Characterization and Morphological Analysis of Summer and Wintertime PM$_{2.5}$ Aerosols Over Urban-Rural Locations in Delhi-NCR

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Abstract
Present study investigates the urban-rural variation of aerosols morphological and chemical characteristics. Summer and winter time 24 hourly sampling for PM$_{2.5}$ was carried out at an urban and rural location in Delhi and National Capital Region (NCR) using a Mini-Volume Air Sampler. High PM$_{2.5}$ concentrations were observed at the urban site (87.3μg/m$^3$, 155.56μg/m$^3$) compared to those at the rural (39.46μg/m$^3$, 91.62μg/m$^3$) in summer and winter seasons respectively. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) were used to characterise the PM$_{2.5}$ aerosols in the urban and rural area in the two seasons. SEM images shows different particle shapes at the urban and rural site in summer and winter seasons. SEM results showed the presence of flaky, aggregates and irregular shaped particles dominated in the urban area in summer season whereas rural area was relatively cleaner. In the winter season, rural site was observed to be dominated by spherical and irregular shaped particles indicating the combustion sources whereas particles were observed in a more concentrated form at the urban site. EDX analysis indicates the varying percentages of C, Cu, Zn, Co, Ni, Fe (representative elements) at both the rural and urban sites in both the seasons. Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) three day backward air mass trajectories
indicated the influence of Western and N-W air masses over Delhi-NCR for both the summer and winter seasons respectively. Further, this study reveals the variability of PM$_{2.5}$ particles morphological and elemental composition in different seasons at urban and rural locations and highlighted the different probable sources associated with them.

**Keywords:** PM$_{2.5}$; SEM-EDX; urban-rural; elemental composition

**INTRODUCTION**

The deteriorating air quality in the megacities and the surrounding rural areas have become a matter of concern in the both the developed and developing world. In India, the PM$_{2.5}$ (particles with diameter $\leq 2.5\mu m$) aerosols monitoring have gained importance over the last decade because of their vital role not only in the regional climate studies but in other aspects, such as the air quality, human health, socio-economic and cultural, as well. The National Capital, Delhi, is experiencing rapid economic growth and urbanization which has resulted in the severe air pollution scenarios in the last few years (Hazarika and Srivastava, 2016). The rapidly increasing population and therefore the increasing energy consumption have also helped in alleviating the problem. The National Capital Region (NCR), comprises of the various towns and villages of three states such as Haryana, Uttar Pradesh and Rajasthan which share their border with Delhi, is one of the commercially important and a rapidly urbanizing region. This increase in air pollution, esp. the PM$_{2.5}$ levels, play a major role in the regional/local climate change because of their small size and large residence time.

Depending upon their composition certain particles can cause "cooling" (e.g. sulphate aerosols) or "heating" (e.g. Black Carbon) by scattering/absorbing the incoming solar radiation (Massling et al. 2015). The morphological properties of the particles are useful in understanding the light scattering properties of the particles (Buseck et al. 2000). Light scattering properties depend upon the particle’s shape and size and refractive index. The shape and size of the particles differ from region-to-region and seasonally, thus changing their optical properties such as Single Scattering Albedo (SSA), Extinction Efficiency ($Q_{ex}$) and Assymetry parameter (g) (Mishra et al. 2015). Therefore, regional and seasonal specific ground based measurements regarding the PM$_{2.5}$ aerosols physical and chemical properties is required in order to understand their optical properties and hence their role in regional climate change.

Imaging techniques, such as Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) coupled with the Energy Dispersive X-Ray Spectroscopy (EDX) are one of the very useful and powerful techniques to gain an insight into the morphological properties of the particulate matter (Paoletti et al. 1999; Casuccio et al. 2004). These properties help in identifying the possible sources of the particles. Detailed review of the particles morphology have been provided by Pošfai and Buseck (2010). These techniques have been used both nationally and internationally to study the physical and chemical properties of the PM$_{2.5}$ aerosols (Tasic et al. 2006; Rodriguez et al. 2009; Pipal et al. 2011; Tiwari et al. 2015).
Many studies regarding the PM$_{2.5}$ characteristics covering different regions/locations like urban, rural, natural background and different seasons have been carried out globally (Viana et al. 2008; Putaud et al. 2010; Khan et al. 2010). Various studies over Delhi have been carried out (Apte et al. 2011; Chelani et al. 2013; Trivedi et al. 2014; Tiwari et al. 2014; Tiwari et al. 2015; Pant et al. 2015) regarding the role of particulate matter and their chemical and morphological properties but the same information regarding the urban and rural scenario are very few (Pipal et al. 2011; Rastogi et al. 2016). The capital Delhi has been reported to have the highest PM$_{2.5}$ concentration among 20 cities in the world (Steering Committee Report 2015). Some studies have focussed on the indoor PM$_{2.5}$ concentration in the rural area (Massey et al. 2009; Joon et al. 2011; Mukhopadhyay et al. 2012) but the outdoor PM$_{2.5}$ studies in the rural area needs to be explored.

