Carbonaceous and Secondary Inorganic Aerosols during Wintertime Fog and Haze over Urban Sites in the Indo-Gangetic Plain

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ABSTRACT

The chemical composition of total suspended particulate (TSP) matter and secondary aerosol formation have been studied during wintertime fog and haze events from urban sites (Allahabad and Hisar) in the Indo-Gangetic Plain. The atmospheric abundances of elemental carbon (EC), organic carbon (OC), water-soluble OC (WSOC) suggest that organic matter is a major component of TSP, followed by concentrations of sulphate and nitrate under varying meteorological conditions. The concentrations of EC, OC, and WSOC show a nearly 30% increase during fog and haze events at Allahabad and a marginal increase at Hisar; whereas inorganic constituents (NH4+ and SO42−) are 2–3 times higher than those during clear days at both the locations. The sulphur and nitrogen oxidation ratios (SOR and NOR) also exhibit significant increases suggesting possible enhancement of secondary formation of SO42− and NO3− during fog and haze events. The significant correlation between NH4+ and SO42− (R2 = 0.66, n = 61) and an NH4+/SO42− equivalent ratio ≥ 1 during fog-haze conditions suggest near-complete neutralization of sulphuric acid by ammonia. In contrast, NH4+/SO42− equivalent ratios are less than 1 during normal days suggesting an NH3-deficient environment and the possible association of SO42− with mineral dust for neutralization. Secondary inorganic aerosol formation and their hygroscopic growth can have significant impact on atmospheric chemistry, air-quality and visibility impairment during fog-haze events over northern India.

Keywords: Elemental carbon; Organic carbon; Secondary inorganic aerosols; Sulphur and nitrogen oxidation ratios; Fog and haze; Indo-Gangetic Plain.

INTRODUCTION

The Indo-Gangetic Plain (IGP) in northern India, stretching from north-west to north-east, is a densely populated region with characteristic emissions from anthropogenic sources. Among the major sources of aerosol, emissions from agricultural-waste and biomass burning dominate during the wintertime (Dec–Feb) (Venkataraman et al., 2005; Rengarajan et al., 2007; Gustafsson et al., 2009; Ram et al., 2010a; Shakya et al., 2010; Rajput et al., 2011; Ram and Sarin, 2011). The transport of mineral aerosol from arid and semi-arid regions of western India, during the summer (April–early June), imparts strong temporal variability in the chemical composition and optical properties of aerosol (Jethva et al., 2005; Chinnam et al., 2006). In addition, lack of year-round precipitation further leads to the high aerosol loading over the entire Gangetic Plain. Measurements of aerosol optical depth (AOD) and absorption aerosol optical depth (AAOD) have characterized IGP as a hotspot for anthropogenic aerosol in south-Asia (Ramanathan et al., 2007).

The enhanced levels of pollutants lead to poor air-quality and several environmental, health and socio-economical issues in Asia (Hameed et al., 2002; Lee and Sequeira, 2002; Husain et al., 2007; Bari et al., 2010; Wan et al., 2010; Zhao et al., 2010). Among these, fog-haze formation and reduction in visibility is of major concern (Watson, 2002; Zhang et al., 2010). The formation of fog and haze is associated with high aerosol loading from anthropogenic sources as well as formation of secondary aerosols via gas-to-particle conversion under favorable meteorological conditions (Reilly et al., 2001; Husain et al., 2004; Sun et al., 2006; Zhang et al., 2010; Fang et al., 2011;). Recent studies suggest that a significant fraction of atmospheric particulate matter (PM) in the Indo-Gangetic Plain are comprised of carbonaceous aerosol (~30–35% of the PM) and water-soluble inorganic species (~10–20% of the PM) over IGP and other locations in India (Tare et al., 2006; Rengarajan et al., 2007; Ram et al., 2010a; Deshmukh et al., 2011; Kothai et al., 2011). During the wintertime, low ambient temperatures (range: ~10–20°C, at times dipping as low as 5°C) and weak winds (< 2 m/s) and boundary layer height (~500–800 m) favour stable atmosphere, leading to poor convective
mixing and accumulation of pollutants in the lower atmosphere (Nair et al., 2007; Ram et al., 2010a).

A large variability in aerosol optical properties and radiative forcing during wintertime haze and fog has been reported over northern India (Ramachandran et al., 2006; Tripathi et al., 2006). The aerosol chemical composition changes through the aqueous phase-reactions on aerosol surfaces (Sun et al., 2006; Biswas et al., 2008; Jihua et al., 2009; Tan et al., 2009) and subsequently, it affects aerosol optical properties during fog-haze conditions. In this manuscript, we report on the changes in chemical composition of atmospheric aerosol, secondary species formation and neutralization processes during fog and haze events through simultaneous measurements of carbonaceous species (EC, OC and WSOC) and water-soluble inorganic ionic constituents (cations: Na\(^+\), K\(^+\), NH\(_4^+\), Ca\(^{2+}\) and Mg\(^{2+}\) and anions: Cl\(^-\), SO\(_4^{2-}\), NO\(_3^-\) and HCO\(_3^-\)) from two urban sites (Allahabad and Hisar) in the IGP. In addition, the formation of secondary inorganic aerosols (NO\(_3^-\) and SO\(_4^{2-}\)) have been assessed under different meteorological conditions (clear days, haze and fog events) by sulphur and nitrogen oxidation ratios (SOR and NOR, respectively).

