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# Enhanced secondary organic aerosol during fog 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 interaction between fogs and carbonaceous aerosols. These aerosols can be formed via gas-to-particle partitioning of various low volatility products of photo-oxidation reactions; particulate organic matter produced by this process is referred to as secondary organic aerosol (SOA). Formation mechanisms have been suggested both in wet aerosols and in fogs and clouds (Blando et al., 2000 ). Mechanisms of SOA production remain poorly understood partly due to the complex nature of multiphase processes likely involved in SOA production. This study has examined the aqueous phase production of SOA and processing of organics and inorganics by fog droplets.

## Method

$PM_1$ samples on filters were collected from mid January to February, 2010 in Kanpur city which is located in the most polluted and densely populated (~ 2.6 million) Indo-Gangetic plain of India (Fig 1). Micro-Pulse Lidar Network (MPLNET), as part of National Aeronautic Space Administration (NASA), was used for identification of fog duration. Organic Carbon (OC), Elemental Carbon (EC) and water soluble organic carbon (WSOC) measurements were carried out by EC-OC analyzer and TOC analyzer, respectively. Trace gases ($O_3$,CO,$SO_2$) and solar flux measurement were carried out by gas analyzer and pyranometer (as part of NASA AERONET), respectively to identify the photo-chemical activity. Meteorological data were measured by atmospheric weather station. EC tracer method (Turpin et al., 1991) was used to estimate the SOA. All the filters and fog water were analyzed for inorganics by ion chromatograph. More details of the findings are included elsewhere (Kaul et al., 2011)

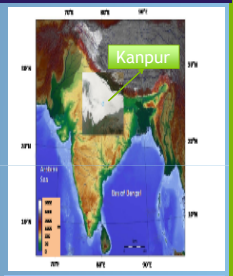


Figure 1: Sampling site, Kanpur (shown by circle) located at 26.5° N, 80.3° E, 142 m msl . Figure shows the spatial scale which can be affected by the event (figure to the scale). Aerial fog information taken from MODIS rapid response (http://aeronet.gsfc.nasa.gov/cgi-bin/bamgomas_interactive)

## Trace Gas and Meteorology

➢ Foggy day is characterized by relatively lesser photo-chemical reactions (Fig 2 A & B)

➢$SO_2$ is scavenged and removed from the atmosphere (Fig 2 A)

➢Stagnant and calm atmospheric condition existed during foggy day

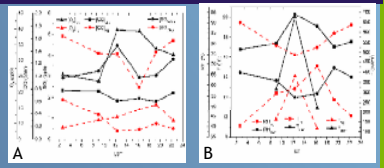


Figure 2: (A) Study average diurnal variation of trace gas during clear and foggy day (B) Study average diurnal variation of relative humidity (RH), solar flux (F) and temperature (T) during clear and foggy day. LST is local standard time (Kaul et al., 2011)

## Secondary Organic Aerosol

Table 1: Behavior of organic carbon (OC) to elemental carbon (EC) ratio as fog is evaporating. LST stands for local standard time (Kaul et al., 2011)

| DATE (YYYY-MM-DD) | LST(hours) 2.625 | 9 | 12.3 |
|---|---|---|---|
| 2010-01-16 | --- | 12.80 | 15.15 |
| 2010-01-18 | 13.87 | 14.45 | 34.43 |
| 2010-01-19 | 15.41 | 17.63 | 15.41 |
| 2010-01-20 | 10.90 | 9.67 | 13.68 |
| 2010-01-21 | 6.19 | 13.24 | 13.31 |
| 2010-01-22 | 6.22 | 10.40 | 13.89 |
| 2010-01-23 | 9.09 | 10.86 | 10.76 |
| 2010-01-25 | 7.98 | 15.14 | 14.28 |
| 2010-01-26 | --- | 8.80 | 10.86 |
| 2010-01-28 | 3.88 | 4.98 | --- |
| 2010-02-13 | 2.77 | 75.10 | 26.70 |

➢Increase of OC/EC ratio as fog evaporates, higher values of OC/EC ratio and SOA indicates SOA formation through aqueous mechanism (Table 1, Fig 3 A )

➢Smaller concentration of biomass tracer, $K^+$ and WSOC during foggy days indicates removal of biomass generated carbon, thus contamination from biomass to estimated SOA is negligible during foggy day (Fig 3-B, 6-A)

➢Temperature and relative humidity had negligible influence on SOA formation (Fig 3-C and D)

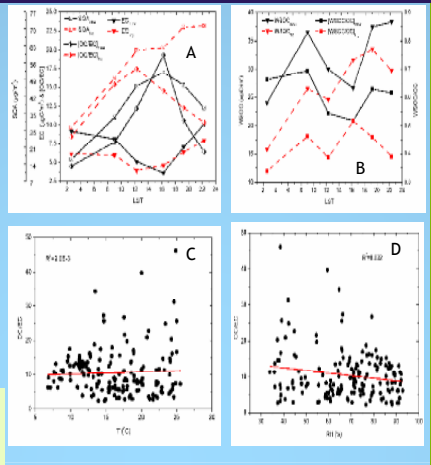


Figure 3: (A) Study average diurnal variation of organic carbon (OC) to elemental carbon (EC) ratio, EC and secondary organic aerosol (SOA) during clear and foggy day (B) Study average diurnal variation water soluble organic carbon (WSOC) and WSOC/OC ratio during clear and foggy day (C) Correlation of OC/EC with temperature (T) (D) Correlation of OC/EC with relative humidity (RH) (Kaul et al., 2011).