Present study is a comparative study of the PM$_{2.5}$ levels, their morphological and chemical properties and possible sources of these particles in the urban and rural locations in Delhi-NCR in both the summer and winter seasons.

**METHODOLOGY**

**Study area**

The Delhi-NCR comprises area of 58332 km$^2$ with a population of 56.88 million. The population of Delhi increased from 13 million in 2001 to 16 million in the year 2011 (Census of India, 2011). Delhi has seen a 3.63% surge in the energy demand from the year 2005 to 2015. Also, in Delhi the number of registered vehicles has been reported to be 8.8 millions (2014-15). Increase in number of vehicles such as cars, taxis, jeeps, auto rickshaws, buses etc. and two-wheelers like scooters and motor cycles has led to an increase in the pollution levels in Delhi (Economic Survey of Delhi, 2014-2015). Delhi-NCR falls in a semiarid climate zone experiencing different seasons during the course of a year namely, Summer (April-June), Monsoon (July-August), Post-Monsoon (September-November), winter (December-January) and spring (February-March). Summers are usually long with temperature going up to as high as 45°C during daytime (Guttikunda and Gurjar, 2012). The winters are generally cold with calm winds and temperatures going as low as 4-5°C. A strong inversion layer forms over the region during the winters. The average annual rainfall in this region is approximately 670mm. The wind direction is generally north-westerly throughout the year except during monsoon period when it is south-westerly. Sampling was carried out for summer (May-June) and winter (December-January) seasons for the year 2015 at two locations in Delhi-NCR briefly described below.

**Sampling sites**

**Urban site**

Shahdara, Delhi (28.68°N, 77.29°E) is one of the oldest and highly urbanized areas of Delhi, consisting both the residential as well as industrial establishments around it.
The sampling site was located near the main Loni Road which is a major arterial road connecting Delhi and Saharanpur, (Uttar Pradesh). It is one of the busiest roads experiencing heavy traffic 24 hours of the day. Loni Road comprises of many shops such as of utilities, local eateries (*dhabhas*), printing presses, mechanics shops or motor repairing shop/workshop and businesses mainly of plywood and timber. The Shahdara Railway Station and Metro Station are located around two kilometers from the sampling site.

**Rural site**

Sampla, Haryana (28.77°N, 76.76°E) in NCR which is situated around 60km away NW of Delhi represented the rural site which was surrounded mainly by the vast agricultural fields. A few factory establishments and one or two brick kilns are established approximately 10kms away from the sampling site. The national highway (NH-10) and Sampla railway station are located approx. 1-1.5 kms away from the sampling site. Sampla is surrounded by the four major cities/towns such as Bahadurgarh, Rohtak, Sonepat and Jhajjar which are around 20-40 kms away from the sampling site. Nearest is the Bahadurgarh (approx. 20kms away) which is an industrial area with industries and factories ranging from shoe manufacturing, steel, textiles and chemicals.