**SAMPLING LOCATIONS, AEROSOL COLLECTION AND METEOROLOGICAL DETAILS**

Ambient aerosol samples were collected at Allahabad and Hisar during Dec 2004 using a high-volume sampler (model APM 450, Environtech, India). The sampler does not have size-selective inlet and thus, all samples correspond to total suspended particulate (TSP) samples. The sampler was calibrated before the field campaign and the flow-rate was suspended particulate (TSP) samples. The sampler was size-selective inlet and thus, all samples correspond to total APM 450, Environtech, India). The sampler does not have

The two sampling sites, Allahabad (24.0°N, 81.9°E) and Hisar (29.2°N, 79.5°E), represent an urban polluted environment in northern India and their locations are shown in Fig. 1. As per Census India report in 2011, the populations of Hisar and Allahabad are 0.3 and 1.2 million, respectively. Both sites are located in a highly agriculture productive region of India and high level of pollution is observed from the burning of cow-dung, agricultural waste and wood-fuel used for residential heating purposes (Badarinath et al., 2009).

The sampling period (Dec 2004) represents wintertime weather conditions over northern India and characterized by calm winds (wind speed < 2 m/s) and low ambient temperature (range: 5–25°C). In addition, lower boundary layer height (~500–800 m) (Nair et al., 2007) and prevailing meteorological conditions (lower temperature and calm winds, and high relative humidity) are conducive to the accumulation of aerosol and pollutants in the lower atmosphere over the IGP. The sampling period was also characterized by a number of fog and haze weather conditions in the Gangetic Plain (Ramachandran et al., 2006; Lal et al., 2008). Thus, these particulate samples provide an ideal opportunity to understand the role of primary (derived from the anthropogenic emissions within the IGP) and secondary aerosol, and local meteorological conditions in the modulation of fog-haze formation. The classification of fog, haze and clear days is based on the visibility, relative humidity (RH) and the notes in the log book during the sampling period (Ramachandran et al., 2006; Lal et al., 2008). When the visibility was in the range of 0.2–0.5 km, 1–2 km and ~10 km; the events were defined as fog, haze and clear days, respectively (Ramachandran et al., 2006). The diurnal plot of three hourly averaged temperature and relative humidity data during clear, haze and fog events at Hisar is shown in Fig. 2. Generally, relative humidity was less than 70 and 80%, respectively, during clear and haze days. In contrast, the RH was higher than 90% (especially in morning hours; see Fig. 2) during foggy days. In addition, some of the intense fog and haze events (e.g. Fig. 1) in the IGP region were also captured by the Moderate Resolution Imaging Spectroradiometer (MODIS) onboard NASA’s Terra satellite captured this image of the region on December 17, 2004.
CHEMICAL ANALYSES OF AEROSOL SAMPLES AND QUALITY CONTROL

All the filters were wrapped in the Aluminum foil after sample collection and were packed in zip-lock bags. Samples were brought to the laboratory and stored in a refrigerator at ~4°C until the analysis. Prior to assessment of total aerosol mass and chemical analysis, samples were equilibrated in a laminar flow bench for ~15–20 h under constant relative humidity (35 ± 5%) and temperature (22 ± 1°C) conditions. The particulate matter (PM) mass ($\mu g/m^3$) was ascertained gravimetrically by weighing full-filter before and after the aerosol sampling, and dividing the aerosol mass (in $\mu g$) by the total volume of air sampled (in units of $m^3$). The mass concentrations of elemental and organic carbon (EC and OC) in ambient aerosol were assessed on the EC-OC analyzer (Sunset Laboratory, USA) using thermo-optical transmittance (TOT) protocol (Rengarajan et al., 2007; Ram et al., 2008). The transmittance signal measured using a laser source (at 678 nm) was used to define the split-point between EC-OC and to correct for the pyrolyzed carbon. Also, OC concentrations were corrected for the carbonate carbon by acidifying the aerosol sample with 6M HCl in a desiccator (for ~6 hrs) and re-analyzing the acidified samples on the EC-OC analyzer. A number of replicate analyses of aerosol samples (n = 6) provide good reproducibility (reported as relative percentage deviation; r.p.d.) for OC (~6%), EC (~8%) and TC (~5%) measurements. In addition, the transmittance signal at 678 nm of the laser source has been used for the determination of absorption coefficient ($b_{abs}$) and mass absorption efficiency ($\sigma_{abs}$) of EC (Ram and Sarin, 2009).

