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Original article

## Study of chemical species associated with fine particles and their secondary particle formation at semi-arid region of India

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## ABSTRACT

The fine particles (PM<sub>2.5</sub>) were collected for 24 h from Agra atmosphere and chemically characterized during the one year study period. The average concentration of PM<sub>2.5</sub> was  $90.21 \pm 20.62 \mu\text{g m}^{-3}$  which is higher than NAAQS and WHO annual standards and their seasonal trend was winter > summer > monsoon. Ionic study indicates that cations were dominant in comparison to anions. Seasonally, F<sup>-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> were higher during summer period and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> were higher during monsoon period while SO<sub>4</sub><sup>2-</sup> was higher during winter season. The ratios Ca<sup>2+</sup>/Na<sup>+</sup>, Mg<sup>2+</sup>/Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> were higher, while Cl<sup>-</sup>/Na<sup>+</sup> ratio was lower than sea water ratio indicating the incorporation of non marine constituents in aerosols. The observed Cl<sup>-</sup>/Na<sup>+</sup> (average 0.71) deviate considerable from the Sea water ratio suggesting either a fractionation of Cl<sup>-</sup> or enrichment of Na<sup>+</sup> as there was significant deviation from marine sources. Linear correlation was observable between nss-Ca<sup>2+</sup> and nss-Mg<sup>2+</sup> with HCO<sub>3</sub><sup>-</sup> throughout the annual seasonal cycle (HCO<sub>3</sub><sup>-</sup>: Ca = 0.59, HCO<sub>3</sub><sup>-</sup>: Mg<sup>2+</sup> = 0.53) suggesting the origination of these species from soil dust. The calculated conversion ratio of 'S' (CR<sub>S</sub>) was lower than 'N' (CR<sub>N</sub>) which suggests that the secondary formation of NO<sub>3</sub><sup>-</sup> aerosol from NO<sub>2</sub> was more predominant than SO<sub>4</sub><sup>2-</sup>. Trajectory analysis indicates that long range transportation also contributes to PM<sub>2.5</sub> mass over the measurement site.

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### 1. Introduction

Atmospheric aerosol particles are complex and multi-component mixture which is originating from both biogenic and anthropogenic sources. These sources are associated with various health effects as well environmental impact. They contain water-soluble inorganic species (ionic species), organic and elemental carbon as well as metals (Onat et al., 2012; Kim et al., 2002, 2004; Pipal et al., 2014a,b). According to an UNEP report, more than 500,000 people are killed worldwide each year by particulate matter (UNEP, 1994). Apart from this, the already published works on aerosols indicates that the airborne ionic species are responsible for a large proportion of the visibility loss and cloud

formation in the air (Penner et al., 2011; Cheng et al., 2011; Jung et al., 2009). Particles can also play a major role in the acidification of precipitation and may affect climate change (Khoder and Hassan, 2008). Moreover, ionic species, such as SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> are the common components of secondary airborne particles and can comprise a large fraction of the particulate matter (PM) in the atmosphere (Wang et al., 2006; Sun et al., 2006). The chemical composition of particles themselves, as well as the variety and amount of compounds adsorbed on their surfaces, are other factors expectedly responsible for the health effects. In the ambient air, coarse particles are mostly derived from soil and sea salt while fine and ultrafine particles are predominantly derived from combustion of fossil fuels (Ruusunen et al., 2011).

The Indo-Gangetic Plain (IGP) is one of the most populated and polluted regions in northern India. Large-scale urbanization, the land use changes, the industrial activities and regional emission sources (biomass burning and fossil fuel) contribute to the high aerosol loading over the entire IGP. The Gangetic Plain experiences extreme variability in the climate over the annual seasonal cycle.

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The dense fog and haze weather conditions during winter, the intense convective mixing in the summer as well as the transport of mineral dust from Pakistan, Afghanistan and the Thar Desert (in western India) impart a characteristic seasonal variability to the aerosol composition. In this context, our study is relevant and presents one year data set on the mass concentrations of  $PM_{2.5}$  and its chemical constituents. Along with the mass, the secondary particles formation in the atmosphere of the semi-arid region (Agra) of India was also investigated.

## 2. Materials and methods

### 2.1. Description of sampling site

Agra ( $27^{\circ} 10' N$   $78^{\circ} 02' E$ ) is located in the north central part of the India and 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, a World Heritage, which is situated on the west bank of the river Yamuna. Agra has about 1,574,542 inhabitants and the population density is about 1093 persons per sq. km (Census, 2011; Kulshrestha et al., 2014) with more than  $10^5$  average traffic loads of vehicles per day and 32,030 generator sets (Kumar and Kumari, 2015; ADA, 2013). In Agra, 60% of the recorded level of pollutants is due to vehicular emissions locally and from three major national highways called NH-2, NH-3 and NH-11 cross the city. Two thirds of its peripheral boundaries are bounded by the Thar Desert of Rajasthan. The major industrial activities in Agra are ferrous and non-ferrous metal casting, rubber processing, lime oxidation and pulverization, engineering works and chemicals. Apart from the local sources, Firozabad glass industry and Mathura refinery are also situated at a distance of 40 km from east and north-west of Agra, respectively.

### 2.2. $PM_{2.5}$ sample collection

Samples of  $PM_{2.5}$  were collected on the roof of building at Department of Chemistry, St. Johns College Agra from 2008 to 2009. Samples of aerosols were collected for 24 h on PTFE by medium-volume air sampler (model: APM 550, Envirotech, New Delhi flow rate: 16.61/min) which was placed about 10 m above the ground. Samples were collected twice in a week for the entire study period. After sampling, the samples were kept in a polyethylene plastic bag immediately and then preserved in a refrigerator at  $4^{\circ} C$  for further chemical analysis. The mass concentration of  $PM_{2.5}$  was ascertained gravimetrically by weighing the filters before and after the sampling.

