



# Seasonal Variation of Carbonaceous Species of PM<sub>10</sub> Over Urban Sites of National Capital Region of India

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Received: 23 December 2019 / Revised: 7 March 2020 / Accepted: 21 March 2020 / Published online: 7 April 2020  
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## Abstract

The air quality of national capital region (NCR) of Delhi, India is becoming more severe day by day because of the anthropogenic activities. To get a better understanding of the ambient air quality of NCR-Delhi, the study of carbonaceous species in particulate matter (PM) is essential. PM<sub>10</sub> samples were collected periodically from the three main urban sites (Faridabad; IGDTUW-Delhi; and CSIR-NPL Delhi,) of NCR-Delhi in the year 2015 to explore the possible sources of carbonaceous species [organic carbon (OC), elemental carbon (EC), and water-soluble organic carbon (WSOC)] in PM<sub>10</sub>. The annual average concentrations of PM<sub>10</sub>, OC, EC, and WSOC were estimated as  $195 \pm 121$ ,  $23.6 \pm 14.4$ ,  $5.2 \pm 4.0$ , and  $15.5 \pm 7.7 \mu\text{g m}^{-3}$ , respectively, at Faridabad, whereas average concentrations of PM<sub>10</sub>, OC, EC, and WSOC were  $274 \pm 141$ ,  $30.8 \pm 19.3$ ,  $9.4 \pm 5.2$ , and  $21.3 \pm 14.3 \mu\text{g m}^{-3}$ , respectively, at IGDTUW, Kashmiri Gate. Concentrations of PM<sub>10</sub>, OC, EC and WSOC were estimated as  $209 \pm 81$ ,  $26.0 \pm 12.8$ ,  $7.9 \pm 5.6$  and  $9.7 \pm 5.9 \mu\text{g m}^{-3}$  at CSIR-NPL. During the study, a significant positive linear trend between OC vs. EC and OC vs. WSOC have been observed for these three sites as ( $R^2=0.64$  and  $R^2=0.76$  at Faridabad;  $R^2=0.66$  and  $R^2=0.87$  at IGDTUW-Delhi; and  $R^2=0.79$  and  $R^2=0.55$  at CSIR-NPL), which indicates the common sources (vehicular emission and/or biomass burning) of carbonaceous aerosols over NCR-Delhi. All these carbonaceous species of PM<sub>10</sub> shows seasonal variation with maxima during winter as well as post-monsoon and minima during monsoon seasons. 5 days backward trajectories of the air masses were calculated which shows the origination of pollutants from local sources along with long-range transport. Furthermore, the secondary and primary organic carbon (i.e., SOC and POC) in PM<sub>10</sub> were also computed and reported.

**Keywords** PM<sub>10</sub> · Carbonaceous aerosols · OC · EC · WSOC · Trajectories

## 1 Introduction

Carbonaceous aerosols (CA) in the surrounding gets special attention in the current years because of their great influences on air visibility, agriculture, water sources, health

and climate (Pant et al. 2015; Sharma et al. 2018). Earlier studies in Delhi have recorded that both primary and secondary sources have a good contribution to the Delhi's poor ambient air quality (Jaiprakash et al. 2017; Pant et al. 2015; Jain et al. 2020; Sharma et al. 2020). Combustion like biomass, fossil fuels and industrial activities leads to the formation of carbonaceous aerosols. These carbonaceous aerosols (CAs) consists both the elemental carbon (EC) also known as black carbon (BC) with the primary pollutants (incomplete combustion of fossil fuels and biomass burning) which has disproportionate emissions in the northern hemisphere shows their dominant (Sharma et al. 2014a, b; Rastogi and Sarin 2009) and organic carbon (OC) with both primary and secondary pollutants (translation of gas to particle VOCs, physical and chemical adsorption) both have a crucial effects on human health, further provides an unhealthy atmosphere as both are constituents of PM<sub>10</sub>. EC or BC helps in the formation of brown clouds which has

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s41810-020-00058-2>) contains supplementary material, which is available to authorized users.

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tendency to dim the Earth's surface thus leading to global warming (Ramanath and Carmichael 2008). Disturbance in the pattern of rainfall also comes into the picture because of EC concentration present in the atmosphere (Ramanathan et al. 2005), i.e., perturbation in the hydrological cycle. Presence of brown carbon makes OC ultraviolet-absorbing and the absorbing capacity of BC is increased by a factor 2–4 when OC acts as a coating (Bond et al. 2006; Fuller et al. 1999; Jacobson 2001, Schnaiter et al. 2005). As a possible sources of CAs can be represented through OC/EC ratio (Kaushal et al. 2018; Rastogi and Sarin 2009; Subhankar and Ambade 2016). OC can be classified to water-soluble organic (WSOC) which has more portions of carbonaceous and water-soluble inorganic carbons (WSIC). The study of WSOC becomes essential because of the hygroscopic surrounding. Studying the concentration, size and chemical composition of particulate matter (PM) at the receptor sites boost the understanding of PM sources and chemical, physical and optical processes, respectively (Putaud et al. 2010; Yin and Harrison 2008), thus driving to an ideas to decrease PM's pollution (Pant and Harrison 2012; Sharma et al. 2016b; 2018). Major factors that influence the composition of the PM are their sources, meteorological parameters, atmospheric chemistry, and anthropogenic activities (Sharma et al. 2014a; Jain et al. 2020).

National Capital Region of Delhi, India covers the 34,144 km<sup>2</sup> area in total with a population of 15.8 million, i.e., 7.6% of the country's urban population, including Delhi city with total area 1483 km<sup>2</sup> has a great influence on the atmospheric routine (Kumar et al. 2017). Furthermore, NCR-Delhi being the hot center of the country leads to an increase in the anthropogenic activities with emissions from biomass burning, vehicular emissions, agriculture activities, fossils fuel, a further rapid increase in the industries, urbanizations, and constructions have a serious influence on the atmospheric chemistry. In addition, the long-range traveled aerosols show a great impact on the concentrations at the receptor sites. The speciality of the locations (Faridabad, IGDTUW-Delhi and CSIR-NPL) being chosen for the present study is because of the huge traffic junction, large agriculture fields, industries, increase in the population which enhances the anthropogenic activities. So it becomes important to understand the atmospheric chemistry and models for such receptor sites to maintain healthy and balanced atmospheric conditions.

To scale down the air pollution over the Delhi-NCR multiple steps have been taken like closing of various factories, introducing Delhi metro route, startup of CNG (compressed natural gas) vehicles, reducing the content of sulphur in diesel (Chowdhury et al. 2019), also the odd–even system (Sharma et al. 2017). Therefore, to maintain a controlled and pleasant atmosphere (air quality) it becomes essential to go through the study of PM over the NCR of Delhi. The

present study of CAs is essential over the NCR-Delhi as a limited study is available over the region. In this paper, we report the seasonal variability of OC, EC, WSOC, SOC and CAs [ $OC \times 1.8 + EC$ ; a conversion factor of  $OC > 1.6$  is suggested for urban aerosols (Zhang et al. 2005; Ram et al. 2010), hence we adopted 1.8 as a factor to convert OC to OM] of PM<sub>10</sub> during January–December 2015 over the urban sites (Faridabad, IGDTUW-Delhi and CSIR-NPL) NCR-Delhi, India.

