Characteristics and Sources of Carbonaceous Aerosols in PM$_{2.5}$ during Wintertime in Agra, India

Tripti Pachauri, Aparna Satsangi, Vyoma Singla, Anita Lakhani, K. Maharaj Kumari*

Department of Chemistry, Faculty of Science, Dayalbagh Educational Institute, Dayalbagh, Agra 282110, India

ABSTRACT

PM$_{2.5}$ samples were collected at traffic, rural and campus sites in Agra during Nov 2010 to Feb 2011 and characterized for carbonaceous aerosols. The average mass concentrations of PM$_{2.5}$ were 308.3 ± 51.8 $\mu g/m^3$, 91.2 ± 17.3 $\mu g/m^3$ and 140.8 ± 22.3 $\mu g/m^3$ at the traffic, rural and campus sites, respectively. The 24-h mass concentrations of PM$_{2.5}$ were significantly higher than the limit of 60 $\mu g/m^3$ prescribed in the National Ambient Air Quality Standards (Indian NAAQS) and 25 $\mu g/m^3$ of those of the WHO (World Health Organization). The average concentrations of OC (organic carbon) and EC (elemental carbon) were 86.1 ± 5.2 and 19.4 ± 2.4 at the traffic site, 30.3 ± 12.9 and 4.0 ± 1.5 at the rural site and 44.5 ± 18.5 $\mu g/m^3$ at the campus one. The contributions of TCA (Total Carbonaceous Aerosol) at the traffic, campus and rural sites were found to be 52, 54 and 58% of PM$_{2.5}$ mass, respectively. A significant correlation was observed between water soluble K$^+$ and OC at the rural ($R^2 = 0.63$) and campus ($R^2 = 0.53$) sites compared to the traffic one ($R^2 = 0.35$). This may be attributed to increased biomass burning emissions at the rural and campus sites. The concentrations of SOC (Secondary Organic Carbon) were estimated based on the minimum OC/EC ratio, and were found to be 15.3 ± 6.3, 8.2 ± 5.8 and 28.8 ± 15.8 $\mu g/m^3$, accounting for 18, 24.7 and 60.7% of total OC at the traffic, rural and campus sites, respectively. The surface morphology of the particles was analyzed by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDX). The results indicated branched chain-like aggregates of carbon bearing spheres at the traffic and rural sites, while at the campus site carbon-rich and minerogenic (mineral dust) particles were the dominant ones.

Keywords: Organic carbon; Elemental carbon; PM$_{2.5}$; SEM/EDX; SOC.

INTRODUCTION

Atmospheric aerosols play an important role in regional air quality, public health, atmospheric chemistry and climate change especially over East Asia (Jacobson, 2001). They are produced from various natural and anthropogenic sources and have significant direct radiative impact through absorption and scattering of incoming radiation (Haywood and Boucher, 2000; Tare et al., 2006). It comprises a mixture of sulfates, nitrates, carbonaceous particles, sea salt, and mineral dust (Hansen et al., 2000). Atmospheric carbonaceous particles have recently gained importance because of their influence on climate and adverse health effects (Frazer, 2002). Carbonaceous matter is usually classified into organic carbon (OC) and elemental carbon (EC). Elemental carbon is a primary pollutant emitted from anthropogenic combustion sources and does not undergo chemical transformations, while OC can be either released directly into the atmosphere from anthropogenic and biogenic sources (primary OC, POC) or formed within the atmosphere through gas-to-particle conversion of volatile organic compounds through photochemical reactions (secondary OC, SOC) (Turpin and Huntzicker, 1995; Cao et al., 2003; Seinfeld and Pandis, 2006). EC possesses a strong capability of absorbing solar radiation and is considered to play an important role in global climate change as it causes positive radiative forcing. It is the second most important component of global warming, after CO$_2$ (Hansen et al., 2000; Jacobson, 2001) while OC is mainly a scattering medium and exerts a negative climate forcing influence (Houghton et al., 2001; Li and Bai, 2009). Despite the evident significance of carbonaceous aerosols in the process of air chemistry and physics information concerning their exact impacts on climatic and environmental processes is still limited because of our poor understanding of its concentrations, chemical composition and formation mechanisms (Jacobson et al., 2000; Li and Bai, 2009; Zhang et al., 2011).

With increasing industrial development and urbanization, the contribution from anthropogenic sources to aerosol loading has significantly increased, especially over the urban/industrial locations of South Asia (Praveen, 2009; Safai et al., 2010; Zhang et al., 2011; Deshmukh et al.,...
2012b, c, d). This significant increase in air pollution resulted from natural as well as anthropogenic aerosols consisting of black carbon (BC), organic carbon, dust, sulfates, nitrates, and fly ash often referred as Atmospheric brown clouds (ABCs) (Ramanathan et al., 2005). Considering the key role of ABCs in atmospheric radiative as well as chemical properties, several experiments have been carried out including Indian Ocean Experiment (INDOEX) to develop emissions inventory for PM$_{2.5}$ (Reddy and Venkataraman, 2000) as well as Black carbon (BC) and organic matter (OM) (Reddy and Venkataraman, 2002a, b). In addition to these studies, there are several studies focusing on the field measurements of carbonaceous aerosols in TSP (Rengarajan et al., 2007; Sudheer and Sarin, 2008; Ram et al., 2008; Ram and Sarin, 2010a; Satsangi et al., 2010; Kumar et al., 2012; Satsangi et al., 2012), PM$_{10}$ (Venkataraman et al., 2002; Ram and Sarin, 2010b) and PM$_{2.5}$ (Ram and Sarin, 2011; Rengarajan et al., 2011) but the detailed information regarding the concentration levels and site to site variation of carbonaceous aerosols in fine particles (PM$_{2.5}$) is still limited in India.

Therefore, the present work has been carried out to compare the relative contribution of carbonaceous species (OC and EC) to PM$_{2.5}$ mass during Nov. 2010 to Feb. 2011 at traffic, rural and campus sites of Agra, India and to identify the possible sources and factors affecting carbonaceous species. An attempt has also been made to characterize the elemental composition and morphology of individual atmospheric particles using SEM-EDX method. During winter season, extensive use of biomass combustion results in significant increase of atmospheric particles and gaseous pollutants which are known to have major impact on local atmospheric chemistry and human health. Thus, in order to evaluate the enhanced pollution the present study mainly emphasizes on characterization of carbonaceous aerosols during wintertime.

