Effect of Various Fog Processing Stages on the Oxidation Process of Organic Aerosol

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Poster
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EGU2019-1609

Photography encouraged

Introduction

- Estimates of global secondary organic aerosol (SOA) budget are still largely uncertain due to poor understanding of its oxidation processes, especially in the heavily polluted region in which biomass burning (BB) sources dominate under fog periods (high relative humidity (RH) and lower temperature (T) conditions).
- Organic aerosol (OA) exhibit various phases (liquid, semisolid, or amorphous solid) depending upon prevailing ambient temperature and RH.
- In fog processing scenario, bulk diffusion coefficients of OH and levoglucosan (a marker of biomass burning OA) enhance as compared to dry atmospheric conditions which subsequent effects on the SOA production due to changes in the diffusivity of oxidant and organics.
- Fog duration varies from minutes to several hours, highly depending on local metrological parameters which change with time of the day like RH, temperature and wind speed. Therefore, to thoroughly understand the fog processing phenomena, as well as its effect on the OA oxidation processes, relatively number of stages during the fog-cycle, are required.

Hypothesis

- Activation fog period and dissipating fog periods represent the period just before (fog formation) and after (evaporation of fog droplets) the fog period, where number concentration of fine droplets, as well as ALWC, are higher, are crucial in any fog life cycle.
- Activation-fog-period and dissipating-fog-period are crucial for this study to separate the combined effect of high ALWC and LWC during pre-fog-period and contrast it with post-fog-period having low ALWC and zero LWC.

Methods and Materials

Site: IIT Kanpur (26.5°N, 80.3°E, and 142 m above mean sea level), located in the center of Indo-Gangetic Plain (IGP)

Study Period: 30th December 2015 to 23rd January 2016

Instrumentation: HR-ToF-AMS, CDP, RH & T Sensor

Selection Criteria for Fog Processing Periods: LWC: Liquid Water Content of fog droplets

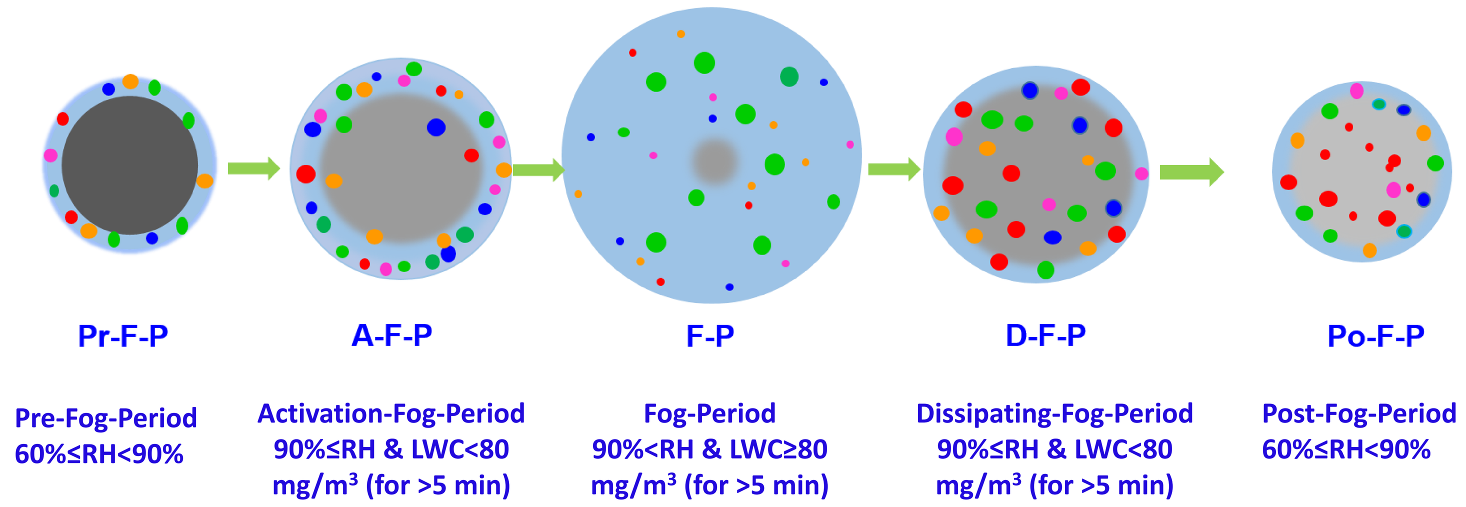


Figure 1. Various stages of fog life cycles.

