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Study of Surface Morphology, Elemental Composition and Origin of Atmospheric Aerosols ($PM_{2.5}$ and PM_{10}) over Agra, India

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ABSTRACT

In situ measurements of PM ($PM_{2.5}$ and PM_{10}) particles were carried out using a medium volume air sampler (offline) and particle number concentrations of PM were measured by a Grimm aerosol spectrophotometer (online) during the study period of 2010–2011. The morphology and elemental composition analyses of PM were performed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS), respectively. The average mass concentrations of $PM_{2.5}$ and PM_{10} were 97.2 and 242.6 μg/m^3 at roadside (RD) and 121.2 and 230.5 μg/m^3 at a semirural (SR) site, respectively. These concentrations were substantially higher than the NAAQS, WHO and USEPA standards. The highest mass and number concentrations of $PM_{2.5}$ and PM_{10} were observed during winter, followed by those during the post-monsoon period and summer, with the lowest in the monsoon period. SEM and EDS analysis of PM indicated the presence of soot, mineral, tarballs, fly ash, aluminosilicates/silica, fluorine, carbon rich, and Cl-Na rich particles. Of these particles, soot, tarballs, and F-C rich particles dominate in $PM_{2.5}$, whereas mineral, aluminosilicates, and Cl-Na rich particles dominate in PM_{10}. The morphology and elemental composition of the particles varied over the seasons due to atmospheric processing. The highest carbon concentration (56%) was observed in $PM_{2.5}$ during summer at the RD, while in the monsoon, post-monsoon period and winter the carbon concentration was ~9% lower at the RD as compared to the SR. However, the concentration of carbon in PM_{10} was ~38% higher at the RD as compared to SR during both summer and winter. Air mass backward trajectory cluster analysis was performed, and the results indicate that the aerosol loadings over Agra are mainly transported from the Middle East and Arabian Sea during the summer and monsoon period, while during the pre-monsoon period and winter the aerosol loadings came from the northern region, and were due to the burning of biomass and coal, as well as other local activities.

Keywords: Mass and number concentration of PM; Physicochemical properties; Carbon analysis; Seasonal variation; Source identification.

INTRODUCTION

Particulate also called aerosol air pollution is caused due to very small liquid and solid particles suspended in the air. They originate from a variety of stationary and mobile sources and may be directly emitted (primary emission) or formed in the atmosphere (secondary emission) by transformation of gaseous emissions (Wilson *et al.*, 2002). Size and chemical composition of ambient particulates strongly influence on human health, visibility and ecosystem etc. thus it is crucial to investigate the physicochemical characteristics of atmospheric particles and also to evaluate their potential toxicity. A large number of health-related studies recognized that fine particles particularly submicron sizes, penetrate deep into lung and exacerbate chronic respiratory and pulmonary diseases (Delfino *et al.*, 2005). Such diseases also induce morphological and functional alterations in human pulmonary epithelial cells (Ramgolam *et al.*, 2009). Apart from this, Elemental composition of particulate plays an important role in the chemical characteristics of Particulate matters (PM) and provides interesting data, not only for the evaluation of its impact on human health (Marmur *et al.*, 2006), ecology and environment (Braga *et al.*, 2005) but also for the identification of specific emission sources (Voutsa *et al.*, 2002).

Moreover, Surface area dominates in all size of particles ($PM_{2.5}$: d < 2.5 μm, PM_{10}: d < 10 μm) and mass dominates in coarse mode particulate matter (PM_{10}: d < 10 μm) in the atmosphere. Surface area may become more essential to ecological impact assessment as recognition of the oxidizing

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capacity of $PM_{2.5}$, their interactions with other pollutants such as ozone and their processes, soil disturbances, hygroscopic fine PM expanding with humidity to a coarse mode, and gas condensation directly onto pre-existing coarse particles.

Particulate matter ($PM_{2.5}$) contains organic (soot, polycyclic aromatic hydrocarbon (PAHs)), inorganic compounds (metals, sulfates, nitrates, and other inorganic species), acid salts, biological elements such as endotoxins, allergens, and pollen fragments and combinations of both organic and inorganic constituents (Sielicki *et al.*, 2011). Due to the excess amount of these pollutants, disturbs the equilibrium of soil which ultimately changes the acidity of soils leading to soil disturbance.

Any cost-effective air pollution control policy cannot be planned without a robust knowledge of the main contributors to atmospheric aerosol concentration. The high number of possible sources and the fast variations of their relative contribution to the atmospheric aerosol make this goal attainable only if the highest possible number of information about particle dimension, shape and chemical composition are known. Apart from this the characteristics of the sampling sites and meteorological situation during the observation periods are also important.

Electron scanning microscopy coupled with energy dispersive spectrometer (SEM-EDS) analysis can provide substantial information on the elemental composition, mineral types, size distribution, and morphology of the airborne particle, which cannot be achieved by bulk chemical analysis alone (Sharma and Srinivas 2009; Srivastava *et al.*, 2009; Pachauri *et al.*, 2013). SEM-EDS is an analytical method for surface elemental analysis, with a potential detection limit of 0.1–0.5 wt.% for most elements (Haley *et al.*, 2006). A spatial resolution < 10 nm can be achieved using this technique, which provides a basis for the generation of quantitative and qualitative elemental data for individual particles. The application of SEM-EDS can provide additional information concerning the composition, source, formation, transport, reactivity, transformation reactions and the number and volume- size distribution of atmospheric aerosols (Ma *et al.*, 2001). During the last few decades, SEM-EDS has been successfully applied to the chemical and physical characterization of individual particles (Xie *et al.*, 2005; Slezakova *et al.*, 2008; Pipal *et al.*, 2011). In order to improve air quality, efforts must be made to understand the physical and chemical characteristics of airborne PM ($PM_{2.5}$ and PM_{10}) and to identify their origins. In mixed environmental sample, the total number and total surface area of atmospheric particles increase exponentially as diameter of the particles decreases. However, the total particulate mass of a substance generally decreases exponentially with decrease in particle diameter.

PM are strongly affected by meteorological parameters such as precipitation, mixing layer height, temperature, air mass origin and season (Jacob *et al.*, 2009; Spindler *et al.*, 2010). Weather change is supposed to have direct and indirect effects on urban PM which in fact depends on sampling season, air mass origin and temperature. Fransen *et al.* (2012) observed the higher levels of PM during the winter months due to more frequent temperature inversions in winter months combined with lack of precipitation (Aryal *et al.*, 2008, 2009)

The characterizations of PM are very important to perceive the morphological features of particle and their elemental composition and it can also provide the fundamental evidence for policy decision. The data is also very useful to analyze physicochemical characteristics, variability of particles in different seasons and their origin**.** In this connection, the present study has been conducted covering the following objectives (i) to determine the mass, number concentration level and morphology of PM ($PM_{2.5}$ and PM_{10}) (ii) identification of elemental composition and (iii) source identification of aerosols over a World Heritage city at Agra, India during the period of 2010–2011.

