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Research Article

## Wintertime characterization of Carbonaceous and Inorganic constituents of PM<sub>2.5</sub> and PM<sub>10</sub> aerosols at an urban site of North Central India

Tripti Pachauri<sup>\*1</sup>, Ram Kumar Saraswat<sup>2</sup>, Anita Lakhani<sup>1</sup> & K. Maharaj Kumari<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Dayalbagh Educational Institute, Dayalbagh, Agra, India

<sup>2</sup> Department of Chemistry, School of Sciences, St. Johns College, Agra, India

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**Abstract:** Aerosol mass concentrations and chemical composition of PM<sub>2.5</sub> and PM<sub>10</sub> were studied during winter season at an urban site (Agra) of North Central India. Weekly samples were collected during winter season from October 2012 to February 2013. The average mass concentrations were found to be  $116.4 \pm 39$  and  $310.5 \pm 42.9$   $\mu\text{g}/\text{m}^3$  for PM<sub>2.5</sub> and PM<sub>10</sub> indicating the combined impact of local anthropogenic emissions and meteorological conditions. On average, the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  accounted for 46 and 48% of total WSIS in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. The average ratio of  $\sum C/\sum A$  is  $> 1$  suggesting the alkaline nature of aerosols. The average concentrations of OC and EC were found to be  $35.8 \pm 19.2$   $\mu\text{g}/\text{m}^3$  and  $4.8 \pm 1.3$   $\mu\text{g}/\text{m}^3$  in PM<sub>2.5</sub> while  $113 \pm 23.5$   $\mu\text{g}/\text{m}^3$  and  $16.3 \pm 6.3$   $\mu\text{g}/\text{m}^3$  in PM<sub>10</sub>. A good OC – EC correlation for both PM<sub>2.5</sub> and PM<sub>10</sub> indicated the presence of common dominant sources for carbonaceous aerosols. The average concentration of TCA was found to be  $62.6 \pm 31.6$  and  $190 \pm 35.8$   $\mu\text{g}/\text{m}^3$  in PM<sub>2.5</sub> and PM<sub>10</sub> indicating the dominance of carbon rich aerosols. On average, SOC accounted for 43.8 and 34.5% of total OC. High contribution of SOC to total OC may be probably due to the combined emissions of anthropogenically originated VOCs as well as naturally emitted terpenes.

**Keywords:** Water soluble ions, Organic carbon, Elemental carbon, SOC, SEM/EDX

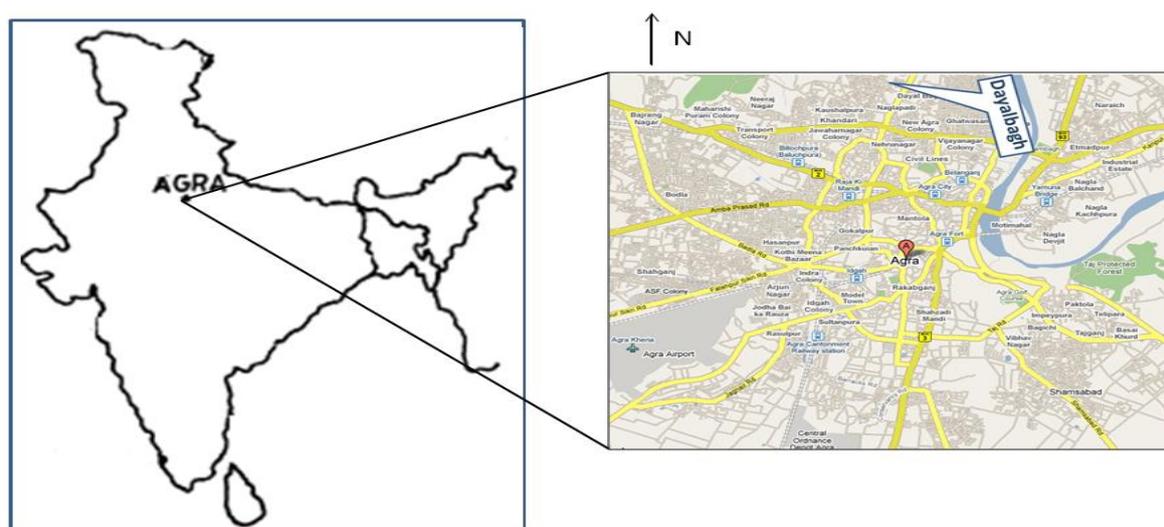
## INTRODUCTION

Aerosols particles mainly consists of water-soluble inorganic species (WSIS), elements and carbonaceous species which constitutes a major fraction of fine aerosol<sup>1, 2</sup>. The concentrations of aerosol particles are mainly influenced by meteorological factors, geographic conditions and particle emissions sources. The characteristic properties of aerosols are due to their water soluble components, e.g. magnesium, sodium, potassium, calcium, ammonium, nitrate, sulphate, chloride<sup>3</sup>, organic compounds, elemental carbon and metals that originate from a wide range of sources through a series of complex mechanisms<sup>4</sup>.

Thus, in order to understand the chemical composition, sources and formation mechanism of fine (PM<sub>2.5</sub>) as well as coarse (PM<sub>10</sub>) particles, several studies have been carried out in a large variety of environments worldwide<sup>5-9</sup>. However, only few studies reports simultaneous measurements of PM<sub>2.5</sub> and PM<sub>10</sub> aerosol particles<sup>2, 10, 11</sup>. On the other hand, the detailed information regarding the chemical composition, concentration, sources and formation mechanism of PM<sub>2.5</sub> as well as PM<sub>10</sub> aerosols is still limited in India. The purpose of the present study is to quantify the relative contribution of water soluble inorganic ions and carbonaceous species in PM<sub>2.5</sub> and PM<sub>10</sub> mass, to identify the possible sources and factors affecting aerosol composition during winter season at Agra, an urban location of Indo- Gangetic plain.