**MATERIALS AND METHODS**

*Description of Sampling Sites*

Agra (27°10’N, 78°05’E, and 169 m.s.l.) is located in the north central part of India. It is the home of world famous heritage monument Taj Mahal. It is bounded by the Thar Desert of Rajasthan on its South East, West and North West peripheries and is therefore, a semiarid area with a marked monsoon season.

In the present study, three sites were selected for the collection of PM$_{2.5}$ samples in Agra (Fig. 1): traffic (National Highway II), rural (Lal Gadi) and campus site (Dayalbagh Educational Institute). The site descriptions are as follows.

National Highway II: It is the busiest highway of Agra. This site is influenced by heavy traffic flow with more than 10$^5$ average traffic loads of vehicles per day (Satsangi et al., 2012). It lies about 3 km away from the industrial area (Nunhai). The sampler was mounted on the rooftop of a roadside house (8 m away from road) about 15 m height above the ground.

Lal Gadi: This is small village situated at the northern outskirts of Agra city. This site is surrounded by agricultural fields with minimal traffic/industrial activity. Coal, wood, crop residues and cowdung cakes are mainly used as fuel for cooking purpose. Agricultural activities predominate throughout the year (Kulshrestha et al., 2009). The sampler was installed on the rooftop of a one story small house about 12 m above the ground levels.

Dayalbagh Educational Institute: This campus site is about 10 km away from the industrial sector of the city. The Institute campus lies by the side of the road that carries mixed vehicular traffic on the order of 10$^4$ vehicles in a day (Satsangi et al., 2012). This site is surrounded by

![Fig. 1. Location of Agra indicating traffic, rural and campus sites.](image)
small residential community. Therefore, it represents mixed area of traffic and residential environments. The sampler was placed on the roof of Science Faculty building about 12 m above the ground level.

**Sample Collection and Quality Control**

PM$_{2.5}$ samples (n = 48; 16 samples per site) were collected using Fine Particulate Sampler (Envirotech APM 550) operated at a constant flow rate of 16.6 L/min on pre-weighed 47 mm quartz fibre filters (Palfflex, Tissuquartz). Simultaneously sampling was done for 24 h with frequency of once a week at all the three sites during winter season from Nov 2010 to Feb 2011. Before exposure, the quartz fiber filters were pre-heated in a muffle furnace at 800°C for 3 h to remove organic impurities. Filters were weighed thrice before and after sampling using four digit balance (Mettler, Toledo, reading precision 10 μg). Before weighing the samples were equilibrated in desiccators at 20–30°C and relative humidity of 20–35% in humidity controlled room for 24 h. The conditioned and weighed PM$_{2.5}$ filters were placed in cassettes and placed inside polyethylene zip-lock bags and taken to the field for sampling to avoid contamination of the filters on the way. Laboratory blank filters (n = 4) were also collected to reduce gravimetric bias due to filter handling during and after sampling. Filters were handled only with tweezers coated with Teflon tape to reduce the possibility of contamination. After weighing the samples were wrapped in aluminum foil and sealed in polyethylene zip-lock bags and stored in deep freezer at -4°C until the time of analysis to prevent the degradation of organic compounds due to photo-oxidation. It was assumed that the collected particulate matter was uniformly distributed over the entire area of filters.

The fine particulate sampler is designed to work at a constant flow rate of 16.67 ± 0.83 L/min. The flow rate of the sampler was calibrated before every sample through Gas Flow Meter for “Leak Test” in order to avoid any air leakage and to check accurate flow of air to the sample. Daily flow rate calculations (gas meter reading/timer reading) were made to make sure that the fluctuations in flow rate are within the range. Glass fibre filter in the wins impactor was changed after 48 h of sampling or when the filter gets clogged. The filter in the wins impactor was rinsed with 3–4 drops of silicon oil at regular intervals as per the need. Periodic cleaning of the sampler was done to make the sampler dust free so that the dust on the sampler may not be counted with the mass concentration of the sample.

Blank test was also monitored by using operational blanks (unexposed filters), which were processed with field samples. The blank filters were taken once a month. They were exposed in the field when the field-sampling box was opened to remove and replace field samples. Field blank values were very low (0.2 ± 0.1 μg), typically below or around the method detection limits (0.28 ± 0.1 μg/m$^3$, using 3σ values of total procedural blank concentrations of the filter).

**Carbonaceous Species Analysis and Quality Control**

A portion of filter samples (1.5 cm$^2$) was cut and analyzed for OC and EC by a thermal/optical Carbon Aerosol Analyzer (Sunset Laboratory, Forest Grove, OR) using NIOSH 5040 (National Institute of Occupational Safety and Health) protocol based on Thermal Optical Transmittance (TOT). A detailed procedure for the analysis of OC-EC has been described in Satsangi et al. (2012).

Standardization of the Instrument was carried out by sucrose solution (3.2 μg/μL). A solution of 10 μL gives 32.0 ± 1.8 μg OC. For quality control, the analyzer was calibrated using a blank punch of pre-heated Quartz Fiber Filter and standard sucrose solutions every day. Sampled quartz filters were also analyzed similarly for blank corrections. The overall blank concentrations from the quartz filters for OC and EC were 0.5 ± 0.2 and 0.0 ± 0.02 μg/cm$^2$, respectively. These were subtracted from the measured OC and EC concentrations in the aerosol samples. The detection limit, precision and accuracy of OC and EC is given in Table 1.

**Water-Soluble K$^+$ Analysis and Quality Control**

Water soluble K$^+$ was analyzed by using Dionex ICS 1100 Ion Chromatograph system (Dionex Corp, Sunnyvale, CA) equipped with guard column (CG12A), analytical column (CSRS 300), and cation self-regenerating suppressor (CSRS 300). To extract, half of each filter was sonicated for 45 min in 1% HNO$_3$ (Parmar et al., 2001) and K$^+$ was eluted using 20 mM Methane Sulfonic Acid as an eluent (mobile phase). A series of K$^+$ standards were used in order to quantify the resulting peak from the ion chromatography. Detection limit, precision and accuracy of K$^+$ are 0.06 ppm, 3.7% and 1.5%, respectively (Satsangi et al., 2012). For quality control, unloaded filter was extracted as described above and analyzed for blank corrections and subtracted from the measured K$^+$ concentrations in the aerosol samples.

