Water Soluble Ionic Species in Atmospheric Aerosols: Concentrations and Sources at Agra in the Indo-Gangetic Plain (IGP)

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ABSTRACT

This study presents a comprehensive set of 2 years of data (January 2009–December 2010) on the chemical composition of ambient aerosols collected at a university campus in Agra, which lies on the Indo-Gangetic Plain (IGP). The average concentration of total suspended particles (TSP) was $213.2 \pm 91.4 \mu g/m^3$. The most abundant ions in TSP were $Ca^{2+}$, $NO_3^-$ and $SO_4^{2-}$, which contributed about 3.2%, 3.1% and 2.7%, respectively. TSP and most of the ions, such as $F^-$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $NH_4^+$ and $K^+$, had the highest mass concentrations in winter, while higher mass concentrations of $Ca^{2+}$ and $Mg^{2+}$ were found in summer. Higher ionic concentrations during the winter season may be attributed to a combined effect of biomass burning and meteorological conditions (low temperature, wind speed and mixing height). The $[NO_3^-]/[SO_4^{2-}]$ ratio at the present sampling site was $1.1 \pm 0.4$, which indicates that there were equal contributions from both stationary sources and vehicles. In winter, high $[NO_3^-]/[SO_4^{2-}]$ ratios ($1.7 \pm 0.4$) could be due to the extensive use of fuelwood and cowdung cakes to combat the cold. The acidity in aerosols is neutralized by the alkaline species, as indicated by the correlation between $NO_3^-$ and $SO_4^{2-}$ and sum of ($Ca^{2+}$, $Mg^{2+}$ and $NH_4^+$). $Ca^{2+}$ is the major acid neutralizing cation in the aerosols, followed by $Mg^{2+}$ and $NH_4^+$. The crustal source contribution was observed based on the ratios of various ions with respect to $Ca$ in soil and aerosol. On the basis of backward trajectories and the associated concentrations of the ions, the aerosol samples were classified into sectors in relation to their origin to determine the related sources. The major sources of water soluble ions identified at Agra are biomass combustion and local soil.

Keywords: Cations; Anions; Neutralization; Back trajectories.

INTRODUCTION

Airborne particulate matter is important and unique among air contaminants because of their potential complexity in terms of both chemical composition and physical properties (Balasubramanian et al., 2003). They have been broadly studied in the last decade for their potential health impact (EPA, 1996; Schwartz et al., 1996; Khan et al., 2010). Atmospheric aerosols vary markedly in size, chemical composition, quantity and distribution in the atmosphere (Andreae, 1995; Mouli et al., 2003). Studies conducted on aerosol particles have great importance in affecting atmospheric radiation that can lead to climate forcing (Charlson et al., 1992), cloud formation and atmospheric photochemical reactions and the light extinction effect that influence global weather changes (Seinfeld and Pandis, 1998; Tsai et al., 2003). In addition, these particulates are responsible for much of the reduction in visibility that occurs in urban areas (National Research Council, 1993). Therefore, in order to understand the effect of atmospheric aerosols, it is essential to know their detailed chemical composition. The water-soluble ions constitute a major fraction of dry particulate matter in tropospheric aerosols. The ionic composition of an aerosol determines to a large extent its acidity, influencing the partitioning of water-soluble, semi-volatile compounds between the gas phase and aerosol particles (Fridlind and Jacobson, 2000).

Water-soluble inorganic species (WSIS) are usually significant components of atmospheric particles. They are influenced mainly by meteorological factors, geographic conditions and particle emissions like emissions from industries, traffic, agricultural activities and natural sources. The characteristic properties of aerosols are due to their water soluble components, e.g., magnesium, sodium, potassium, calcium, ammonium, nitrate, sulphate, chloride (Tsai and Kuo, 2005), organic compounds, elemental carbon and metals (Mariani and Mello, 2007) that originate from a wide range of sources through a series of complex mechanisms. These atmospheric particles are introduced directly into the atmosphere from natural causes, like sea spray and erosion, volcanic eruptions or from anthropogenic pollution sources (Ali-Mohamed, 1991; Ali-Mohamed et al., 1995; Ali-
The concentration and distribution of water soluble ions may indicate source contributions, chemical transformations in the atmosphere and their potential adverse effects (Mariani and Mello, 2007). Several researchers have attempted to study the chemical composition and mass size distribution of atmospheric aerosols at different places (Shrestha et al., 2000; Wu et al., 2006; Pio et al., 2008; Stone et al., 2011; Hu et al., 2012; Tsai et al., 2012). In India also, studies on chemical characterization and mass size distribution of water soluble ionic constituents in aerosols have been conducted (Khemani et al., 1985; Safai et al., 1993; Tripathi et al., 1996; Kumar et al., 2003; Rastogi and Sarin, 2005; Kumar et al., 2006; Safai et al., 2008; Kulshrestha et al., 2009; Safai et al., 2010; Deshmukh et al., 2011; George et al., 2011; Ram et al., 2012). Few studies have been carried out in the Indo-Gangetic plain to characterize TSP (Kulshrestha et al., 1998; Parmar et al., 2001; Kumar et al., 2007; Ram et al., 2010; Ram et al., 2012). The IGP covers a vast area from 21.75°N; 74.25°E to 31.0°N; 91.5°E in the Indian subcontinent and experiences extreme variability in the climate over the annual seasonal cycle. The large scale urbanization, changes in land use, industrial activities, and regional emission sources (biomass burning and fossil fuel) contribute a significant fraction to high aerosol loading over the entire Indo Gangetic Plain (IGP), one of the most populated and polluted regions in Northern India. As Agra lies in the IGP, it is also influenced by its variable climatic conditions.