MATERIAL AND MEASUREMENTS

Study Area

Agra (27°10′N, 78°02′E), is located in the North central part of the India, about 204 km of south of Delhi in the state of Uttar Pradesh. It is one of the most famous tourist spots because of the presence of Taj Mahal which is situated on the west bank of river Yamuna. The climate during the summer is hot and dry with temperature ranging from 32 to 48°C. The downwind is south-southeast 29% and northeast 6% at the time of summer. The monsoon season is hot and humid; temperature ranges from 24 to 36°C and the relative humidity ranges from 70 to 90%. The pre-monsoon and monsoon seasons are dominated by strong northeast and southeast winds. In winter the temperature ranges from 3.5 to 30.5°C and downwind West-North-West 9.4% and North-North-West 11.8% (IMD, 2009). The atmospheric pollution load is high because of downwind sources like, oil refinery at Mathura (50 km far from the centre of the city) from where pollutants may be transported to different areas (Kumar *et al.*, 2007). Agra has about 13,11,000 total inhabitants and the population density is about 21,148 persons per sq km with 386,635 vehicles registered and 32,030 generator sets (Pipal *et al.*, 2011, 2014). In Agra, 60% pollution is due to vehicles and three highways (NH-2, NH-3 and NH-11) cross the city. Vehicular traffic on these highways is high (10^5 vehicles per day) (Kulshrestha *et al.*, 2009, 2009a). The ferrous and non ferrous metal casting, rubber processing, lime oxidation and pulverization, engineering works and chemicals are the major industrial activities in Agra. Apart from the local sources, Firozabad glass industry is situated at a distance of 40 km east of Agra. It is also influenced from Indo Gangetic plain (IGP) and semi arid tracts of Rajasthan which are most aerosols polluted places in India. During study period, two different sites were chosen over Agra for the sampling of atmospheric particles i.e., roadside (RD) and semirural (SR) sites (Fig. 1).

Sampling and Analysis

Sampling Protocol

Sampling of PM ($PM_{2.5}$ and PM_{10}) were carried out on the roof of buildings of RD and SR sites from April 2010 to January 2011 which covers all the four seasons (summer:

Fig. 1. Map of Agra city (27°10′N, 78°02′E) showing the sampling sites.

April–June, monsoon: July–Sep, post-monsoon: Oct–Nov and winter: Dec.–Jan). Aerosol samples were collected for 24 h on PTFE and glass fiber filters for PM by a medium-volume sampler (model: APM 550, Envirotech, New Delhi flow rate: 16.6 L/min). The sampler was set up at a place about 6 m above the ground. The samples were put in polyethylene plastic bags immediately after sampling and then preserved in a refrigerator. Grimm 31-Channel Portable Aerosol Spectrometer model No.1.109 was used for the monitoring of particulate number concentrations for same period, which runs at a constant flow rate of 1.2 L/min ± 5% with controller for continuous measurement. The sampled particles are measured by the physical principle of light scattering technique. Each single particle is illuminated by a defined laser light and each scattering signal is detected at an angle of 90° by a photo diode. The light source is provided by a laser diode at a wavelength of 675 nm, which then passes several collimator lenses to get a wide, but very flat, light band. The aerosol spectrophotometer measured the particle range from > 0.25–32 µm, out of these sizes particles we are reporting here < 2.5 µm and < 10 µm size range particles.

The aerosol mass concentrations of $PM_{2.5}$ and PM_{10} were ascertained gravimetrically by weighing the filters before and after the sampling. Prior to weighing, all filters were conditioned at a relative humidity of 40 ± 5% and temperature of 22 ± 1°C for 5–6 h. The repeat measurement of the filter weights provide an uncertainty of ± 1 mg which corresponds to an overall error of 15% in the aerosol mass concentration. Whereas quality control in monitoring was made to check the daily flow rate calculation to make sure that the fluctuation in flow rate was within the range.

The cascaded impactor was used to classify aerosols depending on their sizes of 10–2.5 µm ($PM_{10-2.5}$) and less than 2.5 µm ($PM_{2.5}$). The impactor filter was changed after 48 h of sampling or when the filter gets clogged. 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 mass concentration of the sample. Same procedure was taken with Grimm spectrophotometer. This is a very important part for monitoring of atmospheric particles to attain the quality work.

SEM-EDS Analysis of Aerosols

Analysis of PM were performed using electron scanning microscopy (SEM, JEOL Model JSM-6390LV) coupled with energy dispersive spectrometer (EDS, JEOL Model JED-2300) for determination of morphology and elemental composition of airborne particles. Approximately one fourth of filter paper of PTFE and glass fibre were cut and coated with gold to prepare the samples for SEM-EDS analysis. Three images of one sample were taken at a magnification of X1500, X5000, X10000. EDS spectra of individual particles were obtained after scanning an electron beam with an accelerating voltage of 15–30 kV for determination of individual elemental composition of particles. This can provide rapid qualitative, or with adequate standards, quantitative analysis of elemental composition with a sampling depth of 1–2 microns (Sielicki *et al.*, 2011).

Meteorological Status over World Heritage Site in North India

Meteorological parameters such as atmospheric temperature (Tem.), wind direction (WD), wind speed (WS) and relative humidity (RH) were monitored at Agra station

by automatic weather monitor (Envirotech WM251). Average values of Tem, WS, WD and RH during study period were 27.09°C, 3.35 m/s, 189.06 degree and 54.14% over Agra and their day to day variability were depicted in Fig. 2. WS and WD were observed higher during summer (WS: 4.02 m/s and WD: 196.13 degree) followed by winter and post-monsoon and lowest in monsoon (WS: 3.63 m/s and WD: 152.90 degree). Whereas the Tem was higher during summer and lower in during winter and in the case of RH it was higher during monsoon (69.26%) followed by winter and post-monsoon and lowest during the summer period (34.49%). The relative humidity was higher more than 46% for most of the study period except summer period; it is due to temperature along with the dry weather conditions.

RESULTS AND DISCUSSION

PM Mass Concentrations

The average mass concentrations of $PM_{2.5}$ and PM_{10} were 97.21 μg/m^3, varied from 33.00–170.23 μg/m^3 and 242.57 μg/m^3, varied from 7 1.35–377.36 μg/m^3 at roadside (RD) whereas at semirural (SR) site, it were 121.20 μg/m^3, varied from 89.12–183 μg/m^3 and 230.52 μg/m^3 varied from 111–344 μg/m^3 respectively in entire study. This indicates that the observed values of PM are substantially higher than the annual standards stipulated by central pollution control board (nodal agency of Government of India) called national ambient air quality standard (NAAQS: 40 μg/m^3 for $PM_{2.5}$ and 60 μg/m^3 for PM_{10}) and (World Health Organization: 25 μg/m^3 for $PM_{2.5}$ and 50 μg/m^3 for PM_{10}). It also, perceived average yearly mass PM concentrations seem to be exceeding the limit values of standards of United States Environmental Protection Agency (USEPA: 15 μg/m^3) and European Union (EU: 20 μg/m^3) standards of $PM_{2.5}$.

The present levels of PM are compared with other studies which were carried out over IGP and were found similar and some variability than the earlier reported values of PM (Table 1). Apart from this the study also compared with other studies done in other part of the world indicating higher concentration except some studies.

The higher level of $PM_{2.5}$ and PM_{10} over Agra may be attributed to the combined effect of metrological conditions and anthropogenic emissions such as vehicular exhaust, waste incineration, coal and biomass and bio-fuel combustion and re-suspended soil dust over Agra.

