Seasonal Variations in Water Soluble Inorganic Ions, OC and EC in PM$_{10}$ and PM$_{>10}$ Aerosols over Delhi: Influence of Sources and Meteorological Factors

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ABSTRACT

The PM$_{10}$ and particles of greater than 10 µm aerodynamic diameter (henceforth referred as PM$_{>10}$) collected over Delhi exceeded the National Ambient Air Quality Standards (100 µg m$^{-3}$) with an annual average of 215 µg m$^{-3}$ and 495 µg m$^{-3}$, respectively. The water soluble inorganic ions (WSII) were higher throughout the year in PM$_{10}$ (13.5%) than in PM$_{>10}$ (5%). SO$_4^{2-}$ dominated over NO$_3^−$ ions and contributed 54% to the total WSII in PM$_{10}$. NO$_3^−$ and Ca$^{2+}$ were dominant ions in PM$_{>10}$. NH$_4^+$ during winter and autumn, and Ca$^{2+}$ in summer PM$_{10}$ samples were the major acid neutralizing species. The WSII showed monthly and seasonal changes. The total carbon (TC = EC + OC) constituted 8.8%–47.8% of total PM$_{10}$ mass, and OC and EC varied from 9.91 to 37.06 µg m$^{-3}$ and 5.42 to 22.23 µg m$^{-3}$ during the year-long sampling period. The SOC contributed more to OC in summers and the char (EC1) dominated over soot (EC2 + EC3) in EC fractions throughout the year. In summer samples, secondary OC (SOC) contributed 81% to OC and the OC/EC ratio was 3.61 suggesting the possible role of mineral dust and high photochemical activity in SOC production. For the eight different fractions, three dominant sources were identified, coal combustion, biomass burning, and motor vehicle exhaust for OC1, OC2 and OC3; vehicle exhaust for OC4, OP, EC2 and EC3; and biomass and coal combustion for EC1. The seasonal changes in the WSII and carbon concentrations in PM$_{10}$ and PM$_{>10}$ are attributed to both the sources and the meteorological conditions in and around the study area.

Keywords: Soluble ions; Carbon fractions; Processes; Air quality.

INTRODUCTION

Rapid urbanization and industrialization have negatively impacted the air quality of India and China resulting in serious health issues (Li et al., 2014; Pant et al., 2015). In India, air quality has been identified as one of the top five reasons of mortality and morbidity (Lim et al., 2012). The ambient air quality in New Delhi quite often exceeds the National Ambient Air Quality Standards (NAAQS) making it a health risk (Guttikunda and Goel, 2013; Guttikunda et al., 2014; Trivedi et al., 2014; Pant et al., 2015). Guttikunda and Goel (2013) found that “the health impacts analysis of air pollution in Delhi estimates 7,350–16,200 premature deaths and 6.0 million asthma attacks per year”. The PM$_{2.5}$ and PM$_{10}$ particles are largely responsible for poor air quality in Delhi (Trivedi et al., 2014; Pant et al., 2015). These particles also play very wide role in climate studies (Ramana et al., 2010), visibility (Singh and Dey, 2012) and atmospheric chemistry (Seinfeld and Pandis, 2006). Chemically, they are composed of water soluble inorganic ions (WSII), organic compounds, organic and elemental carbon and crustal materials. In general, WSII and carbon content account for more than one third of the PM$_{10}$ mass in urban environments (Ytrri et al., 2007; Gu et al., 2010; Pavuluri et al., 2011; Zhang et al., 2011). The WSII in aerosols serve as a good proxy for the pollution sources and help in understanding the chemical reactions in ambient atmosphere (Wang et al., 2006; Radhi et al., 2010). Carbon content includes elemental carbon (EC) and organic carbon (OC). The EC, does not undergo chemical transformations in the atmosphere, is directly emitted by fossil fuel and biomass combustion. The OC includes primary organic carbon (POC), directly emitted from combustion sources and secondary organic carbon (SOC), formed via photochemical reactions involving POC or by gas to particle conversion from volatile organic compounds. Further, the physio-chemical characteristics of ambient aerosols are influenced by both, prevailing meteorological factors (temperature, humidity, wind velocity and precipitation) (Trivedi et al., 2014) and the geographical location (topography and proximity to the sources (Yadav and Rajamani, 2006; Radhi et al., 2010).

Recently, a few studies have been carried out in the parts of northern India, especially over the Indo-Gangetic Plains,
to understand the characteristics, composition and sources of aerosols (Rengarajan et al., 2007, Ram and Sarin, 2009, 2010, 2011; Ram et al., 2012; Trivedi et al., 2014; Pant et al., 2015 and references therein). However, the year round information on WSII and carbon content over Delhi is unavailable despite the fact that this region encounters multiplicity of PM$_{10}$ sources (Yadav and Rajamani, 2004, 2006) and pronounced seasonal changes in meteorological conditions. In the present study, PM$_{10}$ (< 10 µm aerodynamic diameter) and PM$_{2.5}$ (< 2.5 µm aerodynamic diameter) were collected on year round basis over Delhi and characterized for WSII, OC and EC mass concentrations to understand their sources, chemical processes and seasonal variations.