Few sporadic studies on size differentiated concentrations of TSP and the major cations and anions have been reported during December 1992 to March 1993 (Kulshrestha et al., 1998) and during July to September 1998 (Parmar et al., 2001) at Agra. Chemical characterization of aerosols, their mass size distribution studies and its variation in different seasons at Dayalbagh, Agra has also been reported by Kumar et al. (2007). Earlier study by Safai et al. (2008) at Agra reported chemical characterization of aerosols only during a specific land campaign (December 2004) for intense foggy or hazy days. In this paper, a systematic study of chemical characterization of water soluble fraction of TSP matter has been presented with data from two consecutive years (2009–2010) and seasonal variation has also been discussed. For the first time, an attempt has been made to determine the transport of air masses to Agra from different sectors and study its influence on the ionic concentrations. The study also investigates the possible sources that may be responsible for the variation in the concentrations.

**MATERIALS AND METHODS**

**Sampling Location**

Agra (27°10′N, 78°05′E) lies in the Indo-Gangetic plain. Its borders touch Rajasthan to its west and south, the district of Firozabad to its East and the district of Mathura to its North. The Mathura oil refinery is about 40 km to the northwest of the study site and lies in the upwind direction as winds are mostly from west and northwest sector. Industrial activities of Agra include rubber processing, engineering and a few ferrous casting industries based on natural gas. Agra has continental type of climate. Climatically, the city observes dry climate during summers and winters. Temperature ranges from 2°C (in winter) to 45°C (in summer). Wind speed is generally 1 to 14 km/hr. Relative humidity is about 70%.

Aerosol samples were collected on the roof (about 12 m height) of the Science Faculty building of Dayalbagh Educational Institute campus, which lies to the north of Agra city. It is surrounded by a variety of deciduous trees and agricultural fields. The main crops that are grown are rice and wheat, which are grown in rotation. Others include maize, pulses and pearl millet. The soil is sandy and calcareous by nature. There is no industry in this area. The sampling site lies by the side of a road that carries mixed vehicular traffic, moderate (of the order of 1000 vehicles) during the day. The campus lies about 2 km north of the NH-2 which has dense vehicular traffic (100,000 vehicles) throughout the day and night (Kumar et al., 2007; Singla et al., 2011; Satsangi et al., 2012). The surrounding area is completely free of construction or tall tree which could obstruct wind flow. Fig. 1 shows the location of sampling site in India.

![Fig. 1. Location of Sampling Site in Agra.](image-url)
**Aerosol Collection and Gravimetric Analysis**

Sampling was carried out from January 2009 to December 2010. One sample was collected on every Wednesday. However, samples were not collected when there was heavy rainfall. Samples could not be collected when the sampler was out of order. A total of 80 samples were collected during this period. TSP samples were collected on Whatman filter paper sheets (20.3 cm × 25.4 cm) using high volume sampler Envirotech APM 460. The sampler was periodically calibrated to keep a check on the flow rate. The mass concentrations were determined gravimetrically using electronic microbalance (Mettler AJ150). Each filter was weighed before and after sampling, and the net mass was obtained by difference of two weights. The exposed filters were stored in a refrigerator at ~4°C before chemical analysis.

**Chemical Analysis of Water-Soluble Ions**

After sampling, each filter paper was weighed and stored in desiccator until analysis. For the analysis, each filter paper was divided into two parts. One part was extracted with deionized water while another part was extracted with 1% nitric acid (v/v) for the cation analysis. The concentrations of major anions (F –, Cl –, NO3 –, and SO4 2–) and major cations (Na+, K+, Ca2+ and Mg2+) were analyzed by Ion Chromatography using Dionex ICS 1100 Ion Chromatograph. 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) with 6.0 mM NaOH as eluent while for cation analysis, system was equipped with guard column (CG12A, 4 × 50 mm), analytical column (CS12A, 4 × 250 mm) and cation self-regenerating suppressor (CSRS) using 20.0 mM MSA (methylene sulphonic acid) as eluent. For sample introduction in the chromatograph, the solutions were injected through a 25 µL loop. The flow rate of both eluents was 1.0 ml/min. Calibration was done by a set of standard containing either anions, or cations to be determined.

**Meteorological Parameters**

Agra lies in the subtropical climatic belt. It is about 1500 km away from the sea and shows extreme variation in temperature with hot summers and chilly winters. An automatic weather station (Envirotech WM 271) is installed about 12 m above the ground level at the roof of Science Faculty Building. It is used to measure surface meteorological parameters like temperature (maximum and minimum), relative humidity, wind speed, wind direction, precipitation and air pressure, simultaneously. The instrument has been programmed to collect meteorological data at an interval of 1 minute which is downloaded and computed through software. Generally, air temperature, relative humidity, and air pressure are rather low and wind speed is high, corresponding to the prevalence of the westerly winds during the summer season. Relative humidity is highly variable from 25–99%. During winters, the winds blow from the NE, E and SE sectors with a calm period of approximately 75%.