## MATERIALS AND METHODS

**Site description and sample collection:** The sampling site is located in Agra (North Central India, 27°10' N, 78°05' E). It is the home to the world famous heritage monument Taj Mahal. It lies in a semi-arid zone, adjacent to the Thar Desert of Rajasthan. Agra's climate is tropical and strongly influenced by the Aeolian dust blown from the Asian subcontinent and Thar Desert of Rajasthan. The major industrial activities are ferrous and non-ferrous metal casting, rubber processing, electroplating industry, pulverization and engineering works. Agra is famous for Petha (famous Indian confectionary) and shoe industries which contribute to aerosol loading through their solid waste dumping and incineration.

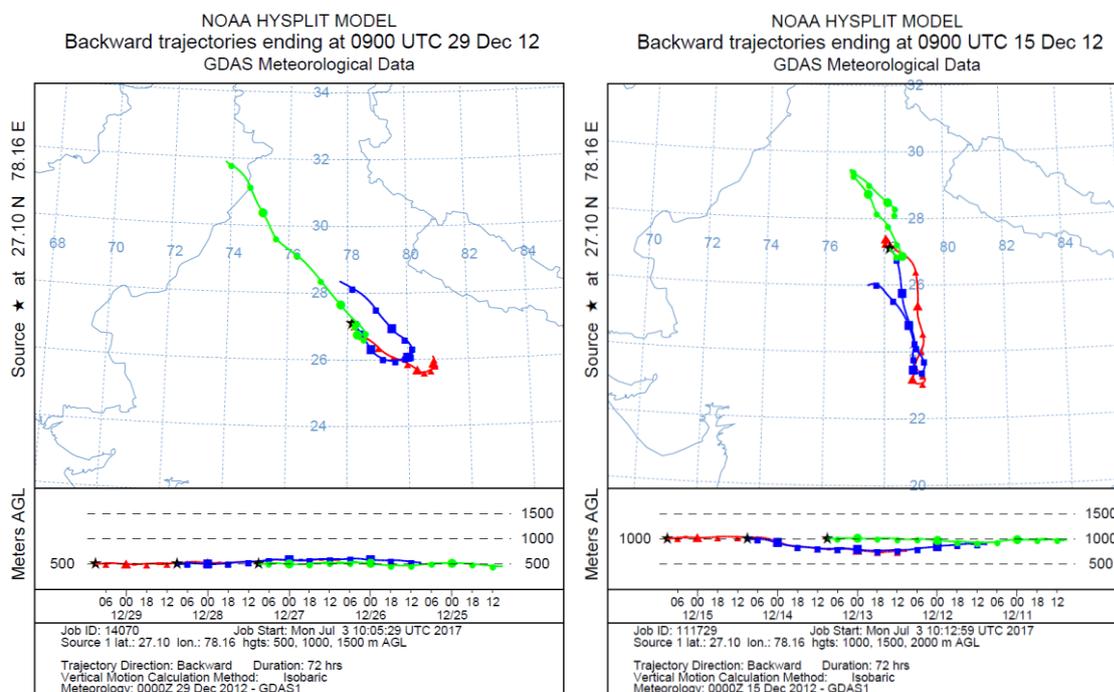


**Fig 1.** Location of sampling site.

Sampling was carried out at Dayalbagh Educational Institute Campus in Dayalbagh, lying towards north of Agra city (Fig 1). It is a suburban site with a small residential community lying immediately

outside the city where agricultural activities predominate. All PM<sub>2.5</sub> and PM<sub>10</sub> samples were collected using Fine Particulate Sampler (Envirotech APM 550) operated at a constant flow rate of 16.6 Lmin<sup>-1</sup> on pre-weighed 47 mm quartz fibre filters (Pallflex, Tissuquartz). Sampling was done for 24 h with frequency of once a week from October 2012 to February 2013 both for PM<sub>2.5</sub> and PM<sub>10</sub>. Before exposure, the quartz fiber filters were pre-heated in a muffle furnace at 800°C for 3 h to remove organic impurities. Filter papers were weighed thrice before and after sampling using four digit balance (Mettler, Toledo). 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.

**Meteorological conditions:** During the measurement period (October 2012 - February 2013), meteorological conditions such as ambient temperature, rainfall, relative humidity, wind speed and wind direction were monitored through an automatic weather monitoring system (Envirotech's Wind Monitor WM271) mounted on the roof of Science Faculty building, 12m above the ground level. Five days air mass back trajectories were calculated by HYSPLIT model, (<http://www.arl.noaa.gov/ready/hysplit4.html>) indicated that the air parcel typically originated from surrounding areas of Agra and thus show dominance of anthropogenic sources (Fig 2a,b). These air masses under the influence of different local emissions change the aerosol characteristics and give rise to increased levels of particulate mass.



**Fig 2.** (a, b) Five-day air-mass back trajectories during Dec and Jan indicating and contribution from localized sources.

**Carbonaceous analysis and quality control:** A portion of filter samples (1.5 cm<sup>2</sup>) 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)<sup>12</sup>. The analytical procedure for OC–EC has been described in our previous paper by Pachauri *et al.*<sup>13</sup>

**Water-soluble ions analysis and quality control:** The concentrations of major anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and major cations (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) in aerosol samples were determined by using Dionex ICS 1100 Ion Chromatograph system (Dionex Corp, Sunnyvale, CA). To extract the

water-soluble cations, loaded filter paper was sonicated for 45 min in 1% HNO<sub>3</sub> and major cationic concentrations were determined using 20mM Methane Sulfonic Acid as an eluent. For cation analysis, the system is equipped with guard column (CG12A, 4×50 mm), analytical column (CS12A, 4×250 mm) and cation self-regenerating suppressor (CSRS) while anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were extracted using deionized water. The major anions were analyzed by the system equipped with guard column (AS11, 4×50 mm), analytical column (AS11, 4×250 mm) and anion self-regenerating suppressor (ASRS Ultra II) using 6 mM NaOH as an eluent.

**SEM- EDX Analysis:** PM<sub>2.5</sub> aerosol samples 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). Approximately 600 particles were analyzed on each filter paper. 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.