## 2 Methodology

### 2.1 Sites Description

India is divided into five major sections the east, west, north, south and the central part. NCR-Delhi being in the central measures great influence on its atmosphere due to Indo-Gangetic plain (IGP) in the east, the Thar desert in the west, the Himalayas in the north, and the hot plains in the south region, which reflects NCR-Delhi as the most polluted megacity in the world. Based on downwind direction (north-west to south-east) sampling of PM<sub>10</sub> samples was carried out at the terraces of three urban sites of NCR-Delhi [(National Institute of Technology, Faridabad (28°38' N, 77°10' E; industrial area); Indira Gandhi Technical University for Women (IGDTUW), Kashmiri Gate-Delhi (28°66' N, 77°23' E; urban area) and (CSIR-National Physical Laboratory, New Delhi (28°38' N, 77°10' E; urban area)]. These sampling sites (Fig. 1) reflect a quite urban atmosphere, with huge traffic junctions, construction sites, small scale industries and garbage pile up on the roadsides. As Faridabad have traffic junctions, garbage in the open space, agriculture fields and industries. IGDTUW-Delhi located just a few meters from the highly dense traffic junction, i.e., ISBT (Inter State Bus Terminal) network, and some rural locations nearby it and CSIR-NPL is surrounded by a highly running traffic and the agriculture fields. In addition, for these three locations there is in homogeneity in temperature during the whole years, i.e., over the three monitoring sites mercury drops to 2 °C during the months January–February (winter) and mercury rises up to 48 °C during the month March–May (summer) further temperature is calm during the rainy season, i.e., June–September (monsoon) as well as post-monsoon (October–November) seasons. The average temperature, RH and wind speed (WS) at the sampling site CSIR-NPL is recorded as 25 °C, 55% (25–77%) and 1.5 m s<sup>-1</sup> (range 0.6–4.5 m s<sup>-1</sup>), respectively (Sharma et al. 2014a).

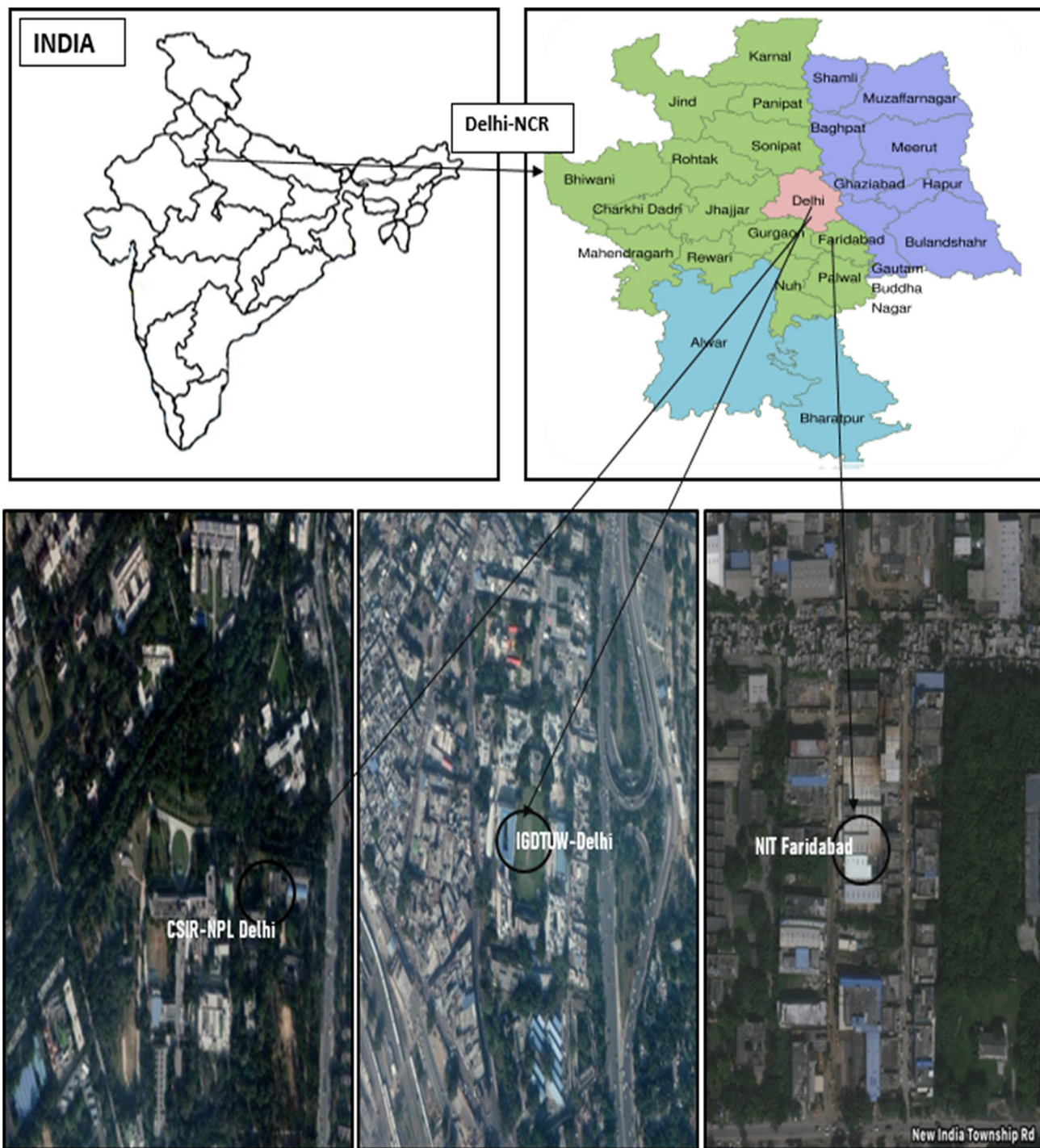


Fig. 1 Map of sampling sites

## 2.2 PM<sub>10</sub> Sampling

Ambient PM<sub>10</sub> samples were collected from New Industrial of Town (NIT), Faridabad ( $n = 33$ ), Indira Gandhi Technical University for Women (IGDTUW-Delhi) Delhi ( $n = 67$ ) and CSIR-National Physical Laboratory, New Delhi ( $n = 115$ )

during January–December 2015 at height of 10 m above the ground level (AGL). Number of PM<sub>10</sub> samples collected in each season for all the three locations are summarized in Table S1 (in supplementary information). Before sampling the quartz microfiber filters (QM-A) were pre-combusted at 550 °C for 5 h to remove organic artifacts and



desiccator-stored for 24 h before the initial weight of the filters. 24 h sampling was done using a high volume sampler with flow rate  $1.12 \text{ m}^3 \text{ min}^{-1}$  (accuracy  $\pm 2\%$ ; flow of the sampler was calibrated using National Standards). The concentration of  $\text{PM}_{10}$  ( $\mu\text{g m}^{-3}$ ) was calculated on the basis of the difference between initial and final weights of the filters measured by a micro balance (resolution:  $\pm 10 \mu\text{g}$ ) was determined by dividing the amount of total volume passed during the sampling. After that  $\text{PM}_{10}$  filters were stored in the deep freezer at  $-20 \text{ }^\circ\text{C}$  prior to analysis. Furthermore, the samples were carried out for the chemical analysis, i.e., for the determination of concentrations of organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC).