**SEM-EDX Analysis**

PM$_{2.5}$ samples collected from different sites were analyzed by SEM-EDX at National Institute of Oceanography, Goa. The SEM-EDX analysis was carried out with the help of computer controlled field emission scanning electron microscope SEM (JSM-5800 LV) equipped with an energy dispersive X-ray system (Oxford 6841). The dry and loaded quartz fiber filters were punched in 1 mm$^2$ from the centre of each sample. All the samples were mounted on plastic stubs for gold coating. A very thin film of gold (Au) was deposited on the surface of each sample using vacuum coating unit called Gold Sputter Coater (SPI-MODULE) which can prepare 6 samples at a time. The fine coating of gold makes the samples electrically conductive. The samples were placed in the corner of SEM-EDX chamber. The working conditions were set at an accelerating voltage of 20 kV, a beam current of 40–50 μA and a Si (Li) detector 10 mm away from the samples to be analyzed. X-Ray detection limit is ~0.1%. The Oxford ISIS EDS system with 133 eV resolutions is capable of collecting spectrum from multiple points, lines across the interface and elemental mapping.

EDX analysis was carried out at each analysis point and the elements present were both qualitatively and quantitatively measured. Approximately 100 particles were analyzed on each filter. The EDX spectra of blank Quartz fiber filter was also obtained and their composition was manually subtracted.
during the evaluation of the EDX spectra of individual aerosol particles

**Meteorological Data Analysis**

The climate of Agra is divisible into three distinct seasons; summer (March–June), monsoon (July–September) and winter (October–February) (IMD report, 2009). The winter season is associated with cold and stable conditions with low ambient temperature which sometimes drops below 2°C. Relative humidity in the winter ranges between 41.8 and 91.4%. Meteorological data viz. ambient temperature, rainfall, relative humidity, wind speed and wind direction were recorded through an automatic weather monitoring system (Envirotech’s Wind Monitor WM271) mounted on the roof of Science Faculty building, 12 m above the ground level. It was programmed to collect data at 1 min. interval and store them in memory to be downloaded to a computer. The weather conditions were very cold and calm during winter season (46.8% calm, Fig. 2). The wind speed varied in a range of 0.4 to 7 m/s. The temperature varied from 3 to 31°C whereas relative humidity varied between 41 and 91%. Table 2 shows the mean and ranges for meteorological parameters during the sampling period.

**Back Trajectory Analysis**

In order to identify the source and transport pathways of the airborne particles arriving at the sampling site, the air mass backward trajectory analysis was carried out. These air mass back-trajectories were obtained from the final run data archive of Global Data Assimilation System model using NOAA (National Oceanic and Atmospheric Administration) Air Resource Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (http://www.arl.noaa.gov/ready/hysplit4.html (accessed via NOAA ARL Realtime Environmental Applications and Display System (READY) website http://ready.arl.noaa.gov). The five-day back trajectory analysis of winter months was simulated at 12:00 hrs (local time) at 500, 1000 and 1500 m above the ground level and has been represented in Figs. 3(a) and 3(b). The results indicate short trajectories originating from local areas around Agra indicate the dominance of anthropogenic emission sources.

### Table 1. Method Detection Limit, precision, accuracy and number of field blanks below detection limits of different species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Method Detection Limit</th>
<th>Precision (%)</th>
<th>Accuracy (%)</th>
<th>No. of Field Blanks Below Detection Limit (n = 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$ (µg/m³)</td>
<td>0.28</td>
<td>2.1</td>
<td>1.3</td>
<td>6</td>
</tr>
<tr>
<td>OC (µg/cm²)</td>
<td>0.2</td>
<td>1.7</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>EC (µg/cm²)</td>
<td>0.01</td>
<td>1.5</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>K⁺ (ppm)</td>
<td>0.06</td>
<td>3.7</td>
<td>1.5</td>
<td>5</td>
</tr>
</tbody>
</table>

**Fig. 2.** A wind rose plot for winter season showing 46.8% calm wind at Agra.

### Table 2. Mean and ranges for meteorological parameters at sampling site Agra during Nov 2010–Feb 2011.

<table>
<thead>
<tr>
<th>Month</th>
<th>Temperature (°C)</th>
<th>Rainfall (mm)</th>
<th>Relative Humidity (%)</th>
<th>Vapor Pressure (kPa)</th>
<th>Wind Speed (m/s)</th>
<th>Wind Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>November 2010</td>
<td>21 (10–31)</td>
<td>0.0 (0–0.1)</td>
<td>57 (41–61)</td>
<td>1.6 (1–1.8)</td>
<td>2.8 (1.2–3.6)</td>
<td>NE</td>
</tr>
<tr>
<td>December 2010</td>
<td>19 (12–29)</td>
<td>0.1 (0–0.2)</td>
<td>61 (48–77)</td>
<td>1.3 (0.9–2.4)</td>
<td>3.1 (2.1–7)</td>
<td>NE</td>
</tr>
<tr>
<td>January 2011</td>
<td>11 (3–18)</td>
<td>0.4 (0–0.6)</td>
<td>78 (56–91)</td>
<td>1 (0.7–1)</td>
<td>3.8 (0.4–4.6)</td>
<td>N</td>
</tr>
<tr>
<td>February 2011</td>
<td>23 (8–28)</td>
<td>0.1 (0–1)</td>
<td>68 (51–82)</td>
<td>1.2 (0.4–2)</td>
<td>5.2 (0.9–6.8)</td>
<td>NW</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Concentration Levels of PM$_{2.5}$

The mass concentrations of PM$_{2.5}$ ranged from 210.8 to 381.7 $\mu$g/m$^3$ at traffic site, 72.9 to 118.2 $\mu$g/m$^3$ at rural site and 101.3 to 163.9 $\mu$g/m$^3$ at campus site, respectively. At the three sites, the average mass concentrations ranked in the order of traffic (308.3 ± 51.8 $\mu$g/m$^3$) > campus (140.8 ± 22.3 $\mu$g/m$^3$) > rural (91.2 ± 17.3 $\mu$g/m$^3$) sites as shown in Table 3. The average daily concentration of PM during the measurement period exceeded the 24 hour NAAQS of India (60 $\mu$g/m$^3$; http://www.cpcb.nic.in/National_Ambient_Air_Quality_Standard.php) and WHO (25 $\mu$g/m$^3$; whqlib.doc.who.int/hq2006/WHO_SDE_PHE_OEH_06.02_eng.pdf) 24-h guidelines 100% of the time, respectively.

At traffic site, the concentrations levels were 2.2 and 3.3 times higher than campus and rural site which may be attributed to higher vehicular emissions and resuspended road dust. On the other hand, various local sources such as vehicular exhaust, waste incineration and residential heating around campus site and coal as well as biomass combustion at rural site were the dominant sources contributing significantly to PM$_{2.5}$ mass. In addition to these anthropogenic emissions, the stable meteorological conditions during winter season (high RH and low wind speed) favor the accumulation of pollutants. A wind rose (WR) plot of winter months showed low and steady wind speed (mainly confined to 0–1 m/s; Fig. 2). These climatic conditions i.e. less dispersion and low mixing heights or lower boundary layer height, typically 500–1000 m (Nair et al., 2007) during winter months help the ambient particles to remain for longer time in the atmosphere. These stagnant meteorological conditions is also supported by the results of back trajectory analysis that shows that the site is under the influence of different local emissions and account for increased levels of particulate mass (Fig. 3(a) and 3(b)).