## RESULTS AND DISCUSSION

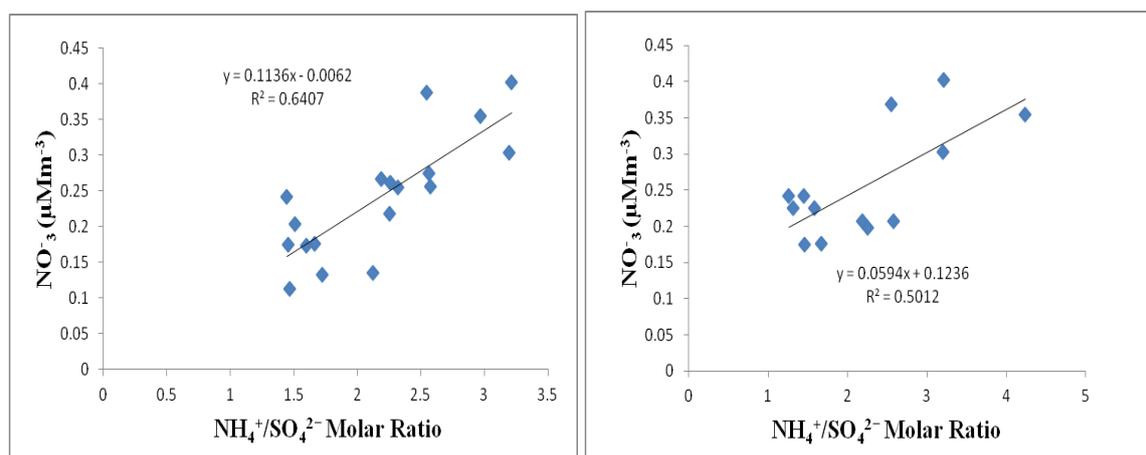
**Concentration levels and chemical composition of PM<sub>2.5</sub> and PM<sub>10</sub>:** Mass concentration is the key criteria for the assessment of air quality. At the present site, the mass concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> during winter season ranged from 49.7 to 163.6 and 267.6 to 410.6 µg/m<sup>3</sup>, respectively. The average mass concentrations were found to be 116.4 ± 39 and 310.5 ± 42.9 µg/m<sup>3</sup> for PM<sub>2.5</sub> and PM<sub>10</sub> as shown in Table 1. The results indicated that the fine particles (PM<sub>2.5</sub>) contribute about one third of PM<sub>10</sub> fraction accounting for about 36 % of total PM<sub>10</sub> mass. The average daily concentration of PM during the measurement period exceeded the 24 hour National Ambient Air Quality Standard ([http://www.cpcb.nic.in/National\\_Ambient\\_Air\\_Quality\\_Standard.php](http://www.cpcb.nic.in/National_Ambient_Air_Quality_Standard.php)) of India which has been assigned to 40 and 60 µg/m<sup>3</sup> for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively.

Higher level of particulate matter at this sampling site may be attributed to the combined impact of climatic conditions and anthropogenic emissions by various local sources such as vehicular exhaust, waste incineration, coal and biomass combustion as well as resuspended dust. These climatic conditions (i.e. less dispersion and low mixing heights) during winter months helps the ambient particles to be remain for longer time in the atmosphere. The air mass back-trajectories were simulated using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model which is based on the GDAS Meteorological Data<sup>14</sup>. The results also indicated the effect of localized sources during winter months (December, January and February).

**Water soluble ionic concentrations in PM<sub>2.5</sub> and PM<sub>10</sub>:** Water-soluble inorganic ions comprise a large part of aerosol particles and play an important role in the atmosphere. In the present study, the sum of total water-soluble ionic species (WSIS) contributed an average of 37.6 ± 8.2% to total PM<sub>2.5</sub> mass. The average mass concentrations of various ions ranked in the order of SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Ca<sup>2+</sup> > Na<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > K<sup>+</sup> > Mg<sup>2+</sup> > F<sup>-</sup>. On the other hand, the sum of WSIS in PM<sub>10</sub> ranged from 80.5 to 129.4 µgm<sup>-3</sup> (average: 98.3 ± 13.6 µgm<sup>-3</sup>, Table 1) and constituted about 30.8% of PM<sub>10</sub> mass concentration. The order of percentage contribution of each ionic species to WSIS in PM<sub>10</sub> is as follows: SO<sub>4</sub><sup>2-</sup> (24%) > Ca<sup>2+</sup> (19%) > NO<sub>3</sub><sup>-</sup> (17%) > Cl<sup>-</sup> (16.5%) > Na<sup>+</sup> (8.5%) > NH<sub>4</sub><sup>+</sup> (7%) > K<sup>+</sup> (5%) > Mg<sup>2+</sup> (2.5%) > F<sup>-</sup> (0.5%).

**TABLE 1.** The average concentrations ( $\pm 1\sigma$ ) of particulate matter (PM), carbonaceous species (OC and EC), WSIS in PM<sub>2.5</sub> and PM<sub>10</sub> samples. The average ratios ( $\pm 1\sigma$ ) and neutralization factors (NF) are also given.

