Chemical and Microphysical Properties of Aerosol during Foggy and Nonfoggy Episodes over a Typical Location in Indo-Gangetic Plain

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Introduction

Frequent and extended fog episodes over the Indo-Gangetic Plain during winter make it an ideal site to study the role of fog in altering chemical and microphysical properties of aerosol. Fog processes both organic and inorganic compounds. It scavenges organic, inorganic compounds and aerosols. It can produce secondary organic aerosol (SOA) by aqueous phase processing of organic compounds (Kaul et al., 2000; Kaul et al., 2011). Inorganic compounds like sulfates help in formation of more organic phase by oligomerization. Aerosol of acidic nature increases the formation of SOA. The formation of SOA can be reflected by changes in organic carbon and growth in diameter of aerosol. Positive matrix factorization can be used to understand the influence of fog on emission sources and vice versa.

Methodology

PM samples on filters were collected during foggy and nonfoggy episodes from mid January to February, 2010 in Kanpur city which is located in Indo-gangetic plain of the India (Fig 1). Characterization of foggy and nonfoggy episodes are detailed elsewhere (Kaul et al., 2011). Carbon content of aerosol and fogwater were measured by EC-OC analyzer and TOC analyzer. Trace gases (O3, CO, SO2), meteorology and solar flux measurements were carried out by gas analyzers, automatic weather station and a pyranometer (a part of MPLNET, ISRO) to identify the pollution chemistry, EC tracer method (Turpin et al., 1995) was used to estimate the SOA. All the filters and fogwater samples were analyzed for inorganic ions (ion chromatograph). More details of the findings are included elsewhere (Kaul et al., 2011). Positive matrix factorization (PMF) tool for source apportionment were employed to understand the emission sources of pollutants.

Meteorology and Trace Gas

Drastic change in meteorology and trace gas concentrations before and after 1st week of February which may be due to stagnant and calm conditions (Fig 2 A & B)

SO2 is scavenged and removed from the atmosphere (Fig 2 B) during foggy episodes

Less O3 during foggy episodes indicates reduced photo-oxidation (Fig 2 B)

Table 1: Ordinary linear regression coefficient between inorganic species and organic carbon concentrations of fog droplets of different size

<table>
<thead>
<tr>
<th>Species/Organic Carbon (OC)</th>
<th>Organic Carbon (OC)</th>
<th>16-22 µm</th>
<th>16-18 µm</th>
<th>&lt; 4 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td>0.07</td>
<td>0.51</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>NO3</td>
<td>0.34</td>
<td>0.89</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>0.98</td>
<td>0.83</td>
<td>0.78</td>
<td></td>
</tr>
</tbody>
</table>

Ordinary linear regression coefficient between sulfate concentration in aerosol and SOA during fog evaporation (R² = 0.24) and foggy episode (R² = 0.24)

Similar poor correlation between SOA and nitrate concentration in aerosol

Thus, no trace of organo-sulfate and organo-nitrate formation in aerosol during foggy episodes and fog evaporation

Positive sign of organo-sulfate, organo-nitrate formation in fog droplets

Acidic nature of aerosol on enhanced SOA formation is not seen (Fig 3 D)

Enhanced secondary production of sulfate and ammonium during foggy episodes whereas nitrate is rather scavenged more during foggy episodes (Fig 3 C)

POA, WSOC and WSC are observed to be scavenged (Fig 4 A)

SOA is higher during foggy episodes due to its aqueous production

Higher TC and DM during foggy episodes is due to reduced dispersion and growth is size of the aerosol (Fig 4 A)

Positive aerosol diameter growth rate during fog evaporation is due to SOA formation (Fig 4 B); secondary inorganic aerosols also contributes to such growth in diameter

Lower GSD during foggy episodes may be due to scavenging of larger size aerosols by fog droplets

Table 2: Ordinary linear regression coefficient (R²) between measured and modeled species

<table>
<thead>
<tr>
<th>Species/Organic Carbon (OC)</th>
<th>Organic Carbon (OC)</th>
<th>16-22 µm</th>
<th>16-18 µm</th>
<th>&lt; 4 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.98</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NH4</td>
<td>0.20</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO4</td>
<td>0.66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WSOC</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Microphysical Properties

Figure 3: Temporal variation of (A) water soluble inorganic carbon (WSIC), (B) water soluble organic carbon (WSOC), (C) secondary organic aerosol (POA), (D) primary organic aerosol (POA) and (E) secondary organic aerosol (SOA) during foggy episodes.

Figure 4: (A) Temporal variation of total concentration (TC), geometric standard deviation (GSD) and modal diameter (Dm) (B) The aerosol diameter growth rate upon fog evaporation from 9.0 to 13.3 local standard time (hours) D = aerosol mobility diameter

Summary and Conclusions

The enhanced production of secondary organic aerosol (SOA) during foggy episodes is due to its aqueous phase production. The interaction of organics with inorganics leads to formation of organo-sulfate and organo-nitrate inside the fog droplets, similar formation in the aerosol upon fog evaporation and foggy episodes was not observed due to likely scavenge and wet removal. Fog droplet scavenges both organic and inorganics species. Formation of SOA caused growth in diameter of aerosol during fog evaporation. The biomass and secondary source contributes considerably to water soluble organic carbon (WSOC), contribution in other sources is relatively small. Refractory, dust and secondary are the major emission sources during foggy episodes, their strength decrease after calm conditions disappear, preferably after 1st week of February. Biomass burning during foggy episodes and before of 1st week of February contributed relatively lesser to aerosol due to scavenging of biomass burn aerosol.

References


Positive Matrix Factorization (PMF) Source Apportionment

Figure 5: Emission source profile during the study period and corresponding relative contribution during foggy and nonfoggy episodes for mineral dust (Fig U1 to D1), biomass burning (Fig U2 to D2), refractory (Fig U3 to D3) and secondary (Fig U4 to D4). WSOC is water soluble organic carbon

Four emission sources were resolved viz. mineral dust, biomass burning, refractory and secondary (Fig U1 to U4 and D1 to D4)

Almost all the sources contributed considerably to emission before 1st February except biomass burning because biomass generated aerosols are hygroscopic and are scavenged and removed from the atmosphere

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