**SAMPLING DETAILS**

Aerosol sampling was performed at the roof top of School of Environmental Sciences, Jawaharlal Nehru University (JNU), New Delhi. The university is a residential academic institution located on the famous Delhi ridge with vast vegetation cover. The ambient particles were collected over 24 hour period, with a frequency of 3 to 5 samples per month from January to December using high volume sampler (Envirotech make, model: APM 460 BL). The PM$_{10}$ samples were collected on quartz filter paper while the PM$_{2.5}$ were collected in the cup fitted below the cyclone chamber simultaneously in the same equipment. All the filter papers were pre-baked at 500°C and were desiccated for 24 hours before weighing them prior to and after the sampling. To account for any artifacts introduced during the sample collection and handling, field blank filters were also collected in each month by exposing filters in the sampler but not drawing air through them.

New Delhi, located in tropical climate zone (28°35′N and 77°12′E; 218 m MSL), the capital city of India is one of the most polluted cities of India. New Delhi represents a climatic transition zone from semi-arid in the west to sub-humid in the east. The summers are characterized by high intensity SW winds and open atmospheric conditions with temperature varying between 35°C to 45°C whereas NW low intensity winds dominate winters with 0 to 10°C temperature conditions and relative humidity close to 100%. The meteorological data for the study period were taken from an automatic weather station (AWS), installed at about 15 m above the ground level on the roof top of School of Social Science building adjacent to the sampling site in JNU, New Delhi and are provided in supplementary Table S1. Three coal based thermal power plants (combined capacity ~1,100 MW) and vehicular emissions are the major sources of air pollution in Delhi. In 2011–2012, the vehicular population was approximately 7.5 million (Economic Survey of Delhi). A recent study by Yadav et al. (2016) have reported contributions of different sources for PM$_{10}$ as crustal materials (21%), industrial and vehicular emissions (23%), and wind assisted transport and re-suspension of surface dust (56%) and for PM$_{2.5}$ as primary crustal (59%), crustal dust (26%) and anthropogenic (15%). The sampling site acts as a receptor site for the pollutants from surrounding regions (Tandon et al., 2010; Kumar and Yadav, 2013). The relevant characteristics of the study area can be accessed from elsewhere (Yadav and Rajamani, 2004, 2006).

To identify the influence of air masses originating from different directions, the backward trajectory analysis for the sampling periods was conducted using the HYPLIT model, developed by NOAA/ARL (Draxler and Rolph, 2013). The careful analysis of backward trajectories during the sampling period indicated that Delhi receives winds from four dominant sectors of air mass origin (Fig. 1). Summers are dominated by high intensity south-south westerly winds which pass through the great Indian Thar Desert and transport dust particles in Delhi region. The north and north west air mass back trajectories during winters find their origin in the regions of Pakistan and Afghanistan and crosses the agriculture dominated neighboring states Haryana, Punjab and Himachal Pradesh before reaching to Delhi. The autumn period air mass back trajectories carry the anthropogenic emissions dominated by crop residue burnings from the neighboring states. The rainy season is primarily on account of Indian monsoon and winds passes through Indo Gangetic plains before reaching to Delhi during July to September.

**ANALYTICAL DETAILS**

**Extraction and Analysis Procedures for WSII**

The WSII were extracted from each sample filter paper in 20 mL of Milli Q water using ultrasonic shaker. All the extraction solutions, after filtering through 0.2 µm size filter papers, were stored in high-density polyethylene bottles and kept in the refrigerator at 4°C until analysis. The pH of sample solution was taken using pH meter (model Eutech 510) following three point calibration. Major cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$ and NH$_4^+$) and anions (F$^-$, Cl$^-$, NO$_3^-$ and SO$_4^{2–}$) were analyzed using Metrohm Ion Chromatograph (IC) model 882 Compact IC plus1 pro1 equipped with conductivity channel. For cation analysis, 1.7 mM nitric acid and 0.7 mM dipicolinic acid was used as eluents and the flow rate was maintained at 0.9 mL min$^{-1}$ in Metrosep C4-150/4.0 column. For anion analysis, 3.2 mMol Sodium carbonate and 1 mMol Sodium bicarbonate were used as eluents and the flow rate was maintained at 0.7 mL min$^{-1}$ in the Metrosep A Supp 5-150/4.0 column. Sample extraction and storage, and WSII analysis were carried out in a metal free positive pressure clean laboratory having 1000 class air flow in the lab and 100 class air flow in the fume hoods. Lab and field filter blanks (kept inside the sampler, but not used for air filtering) were prepared and analyzed together with the samples, following the same procedures; obtained values were routinely subtracted from the sample values. The efficacy of the water soluble extraction protocol was checked by re-extracting the WSII from the previously extracted sample filter papers in the same manner and extraction efficacy (in % units) was calculated as:

$$\left(\frac{C_1}{C_1 + C_2}\right) \times 100$$  \hspace{1cm} (1)

where $C_1$ and $C_2$ are the concentration of WSII during 1$^{st}$ and 2$^{nd}$ extractions, respectively. The average value of
Fig. 1. Representative air back trajectories over Delhi for different seasons taken from NOAA (source: Draxler and Rolph, 2013; http://www.arl.noaa.gov/HYSPLIT.php).

extraction efficiency for all ions was recorded in the range of 90–100%. The possible losses of ions during the process of extraction and filtration were investigated by spiking the samples with standard solution of known concentrations and the spiked filter papers were subjected to extraction following the same procedure as applied to sample filter papers. The experiments (n = 6) showed that the average recoveries of ions from quartz filter papers were in the range of 92–100%. Multi-ion serially diluted standard solution made from the stock standard solutions procured from E-Merck, Germany were used for calibration and testing the instrumental stability during the IC analysis. The accuracy, precision and recovery data for individual ionic species analyzed on IC are provided in the supplementary Table S2.