Species ( $\mu\text{gm}^{-3}$ )	PM <sub>2.5</sub> (n = 20)		PM <sub>10</sub> (n = 20)		PM <sub>2.5</sub> / PM <sub>10</sub>
Mass	116.4 $\pm$ 39	49.7 – 163.6	310.5 $\pm$ 42.9	267.6 – 410.6	0.37 $\pm$ 0.03
Na <sup>+</sup>	4.5 $\pm$ 1.2	2.2 – 6.4	8.1 $\pm$ 1.8	5.4 – 12.4	0.56 $\pm$ 0.05
NH <sub>4</sub> <sup>+</sup>	4 $\pm$ 1.2	2.3 – 6.7	7.2 $\pm$ 2.1	3.3 – 11.3	0.56 $\pm$ 0.04
K <sup>+</sup>	3.2 $\pm$ 1.2	1.9 – 6.1	4.8 $\pm$ 0.8	3.1 – 5.8	0.67 $\pm$ 0.07
Mg <sup>2+</sup>	$\pm$ 0.4	0.2 – 1.9	2.2 $\pm$ 0.4	1.6 – 2.9	0.50 $\pm$ 0.04
Ca <sup>2+</sup>	5.1 $\pm$ 1.8	3.1 – 9.3	18.9 $\pm$ 4.8	8.3 – 25.4	0.28 $\pm$ 0.02
F <sup>-</sup>	0.3 $\pm$ 0.2	0.01 – 0.7	0.5 $\pm$ 0.2	0.2 – 0.8	0.61 $\pm$ 0.04
Cl <sup>-</sup>	7.1 $\pm$ 2.9	2.6 – 12.2	16.4 $\pm$ 4.2	11.3 – 24.4	0.43 $\pm$ 0.1
NO <sub>3</sub> <sup>-</sup>	5.9 $\pm$ 2.4	2.3 – 10.7	17.1 $\pm$ 5.1	10.8 – 24.9	0.34 $\pm$ 0.02
SO <sub>4</sub> <sup>2-</sup>	9.7 $\pm$ 4	4.3 – 18.7	23 $\pm$ 4.4	14.8 – 28.8	0.43 $\pm$ 0.03
$\Sigma A$	23.1 $\pm$ 8.8	11.4 – 44	56.6 $\pm$ 9.4	42.2 – 63.7	–
$\Sigma C$	19 $\pm$ 6.3	11.5 – 34.7	41.5 $\pm$ 8.8	25.9 – 48.9	–
$\Sigma C/\Sigma A$ ( $\mu\text{eq}$ )	1.3 $\pm$ 0.3	0.8 – 1.4	1.6 $\pm$ 0.4	0.9 – 2.1	–
EC	4.8 $\pm$ 1.3	2.6 – 7.1	16.3 $\pm$ 6.3	6.6 – 20.8	0.29 $\pm$ 0.02
OC	35.8 $\pm$ 16.3	13.6 – 66.2	113 $\pm$ 23.5	68.5 – 126	0.31 $\pm$ 0.02
TCA	62.6 $\pm$ 31.6	26.3 – 98	190 $\pm$ 35.8	117 – 221.6	0.32 $\pm$ 0.01
OC/EC	6.8 $\pm$ 3.1	3.1 – 8.1	7.1 $\pm$ 1.6	4.6 – 8.6	–
% TCA	54 $\pm$ 20	18.7 – 77.5	56.6 $\pm$ 8.2	51 – 69.4	–
% WSIS	37.6 $\pm$ 8.2	20.8 – 47.2	30.8 $\pm$ 3.4	28 – 34	–
NO <sub>3</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	0.65 $\pm$ 0.2	0.2 – 0.8	0.78 $\pm$ 0.2	0.5 – 0.9	–
NF (Ca)	0.6 $\pm$ 0.2	0.4 – 1.1	$\pm$ 0.4	0.4 – 1.4	–
NF (NH <sub>4</sub> )	1.1 $\pm$ 0.3	0.5 – 1.3	0.6 $\pm$ 0.2	0.3 – 0.9	–
NF (Mg)	0.2 $\pm$ 0.1	0.1 – 0.5	0.5 $\pm$ 0.2	0.2 – 1	–



**Fig 3.** Correlation between NH<sub>4</sub><sup>+</sup>/ SO<sub>4</sub><sup>2-</sup> molar ratio and NO<sub>3</sub><sup>-</sup> concentrations in PM<sub>2.5</sub> and PM<sub>10</sub>.

Among the various ionic species, SO<sub>4</sub><sup>2-</sup> was the most abundant chemical component and accounted for nearly 23% of total mass of WSIS in both PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. On average, the concentrations of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> accounted for 46 and 48% of total WSIS in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. Atmospheric SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> are formed through gas- to- particle conversion processes when their gaseous precursor's viz. SO<sub>2</sub> and NO<sub>2</sub> gets oxidized. These precursor gases are emitted from various industrial, vehicular and domestic activities<sup>15, 16</sup>. Particulate ammonium may originate by

reaction of  $\text{NH}_3$  vapours with acidic gases such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  or ammonia vapour may react or condense on an acidic particle surface of anthropogenic origin and accumulate in fine mode<sup>15</sup>. The stability of the products  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{Cl}$  are different and depend upon temperature and relative humidity<sup>5</sup>. Ammonium sulphate is most stable while  $\text{NH}_4\text{Cl}$  is most volatile; hence  $\text{NH}_3$  prefers to react with  $\text{H}_2\text{SO}_4$ . Table 2 and 3 shows the correlation matrix among the carbonaceous and WSIS in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  samples collected at Agra. The result indicated that  $\text{NH}_4^+$  is show good correlation with  $\text{SO}_4^{2-}$  ( $r = 0.65$ ),  $\text{NO}_3^-$  ( $r = 0.58$ ) and  $\text{Cl}^-$  ( $r = 0.53$ ) in  $\text{PM}_{2.5}$  than in  $\text{PM}_{10}$   $\text{SO}_4^{2-}$  ( $r = 0.58$ ),  $\text{NO}_3^-$  ( $r = 0.55$ ) and  $\text{Cl}^-$  ( $r = 0.48$ ). These results suggest that ammonia has strong affinity for  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  acids for the formation of ammonium salts in fine-mode. It may be observed that appreciable amount of ammonia is present in fine as well coarse mode due to the presence of cattle shed at a distance of 0.5 km and use of fertilizers in agricultural fields surrounding the sampling site which may act as a major sources of  $\text{NH}_3$  gas.

**TABLE 2:** Correlation matrix among the carbonaceous and WSIS in  $\text{PM}_{2.5}$  samples from Agra. Values in bold indicates significance at 0.001 probability level.

	$\text{PM}_{2.5}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	OC	EC
$\text{PM}_{2.5}$	1											
$\text{Na}^+$	0.210	1										
$\text{NH}_4^+$	0.476	<b>0.518</b>	1									
$\text{K}^+$	0.419	0.238	0.324	1								
$\text{Mg}^{2+}$	0.438	0.391	<b>0.759</b>	0.297	1							
$\text{Ca}^{2+}$	0.446	0.206	-0.090	0.563	<b>0.661</b>	1						
$\text{F}^-$	-0.496	-0.173	-0.098	0.050	-0.271	-0.276	1					
$\text{Cl}^-$	<b>0.711</b>	0.347	<b>0.573</b>	<b>0.681</b>	0.181	0.311	-0.46	1				
$\text{NO}_3^-$	<b>0.703</b>	0.491	<b>0.581</b>	0.308	<b>0.528</b>	<b>0.508</b>	-0.45	0.231	1			
$\text{SO}_4^{2-}$	<b>0.663</b>	0.502	<b>0.630</b>	0.381	0.257	<b>0.512</b>	-0.35	<b>0.793</b>	<b>0.737</b>	1		
OC	<b>0.647</b>	0.247	0.184	<b>0.589</b>	0.369	0.386	-0.45	<b>0.585</b>	0.526	0.316	1	
EC	0.339	0.486	0.381	<b>0.495</b>	0.453	0.185	-0.25	<b>0.456</b>	0.397	0.175	<b>0.851</b>	1