## 2.3 Chemical Analysis

The OC, EC and WSOC of  $\text{PM}_{10}$  were analyzed with following instrumentation and methodology. The instruments used in chemical analysis were calibrated using respective standards and traceable to SI. The QA/QC of all the instruments were performed during the analysis of the samples and described in each section.

### 2.3.1 OC and EC analysis

For OC and EC concentrations of  $\text{PM}_{10}$  filters along with a blank (to remove background error) were analyzed using thermal/optical carbon analyzer (DRI Model 2001A, M/s. Atmoslytic Inc., Calabasas, CA, USA) by “IMPROVE-A Protocol” based on the principle of preferential oxidation of organic and elemental carbon compounds at different temperature (Chow et al. 2004). The analyzer operates like initially liberating carbon compounds under different temperature (OC1, OC2, OC3, and OC4 at  $140 \text{ }^\circ\text{C}$ ,  $280 \text{ }^\circ\text{C}$ ,  $480 \text{ }^\circ\text{C}$ , and  $580 \text{ }^\circ\text{C}$ , respectively, EC fractions EC1, EC2, and EC3 at  $580 \text{ }^\circ\text{C}$ ,  $740 \text{ }^\circ\text{C}$  and  $840 \text{ }^\circ\text{C}$ , respectively), converting these carbon compounds to carbon dioxide ( $\text{CO}_2$ ) by passing the volatilized carbon compounds through an oxidizer manganese dioxide ( $\text{MnO}_2$ ), further in presence of methanator and hydrogen-enriched nickel catalyst,  $\text{CO}_2$  is converted to methane ( $\text{CH}_4$ ) thus by quantifying  $\text{CH}_4$  using flame ionization detector (FID). The calibration of the instruments, standards used for calibration and details about the analytical procedure for OC and EC are summarized in our previous paper and reference therein (Sharma et al. 2014a). Each  $\text{PM}_{10}$  samples were analyzed in triplicate with field blank filters and estimated the OC and EC concentration with 3–7% of repeatability errors. The carbonaceous aerosols (CAs) is calculated as sum of organic matter ( $\text{OM} = 1.8 \times \text{OC}$ ) and elemental carbon of  $\text{PM}_{10}$  (Srinivas and Sarin 2014). A conversion factor of  $\text{OC} > 1.6$  is suggested for urban aerosols (Zhang et al. 2005).

### 2.3.2 WSOC analysis

As sample contains both total water soluble organic carbon (TOC) and total water soluble inorganic carbon (IC) collectively known as total water soluble carbon (TC) (WSOC or  $\text{TOC} = \text{TC} - \text{IC}$ ). For the analysis of the WSOC,  $\sim 4.0 \text{ cm}^2$  area of each deposited  $\text{PM}_{10}$  filter was extracted (sonication for 45 min three runs at  $50 \text{ }^\circ\text{C}$ ) in 25 ml Milli-Q water (resistivity:  $18.2 \text{ M}\Omega\text{-cm}$ ) followed by the filter (to free insoluble particle) through  $0.2 \mu\text{m}$  membrane filters using a syringe. Furthermore, 5 ml of each sample was filled in the vials and proceed for analysis using the instrument Total Organic Carbon Analyzer (TOC-LCPH/CPN, M/s. Shimadzu, Japan) based on the principle of non-dispersive infra-red (NDIR) method. Where the condition maintained as supply gas pressure  $\sim 200\text{--}250 \text{ kPa}$ , carrier gas flow  $150 \text{ ml min}^{-1}$ , furnace temperature  $680 \text{ }^\circ\text{C}$ , dehumidifier temperature  $0.8 \text{ }^\circ\text{C}$ , NDIR temperature  $66.2 \text{ }^\circ\text{C}$ . Calibration was performed using operationally followed by standards procedure (Rai et al. 2020). For TC calibration, standard potassium hydrogen phthalate and for IC calibration, standard  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  were used (Rai et al. 2020). Field blank samples were also run to remove the background error at the beginning and after every 10 samples (repeatability errors: 3–10% based on triplicate analysis). The details analytical procedure of WSOC analysis of  $\text{PM}_{10}$  samples are summarized in Rai et al. (2020).

The water soluble inorganic ionic components (cations:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , anions:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) of  $\text{PM}_{10}$  samples of CSIR-NPL have been analyzed by Ion Chromatograph (Model: DIONEX-ICS-3000, USA). The analytical error (repeatability) was estimated to be 3–7% based on triplicate ( $n=3$ ) analysis. Details of water soluble inorganic ions analysis of  $\text{PM}_{10}$  are discussed in Sharma et al. (2014a).

## 2.4 Meteorological parameters and trajectory analysis

Concerning with the meteorological parameter data as wind speed (WS, accuracy  $\pm 2\%$ ), wind direction (WD, accuracy  $\pm 3^\circ$ ), temperature (T, accuracy  $\pm 1 \text{ }^\circ\text{C}$ ) and relative humidity (RH, accuracy  $\pm 2\%$ ) which shows a relative contribution in enhancing the particulate concentrations were collected using automatic weather stations (AWS) (installed at CSIR-NPL and IGDTUW/DPCC, at  $\sim 10 \text{ m AGL}$ ; AWS was not available at Faridabad site). For Faridabad, the meteorological parameters were collected from the India Meteorological Department ([www.imd.gov.in](http://www.imd.gov.in)).

Composition of atmospheric aerosols is influenced by its source region and transport pathway. To identify the possible transport pathways of  $\text{PM}_{10}$  from their potential sources of origins to sampling sites, 5 days backward trajectory

calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model have been traced (Draxler and Rolph 2003). Air mass back-trajectories for each experimental day for 500 m above the ground level (AGL) during January–December 2015 have been calculated (using GDAS meteorological data). HYSPLIT was run every day starting at 0500 h, UTC (Universal Coordinate Time), at a starting height of 500 m AGL on an hourly basis. This height was chosen to diminish the effects of surface friction and to represent winds in the low boundary layer. The PM has the ability to travel long distance; therefore, 5 days were selected to calculate backward trajectories using HYSPLIT.