Table 3 summarizes comparison of PM$_{2.5}$ mass levels in India and other cities of the world during winter period. On comparison with other traffic site, the mean concentrations were much higher than the values reported at other traffic dominated sites like Kathmandu, Nepal, Polytechnic University, China, Beijing Normal University, China and Milan, Italy, Durg city, Chhattisgarh (215 $\mu$g/m$^3$; Deshmukh et al., 2011) and Raipur (268 $\mu$g/m$^3$; Deshmukh et al., 2013b) but lower than the Industrial site of China, Xian. At rural site, the mean concentrations were much lower than the values reported at other rural sites like Wusumu, Jinan and Miyun but comparable with Linan. However, the mean concentration was much higher than reported at Rancha, Jordan. The levels of PM$_{2.5}$ at Dayalbagh University campus was found to be comparable with Jilin University, China but higher than National University campus, Singapore, Gwangju University campus, Korea, Jimei University, China, Institute of Geochemistry, Chinese Academy of Sciences, Wushan, China. However, the mass concentration was found to be lower than Zhongshan University, Guangzhou, China, Tsinghua University, Beijing, China and University of Engineering & Technology campus, Lahore, Pakistan and Pandit Ravi Shankar Shuklia University, Raipur (225 $\mu$g/m$^3$; Deshmukh et al., 2013a). A clear distinction observed between the concentration levels at Agra and other sites is largely due to variation of site and source emissions.
Table 3. Comparison of PM$_{2.5}$, OC and EC concentrations during winter period in India and other cities in the world.

<table>
<thead>
<tr>
<th>Location</th>
<th>Site</th>
<th>Period</th>
<th>PM$_{2.5}$ (µg/m$^3$)</th>
<th>OC (µg/m$^3$)</th>
<th>EC (µg/m$^3$)</th>
<th>OC/EC</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xiamen, China</td>
<td>Jimei University</td>
<td>Jan 2010</td>
<td>99.9 ± 5.17</td>
<td>28.9 ± 4.3</td>
<td>4.5 ± 0.4</td>
<td>6.5 ± 1</td>
<td>Zhang et al. (2011)</td>
</tr>
<tr>
<td>Gwangju, Korea</td>
<td>University Campus</td>
<td>Nov 2008–Feb 2009</td>
<td>8.8–111.0</td>
<td>2.13–19.52</td>
<td>0.67–10.1</td>
<td>1.4–7.9</td>
<td>Park and Cho (2010)</td>
</tr>
<tr>
<td>Changchun, China</td>
<td>Jilin University</td>
<td>Jan 2003</td>
<td>140.5 ± 28.6</td>
<td>39.2 ± 8.7</td>
<td>13.5 ± 2.9</td>
<td>2.9</td>
<td>Cao et al. (2007)</td>
</tr>
<tr>
<td>Guangzhou, China</td>
<td>Zhongshan University</td>
<td>Jan 2003</td>
<td>156.0 ± 93.6</td>
<td>41.1 ± 29.6</td>
<td>14.5 ± 9.9</td>
<td>2.8</td>
<td>Cao et al. (2007)</td>
</tr>
<tr>
<td>Wushan, Guangzhou, China</td>
<td>Institute of Geochemistry, Chinese Academy of Sciences</td>
<td>Feb–March 2005</td>
<td>129.9 ± 86.3</td>
<td>23.9 ± 19.9</td>
<td>4.4 ± 2.2</td>
<td>5.0</td>
<td>Duan et al. (2007)</td>
</tr>
<tr>
<td>Singapore</td>
<td>National University Campus</td>
<td>Jan–Dec 2000</td>
<td>10–69 (27.2)</td>
<td>7.34</td>
<td>3.26</td>
<td>-</td>
<td>Balasubramanian et al. (2003)</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Tsinghua University</td>
<td>Nov 1999–March 2000</td>
<td>175.9</td>
<td>31.49</td>
<td>11.08</td>
<td>-</td>
<td>He et al. (2001)</td>
</tr>
<tr>
<td>Rachma, Jordan</td>
<td>Rural</td>
<td>Jan–Dec 2007</td>
<td>25 ± 7</td>
<td>2.2 ± 0.2</td>
<td>0.45 ± 0.1</td>
<td>5.0</td>
<td>Schneidermesser et al. (2010)</td>
</tr>
<tr>
<td>Wusumu, China</td>
<td>Rural</td>
<td>Jan 2006</td>
<td>115.6</td>
<td>28.6</td>
<td>3.2</td>
<td>-</td>
<td>Han et al. (2008)</td>
</tr>
<tr>
<td>Miyun, China</td>
<td>Rural</td>
<td>Dec 2001</td>
<td>683.1 ± 233</td>
<td>72.6 ± 24</td>
<td>37 ± 29</td>
<td>3.2</td>
<td>Dan et al. (2004)</td>
</tr>
<tr>
<td>Linan, China</td>
<td>Rural</td>
<td>Oct–Dec 1999</td>
<td>90 ± 47</td>
<td>44 ± 25</td>
<td>3.4 ± 1.7</td>
<td>-</td>
<td>Xu et al. (2002)</td>
</tr>
<tr>
<td>Jinan, China</td>
<td>Rural</td>
<td>March 2006–Feb 2007</td>
<td>146.8</td>
<td>35.24</td>
<td>5.67</td>
<td>-</td>
<td>Yang et al. (2012)</td>
</tr>
<tr>
<td>Hok Tsui, China</td>
<td>Rural</td>
<td>Winter 2006–2007</td>
<td>-</td>
<td>6.23</td>
<td>2.78</td>
<td>-</td>
<td>Huang et al. (2012)</td>
</tr>
<tr>
<td>Xian, China</td>
<td>Industrial</td>
<td>January 2003</td>
<td>375.2 ± 143</td>
<td>102 ± 33</td>
<td>21.6 ± 5.4</td>
<td>4.7</td>
<td>Cao et al. (2007)</td>
</tr>
<tr>
<td>University, China</td>
<td>Polytechnic University</td>
<td>Nov 2000–Feb 2001</td>
<td>52.5 ± 5.4</td>
<td>11.2 ± 1.8</td>
<td>6.4 ± 1.2</td>
<td>1.8</td>
<td>Ho et al. (2006)</td>
</tr>
<tr>
<td>Polytechnic</td>
<td>University, China</td>
<td>Nov 2000–Feb 2001</td>
<td>204.5</td>
<td>47.6</td>
<td>70.9</td>
<td>0.7</td>
<td>Lonati et al. (2005)</td>
</tr>
<tr>
<td>Polytechnic</td>
<td>University, China</td>
<td>Dec 2001</td>
<td>257.6 ± 85.8</td>
<td>41.2 ± 20.8</td>
<td>31.6 ± 31</td>
<td>7.4</td>
<td>Dan et al. (2004)</td>
</tr>
<tr>
<td>Polytechnic</td>
<td>University, China</td>
<td>Jan–Feb 2002</td>
<td>60 ± 22.9</td>
<td>10.6 ± 3.7</td>
<td>6.1 ± 1.8</td>
<td>1.7</td>
<td>Cao et al. (2003)</td>
</tr>
<tr>
<td>Polytechnic</td>
<td>University, China</td>
<td>Nov 2000–Feb 2001</td>
<td>50.9</td>
<td>9.4</td>
<td>5.8</td>
<td>-</td>
<td>Ho et al. (2003)</td>
</tr>
<tr>
<td>Kanpur, India</td>
<td>Urban</td>
<td>Oct 2008</td>
<td>74–324</td>
<td>47.0</td>
<td>7.7</td>
<td>-</td>
<td>Ram and Sarin (2011)</td>
</tr>
<tr>
<td>Ahmedabad, India</td>
<td>Urban</td>
<td>Dec 2006–Jan 2007</td>
<td>55.7 ± 17</td>
<td>18.3 ± 5.9</td>
<td>3.0 ± 0.9</td>
<td>6.2</td>
<td>Rengarajan et al. (2011)</td>
</tr>
<tr>
<td>Agra, India</td>
<td>Dayalbagh University campus (n = 16)</td>
<td>Nov 2010–Feb 2011</td>
<td>140.8 ± 22.3</td>
<td>44.5 ± 18.5</td>
<td>5.0 ± 1.4</td>
<td>8.1</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>Rural (n = 16)</td>
<td>Nov 2010–Feb 2011</td>
<td>91.2 ± 17.3</td>
<td>30.3 ± 12.9</td>
<td>4.0 ± 1.5</td>
<td>7.4</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>Traffic (n = 16)</td>
<td>Nov 2010–Feb 2011</td>
<td>308.3 ± 51.8</td>
<td>86.1 ± 5.2</td>
<td>19.4 ± 2.4</td>
<td>4.4</td>
<td>Present study</td>
</tr>
</tbody>
</table>
Concentration of Carbonaceous Species in PM$_{2.5}$