**PM$_{2.5}$ sampling**

**Sampling and quality control**

Sampling for PM$_{2.5}$ was carried out with the Tactical Air Sampler (TAS) Mini-Vol® Air sampler (Airmetrics) with a constant flow rate of 5L/min for 24 hours a day. The sampler works with a rechargeable lead-acid battery with a 24 hour backup with low flow and low battery shut-offs. PM2.5 sampling was carried out using Whatmann quartz fibre filters (47mm) for 5 days each in both the summer and winter seasons at Shahdara and Sampla respectively. The sampler was placed at a height of 1.5 meters above the floor level of the second floors of residential buildings at each sampling site throughout the study. Filter papers were kept in dessicator with silica gel for 24 hours both pre and post-sampling. Blank filters were also treated in the same way. The sampler pump draws air at the rate of 5litres/minute, which is made to pass through an impactor leading to collection of PM$_{2.5}$ on a quartz filter paper. After sampling the samples were put in the aluminium foil covered petri dishes which were sealed with the plastic cover and cellotape and stored in the refrigerator till further analysis. Samples were weighed pre and post-sampling using microbalance (SARTORIUS GD603) with 0.0001mg accuracy. Care was taken to handle the samples with the forceps all the time. Weight of the samples was calculated gravimetrically. Field and lab blank samples were collected and their concentrations were subtracted from the measured concentrations. Total of 20 samples were collected at both the sampling sites in the summer and winter seasons. The average temperature and relative humidity during the sampling in Delhi-NCR in summer and winter months were 32.8°C, 50.7% and 13.4°C, 66.0% respectively (www.wunderground.com).
SEM-EDX Analysis

SEM-EDX technique was used to analyze PM$_{2.5}$ samples collected from the two sites at Advanced Instrumentation Research Facility (AIRF) in Jawaharlal Nehru University (JNU), New Delhi. The SEM-EDX analysis was carried out with the help of a computer controlled scanning electron microscope SEM (Carl Zeiss EVO 40, Cambridge) coupled with an energy dispersive X-ray (EDX) system (Bruker X-Flash detector 3010, Germany). Prior to the SEM analysis, the samples were mounted on aluminium stubs using double sided carbon tape for gold coating to make the samples electrically conductive. A very thin film of gold (Au) was deposited on the surface of each sample in vacuum coating unit called Gold Sputter Coater (POLARON-SC7640, UK). The samples were placed in the vacuum chamber of SEM instrument at the designated positions for analysis. The SEM working conditions were set at an accelerating voltage of 20 kV, a beam current of 40 - 50μA. The images were recorded at different magnifications 5000x, 10000x, 15000x with a resolution of 20nm. The EDX analysis system consists of Silicon Drift detector with 129eV resolutions and detection limit of 0.1% is capable of collecting spectrum from different points and elemental mapping. A quantitative and qualitative analysis of the elements was done using EDX analysis. The EDX spectra of blank quartz fiber filter was also measured and subtracted from the samples EDX spectra.

Backward trajectory Analysis

NCEP re-analysis data have been downloaded from the NOAA website (ftp://ftp.arl.noaa.gov/pub/archives/reanalysis) for Hybrid Single-Particle Lagrangian Integrated Trajectory (HYPLIT) model configuration. HYPLIT model control file has been configured to run model at different heights for the three days backward trajectory analysis in both the summer and winter season.

RESULTS AND DISCUSSION

Seasonal variation of PM$_{2.5}$

The average concentration of PM$_{2.5}$ at the urban (Shahdara) site was found to be relatively higher as compared to the rural site (Sampla) in both the summer and winter seasons. The average PM$_{2.5}$ concentration in the urban site was measured to be 87.33μg/m$^3$ and 155.56μg/m$^3$ and in rural was 39.46μg/m$^3$ and 91.62μg/m$^3$ in the summer and winter seasons respectively (Figure 2). The average, minimum, maximum concentrations and standard deviation at urban and rural locations in both summer and winter seasons respectively are listed in table 1.
Table 1. The average, minimum, maximum and standard deviation (S.D) of PM\textsubscript{2.5} concentration (µg/m\textsuperscript{3}) at urban and rural location in summer and winter season.

<table>
<thead>
<tr>
<th>Location</th>
<th>Summer</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg. (µg/m\textsuperscript{3})</td>
<td>Min. (µg/m\textsuperscript{3})</td>
</tr>
<tr>
<td>Shahdara (Urban)</td>
<td>87.30</td>
<td>41.66</td>
</tr>
<tr>
<td>Sampla (Rural)</td>
<td>39.46</td>
<td>33.33</td>
</tr>
</tbody>
</table>

The standard deviation of PM\textsubscript{2.5} was observed to be highest at the urban site in winter than in summer and lowest at the rural site in summer season. These average daily concentrations at both the sites exceeded the 24 hourly average levels of Central Pollution Control Board (CPCB)-NAAQS PM\textsubscript{2.5} level (60 µg/m\textsuperscript{3}), WHO guidelines (25 µg/m\textsuperscript{3}) & US-EPA standards (35 µg/m\textsuperscript{3}) except in the summer season at the rural site which were below the prescribed 24 hourly CPCB-NAAQ Standards but exceeded those of US-EPA and WHO standards.