### 3 Results and Discussion

#### 3.1 Concentration of PM<sub>10</sub>

The statistical summary of the PM<sub>10</sub> and their chemical species (OC, EC, WSOC, CAs, and SOC) along with seasonal variations for all the monitoring sites are presented in Table 1. During the study period, the annual average concentrations of PM<sub>10</sub> along with the standard deviation ( $\pm$ SD at  $1\sigma$ ) over Faridabad, IGDTUW-Delhi and CSIR-NPL were  $195 \pm 121 \mu\text{g m}^{-3}$ ,  $275 \pm 141 \mu\text{g m}^{-3}$ , and  $209 \pm 81 \mu\text{g m}^{-3}$ , respectively (ranges 44–570  $\mu\text{g m}^{-3}$ , 58–584  $\mu\text{g m}^{-3}$ , and 69–476  $\mu\text{g m}^{-3}$ , respectively). The observed concentration is much higher than the concentration reported in Jain et al. (2019) ( $133 \mu\text{g m}^{-3}$ ) at Delhi, whereas the PM<sub>10</sub> concentration reported by Perrino et al. 2011 ( $183 \mu\text{g m}^{-3}$ ), Tiwari et al. 2013 ( $161 \pm 80 \mu\text{g m}^{-3}$ ) are close to the concentration of PM<sub>10</sub> recorded over Faridabad. Kulshrestha et al. 2009 ( $219 \pm 84 \mu\text{g m}^{-3}$ ) recorded the PM<sub>10</sub> concentration is close to the concentration over CSIR-NPL. Furthermore, Mandal et al. 2014 ( $285 \pm 26 \mu\text{g m}^{-3}$ ) studied similar PM<sub>10</sub> concentration to IGDTUW-Delhi. IGDTUW-Delhi reflected the higher mass concentration ( $275 \pm 141 \mu\text{g m}^{-3}$ ) compared to the other two sites with huge variations because of the accumulation of particles from the huge traffic influence of ISBT (inter-state bus terminal) and Indo-Gangetic plain (IGP) as well as local sources like traffic, biomass burning, secondary aerosols, fossil fuel combustion and industrial emissions etc. (Gadi et al. 2019). Observed annual average concentration values are reported to be more than double as compared to the guidelines of National Ambient Air Quality Standard (NAAQS) (for 24 h:  $100 \mu\text{g m}^{-3}$  and for annual:  $60 \mu\text{g m}^{-3}$ ) provided by Central Pollution Control Board (CPCB) of India, and four times greater according to World Health Organization (WHO) ( $50 \mu\text{g m}^{-3}$ ).

During winter, Faridabad hits the PM<sub>10</sub> concentration to  $348 \pm 147 \mu\text{g m}^{-3}$ , while IGDTUW-Delhi to  $294 \pm 143 \mu\text{g m}^{-3}$  which is lower than the result reported by Gupta et al. 2018 ( $369 \pm 220 \mu\text{g m}^{-3}$ ) and CSIR-NPL

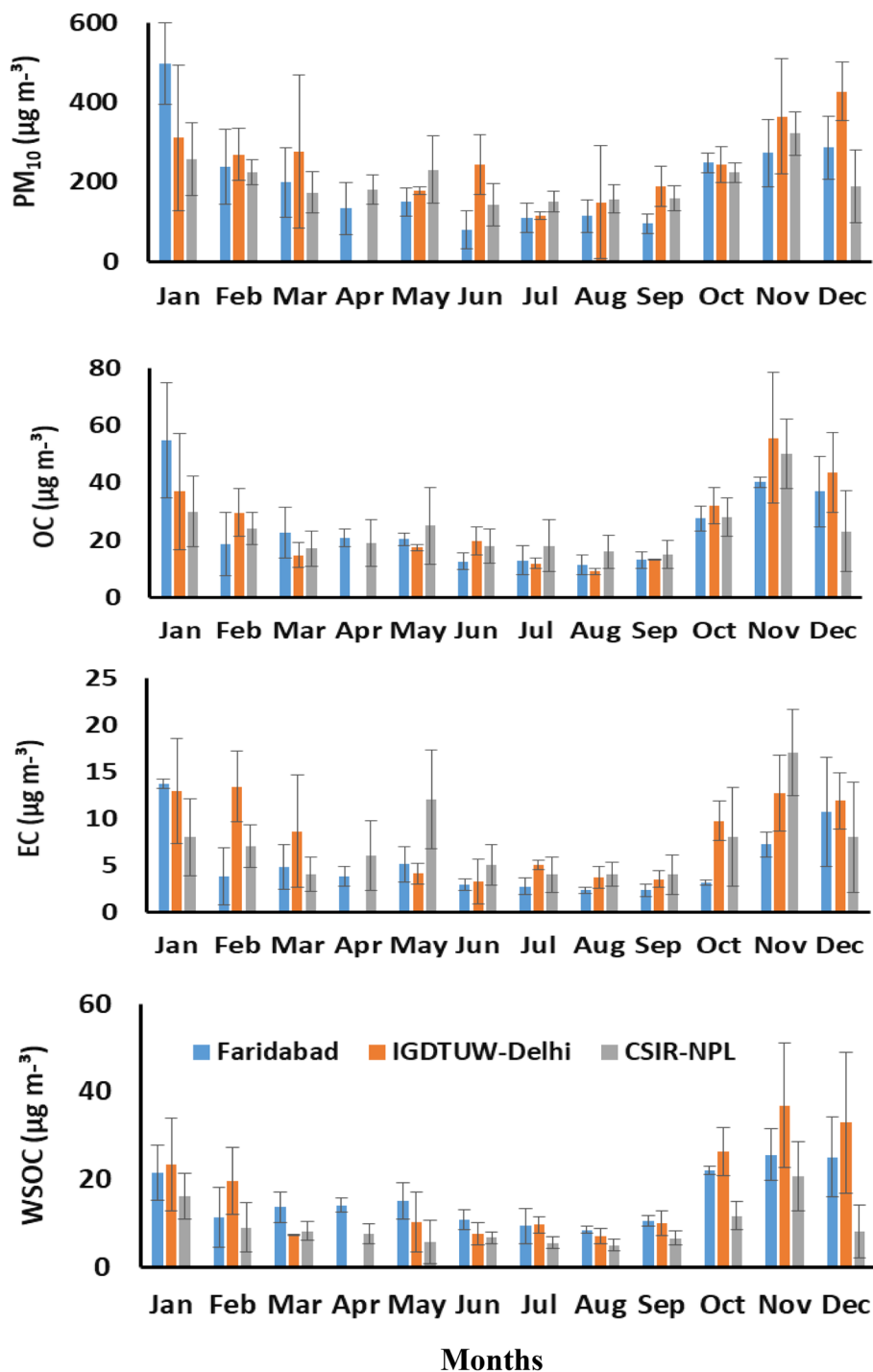
to  $237 \pm 60 \mu\text{g m}^{-3}$  which is close to the result reported by Jain et al. (2018) ( $249 \pm 103 \mu\text{g m}^{-3}$ ). Higher concentration of PM<sub>10</sub> over Faridabad may attribute to the traffic, burning waste in open, biomass burning, small and large scale industries, agricultural activities and mining of sandstone for the construction purpose of national highway also low temperature in winter results in formation of thick smog resulting high concentration (Gupta et al. 2018). Whereas IGDTUW-Delhi and CSIR-NPL showed higher mass concentration during post-monsoon (October–December), i.e.,  $343 \pm 118 \mu\text{g m}^{-3}$  and  $304 \pm 75 \mu\text{g m}^{-3}$ , respectively, may be contributed by crop residue (biomass burning) in Punjab and Haryana (through regional transportation of pollutants) and local sources like vehicular emissions, soil dust and secondary aerosols as well as also affected by festivals Diwali (huge amount of fire crackers were used during this festival) etc., (Shivani et al. 2019). The concentration of PM<sub>10</sub> was found to be lower during monsoon season at all the sites and higher during winter (January) at Faridabad and during post-monsoon (December) at IGDTUW-Delhi and CSIR-NPL (Figs. 2, 3). The seasonal variation in the concentration of PM<sub>10</sub> among the seasons might be due to influence meteorological parameters and the potential sources of the PM. Seasonal PM<sub>10</sub> concentration for Faridabad varies as winter > post-monsoon > summer > monsoon, whereas for IGDTUW-Delhi and CSIR-NPL varies like post-monsoon > winter > summer > monsoon (Fig. 3). Collectively the climatic conditions (lower mixing height) and biomass burning (crop residue, wood and dungcake) as well as fossil fuel combustions are influencing during post-monsoon as well as winter seasons. During summer and monsoon seasons (i.e., wet seasons) heavy rainfalls wash out the pollutants resulting in a lower concentration of PM<sub>10</sub> at the sampling sites (Jain et al. 2019).