### 2.3. Extraction of $PM_{2.5}$ samples

Half portion of PTFE (47 mm in diameter) were cut and put into beaker and then digested in beaker by ultrasonicator using Mili-Q water for 2 h followed by filtration and make up to 25 ml solution. The chemical analysis of aerosols samples was done by using Ion chromatography and Atomic Absorption Spectrometer (AAS). Ion chromatograph (DX100) was used for the analysis of  $Cl^{-}$ ,  $SO_4^{2-}$  while  $NO_3^{-}$ ,  $NH_4^{+}$  was measured by UV-Vis spectrophotometer (Spectronic -20D). Ammonium ( $NH_4^{+}$ ) reacts with phenol and hypochlorite in the presence of a catalyst (sodium nitroprusside) to produce a blue colored indophenol dye. The analysis of cations i.e.  $Na^{+}$ ,  $K^{+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  were done by AAS (Perkin Elmer-AAnalyst 100). Reproducibility test demonstrates the stability of the analytical instruments. Analysis of the same standard solution was repeated 10 times on IC and AAS The relative standard deviation was ranged in between 0.62% and 5.8% for all analyzed species which indicates about 95% reproducibility of measured species.

### 2.4. pH measurement of $PM_{2.5}$ samples

The pH values of extracted samples were also measured to know the nature of samples. Alkalinity of aerosols can be directly measured by the pH of aerosol filtrates. It is well known that high pH values of aerosol results from the basic cations such as  $Na^{+}$ ,  $Mg^{2+}$ ,  $K^{+}$ ,  $Ca^{2+}$  and  $NH_4^{+}$  whereas acidic water soluble anions such as  $SO_4^{2-}$ ,  $NO_3^{-}$  and  $Cl^{-}$  decreases the aerosols filtration. The pH of  $PM_{2.5}$  aerosol at Agra ranged from 6.2 to 9.1 (mean: 7.65, SD: 0.94) with a blanks mean value of 6.8. The mean value of pH (7.65) is little lower than blank value indicates that although Agra was not facing acid problem, but if present level of emission continue then it would face the acidification problem in near decades.

### 2.5. Quality control in monitoring and analysis

The sampler is designed to work at a constant flow rate of  $16.67 \pm 0.83$  L/min. Daily flow rate calculations (gas meter reading/timer reading) were being made to make sure that the fluctuations in flow rate are within the range or not. Filter in the wins impactor needs to be changed after 48 h of sampling (Chow et al., 1998; Pipal et al., 2014a,b) or when the filter gets clogged as per the operator's judgment. The filter should be immersed in 3–4 drops of silicon oil at regular intervals as per the need. Field blanks (unexposed filter papers) filter paper was also monitored for background contamination which was processed with samples. It was exposed in the field for few seconds, were collected thrice during the season. Background contamination was eliminated by subtracting the field blank values from concentrations of the samples. Usually, field blank values were very low, typically below or around the detection limits. The detection limits for anions ( $F^{-}$ ,  $Cl^{-}$ ,  $NO_3^{-}$  and  $SO_4^{2-}$ ) are  $< 0.01$  ppm with 0.3 ml/min eluent flow rate while for cations ( $NH_4^{+}$ ,  $K^{+}$ ,  $Na^{+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  are 0.02, 0.04, 0.02, 0.06 and 0.04 ppm with 0.25 ml/min eluent flow, respectively.

## 3. Results and discussion

### 3.1. Mass concentration of particulate matter ( $PM_{2.5}$ )

The average concentration of  $PM_{2.5}$  was  $90.21 \pm 20.62 \mu g m^{-3}$  during the entire study period. This obtained value is considerable higher than the NAAQS (<http://www.cpcb.nic.in/National-Ambient-Air-Quality-Standards.php>,  $PM_{2.5}$ :  $40 \mu g m^{-3}$ ), WHO (<http://www.euro.who.int/document/E87950.pdf>,  $PM_{2.5}$ :  $10 \mu g m^{-3}$ ) and USEPA (<http://www.epa.gov/air/criteria.html>,  $PM_{2.5}$ :  $15 \mu g m^{-3}$ ) annual standards. Monthly analysis of PM indicates the higher concentration of PM in month of Jan and lowest in the month of May (Fig. 1). Variations in mass concentration of  $PM_{2.5}$  were observed due to different emissions sources at Agra as the site is located near to semi arid regions; IGP and That desert. Over all significantly higher concentration of fine particles may be due to combined effect of climatic conditions and anthropogenic emissions such as vehicular exhaust, waste incineration, coal and biomass and bio-fuel combustion and re-suspended soil dust. The lower concentration of  $PM_{2.5}$  in the month of May may be due to the dilution effects of air pollutants because of the high speed winds.

Seasonal analyses indicates the higher concentration was during winter followed by summer and lower during the monsoon period and follows the trend as winter > summer > monsoon (Fig. 1). The accumulation of particles especially in fine size due to thermal inversion is the major cause for these high concentrations of  $PM_{2.5}$  over north region of India during the winter period (Pipal et al., 2011, 2014a,b). The source for these particles could mostly be from the local emission sources such as combustion of biomass, bio

