

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 processing of organic compounds (Blando et al., 2000; Kaul et al., 2011). Inorganic compounds like sulfate 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

PM₁ 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 NASA), respectively to identify the photochemical activity. EC tracer method (Turpin et al., 1991) was used to estimate the SOA. All the filters and fogwater samples were analyzed for inorganic by ion chromatograph. More details of the findings are included elsewhere (Kaul et al., 2011). Positive matrix factorization (PMF) as a tool for source apportionment were employed to understand the emission sources of pollutants.

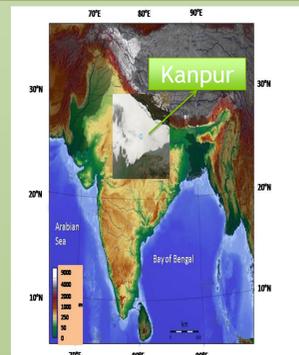


Figure 1: Sample site is shown by a circle. The map is overlapped with aerial image of fog (image to the scale) taken from MODIS rapid response (http://aeronet.gsfc.nasa.gov/cgi-bin/bamgomas_interactive). This figure shows that a large part of the area is affected by fog during winter.

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)

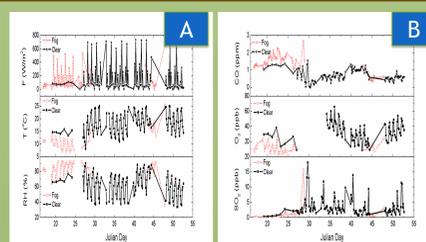


Figure 2: (A) Temporal variation of solar flux (F), temperature (T) and relative humidity (RH) during foggy and nonfoggy episodes (B) Trace gas concentrations (CO, O₃, SO₂) during foggy and nonfoggy episodes

Chemical Properties

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

species/OC	Organic Carbon (OC)		
	16-22 μm	4-16 μm	< 4 μm
NH ₄ ⁺	0.07	0.51	0.93
NO ₃ ⁻	0.34	0.89	0.82
SO ₄ ²⁻	0.09	0.63	0.70

> 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 (Table 1)

> Acidic nature of aerosol on enhanced SOA formation was 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 WSIC are observed to be scavenged

> SOA is higher during foggy episodes due to its aqueous production

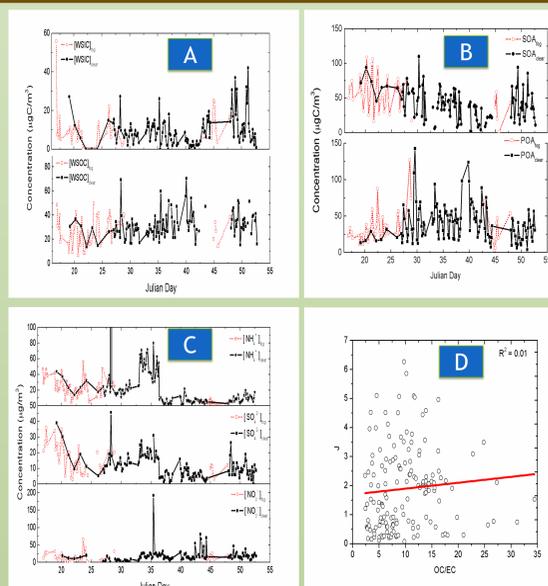


Figure 3: Temporal variation of (A) water soluble inorganic carbon (WSIC), water soluble organic carbon (WSOC), (B) primary organic aerosol (POA) and secondary organic aerosol (SOA), more details on SOA can be found in Kaul et al., 2011 and (C) ammonium, sulfate and nitrate during foggy and nonfoggy episodes; (D) Ordinary linear regression between J (J=[NH₄⁺]/[2SO₄²⁻]+[NO₃⁻]) and organic carbon (OC) to elemental carbon (EC) ratio

Microphysical Properties

> Higher TC and D_m 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 aerosol also contributes to such growth in diameter

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

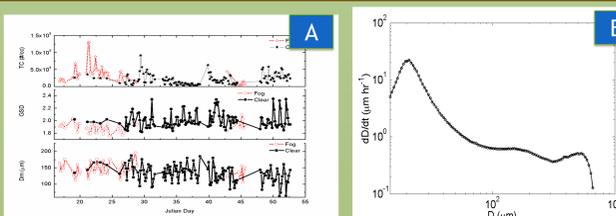


Figure 4: (A) Temporal variation of total concentration (TC), geometric standard deviation (GSD) and modal diameter (D_m) (B) The aerosol diameter growth rate upon fog evaporation from -9.0 to -13.3 local standard time (hours). D is aerosol mobility diameter

References

Blando, J. D.; Turpin, B. J., Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility. *Atmos. Environ.* 2000, 34, (10), 1623-1632.
 Kaul, D. S., et al., Secondary Organic Aerosol: A Comparison between Foggy and Nonfoggy Days, *Environmental Science & Technology*, 2011, DOI: 10.1021/es201081d
 Turpin, B. J.; Huntzicker, J. J., Secondary formation of organic aerosol in the Los Angeles basin: A descriptive analysis of organic and elemental carbon concentrations. *Atmos. Environ. Part A. General Topics* 1991, 25, (2), 207-215.