On the basis of data recorded during the study period, following observations were made (Table 1). In summer, the average maximum and minimum temperature varies from 30.0 to 40.0°C. May and June are the hottest months having maximum temperature over 40°C. Average wind speed is around 4.7 km/hr and relative humidity ranges from 12 to 44% (average = 29.1%) during summer. Dust storms are most frequent in May and may also occur in April and June which last for a period of 30 minutes to 2 hours. The frequency of dust storms in northern and northwestern India is high with wind speed ranging from 8 to 14 km/hr. The increased wind speed causes uplifting and transport of desert dust which causes reduced visibility (800 m–1 km). The strong winds during these dust storms carry large amount of dust, causing severe air pollution. In monsoon, weather is hot and humid, average maximum and minimum temperature ranges from 27.5 to 35.7°C and relative humidity varies from 65 to 98%. During post monsoon season, minimum and maximum temperature varies from 20.0 to 30.0°C and relative humidity is around 66%. In winter, the temperature ranges between 12.0 to 23.0°C. The year’s coldest months are December and January, when temperatures average around 10–15°C. The hallmark of the season is the heavy fog, which frequently disrupts daily life; fog grows thick enough to hinder visibility and disrupt air travel 15–20 days annually. Wind speed and relative humidity were 1.0 km/hr and 70.5% during winter.

**RESULTS AND DISCUSSION**

**Concentration of TSP**

The statistics of TSP concentrations at Dayalbagh, Agra are presented in Table 2. TSP concentrations varied from 67.7 to 395.6 µg/m^3 with an annual average of 213.2 ± 91.4 µg/m^3. Our concentrations of TSP mass are comparable to earlier studies reported in the Indo-Gangetic plain: 177.4 ± 63.9 µg/m^3 (Hisar, Rengarajan et al., 2007) and 194.0 ± 38.0 µg/m^3 (Jaduguda, Ram and Sarin, 2010).

TSP concentrations show strong seasonal variation at Agra, the highest TSP concentration of 301.3 ± 56.1 µg/m^3 was observed in winter (December–February) and lowest concentration of 117.2 ± 52.1 µg/m^3 was observed in monsoon (July–September). TSP concentrations in post-monsoon (October–November) and summer (March–June)

### Table 1. Average meteorological parameters during the study period.

<table>
<thead>
<tr>
<th>Season</th>
<th>Number of Samples</th>
<th>Maximum Temperature (°C)</th>
<th>Minimum Temperature (°C)</th>
<th>Relative Humidity (%)</th>
<th>Wind speed (km/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>25</td>
<td>40.5 ± 4.3</td>
<td>30.0 ± 2.6</td>
<td>29.1 ± 13.0</td>
<td>4.7 ± 2.3</td>
</tr>
<tr>
<td>Monsoon</td>
<td>17</td>
<td>35.7 ± 3.1</td>
<td>27.5 ± 3.1</td>
<td>75.2 ± 12.2</td>
<td>1.7 ± 1.2</td>
</tr>
<tr>
<td>Post Monsoon</td>
<td>21</td>
<td>29.8 ± 3.3</td>
<td>20.2 ± 3.3</td>
<td>66.2 ± 14.9</td>
<td>1.3 ± 0.6</td>
</tr>
<tr>
<td>Winter</td>
<td>17</td>
<td>15.0 ± 1.6</td>
<td>6.7 ± 2.7</td>
<td>70.5 ± 12.7</td>
<td>1.0 ± 0.7</td>
</tr>
</tbody>
</table>
were 262.4 ± 82.5 µg/m^3 and 208.1 ± 63.4 µg/m^3, respectively. Winter and post monsoon concentrations were 1.4 and 1.2 times higher than the annual average of TSP recorded at Agra. In summer the concentrations were at a level of the annual average of TSP while in monsoon lowest TSP concentrations were recorded. On applying t test at 95% confidence level, it was observed that there was statistically significant difference (p = 0.001) in TSP concentration in the above season as compared to those in summer, winter and post monsoon.