The average concentrations of OC, EC, OC/EC ratio and TCA (total carbonaceous aerosol) show strong site variation with the highest concentration at traffic site followed by rural and campus sites, respectively. The average concentration of OC was 86.1 ± 5.2, 30.3 ± 12.9 and 44.5 ± 18.5 μg/m$^3$ at traffic, rural and campus sites, respectively. The OC mass concentration at traffic site was about 2.8 and 1.9 times higher than rural and campus sites, respectively. This may be attributed to increased emissions from vehicular exhaust. The emissions from automobile exhaust are the main sources of VOCs (Volatile organic compounds) emitted anthropogenically. Kerbachi et al. (2006) reported that near heavy road traffic, mobile sources account for 75–85% of the aromatic VOCs emissions of which 70% is from automobile exhaust. During winter season dispersion and dilution of pollutants is restricted due to temperature inversion phenomenon and low mixing heights which causes accumulation of these organic compounds and hence, high levels of OC was observed. However, the EC concentrations were found to be 19.4 ± 2.4, 4.0 ± 1.5 and 5.0 ± 1.4 μg/m$^3$ at traffic, rural and campus sites, respectively. Furthermore, the percentage contribution of OC to PM$_{2.5}$ mass was found to be 28%, 33% and 31.6% while EC contribute 6.2%, 4.3% and 3.5% to PM$_{2.5}$ mass concentrations at traffic, rural and campus sites, respectively. The results show that OC contribute nearly one third of fine particulate mass at rural and campus site while found to be lower at traffic site. On applying t-test, the variations in OC and EC concentrations at different sites was observed to be statistically significant. The critical value of $t$ ($P = 0.05$) for 30 degrees of freedom is 2.04; since the experimental value of $t$ is greater than this value (18.2, 16.4 and 14.9 between traffic, campus and rural sites) the difference between the results are significant at the 5% level. These results indicated that carbonaceous aerosols at Agra were influenced more or less by local factors at various types of sampling sites.

In Table 3 levels have been compared with only those sites where carbonaceous aerosols was analyzed by NIOSH method using thermal/optical carbon analyzer and data was for winter period and sites have similar characteristics. As shown in Table 3, OC and EC concentrations at traffic site were much higher than the values reported at other traffic dominated sites like Kathmandu, Nepal, Polytechnic University, China, but lower than the Industrial site of China, Xian. It is interesting to note that the levels of OC was found to be lower than the present study but EC levels were drastically higher at Beijing Normal University, China and Milan, Italy. On comparison with other rural sites of China the levels of OC and EC were found to be comparable with the concentrations at Wusumu but lower than reported at Miyun and Jinan. However, the mean concentration was much higher than reported at Raelma, Jordan and Hok Tsui. At Dayalbagh University campus, the OC concentration levels was found to be comparable with Zhongshan University, Guangzhou, China but higher than National University campus, Singapore, Gwangju University campus, Korea, Jimei University, China and Institute of Geochemistry, Chinese Academy of Sciences, Wushan, China. However, EC mass concentration was found to be lower than Zhongshan University, Guangzhou, China, Tsinghua University, Beijing, China and University of Engineering & Technology campus, Lahore, Pakistan. On comparison with Dayalbagh University campus, the levels of OC and EC reported at two urban sites of India were found to be higher at Kanpur while lower at Ahmedabad. This observed variation may be due to the different source emissions at different sites.