![Summer-Winter PM\textsubscript{2.5} Concentration Variation](image_url)

Figure 1. PM\textsubscript{2.5} concentration at the sites Shahdara (urban) and Sampla (rural).
Figure 2. SEM images of PM$_{2.5}$ particles in summer season at the urban (2a) and rural site (2b) in Delhi-NCR.
The measured PM$_{2.5}$ concentrations were found to be consistent with the previous studies. During the summer season (Table 2), the measured PM$_{2.5}$ concentration in the Shahdara area was found to be higher than the concentrations reported in various cities such as Chattisgarh (Durg City), Chennai, Pune, Lucknow and cities outside India like Yokohama (Japan) but lower than those reported in Agra and Kanpur. During the winter season, measured concentrations were found to be higher than Chennai, Pune and Yokohama (Japan) but lower than Kanpur, Chattisgarh and Jinan (China) but lie in between those reported at Lucknow. The PM$_{2.5}$ concentrations in the present study were also compared with the other studies reported previously over Delhi. PM$_{2.5}$ concentrations were observed to be higher during the winter season than those reported by Tiwari et al. (2015) but lower than other studies (Trivedi et al. 2014; Pant et al. 2015) and during the summer season, measured concentration was higher than Pant et al. (2015) but almost comparable to Trivedi et al. (2014).

Table 2. Seasonal PM$_{2.5}$ concentrations (μg/m$^3$) in urban areas in India and outside India.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Summer</th>
<th>Winter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delhi, India</td>
<td>87.3</td>
<td>155.56</td>
<td>Present study</td>
</tr>
<tr>
<td>Yokohama, Japan</td>
<td>20.80±6.3</td>
<td>21.15±9.5</td>
<td>Khan et al., (2010)</td>
</tr>
<tr>
<td>Agra, India</td>
<td>90.14±7.21</td>
<td>-</td>
<td>Pipal et al., (2011)</td>
</tr>
<tr>
<td>Chattisgarh, India</td>
<td>83.5</td>
<td>215.0</td>
<td>Deshmukh et al., (2011)</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>65.4±16.8</td>
<td></td>
<td>Hou et al., (2011)</td>
</tr>
<tr>
<td>Jinan, China</td>
<td>143.25</td>
<td>204.89</td>
<td>Yang et al., (2012)</td>
</tr>
<tr>
<td>Fuzhou, China</td>
<td>23.58</td>
<td>59.81</td>
<td>Xu et al., (2012)</td>
</tr>
<tr>
<td>Chennai, India</td>
<td>67.0</td>
<td>74.0</td>
<td>Srimuruganandam and Nagendra, (2012)</td>
</tr>
<tr>
<td>Lucknow, India</td>
<td>34.3-71.0</td>
<td>144.7-189.3</td>
<td>aPandey et al., (2013)</td>
</tr>
<tr>
<td>Kerala, India</td>
<td>12.37-25.6</td>
<td>-</td>
<td>bRagi et al., (2013)</td>
</tr>
<tr>
<td>Delhi, India</td>
<td>-</td>
<td>117±79.1</td>
<td>cTiwari et al., (2015)</td>
</tr>
<tr>
<td>Delhi, India</td>
<td>86.4±26.8</td>
<td>221.1±94.7</td>
<td>Trivedi et al., (2014)</td>
</tr>
<tr>
<td>Delhi, India</td>
<td>58.2±35.0</td>
<td>276.9±99.9</td>
<td>dPant et al., (2015)</td>
</tr>
<tr>
<td>Pune, India</td>
<td>76.1±25.5</td>
<td>97.8±30.5</td>
<td>Yadav et al., (2015)</td>
</tr>
</tbody>
</table>

a,b Concentrations from lower to higher level  
c 4h sampling concentration  
d 12h sampling concentration
From Table 3, the measured concentration at the rural site during winter season is comparable to those reported at other rural sites (Xu et al. 2002; Pachauri et al. 2013) but higher than Rachma (Jordan) and lower than that in Agra (Kulshrestha et al. 2009), Wusumu (China) and Jinan (China). Measured rural concentration during the summer season was found to be higher than Ragi et al. (2013) but lower than the rest of the other studies. The studies regarding the PM$_{2.5}$ concentrations during summer season are very few may be because winter season is most important as far as air quality of a region with respect to PM$_{2.5}$ concentration is concerned.