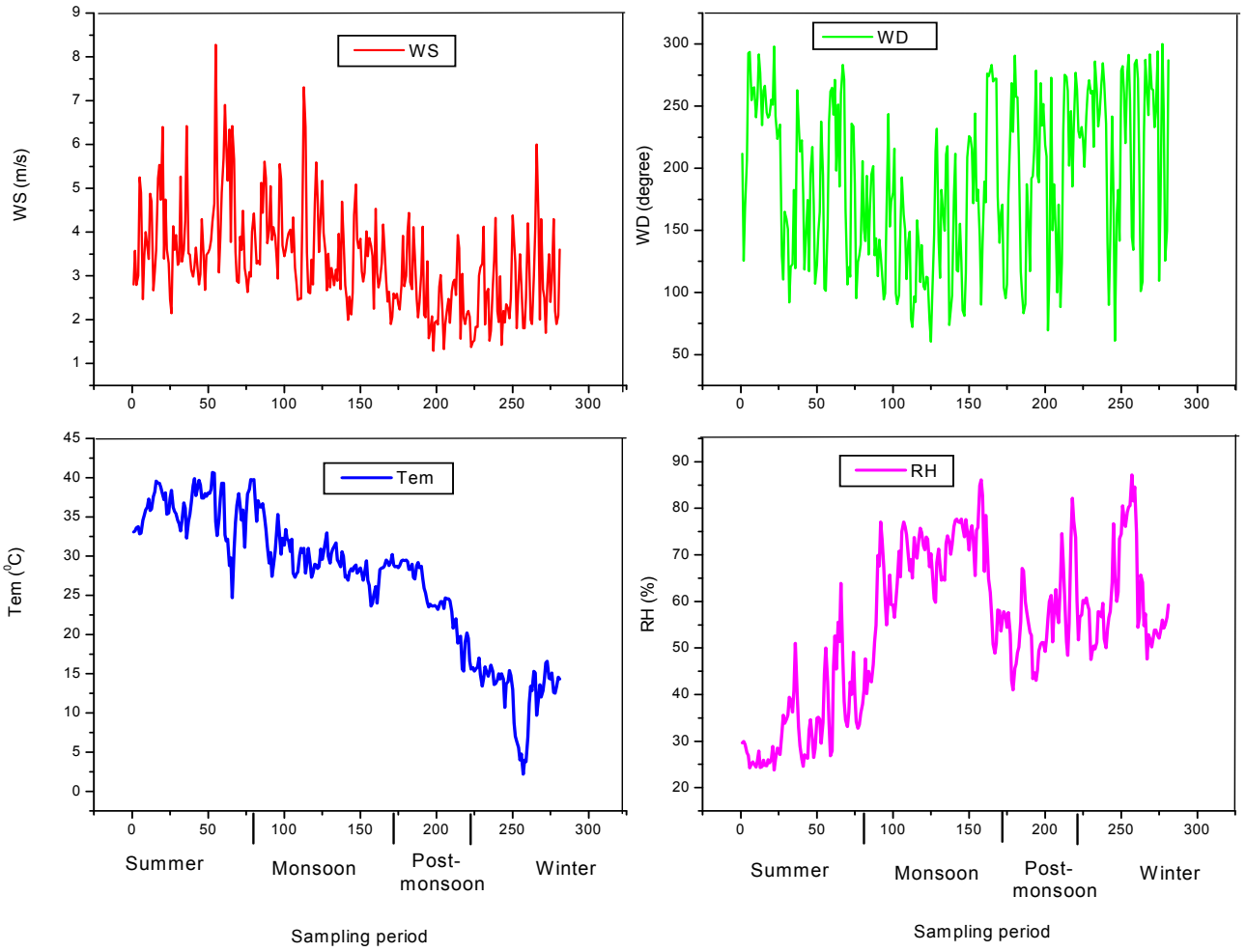

Fig. 2. Day to day variability of meteorological parameters (WS = wind speed, WD = wind direction, Tem = temperature and RH = relative humidity) over Agra.

Table 1. Comparison of $PM_{2.5}$ and PM_{10} concentrations in present study over Agra with earlier reported mass concentrations of PM in different parts of northern India and other global locations.

Place	$PM_{2.5}$	PM_{10}	References
Agra RD	97.2	242	Present study
Agra SR	121.2	230.5	Present study
Delhi	148.4 ± 67		Dey *et al.*, 2012
Delhi	97 ± 56	219 ± 84	Tiwari *et al.*, 2010
Delhi	123 ± 87	208 ± 14	Guttikunda, and Calori, 2013
Lucknow	101.05 + 22.5	204.0 + 26.7	Pandey *et al.*, 2012
Kanpur	95	281	Sharma and Maloo, 2005
Patiala	57 ± 2	97 ± 2	Awasthi *et al.*, 2011
Agra	136	170	Kulshrestha *et al.*, 2009
Lahore, Pakistan	91	489	Colbeck *et al.*, 2011
Beijing, China	86.6		Zhao *et al.*, 2009
Taipei, Taiwan	21.82 ± 7.5	39.45 ± 11.6	Gugamsetty *et al.*, 2012
Haarlemmerweg, Germany	17.8	27.5	Boogaard *et al.*, 2011

Fig. 3 shows the monthly trends of $PM_{2.5}$ and PM_{10} mass concentration at RD as well as SR sites. Higher concentrations of $PM_{2.5}$ was observed in the month of December but in the case of PM_{10} it was during November while lower was in the month of July at RD. Whereas at SR, the $PM_{2.5}$ and PM_{10} followed the same trend as higher in the months of December and lower in the months of August.

Seasonal analysis of PM mass concentrations showed a large variability among the seasons (Fig. 4), where it was found to be higher for $PM_{2.5}$ concentration during winter (185.7 (RD) and 235.4 (SR) $\mu g/m^3$) followed by post-monsoon (92.1 (RD) and 108.7 (SR) $\mu g/m^3$) > summer (90.1 (RD) and 89.1 (SR) $\mu g/m^3$) > monsoon (28.0 (RD) and 80.9 (SR) $\mu g/m^3$). However for PM_{10}, it was in the order of winter (328.9 (RD) and 384.5 (SR) $\mu g/m^3$) > post-monsoon (337.88 (RD) and 252.25 (SR) $\mu g/m^3$) > summer (278.7 (RD) and 234.5 (SR) $\mu g/m^3$) > monsoon (28.0 (RD) and 67.8 (SR) $\mu g/m^3$) respectively. The seasonal characteristics of $PM_{2.5}$ and PM_{10} concentrations in Agra can also be explained as the combined impact due to weather conditions, local emissions as well as long range transport of pollutants. These higher concentrations of fine particles during the winter period were due to low wind speed, low mixing height as well as low temperature. During stable and cold conditions, the pollutant could not disperse and accumulate (Tiwari *et al.*, 2012). The relatively higher concentrations of PM were observed during winter and post-monsoon seasons in comparison to summer and monsoon season at both sites. The trend of PM concentrations at both sampling sites were observed in the order of winter > post-monsoon > summer > monsoon. This fact was also observed by other previous studies conducted over IGP region (Mishra *et al.*, 2012). Kulshrestha *et al.* (2009a) also found higher concentration of $PM_{2.5}$ and PM_{10} during winter season which also suggest that the higher concentration of PM during winter may be due to variations in WS, low Tem and moderate RH which resulted towards the poor dilution of pollutants during this season. It was also observed that higher concentrations during winter and post-monsoon seasons (low temperature) due to very frequent and persistent thermal inversion and foggy conditions at ground level causing a considerable amount of aerosols to accumulate in the lower layers of the atmosphere. Apart from this, impact of festival (Deewali) and massive biomass burning of crops residue over the western part of India, especially Haryana and Punjab states play a crucial role in enhancement of fine mode aerosols mass concentrations during winter and post-monsoon (Tiwari *et al.*, 2010; Awasthi *et al.*, 2011). Moreover, Agra is affected with high concentrations of aerosols load (Taneja *et al.*, 2008; Kulshrestha *et al.*, 2009; Pipal *et al.*, 2010) due to its semi arid climatic conditions, resuspension of crustal load and calm wind regions during winter time. Variations in PM mass during summer is due to influence of moderately high winds, temperature, convective mixing and dust particles derived from the disturbed soil is lifted in the atmosphere (detail description given in the later section 5). The lower concentrations of aerosols were observed during monsoon season at both sites due to wash out effect from the atmosphere by wet removal and hygroscopic growth of particles in the presence of high moisture (Kulshrestha *et al.*, 2009; Kumar and Sarin, 2009; Verma *et al.*, 2010; Deshmukh *et al*., 2011).