**OC/EC Analysis**

A 0.5 cm² punch from the filter was analyzed for eight carbon fractions following the IMPROVE_A thermal/optical reflectance (TOR) protocol on a DRI model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA) (Cao et al., 2007; Chow et al., 2007). The analyzer works on preferential oxidation of organic carbon and elemental carbon at different temperatures. This produced four OC fractions (OC1, OC2, OC3 and OC4 at 140°C, 280°C, 480°C and 580°C in a helium [He] atmosphere), OP (a pyrolyzed carbon fraction); and three EC fractions (EC1, EC2 and EC3 at 580°C, 740°C and 840°C in a 2% O₂ and 98% He atmosphere) wherein the corrected EC1 is equal to EC1 minus OP. IMPROVE_TOR OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as
EC1 + EC2 + EC3 – OP (Chow et al., 2007). The EC is further divided into char (EC1 – OP) and soot (EC2 + EC3) (Han et al., 2009). The instrument performance was checked against the internal standards after the analysing every 10 samples. All the reported concentrations were corrected for laboratory and field blanks.

RESULTS AND DISCUSSIONS

Based on the climatic conditions and the air back trajectory analysis (Fig. 1) and following the classifications of seasons as per Indian Meteorological Department, India (http://www.imd.gov.in/Welcome%20To%20IMD/Welcom e.php), the present study is divided into four seasons, winter (December–March), summer (April–June), rainy (July–September) and autumn (October and November). The data are discussed on annual, seasonal and monthly average basis in subsequent sections.

Aerosol Load: Seasonal and Monthly Variations

The PM10 and PM>10 load ranged from 46 to 900 µg m–3 and from 76 to 1791 µg m–3 during the sampling period with an annual average of 215 ± 176 µg m–3 and 495 ± 459 µg m–3, respectively (Table 1). The monthly average aerosol loads are plotted in Fig. 2(A) with the seasonal averages in Fig. 2(B). The average PM10 load was highest in winter followed by summer, autumn and rainy season, while PM>10 load was highest in summer followed by winter, autumn and rainy season. The summer months encountered highest load of 900 µg m–3 (summer ave. = 239 µg m–3) for PM10 and 1791 µg m–3 (summer ave. = 720 µg m–3) for PM>10 during the sampling period and the World Health Organization’s highest load of 900 µg m–3 (summer ave. = 239 µg m–3) for autumn and rainy season. The summer months encountered with an annual average of 215 ± 176 µg m–3 and 495 ± 459 µg m–3, respectively (Table 1). The monthly average aerosol loads are plotted in Fig. 2(A) with the seasonal averages in Fig. 2(B). The average PM10 load was highest in winter followed by summer, autumn and rainy season, while PM>10 load was highest in summer followed by winter, autumn and rainy season. The summer months encountered highest load of 900 µg m–3 (summer ave. = 239 µg m–3) for PM10 and 1791 µg m–3 (summer ave. = 720 µg m–3) for PM>10 with high intra month variations (see error bars in Fig. 2). This suggests that the summer time dust storms are contributing more to PM>10 compared to PM 10 and 1791 µg m –3 (summer ave. = 720 µg m–3) for PM>10, the ion’s mass concentrations (µg m–3) were converted to nano equivalents (neq m–3) (Shen et al., 2007). The ∑ anions/∑ cations ratio in PM10 was 1.07, 1.05, 0.99 and 0.87 for winter, autumn, rainy and summer season samples, respectively. The correlation coefficient of 0.93 and 0.97 among ∑ anion and ∑ cation in PM10 and PM>10, respectively, indicated that major WSII have been identified with good reliability.

Annual Ionic Concentrations

The total WSII accounted for 13.5% of total PM10 load compared to 5% in PM>10 load (Table 1), an observation similar to Deshmukh et al. (2012). Hueglin et al. (2005) have reported nearly similar contributions of WSII to aerosols for an urban site in Switzerland. The percentage contributions of each ionic species to total WSII in PM10 and PM>10 load are shown in Figs. 3(A) and 3(B), respectively. In PM10, SO4 2– ions contribute maximum (54%) followed by NH4 +, NO3 – and Ca2+ to the total WSII (Fig. 3(A)). Pavuluri et al. (2011) have reported dominance of SO4 2– in PM>10. Higher Ca2+ in PM>10 is associated with higher PM10 load during winters compared to monsoon. The neutralizing species (calcium and magnesium) are dominant in PM>10 (Hueglin et al., 2005).

To calculate the ionic balance among WSII in PM10 and PM>10, the ion’s mass concentrations (µg m–3) were converted to nano equivalents (neq m–3) (Shen et al., 2007). The ∑ anions/∑ cations ratio in PM10 was 1.07, 1.05, 0.99 and 0.87 for winter, autumn, rainy and summer season samples, respectively. The correlation coefficient of 0.93 and 0.97 among ∑ anion and ∑ cation in PM10 and PM>10, respectively, indicated that major WSII have been identified with good reliability.