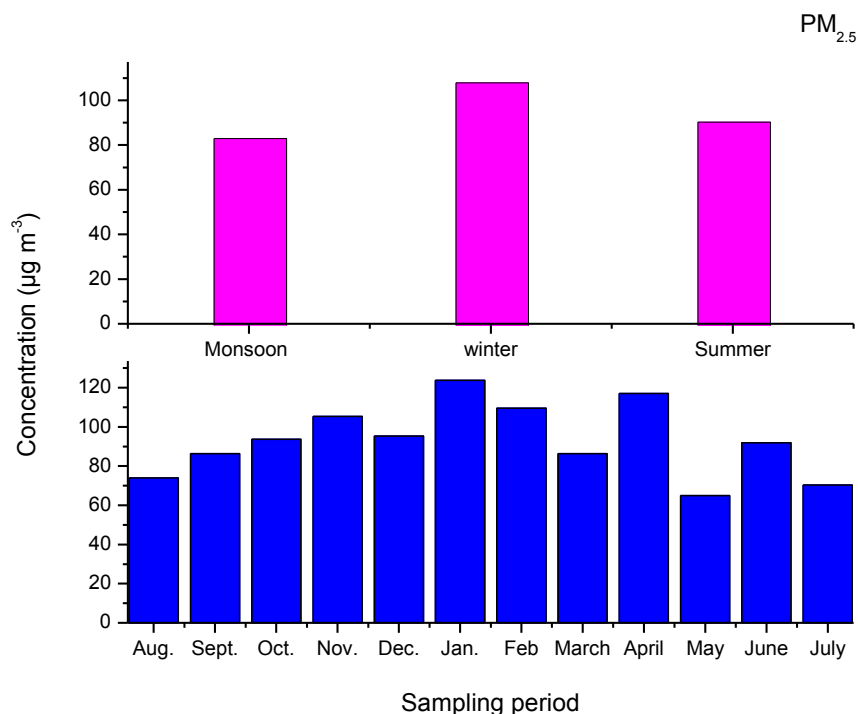


Fig. 1. Mass concentration of particulate matter (PM<sub>2.5</sub>) at Agra.

and fossil fuels (Pipal et al., 2011, 2014a,b). Awasthi et al. (2011) also reported that higher PM<sub>2.5</sub> concentration over northern part of India was due to biomass burning which was transported from western part of India. Kulshrestha et al. (2009) reported high loadings of PM<sub>2.5</sub> (195 µg m<sup>-3</sup>) in another study over Agra. The present results (90 µg m<sup>-3</sup>) are also compared with other studies reported by various authors over IGP region and given in Table 1. It was found that present study was similar and sometimes lower than the earlier reported values of fine particles over IGP region. Table 1 also shows the meteorological parameters such as temperature and relative humidity.

### 3.2. Characteristics of inorganic ionic species in PM<sub>2.5</sub>

Chemical constituents of PM<sub>2.5</sub> were characterized in terms of major cations (Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>) and anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) during one year study cycle. Fig. 2 shows the monthly trends of ionic species which indicates that Na<sup>+</sup> was

dominant in cations except some period of study (Nov–Dec) while NO<sub>3</sub><sup>-</sup> was abundant in anions followed by SO<sub>4</sub><sup>2-</sup> during the whole studied period. Fig. 3 shows the variations and relationship between total cations and total anions which indicates that cations were dominant in comparison to anions during whole study. Table 2 also depicts the seasonal values of ionic species along with their standard deviation. As evident from the Table, the concentration of F<sup>-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> were higher during summer period whereas other chemical species such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> were higher during monsoon period except SO<sub>4</sub><sup>2-</sup> which was higher during winter season. Table 3 shows the monthly values of some chemical components during the study period.

To see the completeness of the measured parameters in PM<sub>2.5</sub> samples, charge balance between total cations ( $\sum^+$ : Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>) and total anions ( $\sum^-$ : F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were determined in the water extract of PM<sub>2.5</sub>. The total equivalent of anions was plotted against the total equivalent of cations (Fig. 4a). The slope of regression line was lower than unity (slope = 0.98, r = 0.59 significant P < 0.001) which might be attributed to unmeasured anions, which are not counted in the calculation. The main anions which may cause the lower slope (i.e., imbalance) are bicarbonate, organic ions (formic acid acetate) and NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and Br<sup>-</sup>. Fig. 4b shows the plot between the difference of  $\sum^+$  cations and  $\sum^-$  anions i.e., called excess amount of cations and HCO<sub>3</sub><sup>-</sup> which indicates that cations consisted some parts of HCO<sub>3</sub><sup>-</sup> (r = 0.63, slope: 0.58), therefore, cations and anions are not neutralized. The previous studies from the Indian region (Kulshrestha et al., 1998; Venkataraman et al., 2002; Satsangi et al., 2014) had reported on cations excess in the ion balance of water extracts, which is largely attributed to the large amount of HCO<sub>3</sub><sup>-</sup> ions. Measurement of HCO<sub>3</sub><sup>-</sup> in the ambient aerosols provides better insight into the chemical transportation process occurring during transport of aerosols, such processes are relatively important over the region like arid and semiarid, which contributes large inputs of mineral dust into the atmosphere.

Table 1

The comparison of the present results with earlier reported studies over IGP region along with meteorological parameters.

Place	PM <sub>2.5</sub> (µg m <sup>-3</sup> )	References	Months	Temp.	RH
Agra	90.21 ± 20.62	Present study	Aug.	29.69	76.85
Agra	195	Kulshrestha et al., 2009	Sept.	30.22	64.25
Agra	90.16 ± 7.21	Pipal et al., 2011	Oct.	28.55	51.41
Delhi	148.4 ± 67	Dey et al., 2012	Nov.	22.71	54.35
Delhi	97 ± 56	Tiwari et al., 2010	Dec.	17.4	61.36
Delhi	122.3 ± 90.7	Tiwari et al., 2013	Jan.	15.59	59.42
Delhi	123 ± 87	Guttikunda and Calori, 2013	Feb.	18.57	58.38
Lucknow	101.05 ± 22.5	Pandey et al., 2012	March	22	57.8
Kanpur	95	Sharma and Maloo, 2005	April	31.86	25.6
Kanpur	37.6	Ghosh et al. 2014	May	34.24	43.34
			June	32.67	52.96
			July	29.96	80.67

Temp.: Temperature.  
RH: Relative humidity.