Particle Number Concentrations (PNC)

Fig. 5 shows the monthly variations of particle number concentration of PM in particle per liter. The total average number concentrations of PM_{10} and $PM_{2.5}$ were 5.82 and 5.76 particles/liters (log) at RD while at SR site it, was 5.93 and 5.90 particles/liters (log) respectively. On seasonal analysis, the higher number concentrations of $PM_{2.5}$ and PM_{10} were found during winter followed by post-monsoon, summer and monsoon season at both sites. Higher number concentrations during winter was because of the lower temperature which is likely to favor particle formation by condensation; moreover, it is also affected by vehicular emission density, boundary layer depth, restriction of particles to transport and freezing of particles due to low level inversion (Duan *et al.*, 2007; Awasthi *et al.*, 2011; Fransen *et al.*, 2012). The lower particle number concentrations were observed during summer at both sites it was due to higher WS and Tem. In such conditions, the formations of new particles are lesser due to tremendous increase in internal

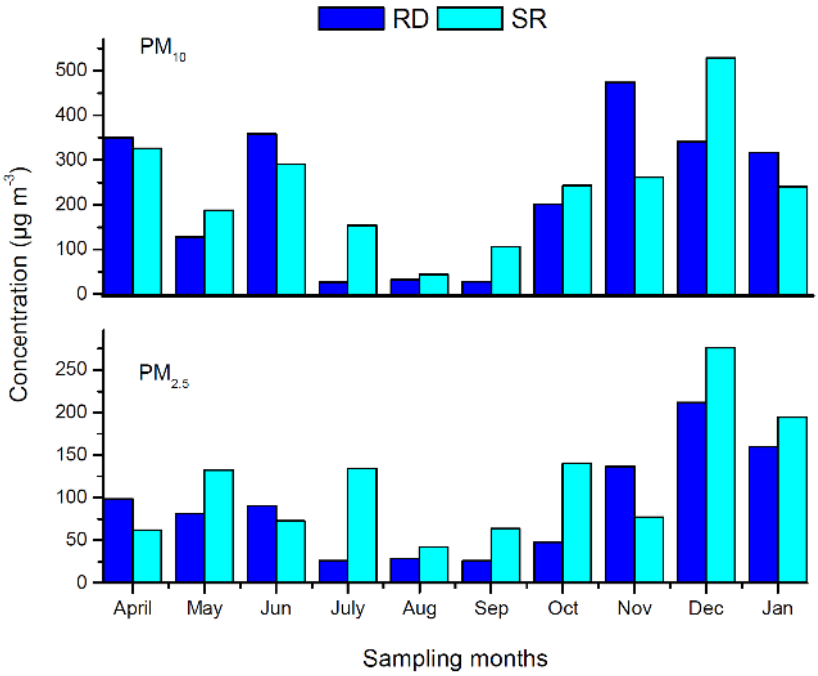

Fig. 3. Monthly mass concentrations of PM (µg/m^3).

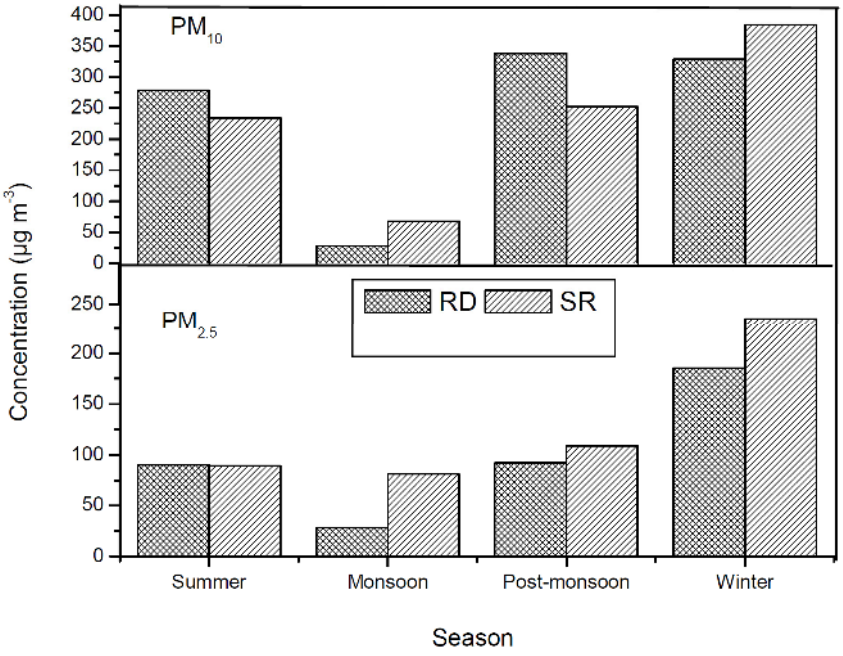

Fig. 4. Season wise trends of PM concentrations.

turbulence mixing into the atmosphere. The particle number concentrations of $PM_{2.5}$ and PM_{10} were higher at SR site in comparison to RD in the month of December while rest of months; it was observed similarity in its variations. This higher concentrations in the months of December over SR may be due to agricultural activities, coal burning, selum factories, and resuspended dust particles because of loose soil at this site, most of particles are generated from stationary sources which are the main reasons for the higher number concentrations. The particles number concentrations increases exponentially as diameter of particles decreases (Sharma and Srinivas, 2009).

Morphological Analysis of Atmospheric PM over Agra

Microscopic and elemental composition analysis of atmospheric aerosols (PM) collected at two different sites (RD and SR) were made by SEM and EDS technique during different seasons and depicted in Figs. 6 and 7 respectively. On the basis of these images and elemental composition of PM, it was classified into following groups

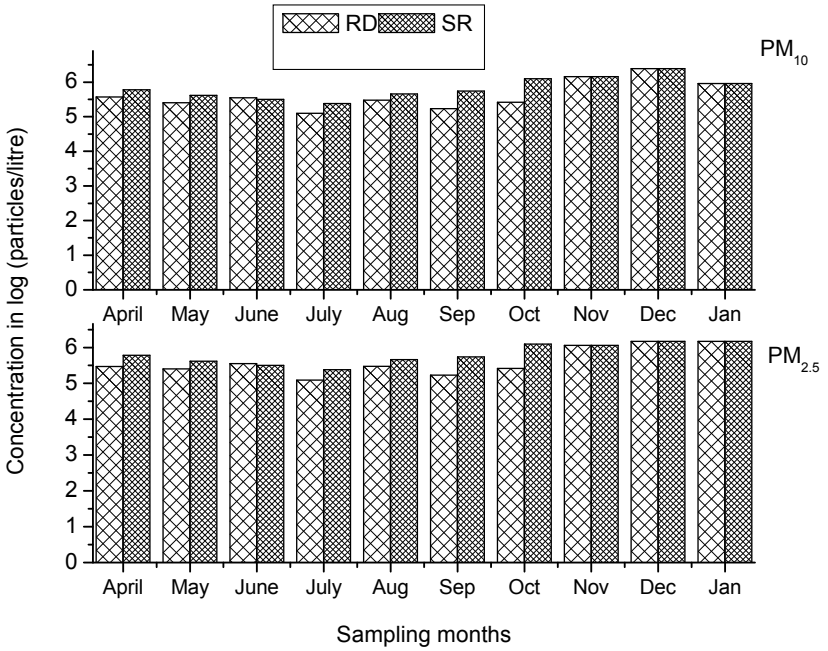

Fig. 5. Monthly trends of number concentrations in log (particle/liter) of $PM_{2.5}$ and PM_{10}.

i.e., soot particles, mineral particles, tarball, fly ash, aluminosilicates/silica, fluorine/carbon rich, Na-Cl rich particles over Agra.

