Combined effects of organic aerosol loading and fog processing on organic aerosols oxidation, composition, and evolution
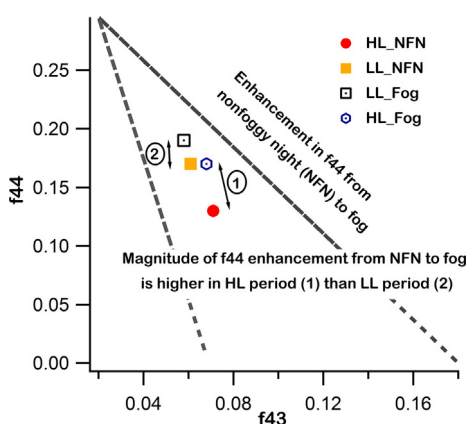
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Chemical characterization of ambient non-refractory submicron aerosols (NR-PM$_1$) was carried out in real time at Kanpur, India. The measurements were performed during the winter (December 2014 to February 2015), and comprised of two very distinct high and low aerosol loading periods coupled with prevalent foggy conditions. The average non-refractory submicron aerosol loading varied significantly from high (HL, ~240 μg/m^3) to low loading (LL, ~100 μg/m^3) period and was dominated by organic aerosols (OA) which contributed more than half (~60%) of the measured aerosol mass. OA source apportionment via positive matrix factorization (PMF) showed drastic changes in the composition of OA from HL to LL period. Overall, O/C (oxygen to carbon) ratios also varied significantly from HL (=0.59) to LL (=0.69) period. Fog episodes (n = 17) studied here seem to be reducing the magnitude of the negative impact of OA loading on O/C ratio (OA loading and O/C ratio are anti-correlated, as higher OA loading allows gas to particle partitioning of relatively less oxidized organics) by 60% via aqueous processing. This study provided new insights into the combined effects of OA loading and fog aqueous processing on the evolution of ambient organic aerosols (OA) for the first time.

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1. Introduction

Submicron ambient aerosols have an impact on radiative climate forcing and can adversely affect human health (Jacobson et al., 2000; Seinfeld and Pankow, 2003; Jimenez et al., 2009). Most Indian cities suffer from poor air quality, and numerous studies have reported very high pollution levels in all the major cities of India (Venkataraman et al., 2002; Gurjar et al., 2004; Gupta et al., 2006; Sarkar et al., 2010; Joseph et al., 2012). Kanpur, being a major industrial hub and having a population of 4.5 million also suffers from serious air pollution (National Ambient Air Quality Standards, 2012). Numerous offline, 4–8 h long filter based field studies (Kaul et al., 2011, 2012; Ram and Sarin, 2011; Gupta and Mandariya, 2013; Singh et al., 2014) reported very high PM_1 loadings ranging between 100 and 200 μg/m^3 in Kanpur, especially during winter. Although useful; these studies were unable to capture organic aerosol (OA) evolution (gradual changes in nature and properties of OA via aging, volatilization and mixing with a different type of OA (Heald et al., 2010)), which usually occurs over shorter time scales. Advancement in mass spectrometry technique and the arrival of Aerodyne aerosol mass spectrometer (AMS) (DeCarlo et al., 2006; Canagaratna et al., 2007) has provided some in depth information about the real time evolution of OA (Hallquist et al., 2009; Heald et al., 2010). Around the globe, many fields and laboratory studies have been performed using AMS; however, online/AMS based studies have rarely been conducted in the South Asia, world's most populous region. So, very limited information is available about OA evolution and properties from this region (Bhattu and Tripathi, 2015). Thus, the goal of this study was to explore the impact of different parameters like organic aerosol (OA) loading and fog on the real-time evolution of aerosol composition and oxidation (O/C ratio) ratios.

O/C ratio of SOA or OOA (Secondary or Oxidized organic aerosol) is usually negatively correlated with OA loading as reported by a few chamber (Kang et al., 2011; Pfaffenberger et al., 2013) and ambient studies (Ng et al., 2011a; Bhattu and Tripathi, 2015). Higher OA concentration promotes more gas to particle conversion of less oxidized, semi volatile organics (Kang et al., 2011; Ng et al., 2011a). A laboratory (Kang et al., 2011) study has also indicated that the slope of this anti-correlation between O/C ratio, and OA loading depends on aerosol loading regime. However, such dependence has not yet been reported from field studies and the causality for this observation has not been explored in either laboratory or field studies. Observed high and low OA loading conditions in this current study provided a unique opportunity to explore this OA loading-dependent SOA oxidation under ambient conditions. During winter of every year, Kanpur is affected by several fog episodes of short (3 h) to long durations (17 h) that severely hampered regular activities of local people. Fog episodes can also contribute to the formation of secondary organic aerosols (SOA) via aqueous phase oxidation, as reported in several previous field and lab studies (Dall'Osto et al., 2009; Kaul et al., 2011; Ge et al., 2012; Li et al., 2013; Chakraborty et al., 2015).