Seasonal and Monthly Variations

The season wise percentage contributions of WSII to the total PM10 and PM>10 are given in Table 1. The WSII were lowest in PM10 and PM>10 during summer season as compared with the NAAQS limits by nearly 15 times. The ambient PM10 load did not meet the NAAQS in winters and summers, but the PM10 load was higher during winters. The large scale open biomass burning and use of more coal in the thermal power plants to meet the excess energy demands are possible sources for PM10 during winters. In addition, the reduced mixing height due to temperature inversions during winters restrict the dispersion of fine particles and result in the accumulation of PM10 near the surface (Ram et al., 2012). In autumn season, PM10 load was higher in November compared to October month due to the burning of fire crackers during Diwali festival in North India (Tandon et al., 2008). Similar trends have been observed previously by Yadav and Rajamani, 2004; Rastogi and Sarin, 2009 based on their seasonal sampling done at different locations in north India.

Further, the PM10 load (annual ave. = 176 µg m–3) exceeded the Indian NAAQS for PM10 (100 µg m–3 for a 24 hour period averaging time and 60 µg m–3 for annual average) during the sampling period and the World Health Organization’s criteria (20 µg m–3). PM10 load has intermittently exceeded the NAAQS limits by nearly 15 times. The ambient PM10 load did not meet the NAAQS in winters and summers, but was within the limits in rainy and autumn seasons. Such high PM10 concentrations are largely responsible for increased pulmonary and cardio vascular diseases during winters and for the breathing and allergen related diseases during summer in this region (Yadav et al., 2007; Lim et al., 2012; Guttikunda and Goel, 2013).
Table 1. Seasonal and annual mean concentrations of load and water soluble inorganic ions (WSII) in PM$_{10}$ and PM$_{>10}$ collected over Delhi (± indicate standard deviation in the respective data).

<table>
<thead>
<tr>
<th></th>
<th>Winter (n = 16)</th>
<th>Summer (n = 11)</th>
<th>Rainy (n = 9)</th>
<th>Autumn (n = 7)</th>
<th>Annual Average (n = 43)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(December, January, February, March)</td>
<td>(April, May, June)</td>
<td>(July August, September)</td>
<td>(October, November)</td>
<td></td>
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<tr>
<td>Load</td>
<td>245 ± 117</td>
<td>239 ± 221</td>
<td>86 ± 45</td>
<td>163 ± 84</td>
<td>215 ± 176</td>
</tr>
<tr>
<td></td>
<td>220 ± 20</td>
<td>720 ± 462</td>
<td>82 ± 05</td>
<td>154 ± 20</td>
<td>495 ± 459</td>
</tr>
<tr>
<td>pH</td>
<td>4.92 ± 0.67</td>
<td>6.68 ± 0.36</td>
<td>6.30 ± 0.21</td>
<td>5.16 ± 0.65</td>
<td>6.06 ± 0.89</td>
</tr>
<tr>
<td></td>
<td>6.95 ± 0.41</td>
<td>7.02 ± 0.17</td>
<td>7.02 ± 0.14</td>
<td>6.81 ± 0.07</td>
<td>6.99 ± 0.18</td>
</tr>
<tr>
<td>F</td>
<td>0.53 ± 0.45</td>
<td>0.25 ± 0.15</td>
<td>0.01 ± 0.06</td>
<td>0.02 ± 0.07</td>
<td>0.24 ± 0.45</td>
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<td></td>
<td>0.03 ± 0.02</td>
<td>0.22 ± 0.09</td>
<td>0.01 ± 0.02</td>
<td>0.03 ± 0.01</td>
<td>0.14 ± 0.12</td>
</tr>
<tr>
<td>Cl</td>
<td>0.61 ± 0.36</td>
<td>1.23 ± 1.01</td>
<td>0.12 ± 0.01</td>
<td>0.18 ± 0.12</td>
<td>0.78 ± 1.40</td>
</tr>
<tr>
<td></td>
<td>4.05 ± 1.89</td>
<td>3.67 ± 1.62</td>
<td>1.01 ± 0.63</td>
<td>1.45 ± 0.59</td>
<td>3.02 ± 1.80</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>2.13 ± 1.28</td>
<td>4.36 ± 3.32</td>
<td>0.40 ± 0.12</td>
<td>2.93 ± 2.59</td>
<td>3.06 ± 3.04</td>
</tr>
<tr>
<td></td>
<td>2.83 ± 0.16</td>
<td>5.34 ± 1.95</td>
<td>0.98 ± 0.40</td>
<td>2.79 ± 0.41</td>
<td>4.05 ± 2.32</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>31.2 ± 21.5</td>
<td>10.8 ± 3.10</td>
<td>12.6 ± 10.3</td>
<td>13.4 ± 3.77</td>
<td>15.69 ± 12.9</td>
</tr>
<tr>
<td></td>
<td>1.89 ± 0.79</td>
<td>4.46 ± 1.69</td>
<td>0.74 ± 0.20</td>
<td>2.18 ± 0.14</td>
<td>3.30 ± 2.04</td>
</tr>
<tr>
<td>Na</td>
<td>0.67 ± 0.24</td>
<td>1.03 ± 0.46</td>
<td>0.73 ± 0.59</td>
<td>0.16 ± 0.05</td>
<td>0.80 ± 0.59</td>
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<tr>
<td></td>
<td>0.27 ± 0.11</td>
<td>1.07 ± 0.52</td>
<td>0.13 ± 0.01</td>
<td>0.29 ± 0.24</td>
<td>0.74 ± 0.59</td>
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<tr>
<td>NH$_4$</td>
<td>8.64 ± 5.52</td>
<td>0.69 ± 0.48</td>
<td>2.99 ± 2.63</td>
<td>2.88 ± 1.79</td>
<td>3.00 ± 5.19</td>
</tr>
<tr>
<td></td>
<td>0.30 ± 0.13</td>
<td>0.53 ± 0.31</td>
<td>0.02 ± 0.01</td>
<td>0.21 ± 0.14</td>
<td>0.39 ± 0.32</td>
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<tr>
<td>K</td>
<td>2.25 ± 0.81</td>
<td>1.62 ± 0.68</td>
<td>0.44 ± 0.25</td>
<td>3.04 ± 2.67</td>
<td>1.73 ± 1.23</td>
</tr>
<tr>
<td></td>
<td>0.48 ± 0.16</td>
<td>1.20 ± 0.59</td>
<td>0.11 ± 0.04</td>
<td>0.38 ± 0.17</td>
<td>0.85 ± 0.65</td>
</tr>
<tr>
<td>Ca</td>
<td>2.01 ± 1.14</td>
<td>5.31 ± 3.05</td>
<td>1.51 ± 0.71</td>
<td>1.42 ± 0.64</td>
<td>1.73 ± 1.23</td>
</tr>
<tr>
<td></td>
<td>3.24 ± 0.16</td>
<td>4.45 ± 1.63</td>
<td>1.04 ± 0.22</td>
<td>2.24 ± 0.19</td>
<td>3.50 ± 1.85</td>
</tr>
<tr>
<td>Mg</td>
<td>0.14 ± 0.12</td>
<td>0.44 ± 0.24</td>
<td>0.10 ± 0.03</td>
<td>0.13 ± 0.08</td>
<td>0.28 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>0.20 ± 0.02</td>
<td>0.46 ± 0.18</td>
<td>0.06 ± 0.01</td>
<td>0.19 ± 0.06</td>
<td>0.33 ± 0.22</td>
</tr>
<tr>
<td>WSII</td>
<td>48.24</td>
<td>13.30</td>
<td>25.72</td>
<td>18.92</td>
<td>29.09</td>
</tr>
<tr>
<td>% WSII$^\wedge$</td>
<td>19.70</td>
<td>6.04</td>
<td>9.93</td>
<td>22.09</td>
<td>16.32</td>
</tr>
</tbody>
</table>