Contribution of Carbonaceous Species to PM$_{2.5}$

Total carbonaceous aerosol was calculated by the sum of EC and organic matter (OM) which was estimated by multiplying the amount of OC by 1.6 (for urban) and 2.1 (for non-urban) (TCA = 1.6 × OC + EC) (Turpin and Lim 2001; Cao et al., 2003; Rengarajan et al., 2007). The average concentration of TCA was 157.3 ± 10.6, 61.3 ± 22.1 and 76.3 ± 30.5 μg/m$^3$ at traffic, rural and campus sites, respectively. TCA contribute 52, 54 and 58% to total PM$_{2.5}$ mass at traffic, campus and rural sites indicating that the fine particles at all the three sampling sites are enriched with carbonaceous species. Higher contribution of TCA may be attributed to higher emission sources of carbonaceous aerosols as well as unfavorable meteorological conditions like low wind speed, low mixing height, frequent inversion etc. that results in stagnation of the pollutants. Various studies conducted in India during winter season also report high TCA contribution (as high as 60%) to PM$_{10}$ mass at Kanpur (Ram et al., 2010b) and almost 58% to PM$_{2.5}$ mass at Ahmedabad (Rengarajan et al., 2011). Increased levels of TCA at traffic site may be attributed to high vehicular emissions mixed with some industrial emissions from industrial area (nearly 3 km away). On the other hand, increased emissions from extensive biomass burning (coal, fuel wood, cow dung cakes etc) were the dominant source contributing to carbonaceous aerosols at rural site as well as campus site. According to the emission inventory models, biofuel/biomass burning account for 50 to 90% of carbonaceous aerosol emission from south Asia and for India, it is ~70% (Gustafsson et al., 2009; Rengarajan et al., 2011). In India, for the year 1990, burning of biomass and fossil fuels contributed about 64% and 36% to the total fuel consumption respectively (Venkataraman et al., 1999). The largest contributions were from the burning of wood (33%), coal (30%), animal waste (14%), and agricultural residues (13%) (Deshmukh et al., 2010b). Most of the biomass burned in India is used as fuel for cooking and heating on the other hand the major fossil fuels burnt are coal and diesel (Venkataraman et al., 1999). Mayol-Bracero et al. (2002) during INDOEX (Indian Ocean Experiment) reported that biomass burning accounts for ~20% and fossil fuel ~80% of the total carbonaceous aerosol emission, whereas the observation from the Bay of Bengal during winter time suggested more than 80% from biomass burning. This observed biomass burning was mainly in the form of biofuel combustion, which is widely used in India, mainly for household purposes (Olivier et al., 1994; Reddy and Venkataraman, 2002a).

A significant correlation between water soluble K$^+$ and
OC abundances further supports that the biomass burning emissions are the main source of carbonaceous species at rural (R² = 0.63) and campus (R² = 0.53) sites, respectively (Fig. 4). Xu et al. (2012) has also reported a good correlation between K⁺ and OC (0.77) during winter season in Fuzhou, China. Due to release of K⁺ during combustion processes, it is generally used as an index of biomass burning (Deshmukh et al., 2010a; Deshmukh et al., 2012a). The K⁺/OC and K⁺/EC ratios can be used to characterize the emission sources biomass burning in comparison with fossil fuel. Relatively high K⁺/EC ratios have been reported for biomass burning (range: 0.21–0.46) and low ratios for fossil fuel emissions (range: 0.025–0.09) (Andreae 1983; Ram and Sarin, 2010a). A ratio of K⁺/EC reported at various sites of India varied from 0.30–0.69 at Allahabad, 0.08–0.19 at Jaduguda and 0.15–0.98 at Kanpur (Ram and Sarin, 2010a), 0.28–1.21 at Hisar (Rengarajan et al., 2007). Table 4 shows the K⁺/OC and K⁺/EC ratios from selected sites of India. In the present study, K⁺/EC ratios at rural site ranges from 0.3 to 0.69 with an average value of 0.53 while at campus site it varies from 0.2 to 0.59 with an average value of 0.48. The relatively higher value of K⁺/EC ratios indicates biomass burning emissions. However, at traffic site, the average value of K⁺/EC ratio (0.08 ± 0.03) was found to be indicative of fossil fuel emissions.

**Relationship between OC and EC**

The origin of OC and EC can be evaluated by the relationship between OC and EC (Turpin and Huntzicker, 1995; Chow et al., 1996; Li and Bai, 2009). A good OC-EC correlation with correlation coefficient (R) of 0.87 (± 0.3 and ± 11.2 error in slope and intercept), 0.94 (± 2.3 and ± 0.9 error in slope and intercept) and 0.79 (± 3.8 and ± 1.2 error in slope and intercept) were obtained for traffic, rural and campus site respectively (Fig. 5). These results indicated the presence of common dominant sources for OC and EC (biomass burning, coal combustion and motor vehicular exhaust) because the relative rates of OC and EC would be proportional to each other. The variation of regression slope (1.8–8) might have been resulted from the site variability (different source emissions), meteorological factors and SOC (secondary organic carbon) formation.

The mass ratios of OC to EC (OC/EC) are used to interpret the emission and transformation characteristics of carbonaceous aerosol. They are influenced by emission sources of OC and EC, secondary organic aerosol (SOA) formation and different removal rates by deposition of OC and EC (Cachier et al., 1996). If the OC/EC ratios exceed 2.0, it suggests secondary organic aerosol formation in addition to primary emission sources. Thus, OC/EC ratios have been used to indicate the presence of primary as well as secondary organic aerosols (Chow et al., 1996). Several studies have reported OC/EC ratio for various emission sources which includes vehicular exhaust (OC/EC: 2.5–5.0, Schauer et al., 2002), coal smoke (OC/EC: 2.5–10.5, Chen et al., 2006), kitchen emissions (OC/EC: 4.3–7.7, See and Balasubramanium, 2008) and biomass burning (OC/EC: 3.8–13.2, Zhang et al., 2007). It should be noted that the OC/EC ratios presented above were measured by TOT method, which were comparatively higher than those by

![Fig. 4. Correlation between OC and K⁺ mass concentration collected at traffic, rural and campus sites of Agra.](image)