Highest TSP concentrations during winter may be attributed to low temperature of about 2°C and increased heating activities (in order to keep themselves warm, people burn coal, vegetation debris and other waste materials). Low wind speed and low mixing height results in stagnation of the pollutants. In summer season, TSP concentrations are low as compared to other seasons. This is because high temperature due to long periods of solar radiation, high wind speed and greater mixing height favour dispersion of air pollutants in summer. This season also experiences the influence of dust events. These dust events originate from Thar Desert and may lead to high TSP concentrations of over 350 µg/m^3. Such high TSP concentrations have been excluded from the summer average concentrations. Earlier studies by Dey et al. (2004), Jethva et al. (2005), Badarinath et al. (2007) and Ram et al. (2008) also report that the transport of dust occurs from Pakistan and Afghanistan through the Thar Desert to the northern part of India during the months of March to June. Chinnam et al. (2006) have also reported the transport of air pollutants from Thar Desert during dust storms. To identify the sources and transport pathways of the chemical components in the atmospheric aerosols, air mass backward trajectory analysis was carried out. These air mass back-trajectories were simulated using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model which is based on the GDAS Meteorological Data (Draxler and Rolph, 2003). The air mass back trajectories of summer season were simulated at 12:00 hrs (local time) at 500 m above the ground level and have been represented in Fig. 2 which supports the transport of dust from Thar Desert. The effect of localized sources is also supported by air mass back trajectories of winter months, December, January and February. In the monsoon season, TSP concentrations are low with an average of 117.2 ± 52.1 µg/m^3. This is probably due to the scavenging of aerosol particles by rainfall under the influence of southwest monsoon. During post monsoon months, a different monsoon cycle, the northeast (retreating) monsoon brings dry, cool, and dense central Asian air masses to large parts of India. Winds flow from the Himalayas to southwest across the country. This results in clear and sunny days due to the rise in temperature. This period marks the transition from wet to dry seasonal conditions. This season also experiences the flow of air masses from northwest region in addition to the local emissions as seen from the back trajectories of post monsoon season.


<table>
<thead>
<tr>
<th></th>
<th>F^-</th>
<th>Cl^-</th>
<th>NO_3^-</th>
<th>SO_4^-2</th>
<th>Na^+</th>
<th>NH_4^+</th>
<th>K^+</th>
<th>Mg_2^+</th>
<th>Ca_2^+</th>
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</thead>
<tbody>
<tr>
<td><strong>Mass Concentrations (µg/m^3)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mean</td>
<td>213.2</td>
<td>0.3</td>
<td>4.6</td>
<td>6.7</td>
<td>5.9</td>
<td>4.0</td>
<td>2.7</td>
<td>3.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Min</td>
<td>67.7</td>
<td>0.1</td>
<td>1.0</td>
<td>1.1</td>
<td>1.7</td>
<td>0.6</td>
<td>0.3</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Max</td>
<td>395.6</td>
<td>0.9</td>
<td>14.1</td>
<td>22.3</td>
<td>15.9</td>
<td>11.6</td>
<td>9.2</td>
<td>11.3</td>
<td>4.8</td>
</tr>
<tr>
<td>SD</td>
<td>91.4</td>
<td>0.2</td>
<td>3.1</td>
<td>5.0</td>
<td>3.6</td>
<td>2.7</td>
<td>2.2</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Mass Percentages in TSP (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.1</td>
<td>2.2</td>
<td>3.1</td>
<td>2.7</td>
<td>1.9</td>
<td>1.2</td>
<td>1.6</td>
<td>0.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Min</td>
<td>0.1</td>
<td>1.5</td>
<td>1.6</td>
<td>2.5</td>
<td>0.9</td>
<td>0.4</td>
<td>1.2</td>
<td>0.1</td>
<td>1.9</td>
</tr>
<tr>
<td>Max</td>
<td>0.2</td>
<td>3.6</td>
<td>5.6</td>
<td>4.0</td>
<td>2.9</td>
<td>2.3</td>
<td>2.9</td>
<td>1.2</td>
<td>5.3</td>
</tr>
<tr>
<td>SD</td>
<td>0.2</td>
<td>3.4</td>
<td>5.5</td>
<td>3.9</td>
<td>3.0</td>
<td>2.5</td>
<td>2.4</td>
<td>1.1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

**Ion Balance**

An ion balance check was conducted in order to assess the quality of the analysis. The ion balance expressed by the sum of the equivalent concentration (µequi/m^3) of cation-to-anion (C/A) is a good indicator to study the acidity of the environment. Ion balance was calculated assuming that the major cations (Na^+, K^+, Mg_2^+, Ca_2^+ and NH_4^+) and anions (Cl^-, NO_3^- and SO_4^-2) account for most of the ions in the solution. According to the principle of electroneutrality of solutions, total cation equivalents (CE) must be equal to the total anion equivalents (AE). CE is calculated as a sum of each cation concentration divided by its equivalent weight. For example, 1.8 µg/m^3 of Ca_2^+ expressed as equivalents m^-3 is 1.8/20 = 0.0898 µequiv/m^3, AE is calculated likewise as the sum of each anion concentration divided by its equivalent weight. The average of the sum of equivalent anions was 0.92 while the average of the sum of equivalent cations was 1.09.

Percent ion difference was calculated as follows:

\[
\% \text{ Ion difference} = 100 \times \frac{(CE - AE)}{(CE + AE)} \quad (1)
\]

Total percent ion difference was 8.6% which was well within acceptable range (Criteria specified by the Global Atmospheric Watch programme of World Meteorological Organization (WMO, 1994). A small anion deficiency may be due to unanalyzed carbonate/bi-carbonate, and organic anions such as acetate, formate. A regression analysis of total anions versus total cation concentrations yielded a linear relationship with a slope of 0.54, intercept 0.08, and a high co-efficient of determination (r^2) of 0.83, indicating good data quality. The calibration uncertainties for all analytes were observed within 5%.
Concentrations of Water Soluble Ions

Water-soluble ions comprise a large part of aerosol particles and play an important role in the atmosphere. In this study, nine major water-soluble inorganic components were detected (F\(^-\), Cl\(^-\), NO\(_3\)^-, SO\(_4^{2-}\), Na\(^+\), NH\(_4^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)), their mass concentrations are presented in Table 2. The sum of the water-soluble ionic species (WSIS) ranged from 12.4 to 98.4 \(\mu g/m^3\) with an average of 40.5 ± 34.7 \(\mu g/m^3\) and constituted about 20% of the TSP concentration. At other Indian sites of Indo-Gangetic plain, similar WSIS has been reported: Hisar, WSIS ranged from 14.1 to 78.3 \(\mu g/m^3\) and constitute about 26% while at Manora Peak WSIS constituted about 18.8% of the TSP concentration (Rengarajan et al., 2007).