*$^\wedge$ indicate percentage of total sum of all water soluble inorganic ions in the total load of respective size. All ionic data and mass loads are in µg m$^{-3}$ units.
Fig. 2. Mass concentrations of PM$_{10}$ and PM$_{>10}$ (> 10 µm aerodynamic diameter) collected during different months (panel A). Seasonal averages are shown in panel B. Relative Humidity influences particle growth and formation of secondary pollutants in atmosphere in tropical climate (Kong et al., 2015). The seasonal variations in ionic concentrations in PM$_{10}$ and PM$_{>10}$ are shown in Fig. 4. Sulphate concentration was found to be higher in PM$_{10}$ compared to PM$_{>10}$ in all seasons and the highest concentration of SO$_4^{2-}$ (31.2 ± 21.5 µg m$^{-3}$) was found in winter compared to other seasons. The NO$_3^-$ showed the highest concentration during summer followed by autumn, winter, and rainy season in both PM$_{10}$ and PM$_{>10}$. Unlike sulphate ions, nitrate was higher in PM$_{>10}$ compared to PM$_{10}$. The higher concentrations of nitrate in PM$_{>10}$ and in summer season need a suitable explanation. NO$_x$ is emitted by vehicular emissions, power plant, refineries, and biomass burning and its concentration in the atmosphere is influenced by meteorological factors like temperature and relative humidity (Wang et al., 2006). Nitrate ions are formed in atmosphere by the homogeneous gas phase transformation and oxidation from NO$_x$ to nitric acid, which then gets neutralized by ammonia to form ammonium nitrate. Coarse mode NO$_3^-$ can be formed by the reaction of mineral aerosols with gaseous nitric acid (Wolff, 1984; Radhi et al., 2010). Radhi et al. (2010) have proposed that the reaction among nitric acid and sodium chloride and calcium carbonate in Australian desert aerosols result in higher nitrate concentration (> 70%) in aerosols. Thus, the desert aerosols transported from the Thar desert in west of Delhi play an important role as a sink for nitric acid by providing an alkaline surface area for reaction of nitrogen oxides (Tabazadeh et al., 1998).