The inorganic constituents, cations (Na$^+$, K$^+$, NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$) and anions (Cl$^-$, SO$_4^{2-}$ and NO$_3^-$) in the water-extract of aerosol samples, were measured using an ion chromatograph (Dionex-500) whereas water-soluble organic carbon (WSOC) was analyzed using a total organic carbon (TOC) analyzer (Shimadzu, TOC-5000A) (Ram and Sarin, 2010). The mass concentration of bicarbonate ion (HCO$_3^-$) was measured using a 0.005 M HCl and fixed endpoint titration method in an auto-titration system. The experimental details for the measurement of inorganic constituents and WSOC are described in our recent publication (Ram and Sarin, 2010). The reproducibility (as r.p.d.) of replicate analyses of water-extracts for K$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ were better than 3% while it was ~6% for NH$_4^+$ analysis (n = 4). All the reported data of carbonaceous species (EC, OC and WSOC) and inorganic ionic constituents (cations and anions) are corrected for their respective procedural blanks (Ram and Sarin, 2010; Ram et al., 2010a).

| Table 1. The 24-hr average meteorological data, NO$_2$ and SO$_2$ concentrations during the clear days, haze and fog events at two sampling sites (Hisar and Allahabad) in northern India. |

<table>
<thead>
<tr>
<th>Species</th>
<th>Hisar$^a$</th>
<th>Allahabad</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clear days</td>
<td>Haze events</td>
</tr>
<tr>
<td></td>
<td>(6, 8, 15 Dec)</td>
<td>(11, 17, 28 Dec)</td>
</tr>
<tr>
<td>RH (%)$^b$</td>
<td>46.7 ± 9.9</td>
<td>62.3 ± 8.5</td>
</tr>
<tr>
<td>Temperature (°C)$^c$</td>
<td>17.5 ± 0.4</td>
<td>16.7 ± 1.1</td>
</tr>
<tr>
<td>Wind speed (m/s)$^d$</td>
<td>0.6 ± 0.1</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>Visibility range (km)$^e$</td>
<td>~10.0</td>
<td>1.0–2.0</td>
</tr>
<tr>
<td>NO$_2$ (μg/m$^3$)$^{f,g}$</td>
<td>23.3 ± 7.1</td>
<td>31.5 ± 7.6</td>
</tr>
<tr>
<td>SO$_2$ (μg/m$^3$)$^{f,g}$</td>
<td>11.0 ± 1.7</td>
<td>15.6 ± 4.6</td>
</tr>
</tbody>
</table>

$^a$Classification of fog, haze events and clear days as per Ramachandran et al. (2006); Lal et al. (2008).

$^b$Daily-average data for relative humidity (RH), temperature and wind speed. The fog and haze events persist only for few hrs (when RH > 80%; see Fig. 1), the 24-hr averaging resulted in lower RH during fog and haze events.

$^{f,g}$Daily-average NO$_2$ and SO$_2$ concentrations at Allahabad is adopted from Kulshreshtha et al. (2009) and those at Hisar from Lal et al. (2008).
RESULTS AND DISCUSSION

Total Suspended Particulate Matter

The average mass concentrations of total suspended particulate (TSP), carbonaceous species (OC, EC and WSOC) and inorganic species during clear days, haze and fog events are presented in Table 2 and their fractional contribution is shown in Fig. 3. Among the measured chemical species, organic matter (OM = 1.6 × OC) contributes ~25–30% of the TSP mass whereas the absorbing EC mass is only 2% at Allahabad and Hisar (Fig. 3). Organic matter often contains functional groups which comprise of elements such as oxygen, nitrogen and sulphur and an appropriate conversion factor is needed to account for these elements. The conversion factor (i.e. OM/OC ratio) is highly variable (range: 1.4–2.1) (Turpin and Lim, 2001) and depends on the sources of organic aerosol, location and environment (urban, rural or high-altitude). In this study, we have used a value of 1.6 to estimate the OM concentration at the urban sites (Rengarajan et al., 2007; Ram et al., 2010; Turpin and Lim, 2001). SO4− contributes ~7% to the TSP mass at both sites, followed by NO3− (8% at Hisar and 4% at Allahabad) and NH4+ (4% at Hisar and 2.5% at Allahabad). In addition, carbonaceous and inorganic species together contribute ~60% of the aerosol mass at Hisar whereas their contribution is ~50% at Allahabad (Fig. 3). The contribution of unidentified matter (UM), estimated by taking difference of OM, EC and inorganic constituents from the TSP, is of the order of 40% at Hisar and ~50% at Allahabad. The unidentified matter mainly consists of mineral dust with dominant contribution from carbonate-rich minerals (such as CaCO3, MgCO3, dolomite [CaMg(CO3)2]), calcium sulphate (or Gypsum), and alumino-silicates (Krueger et al., 2004; Rengarajan et al., 2007; Zhang et al., 2010). The high-level of Ca2+ concentration in our samples (Table 2) and neutralization of acidic species by mineral aerosol (Table 3) and section 4.5) further attests our inference.

Mass Concentrations of Carbonaceous and Inorganic Species

The average mass concentrations of OC and EC are 49.0 ± 14.1 and 6.2 ± 2.0 μg/m3, respectively at Allahabad and those at Hisar are 30.9 ± 17.9 and 3.8 ± 1.4 μg/m3, respectively. Although, mass concentrations of OC and EC are relatively higher at Allahabad; their fractional contribution is similar at both the urban sites (Fig. 3). In addition, mass concentrations of OC and EC at Hisar and Allahabad are also similar with a recent data acquired during the wintertime from Kanpur, an urban site located at the center of the IGP (Ram et al., 2010a). However, mass concentrations of OC and EC at urban sites in the IGP are an order of magnitude higher compared to those at high-altitude site (Manora Peak) in the central Himalaya (Ram et al., 2010b). The average mass concentration of WSOC is 17.7 ± 5.9 and 15.3 ± 7.6 μg/m3 at Allahabad and Hisar, and average WSOC contributes ~32 and 36% of total OC, respectively.