Fog Events: 04 Number

Fog Processing Periods: 05 Numbers

Data Analysis: Wind speed (WS) and wind direction (WD) were obtained from NOAA ARL dataset. Aerosol liquid water content (ALWC) associated with inorganic species was predicted using E-AIM-IV model.

Results

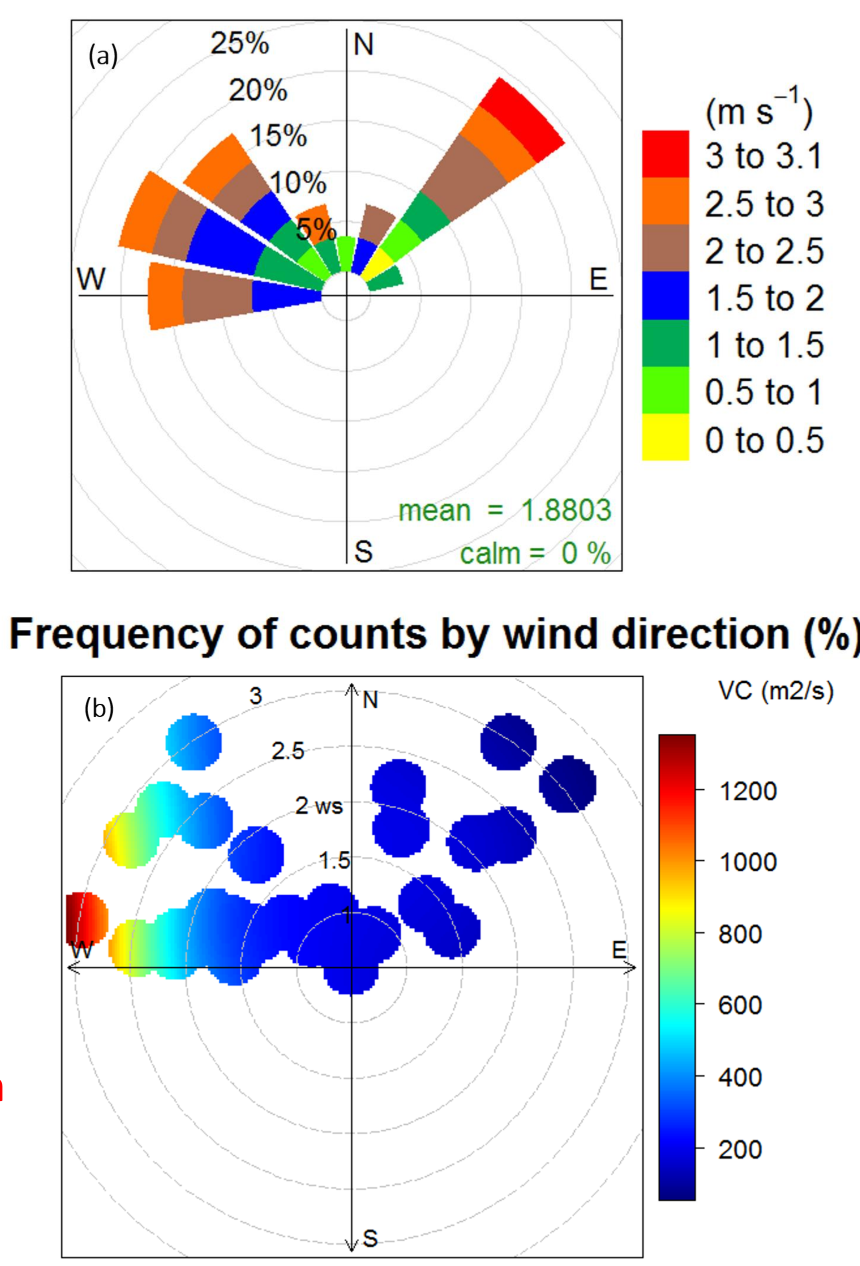
1. Average meteorological parameters for fog processing periods

Table 1. Fog processing period's average±standard deviation meteorological parameters: solar radiation (SR), planetary boundary layer (PBL), F (fine fog droplets, diameter: 4-16 μm), M (Medium fog droplets, diameter: 16-22 μm), C (Coarse fog droplets, diameter: >22 μm), LWC (fog droplets liquid water content), ALWC (aerosol liquid water content).

