

Fog and organic aerosol interaction: Chemistry, composition and significance

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Introduction:

Organic aerosols (OA) can contribute up to 90% of the submicron aerosol mass and exert significant influence on overall aerosol properties. Fog is a natural weather phenomenon which results in severe visibility degradation. However, fog droplets are also act as an efficient medium for processing of different aerosol species. Studies on fog and OA interactions are rare, especially from South Asia. Majority of those few field studies has reported an increase OA oxidation level and production of enhanced secondary OA [Ervens *et al.*, 2011].

Methodology:

We have also conducted real time measurement of ambient OA during the foggy period of Dec-February during the 2012-2016 period. For the first time, we have deployed High resolution Time of Flight-Aerosol Mass Spectrometer (HR-ToF-AMS) in India and South Asia to understand real time evolution of OA. To better isolate fog impact, while campaign dataset is divided into pre-fog (5-10 pm), fog (10pm-8am), post-fog (8am-5pm) time periods. Similar time frames from the non-foggy period are termed as non-pre-fog, non-fog, non-post-fog. Size resolved fog water samples were also collected to understand the OA chemistry occurring inside the droplets.

Results and discussions:

Our results indicate that during fog events OA oxidation level (O/C) can increase upto 15-20% from pre-fog levels. Apart from that a possible change in oxidation mechanism has also been identified, as slope of H/C vs O/C plot becomes much shallower during foggy/hazy period. Composition of OA during fog showed complete dominance of oxidized (secondary) OA. These characteristics are absent from non-pre-fog to non-foggy period, indicating the role of fog (aqueous) processing. To

gain more insight, collected size resolved fog water samples (coarse, medium and fine fog droplets) were analyzed. OA present inside finer droplets are found to be more oxidized (higher O/C ratio) and less volatile than OA present in larger droplets. A simple box model reveals that presence of higher quantities of transition metals like Fe, Cu lead to enhanced production of OH radicals inside the fine droplets thus leading to more oxidized OA formation. A continuous increase in OA O/C ratio is observed during a fog event; from fog formation to fog dissipation. Same enhancement was absent during non foggy nights. It is also found that night time in fog oxidation can be as efficient as daytime photochemical oxidation. Fog processing of OA seemed to be effective under both high (HL) and low (LL) OA loading conditions. In traditional gas to particle conversion route of SOA formation, OA loading and O/C ratio are anti-correlated. In this study also a strong anti-correlation between OA loading and O/C ratio is observed, however, slope of this anti-correlation is much steeper under LL condition than HL one, clearly indicating a loading regime dependency. On the contrary to gas SOA formation, fog/aqueous processing depends on fog LWC (liquid water content) and not on OA loading. Due to this, difference between O/C ratio (LL O/C - HL O/C = 0.12) of HL and LL periods is higher during non-foggy period dominated by gas phase SOA formation compared to foggy period (LL O/C - HL O/C = 0.05). As fog processing produces highly oxidized aqSOA independent of loading conditions, so during fog, OA O/C ratio enhanced effectively under both the loading condition. These findings indicate that global models should include fog/cloud droplet size based aqueous chemistry into their models to accurately predict SOA mass and properties.

Ervens, B., B. J. Turpin, and R. J. Weber (2011), Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11(21), 11069–11102, doi:10.5194/acp-11-11069-2011.