The mass concentrations of cations follow the trend: NH4+ > Ca2+ > K+ > Na+ > Mg2+ at Allahabad and Hisar. Trend for anions is: SO42− > NO3− > HCO3− > Cl− for the samples collected at Allahabad and NO3− > SO42− > HCO3− > Cl− at Hisar. The average water-soluble inorganic species (WSIS: sum of the cations and anions) mass is 61.0 ± 45.6 μg/m3 at Allahabad and Hisar, and contribute ~20 and 25% of the TSP mass, respectively. The fractional contribution of individual cation and anion (to WSIS mass) at both sampling sites is presented in Fig. 4. Among anions; SO42−, NO3− and HCO3− are the major contributor to the WSIS mass whereas NH4+, Ca2+ and K+ cations contribute significantly toward the WSIS mass (Fig. 4). The mass concentrations of NH4+, SO42− and NO3− at Allahabad contribute ~12, 33 and 20% of the WSIS mass, respectively (Fig. 4). The contribution of SO42− and NO3− is similar (~28 and 29% of

Table 2. Mass concentrations (± 1 s) of carbonaceous (OC, EC and WSOC) and selected inorganic species (in the units of μg/m3) during the clear days, haze and fog events at two sampling sites in northern India. Aerosol absorption coefficient (baabs; unit: M/m) and mass absorption efficiency (σabs; unit: m2/g) of EC, at 678 nm, is also given. The scattering coefficient (bscat; at 678 nm) is estimated using an average mass scattering efficiency of 3.0 m2/g (Ram et al., 2012).

<table>
<thead>
<tr>
<th>Species</th>
<th>Clear</th>
<th>Haze</th>
<th>Fog</th>
<th>Clear</th>
<th>Haze</th>
<th>Fog</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSP</td>
<td>147 ± 21</td>
<td>199 ± 19</td>
<td>162 ± 29</td>
<td>212 ± 45</td>
<td>247 ± 42</td>
<td>302 ± 95</td>
</tr>
<tr>
<td>OC</td>
<td>31.5 ± 9.7</td>
<td>34.9 ± 12.8</td>
<td>31.6 ± 8.8</td>
<td>33.8 ± 9.5</td>
<td>45.1 ± 8.5</td>
<td>60.1 ± 12.7</td>
</tr>
<tr>
<td>EC</td>
<td>3.5 ± 1.0</td>
<td>4.0 ± 1.4</td>
<td>4.1 ± 1.3</td>
<td>5.0 ± 2.1</td>
<td>6.4 ± 2.5</td>
<td>6.9 ± 2.6</td>
</tr>
<tr>
<td>WSO2C</td>
<td>9.4 ± 3.9</td>
<td>11.3 ± 3.7</td>
<td>11.8 ± 2.1</td>
<td>12.5 ± 4.8</td>
<td>19.0 ± 5.4</td>
<td>21.3 ± 1.7</td>
</tr>
<tr>
<td>Na+</td>
<td>0.7 ± 0.1</td>
<td>0.8 ± 0.2</td>
<td>0.7 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.8 ± 0.2</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>K+</td>
<td>2.5 ± 0.7</td>
<td>2.6 ± 0.6</td>
<td>2.7 ± 0.7</td>
<td>1.8 ± 0.4</td>
<td>2.5 ± 0.4</td>
<td>2.9 ± 0.5</td>
</tr>
<tr>
<td>Ca2+</td>
<td>3.4 ± 0.4</td>
<td>4.4 ± 0.8</td>
<td>2.7 ± 1.0</td>
<td>5.8 ± 1.2</td>
<td>5.2 ± 2.2</td>
<td>6.2 ± 2.4</td>
</tr>
<tr>
<td>Mg2+</td>
<td>0.3 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>0.6 ± 0.1</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>NH4+</td>
<td>3.2 ± 2.6</td>
<td>6.8 ± 1.9</td>
<td>9.7 ± 3.8</td>
<td>2.9 ± 1.1</td>
<td>7.3 ± 2.3</td>
<td>8.5 ± 2.8</td>
</tr>
<tr>
<td>Cl−</td>
<td>0.4 ± 0.4</td>
<td>0.4 ± 0.1</td>
<td>0.4 ± 0.1</td>
<td>0.1 ± 0.1</td>
<td>0.1 ± 0.1</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>NO3−</td>
<td>9.9 ± 5.3</td>
<td>16.7 ± 4.2</td>
<td>17.1 ± 5.6</td>
<td>5.5 ± 1.9</td>
<td>9.9 ± 3.7</td>
<td>12.4 ± 6.0</td>
</tr>
<tr>
<td>SO42−</td>
<td>7.0 ± 2.9</td>
<td>12.7 ± 1.8</td>
<td>17.3 ± 6.1</td>
<td>10.8 ± 2.8</td>
<td>18.6 ± 2.6</td>
<td>23.6 ± 8.6</td>
</tr>
<tr>
<td>babs</td>
<td>39.4 ± 6.7</td>
<td>40.0 ± 15.7</td>
<td>49.3 ± 6.2</td>
<td>56.4 ± 14.2</td>
<td>72.9 ± 25.5</td>
<td>71.9 ± 10.6</td>
</tr>
<tr>
<td>σabs</td>
<td>12.2 ± 1.0</td>
<td>11.2 ± 3.1</td>
<td>12.0 ± 2.8</td>
<td>11.9 ± 3.0</td>
<td>12.0 ± 3.0</td>
<td>11.4 ± 4.1</td>
</tr>
<tr>
<td>bscat</td>
<td>441 ± 63</td>
<td>597 ± 57</td>
<td>486 ± 87</td>
<td>636 ± 135</td>
<td>741 ± 126</td>
<td>906 ± 285</td>
</tr>
</tbody>
</table>
Fig. 3. TSP mass closure at urban Hisar and Allahabad for the samples collected during Dec 2004. OM refers to the organic matter \( (= 1.6 \times OC) \), WSIS \(^s\) (sum of inorganic species excluding \( SO_4^{2-} \), \( NO_3^- \) and \( NH_4^+ \)) and unidentified matter (UM) is defined as TSP – OM – EC – WSIS \(^s\).