**TABLE 3:** Correlation matrix among the carbonaceous and WSIS in  $\text{PM}_{10}$  samples from Agra.

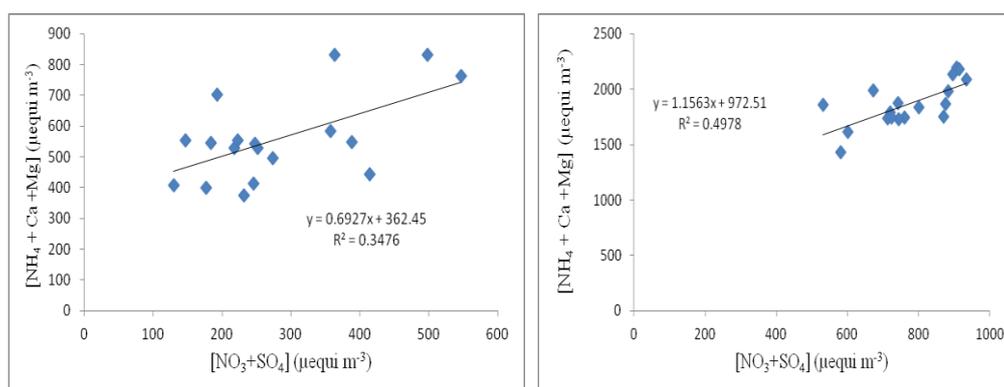
	$\text{PM}_{10}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	OC	EC
$\text{PM}_{10}$	1											
$\text{Na}^+$	0.854	1										
$\text{NH}_4^+$	0.926	0.891	1									
$\text{K}^+$	0.661	0.686	0.603	1								
$\text{Mg}^{2+}$	0.241	-0.069	-0.180	-0.08	1							
$\text{Ca}^{2+}$	0.432	0.546	0.440	0.418	0.721	1						
$\text{F}^-$	0.128	0.309	0.183	0.228	0.277	0.205	1					
$\text{Cl}^-$	0.701	0.490	0.481	0.408	0.113	0.298	-0.18	1				
$\text{NO}_3^-$	0.279	0.395	0.551	0.376	0.205	0.606	-0.16	0.396	1			
$\text{SO}_4^{2-}$	0.115	0.394	0.582	0.713	0.190	0.591	-0.50	0.139	0.580	1		
OC	0.794	0.882	0.832	0.508	-0.07	0.770	0.18	0.501	0.131	-0.27	1	
EC	0.672	0.614	0.620	0.488	0.200	0.617	0.44	0.445	-0.18	-0.84	0.845	1

The  $\text{NH}_4^+/\text{SO}_4^{2-}$  molar ratios for the formation of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  are 2:1 and 1:1, respectively. In the present study,  $\text{NH}_4^+/\text{SO}_4^{2-}$  molar ratios were  $2.8 \pm 1.0$  and  $2.1 \pm 0.8$  in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ , respectively. The ratio is  $>2$  in both  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  samples suggesting their predominant existence as  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  salts. The formation of  $\text{NH}_4\text{NO}_3$  by chemical neutralization at the present site is supported by positive correlation between  $\text{NH}_4^+/\text{SO}_4^{2-}$  molar ratios and  $\text{NO}_3^-$

concentrations ( $r = 0.8$  in  $PM_{2.5}$  and  $r = 0.7$  in  $PM_{10}$ , Figure 3). At Hisar, Rengarajan *et al.*<sup>17</sup> had also reported significant positive correlation ( $r = 0.82$ ) between  $NH_4^+/SO_4^{2-}$  molar ratios and  $NO_3^-$  concentrations in TSP. The incorporation of  $NO_3^-$  to the particulate phase is not favored when  $NH_4^+/SO_4^{2-}$  ratio is low<sup>17, 18</sup>. Thus, it may be concluded that  $NH_4^+$  primarily exists in the form of  $(NH_4)_2SO_4$  and  $NH_4NO_3$  both in  $PM_{2.5}$  and  $PM_{10}$  aerosols at Agra.

The crustal elements ( $Ca^{2+}$  and  $Mg^{2+}$ ) found in the coarse-mode mainly originate from disturbed soils. A strong correlation between  $Ca^{2+}$  and  $Mg^{2+}$  ( $r = 0.72$ ) in  $PM_{10}$  also indicate that these mineral aerosols dominate in coarse fraction. As described above, the relatively low association of  $NH_4^+$  with  $NO_3^-$  and  $SO_4^{2-}$  in the coarse-mode suggests that the role of water soluble  $Ca^{2+}$  is important for the neutralization of acidic species ( $NO_3^-$  and  $SO_4^{2-}$ )<sup>11,19</sup>. This could be explained by the neutralization factors (NF defined as the ratios of equivalent concentration of,  $Ca^{2+}$  and  $Mg^{2+}$  to  $NO_3^-$  and  $SO_4^{2-}$ ) which are presented in Table 1. The results show higher values of NF for  $Ca^{2+}$  suggesting the possible association of  $NO_3^-$  and  $SO_4^{2-}$  with  $Ca^{2+}$  in coarse mode. This probable relationship is also indicated by good correlation of  $Ca^{2+}$  with  $SO_4^{2-}$  ( $r = 0.59$ ) and  $NO_3^-$  ( $r = 0.6$ ) in  $PM_{10}$ . In general,  $NO_3^-$  exists in fine mode as  $NH_4NO_3$  whereas in coarse mode a portion of released  $HNO_3$  (after neutralization with  $NH_3$ ) and/or  $H_2SO_4$  can react with alkaline mineral dust to form  $Ca(NO_3)_2$  and/or  $CaSO_4$  in the coarse-mode<sup>19-21</sup>. Wang *et al.*<sup>22</sup> also reported that the lower temperature in winter favor the shift from the gas phase of nitric acid to the particle phase of nitrate which could lead to the formation of coarse mode nitrate. In  $PM_{2.5}$ , the NF value for  $NH_4^+$  is relatively higher as compared to that in  $PM_{10}$  which can be attributed to greater affinity of ammonia for  $H_2SO_4$  and  $HNO_3$  acids in the fine-mode. Thus, particulate  $NH_4^+$  is the major neutralizing agent in  $PM_{2.5}$ , whereas  $Ca^{2+}$  plays an important role in the neutralization of the acidic species ( $NO_3^-$  and  $SO_4^{2-}$ ) in the coarse mode ( $PM_{10}$ ) aerosols.

