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Secondary organic aerosol over an urban environment in a semi–arid region of western India

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ABSTRACT

Carbonaceous species in PM_{10} and $PM_{2.5}$ samples, collected from an urban location at Ahmedabad in India during summer, were analyzed to study variability in water–soluble organic carbon (WSOC) and secondary organic carbon (SOC) along with atmospheric water vapor content. A significant correlation between WSOC and SOC was found indicating major contribution of soluble organic compounds by secondary organic aerosol formation. A strong inverse dependence of WSOC and SOC on atmospheric water vapor content is observed in both PM_{10} and $PM_{2.5}$ (at <45% relative humidity, RH) during daytime; whereas data collected during monsoon season at higher RH conditions do not exhibit such relation. Aerosol liquid water content (LWC) calculated from thermodynamic equilibrium model suggests that the decrease in secondary organic aerosol (SOA) with increase in RH occurs when LWC is absent or insignificant amount. The inverse correlation in summertime indicates possible decrease in the extent of heterogeneous photochemical oxidation of precursor volatile organic compounds on mineral aerosol surface with increase in ambient water vapor. These results have implications for SOA estimations on regional scales especially in arid and semi–arid regions where significant amount of fine mineral dust is present.

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1. Introduction

Carbonaceous aerosol, a major contributor to atmospheric fine particulate matter, has potential impact on air quality and regional climate (Menon et al., 2008). Organic aerosol is a poorly understood category that constitutes a substantial portion of ambient aerosol and is ubiquitously present in Earth's atmosphere (Kanakidou et al., 2005). A large fraction of organic aerosol, both natural and anthropogenic, is of secondary origin, produced by oxidation of volatile organic compounds (VOC) (Seinfeld and Pankow, 2003; Zhang et al., 2007; Kroll and Seinfeld, 2008). Secondary organic aerosol (SOA) estimates based on VOC fluxes suggest their dominance over the primary component on a global scale. Though several precursors originate from industrial and automobile emission sources, the dominant fraction of the global SOA budget is thought to be from biogenic VOCs (Kanakidou et al., 2005). Contribution of SOA from anthropogenic precursors to the global SOA budget could be significantly higher than the earlier estimates (de Gouw et al., 2005; Volkamer et al., 2006). However, it has been reported that atmospheric models underestimate organic aerosol mass not only within the boundary layer but at higher altitudes as well (Morris et al., 2006; Goldstein and Galbally, 2007; Yu et al., 2008). The discrepancies associated with these estimated fluxes, as much as an order of magnitude; arise largely due to poor understanding of the formation mechanisms of SOA from the precursors and their controlling factors (Hallquist et al., 2009).

Atmospheric water vapor may impact the concentration of SOA mass, considering equilibrium absorptive partitioning of semi–volatile organic compounds (Seinfeld and Pankow, 2003). Also,

ambient relative humidity is proposed as a factor influencing SOA formation by controlling liquid water content (LWC) in aerosol, which in turn, may promote partitioning of semi–volatile oxidation products of SOA precursors between particle and gas phases and/or heterogeneous reactions of water–soluble organic compounds (Volkamer et al., 2009). Partitioning of carboxylic acids is reported to have a strong influence on RH and it enhances with increase in RH (Falkovich et al., 2004; Hatch et al., 2007). Studies involving simultaneous measurement of particle and gas phase water–soluble organic carbon (WSOC) by Hennigan et al. (2008) revealed that a significant increase in partitioning of WSOC to the particle phase at elevated RH (>70%) occurs. This suggests that such gas–aerosol partitioning of soluble organic compounds and subsequent particle/aqueous phase reactions are important pathway for SOA formation (Ervens et al., 2011). Nguyen et al. (2011) studied effect of RH on isoprene photo–oxidation to produce SOA under humid (90% RH) and dry (<2% RH) conditions. Their results indicated significant change in SOA composition but not any detectable difference in rate and extent of SOA mass increase. In certain circumstances, condensation reactions were suppressed in humid conditions because water is formed as a product as reported by Zhang et al. (2011). Tillmann et al. (2010) studied influence of RH on SOA formation from ozonolysis of α–pinene. Their results provided evidence for increase in SOA yield at humid conditions than at dry conditions. Thus, several reported studies demonstrate, both laboratory experiments as well as field measurements, inconsistencies existing in assessment of effect of RH on SOA formation in ambient atmosphere and need for further investigation on these processes (Dommen et al., 2006; Healy et al., 2009; Zhang et al., 2011).