Thus, secondary inorganic aerosol (SIA: \( NH_4^+ \), \( SO_4^{2-} \) and \( NO_3^- \)) contribute \( \sim 65 \) and \( \sim 70\% \) of the WSIS mass at Allahabad and Hisar, respectively.

**Chemical and Absorption Properties of Aerosol during Clear Days, Haze and Fog Events**

In general, total suspended particulate (TSP) and concentrations of selected chemical species (EC, OC, WSOC, \( NH_4^+ \), \( SO_4^{2-} \) and \( NO_3^- \)) increases during haze and fog events. Although, fog and haze events persist only for few hrs (when RH > 80%; see Fig. 1), the increase in daily mass concentrations of chemical species were significant at both sites. The average ratios of mass concentrations of selected chemical constituents during fog and haze events, with respect to those during clear days, at Allahabad and Hisar are shown in Fig. 5. The average TSP mass increases by \( \sim 25\% \)–\( 50\% \) during haze-fog events at Hisar and Allahabad. The mass concentrations of OC, EC and WSOC also exhibit an increase of \( \sim 30\% \) (Fig. 5). However, their fractional contribution (to TSP) increases only 5\% during foggy days. The OC/EC and WSOC/OC ratios are also similar during clear days, haze and fog events at both the sampling sites (Table 3).

Secondary organic carbon (SOC), estimated using the EC tracer method, contributes \( \sim 30\% \) of total OC at urban sites in the Gangetic Plain during wintertime (Ram and Sarin, 2010). The EC tracer approach provides an easier and convenient method to estimate SOC concentration. However, the estimated SOC concentration can be associated with some degree of uncertainty due to varying nature and source strength of primary emissions (biomass vs. fossil fuel emissions) and changes in the primary OC/EC ratio. Biomass burning emissions dominate in the IGP during winter months (Rengarajan et al., 2007; Gustafsson et al., 2010; Ram and Sarin 2010; Ram et al., 2012). Therefore, primary OC/EC ratio from biomass burning emission sources is reasonably constant so that the estimation of SOC is quite reliable in the present study. In addition, mass concentrations of K\(^+\), a tracer of biomass burning emissions, shows an increase (~35–60\%; Table 2) at Allahabad suggesting that strength of biomass burning emissions was higher during haze and fog events. In addition, absorption coefficient (\( b_{abs} \)) also exhibits an increase by ~25–30\% during haze and fog events (Table 2). Since, mass absorption efficiency (\( \sigma_{abs} \)) remains similar during haze and fog events; the increase in absorption coefficient is attributed to the increase in EC mass concentration.

The mass concentrations of secondary inorganic aerosol (SIA: \( NH_4^+ \), \( SO_4^{2-} \) and \( NO_3^- \)) show a factor of 2–3 increase during haze and fog events (Table 2, Fig. 5). Among secondary inorganic aerosol; \( NH_4^+ \) shows the maximum increase followed by \( SO_4^{2-} \) and \( NO_3^- \) at both sites (Fig. 5). The fractional contribution of EC, OM and secondary inorganic aerosol during clear days, haze and fog events are presented in Fig. 6. It is observed that the contribution

<table>
<thead>
<tr>
<th>Table 3. Ratios of selected chemical species during clear days, haze and fog events at Hisar and Allahabad.</th>
<th>Hisar</th>
<th>Allahabad</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPECIES</td>
<td>Haze</td>
<td>Fog</td>
</tr>
<tr>
<td><strong>OC/EC</strong></td>
<td>8.9 ± 0.5</td>
<td>8.6 ± 0.4</td>
</tr>
<tr>
<td><strong>WSOC/OC</strong></td>
<td>0.29 ± 0.05</td>
<td>0.33 ± 0.03</td>
</tr>
<tr>
<td><strong>WIOC/EC</strong></td>
<td>6.3 ± 0.6</td>
<td>5.8 ± 0.5</td>
</tr>
<tr>
<td><strong>NH_4^+/SO_4^{2-}</strong> (equivalent)</td>
<td>0.9 ± 0.6</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td><strong>NO_3^-/Ca^{2+}</strong> (molar)</td>
<td>1.5 ± 0.7</td>
<td>2.2 ± 0.7</td>
</tr>
<tr>
<td><strong>SO_4^{2-}/Ca^{2+}</strong> (molar)</td>
<td>0.8 ± 0.3</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td><strong>NF (NH_4^+)</strong></td>
<td>0.48 ± 0.32</td>
<td>0.70 ± 0.08</td>
</tr>
<tr>
<td><strong>NF (Ca^{2+})</strong></td>
<td>0.72 ± 0.49</td>
<td>0.41 ± 0.06</td>
</tr>
<tr>
<td><strong>NF (Mg^{2+})</strong></td>
<td>0.10 ± 0.07</td>
<td>0.07 ± 0.01</td>
</tr>
</tbody>
</table>