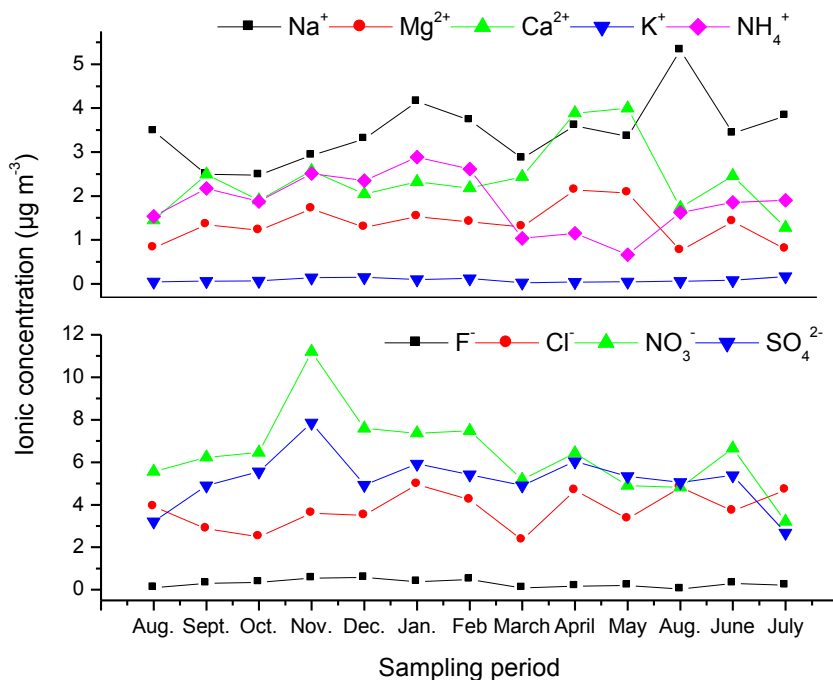


Fig. 2. Concentrations of inorganic species (cations and anions) during the study period.

Table 3  
Monthly values of CR<sub>N</sub>, CR<sub>S</sub>, O<sub>3</sub>, NO<sub>2</sub>, and NH<sub>4</sub><sup>+</sup> during the study period.

Months	CR <sub>N</sub>	CR <sub>S</sub>	O <sub>3</sub> (µg m <sup>-3</sup> )	NO <sub>2</sub>	NH <sub>4</sub> <sup>+</sup>
Aug.	0.28	0.09	16.00	14.30	1.54
Sept.	0.19	0.10	26.20	25.80	2.17
Oct.	0.13	0.12	72.50	40.30	1.87
Nov.	0.22	0.14	78.20	38.30	2.50
Dec.	0.14	0.10	53.30	45.50	2.30
Jan.	0.13	0.12	47.40	46.80	2.80
Feb.	0.16	0.12	59.63	43.53	2.53
March	0.15	0.18	64.90	29.30	1.04
April	0.20	0.32	46.90	24.50	1.15
May	0.34	0.29	27.20	9.30	0.66
June	0.13	0.09	34.10	17.30	1.18
July	0.20	0.25	21.90	12.50	1.59

CR<sub>N</sub>: Conversion ratio of nitrogen.  
CR<sub>S</sub>: Conversion ratio of sulfur.

In the present study, HCO<sub>3</sub><sup>-</sup> were not determined analytical and their concentration were estimated on the basis of equilibrium between CO<sub>3</sub><sup>2-</sup> dissolve HCO<sub>3</sub><sup>-</sup> using the following equation (EANET, 2000).

$$[\text{HCO}_3^-] (\text{neq ml}^{-1}) = 1.24 \times 10^{(\text{pH}-5.35)} \quad (1)$$

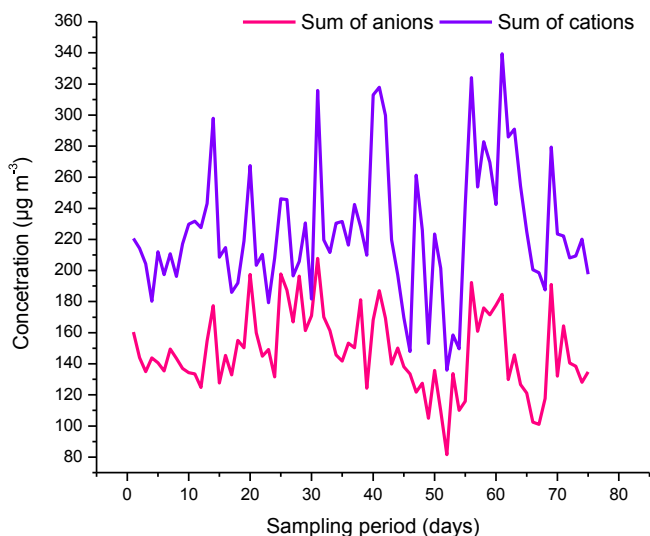


Fig. 3. Trend of sum of cations (Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>) and sum of anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) during the study period.

Table 2  
Season wise trend of ionic species such as cations and anions along with HCO<sub>3</sub><sup>-</sup> (µg m<sup>-3</sup>).

		F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>
Monsoon	Average	0.15	3.77	5.59	4.49	1.01	1.96	1.82	3.66	0.05	0.57
	SD	0.13	1.21	1.15	1.28	0.40	0.57	0.61	1.45	0.02	0.78
Winter	Average	0.14	3.32	5.00	5.17	1.68	3.24	0.94	3.09	0.03	0.57
	SD	0.08	1.40	1.65	1.71	0.67	1.24	0.44	1.04	0.02	0.30
Summer	Average	0.16	3.48	4.85	5.01	1.77	3.31	0.82	3.16	0.04	0.62
	SD	0.07	1.50	1.95	1.91	0.70	1.34	0.43	1.14	0.02	0.29

SD: standard deviation.