Among the ionic species, NO\(_3^-\) and Ca\(^{2+}\) were the most abundant chemical components (6.7 \(\mu g/m^3\)) and each accounted for 18.7% of the total mass of ions and 3.1% of TSP mass. Of all the other inorganic species, SO\(_4^{2-}\) had the highest concentration of 5.9 \(\mu g/m^3\), followed by 4.6 \(\mu g/m^3\) for Cl\(^-\), 4.0 \(\mu g/m^3\) for Na\(^+\), 3.5 \(\mu g/m^3\) for K\(^+\), 2.7 for NH\(_4^+\), 1.4 \(\mu g/m^3\) for Mg\(^{2+}\) and 0.3 \(\mu g/m^3\) for F\(^-\).

Sources and Formation of Sulphate and Nitrate

In India, a comprehensive, spatially resolved (0.25° × 0.25°) fossil fuel consumption database and emissions inventory has been reported by Reddy and Venkataraman...
Based on emissions in the years 1996–1997. According to it, gasoline and diesel fuel contain 0.2% and 1.0 to 1.8% sulphur by weight, respectively. The sulphur content of coal in Uttar Pradesh is 0.6% (Reddy and Venkataraman, 2002a). Ohara et al. (2007) also developed an emission inventory for Asia (Regional Emission inventory in Asia (REAS) Version 1.1) for the period 1980–2020 which shows that in India the estimated ratio of NO\textsubscript{x} to SO\textsubscript{x} is 1:1.9 from power plants, 1:3.7 from industry, 1:2 from vehicular activity (Arimoto et al., 1996). Further evaluation of SO\textsubscript{4}/Ca\textsuperscript{2+} ratio in winter at the present site as in winter, to combat the cold, fuelwood and cowdung cakes are consumed extensively.

Speciation of Water Soluble Ions

Aerosols show acidic nature mainly due to the presence of SO\textsubscript{4}\textsuperscript{2–} and NO\textsubscript{3}\textsuperscript{–} anions. SO\textsubscript{4}\textsuperscript{2–} and NO\textsubscript{3}\textsuperscript{–} ions are produced by the oxidation of the gaseous precursors (SO\textsubscript{2} and NO\textsubscript{x}) in the atmosphere and are neutralized by mineral aerosols and ammonia (Han et al., 2007). The correlation between NO\textsubscript{3}\textsuperscript{–} and SO\textsubscript{4}\textsuperscript{2–} with Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and NH\textsubscript{4}\textsuperscript{+} suggests that the acidity in aerosols is neutralized by the alkaline species (Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and NH\textsubscript{4}\textsuperscript{+}) which act as neutralizing agent or buffer. Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and NH\textsubscript{4}\textsuperscript{+} react with H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3} to form their salts of NO\textsubscript{3}\textsuperscript{–} and SO\textsubscript{4}\textsuperscript{2–}. This is further confirmed by linear regression between the sum of (NO\textsubscript{3}\textsuperscript{–} + SO\textsubscript{4}\textsuperscript{2–}) and (Ca\textsuperscript{2+} + NH\textsubscript{4}\textsuperscript{+} + Mg\textsuperscript{2+}) as shown in Fig. 3. The correlation coefficient was 0.71. Earlier studies at the present site also report Ca\textsuperscript{2+} to be the major neutralizing agent. The studies reveal that Ca\textsuperscript{2+} and Mg\textsuperscript{2+} are predominantly coarse mode particles and NH\textsubscript{4}\textsuperscript{+} exists in fine mode (Kulshrestha et al., 1995).

The acid neutralization capacity of different cations can also be estimated by calculating the Neutralization Factors (N\textsubscript{f}) with respect to the particular cation. The calculation of these factors is based on the fact that NO\textsubscript{3}\textsuperscript{–} and SO\textsubscript{4}\textsuperscript{2–} are the major acidifying anions and Ca\textsuperscript{2+}, NH\textsubscript{4}\textsuperscript{+}, Mg\textsuperscript{2+} and K\textsuperscript{+} are major acid neutralizing cations in the aerosols. The neutralization factor may be calculated as:

\[
N_{f}(\text{Ca}^{2+}) = [\text{Ca}^{2+}]/[\text{SO}_{4}^{2–}] + 2[\text{NO}_3^-] \quad (2)
\]

\[
N_{f}(\text{Mg}^{2+}) = [\text{Mg}^{2+}]/[\text{SO}_{4}^{2–}] + 2[\text{NO}_3^-] \quad (3)
\]

\[
N_{f}(\text{NH}_4^+) = [\text{NH}_4^+]/2[\text{SO}_{4}^{2–}] + [\text{NO}_3^-] \quad (4)
\]