#### 3.2 Concentrations of OC, EC and WSOC in PM<sub>10</sub>

Carbonaceous aerosols (CAs) which has origination from both primary and secondary pollutants show a crucial role in visibility degradation, atmospheric chemistry and regional as well as global climate change. Statistical summary of OC, EC, WSOC, CA and SOC of PM<sub>10</sub> along with seasonal changes are tabulated in Table 1. In the present study, annual concentration of OC at Faridabad was recorded as  $23.6 \pm 14.4 \mu\text{g m}^{-3}$  (range 1.7–69.1  $\mu\text{g m}^{-3}$ ). Similarly at IGDTUW-Delhi and CSIR-NPL, concentration of OC was recorded as  $30.8 \pm 19.3 \mu\text{g m}^{-3}$  (range 7.8–79.4  $\mu\text{g m}^{-3}$ ) and  $26.0 \pm 12.8 \mu\text{g m}^{-3}$  (range: 2–72  $\mu\text{g m}^{-3}$ ), respectively. A similar result ( $22.7 \pm 7.3 \mu\text{g m}^{-3}$ ) was reported by Sharma et al. (2016a) in Delhi. Seasonal trends of OC concentration at Faridabad observed as winter ( $35.7 \pm 22.1 \mu\text{g m}^{-3}$ ) > post-monsoon ( $34.4 \pm 8.4 \mu\text{g m}^{-3}$ ) > summer ( $21.2 \pm 4.4 \mu\text{g m}^{-3}$ ) > monsoon ( $12.5 \pm 3.7 \mu\text{g m}^{-3}$ ).



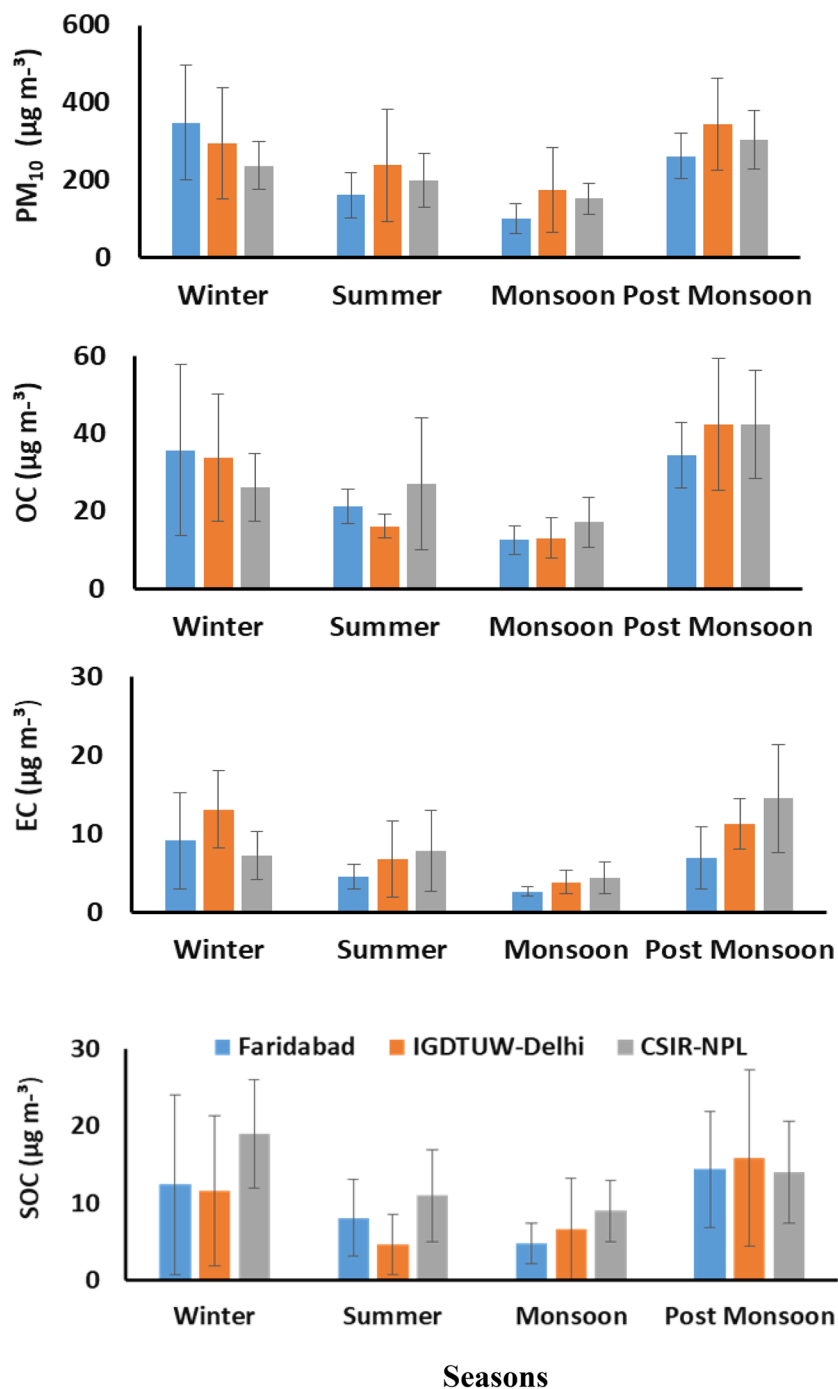
**Fig. 2** Monthly average concentrations of the carbonaceous species (OC, EC, and WSOC) of PM<sub>10</sub> over Faridabad, IGDTUW, and CSIR-NPL of NCR-Delhi