**Table 3.** Seasonal PM$_{2.5}$ concentrations (μg/m³) in rural areas in India and outside India.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Summer</th>
<th>Winter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haryana, India</td>
<td>39.46</td>
<td>91.62</td>
<td>Present study</td>
</tr>
<tr>
<td>Linan, China</td>
<td>-</td>
<td>90.0±47.0</td>
<td>Xu et al. (2002)</td>
</tr>
<tr>
<td>Miyun, China</td>
<td>-</td>
<td>683.1±233</td>
<td>Dan et al. (2004)</td>
</tr>
<tr>
<td>Rachma, Jordan</td>
<td>-</td>
<td>25.0±7.0</td>
<td>Schneidenessser et al. (2010)</td>
</tr>
<tr>
<td>Wusumu, China</td>
<td>50.7</td>
<td>115.6</td>
<td>Han et al. (2008)</td>
</tr>
<tr>
<td>Agra, India</td>
<td>59.6±20.6</td>
<td>127.0±53.9</td>
<td>Kulshrestha et al. (2009)</td>
</tr>
<tr>
<td>Jinan, China</td>
<td>69.56</td>
<td>146.8</td>
<td>Yang et al. (2012)</td>
</tr>
<tr>
<td>Agra, India</td>
<td>-</td>
<td>91.2±17.3</td>
<td>Pachauri et al. (2013)</td>
</tr>
<tr>
<td>Agra, India</td>
<td>89.12 ±37.94</td>
<td>-</td>
<td>Pipal et al. (2011)</td>
</tr>
</tbody>
</table>

*Concentrations from lower to higher level

The months of April-June characterise the summer season in the North India. During the summer season, high atmospheric boundary layer and strong surface winds leads to the proper dispersion of pollutants and therefore, less concentration near the surface. This might be true up to a point in the rural areas as anthropogenic pollution sources are far and few as compare to urban areas where they are present in large numbers, thus, effectively keeping the pollution level high even during the summer season. The other sources of PM$_{2.5}$ aerosols in the rural region may also include the biomass burning (April-May; October-December), bio-fuels (wood and cow-dung cakes) for cooking purposes, transport of pollutants by wind from the nearby industrial areas and brick kilns (Guttikunda and Calori 2013). Heavy metals along with the dust are also carried by the wind during the summer season, further aggravating the air pollution and affecting the visibility (Pandithurai et al. 2008). High level of PM$_{2.5}$ concentration over Delhi in both the summer and winter seasons could
be because of significant amount of anthropogenic emissions such as vehicular, coal based thermal power plants, which are also a source of sulphates, nitrates and carbonaceous aerosols such as black carbon, brick kilns, dust from large scale constructional activities, especially, in the urban areas, the burning of wood, coal, garden cuttings, and dead leaves (Prasad et al. 2006; Chowdhury et al. 2007; CPCB, 2010; Guttikunda and Calori, 2013; Sharma et al. 2014). PM$_{2.5}$ concentrations during winter in the Delhi-NCR are also affected by meteorological conditions (calm or no winds and lower inversion height) leading to poor dispersion of pollutants causing them to accumulate near the surface. The high level of anthropogenic aerosols during the winter greatly affects the visibility of the region which badly hits the transport sector both (air and ground), safety of the public, business and tourism (Singh and Dey, 2012). Haziness of the sky, as a result of anthropogenic aerosols, further plays an important role in the solar irradiance attenuation studies (Ramanathan et al. 2001). As solar radiation is one of the major driving force of various earth and life processes, understanding the role of the aerosols interactions with the incoming solar radiation is very important for various scientific, academic and industrial applications. Higher the concentration of the aerosols, higher will be the attenuation of the incoming solar radiation.