Soot Particles

Soot particles are clearly distinguishable from other aerosol types due to its unique morphology as they are abundant in fine mode in the present study (Figs. 6 and 7). Morphology of soot particles varied from chains to simple clusters, with size 1–2 μm which depend on different types of fuels, burning conditions, and atmospheric processes (Yue *et al.*, 2006). The soot aggregates particles were abundant at RD than at SR area due to vehicular emissions which are dominant at RD site, suggesting vehicular pollution over this site. These particles are primarily emitted from biomass burning and incomplete fossil fuel combustion are mainly composed of fine particles (Lu *et al.*, 2011) and has attracted special attention nowadays, mainly due to their contribution to climate change (global warming), reduced visibility, and adverse health effects (Venkataraman *et al.*, 2005).

Fly Ash Particles

The fly ash particles contain mainly aluminosilicates characterized by silicon with varying amount of magnesium, potassium, calcium and iron (Feng *et al.*, 2009) with smooth shape and byproduct of coal burning (Figs. 6(a), 6(b), 6(g) and 6(h)). These particles originate from various kinds of combustion processes (vehicular emissions, and other urban anthropogenic sources) and coal combustion. The size ranges of fly ash particles are between 50 to 1 μm, with amorphous, spherical, irregular shape (Lu *et al.*, 2011). These particles are mostly smooth, spherical dominated by Si and Al and observed in coarse particles (PM_{10}) at both sites (Figs. 6 and 7). However, smaller fly ash airborne particles with a diameter of less than 10 μm are taken into special consideration because these particles are regarded as respirable and may cause damage to the respiratory system of humans (Iordanidis *et al.*, 2008). Moreover, fly ash particles are regarded as a very toxic material owing to its high concentrations of leachable heavy metals and in some cases to the presence of chlorinated organic compounds.

Mineral Particles

Mineral particles with irregular shape were observed in coarse particle which may be mainly derived from natural sources such as soil dust, resuspension of dust from road, crust and some other anthropogenic activities such as construction and vehicles (Li *et al.*, 2010). Furthermore, the mineral particles observed in Agra air can be divided into two types, one with irregular, crystal, flaky and round shapes at RD during all seasons (Fig. 6) and the other with regular, rod like and elongated shape at both sites (Figs. 6 and 7) in PM_{10} during summer and monsoon. These mineral particles consisted of Al, Si, O, C, Mg, K and Ca, indicating the presence of $CaCO_3$ which are most likely from geological sources (Lu *et al.*, 2008; Satsangi and Yadav, 2014) and were found during winter season over Agra. These calcium carbonate particles are observed in the form calcite ($CaCO_3$) particles which react with HCl via the heterogeneous reaction pathway resulted in the $CaCl_2$ in the atmospheric during the winter period (Kelly and Wexler, 2005). The Ca-containing compounds such as carbonate making up dust particles are favorable for the uptake of chloride precursor gases (HCl) and that the products of this reaction are hygroscopic salts. $PM_{2.5}$ is composed of minerals and soot aggregates, which are mainly from vehicular exhaust emission which dominates at RD (Lu *et al.*, 2011).

Tarball Particles

Fig. 6 shows the tarball particles which are spherical,

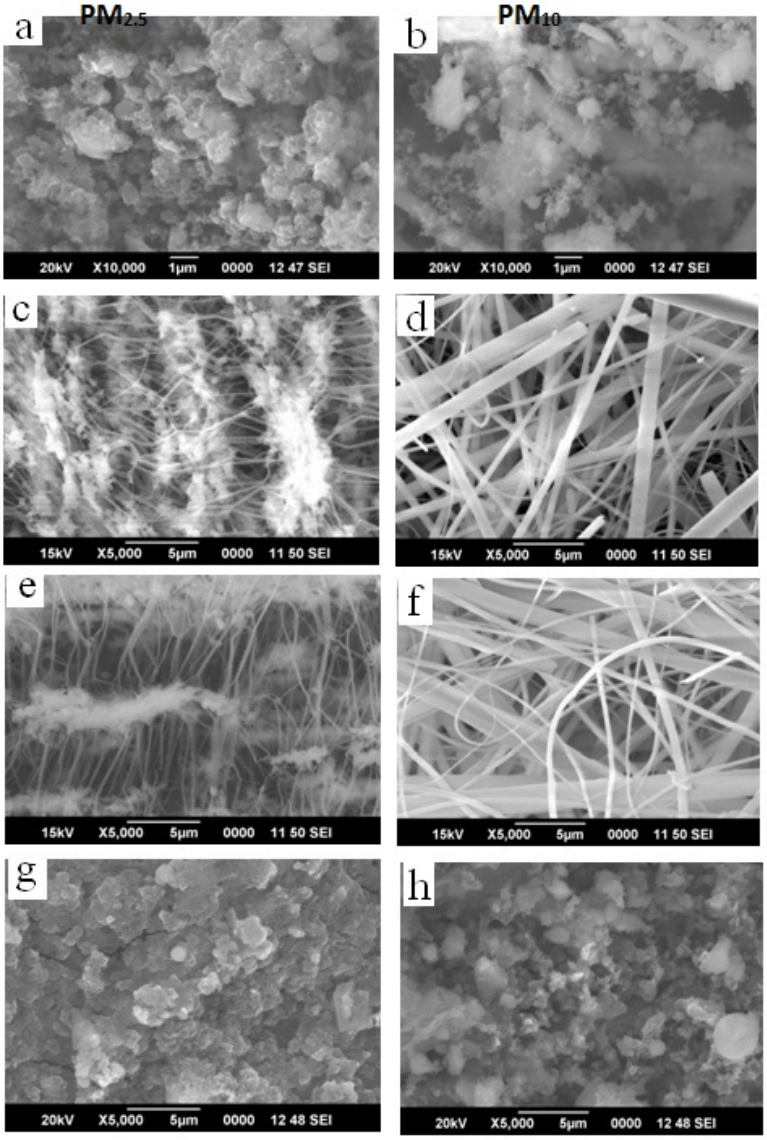

Fig. 6. Morphologies of $PM_{2.5}$ and PM_{10} at RD site during the entire study period (a–b: summer, c–d: monsoon, e–f: post-monsoon and g–h: winter).

amorphous and are not aggregated with other particles. The composition of tarball particles were observed dominated by carbon, oxygen with traces of S and K, which is similar as observed in other studies also in fine mode (Posfai *et al.*, 2004). The individual elemental percentage of these particles is different from our previous study (Pipal *et al.*, 2011) and having cluster, spherical, irregular shape at RD where these particles originated from fuel oil combustion.