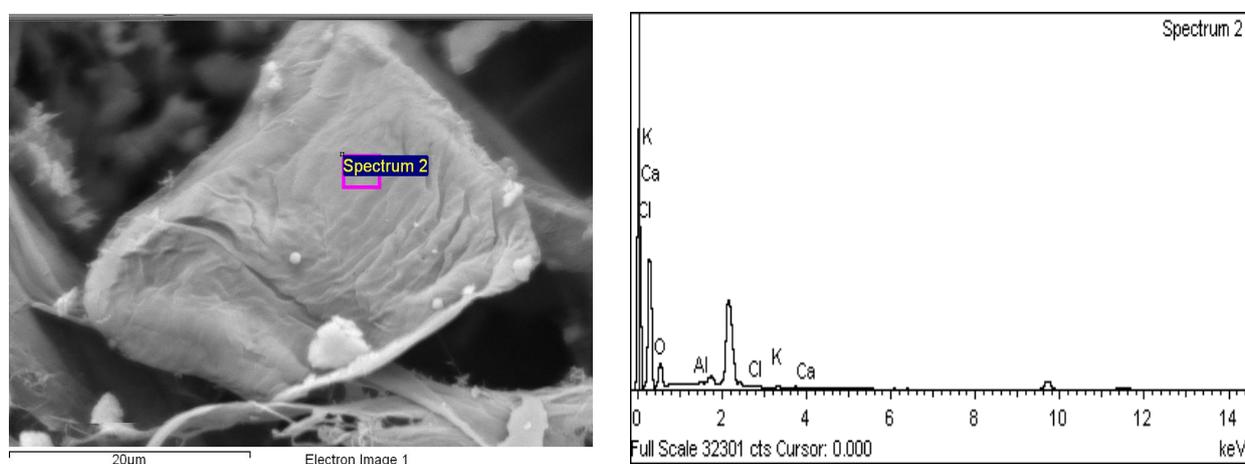
The acid neutralization capacity of different cations can also be estimated by the correlation between  $NO_3$  and  $SO_4$  with Ca, Mg and  $NH_4$  which suggests that the acidity in aerosols (mainly due to the presence of  $NO_3$  and  $SO_4$ ) is neutralized by the alkaline species (Ca, Mg and  $NH_4$ ) which act as neutralizing agent or buffer. This is further confirmed by linear regression between the sum of ( $NO_3+SO_4$ ) and ( $Ca+NH_4+Mg$ ) as shown in Figure 4. The correlation coefficient was 0.58 and 0.7 in  $PM_{2.5}$  and  $PM_{10}$ , respectively. Earlier studies at the present site had also reported that the basic nature of coarse mode aerosols is primarily due to soil-derived alkaline components, Ca and Mg while in fine mode  $NH_4$  is the major neutralizing agent<sup>5,23</sup>.



**Fig. 4** Regression between  $NO_3$  and  $SO_4$  with Ca, Mg and  $NH_4$  in  $PM_{2.5}$  and  $PM_{10}$  aerosols.

A good correlation was observed between  $NO_3^-$  and  $SO_4^{2-}$  in  $PM_{2.5}$  ( $r = 0.79$ ) than in  $PM_{10}$  ( $r = 0.58$ ). This correlation implied that precursors of these species were released from similar emission sources such as coal burning, vehicular exhaust or industrial emissions especially in case of  $PM_{2.5}$  aerosols but in  $PM_{10}$  some fraction of  $NO_3^-$  and  $SO_4^{2-}$  may probably be contributed by crustal sources. In addition

to these sources, internal mixing and meteorological conditions might also play some roles for the good correlation. Earlier studies on chemical characterization of aerosols at this site also show that  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are partly soil derived and partly of secondary origin formed by heterogeneous reactions of gaseous  $\text{SO}_2$  and  $\text{HNO}_3$  on soil particles<sup>5,23</sup>. This may be further confirmed by determining the ratios of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions with respect to Ca in soil (by assuming all suspended Ca to be soil derived). The results indicated that in  $\text{PM}_{2.5}$  around 30% of  $\text{NO}_3$  and  $\text{SO}_4$  in aerosols have been derived from local soil as their ratios are close to the corresponding ratios in the local soil whereas about 50%  $\text{NO}_3$  and  $\text{SO}_4$  in  $\text{PM}_{10}$  aerosols have been derived from local soil while other fraction of these ions are contributed from other local anthropogenic sources.  $\text{NO}_3^-/\text{SO}_4^{2-}$  ratio may provide some idea about the contribution of different major anthropogenic activities. If this ratio is  $>1$  it indicates greater contribution of  $\text{NO}_3$  that is emissions from mobile sources (vehicular emissions) whereas if this ratio is  $<1$ , it shows greater contribution of  $\text{SO}_4$  which shows the dominance of stationary sources (industrial activities) over vehicular activity<sup>24</sup>. The average ratio was found to be  $0.65 \pm 0.2$  and  $0.78 \pm 0.2$  in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ , respectively. The ratios are  $<1$  indicating slight dominance of  $\text{SO}_4$ . This might be due to great coal consumption during winter season which has higher sulphur content.