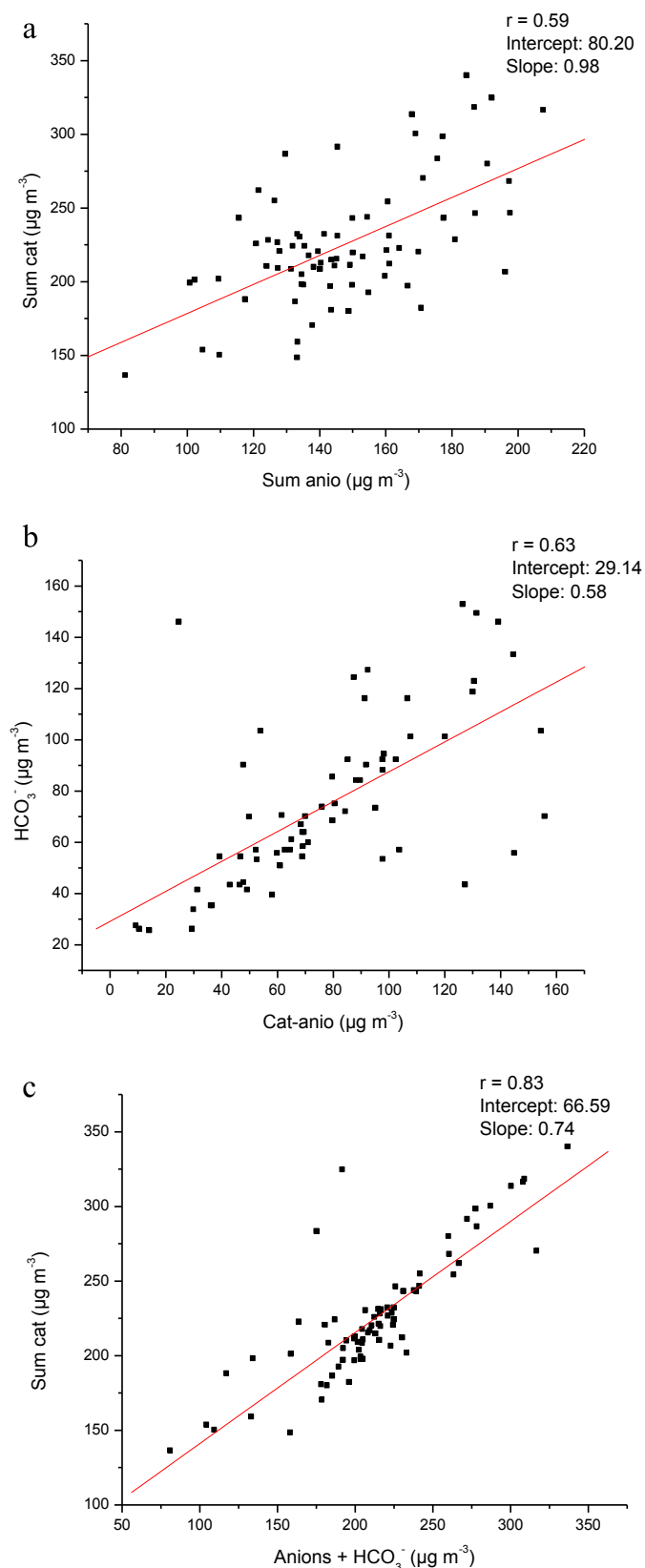


Fig. 4. a: Plot between  $\sum$ cations and  $\sum$ anions. b: Plot between  $\text{HCO}_3^-$  and cations-anions. c: Plot between  $\sum$ cations and  $\sum$ anions +  $\text{HCO}_3^-$ .

The mean concentration of  $\text{HCO}_3^-$  (neq  $\text{ml}^{-1}$ ) inclusion of concentration of  $\text{HCO}_3^-$  to anions sum the slope of the regression line slightly lower than the unity (slope = 0.74,  $r = 0.83$ ) which indicates that almost all of the ions have been quantified (Fig. 4c).

In order to determine the marine influence on the  $\text{PM}_{2.5}$  composition, Sea salt ratios were calculated using  $\text{Na}^+$  as reference element (Parmar et al., 2001). It is evident from Table 4 that ratios of  $\text{Ca}^{2+}/\text{Na}^+$ ,  $\text{Mg}^{2+}/\text{Na}^+$  and  $\text{SO}_4^{2-}/\text{Na}^+$  were higher, while for  $\text{Cl}^-/\text{Na}^+$  ratio was less than Sea water ratio. Aerosol composition may be affected by local terrestrial sources. Al, Fe, Ca, and Si are the good tracer of soil but we could not select them as reference element because Al and Si were not determined in sample. And also a significant fraction of Ca and Fe is also emitted from anthropogenic activities (ferrous and non ferrous foundries are situated in Agra). Therefore, Mg has been chosen as a reference element considering all Mg to be soil originated. The ratios of various ions with respect to Mg in soil and  $\text{PM}_{2.5}$  are presented in Table 4. It was found that ratios were very much higher ( $\text{Cl}^-/\text{Mg}^{2+}$ ) in the month of June. Moreover,  $\text{Cl}^-/\text{Mg}^{2+}$  and  $\text{Na}^+/\text{Mg}^{2+}$  were close to corresponding ratios in local soil. This shows that  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$  are the mainly soil derived while  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are contributed from other sources. In order to determination of other sources, excess concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were calculated. On the basis of this, it is found that 52–69% for  $\text{SO}_4^{2-}$  and 76–88% for  $\text{Mg}^{2+}$  contribution from industries. It is evident from table that ratios of  $\text{Ca}^{2+}/\text{Na}^+$ ,  $\text{Mg}^{2+}/\text{Na}^+$  and  $\text{SO}_4^{2-}/\text{Na}^+$  were very much higher in winter and summer compare to monsoon seasons while for  $\text{Cl}^-/\text{Na}^+$  ratio was less than sea water ratios. Higher deviation in ratios indicates that incorporation of non marine constituents in  $\text{PM}_{2.5}$  aerosols due to the distance of the sampling location from the Sea as Agra is situated about 1500 km away from both Bay of Bengal and the Arabian Sea. The observed  $\text{Cl}^-/\text{Na}^+$  (average 0.71) deviate considerably from the Sea water ratio suggesting either a fractionation of  $\text{Cl}^-$  or enrichment of  $\text{Na}^+$  using this as reference element for sea salt concentration, nss component has been calculated (Wang et al., 2006; Lee and Hieu, 2013). The non sea salt components of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  are varied from 52% to 96% which suggest the non influence of marine sources.