Aluminosilicates and Silica

Aluminosilicates and silica were observed to be most abundant particles in PM at both sites. It is characterized by high contents of Si and Al with varying Mg, K, Fe and Ca in PM_{10} (Figs. 6–7 and Table 2). They are typically terrigeneous minerals therefore, a large fraction of the particles identified as aluminosilicates which can be attributed to eolian dispersion of soil particles. Aluminosilicates having high content of Al, Si and K (Table 2) during summer and winter might have originated from crustal sources and agriculture activities. These particles contain predominantly silicon as silica (e.g., quartz) which originates from soil and crust (Cong *et al.*, 2010).

Fluorine/Carbon Rich Particles

Fluorine and carbon rich particles were mainly abundant in fine particles which show the cluster and lattice shape particle morphology at both sites (Figs. 6 and 7) in monsoon and post-monsoon. Fluorine related particles could be emitted from the industries that either manufactured fluorine based chemicals or by coal burning (Prather *et al.*, 1990), fertilizers and pesticide uses, which are most commonly used in activities at SR site. Water in Yamuna River that flow over rocks rich in fluorine containing minerals such as fluorspar may naturally contain dissolved fluoride (Prather *et al.*, 1990). This fact is also supported by trajectory analysis which indicates that during the monsoon period

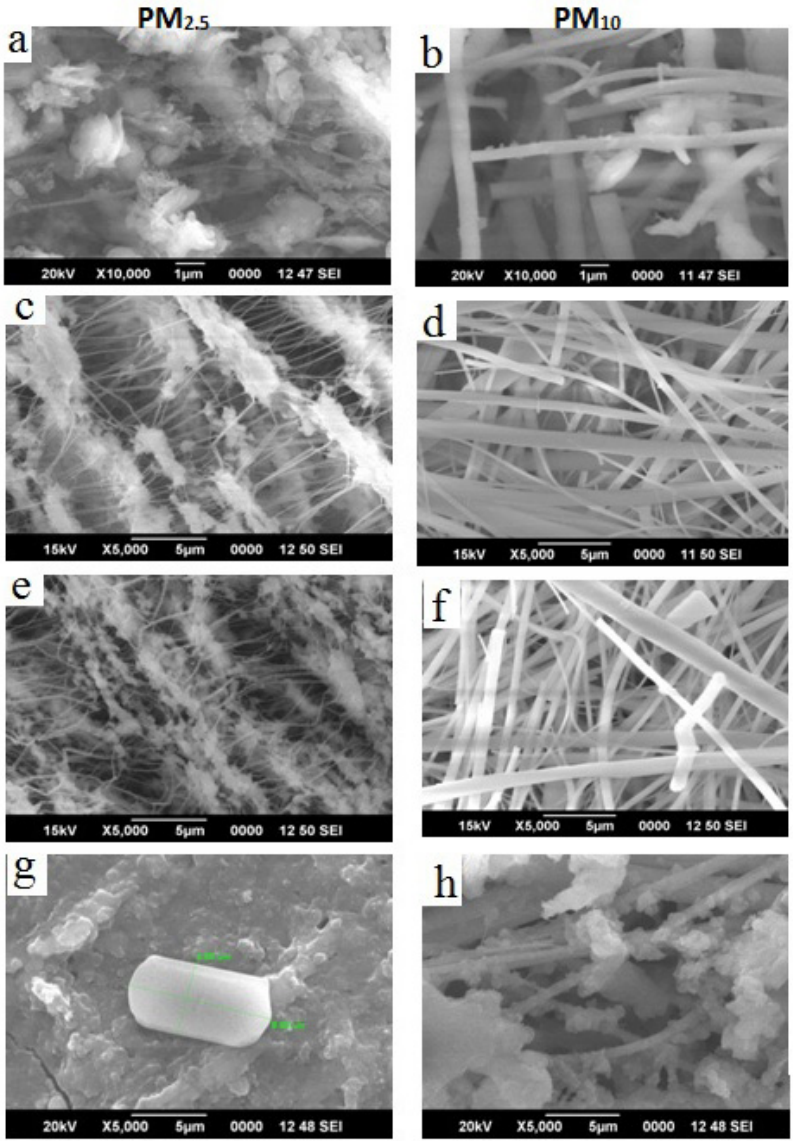

Fig. 7. Morphologies of $PM_{2.5}$ and PM_{10} at SR site during the entire period of study (a–b: summer, c–d: monsoon, e–f: post-monsoon and g-h: winter).

the path of aerosol particles coming from Arabian Sea over Agra (Section 5, Fig. 8). The second group of carbon rich particles was also observed which are originated from vehicular activities (Srivastava *et al.*, 2009).

Cl-Na Rich Particles

Figs. 6–7 indicates that the Cl rich particles associated with trace Si and K in fine particles during the winter period (Table 2), which are great abundance of spheroidal particles with smooth texture. These are usually originated by activities like farming and burning activities around the SR site (Shi *et al.*, 2008). The group of sodium chloride (Cl-Na rich 4.16% relative abundance) was observed in coarse particles which are originated from sea spray and other natural and anthropogenic activities (Campos-Ramos *et al.*, 2009). Moreover, chloride is also converted into sodium chloride and calcium chloride in the atmosphere which may be due to the secondary particles formation. The contributions of marine is also seen and confirm by trajectory analysis which indicates that these types of particles are transported from Arabian Sea passing south part then enter into north region of India (discussed in detail in the later section 5). Highly soluble salts such as calcium chloride ($CaCl_2$) are formed as a result of heterogeneous reactions of dust particles with chloride precursor gases in the marine atmosphere. The chloride formation is expected to play an important role in enhancing the hygroscopicity of dust particles.

On the basis of above discussion the study concluded that different type morphologies of particles were observed in different seasons at RD and SR and are further compared with other studies which were done in other parts of the world (Table 3) and are discussed as follow. In Mexico, porous texure, ultrafine agglomerate, irregular, spheroidal, edge defined crystal tabular and agglomerate shaped particles were observed based on SEM-EDX analysis (Campos-Ramos *et al.*, 2009). Particles have a variety of morphologies such

Table 2. Elemental composition of fine ($PM_{2.5}$) and coarse (PM_{10}) particulate matter at roadside (RD) and semirural (SR) site (%).

RD								
Elements	$PM_{2.5}$				PM_{10}			
	Summer	Monsoon	Post-monsoon	Winter	Summer	Monsoon	Post-monsoon	Winter
C	53.79	28.23	23.68	83.07	23.63	56.54		42.06
O	43.24			8.64	48.81		55.91	18.71
F		71.77	76.32					
Na				0.44	5.66	11.71	12.46	2.61
Mg				0.59	1.13	1.53	1.53	1.52
Al	0.65				3.37	2.93	3.08	5.46
Si	0.95			0.83	15.41	24.48	25.3	21.33
S	0.69			1.5				1.27
Cl				3.76				1.55
K	0.68			1.17	0.81	0.55		2.47
Ca						2.26	1.81	2.93
Fe					1.18			0.05
SR								
Elements	$PM_{2.5}$				PM_{10}			
	Summer	Monsoon	Post-monsoon	Winter	Summer	Monsoon	Post-monsoon	Winter
C	34.37	28.73	29.2	87.96	16.53		55.25	30.74
O	55.81			4.94	53.61	53.88		17.71
F		71.27	70.8					
Na	1.29				5.99	14.2	12.67	3.34
Mg	1.33				1.8	1.78	1.29	1.48
Al	2.15			0.65	3.06	3.08	3.19	5.74
Si	3.14				15.15	25.2	25.57	21.62
S								2.01
Cl				4.94				9.37
K	0.46			1.52	0.97			2.36
Ca	0.76				2.03	1.86	2.03	2.95
Fe	0.68				0.87			2.69

as chain aggregate, solid irregular, and more liquid/spherical shapes which was shown by microscopic examination (Reid *et al.*, 2005). Particulate morphology of PM_{10} i.e., irregular diamond, agglomerate, sphere, floccule, column or stick were identified in Shijiazhuang City, China (Wang *et al.*, 2010). Elongated and bar shape, irregular and regular shape, fluppy morphology, and round or coated with other fine particles was inferred in Guangzhou City (Feng *et al.*, 2009). Chain and cluster like shape (Li *et al.*, 2010), amorphous (Cong *et al.*, 2010), flacky and vascular shape (Cheng *et al.*, 2009) and rod like particles (Cheng *et al.*, 2009) was also observed. Though, such studies have identified the shapes and sizes of particles, but not many studies have been done to explore the effect of seasons.