Whereas at IGDTUW-Delhi OC concentration trend was observed as post-monsoon ( $42.3 \pm 16.9 \mu\text{g m}^{-3}$ ) > winter ( $33.8 \pm 16.4 \mu\text{g m}^{-3}$ ) > summer ( $16.1 \pm 3.0 \mu\text{g m}^{-3}$ ) > monsoon ( $13.0 \pm 5.2 \mu\text{g m}^{-3}$ ). Further for CSIR-NPL order of OC was observed as post-monsoon ( $42.4 \pm 14.0 \mu\text{g m}^{-3}$ ) > summer ( $27 \pm 17 \mu\text{g m}^{-3}$ ) > winter ( $26.2 \pm 8.7 \mu\text{g m}^{-3}$ ) > monsoon ( $17.1 \pm 6.4 \mu\text{g m}^{-3}$ ) which is comparatively lower than the result mentioned by Gupta et al. (2018) in Delhi. Thus all the

three sites had similar seasonal trend of OC concentration was observed. The average EC concentration at Faridabad was reported as  $5.2 \pm 4.0 \mu\text{g m}^{-3}$  (range 1.7–15.7  $\mu\text{g m}^{-3}$ ) (~3% of PM<sub>10</sub>), for IGDTUW-Delhi it was reported as  $9.4 \pm 5.2 \mu\text{g m}^{-3}$  (range 0.8–24.0  $\mu\text{g m}^{-3}$ ) (~3% of PM<sub>10</sub>) and further for CSIR-NPL it was observed as  $7.9 \pm 5.6 \mu\text{g m}^{-3}$  (range 2–28  $\mu\text{g m}^{-3}$ ) (~4% of PM<sub>10</sub>) which is in agreement with the result reported by Sharma et al. (2016b)

**Fig. 3** Seasonal average concentrations of the carbonaceous species (OC, EC, WSOC and SOC) of  $PM_{10}$  at Faridabad, IGDTUW, and CSIR-NPL of NCR-Delhi



as  $8.7 \pm 4.0 \mu\text{g m}^{-3}$  over Delhi. Ordering the EC seasonal concentration trends over the monitoring sites, Faridabad showed the trend as winter ( $9.1 \pm 6.1 \mu\text{g m}^{-3}$ ) > post-monsoon ( $6.9 \pm 4.0 \mu\text{g m}^{-3}$ ) > summer ( $21.2 \pm 4.4 \mu\text{g m}^{-3}$ ) > monsoon ( $2.6 \pm 0.6 \mu\text{g m}^{-3}$ ), whereas IGDTUW-Delhi winter ( $13.1 \pm 4.9 \mu\text{g m}^{-3}$ ) > post-monsoon ( $11.3 \pm 3.3 \mu\text{g m}^{-3}$ ) > summer ( $6.8 \pm 4.9 \mu\text{g m}^{-3}$ ) > monsoon ( $3.8 \pm 1.5 \mu\text{g m}^{-3}$ ), which is in similar with values reported by Gupta et al. (2018). Further for CSIR-NPL post-monsoon ( $14.5 \pm 6.9 \mu\text{g m}^{-3}$ ) > summer ( $7.8 \pm 5.1 \mu\text{g m}^{-3}$ ) > winter

( $7.2 \pm 3.1 \mu\text{g m}^{-3}$ ) > monsoon ( $4.4 \pm 2.0 \mu\text{g m}^{-3}$ ) in Delhi. Approximately 10–90% of the OC content in the atmosphere is accounted through WSOC depending on the source loading on the sampling sites and a major part in the atmospheric OC (Ram et al. 2012; Rai et al. 2020). The annual average WSOC at Faridabad, IGDTUW-Delhi and CSIR-NPL were recorded as  $15.5 \pm 7.7 \mu\text{g m}^{-3}$  (range 3.0–33.6  $\mu\text{g m}^{-3}$ ),  $21.3 \pm 14.3 \mu\text{g m}^{-3}$  (range 3.7–63.1  $\mu\text{g m}^{-3}$ ) and  $9.7 \pm 5.9 \mu\text{g m}^{-3}$  (range 2.6–33  $\mu\text{g m}^{-3}$ ), respectively. IGDTUW-Delhi was recorded the highest WSOC



( $21.3 \pm 14.3 \mu\text{g m}^{-3}$ ) concentration among all the three sites. Moving to the seasonal WSOC concentration, the three sites trended in a similar way, i.e., post-monsoon > winter > summer > monsoon evident from Figs. 2, 3. A similar pattern is reported by Ram et al. (2012) at the various locations over the IGP region. Variation in the boundary layer dynamics, local sources, i.e., emission from incomplete combustion of fuel, biomass burning, and industries there are an irregular pattern of the concentrations (Jain et al. 2019). Furthermore, the concentrations of OC, EC, and WSOC are higher during post-monsoon (October–December) and lower in monsoon. During monsoon, OC and EC concentrations are almost 2–3 times lower compared to winter and post-monsoon, because the meteorological conditions are unfavorable for re-suspension and dispersion of PM due to intense precipitation (Jain et al. 2020).

The OC/EC ratio plays an important characteristic for the examination of source type or source emissions or combustion materials (Pio et al. 2011). So, inferring to emission sources of carbonaceous aerosols the annual OC/EC ratio over Faridabad has been recorded as 5.1, whereas for IGDTUW-Delhi and CSIR-NPL were 3.8 and 4.0, respectively. Furthermore, the scatter plot shows a significant relationship ( $R^2=0.79$  at CSIR-NPL;  $R^2=0.66$  at IGDTUW-Delhi and  $R^2=0.64$  at Faridabad) between OC

vs. EC suggesting common emission sources (originating from combustion sources) like biomass burning or/and fossil fuel combustion (Fig. 4). The OC/EC ratio of road traffic emissions generally varies between 1.4 and 4 for gasoline catalyst vehicles and from 0.3 to 1 for diesel vehicles (Salameh et al. 2015; Amato et al. 2009). Large values (between 4 and 12) of this ratio are generally found for biomass burning emissions (Szidat et al. 2006; Ram et al. 2010). Analysis of stable carbon isotopic composition of  $\text{PM}_{10}$  indicated that the vehicular emissions and biomass burning are the major sources of  $\text{PM}_{10}$  over the sampling site of NCR-Delhi (Sharma et al. 2015; 2017). To infer the extent of secondary aerosols formation WSOC/OC were calculated over Faridabad, IGDTUW-Delhi and CSIR-NPL as 0.65, 0.69, and 0.37, respectively. The scatter plots shows the significant linear correlation between OC vs. WSOC ( $R^2=0.76$  at Faridabad,  $R^2=0.87$  at IGDTUW-Delhi and  $R^2=0.55$  at CSIR-NPL, respectively) signifying that both the species (OC, WSOC) are emitted from same primary sources under similar secondary process (Fig. 4). Because of the low solubility of organic species from the combustion of fuels, the WSOC/OC for vehicular emission is low compared to biomass burning emission. Furthermore, the ratio  $\text{K}^+/\text{OC}$ ,  $\text{K}^+/\text{EC}$  for CSIR-NPL has been reported as 0.17 and 0.39 which is in agreement with the result reported by Sharma