**Table 4. Comparison of the average K⁺/OC and K⁺/EC ratios in India.**

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>Time period</th>
<th>K⁺/OC</th>
<th>K⁺/EC</th>
<th>Emission sources</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dayalbagh University campus, Agra</td>
<td>Nov 2010–Feb 2011</td>
<td>0.05 ± 0.11</td>
<td>0.48 ± 0.2</td>
<td>Biomass burning</td>
<td>Present study</td>
</tr>
<tr>
<td>Rural, Agra</td>
<td>Nov 2010–Feb 2011</td>
<td>0.13 ± 0.1</td>
<td>0.53 ± 0.27</td>
<td>Biomass burning</td>
<td>Present study</td>
</tr>
<tr>
<td>Traffic, Agra</td>
<td>Nov 2010–Feb 2011</td>
<td>0.3 ± 0.1</td>
<td>0.08 ± 0.03</td>
<td>Fossil fuel emissions</td>
<td>Present study</td>
</tr>
<tr>
<td>Kanpur</td>
<td>Oct–2008</td>
<td>0.06 ± 0.02</td>
<td>0.28 ± 0.1</td>
<td>Biomass burning</td>
<td>Ram and Sarin (2011)</td>
</tr>
<tr>
<td>Kanpur</td>
<td>Jan–Feb 2007</td>
<td>0.04 ± 0.01</td>
<td>0.42 ± 0.18</td>
<td>Biomass burning</td>
<td>Ram and Sarin (2010a)</td>
</tr>
<tr>
<td>Allahabad</td>
<td>Dec 2004</td>
<td>0.05 ± 0.01</td>
<td>0.44 ± 0.11</td>
<td>Biomass burning</td>
<td>Ram and Sarin (2010a)</td>
</tr>
<tr>
<td>Hisar</td>
<td>Dec 2004</td>
<td>0.08 ± 0.02</td>
<td>0.64 ± 0.19</td>
<td>Biomass burning</td>
<td>Rengarajan et al. (2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.04–0.13</td>
<td></td>
<td>Agricultural waste burning</td>
<td></td>
</tr>
</tbody>
</table>
In the present study, the ratio of OC/EC were in the range of 3.6–5.2, 5.5–8.7 and 4.5–11.9, with the averages of 4.4 ± 0.3, 7.5 ± 1.1 and 8.1 ± 2.4 at traffic, rural and campus sites, respectively. This variation might be due to different surroundings at all the three sites. The ratios were similar to that reported in the literature for vehicular exhaust at traffic site, coal smoke, kitchen emissions and biomass burning at rural site while all the above sources contribute to OC/EC ratio at campus site. The OC/EC ratio is mostly greater than 2 for most of the samples indicating the dominance of OC derived from various burning sources (coal, biomass and biofuel) as well as the presence of secondary organic particles. However, high ratios could also be attributed to winter season. During winter months, several reasons are responsible for high OC/EC ratios namely: increased residential combustion of coal and wood contribute more to OC than EC, resulting in increased emission of volatile organic precursors, the stagnant meteorological conditions (low mixing layer height) resulted in more SOA formation in wintertime, more semi-volatile organic compounds condensed into aerosol in lower temperature. The high wintertime OC/EC ratio have also been observed in many studies of China like Beijing (Dan et al., 2004), Guangzhou and Hong Kong (Duan et al., 2007), Taiyuan (Meng et al., 2007), Tianjin (Li and Bai, 2009) and Shanghai (Feng et al., 2009).

**Estimation of Secondary Organic Carbon (SOC)**

The direct separation and quantification of primary organic carbon (POC) and secondary organic carbon (SOC) are difficult. Therefore, minimum OC/EC ratio method has received widespread application for the estimation of secondary organic carbon (Turpin and Huntzicker, 1995; Castro et al., 1999). This approach suggests samples having low OC/EC ratio contain almost exclusively primary carbonaceous compounds. So concentration of SOC can be estimated from primary carbonaceous compounds and TOC (total organic carbon) using following equation:

\[
SOC = TOC - POC
\]  

where, \(OC/EC\) is the value of the lowest OC/EC ratio. Since the ratios of OC/EC is usually affected by many factors such as types of emission sources, temporal and spatial variation, ambient temperature etc. Therefore, the measurements of POC and SOC are semi-quantitative (Castro et al., 1999). The observed values of (OC/EC)min in this study were 3.6, 5.5 and 5.1 at traffic, rural and campus sites, respectively. These values are close to that reported at some sites of China, Shanghai (2.2–5.3, Feng et al., 2009), Guangzhou (2.3–4.5, Duan et al., 2007) and India, Ahmedabad (4.7, Rengarajan et al., 2011) Allahabad (5.7, Ram and Sarin, 2010a), Mt Abu (3.4–4.8, Ram and Sarin 2008) and Manora Peak (4.8–6.5, Ram and Sarin, 2008).

The calculated average concentrations of SOC at three sampling sites using the minimum OC/EC ratio are given in Table 5. The SOC concentration in PM2.5 samples ranged from 2.2–25.3 \(\mu g/m^3\) at traffic site, 2.7–17.3 \(\mu g/m^3\) at rural site and 5.4 to 50.1 \(\mu g/m^3\) at campus site. The average concentration of SOC were 15.3 ± 6.3, 8.2 ± 5.8 and 28.8 ± 15.8 \(\mu g/m^3\) accounting for 18, 24.7 and 60.7% of total OC, at traffic, rural and campus sites, respectively. Among the three sites, highest contribution of SOC was observed at campus site followed by rural and traffic sites. During winter season, stable atmospheric conditions strengthen atmospheric oxidation and enhance the condensation of volatile secondary organic compounds (VSOCs) on pre-existing aerosol (Strauder et al., 1999; Duan et al., 2007). The formation of SOA occurs both with the oxidation of naturally emitted terpenes and with anthropogenic volatile organic compounds (VOCs) (Ho et al., 2006).

At campus site, high SOC concentration (55% of TC = OC + EC) may be attributed to combined effect of anthropogenically emitted VOCs (namely benzene, toluene and xylene, BTX) from combustion sources as well as naturally emitted terpenes (as the site is surrounded by deciduous trees which emit terpenes). Singla et al. (2012) have also monitored and reported high concentrations of VOCs during the same study period. These emitted VOCs
were assumed to act as source for secondary aerosol formation. At rural site, the carbonaceous particles were mainly of primary origin (66% of TC) because of increased biofuel and biomass burning emissions while some percentage of SOC (22%) may be contributed by oxidation of naturally emitted terpenes from deciduous trees surrounding the rural site. However, at traffic site POC contribution to TC is highest (67%) probably due to increased primary emissions from Diesel and Gasoline vehicles. At this site, high EC/TC percentage (18%) is observed which also indicates the dominance of fossil fuel combustion. SOC contributes only a small fraction of TC (15%) at this traffic dominated site as a result of oxidation of anthropogenically emitted VOCs from vehicles (> 10^5 vehicles/day).

These results were in agreement with other studies of India that reported high contribution of SOC to total OC especially during winter season at Beijing (64%, Dan et al., 2004; Tianjin (46.9%, Li and Bai, 2009), Xiamen (60.1%, Zhang et al., 2011). In India, the estimated concentrations of SOC contribute (~45% during day) and (~35% during night) (Ram and Sarin, 2011) and (12−42%, Rengarajan et al., 2011) of OC in PM2.5 samples during winter season.