Meteorology Parameter	Fog Processing Period				
	Pr-F-P	A-F-P	F-P	D-F-P	Po-F-P
RH (%)	83.7±6.7	93.1±1.2	94.4±1.3	94.1±2.1	75.5±8.8
T (°C)	13.0±2.9	10.1±2.7	6.8±2.4	8.8±3.8	16.3±3.8
WD (° from N)	232.4±134.4	147.4±140.2	216.2±134.4	210.1±124.0	218.1±113.5
WS (m/s)	2.1±0.8	1.9±0.7	1.5±0.6	1.5±0.4	1.9±0.5
PBL (m)	7.5±15.0	25.2±3.5	45.3±34.2	399.6±339.3	858.8±426.5
SR (W/m^2)	0	0	19.9±23.2	156.4±109.1	479.4±157.6
Fractional of Fog Droplets Number Concentration (%)		83.2±6.0 (F) 6.3±2.4 (M) 10.5±4.1 (C)	69.7±8.1 (F) 11.1±3.0 (M) 19.2±6.4 (C)	84.3±15.8 (F) 5.1±5.5 (M) 10.6±11.9 (C)	
LWC (mg/m^3)		29.9±15.9	173.7±74.8	15.3±20.5	
ALWC ($\mu g/m^3$)	207.9±111.1	512.8±128.9	440.0±283.2	541.9±220.4	144.1±108.8

- **Wind speeds were found to be ranging from 0.5 -3.1 m/s (1.9±0.7 m/s), which results in a stable atmospheric condition.**
- **VC≤ 2000 m^2/s indicates the "bad" category from pollution dispersion point of view during various fog life cycles.**
- **Suggest that OOA formation is most likely of local origin**

Figure 2. (a) Wind rose plot and bivariate polar plot for (b) ventilation coefficient (VC) based on 3.5 hourly data.