### 3.3. Correlation coefficient

Linear correlation was observed between nss- $\text{Ca}^{2+}$ , nss- $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  throughout the annual seasonal cycle. ( $\text{HCO}_3^-$ :  $\text{Ca}^{2+} = 0.59$ ,  $\text{HCO}_3^-$ :  $\text{Mg}^{2+} = 0.53$ ) which suggest that the origin ionic species was from soil dust. Nss- $\text{Ca}^{2+}$  and nss- $\text{Mg}^{2+}$  also correlated with nss- $\text{SO}_4^{2-}$  and they could be arise due to their origin from same sources (from soil) or as *in situ* formation of  $\text{CaSO}_4$  at the surface of mineral dust during the atmospheric excess pollution (Wu and Okada, 1994). In the former case, we would expect very good correlation among both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with nss- $\text{SO}_4^{2-}$ , which is not applicable for our data. As evident from Table 5 although,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was correlated with  $\text{SO}_4^{2-}$  but data is largely scattered which suggests the dominance of *in situ* formation of  $\text{CaSO}_4$  (nss  $\text{SO}_4^{2-}$ :  $\text{Ca}^{2+}$ ) and  $\text{MgSO}_4$  (nss- $\text{SO}_4^{2-}$ :  $\text{Mg}^{2+}$ ) an aerosol surface. The correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.80$ ),  $\text{NH}_4^+$  and  $\text{K}^+$  with  $\text{NO}_3^-$  (0.50–0.59) and  $\text{NO}_3^-$  and  $\text{K}^+$  with  $\text{F}^-$  was also observed. This indicates that these chemical species may be originating from similar sources.

The sources of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in the atmosphere are the oxidation of their gaseous precursors  $\text{NO}_2$  and  $\text{SO}_x$ , respectively, entered into the atmosphere from various anthropogenic activities. Both  $\text{NO}_3^-$  and nss- $\text{SO}_4^{2-}$  produced from coal combustion, biomass and vehicular emission (Seinfeld and Pandis, 1998). The  $\text{NO}_3^-/\text{nss-SO}_4$  ratios varies from 0.51 to 2.7 with an average of 1.16, 1.46 of  $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$  has been used as an indicator of the relative

**Table 4**  
Ratios of ionic species over Agra.

	Cl <sup>-</sup> /Na <sup>+</sup>	K <sup>+</sup> /Na <sup>+</sup>	Ca <sup>2+</sup> /Na <sup>+</sup>	Mg <sup>2+</sup> /Na <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup> /Na <sup>+</sup>	Cl <sup>-</sup> /Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup> /Mg <sup>2+</sup>
Aug	0.73	0.01	0.51	0.48	0.46	4.79	3.93
Sept	0.74	0.02	1.20	1.06	1.00	2.13	3.64
Oct	0.64	0.02	0.91	0.96	1.10	2.04	4.56
Nov	0.81	0.03	1.04	1.16	1.32	2.11	4.60
Dec	0.68	0.03	0.72	0.76	0.73	2.72	3.83
Jan	0.77	0.02	0.68	0.73	0.72	3.24	3.86
Feb	0.73	0.02	0.70	0.75	0.73	3.00	3.85
March	0.55	0.01	1.00	0.87	0.85	1.81	3.77
April	0.88	0.01	1.39	1.25	0.83	2.19	2.83
May	0.64	0.01	1.41	1.18	0.79	1.61	2.58
June	0.59	0.01	0.39	0.29	0.45	6.39	6.71
July	0.701	0.01	0.93	0.88	0.83	2.61	3.80
<b>Average</b>	<b>0.71</b>	<b>0.02</b>	<b>0.91</b>	<b>0.87</b>	<b>0.82</b>	<b>2.89</b>	<b>4.0</b>
<b>SD</b>	<b>0.01</b>	<b>0.01</b>	<b>0.32</b>	<b>0.28</b>	<b>0.24</b>	<b>1.39</b>	<b>1.03</b>

SD: standard deviation.

importance of stationary (coal combustion and biomass burning) as mobile sources (vehicular emissions) of S and N in the atmosphere. Higher NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> mass ratios described the predominance of mobile sources over stationary sources of pollution at the present study site which is nearby busy road traffic therefore; the sufficient amount of NOx was present due to vehicular emissions. The emission ratio of NOx and SO<sub>2</sub> from all pollutants sources over India average around 0.75 (Garg et al., 2001). Higher ratios are compared with the present site which is nearby the traffic junction. In India, transport section contributed the 32% NOx and 7.8% SO<sub>2</sub> while biomass burning and industry 18.7 and 19.2 for NOx and 5.2 and 34.4 for SO<sub>2</sub> emission (Garg et al., 2001, 2002).

To investigate the oxidation process of S and N, the conversion ratios (CR) of 'S' (CR<sub>S</sub>) and 'N' (CR<sub>N</sub>) were calculated by using following equations (Wang et al., 2006).

$$CR_S = n - SO_4^{2-} [S] / (n - SO_4^{2-} + n - SO_2 [S]) \quad (2)$$

$$CR_N = NO_3^- [N] / (NO_3^- [N] + NO_2 [N]) \quad (3)$$

where SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> are the aerosol concentration as S and N, respectively, SO<sub>2</sub> and NO<sub>2</sub> are gases phase concentration for same period. These conversion ratios could be an indication of the secondary transformation processes. The average values of CR<sub>S</sub> were 0.12, 0.12 and 0.22 in the monsoon, winter and summer seasons, respectively. The corresponding average values for CR<sub>N</sub> were 0.22, 0.16 and 0.21, respectively. The monthly variation in CR<sub>S</sub> and CR<sub>N</sub> is given in Table 3. Earlier studies done by Pierson et al. (1979) and Truex et al. (1980) have suggested that in case of primary pollutants the value of photochemical oxidation ratio was lower than 0.10, while *in situ* formation (gaseous oxidation) the value of ratio was greater than 0.10 (Ohta and Okita, 1990). Considering their ratios in