**SEM/EDX Characterization of PM2.5 Samples**

Morphological characteristics (texture, edges and size) of ambient atmospheric particles collected from different sites were compared in order to determine their origin. The surface morphology of the particles collected from the traffic site indicated to have branched aggregates of carbonaceous matter. SEM images of the BC particles collected from the exhaust pipe of a petroleum car show similar co-aggregates of nanometer-sized BC particles (50−100 nm) (Fu et al., 2006). Bang et al. (2004) also observed aggregates of crystalline or nano crystalline particulates, ranging from as few as 2 to more than 1000 nanocrystals and amorphous branched clusters of carbonaceous spherules originated from fuel combustion processes including diesel exhaust (DPM; diesel particulate matter). Various other studies have also reported the presence of carbon chain agglomerates derived from fossil fuel combustion (Murr and Bang, 2003; Sachdeva and Attri, 2008; Edgerton et al., 2009). The results of single particle analysis indicated the presence of carbon as well as Pb bearing particles. The carbon particles were dominated by C, O (> 90% relative contribution by weight) and traces of chloride. These carbon rich particles have nearly spherical morphology and porous surface configuration which facilitates the surface deposition of OC functional groups (Hansen, 2005) (Fig. 6(a)). Pb bearing particles as shown in Fig. 6(b) also have high percentage of C (> 85% relative contribution by weight) and traces of chloride. Sitzmann et al. (1999) has also reported the presence of Pb particles in road traffic samples in London.

At rural site, burning of coal, wood and other combustibles substances produced clustered and branched carbonaceous particles as illustrated in Figs. 6(c) and 6(d). These soot particles were dominated by chain like aggregates of carbon bearing spheres. Various studies have reported that the morphology of carbonaceous particle originated from combustion processes varied from soot chains to complex structures, which depend on fuels, burning conditions and atmospheric processes (Cong et al., 2009; Pósfai and Buseck, 2010; Tumolva et al., 2010). These branched clusters results from the interconnection of often hundred of carbonaceous spherules which stick together through a combination of adhesive surface forces and partial coalescence which occur at high temperature common during combustion (Murr and Bang, 2003). In the present study, some individual carbonaceous spherules with traces of chloride were also found. Similar type of carbon-rich particles associated with Cl and Si traces originated from burning has also been reported by various studies (Shi et al., 2003, 2005) while Sachdeva and Attri (2008) have reported biomass soot aggregates with elongated flattened fiber like structure. Li et al. (2003) and Pósfai et al. (2003) has also reported biomass burning influenced aerosol during single particle analysis. Analysis of individual particles collected from campus site was differentiated into two types of particles: carbon rich particles (Fig. 6(e)) and minergenic (mineral dust) particles (Fig. 6(f)). Carbon rich particles were clearly characterized by chain like and “fluffy” appearance while minergenic particles were of irregular shape. These particles were strongly enriched with carbon (> 98% relative contribution by weight) while minergenic particles were a complex mixture of carbon rich particle containing varying amount of soil related components like Na, K, Mg, Ca and Al. The weight percentage of different elements present in mineral dust particles were in order of Ca (29) > Na (22) > C (16) > Al (14) > K (16) > Mg (3). These particles indicated that carbon rich particles were internally mixed with the mineral dust particles of local origin. Earlier study by Li et al. (2010) has also reported such type of particles during individual particle analysis in the coastal city of South China. The SEM/EDS characterization of airborne particles at Agra by Pipal et al. (2011) also show the dominance of particles rich in carbon and soil related elements. Edgerton et al. (2009) have reported that soot particles containing trace amounts of potassium are indicative of wood burning. In the present study, few carbon rich particles with traces of K and Cl (15−20% relative contribution by weight) indicating the contribution of wood burning emissions.

**CONCLUSIONS**

Organic carbon (OC) and elemental carbon (EC) were
Fig. 6. *Scanning electron images and energy dispersive X-ray spectra: (a) A single carbon particle with nearly spherical morphology dominated by C and O (> 90%) along with traces of chloride (b) A PbCl₂ particle (c) Scanning electron images of branched clusters of soot particles embedded in the filter paper. (d) The texture of branched cluster of soot particles (> 98% relative contribution by weight) with a high magnification (e) A single soot particle with characterized by chain-like and “fluffy” appearance (f) A irregular shaped minerogenic particle characterized by complex mixture of carbon rich particle containing varying amount of soil related components like Na, K, Mg, Ca and Al. *Images a and b collected at rural site, Images c and d collected at traffic site, Images e and f collected at campus site.
measured in PM$_{2.5}$ at traffic, rural and campus sites of Agra, India. Weekly samples were collected during winter season from November 2010 to February 2011. During the sampling period, 24 h average mass concentrations ranged from 210–381 μg/m$^3$, 101–163 μg/m$^3$ and 72–118 μg/m$^3$ at traffic, campus and rural sites, respectively. Relatively high mass concentrations at traffic site may be attributed to higher vehicular emissions and resuspended road dust. The average concentration of OC ranged from 77–95, 16–51 and 28–68 μg/m$^3$ while EC ranged from 12–18, 2–6 and 3–7 μg/m$^3$ at traffic, rural and campus sites, respectively. TCA contributed about 52 to 58% of PM$_{2.5}$ mass at different which is probably due to increased emission sources and less dispersion during winter period. High K$^+$/EC ratios at rural and campus sites indicated biomass burning emissions while low ratios at traffic site show that fossil fuel emissions were dominant. A good OC-EC correlation with correlation coefficient (R) of 0.87, 0.94 and 0.79 at traffic, rural and campus sites suggested the presence of common dominant sources for OC and EC. Low SOC concentrations at rural and traffic sites revealed primary origin of carbonaceous particles. SEM/EDX analysis of particles shows the dominance of clusters or aggregates of carbon particles at traffic and rural sites while at campus site carbon rich particles with “fluffy” appearance and minerogenic particles with irregular shape were found.

ACKNOWLEDGEMENTS

The authors are grateful to the Director, Dayalbagh Educational Institute Agra; Head, Department of Chemistry; for facilities provided; Dr. Shyam Prasad and Mr. Vijay Khedekar, National Institute of Oceanography, Goa for SEM-EDX analysis of aerosol samples and Department of Science and Technology, DST project No.: SR/S4/AS.273/07, New Delhi for financial assistance.

REFERENCES


Deshmukh, D.K., Deb, M.K., Tsai, Y.L. and Mkoma, S.L. (2010a). Atmospheric Ionic Species in PM$_{2.5}$ and PM$_1$. 988