2. Effect of various fog processing stages on OA, composition, and oxidation processes

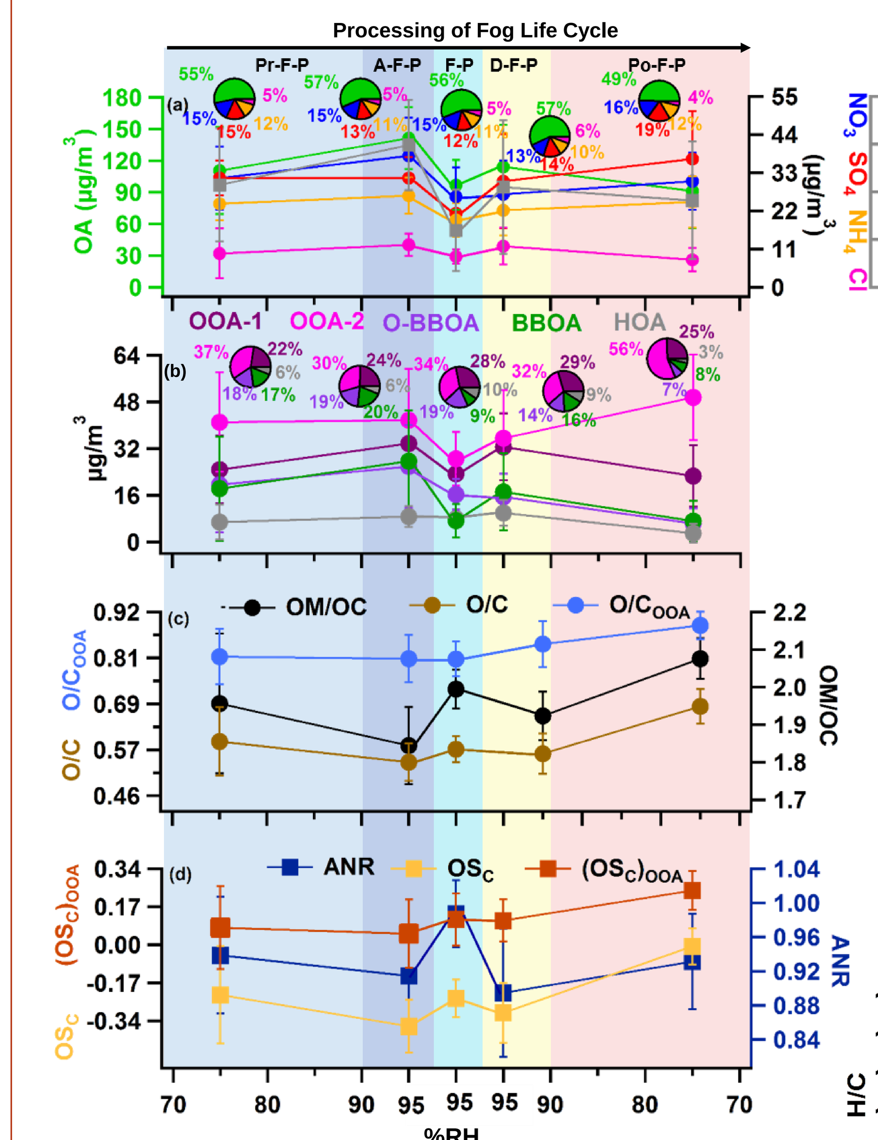


Figure 3. The overview of the variation in overall value of various parameters for the various fog processing periods during the course of fog life cycles .

- A-F-P was observed as heavily polluted period (249.8±47.8 $\mu g/m^3$) while F-P period was least polluted (153.1±37.8 $\mu g/m^3$) indicating the wet removal through grown fog droplets.
- Aerosol in A-F-P and D-F-P were observed acidic as well as with high ALWC.
- OOA-1 processed mainly through biomass burning (BB) emission suggesting is a good surrogate of aqueous SOA, and it gets enhanced significantly under high biomass-burning emissions during A-F-P and D-F-P under acidic aerosol conditions.
- O/C of OA and OOA varied during the all fog processing periods with a maximum during Po-F-P, however low O/C during A-F-P and D-F-P was observed to associate with high OA loading.

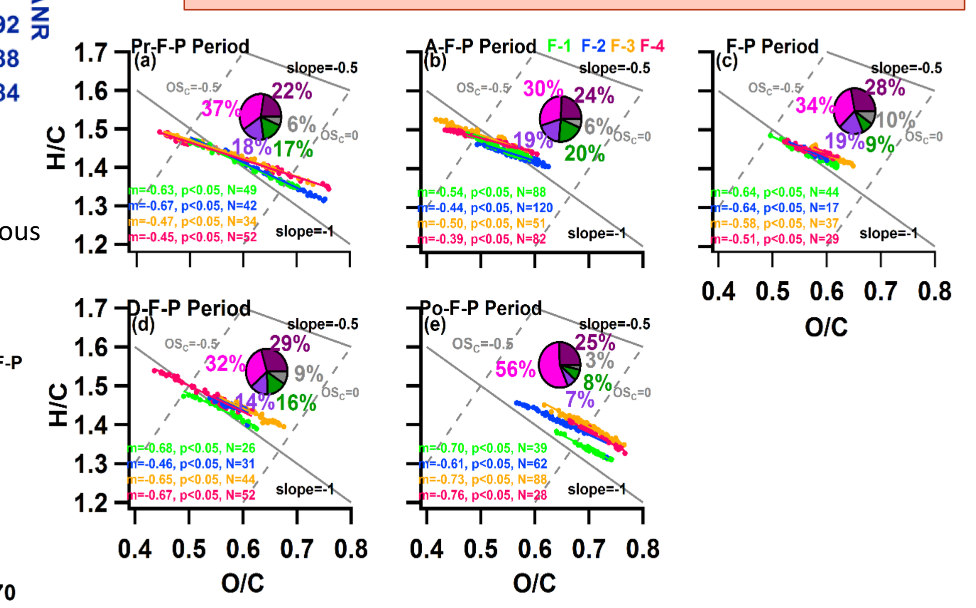


Figure 4. Evolution of OA oxidation processes in terms of elemental ratio.