**Table 5**  
Correlation between the inorganic ions.

	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>
Cl <sup>-</sup>	-0.04	1									
NO <sub>3</sub> <sup>-</sup>	<b>0.57</b>	0.16	1								
SO <sub>4</sub> <sup>2-</sup>	0.23	0.21	<b>0.49</b>	1							
Mg <sup>2+</sup>	0.17	0.18	0.33	<b>0.40</b>	1						
Ca <sup>2+</sup>	-0.11	0.20	0.33	<b>0.35</b>	<b>0.83</b>	1					
NH <sub>4</sub> <sup>+</sup>	<b>0.46</b>	0.25	<b>0.50</b>	0.20	-0.10	-0.21	1				
Na <sup>+</sup>	-0.20	<b>0.80</b>	-0.10	0.17	0.01	0.05	0.05	1			
K <sup>+</sup>	<b>0.70</b>	0.22	<b>0.59</b>	0.31	0.11	-0.07	<b>0.51</b>	0.11	1		
HCO <sub>3</sub> <sup>-</sup>	-0.22	0.28	-0.10	0.13	<b>0.53</b>	<b>0.59</b>	-0.12	0.22	-0.11	0.11	1

Bold values indicate that the correlation is significant at the 0.01 level.

the present aerosol, the values of CR<sub>S</sub> and CR<sub>N</sub> was found to be higher than 0.10, which clearly shows that secondary formation of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> occurred in all the seasons. The values of CR<sub>N</sub> were higher than CR<sub>S</sub> values which suggests that the secondary formation of NO<sub>3</sub><sup>-</sup> aerosol from NO<sub>2</sub> was more predominant than SO<sub>4</sub><sup>2-</sup>. Abundance of NO<sub>3</sub><sup>-</sup> was dominated by local pollution sources as the sampling site is very near too busy road. There are many mechanism reported for the formation of SO<sub>4</sub><sup>2-</sup> from SO<sub>2</sub> such as gas phase reaction of SO<sub>2</sub> and OH• radical, or transportation processes (metal catalyzed oxidation or H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> oxidation) and in cloud processes etc. since gas phase oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> by OH radicals is strong formation of temperature (Seinfeld, 1986). Therefore, higher secondary ratios were expected in summer (as higher temperature processes higher concentration of OH radicals). On applying the t-test, present data significantly show higher values in summer (0.22) than winter and monsoon (0.14 and 0.12) indicate the dominate mechanism of formation of SO<sub>4</sub><sup>2-</sup> from SO<sub>2</sub>. The slope of the regression lines between (SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>) and NH<sub>4</sub><sup>+</sup> larger than one indicating an incomplete neutralization system. The extent of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> neutralization was possible under estimated because of the evaporation which was not considered.

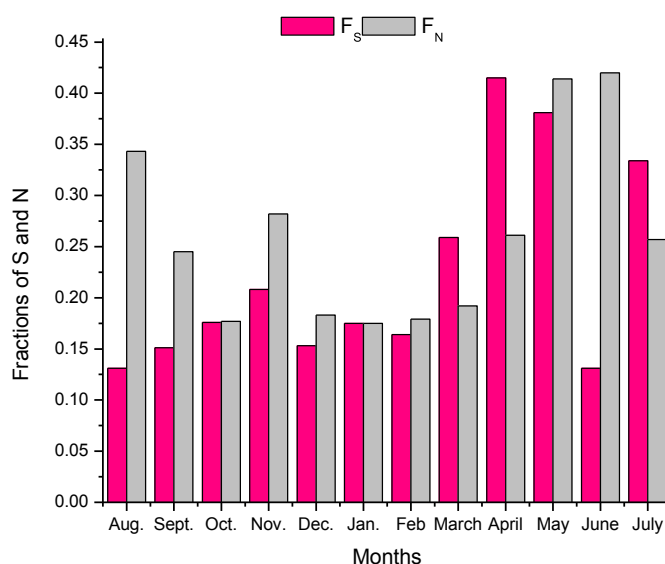
For the estimation of conversion ratios of sulfur (F<sub>S</sub>) and nitrogen (F<sub>N</sub>), the following equations have been used:

$$F_S = nss - SO_4^{2-} [S] / (nss - SO_2 [S] + SO_4^{2-} [S]) \quad (4)$$

$$F_N = nss - NO_3^- [N] / (nss - NO_2 [N] + NO_3^- [N]) \quad (5)$$

where nss-SO<sub>4</sub><sup>2-</sup> [S] and SO<sub>2</sub> [S] are the non sea salt SO<sub>4</sub><sup>2-</sup> and gas phase SO<sub>2</sub> concentration as sulfur, respectively and same for the nitrogen.

The conversion of S (IV) to SO<sub>4</sub><sup>2-</sup> is an important route for forming sulfate. The oxidation may be carried out by several oxidizing species including O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> and reaction may be catalyzed or un-catalyzed. However, oxidation by H<sub>2</sub>O<sub>2</sub> predominates only at lower pH (pH < 5) (Seinfeld, 1986), which was not possible in present case as the pH of aerosols was in alkaline condition. So, the oxidation by H<sub>2</sub>O<sub>2</sub> was ruled out. Oxidation of SO<sub>2</sub> by O<sub>3</sub> is strongly pH dependant and is most efficient at high pH. Therefore, it is speculation in present conditions, oxidation would proceed to some extent by O<sub>3</sub>, although, O<sub>3</sub> is photo-chemically