The role of Cl\textsuperscript{–} in acidity and that of Na\textsuperscript{+} in alkalinity is negligible as it is assumed that these ions originate solely

![Fig. 3. Regression between NO\textsubscript{3}\textsuperscript{–} and SO\textsubscript{4}\textsuperscript{2–} with Ca, Mg and NH\textsubscript{4}\textsuperscript{+}](image)
from sea in the form of sea salt which is neutral. It is observed that Ca\(^{2+}\), Mg\(^{2+}\) and NH\(_4^+\) were the major neutralizing components with average neutralization factors of 1.2 ± 0.9, 0.7 ± 0.6 and 0.5 ± 0.4, respectively.

In addition to the neutralization by mineral aerosols (Ca\(^{2+}\) and Mg\(^{2+}\)), the acidity is also neutralized by NH\(_4^+\) ions. In ammonia (NH\(_3\)) rich environments, neutralization of the sulphuric acid (H\(_2\)SO\(_4\)) is favoured leading to the formation of ammonium sulphate, (NH\(_4\))\(_2\)SO\(_4\), and ammonium hydrogen sulphate, NH\(_4\)HSO\(_4\). Excess NH\(_3\) will then react with HNO\(_3\) to form ammonium nitrate (NH\(_4\))NO\(_3\) (Koutrakis et al., 1992; Pathak et al., 2009).

Particulate phase NH\(_4^+\) concentrations can be calculated using the stoichiometric ratios of the different compounds and compared with actual measurements. Ammonium was calculated from nitrate and sulfate, based on the assumption that all nitrate is in the form of NH\(_4\)NO\(_3\) and all sulfate is in the form of either (NH\(_4\))\(_2\)SO\(_4\) (calculated ammonium = 0.38 sulfate + 0.29 nitrate) or NH\(_4\)HSO\(_4\) (calculated ammonium = 0.192 sulfate + 0.29 nitrate) (Chow et al., 1996). Fig. 4 shows the comparison of measured NH\(_4^+\) with that of calculated NH\(_4^+\). The results show that there is reasonable agreement between the measured and calculated NH\(_4^+\) concentrations, especially when (NH\(_4\))\(_2\)SO\(_4\) is assumed.

The NH\(_4^+\)/SO\(_4^{2-}\) molar ratios for the formation of (NH\(_4\))\(_2\)SO\(_4\) and NH\(_4\)HSO\(_4\) are 2:1 and 1:1, respectively. In the present study, NH\(_4^+\)/SO\(_4^{2-}\) molar ratios show a large variability and range from 0.4 to 4.4, with an annual average of 1.8 ± 1.0. The formation of NH\(_4\)NO\(_3\) by chemical neutralization at the present site is supported by a significant positive correlation (Fig. 5) between NH\(_4^+\)/SO\(_4^{2-}\) molar ratios and NO\(_3^{-}\) concentrations (r = 0.70, p > 0.001). Rengarajan et al. (2007) also obtained similar result at Hisar, i.e., significant positive correlation (r = 0.82, p > 0.001) between NH\(_4^+\)/SO\(_4^{2-}\) molar ratios and NO\(_3^{-}\) concentrations and had concluded that low NH\(_4^+\)/SO\(_4^{2-}\) ratio do not favour the incorporation of NO\(_3^{-}\) to the particulate phase. It may, thus, be concluded that NH\(_4^+\) exists in the form of (NH\(_4\))\(_2\)SO\(_4\), NH\(_4\)HSO\(_4\) and NH\(_4\)NO\(_3\) in the aerosols at Agra.

The abundance of Ca\(^{2+}\) in the atmosphere could be due to its high concentration in local soil and the construction activities distributed all over the city which may lead to the formation of Ca(NO\(_3\))\(_2\) and CaSO\(_4\). The major sources of NH\(_4^+\) compounds may be animal farming, fertilizers, and organic decomposition. This may be true for the present site as it is surrounded by agricultural fields and a casttle yard lies about 400 m away towards northwest of the sampling site.

![Fig. 4. Comparison between Calculated and Measured NH\(_4^+\).](image)

![Fig. 5. Correlation between NH\(_4^+\)/SO\(_4^{2-}\) molar ratio and NO\(_3^{-}\) concentrations.](image)
Source Characterization of Water Soluble Ions

Ionic Correlation

The correlation between ions suggests the likely sources of pollutants and also indicates the gaseous reactions occurring in the atmosphere. Bivariate correlations have been identified to specify the chemical forms of the major ions, F+, Cl−, NO3−, SO42−, NH4+, Na+, K+, Mg2+ and Ca2+ in the atmospheric aerosols of Agra. Table 3 shows the correlation coefficients among these major ions. Aerosol samples show good correlation (r = 0.71) between NO3 and SO4 that indicates that a portion of these may have originated from a similar source. It may also be possible that a fraction of NO3 and SO4 could be associated with Ca, Mg and NH4 after the neutralization process. This is supported by the significant correlation between Ca and NO3 (r = 0.91), Ca and SO4 (r = 0.76), Mg and NO3 (r = 0.76), Mg and SO4 (r = 0.53). Ca and Mg which are vital components of soil show good correlation between each other (r = 0.74) which suggests that they possess a common source. The important molecular species of Ca and Mg could be Ca(NO3)2, CaSO4, Mg(NO3)2 and MgSO4.