**SEM Analysis**

Seasonal variation in the particles morphology could be seen at both the urban and rural sites through SEM application. The flaky, free, aggregated and irregular shaped particles (Figure 2a) were found to be dominated in the urban areas during the summer season. The SEM results show that the rural area samples were relatively cleaner (Figure 2b) as compared to the urban area samples. However, ultrafine and spherical shaped particles were found to be present in the rural samples during the summer season but not in significant amount. The long tubular structures represent the quartz filter fibres in all the SEM images. During winter season, the spherical, aggregated and irregular shaped particles were found to be dominated in both the urban and rural areas. The individual spherical, irregular shaped particles, which were embedded in fibre filters, were more prominently observed at the rural site (Figure 3b) as compared to the urban site where particles were observed to be in a much more concentrated form on the fibre filter strands (Figure 3a). Particles with spherical shape and smooth surfaces are generally characterised by the combustion processes at high temperatures (Tasic et al. 2006). Various atmospheric models consider the spherical shape of the particles for solar attenuation studies (Buseck et al. 2000). Irregular shaped particles could be formed as result of aggregation (Rodriguez et al. 2009). Similar results have been reported in other studies (Tasic et al. 2006; Pipal et al. 2011; Tiwari et al. 2015). Soot particles were observed as aggregates of smaller particles at both the rural and urban sites in the winter and at urban site in summer season. These aggregates are often irregular shaped of different sizes. Soot particles are also known to cause the “heating” of the atmosphere by absorbing the incoming solar irradiance (Tiwari et al. 2015). Also, different processes of particle formation results in different morphologies of the particles. Coagulation processes also result in irregular particles.
in the fine mode fraction. Breed et al. (2002) reported contribution of combustion processes more to the fine mode fraction. In rural areas, combustion processes generally include burning of biomass seasonally and bio-fuels for various purposes such as cooking whereas in urban areas there are numerous combustion processes as discussed above. Though the SEM analysis is a powerful tool to determine the shape and size of the PM$_{2.5}$ particle but it still has some limitations. For example, the SEM analysis cannot tell the presence of the hollow spherical particles. Given the complex fibre structure of the quartz fibre filter, manual SEM analysis of the collected particles is often limited by the heavily loaded samples which makes it difficult for the individual particles to be analyzed effectively (Casuccio et al. 2004).

Figure 3. SEM images of PM$_{2.5}$ particles in winter season in the urban (3a) and rural area (3b) in Delhi-NCR.
EDX Analysis:

Figures 4 and 5 respectively show summer and winter variability of the elemental composition of the PM$_{2.5}$ aerosols at the urban and rural sites in Delhi-NCR.

**Figure 4.** EDX results of elements in PM$_{2.5}$ for urban and rural sampling sites during summer.

**Figure 5.** EDX results of elements in PM$_{2.5}$ for urban and rural sampling sites during winter.
Trace elements

In summer season, the concentration of Zn was observed to be higher at the urban site than the rural site, but was comparable in the winter season at both the sites. In urban area, Cu was found to be slightly higher in winter than summer whereas, in the rural area, Cu concentration was observed to be higher in summer season than winter. Similar variation for Ni was also observed i.e. higher values during summer (rural site) and winter (urban site) seasons. However, the concentrations of Fe and Co were found to be decreasing in winter than summer season at both the sites. Again, Fe and Co were found to be higher in rural area in both the summer and winter seasons as compare to urban area. Presence of Zn and Ni at rural site could be due to diesel-fuelled trucks plying on NH-10 throughout the day and tractors used for the agricultural purposes (Reff et al. 2009). Delhi has two major coal based thermal power plants, large amount of industrial and vehicular (including tire wear and brake lining) emissions, combustible processes using coal and oil which could be the sources of Ni, Cu, Zn and Fe (Hays et al. 2011; Sahu et al. 2011b; Patil et al. 2013; Farao et al. 2014; Pant et al. 2015). Zn has also been associated with incineration (Harrison et al. 1997). Fugitive dust, paints and varnishes for buildings doors and windows have been reported as sources of Co (Srivastava and Jain, 2007; Reff et al. 2009).