The NH$_4^+$ concentrations were more in PM$_{10}$ as compared to PM$_{>10}$ and highest in winters as compared to other seasons. Calcium was higher or nearly equal in PM$_{>10}$ compared to PM$_{10}$ except that PM$_{10}$ has high Ca$^{2+}$ in summers. The Ca$^{2+}$ concentration in aerosols increased during April–June, and the highest concentration of Ca$^{2+}$ (10.48 µg m$^{-3}$ in PM$_{10}$ and7.11 µg m$^{-3}$ in PM$_{>10}$) was recorded during a dust storm day on June 2, 2010. Carbonate of calcium and magnesium...
transported by dust storms or through local re-suspension of dust are dominant sources of Ca\(^{2+}\) in aerosols. K\(^+\), an indicator of biomass burning, was higher (3.04 ± 2.67 µg m\(^{-3}\)) in autumn followed by winters (2.25 ± 0.85 µg m\(^{-3}\)) compared to summer season. The high concentrations of K\(^+\) during autumn season are due to its emissions from fireworks on the occasion of Diwali festival (5\(^{th}\) November, 2010) as K\(^+\) is extensively used in fireworks and emitted in particulate matter form during cracker burning (Tandon et al., 2008), whereas winter time K is associated with biomass burning (Yadav et al., 2006, Ram et al., 2012). This region encounters large scale biomass burning by the general public to get rid of near zero temperature condition in whole northern India. Chloride showed the highest concentration during winter season. Cl\(^-\) comes from burning of fossil fuel (coal combustion), brick kilns, biomass burning etc. Sea salt aerosols (NaCl) react with atmospheric SO\(_2\) and NO\(_x\) to form Na\(_2\)SO\(_4\) and NaNO\(_3\) salts and release hydrochloric acid (HCl) into the atmosphere (Radhi et al., 2010; Tobo et al., 2010). It then gets transformed from gaseous phase to particle phase via neutralization reaction with ammonia (Meskhidze et al., 2005).

**Neutralization Factors**

The equivalent ratios of NH\(_4\)\(^+\)/(NO\(_3\)\(^-\) + SO\(_4\)\(^{2-}\)) were calculated, the value of 1.0 would indicate the complete neutralization of HNO\(_3\) and H\(_2\)SO\(_4\) by NH\(_4\)\(^+\) (Kumar et al., 2014) This ratio in PM\(_{10}\) varied from 0.03 to 0.8. This indicates that there could be cations other than NH\(_4\)\(^+\) which neutralizes acidic species in PM\(_{10}\). The correlation coefficient between NO\(_3\)\(^-\) + SO\(_4\)\(^{2-}\) and Ca\(^{2+}\) + Mg\(^{2+}\) + NH\(_4\)\(^+\) (R\(^2\) = 0.87) suggests that the acidity in PM\(_{10}\) is also neutralized by Ca\(^{2+}\) and Mg\(^{2+}\). The calculated values of the neutralization factors (NF) for the different seasons are shown in Table 2. In PM\(_{10}\), NH\(_4\)\(^+\) was the major neutralizing agent for the acidic species during winter and autumn season and Ca\(^{2+}\) was the major neutralizing agent in the summer samples (ave. NF = 0.94). The Ca\(^{2+}\) was dominant neutralizing agent in PM\(_{10}\) of all seasons. The carbonate of primary and secondary origin in the aerosols over Delhi are largely responsible for high calcium content (Yadav and Rajamani, 2004; Shen et al., 2007). The CO\(_3\)\(^{2-}\) content in aerosols affects the uptake of SO\(_2\) and NO\(_x\) and their conversion to SO\(_4\)\(^{2-}\) and NO\(_3\)\(^-\) on the particle surface as well as the removal of HNO\(_3\) and H\(_2\)SO\(_4\) from the gas phase (Dentener et al., 1996; Zhang et al., 2011).
Fig. 4. Seasonal concentrations of individual ionic species in PM$_{10}$ and PM$_{>10}$ (> 10 µm aerodynamic diameter).

**OC and EC CONTENT IN PM$_{10}$**

Total carbon content in PM$_{10}$ over Delhi was dominated by OC in comparison to EC and was highest (54.37 µg m$^{-3}$) in autumn and lowest (15.76 µg m$^{-3}$) in rainy season (Table 3). Therefore, TC and OC follow similar seasonal patterns. The TC contributed 22%, 8.8%, 18.3%, and 47.8% of total PM$_{10}$ mass in winter, summer, rainy and autumn samples, respectively. OC and EC varied from 9.91 to 37.06 µg m$^{-3}$ and 5.42 to 22.23 µg m$^{-3}$ during the year round sampling. The monthly and seasonal average concentrations of OC and EC are plotted in Fig. 5.

The OC/EC ratio was minimum during rainy season
compared to other seasons. This is attributed to the limited outdoor biomass and fossil fuel (coal) combustion activities on account of wet ambient conditions as well as to the removal of particles by rainwater and the process is termed as rain wash out process. Similar observations about low OC and EC in PM$_{10}$ of two different sites in India due to wet removal of particles during rainy season have also been made by Panicker et al. (2015). The higher OC in autumn season could be linked to the higher plant productivity soon after rainy season and high EC (17.3 µg m$^{-3}$) is a result of biomass burning that happens to clear crop fields after harvesting and for domestic purposes as autumn coincides with the festival season in India. During winters, both OC and EC are higher but among the two, OC (24.9 µg m$^{-3}$) is higher with the festival season in India. During winters, both OC and EC in Delhi’s PM$_{10}$ aerosols were higher as compared to megacities like Chennai (9.1 and 6.5 µg m$^{-3}$) (Pavuluri et al., 2011), Ahmedabad (12.8 and 2.1 µg m$^{-3}$) (Rastogi and Sarin, 2009), Mumbai (25.3 and 12.6 µg m$^{-3}$)(Venkataraman et al., 2002), and Beijing, China (21.2 and 8.9 µg m$^{-3}$) (Zhang et al., 2007). This was so because Chennai and Mumbai are coastal cities, and Ahmedabad too has coastal influence, whereas Delhi is an inland site.