A previous filter based study at the same location reported 60% enhancement OC/EC ratio during fog events (Kaul et al., 2011) compared to non-foggy period. Online AMS based studies carried out in Fresno, California and Hong Kong, (Ge et al., 2012; Li et al., 2013) observed slightly enhanced O/C ratio and f44 (= m/z 44/total OA). In AMS, m/z 44 or CO_2^+ fragment is considered to be a marker for carboxylic acid moieties (Takegawa et al., 2006a) and f44 represents the fractional contribution of m/z 44. Enhanced f44 levels during fog and haze events indicate the formation of more aged/oxidized of OA, highlighting the impact of aqueous processing of the submicron aerosols. Lee et al. (2012) performed laboratory oxidation of cloud water samples and particulate organics collected at a mountain site. They reported significant enhancement in organic mass, f44, and O/C ratio due to functionalization for cloud water samples. However, as oxidation progresses these enhancements slowed down possibly due to the dominance of fragmentation. On the contrary, they found that organic aerosols extracted from the filters became more volatile and lost organic mass due to the dominance of fragmentation from the very beginning of the oxidation process. During 2012–13 winter, enhancement in f44, O/C ratio and OOA contribution during fog events has already been reported at this location from an AMS based study (Chakraborty et al., 2015). Collett et al. (2002, 2008) reported high concentrations of dicarboxylic acids in fog water from different places of US. They also reported preferential scavenging of more oxidized wood burning aerosols than less oxidized vehicular exhaust. Gilardoni et al. (2014) from a study in Po Valley also reported a good correlation between organic aerosol scavenging and O/C ratio. So, the impact of cloud/fog processing on OA oxidation has been reported around the globe with considerable details. However, combined effects of two parameters; OA loading and aqueous oxidation with different impacts on OA oxidation level (O/C ratio) have never been studied anywhere. OA loading decreases O/C ratio as mentioned earlier, however, aqueous oxidation/processing can enhance the OA oxidation level and depends more on aerosol/fog/cloud liquid water content (LWC) rather than OA loading (Volkamer et al., 2009; Ervens et al., 2011). Therefore, it would be interesting to examine the combined effects of OA loading and fog/aqueous processing on existing OA composition and oxidation at this polluted location.

2. Materials and methods

2.1. Site of study and measurement period

Measurements were performed in the campus of Indian Institute of Technology (IIT) Kanpur (26.46°N, 80.33°E, and 142 m above sea level) from 18 Dec 2014–10 February 2015. Kanpur is a large city of ≈4.5 million (GOI, 2011) population and located in the center of the Gangetic Plain (GP), but having very poor air quality (National Ambient Air Quality Standards, 2012). IIT Kanpur is located upwind of the city center and within the city boundaries. Based on NR-PM$_1$ (non-refractory submicron aerosols; part of the submicron aerosols that evaporates within few seconds at 600 °C (Zhang et al., 2005c)) loading, the entire campaign was divided into two separate periods. The 1st period (termed as high loading, HL) was from 18 Dec 2014–01 Jan 2015 with an average NR-PM$_1$ loading of 239 ($\pm$73) μg/m^3, and several frequent fog events (10 events in 15 days). The 2nd period (low loading, LL) was from 02 January 2015–10 February 2015 with an average NR-PM$_1$ loading of 101 ($\pm$39) μg/m^3, and several but infrequent fog events (7 events in 40 days), respectively. Meteorological parameters and CO concentrations for both the periods are listed in Table 1.

RH & T values were obtained from Vaisala RH & T sensor (Model: HMT 331), deployed at the same laboratory along with other instruments. Wind speed (DWA 8600, Dynalab Weathertech), precipitation (DTR 8104, Dynalab Weathertech), and solar radiation (CMP 6, Kripp & Zonen) data were obtained from an automated weather station located near vicinity while the PBL heights were obtained from NOAA ARL archive. CO data was obtained from Thermo Fisher CO analyzer (Model: 49i) instrument kept at the rooftop of the laboratory building.

To analyze the effects of fog, we further divided both the HL and LL period into several sub periods like; fog, prefog, non-pre fog, non-foggy night, postfog, non-post fog. Usually, 90% of the total fog hours were confined within 11 pm–8 am time frame, so this period is taken as foggy period. Prefog (PrF) period is considered to be 5 h before the commencement of the fog; 6–11 pm, while postfog (PoF) period is 8 am-6 pm. Identical time periods, taken for non-foggy periods, are termed as non-pre foggy (NPrF, 6–11 pm), non-foggy night (NFN, 11 pm–8 am) and non-post foggy period (NPoF, 8 am–6 pm). Fog can be defined as an atmospheric condition with low visibility (<1 km) and very high RH (close to 100%, WMO, 1996). In absence of visibility measurements, in this study, start of the fog event was marked when LWC (liquid water content) ≥80 mg/m^3 for ≥15 min (Gilardoni et al., 2014) and end of the fog event was marked when LWC < 80 mg/m^3 for >15 min (Fig. S1).