**Fig. 5.** Monthly trends of fractions of sulfur and nitrogen.

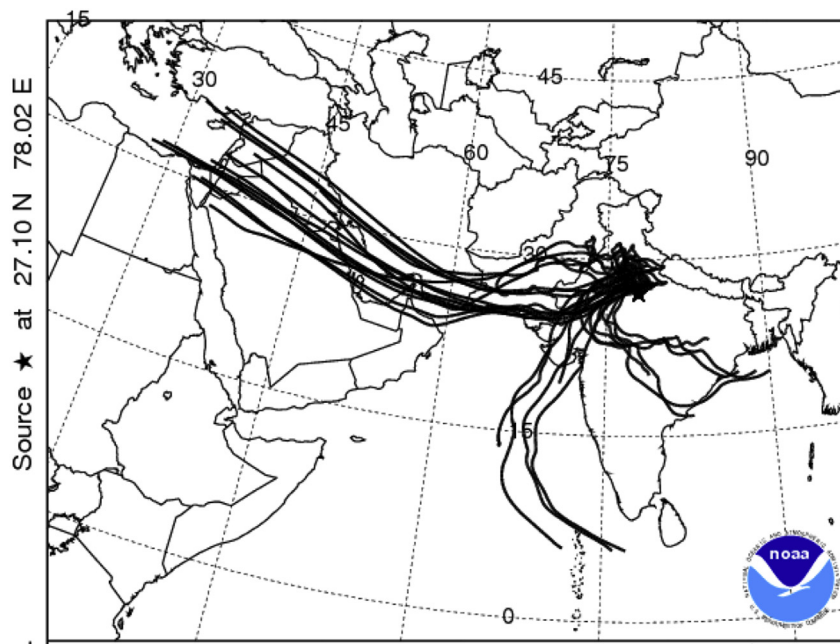


Fig. 6. Air mass backward trajectory clusters analysis at Agra in Jan 2009.

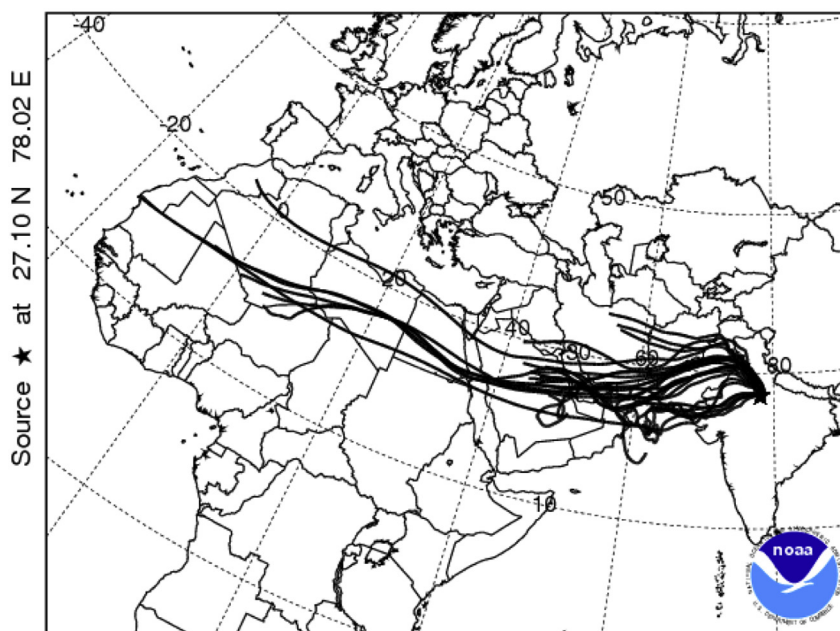


Fig. 7. Air mass backward trajectory clusters analysis at Agra in April 2009.

produced component. Fig. 5 shows monthly variation of the fractions of S and N ( $F_S$  and  $F_N$ ) at Agra which is located north region of India. During the study period, the average  $F_S$  and  $F_N$  was found to be 0.22 and 0.26.  $F_S$  values were found to be higher in the month of April (0.41) while lower during the month of June and Aug (0.31) while in the case of  $F_N$ , it was higher in June (0.42) and lower in Jan (0.17).

#### 3.4. Trajectory analysis

In the present study, the abundance of  $PM_{2.5}$  mass and its chemical species was in the month of Jan and April. Therefore, the

long range transportation of aerosols towards Agra during these months has been performed through trajectory analysis. Figs. 6 and 7 shows the five days air mass backward trajectory clusters analysis (HYSPPLIT Model access via NOAA ARLREADY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>) at Agra at the height of 500 m. This analysis is based on National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPPLIT) 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. This supports the transport of aerosols from the long range transportation from Arabian Sea, Middle Eastern, Thar Desert, Middle East of India and other part of the world over northern Indian region in the month of Jan. Whereas, it was seen in the month of April from Thar desert, south west part of India including other part of the world and neighboring countries such as Pakistan, Afghanistan, Iran, and Turkmenistan (Pipal et al., 2014a,b; Tiwari et al., 2013).

#### 4. Conclusions

Due to high emissions of anthropogenic as well as natural aerosols over IGP these factors inspired to study the atmospheric particles over and around this region. Therefore, aerosol particles ( $PM_{2.5}$ ) were collected at Agra and were characterized in terms of major cations and anions for one year period. The average concentration of  $PM_{2.5}$  was considerable higher than the NAAQS and WHO annual standards. Seasonal analysis of  $PM_{2.5}$  mass concentration follows the trend as winter > summer > monsoon. Amongst, the ionic species  $Na^+$  and  $NO_3^-$  were dominant chemical species during the study period. Seasonal analysis of ionic species reveals that  $F^-$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  were higher during summer period and other chemical species such as  $Cl^-$ ,  $NO_3^-$ ,  $NH_4^+$  and  $K^+$  were higher during monsoon period and  $SO_4^{2-}$  was higher during winter season. The relationship between ionic species indicates that the cations are dominant in comparison to anions during whole study. Ionic ratios indicates that the ratios of  $Ca^{2+}/Na^+$ ,  $Mg^{2+}/Na^+$  and  $SO_4^{2-}/Na^+$  were higher, while ratio between  $Cl^-/Na^+$  ratio was less than sea water ratio which indicates non marine constituents in aerosols. This further indicates that on the aerosol composition there is impact of regional and local terrestrial sources. Linear correlation is observed between nss-Ca, nss-Mg and  $HCO_3^-$  suggesting their origin from soil dust. The value of  $CR_N$  was higher than  $CR_S$  which suggests that the secondary formation of  $NO_3^-$  aerosol from  $NO_2$  was more predominant in comparison to  $SO_4^{2-}$ . The S and N fractions was also calculated and found to be 0.22 and 0.26 for S and N, respectively. The present study is giving the characteristics of fine particulate and it associated chemical species along with their sources over the semi-arid site (Agra). This study will useful to establish the base line of fine particulate matter for policymakers and public awareness and researchers who are working in the field of air pollution.

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