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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## ARTICLE INFO

## ABSTRACT

The fine particles ($PM_{2.5}$) were collected for 24 h from Agra atmosphere and chemically characterized during the one year study period. The average concentration of $PM_{2.5}$ was $90.21 \pm 20.62$ $\mu g$ $m^{-3}$ 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, $F^-$, $Ca^{2+}$ and $Mg^{2+}$ were higher during summer period and $Cl^-$, $NO_3^-$, $NH_4^+$ and $K^+$ were higher during monsoon period while $SO_4^{2-}$ was higher during winter season. The ratios $Ca^{2+}/Na^+$, $Mg^{2+}/Na^+$ and $SO_4^{2-}/Na^+$ were higher, while $Cl^-/Na$ ratio was lower than sea water ratio indicating the incorporation of non marine constituents in aerosols. The observed $Cl^-/Na^+$ (average 0.71) deviate considerable from the Sea water ratio suggesting either a fractionation of $Cl^-$ or enrichment of $Na^+$ as there was significant deviation from marine sources. Linear correlation was observable between nss-$Ca^{2+}$ and nss-$Mg^{2+}$ with $HCO_3^-$ throughout the annual seasonal cycle ($HCO_3^-$: Ca = 0.59, $HCO_3^-$: $Mg^{2+}$ = 0.53) suggesting the origination of these species from soil dust. The calculated conversion ratio of 'S' ($CR_S$) was lower than 'N' ($CR_N$) which suggests that the secondary formation of $NO_3^-$ aerosol from $NO_2$ was more predominant than $SO_4^{2-}$. Trajectory analysis indicates that long range transportation also contributes to $PM_{2.5}$ 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 $SO_4^{2-}$ $NO_3^-$ and $NH_4^+$ 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.

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° 10′ N 78° 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 poly-ethylene plastic bag immediately and then preserved in a refrigerator at 4 °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 $90.21 \pm 20.62$ µg 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 µg m$^{-3}$), WHO (http://www.euro.who.int/document/E87950.pdf, $PM_{2.5}$: 10 µg m$^{-3}$) and USEPA (http://www.epa.gov/air/criteria.html, $PM_{2.5}$: 15 µg 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