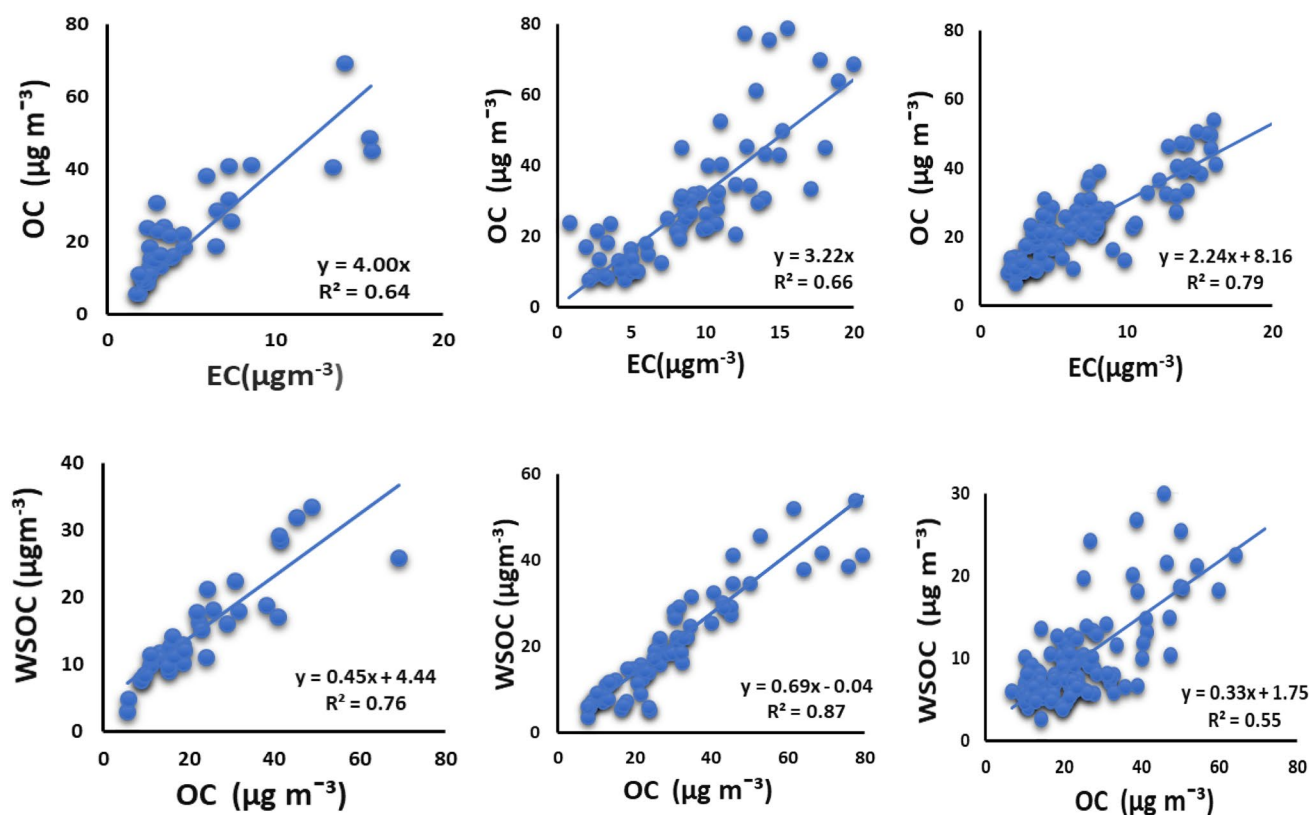


Fig. 4 Scatter plots between OC & EC and WSOC & OC over Faridabad, IGDTUW and CSIR-NPL of NCR-Delhi

et al. (2016c) over Delhi. Figure 5 shows the correlation ( $R^2=0.39$ ) for  $K^+$  vs. OC and ( $R^2=0.44$ ) for  $K^+$  vs. WSOC over the location CSIR-NPL ( $K^+$  data is not available for other two locations). The average and range of OC/EC,  $K^+$ /OC and  $K^+$ /EC ratios in  $PM_{10}$  from Indian and Chinese sites are summarized in Table S2 (in supplementary information).

Primary organic carbon (POC) is estimated using EC tracer method by taking minimum OC/EC ratio for entire study period. Both EC and POC are considered to be originated from combustion sources and EC is a good tracer for POC (Castro et al. 1999). POC is estimated using the following relation:

$$POC = [OC/EC]_{\min} \times [EC] + c, \quad (1)$$

where  $c$  is the contribution from non-combustion sources which is negligible in present case. Secondary organic carbon (SOC) is then computed as the difference of measured OC and estimated POC concentrations ( $SOC = OC - POC$ ). In the present case,  $(OC/EC)_{\min}$  represents the minimum value of OC/EC estimated annually and monthly over the three receptor sites, which differs according to the meteorological conditions and the sources. The annual and seasonal concentrations of SOC at the three sites during the