\(^nF\) stands for neutralization factor.
Fig. 4. Mass closure of water-soluble inorganic species (WSIS) at Hisar and Allahabad.

of SIA increases from 12.5% (during clear days) to 23% (during fog events) at Hisar and 9.4 to 16% at Allahabad. The increase in mass concentrations of NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ can not be attributed to the simultaneous increase in aerosol loading as their fractional contribution is also higher during haze and fog events (Fig. 6). In addition, fractional contribution of UM during fog events decreases to 30% at Hisar and 40% at Allahabad. Furthermore, SO$_4^{2-}$/Ca$^{2+}$ and NO$_3^-$/Ca$^{2+}$ molar ratios are also higher during haze and fog events (Table 3). The mass concentration of Ca$^{2+}$ is similar during clear days, haze and fog events at both sites (Table 2). Thus, the increase in mass concentrations of SO$_4^{2-}$ and NO$_3^-$ can be attributed to secondary formation from their respective precursor gases.

Aerosol absorption coefficient (b$_{abs}$), measured at 678 nm, varies from 24.9 to 54.6 M/m (1 M/m = 10$^{-6}$ 1/m) at Hisar with an average of 39.9 ± 9.1 M/m during Dec 2004. Similarly, b$_{abs}$ ranges from 36.8 to 109.4 M/m (av.: 66.1 ± 17.2 M/m) at Allahabad. Furthermore, absorption coefficient is relatively higher during fog and haze events at both urban sites (Table 2). In contrast, average mass absorption efficiency ($\sigma_{abs}$) of EC at both urban sites (11.1 ± 2.6 m$^2$/g at Allahabad and 11.3 ± 2.2 m$^2$/g at Hisar) are similar during clear, fog and haze events (Table 2). Thus, relatively higher b$_{abs}$ at Allahabad are attributed to the higher EC mass concentrations. The $\sigma_{abs}$ values, obtained in the present study, are relatively higher compared to those reported over Chinese regions; for example 7.7 m$^2$/g (in PM$_{2.5}$ samples collected at urban Guangzhou) (Andreae et al., 2008), 9.3 ± 1.4 m$^2$/g (for PM$_{1.0}$) at urban XinKen (Cheng et al., 2008) and 8.45 ± 1.7 m$^2$/g for aerosol over Beijing during wintertime (Cheng et al, 2011). There is a lack of scattering coefficient (b$_{scat}$) measurements over northern India. However, more recently, Ram et al. (2012) have reported an average mass scattering efficiency of 3.0 ± 0.9 m$^2$/g for PM$_{10}$ samples collected during Oct–Nov 2008 at Kanpur. Assuming this value applicable for TSP samples also, scattering coefficient (at 678 nm wavelength) ranges from 450 to 1600 M/m (at Allahabad) and 201 to 885 M/m (at Hisar) during the observation period. The average

Fig. 5. The mass ratios of selected aerosol constituents, with respect to clear days, during fog and haze events: (a) and (b) at Hisar; (c) and (d) at Allahabad.
absorption and scattering coefficients are summarized in Table 2 and both optical parameters are relatively higher during fog and haze events at Hisar and Allahabad.

**Sulphur and Nitrogen Oxidation Ratios (SOR and NOR)**

The 24-hr average meteorological data including ambient temperature, relative humidity (RH) and wind speed during clear days, haze and fog events at both the sampling sites are presented in Table 1. Although, only NO2 data is available at Hisar; concentration of SO2 and NO2 gases are available at Allahabad. Kulshrestha et al. (2009) have reported that daily-average concentrations of SO2 and NO2 varied from 5 to 43 μg/m3 and 2 to 45 μg/m3, respectively during the sampling period at Allahabad. The average concentration of SO2 at Allahabad during clear days, haze and fog events are: 11.0 ± 1.7, 15.6 ± 4.6 and 17.2 ± 10.9 μg/m3 whereas that of NO2 are: 11.7 ± 2.9, 26.8 ± 9.7, and 17.4 ± 6.2 μg/m3.

It is observed that concentration of precursor gases as well as those of SO2-2 and NO3- increases significantly during haze and fog events. Relative humidity is relatively higher during haze and fog events at Allahabad (Fig. 1). Thus, it is evident that higher RH and concentrations of precursor gases during haze and fog events led to enhanced formation of SO2-2 and NO3- aerosols.