Numerous compounds contribute to SOA formation and are chemically diverse. Direct measurement technique is not available exclusively for SOA, but various indirect methods are effectively used to infer SOA concentrations. A known ratio of organic carbon (OC) to elemental carbon (EC) for primary emissions has been widely used to estimate SOA (Castro et al., 1999; Pio et al., 2011). SOA production from precursor VOCs is generally through oxidation processes which lead to formation of polar functional groups in product compounds. Hence many of the SOA components are likely to be water–soluble, especially those produced from biogenic VOCs, and hence WSOC in aerosol can be considered as a reasonable proxy for SOA concentration (Kondo et al., 2007; Weber et al., 2007). In this study, we investigate the temporal variation of water vapor content and SOA formation in ambient air. It may be noted that identifying the reactions which dominate the RH effect remains difficult, considering the complexities of different reaction pathways and numerous possible oxidation products of SOA precursors. Thus, we currently rely on proxies such as variation in secondary organic carbon (SOC) and WSOC content as indicators of SOA formation.

2. Experimental Method

PM$_{2.5}$ and PM$_{10}$ samples (particles with aerodynamic diameter <2.5 µm and <10 µm, respectively) were collected on Tissuquartz filters (Pall Life Sciences) using two separate mass–flow controlled high–volume air samplers (Tisch Inc., USA) from March 21 to June 23, 2007 once in a week, at Ahmedabad (23°02′N, 72°32′E), an urban location in a semi–arid region of western India. The two samplers were operated from 09:00 hours (local time) to ~19:00 hours for sampling in daytime and rest of the time were operated for collecting night time samples. There were 26 samples (13 each for PM$_{2.5}$ and PM$_{10}$) collected during daytime and 24 samples (12 each for PM$_{2.5}$ and PM$_{10}$) during nighttime (one nighttime sample was not collected on June 7, 2007 due to sampler problem). This set of samples represents the summer season. Another 20 samples (10 each for PM$_{2.5}$ and PM$_{10}$) were collected during daytime over the period of July to October 2007 which represent monsoon season. Nighttime samples were not collected during the monsoon period. Also, regular weekly sampling was not possible during monsoon season because of intermittent rain events.

Mass loading was ascertained gravimetrically by taking filter weights before and after sampling. Filters were equilibrated at a RH of 40±3% before weighing. The samples were stored under freezing temperature until chemical analysis. The concentrations of EC and OC were measured on EC–OC analyzer (Sunset Laboratory) using NIOSH protocol (Birch and Cary, 1996; Rengarajan et al., 2007). A separate aliquot of samples were treated with HCl fumes in order to eliminate carbonate carbon and analyzed on EC–OC analyzer to apply appropriate correction to OC. These samples were collected using high volume samplers without removing VOCs from the air flow. This can introduce a positive sampling artifact by absorbing VOCs on filters, but the sampling is done for extended time period (typically more than 10 hours) and measured OC content is sufficiently large, hence this artifact is likely to be insignificant. Second aliquot of sample was subjected to microwave digestion with HF and HNO$_3$; the resultant solution was diluted and analyzed for Al on ICP–MS (Thermo X–series II). A third aliquot of sample was subjected to water extraction and subsequently WSOC and water–soluble ionic species were determined. WSOC was measured on TOC analyzer (Shimadzu, TOC5000A) with NDIR detector. Water–soluble ionic species (K$^+$, Ca^{2+}, Mg^{2+}, NH$_4^+$, Na$^+$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$) were measured on Ion–chromatography system (DIONEX 500) equipped with suppressed conductivity detector. IonPac® CS12 and AS14 analytical columns were used for the separation of ions in cation and anion analysis respectively. Details of the measurement procedures are described elsewhere (Rengarajan et al., 2007).