The OC/EC ratios in aerosols are used as an empirical method to understand their emission sources (s) and transformation characteristics (Zhang et al., 2007). The OC/EC ratios for biomass burning are expected to be higher (~8) compared to fossil fuel combustion emission (~2) (Mayol-Bracero et al., 2002). In this study, the annual average OC/EC ratio, with a value of 2, indicate the dominance of fossil fuel (coal and vehicular exhausts) emissions compared to biomass burning. On seasonal considerations, OC/EC ratios showed highest value (3.61) during summer and lowest (1.12) in winter. In rainy and autumn season, this ratio was 1.70 and 2.14, respectively. The variations are primarily due the change in EC content from 22.2 µg m$^{-3}$ in winter to 5.4 µg m$^{-3}$ in summers. Again, the high EC is attributed to more operational combustions sources during winters compared to very limited combustion during summers. The summer time high and winter time low OC/EC ratios indicate the cooling efficiency and absorbing nature of aerosol, respectively in this region (Novakov et al., 2005). The seasonal variations could be attributed to either different source for OC and EC which become operational in one season and are limited in other season, photochemical reactions and dust mediated reactions leading to SOC formation, and to the meteorological conditions. In general, OC/EC ratios for most of the urban sites around the world fall in the range of 1.0 to 4.0, and a value of greater than 2 have been considered as indicative of SOC formation in the atmosphere (Cao et al., 2003).

The direct separation and quantification of POC and SOC is difficult using EC-OC analyzer. Here, SOC was calculated as:

$$\text{SOC} = (\text{OC})_{\text{hot}} - \text{POC}$$  \hspace{1cm} (2)

where, POC was estimated following the EC tracer method (Lim and Turpin, 2002) as:

$$\text{POC} = (\text{OC})_{\text{min}} \times (\text{EC})$$  \hspace{1cm} (3)

We have used the minimum OC/EC ratio of the respective
Fig. 5. Mass concentrations of OC and EC in PM$_{10}$ collected during different months. The seasonal averages are given in box.

seasons while calculating the SOC for each season(s). The POC and SOC concentrations are provided in Table 3. The results indicate that the formation of SOC seems to be a viable explanation for high OC/EC ratios in summers. The POC in summer PM$_{10}$ was 3.63 µg m$^{-3}$ whereas SOC was 15.93 µg m$^{-3}$ (nearly four time of POC). During winter POC (14.89 µg m$^{-3}$) dominates over SOC (10.04 µg m$^{-3}$). Therefore, high OC in summer is due to SOC. The low SOC formation has been explained in terms of a weak photochemical activity during winter period (Ram and Sarin, 2010). Biomass burning is largely responsible for nearly equal concentrations of OC and EC during winters.

Ram and Sarin (2009) have reported a common source for the OC and EC based on fairly good correlation among OC and EC in aerosols over northern India. However, a weak correlation was observed between OC and EC. This suggests that OC and EC fractions were not contributed by a single primary source rather could be related to multiple sources, SOA formation and meteorological factors (Cachier et al., 1996).

The relatively lower EC/TC ratios (0.1–0.2) are used as marker of biomass burning sources and higher ratios (~0.5) indicate contribution from fossil fuel combustion (Ram and Sarin, 2010). The EC/TC ratios were greater than 0.2 throughout the sampling period indicating the dominant contribution from fossil fuel combustion sources in this region. In addition, K$^+$/OC and K$^+$/EC ratios are also used to differentiate the biomass burning and fossil fuel combustion sources. Relatively high K$^+$/EC ratios (0.21–0.46) have been reported for biomass burning and low ratios (0.025 to 0.09) for fossil fuel emissions (Andare, 1983; Ram and Sarin, 2010). K$^+$/EC ratio showed the value of 0.23 in comparison to other sites in India, for example 0.30–0.69 at Allahabad, 0.08–0.19 at Jaduguda and 0.15–0.98 at Kanpur (Ram and Sarin, 2010), 0.28–1.21 at Hisar (Rengarajan et al., 2007). Based on the observations, EC/TC ratio supports more fossil fuel combustion, poor correlation of OC and EC, and a fair correlation of K$^+$ and EC; it will be wise to consider the mixing of different sources (biomass burnings, fossil fuel combustion and desert aerosols) under the influence of prevailing meteorological conditions.

The total carbonaceous material (TCM) was estimated (Yttri et al., 2007) as:

$$ TCM = OM + EM $$

where, OM = 1.6 × OC and EM = 1.1 × EC.