## Microphysical Properties

➢Higher TC and Dm during late evening and overnight is due to reduced dispersion and fog formation (Fig 4-A and B)

➢Higher TC and Dm from morning to afternoon (Fig 2) is due to SOA production (Fig 4-A)

➢Lower GSD during foggy day may be due to scavenging of aerosols by fog droplets

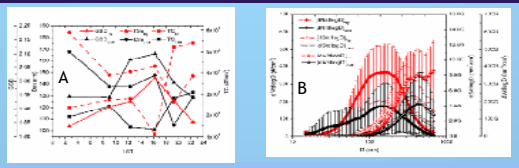


Figure 4: (A) Study average number (N), volume (V) and surface area (S) size distribution of foggy and clear day's aerosols. D is mobility diameter (B) Study average diurnal variations of total number concentration (TC), mode diameter (Dm) and geometric standard deviation (GSD) during foggy and clear days. LST stands for local standard time

## 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.

## Chemical Properties of aerosols and fog droplets

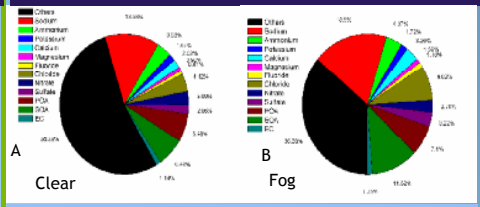


Figure 5: Aerosol chemical composition during nonfoggy (A) and foggy (B) day. POA, SOA and EC stand for primary organic aerosol, secondary organic aerosol and elemental carbon, respectively.

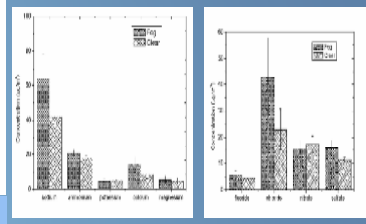

Figure 6: Chemical composition of aerosols during foggy and nonfoggy day.

➢ Carbonaceous aerosol accounts for ~14 % and ~17 % during clear and foggy day. Aerosol composition is dominated mostly by inorganics (Fig 5)

➢ Aerosol during foggy day becomes enriched with almost all inorganic and organic species (Fig 6)

➢ Almost all the inorganics are scavenged by fog droplets, smaller size fog droplets becomes more enriched with inorganics and organics (Fig 7)

➢Despite their wet scavenging, only WSOC, $NO_3$ and $K^+$ are removed form the atmosphere to below nonfoggy concentration

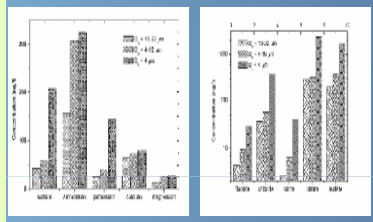

Figure 7: Fog droplets chemical composition of aerodynamic diameter (Da) 4, 16 and 22 µm.

## Positive Matrix Factorization (PMF)

➢Almost all sources contributes to PM mass and biomass contribution during foggy day is less due to scavenging of biomass generated aerosols (Fig 8-A)

➢Biomass burning is the highest contributor to PM mass during nonfoggy day whereas refractory source is the highest contributor during foggy day (Fig 8-A and B)

➢Contribution of WSOC from secondary source is relatively small with most coming from biomass burning (Fig 8-A and B)

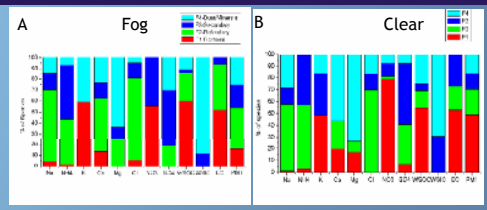


Figure 8: Contribution profile of species during foggy (A) and nonfoggy (B) days.

## Summary and Conclusions

The enhanced production of secondary organic aerosol (SOA) during foggy day is due to its aqueous phase production. Biomass burning did not confound SOA estimate during foggy day due to scavenging of biomass generated aerosols during foggy day. The temperature and relative humidity has negligible influence on SOA formation. Fog droplets scavenges both organics and inorganics, despite their scavenging, only water soluble organic carbon (WSOC), $NO_3$ and $K^+$ was removed from the atmosphere to below nonfoggy day concentration. Secondary production of WSOC is relatively small with most coming from biomass burning. Contribution of biomass burning to PM mass during clear day is more due to reduced scavenging, contribution of refractory sources to PM mass during foggy day is considerable.

## Acknowledgement

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