The acidic species, SO2-2 and NO3-, are generally produced by the oxidation of their precursor gases (SO2 and NOx, respectively) in the atmosphere under the favorable atmospheric conditions via homogeneous and heterogeneous oxidation processes. Homogeneous oxidation processes involves the gas-phase reaction of SO2 with OH radicals and is a temperature dependent process. On the other hand, heterogeneous oxidation reaction of SO2 can take place on dust aerosol surfaces (Bauer et al., 2004; Krueger et al., 2004), aqueous transformation though catalytic oxidation (via H2O2/O3 oxidation in the presence of Mn2+ and Fe3+) (Martin and Good, 1991; Seinfeld and Pandis, 1998; Tursic et al., 2004) and in-cloud scavenging processes (Warneck, 1999). It has been found that gas phase oxidation is more important prior to fog formation and heterogeneous oxidation take over after fog formation (Rattigan et al., 2001a, b). Thus, the conversion of SO2 to sulfate depends on the concentrations of precursor gases and oxidants, cloud cover, availability of surface area and meteorological conditions such as temperature and relative humidity (Liang and Jacobson, 1999; Rattigan et al., 2001a, b). For example, Rattigan et al. (2001b) investigated SO2 oxidation in clouds as a function of droplet size, and found that SO2 oxidation was dominated by hydrogen peroxide when the pH of the cloud water was lower (in the range of 2.8 to 4.7).

Model simulations suggest that aqueous phase reactions contribute ~two-thirds of the total sulfate production in the troposphere (Warneck, 1999; Unger et al., 2006). Since, ambient temperature is similar during clear days, haze and fog events (Table 1); the higher sulfate formation during haze and fog events can not be fully explained only by the homogeneous gas-phase oxidation of sulphur dioxide. Tursic et al. (2004) concluded that heterogeneous reactions under haze conditions can contribute significantly to formation of secondary sulfate aerosol. Recent studies have reported that PM1.0 and PM2.5 contribute ~65–80% of the PM10 mass at Kanpur, an urban site in the Gangetic Plain (Tare et al., 2006; Ram and Sarin, 2011). Thus, conversion of SO2 through heterogeneous reactions (either on surface or aqueous phase) is expected to be higher under favorable meteorological conditions (lower ambient temperature and wind speed, high RH and SO2) and in the presence of higher particle concentration. However, this proposition and heterogeneous reactions needs a detailed investigation in the IGP.

The secondary NO3- formation depends on the concentrations of NOx and NH3, ambient temperature, RH, OH radical (in daytime) and the photochemical activity. In addition; nighttime secondary NO3- formation involves the hydrolysis of dinitrogen-pentaoxide (N2O5) through the heterogeneous reaction on aerosol surfaces and higher relative humidity enhances the heterogeneous hydrolysis of N2O5 (Ravishankara et al., 1997; Jacob, 2000; Pathak et al., 2009). Brown et al. (2004) have suggested that the conversion efficiency of NOx to HNO3 during nighttime can be equivalent to the daytime photochemical conversion. Moreover, Vrekoussis et al. (2006) have found that ~55–65% of the total production of nighttime HNO3 and NO3- were through the heterogeneous reactions of NO3 radical in an anthropogenically-influenced eastern Mediterranean marine boundary layer. The higher abundances of NO2 and high RH may facilitate the secondary NO3- formation during the wintertime in the polluted atmosphere of the IGP (Ram and Sarin, 2011). The presence of particulate nitrate is a temperature dependent equilibrium between ammonia and HNO3 with lower ambient temperature favouring the existence of ammonium nitrate (NH4NO3) (Seinfeld and Pandis, 1998). Furthermore, this equilibrium also depends on concentration of sulfuric acid as NH4NO3 formation follows ammonium sulfate and ammonium bisulfate (see section 4.5).

In order to understand the oxidation of SO2 and NO2 precursor gases, we have investigated the efficiency of oxidation of SO2 to SO2-2 and NO2 to NO3 during clear days, haze and fog events at Allahabad. The sulphur and nitrogen oxidation ratios (SOR and NOR) were calculated using the following equations (Wang et al., 2006; Tan et...
where daily-average concentrations of all the chemical species are reported in molar units. The sulphate concentration represents non-sea salt (nss)-SO$_4^{2-}$ (where nss-SO$_4^{2-}$ = [SO$_4^{2-}$] − 0.2514 × [Na$^+$]) and is corrected for the contribution from sea-salt (Ram et al., 2010). However, the contribution of sea-salt SO$_4^{2-}$ is very low (~0.1–0.2 µg/m$^3$) and contributes only 1% to total SO$_4^{2-}$ in our samples. The average SOR and NOR, at Allahabad, during clear days, haze, and fog events are presented in Table 4. The SOR and NOR show an increase during haze and fog events (with the highest values during fog events) and thus, suggesting higher oxidation of SO$_2$ and NO$_2$ during haze and fog events. The average SOR, at Allahabad, during clear, haze and fog events are 0.39 ± 0.05, 0.45 ± 0.12 and 0.52 ± 0.15, respectively. Similarly, the average NOR, at Allahabad, during haze and fog events are 0.20 ± 0.04 and 0.33 ± 0.11 whereas those at Hisar are 0.30 ± 0.04 and 0.39 ± 0.08, respectively. The NOR values are 0.25 ± 0.08 and 0.23 ± 0.15 during clear days at Allahabad and Hisar, respectively. These values are compared with those over the Chinese region (Table 4). It is noteworthy that total aerosol mass as well as concentrations of SO$_2$ and NO$_3$ is similar over urban sites in India and China but concentrations of SO$_2$ and NO$_2$ are factor of 3–4 times higher over China (Wang et al., 2006; Rengarajan et al., 2007; Jihua et al., 2009; Tan et al., 2009). However, NOR and SOR over Chinese regions, during clear days, are much lower (except at Beijing) than those at Allahabad and Hisar. Thus, the oxidation efficiency of SO$_2$ to SO$_4^{2-}$ and NO$_2$ to NO$_3$ aerosol are relatively higher over Indian regions. The diurnal variation of NO$_x$ concentration were relatively higher (by ~11 ppbv) during the haze condition (compared to clear days) (Lal et al., 2008). This observation suggests an increase in photochemical activity with simultaneous increase in OH production and thus, results in the lower concentrations of non-methane hydrocarbons and NO$_x$ species (Lal et al., 2008). These differences in oxidation efficiency could arise due to the meteorology, photochemical activity, and the levels of OH radical which are expected to be higher in India than China due to the meridional variations in solar flux (Volz et al., 1981; Lal et al., 2008).