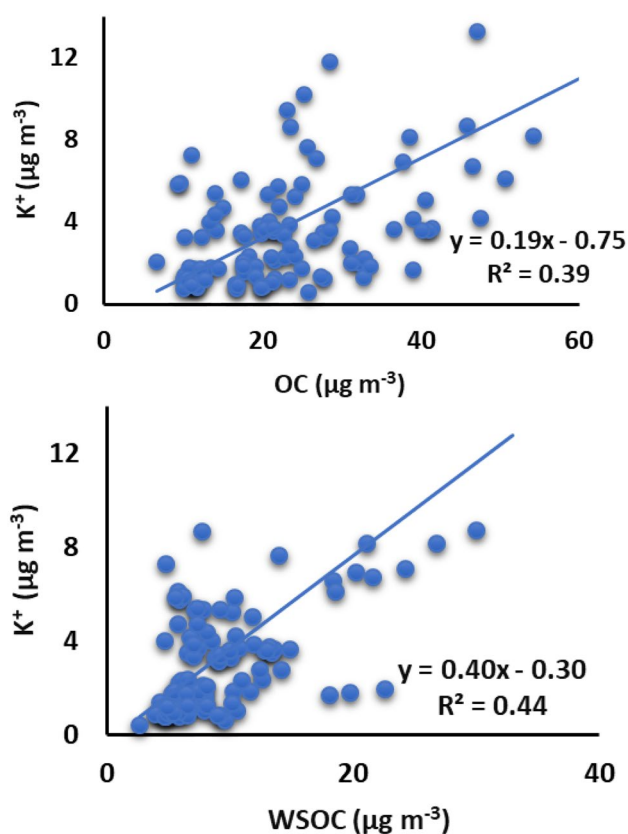


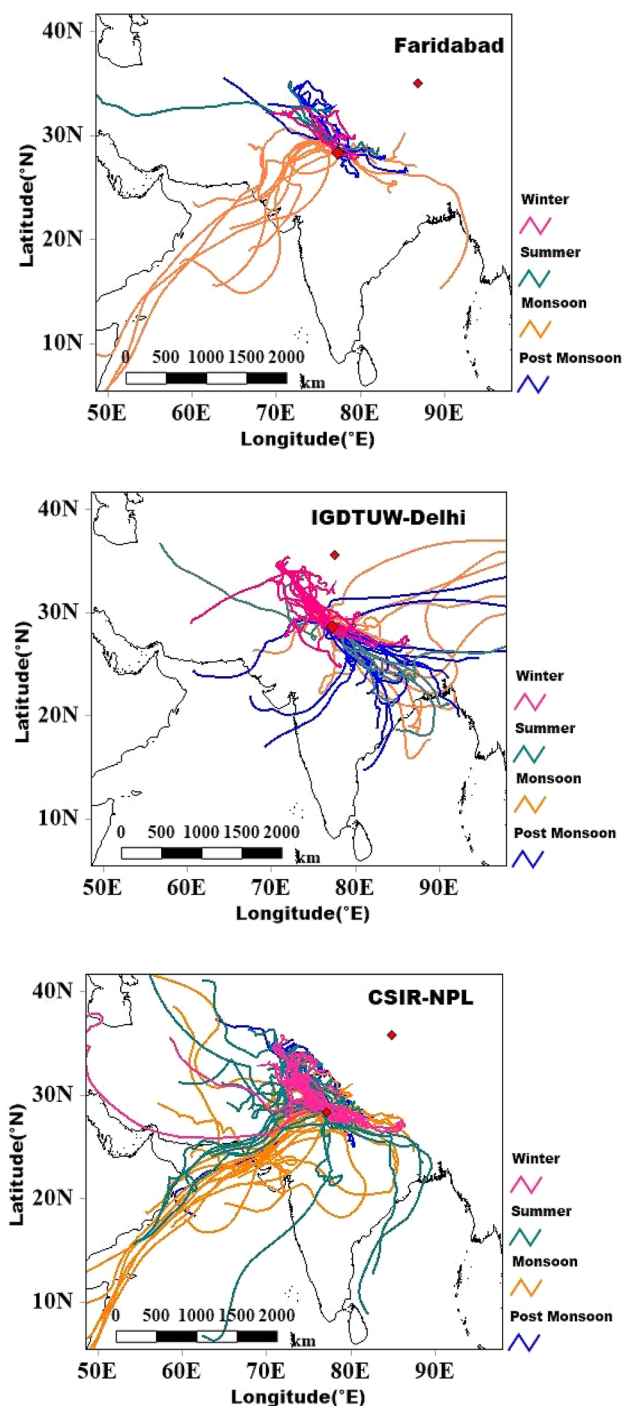
Fig. 5 Scatter plots between  $K^+$  & OC and  $K^+$  & WSOC at CSIR-NPL

study periods are tabulated in Table 1. The concentration of POC over Faridabad, IGDTUW-Delhi and CSIR-NPL were  $15.0 \pm 11.7$ ,  $16.1 \pm 8.9$ ,  $10.5 \pm 7.6 \mu\text{g m}^{-3}$ , respectively (Table 1). Chemical reactions of POC contribute to significant friction of SOC (Ram et al. 2010; Robinson et al 2007). The concentration of SOC was higher during post-monsoon over Faridabad and IGDTUW-Delhi and during winter over CSIR-NPL. Figure 3 depicts the seasonal distribution of SOC over the three monitoring sites of NCR-Delhi. It is clear that the SOC concentration was estimated high during post monsoon. The above discussion summarized the contributor to the  $PM_{10}$  mass concentrations (such as incomplete combustion of fuels, biomass burning, vehicular emission, large and small scale industries). Furthermore, there is also a contribution of the long-range traveled particles which enhance the  $PM_{10}$  concentration at the sampling site of NCR-Delhi. This contribution is studied by trajectories analysis applying the HYSPLIT model.

The path ways of the particles were traced towards the receptor sites of NCR-Delhi using HYSPLIT model (GDAS data sets). Figure 6 depicts the seasonal trajectory of air mass approaching towards the monitoring sites of Faridabad, IGDTUW-Delhi and CSIR-NPL during the year 2015. The trajectory analysis reflected the air parcel pathway to the receptor site Faridabad mainly coming from the south-west and north-west (from the Arabian Sea and Gujarat, Rajasthan, Pakistan and Afghanistan). For IGDTUW-Delhi air parcels showed a contribution from north-east through the IGP region of India. Furthermore, for CSIR-NPL air parcels mostly traveled through the IGP region and from the Arabian Sea passes through some region of Gujarat, Rajasthan, Pakistan, Afghanistan and Bay of Bengal. In winter, air mass flows from north-east to north-west and in summer air mass flows from south-east to south-west. (Sharma et al. 2014a; Jain et al. 2019; Shivani et al. 2019) had also reported the similar air parcel pattern towards the Delhi.

## 4 Conclusion

The study presents the seasonal variation in concentrations of carbonaceous species of  $PM_{10}$  (OC, EC, WSOC, CAs and SOC) over NCR-Delhi, India. The annual  $PM_{10}$  concentration over IGDTUW-Delhi is recorded higher ( $275 \pm 141 \mu\text{g m}^{-3}$ ) followed by CSIR-NPL ( $209 \pm 81 \mu\text{g m}^{-3}$ ) and Faridabad ( $195 \pm 121 \mu\text{g m}^{-3}$ ), because IGDTUW-Delhi reflects influence of heavy traffic load (vehicular emission is more) as compared to other sites. Annual average concentration of OC over Faridabad, IGDTUW-Delhi and CSIR-NPL were  $23.6 \pm 14.4$ ,  $30.8 \pm 19.3$ ,  $26.0 \pm 12.8 \mu\text{g m}^{-3}$ , respectively. Similarly, the annual concentration of EC was  $5.2 \pm 4.0$ ,  $9.4 \pm 5.2$ ,  $7.9 \pm 5.6 \mu\text{g m}^{-3}$ , where EC concentration is observed higher



**Fig. 6** Five days air parcel backward trajectories at Faridabad, IGDTUW-Delhi, and CSIR-NPL of NCR-Delhi

over CSIR-NPL. Post-monsoon (November) reflects a higher concentration of OC over IGDTUW-Delhi, CSIR-NPL, and Faridabad. Furthermore, Faridabad and IGDTUW show a higher concentration of EC during winter and CSIR-NPL reflects higher concentration during post-monsoon (November). Monsoon reflects the lower concentrations, as monsoon

is known as the wet season, rainfall helps in flushing the air pollutants thus resulting in a decrease in the concentrations. In addition, the annual average concentration of WSOC over Faridabad, IGDTUW-Delhi and CSIR-NPL was  $15.5 \pm 7.7$ ,  $21.3 \pm 14.3$ ,  $9.7 \pm 5.9 \mu\text{g m}^{-3}$ , respectively, which is reported higher at Faridabad followed by IGDTUW-Delhi and CSIR-NPL. Plotted trajectory over the receptor sites showed the air-parcel pathway directed from the south-west and the north-west along with the IGP-region. The present study can aid stakeholders and policymakers to incorporate the relevant parameters for carbonaceous aerosols, which influence the air quality of the NCR-Delhi.

**Acknowledgements** The authors are thankful to the Director, CSIR-NPL, New Delhi and Head, Environmental Sciences and Biomedical Metrology Division (ES&BMD), CSIR-NPL, New Delhi for their encouragement and support. Authors thankfully acknowledge the NOAA Air Resources Laboratory for download the air mass trajectories (<http://www.arl.noaa.gov/ready/hysplit4.html>). The authors are thankful to the anonymous reviewers and Editor-in-Chief for their constructive suggestions to improve the manuscript.

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