**Fig. 6** Scanning electron images and energy – dispersive X- ray spectra of: KCl particle with varying amount of soil related components like Ca and Al

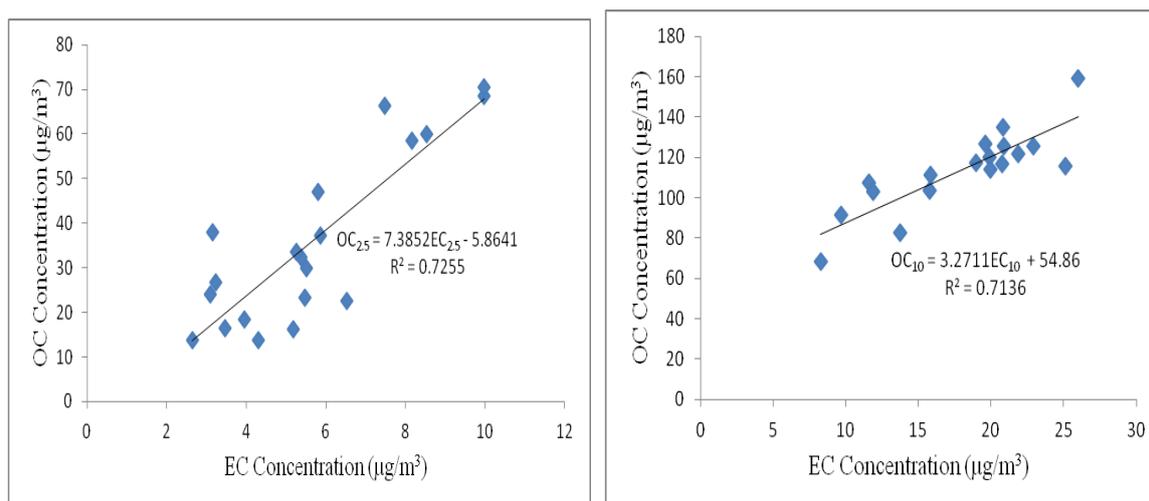
$\text{K}^+$  is generally used as tracer of biomass burning due to its release during combustion processes. Prior studies have also shown that biomass burning is significant source<sup>25-28</sup> of water soluble  $\text{K}^+$ . Cooper<sup>29</sup> had also reported that K may be released into the atmosphere by burning of plant materials and mainly associated with fine mode. Several other studies have measured and reported high concentrations of  $\text{K}^+$  and  $\text{Cl}^-$  in source profile studies of biomass burning and residential wood combustion<sup>30-32</sup>. In the present study, a good correlation between  $\text{K}^+$  and  $\text{Cl}^-$  ( $r = 0.68$ ) in  $\text{PM}_{2.5}$  further confirms that both the tracers of biomass burning were associated with fine mode which could be attributed to enhanced combustion activities during winter. These observations are further supported by the occurrence of KCl particles during SEM/EDX analysis (Fig 6). The presence of KCl particles in young smoke has also been reported by Li *et al.*<sup>32</sup>. In the present study, few carbon rich particles with traces of K and Cl were also found indicating the contribution of wood burning emissions. Edgerton *et al.*<sup>33</sup> have reported that soot particles containing trace amounts of potassium are indicative of wood burning. On the other hand, in  $\text{PM}_{10}$  aerosols they were partly derived from combustion and partly from local crustal sources as nearly 50% of their soil ratio ( $\text{K}/\text{Ca}$  and  $\text{Cl}/\text{Ca}$ ) were close to the corresponding ratios in the local soil.

To evaluate the aerosol acidity/alkalinity the equivalent concentration ratios of cations to anions were calculated separately for each sample measured. In PM<sub>2.5</sub> and PM<sub>10</sub>, the average ratio of total cation to anion ( $\sum C/\sum A$ ) was found to be  $1.4 \pm 0.3$  and  $1.8 \pm 0.6$ , respectively. The results show that both PM<sub>2.5</sub> and PM<sub>10</sub> samples were alkaline in nature indicating the dominance of cations. The alkalinity of aerosols at the present site was also reported in our earlier studies<sup>5,23</sup>.

**Concentration of carbonaceous species in PM<sub>2.5</sub> and PM<sub>10</sub>:** In recent years, carbonaceous aerosols have drawn special attention due to its adverse impacts on environment, visibility and human health<sup>34-36</sup>. 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)<sup>15,37-39</sup>. The average concentrations of OC and EC were found to be  $35.8 \pm 19.2 \mu\text{g}/\text{m}^3$  and  $4.8 \pm 1.3 \mu\text{g}/\text{m}^3$  in PM<sub>2.5</sub> while in PM<sub>10</sub> it was found to be  $113 \pm 23.5 \mu\text{g}/\text{m}^3$  and  $16.3 \pm 6.3 \mu\text{g}/\text{m}^3$ . The OC and EC mass concentration in PM<sub>10</sub> was about 3.1 and 3.3 times higher than in PM<sub>2.5</sub>. Furthermore, the percentage contribution of PM<sub>2.5</sub> to PM<sub>10</sub> in case of OC and EC were 31.6 and 29.4%, respectively. The higher concentration of OC and EC may be attributed to increased emissions from coal and other combustible materials (like burning of wood, cowdung cakes, rubber, tire and vegetation debris) in addition with unfavorable atmospheric dispersion (e.g. low mixing height, frequent inversion etc.).

The total carbonaceous aerosol ( $\text{TCA} = 1.6 \cdot \text{OC} + \text{EC}$ ) constitutes a major fraction of fine aerosol during winter season at Agra. In the present study, the average concentration of TCA was found to be  $62.6 \pm 31.6$  and  $190 \pm 35.8 \mu\text{g}/\text{m}^3$  in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. TCA accounted for an averaged 54 and 56.6% of PM<sub>2.5</sub> and PM<sub>10</sub> mass. This indicates that the carbonaceous fraction accounted for about half of PM<sub>2.5</sub> and PM<sub>10</sub> mass indicating that aerosol particles at the present site are enriched with carbonaceous species. OC shows a good positive correlation with water soluble  $\text{K}^+$  ( $r = 0.58$  in PM<sub>2.5</sub>;  $r = 0.5$  in PM<sub>10</sub>) supporting that the biomass burning emissions are the main source of carbonaceous species. Relatively high  $\text{K}^+/\text{EC}$  ratios have been reported for biomass burning (range: 0.21 – 0.46) and low ratios for fossil fuel emissions (range: 0.025 – 0.09)<sup>7, 26</sup>. In the present study, the  $\text{K}^+/\text{EC}$  ratios range from 0.3 to 0.69 in PM<sub>2.5</sub> while 0.2 to 0.49 in PM<sub>10</sub>. The relatively higher value of  $\text{K}^+/\text{EC}$  ratios indicate biomass burning emissions as the main source of carbonaceous particles in the atmosphere. Similarly, the  $\text{K}^+/\text{OC}$  ratio exhibits a narrow range of 0.04- 0.13 for agricultural waste burning<sup>40</sup> and 0.19 - 0.21 during the wheat straw burning events. Similar results have been observed in our study where the average  $\text{K}^+/\text{OC}$  ratio was found to be 0.04 in PM<sub>2.5</sub> and 0.06 in PM<sub>10</sub> which seems appropriate at the present site as it is surrounded by agricultural fields. After the harvest agricultural waste are burnt which contribute to  $\text{K}^+/\text{OC}$  ratio.