Morphological Changes in PM with Different Seasons and Meteorological Conditions

Morphological analysis of $PM_{2.5}$ and PM_{10} and its comparison with other studies which was carried out in other parts of the world are shown in Table 3. In summer, being a dry atmosphere, strong WS and high Tem persists the particles are spherical, flacky, chain like, fine rod like and cluster whereas in monsoon and post monsoon seasons, the particles appeared in the form of net shape, elongated and lattice shape due to high moisture and humidity. In winter, particles seem rocky, ball shape, capsule type shape, this scavenged morphology has been observed probably because of lower temperature, calm wind, fogy season and combustions of fossil fuels. The soot aggregated particles are mainly observed with chain like shapes due to drier atmosphere in summer and it becomes cluster soot aggregated in monsoon season (Weingartner *et al.*, 1997). Moreover, soot particles adsorb gaseous species and water vapor (Zuberi *et al.*, 2005; Adachi *et al.*, 2008), enhance the production of secondary species such as sulfate and nitrate via catalyzing heterogeneous reactions on their surface (Cofer *et al.*, 1984; Wang *et al.*, 2010). These processes modify the size, shape, mixture state and suspension time of particles and their ability to absorb and scatter radiative energy in the air (Jacobson *et al.*, 2001; Shi *et al.*, 2008; Zhang *et al.*, 2008) and can also indirectly affect hydrological cycles (Jacobson *et al.*, 2001). Large size mineral particles are usually formed from natural dust while fine size particles are due to formation of secondary aerosols into the atmosphere after its interaction and chemical reactions in different seasons. Thus particles suspended in air are associated with different types of sources, and their origin can be traced based on their microscopic and chemical composition (Aragon *et al.*, 2002). Particles size is the single most important determinant of the properties of particles, it has implications for formation,

Table 3. Comparison morphology of atmospheric particles with studies done in other parts of the world.

City	Season	Morphology	Reference
Agra		Spherical, chain, cluster flaky, Rod like shape, irregular, net shape, cylindrical , Crystalline, regular, capsule type, scavenged	Present study
Mexico		Porous texture, ultrafine agglomerated, spheroid, edge defined crystal, tabular and agglomerated shape	Campus-Romas *et al.*, 2009
USA		Chain agglomerated, solid irregular, spherical shape	Reid *et al.*, 2005
Shijiazhuang City, China		Irregular, diamond agglomerated, sphere, floccules, column or stick	Wang *et al.*, 2010
Guangzhou City		Elongated and bar shape, irregular and regular shape, fluppy morphology, and round or coated with other fine particles	Feng *et al.*, 2009
Beijing, China		Chain and cluster like shape	Li *et al.*, 2010
Beijing, China		Amorphous	Cong *et al.*, 2010
Kozani, Greece		Flaky and vascular shape	Iordanidis *et al.*, 2008
Canada		Rod like particles	Cheng *et al.*, 2009
Shanghai		Spherical fly ash, chain like soot aggregated elongated, irregular shape	Yue *et al.*, 2006
Pune		Spherical irregular, Irregular, Cubic Agglomerates of fine particles, short chain	Satsangi and Yadav, 2014

physical and chemical properties, transformation, transport, and removal of particles from the atmosphere. The physical and chemical characteristics of the different sizes aerosol particles in the atmosphere are strongly affected by long-range transport and source characteristics. During transport and aging, particles (fine) of different origin may change their properties due to coagulation and cloud processes as well as due to reactions with gases via various heterogeneous pathways (Niemi *et al.*, 2006).

Elemental Concentrations in PM over Agra

The variations of individual elemental composition of $PM_{2.5}$ and PM_{10} were summarized in Table 2. Major composition of C, O and Si rich particles were observed in $PM_{2.5}$ and PM_{10} particles at RD as well as SR site during the summer period. Fluorine and carbon rich particles were observed in $PM_{2.5}$ and O, Si and Na rich particles in PM_{10} particles at both sites in monsoon and post-monsoon season. However, in winter C, O, Si rich particles are observed in major amount at RD while, C, O, Cl in fine and Si, O, C rich particles were present in PM_{10} at SR site.

During study period, an interesting feature was seen in seasonal analysis of carbonaceous aerosols in $PM_{2.5}$ and PM_{10} particles at both sites. A large variability was observed in case $PM_{2.5}$ as 56% higher concentration were found during summer over RD as compared to SR however in monsoon, post-monsoon and winter period, it was found opposite and were ~9% lower at RD as compared to SR. Whereas in case of PM_{10}, it was observed that ~38% higher concentrations of carbonaceous aerosols were observed at RD as compared to SR during summer and winter. It clearly indicated the higher value of carbon due the impact of vehicular emission. Also, study pointed out that in rural area the dominance of carbonaceous aerosol in $PM_{2.5}$ was due the burring biomass and biofuels during winter. It is clear that in the entire study period the contribution of carbon was found higher in $PM_{2.5}$ at SR site during all seasons except summer due to incomplete combustion of fossil fuels and degradation of carbon containing materials such as vehicle tyres and vegetation takes place around the site (Rogge *et al.*, 1993a, b). The excess of these activities at SR site were also responsible for more carbon contribution at RD during summer period because of strong wind and path (Fig. 8). Therefore, the study concluded that carbon was abundant over Agra due to anthropogenic activities and long range transportation. This fact was also supported by recent studies which have been carried out in Asia focusing on carbon containing species in PM and indicates the significant level of carbonaceous species (Cao *et al.*, 2004; Venkataraman *et al.*, 2005) which are more concern to health as well as ecological effects. As we notice that carbon is playing the principal role in light absorbing and scattering species in the atmosphere which play an important role in the aerosol climatic forcing and visibility degradation, moreover, due to its specific surface properties, carbon provides a good adsorption site for many semi volatile compounds (Jacobson *et al.*, 2001).

The crustal element Si was present in major amount than other crustal elements (14.26–15.31%) in summer, (24.48–25.53%) in monsoon and post-monsoon and (21.37–34.72%) in winter seasons in PM_{10} which originates from soil crust and anthropogenic activities in Agra atmosphere. Si rich particles (40.25% relative abundance) correspond to Si-Al oxides of spheroidal morphology (Figs. 6 and 7) in $PM_{2.5}$ which may be generated by some high temperature process of anthropogenic origin. However, particles with irregular morphology and less than 2.5 μm sizes, associated with Al, Na and Ca may be originated from agricultural fires (Hays *et al.*, 2005). This indicates that the PM in the air, having different kind of chemical composition and its seasonal variability according to its various sources, atmospheric and weather conditions at different areas.