Carbon

Carbon concentration was observed to be higher during winter at both the urban and rural sites, but increase was observed to be higher in the urban area than the rural area in both the summer and winter seasons indicating the effect of numerous sources, such as biomass burning high amount of vehicular, industrial and coal based power plants emissions which are the major sources of carbonaceous aerosols in the atmosphere in urban areas (Prasad et al. 2006; Moreno et al. 2013; Singh et al. 2015) and meteorological conditions. Biannual crop residue burning, using bio-fuels like cow-dung cakes and wood for cooking and heating purposes in rural areas could be the possible sources of carbon content in the rural atmosphere (Rastogi et al. 2016, Pandey et al. 2017). The high amount of carbon in the urban area could indicate the presence of absorbing aerosols in the urban atmosphere. These aerosols absorb the incoming solar irradiance as well as outgoing terrestrial infrared radiation thereby “heating” the atmosphere. This leads to the formation of urban heat island (UHI) indicating the temperature over urban area is higher than the surrounding rural areas (Pandey et al. 2014).

The observed trend in the summer season is: C>Zn>Cu>Ni>Fe ~ Co in Shahdara whereas in Sampla it is Zn>C>Cu>Ni>Fe>Co. However, in winter season observed trend in Shahdara is C>Zn>Cu>Ni>Fe>Co and in Sampla it is C>Zn>Cu>Ni~Fe>Co. Similar trend of Zn > Cu has been observed in Navarra, Spain (Aldabe et al. 2011).

In Delhi, the diesel vehicles and industrial pollution have been ascertained to be the major contributors to the pollution (Srivastava and Jain, 2008) whereas the other sources such as mineral or soil dust, solid waste, gasoline vehicles, or paved road are
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found to be variable. However, in the present study, the variability in the elemental composition at the two sampling sites is not found to be very significant. The characterization and source identification of PM$_{2.5}$ aerosols is very much important as they have large residence time in the atmosphere and can be transported to a long distance with wind thus greatly affecting the air quality and human health. The elemental composition of the aerosols can also be used to study the solar attenuation processes by various elements (e.g. Carbon).

**Trajectory Analysis**

Summer and winter-time three day backward air mass trajectories have been shown in the Figure 6(a) and Figure 6(b) respectively. To understand the movement of air mass at different heights, air mass trajectories were drawn at three different heights levels from ground level i.e. 50m, 500m and 1000m. This was done to understand how different air pollutants, especially aerosols, which have reasonably long residence times, are being transported across various regions. During summertime, air mass originates in the Arabian Sea and gradually moves towards Thar Desert and move further towards the Delhi and NCR (Figure 6a). Delhi-NCR is under the influence of the air masses from North-Western parts mainly Haryana-Punjab and Pakistan (Figure 6b). A downward movement of the air masses have also been seen in the trajectories plots, which depict greater stability conditions. Higher atmospheric stability favours the build up of pollutants in the atmosphere in Delhi-NCR during winter.
CONCLUSION

Measured PM$_{2.5}$ concentrations were higher at the urban site as compared to the rural site in both the summer and winter seasons. Irregular shaped and flaky particles were found to be abundant in summer season whereas in winter, particles were in a concentrated form at the urban site. Rural area SEM results show relatively cleaner with presence of a few ultrafine and spherical particles during the summer season. Spherical, irregular shaped particles dominated in the rural area in the winter season indicating the presence of combustion sources such as biomass burning. Elements such as C, Zn, Cu, Ni, Fe and Co indicating the presence of anthropogenic sources were observed in varying concentrations at both the sampling sites in both the summer and winter seasons. The HYSPLIT three day backward trajectories during the summer season showed a North and North-westerly influence apart from local sources emissions on air mass over Delhi-NCR. The air masses movements show the characteristics of the area over which they passes. The comprehensive studies regarding the aerosols properties need to be carried out further in order to understand the role of aerosols in light scattering processes and hence, the regional /local climate change.

Figure 6. Three-days backward trajectory from NOAA HYSPLIT model over Delhi-NCR during the (a) summer and (b) winter season.
ACKNOWLEDGEMENT

I would like to thank the University Grant Commission (UGC), Government of India for financial support for this study. Authors are also thankful to Advanced Instrumentation Research Facility (AIRF), Jawaharlal Nehru University, New Delhi for facilitating the SEM and EDX analysis.

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