The measured inorganic ionic species are used in an aerosol thermodynamic equilibrium model, ISORROPIA–II (Fountoukis and Nenes, 2007) (http://nenes.eas.gatech.edu/ISORROPIA/), for calculating the LWC in particulate phase. The model was run as "reverse problem" where particle–phase composition, ambient temperature and relative humidity were used as input. This model was used in earlier studies for calculating H$^+$ ion concentration as a measure of aerosol acidity at this site and output had shown consistency with experimental results (Rengarajan et al., 2011a). The SOC is estimated by EC–tracer method assuming minimum OC/EC ratio as the primary ratio (Castro et al., 1999). Meteorological parameters i.e., RH, temperature, wind speed and wind direction were obtained from htpp://www.wunderground.com for Ahmedabad station where the data were collected at a location within 10 km from sampling site. The average values of RH and temperature for sampling duration were calculated from the hourly data for all sampling days. Water vapor pressure was calculated at ambient temperature using RH and saturated vapor pressure obtained by IAPWS (International Association for the Properties of Water and Steam) formulation.

We used the MOZART–4 model to calculate OH, CO and NO$_X$. MOZART–4 (Model for Ozone and Related chemical Tracers, version 4) is a global chemical transport model for the troposphere, simulating 85 gas–phase species and 12 bulk aerosol compounds with the help of 39 photolysis and 157 gas–phase reactions. The chemical mechanism includes an updated isoprene oxidation scheme and treatment of volatile organic compounds. The model is able to reproduce the temporal and spatial distributions of NO$_X$, CO and OH (Peng and Zhao, 2007; Sheel et al., 2010; Srivastava and Sheel, 2013). Five–day air mass back trajectories were calculated using the Hybrid Single–Particle Lagrangian Integrated Trajectory (HYSPLIT4) model from National Oceanic and Atmospheric Administration (NOAA) using Global Data Assimilation System's global data to identify the origin (Draxler and Rolph, 2013) and transport of air masses prior to the sampling location (for 12:30 hours local time).

3. Results

3.1. PM composition during summer season

The average concentrations of aerosol mass and various constituents during summer are presented in Table 1. Average mass concentration of PM$_{2.5}$ is 39.3 µg m^{-3}, which constitutes ~34% of PM$_{10}$ at Ahmedabad during daytime. The corresponding concentration during nighttime is 47 µg m^{-3}; constituting ~31% of PM$_{10}$. Total carbonaceous aerosol mass concentration during daytime and nighttime, calculated as [EC+OCx1.6] (Rengarajan et al., 2007), were 13.6 µg m^{-3} and 21.5 µg m^{-3} in PM$_{2.5}$, whereas in PM$_{10}$, the corresponding concentrations were 19.5 µg m^{-3} and 30.3 µg m^{-3}, respectively. These constitute 34.6% and 45% of PM$_{2.5}$ mass during daytime and at night, while for PM$_{10}$, these are 16.9% and 20%, respectively. OC/EC ratio ranges from 5.7 to 12.6 in fine mode aerosol during daytime whereas range for nighttime ratio is between 2.4 and 15.6. In comparison with studies reported from European region (Vodicka et al., 2013; Mirante et al., 2014), OC/EC ratios over Indian region are higher due to wide spread emission from biomass combustion for domestic purposes (Gustafsson et al., 2009; Ram and Sarin, 2010). Minimum OC/EC ratios for PM$_{2.5}$ samples (3.0 and 2.4) were observed on 25 April and 23 June for nighttime samples. The minimum ratio was obtained for PM$_{10}$ samples on 25 April (3.3). The ratio of 2.4 and 3.3 are used for calculating SOC in PM$_{2.5}$ and PM$_{10}$ respectively, assuming these as primary ratios, (OC/EC)$_{pri}$, following Castro et al. (1999).

$$SOC = OC - EC \times (OC/EC)_{pri} \qquad (1)$$