Although a wide range of values for OM/OC ratios (1.2 to 2.1) have been reported in the literature (Turpin and Lim, 2001) but a factor of 1.6 has been widely accepted as a representative for urban aerosols (Cao et al., 2003). A conversion factor of 1.1 was used to convert EC to EM (Kiss et al., 2002). TCM varied from 13–48% on year round basis and accounted for 48%, 30%, 26% and 13% of the PM$_{10}$ load during autumn, winter, rainy, and summer seasons, respectively. The strong correlation between TCM and PM$_{10}$ ($R^2 = 0.94$) during winter and autumn season implied that both have common source or their sources are interrelated. The average EC and OC concentrations during autumn and winter are 2 to 3 times higher than in summer. The larger contributions of TCM to PM$_{10}$ are attributed to fireworks during Diwali festival (autumn), biomass burning, and enhanced coal consumption for heating purposes and long range transport of TCM from the nearby states of Haryana and Punjab (Ram and Sarin, 2010; Singh and Kaskaoutis, 2014) as compared to summer and rainy seasons.

The Analysis of Eight Carbon Fractions

The eight carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP) have been used to identify the sources of carbonaceous aerosols as each of the fraction differs in their emission sources (Chow et al., 2004). The concentrations of these carbon fractions showed seasonal changes (Fig. 6). The OC2, OC3, OP and EC1 were the most abundant carbon species and each one contributed above 10% to the total carbon irrespective of the sampling season. The high OC1 concentration was observed in autumn season. The OC1 seems to be biogenic in nature as this is the season of
Fig. 6. Percentage contributions of eight carbon fractions to the total carbon content in PM10 collected in different seasons over Delhi.

High plant growth in India. The OC2 is abundant in winter and autumn season samples due to biomass and fossil fuel combustions. The OC4 shows the highest concentration during the summer season and may be associated with the re-suspension of road dust (Chow et al., 2004). The high OP fraction implied that substantial water soluble polar compounds might be present in Delhi atmosphere as observed by Gu et al. (2010) in Tianjin, China and in Delhi by Yadav et al. (2013). The EC1 was found highest during winter season due to biomass and coal combustion and the prevailing meteorological conditions. The percentage contributions of char were more compared to soot to the total EC. The annual average value of char was 11.94 µg m⁻³ similar to that observed by Zhu et al. (2014) for urban environment in Xi'an, China. The analysis of these carbon fractions indicated the multiple emission sources, motor vehicle exhaust, fossil fuel and biomass burnings, and mineral dust.

The Principal component analysis (PCA) had been applied for identifying the sources of eight carbon fraction concentrations analysis in many studies (Cao et al., 2005). For PM₁₀ samples three factors explained 90.49% of the total variance in the data (Table 4). Factor 1, explaining 41.07% of the variance, showed high loading for OC1, OC2 and OC3 indicating the emissions from coal combustion, biomass burning and motor-vehicle exhaust. Factor 2, which explained 38.67% of the variance, had high loadings for OC4, OP, EC2 and EC3, represented vehicle exhaust or formed from condensation of volatile compounds. Factor 3 has loading of only EC1 and marked as biomass and coal combustions source.

**CONCLUSIONS**

The PM₁₀ and PM₉₁₀ load exceeded the Indian NAAQS of 60 µg m⁻³ (24 hours mean) and 100 µg m⁻³ (annual average). The percentage contributions of WSII to the total load were high in PM₁₀ (13.5%) as compared to that in PM₉₁₀ (5%). This suggested that the crustal material which dominated in PM₉₁₀ show limited solubility whereas the winter time aerosols contained more of anthropogenic contributions and secondary pollutants formed by oxidation or neutralization reactions or by heterogeneous (solid- water phase) reactions that were water soluble. The PM₁₀ water soluble chemistry was dominated by SO₄²⁻ (54%) followed NH₄⁺-NO₃⁻ whereas NO₃⁻ and Ca²⁺ were dominant ions in PM₉₁₀. In PM₁₀ samples, NH₄⁺ was the major neutralizing ion except that Ca²⁺ contributed maximally in summer samples. In PM₉₁₀, Ca²⁺ ions were major neutralizing agent in all seasons. Wind assisted transport and intermittent events of severe dust storms were dominant source of PM₁₀ and PM₉₁₀ during summers whereas the biomass burning and the prevailing meteoro logical parameters (low wind speed, lower planetary boundary layer and temperature inversion conditions) were responsible for accumulations of PM₁₀ load during winters. Biomass burning and fire cracking during Diwali festival could contribute during autumn season.

The OC dominated TC and contributed 52.8%, 78.3%, 62.9% and 68.2% of the TC during winter, summer, rainy and autumn seasons, respectively (EC contributed the balance to make up 100% TC). The OC/EC ratio was highest (3.61) during summer compared to winter ratio (1.12). The SOC was maximum (15.93 µg m⁻³ in 19.6 µg m⁻³ OC) during
summer season suggesting the role of mineral dust and high photochemical activity for SOC formation. Further, the poor correlation of OC and EC indicated different sources for OC and EC. K7/EC ratio indicated influence of biomass burning. Among the eight different fractions, three dominant sources were identified, coal combustion, biomass burning and motor vehicle exhaust for OC1, OC2 and OC3; vehicle exhaust contributed OC4, OP, EC2 and EC3; and biomass and coal combustion for EC1. The results suggest that there are multiple carbon sources, proportions of which vary with season. Overall, the monthly and seasonal variations in load, WSII and carbon content of PM10 and PM>10 are influenced by sources, emission strength of sources and the prevailing meteorological conditions during the sampling period. There is an urgent need to control the air pollution sources to safeguard human health in Delhi region.

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SUPPLEMENTARY MATERIAL

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

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