Positive Matrix Factorization (PMF) Source Apportionment

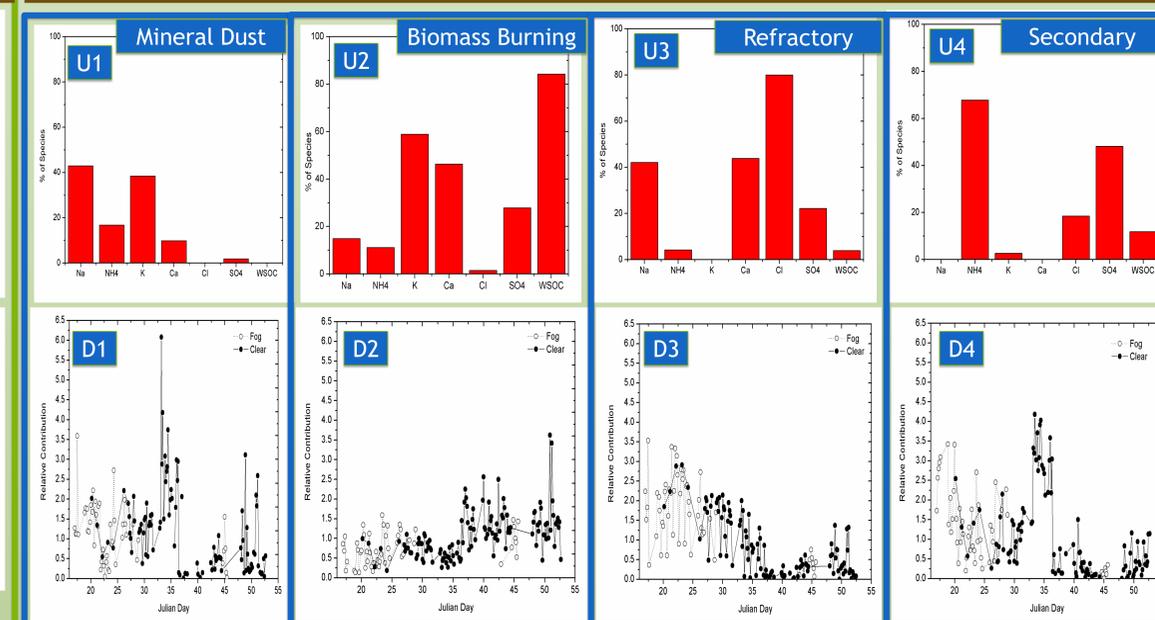


Figure 5: Emission source profile during the study period and corresponding relative contribution during foggy and nonfoggy episodes for mineral dust (Fig U1 to D1), biomass burning (Fig U2 to D2), refractory (Fig U3 to D3) and secondary (Fig U4 to D4). WSOC is water soluble organic carbon

> 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 week of February except biomass burning because biomass generated aerosols are hygroscopic and are scavenged and removed from the atmosphere

> Observed concentration were modeled with reliable significance (Table 2)

> Poor modeling of biomass tracer, K⁺ could be due to its wet scavenging and wet removal from the atmosphere (Table 2)

> Contribution to WSOC from secondary source and biomass is considerable, other sources contributes relatively small amount to WSOC (Fig U1 to U4 and D1 to D4)

Table 2: Ordinary linear regression coefficient (R²) between measured and modeled species. WSOC stands for water soluble organic carbon

Species	R ²
Na	0.98
NH ₄	0.96
K	0.20
Ca	0.55
Cl	0.96
SO ₄	0.66
WSOC	0.99

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 likely to their overnight scavenging and wet removal. Fog droplet scavenges both organic and inorganic species. Formation of SOA caused growth in diameter of aerosol during fog evaporation. The biomass burning and secondary source contributes considerably to water soluble organic carbon (WSOC), contribution from 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 1st week of February contributed relatively lesser to aerosol due to scavenging of biomass generated aerosol.

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