Figure 5 shows good OC – EC correlation with correlation coefficient (R) of 0.85 and 0.84 for PM<sub>2.5</sub> and PM<sub>10</sub> 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 mass ratio OC to EC (OC/EC) can be 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. 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.



**Fig. 5** Correlation between OC and EC concentration in PM<sub>2.5</sub> and PM<sub>10</sub> aerosols.

The ratio of OC/EC ranged from 3.4 to 10.1 and 4.6 to 9.4 with an average of  $6.8 \pm 2.8$  and  $7.1 \pm 1.6$  for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. The highest OC/EC ratio during winter months could be attributed to several reasons namely: increased residential combustion of coal and wood contribute more to OC than EC, resulting in increased emission of volatile organic precursors, the stagnant and dry meteorological conditions resulted in more SOA formation in wintertime, more semi-volatile organic compounds condensed into aerosol in lower temperature. The ratio is similar to that reported in the literature for combined emissions from coal smoke<sup>41</sup> (OC/EC: 2.5 – 10.5, Chen *et al.*,<sup>42</sup> kitchen emissions (OC/EC: 4.3 – 7.7, See and Balasubramaniam, ) and biomass burning<sup>43</sup> (OC/EC: 3.8 – 13.2, Zhang *et al.*<sup>43</sup>). The OC/EC ratio is mostly greater than 2 for most of the samples indicating the relatively high abundance of OC during winter season at Agra. This may be probably due to enhanced contribution from local biomass burning and decrease in the boundary layer height; thus, leading to efficient trapping of aerosols within the boundary layer.

**Levels of secondary organic carbon (SOC):** The direct measurement of secondary organic carbon (SOC), is not possible as it is being derived from the various physical and chemical transformation processes. Rather, they are estimated either by accounting the primary organic carbon (POC) using EC as a tracer and then subtracting it from the total organic carbon (TOC) measured<sup>37, 44</sup> using following equation:  $SOC = TOC - POC$ ;  $POC = EC \times (OC/EC)_{min}$ , where, (OC/EC)<sub>min</sub> 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<sup>44</sup> The observed values of (OC/EC) min in this study were 4.1 and 4.6 for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively.

The calculated SOC concentration using these minimum ratios ranged from 2.2 – 29.3  $\mu\text{g}/\text{m}^3$  and 19.4 – 66.5  $\mu\text{g}/\text{m}^3$  in PM<sub>2.5</sub> and PM<sub>10</sub> samples. The average concentration of SOC in PM<sub>2.5</sub> and PM<sub>10</sub> samples were  $15.7 \pm 3.4$  and  $37.9 \pm 19.5$   $\mu\text{g}/\text{m}^3$  accounting for 43.8 and 34.5% of total OC. High SOC concentration may be attributed to combined effect of anthropogenically emitted VOCs (namely benzene, toluene and xylene, BTX) from combustion and vehicular sources on oxidation contributed small amount of SOC. On the other hand, some naturally emitted terpenes (as the site is surrounded by deciduous trees which emit terpenes) were also assumed to act as source for secondary aerosol formation.

## CONCLUSIONS

During winter season, daily variability in the chemical composition of PM<sub>2.5</sub> and PM<sub>10</sub> aerosols were studied from an urban site (Agra) in the North Central India. The mass concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> ranged from 49.7 to 163.6 and 267.6 to 410.6 µg/m<sup>3</sup>, respectively. The sum of total water-soluble ionic species (WSIS) contributed an average of 37.6 and 30.8% to total PM<sub>2.5</sub> and PM<sub>10</sub> mass. SO<sub>4</sub><sup>2-</sup> was the most abundant chemical component and accounted for nearly 23% of total WSIS in both PM<sub>2.5</sub> and PM<sub>10</sub>. NH<sub>4</sub><sup>+</sup> show good correlation with SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> in PM<sub>2.5</sub> suggesting formation of ammonium salts in fine-mode. Ca and Mg in coarse mode and NH<sub>4</sub> in fine mode were found to be the major neutralizing agents.  $\sum C/\sum A$  ratio was >1 in both PM<sub>2.5</sub> and PM<sub>10</sub> samples indicating alkaline nature of aerosols. The OC and EC concentrations were 35.8 ± 19.2 µg/m<sup>3</sup> and 4.8 ± 1.3 µg/m<sup>3</sup> in PM<sub>2.5</sub> while 113 ± 23.5 µg/m<sup>3</sup> and 16.3 ± 6.3 µg/m<sup>3</sup> in PM<sub>10</sub> aerosols. Both OC and EC were found to be highly correlated indicating the presence of common dominant sources. TCA (Total carbonaceous aerosol) accounted for an averaged 54 and 56.6% of PM<sub>2.5</sub> and PM<sub>10</sub> mass indicating that aerosol particles at the present site are enriched with carbonaceous species. The average OC/EC ratios were 6.8 and 7.1 for PM<sub>2.5</sub> and PM<sub>10</sub> which is similar to the ratio reported for biomass burning emissions. The average SOC (Secondary organic carbon) concentration in PM<sub>2.5</sub> and PM<sub>10</sub> accounted for 43.8 and 34.5% of total OC. The SEM/EDX analysis of PM<sub>2.5</sub> aerosols revealed the dominance of carbonaceous particles during winter season which is also supported by back trajectory analysis indicating the anthropogenic origin of these particles.

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**Corresponding author: Tripti Pachauri**

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

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