NH4+ was closely correlated with SO42− (r = 0.63). As the equivalent ratio of NH4+ to SO42− for NH4HSO4 and (NH4)2SO4 were 0.50 and 1.00, respectively, the slope of 0.2 indicated that the SO42− is incompletely neutralized by NH4+ leading to the formation and existence of both NH4HSO4 and (NH4)2SO4. The correlation between NH4+ and NO3 (r = 0.74) revealed existence of NH4NO3 which is probably formed by the reaction of HNO3 with NH3 on moist soil surfaces. Significant correlation of NH4 with Ca, Mg, Na and K (r = 0.68, 0.62, 0.53 and 0.65, respectively) reflects the influence of agricultural activities carried out in the vicinity of the sampling site (Khwaja and Husain, 1990; Saylor et al., 1992; Satsangi et al., 1998).

Crustal Source Identification

The water soluble ions may originate from mineral dust, anthropogenic activities or may be derived from local soil. Ca and Mg are considered to be of terrigeneous origin. Similar to earlier studies on chemical characterization (Satsangi et al., 1998; Singh et al., 2001; Satsangi et al., 2002), Ca was chosen as a reference element to investigate the effect of local terrestrial sources. This is based on the assumption that all Ca in TSP mass may be soil derived. The ratios of various ions with respect to Ca in soil are presented in Table 4. A comparison of these ratios with aerosol values indicates that about 37 to 66 percentile of aerosol constituents correspond to ratios in soil.

It is found that around 50% of Mg and Cl, 57% of Na and K and 66% of SO4 in aerosols may be derived from soil as their ratios are close to the corresponding ratios in the local soil whereas rest of their fractions may be contributed by other sources. On the other hand, only a small portion of NO3 may have originated from soil as NO3/Ca ratios are close to soil ratios only in about 37% aerosol samples and rest of it may be contributed from other sources.

Seasonal and Route Dependent Variation of Chemical Species

There is a clear evidence of seasonal variation in mass concentrations of all the water-soluble inorganic ions in TSP as shown in Fig. 6. This variation may be due to the influence of meteorological factors and different sources of emissions in different seasons. A coefficient of variance (CV) is defined as the standard deviation (SD) divided by the average concentration. CV was calculated to assess the variation of the major ions in different seasons as shown in Fig. 6. The average concentrations of chemical species in aerosols were arbitrarily classified into four sets based on the air mass backward trajectories as shown in Fig. 7. These four sets were from northwest of India (sector 1), from southwest and central India (sector 2), from southeast India (sector 3) and from east of India (sector 4). In some cases where back trajectories passed through more than one sectors, the sector in which trajectory stayed the longest was selected to assign the source of aerosols. The frequency of trajectory sectors and the contribution of each sector in different seasons have been shown in Fig. 8. As is evident sector 1 (winds from northwest direction) is the dominant sector in all seasons except monsoon and shows significant influence. In winter, the aerosol contribution is also affected by the winds from east of India. In summer, there is maximum contribution from northwest direction.

Most of the ions (F+, Cl−, NO3−, SO42−, NH4+ and K+) showed high mass concentrations in winter which may probably be attributed to the enhanced emissions from heating sources and stagnant atmospheric conditions (low

<table>
<thead>
<tr>
<th>Species</th>
<th>TSP</th>
<th>NH4</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>F</th>
<th>Cl</th>
<th>NO3</th>
<th>SO4</th>
</tr>
</thead>
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<tr>
<td>TSP</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>NH4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.58**</td>
<td>0.53**</td>
<td>1</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.46**</td>
<td>0.65**</td>
<td>0.48</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.53**</td>
<td>0.62**</td>
<td>0.71</td>
<td>0.70**</td>
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<td>Ca</td>
<td>0.50</td>
<td>0.68**</td>
<td>0.39</td>
<td>0.85**</td>
<td>0.74**</td>
<td>1</td>
<td></td>
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<td>F</td>
<td>0.49</td>
<td>0.62**</td>
<td>0.31</td>
<td>0.60**</td>
<td>0.47**</td>
<td>0.65**</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.64**</td>
<td>0.65**</td>
<td>0.45</td>
<td>0.79**</td>
<td>0.66**</td>
<td>0.87**</td>
<td>0.64**</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>NO3</td>
<td>0.61**</td>
<td>0.74**</td>
<td>0.58**</td>
<td>0.89**</td>
<td>0.76**</td>
<td>0.91**</td>
<td>0.72**</td>
<td>0.88**</td>
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<tr>
<td>SO4</td>
<td>0.50</td>
<td>0.63**</td>
<td>0.28</td>
<td>0.67**</td>
<td>0.53</td>
<td>0.76**</td>
<td>0.50</td>
<td>0.74**</td>
<td>0.71**</td>
<td>1</td>
</tr>
</tbody>
</table>