### Nitrogen and sulfur oxidation ratios

<table>
<thead>
<tr>
<th>Site</th>
<th>Time-period</th>
<th>NOR$^a$</th>
<th>SOR$^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allahabad</td>
<td>Dec-04</td>
<td>0.25 ± 0.08</td>
<td>0.20 ± 0.04</td>
<td>0.33 ± 0.11</td>
</tr>
<tr>
<td>Hisar</td>
<td>Dec-04</td>
<td>0.23 ± 0.15</td>
<td>0.30 ± 0.04</td>
<td>0.39 ± 0.08</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>winter-2002</td>
<td>0.06</td>
<td>0.15</td>
<td>0.08</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>summer-2002</td>
<td>0.04</td>
<td>0.22</td>
<td>0.1</td>
</tr>
<tr>
<td>Beijing</td>
<td>2001-04</td>
<td>0.18</td>
<td>0.29</td>
<td>0.17</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>Dec-07-Jan 08</td>
<td>0.09</td>
<td>0.24</td>
<td>0.22</td>
</tr>
</tbody>
</table>

$^a$Nitrogen and sulfur oxidation ratios.
environment and the possible association of NO$_3^-$ with Ca$^{2+}$ and Mg$^{2+}$ as calcium nitrate [Ca(NO$_3$)$_2$] and [Mg(NO$_3$)$_2$], respectively. This is further reflected by the scatter plot between NH$_4^+$ and [NO$_3^-$ + SO$_4^{2-}$] at the two sampling sites (Fig. 7(b)). All the data points, except one, fall below the line with slope of unity indicating that ammonia is not sufficient to completely neutralize the acidic gaseous species and invoke the possible role of mineral aerosol toward the neutralization process. The scatter plot between [Ca$^{2+}$ + NH$_4^+$] and [NO$_3^-$ + SO$_4^{2-}$] indicate nearly complete neutralization of acidic species (Fig. 7(c)). Furthermore, we have calculated the neutralization by the cations (NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$) during clear days, haze and fog events, and neutralization factors (NF; defined as the equivalent ratio of cation to the acidic species) are presented in Table 3. Although, ammonia is the major neutralizing agent of the acidic species at Allahabad and Hisar, Ca$^{2+}$ is the second neutralizing agent. In addition, the neutralization by Ca$^{2+}$ becomes more prominent during clear days at both the sampling sites (Table 3).

CONCLUSIONS AND IMPLICATIONS

Mass concentrations of carbonaceous and inorganic species, together with the oxidation ratios of SO$_2$ and NO$_2$, studied during wintertime, have led us to infer that organic matter is a major constituent of aerosol (~25–30% of TSP mass) in the Indo-Gangetic Plain. Water-soluble inorganic species contribute ~20 and 25% of the TSP mass at Allahabad and Hisar, respectively. A factor of 2–3 increase in the mass concentration of secondary inorganic aerosols (NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$) is observed at the sampling sites in the IGP during haze and fog events. The scattering coefficient is relatively higher at urban sites in the IGP and is closely related to meteorological conditions and aerosol chemical composition. Carbonaceous and inorganic aerosols, associated with high mass scattering efficiencies, contribute significantly to total aerosol mass and scattering coefficient (as evident from the present study). Therefore, the reduction of carbonaceous and inorganic aerosols could effectively improve the visibility over the Gangetic plain during wintertime.

The sulphur and nitrogen oxidation ratios (SOR and NOR) are significantly higher during haze and fog events indicating enhanced oxidation efficiency of precursor gases of SO$_4^{2-}$ and NO$_3^-$. Secondary inorganic aerosol contributes ~65 and 70% of the WSIS mass at Allahabad and Hisar, respectively. The prevailing meteorological conditions (higher RH) and the presence of high levels of pollutants and condensation nuclei may be a likely cause for the fog-haze formation over the IGP which is also favoured under secondary aerosol formation and their hygroscopic growth during the wintertime. Subsequently, changes in morphological features and physico-optical properties of ambient aerosol in the presence of high concentrations of acidic species of the IGP requires detailed investigation in order to understand optical properties and their impact on radiation budget and regional climate.

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