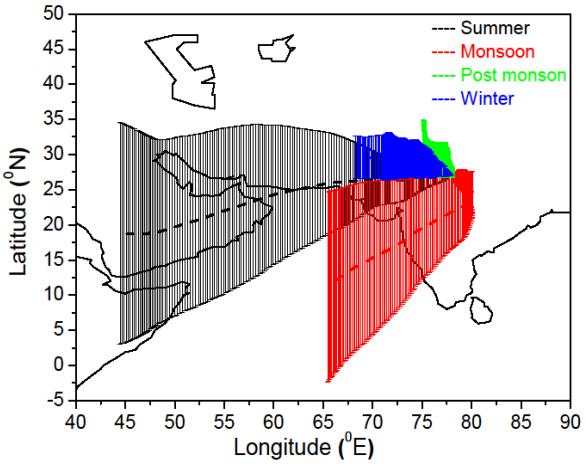

Fig. 8. Seven day air mass backward trajectory clusters analysis at Agra during summer, monsoon, post-monsoon and winter (vertical lines show standard deviation, representing latitudinal air mass spreading).

STATISTICAL AND TRAJECTORY ANALYSIS FOR SOURCE IDENTIFICATION OF PM

In the present study, Pearson correlation between PM and analyzed chemical species were performed for source identification. In addition to this, t-test was also applied to determine the difference in PM mass and number concentrations of aerosols over two different sites. Analysis indicates that the mean values of mass concentrations were 2–3% and number concentrations were 10–12% significantly higher at SR site. The significant correlation (r = 0.62–0.82) was observed amongst mass PM and number concentrations along with elements. The S is correlated with C which is possibly originated from fuel-oil combustion and Mg is correlated with Al, Si, S, K, and Ca, the possible sources of these particles may be similar type over the study region while Al is also good correlate with Si, K, Ca and Si is correlated with Ca, S with K and K with Ca. The presence of Al inferred aluminosilicates probably originate from crustal sources. Silicates are further divided into mafic and felsic (Si and Al rich). Si rich particles correspond to Si-Al oxides possibly generated by some high temperature process of atmospheric origin and crustal dust. Apart from this Al and Si particles also come from cortical, construction activities and ceramic or cement manufacturing (Romero-Guzmán *et al.*, 2012) and the presence of sulfur is due to industrial and mobile transport. It also come from incomplete combustion sources and is mainly associated with carbon and transition metals. The possible sources of K are soil due to the preparing of farmland because SR site is moving towards urbanization and holds construction and agriculture activities which enhance the use of different building materials (cement and sand) (Pipal *et al.*, 2011). The elemental compositions of PM were observed with the help of energy dispersive spectrometer (EDS) which are semi quantitative analyses considering the bulk or individual particles. It is possible to correlate or confirm some chemical species such as C-S, Ca-S-O and Si-Al-O, due to presence of compound derived from incomplete combustion, building tailing materials and aluminosilicates of cortical origin (Romero-Guzmán *et al.*, 2012).

In order to know, the transport pathways of the atmospheric aerosols over the world heritage site (Agra) located in northern part of India, seven days backward trajectory analysis was carried out at height of 500 m on season wise in entire study period based on National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPLIT) model (Draxler and Rolph, 2003). The back trajectory analysis provides a three dimensional (latitude, longitude and altitude) description of the pathways followed by air mass as a function of time by using National Centre for Environmental prediction (NCEP) reanalysis wind as input to the model. The trajectory analysis is very important to identify the origin of source regions and the transport pathways of aerosols to reach the receptor side and also to investigate the aerosol properties and types (Bian *et al.*, 2011).

Fig. 8 shows season wise seven day's air mass backward trajectory at Agra which supports the transport of dust from the long range (Thar Desert and other part of the world) over north Indian region. During the summer period, the air masses appear to be transported from the Middle Eastern at low altitudes and passes over Thar Desert then entering into Agra (north part of India) and IGP (Tiwari and Singh 2013; Tiwari *et al.*, 2013) while in monsoon period, it was coming from Arabian sea passing over south Indian part then enter to Agra and IGP. Marine environment (Arabian sea as well as Bay-of- Bengal) carry mostly sea salt aerosols while traversing through the continental mainland before they reach the measurement site (Reddy *et al.*, 2011).Whereas during winter and post-monsoon it appears from north Indian region and local sources including biomass burning generally occurred during post monsoon period which takes place around the monitoring sites not from long range transport. The trajectory analysis supports our finding as mentioned earlier. Ramachandran and Rajesh (2007) reported the impact of long range transport and meteorological conditions in higher mineral aerosol. The air masses from different source regions lead to the formation of different aerosol types (Reddy *et al.*, 2011). The meteorological parameters play an important role in atmospheric chemistry and photochemistry especially on mineral dust particles. Study done by Kumar and Sarin, (2009) indicates that the air pollutants and its chemical species are affected by long transport due to contrast wind pattern. Due to the strong relation between meteorology and air quality, a changing climate is anticipated to significantly impact air pollution (Mues *et al.*, 2012).

CONCLUSIONS

Morphological and elemental composition analysis of PM provides valuable information for the determination of their physicochemical properties and diverse sources. This analysis is also essential for the assessment of health and ecological effects of airborne particles, which can not be obtained by mass concentration alone, and was not studied, in present study. The average mass concentrations of $PM_{2.5}$

and PM_{10} at present study were 97.21 and 242.57 μg/m^3 at RD while at SR site, it was 121.20 and 230.52 μg/m^3 respectively. These mass concentrations were substantially higher than the standards of NAAQS (40 and 60 μg/m^{3}for $PM_{2.5}$ and PM_{10}), WHO (25 and 50 μg/m^3 for $PM_{2.5}$ and PM_{10}) and USEPA (15 μg/m^3 for $PM_{2.5}$). The average particle number concentrations of $PM_{2.5}$ and PM_{10} were 5.76 and 5.82 particles/liter (log) at RD and 5.90, 5.93 particles/liter (log) at SR site respectively. The higher number concentrations over SR indicate the impact of rural activity apart from long-range transport. Morphology and elemental composition analysis of PM indicated that the dominance of soot particles, mineral particles, tarballs particles, fly ash particles, aluminosilicates/silica particles, fluorine/carbon rich, Cl, Na rich particles at RD whereas at SR site, it was slightly different. Spherical, flaky, chainlike shape, road like, net shape particles were observed at RD while irregular, cluster, and cylindrical, capsule shape and scavenged particle was observed at SR site. During the study period, an interesting feature was seen in seasonal analysis of carbonaceous aerosols in $PM_{2.5}$ and PM_{10} particles at both sites. A large variability was observed (56% higher concentrations) in case of $PM_{2.5}$ during summer over RD as compared to SR, however in monsoon, post-monsoon and winter period, it was found opposite and lower (~9%) at RD as compared to SR. Whereas in the case of PM_{10}, it was observed ~38% higher concentrations of carbonaceous aerosols at RD as compared to SR during summer and winter. It clearly indicated the higher values of carbon are due the impact of vehicular emission. Also, study pointed out that in rural area the dominance of carbonaceous aerosol in $PM_{2.5}$ was due the burning biomass and biofuels during winter.

Significant correlation of $PM_{2.5}$ ($r = 0.68$) and PM_{10} ($r = 0.77$) was observed between sites which indicates that sources of these particles are similar. Backward trajectories were performed and indicates that the impact of long range transport of atmospheric aerosols over Agra during study period. It was observed that the wind passes from Middle Eastern and Arabian Sea over Thar Desert before entering into northern part of India and IGP region during summer and monsoon. Whereas during winter and post-monsoon seasons, it was appeared from north Indian region and localized sources especially biomass burning and other anthropogenic activities.

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