** Correlation is significant (p < 0.01).
Table 4. Ionic ratios with respect to Ca in soil and aerosol.

<table>
<thead>
<tr>
<th></th>
<th>Na/Ca</th>
<th>K/Ca</th>
<th>Mg/Ca</th>
<th>Cl/Ca</th>
<th>NO₃/Ca</th>
<th>SO₄/Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>0.6</td>
<td>0.6</td>
<td>0.3</td>
<td>1.3</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Aerosol</td>
<td>0.8 ± 0.7</td>
<td>0.6 ± 0.5</td>
<td>0.2 ± 0.1</td>
<td>0.9 ± 0.8</td>
<td>1.1 ± 0.7</td>
<td>1.0 ± 0.6</td>
</tr>
<tr>
<td>Percentile</td>
<td>57.1</td>
<td>57.1</td>
<td>50.0</td>
<td>51.8</td>
<td>37.5</td>
<td>66.0</td>
</tr>
</tbody>
</table>

Fig. 6. Seasonal Variation of water-soluble ionic components.

The influence of local emissions during wintertime is evident from the air mass back trajectories depicted in Fig. 2. K⁺ is a useful tracer for pyrogenic aerosols in plants. It is an important component that originates from burning of vegetative material (Hsu et al., 2008). At the present site, K⁺ shows highest concentration in winter (6.2 μg/m³) in contrast to other seasons and K⁺ levels during winter are 1.8 times more than the annual average concentration. This could be attributed to combustion activities which are enhanced in winter. The seasonal variation of F⁻ and Cl⁻ show highest concentration in winter. NO₃⁻ also showed highest concentration in winter followed by post monsoon; NO₃⁻ was 1.5 and 1.7 times higher in post monsoon and winter when compared to the annual average concentration. Secondary components, SO₄²⁻ and NH₄⁺ also show similar variation, showing high concentrations in winter followed by summer and low concentrations in monsoon and post monsoon.

The aerosols classified to sector 1 were associated with high concentrations of chemical species, indicating the higher level of pollution. Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻ and SO₄²⁻ concentrations were relatively high when the trajectories were from the northwest of India (sector 1). Higher mass concentrations of Ca²⁺ and Mg²⁺ were found in summer and post monsoon (Fig. 6). Ca²⁺ and Mg²⁺ are the typical crustal elements and the dry season is favorable for the re-suspension of soil particles. High Ca²⁺ and Mg²⁺ concentrations, in summer, are associated with the dust events which lead to high particulate matter brought by long range transport from Thar Desert and surrounding arid regions which lie to the northwest of sampling site. This is supported by air mass back trajectories which originate from northwest direction (Fig. 2). Significant correlation between ionic species that fall in this sector suggests that these ions were associated with long range transport (Ca and Mg = 0.66; NO₃ and SO₄ = 0.87; Ca and SO₄ = 0.59). The region is also affected by the transport of mineral dust.
in summer from various northwest Asian arid regions including the desert which stretches from Iran through Afghanistan and Pakistan, northwestern India (Thar Desert), and the Arabian Peninsula (Middleton, 1986; Prospero et al., 2002). These mineral dust particles which are transported by long range strongly influence the regional aerosol optical properties over the Indo-Gangetic plain (Singh et al., 2004, 2005; Gautam et al., 2009).

In monsoon (July to September), dominant contribution is from southwest direction (sector 2). The low mass concentrations in this season could be the result of scavenging of aerosol particles by rainfall during the onset of southwest monsoon. The concentrations of \(\text{NH}_4^+\) and \(\text{SO}_4^{2-}\) were found to be lowest in sectors 2 and 3 which have air mass back trajectories arising from Arabian Sea and Bay of Bengal as shown in Fig. 7. This may be due to influence of marine air being transported from over the ocean which is less polluted during the monsoon season. The sea salt ions that fall in this sector show good correlation (Na and Mg, \(r = 0.95\); Na and Cl, \(r = 0.89\); Mg and Cl, \(r = 0.77\)) between each other which suggests that they may be influenced from the southwest monsoon.

In post monsoon season, the aerosol particles are contributed from northwest and eastern parts of India. In
addition to this, small contribution to aerosol concentration is also from southeast direction which is not observed in winter and summer seasons. This may be the result of retreating monsoon. The contribution to aerosol composition from southeast may also be observed in monsoon season to a very small extent.

CONCLUSIONS

The present study conducted on water soluble ions at Agra, India revealed that the average annual TSP concentration at Agra is $213.2 \pm 91.4 \mu g/m^3$. TSP increased by about 1.4 times in winter and decreased in monsoon as compared to the annual average concentration. Ca was the major neutralizing agent followed by Mg and NH$_4$. All the water soluble ionic species show seasonal variation. High concentrations of most of the ions were observed during the winter season which is a combined effect of biomass burning and meteorological conditions (low temperature, low wind speed and low mixing height) whereas lowest concentrations were observed in monsoon due to the scavenging of aerosol particles by rainfall. In summer, long range transport contributes for some of the ionic constituents as evidenced from the air mass back trajectories. The influence of monsoon is evident from the strong correlation between the sea salt ions associated with sectors 2 and 3. It may be concluded that the major sources of water soluble ions at Agra are probably biomass combustion and local soil.

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