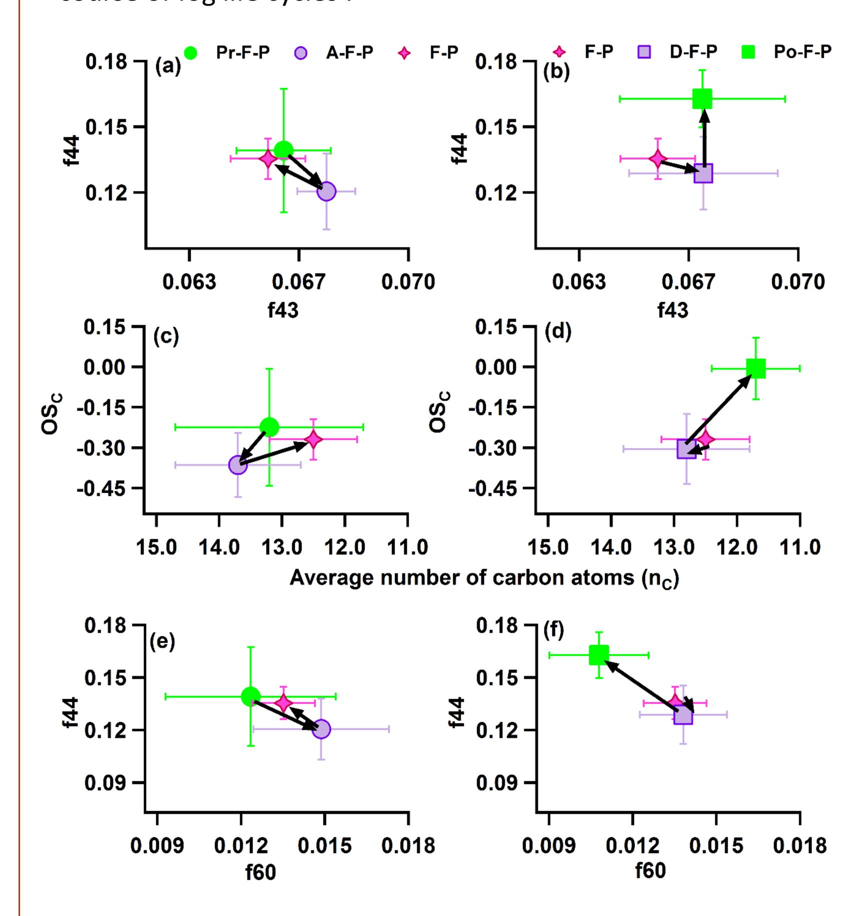


Figure 5. Evaluation OA oxidation processes in terms of formation processes and f43, f44, f60.

- Van Krevelen (VK) slope, O/C ratio, O/C_{OOA}, OS_C and $(OS_C)_{OOA}$, substantially varies throughout all the fog processing periods.
- Oligomerization mechanism possibly significant for the formation of OOA along with functionalization of –OH and carbonyl (aldehyde/ketone) moieties during A-F-P and D-F-P, respectively accompanied by acidic aerosol as well as high aerosol liquid water content (ALWC) condition.
- Fragmentation process can be dominant along with functionalization of –RCOOH or carbonyl (aldehyde/ketone) and –RCOOH moieties during F-P and Po-F-P periods, respectively.

Conclusions

- **Our results suggest that current SOA models should consider crucial A-F-P and D-F-P fog processing periods separately from pre-fog and post-fog, respectively to evaluate oxidative properties and mass concentration of SOA.**
- **Oligomerization and functionalization mechanisms dominating the oxidation processes of OA during A-F-P and D-F-P.**
- **Fragmentation and functionalization mechanisms govern the oxidation process of OA during F-P and Po-F-P**
- **Both activation as well as dissipating fog processing periods have acidic aerosol and high aerosol liquid water content**

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Acknowledgements

We acknowledge the support of IIT Kanpur for providing us with HR-ToF-AMS for PG research and teaching.