Realtime chemical characterization of post monsoon organic aerosols in a polluted urban city: Sources, composition, and comparison with other seasons☆

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ABSTRACT

Real time chemical characterization of non-refractory submicron aerosols (NR-PM$_1$) was carried out during post monsoon (September—October) via Aerosol Mass Spectrometer (AMS) at a polluted urban location of Kanpur, India. Organic aerosol (OA) was found to be the dominant species with 58% contribution to total NR-PM$_1$ mass, followed by sulfate (16%). Overall, OA was highly oxidized (average O/C = 0.66) with the dominance of oxidized OAs (60% of total OA) as revealed by source apportionment. Oxidized nature of OA was also supported by very high OC/EC ratios (average = 8.2) obtained from simultaneous offline filter sampling. High and low OA loading periods have very dramatic effects on OA composition and oxidation. OA O/C ratios during lower OA loading periods were on average 30% higher than the same from high loading periods with significant changes in types and relative contribution from oxidized OAs (OOA). Comparison of OA sources and chemistry among post monsoon and other seasons revealed significant differences. Characteristics of primary OAs remain very similar, but features of OOAs showed substantial changes from one season to another. Winter had lowest OOA contribution to total OA but similar overall O/C ratios as other seasons. This reveals that processing of primary OAs, local atmospheric chemistry, and regional contributions can significantly alter OA characteristics from one season to another. This study provides interesting insights into the seasonal variations of OA sources and evolution in a very polluted and complex environment.

1. Introduction

Submicron size aerosols are an integral part of Earth's atmosphere with significant impacts (direct and indirect) on human health, global climate, and visibility. A large fraction (20—80%) of ambient fine size aerosols is made up of organic aerosols (OA) (Ervens et al., 2011; Hallquist et al., 2009; Jimenez et al., 2009; Ng et al., 2011). Nature of OA can be both primary and secondary, with primary OA (POAs) being directly emitted via biomass burning (BB), volcanic eruptions, fossil fuel combustion, and sea spray. Atmospheric oxidation of VOCs by radicals and oxidants like OH, NO$_3$, O$_3$ and subsequent partitioning of gas phase oxidation products into particulate phase lead to the formation of secondary OA (SOA). Additional SOA can be produced via heterogeneous reactions in cloud/fog droplets and over particulate surface (Ervens et al., 2011; Hallquist et al., 2009). Characterization and evaluation of OA properties are quite challenging because of their different emission sources, variations in atmospheric processing, meteorological factors, differences in physico-chemical properties (solubility, volatility, optical properties, etc.) and long range transport. These spatio-temporal variations make OA characterization a difficult task and lead to inaccurate assessment of its impact on regional climate (Hallquist et al., 2009). Also, the scale of atmospheric processing is rather short thus offline filter based methods with 8—12 h time resolution are inadequate to capture the evolution of OA characteristics. Fortunately, recent advances made in mass spectrometry and the arrival of Aerosol Mass Spectrometers has offered some detailed and unique insights into OA composition, chemistry, characteristics and their temporal evolution. Aerodyne High

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Resolution-Aerosol Mass Spectrometer (HR-ToF-AMS, from now on termed as AMS) (Canagaratna et al., 2007; DeCarlo et al., 2006; Drewnick et al., 2005) is one such widely used instrument, capable of real time characterization of non-refractory submicron aerosols. Utilizing AMS data, one can obtain real time changes occurring in elemental ratios (O/C, H/C, OM/OC) of OA via atmospheric processing, which in turn can provide valuable information about OA evolution and characteristics. By applying additional source apportionment tools like Positive Matrix Factorization (PMF) even further information about OA sources and composition can be obtained. In India, most of the studies conducted till now are offline filter based studies which provided no or insufficient information on OA sources, composition and temporal evolution (Chakraborty and Gupta, 2010; Kaul et al., 2011; Rajput and Sarin, 2014; Ram et al., 2014). Indo Gangetic Plain (IGP) is one of the world's most densely populated region (Bhattu and Tripathi, 2015; Chakraborty et al., 2015; Kaul et al., 2011) with half of India's population residing here. Several major populated and polluted cities are located in IGP and Kanpur is one of them. Very recently, a few AMS based studies (Bhattu and Tripathi, 2015; Chakraborty et al., 2016b, 2015) have been conducted in IGP which showed the dominance of OA in submicron aerosols and provided new insights into OA evolution. However, those studies were mostly carried out during winter thus unable to provide seasonal characteristics, chemistry, and composition of OA. To devise an effective mitigation strategy for severe air pollution in IGP region, a holistic picture of OA with seasonal characteristics and sources is desired. Hence, it is imperative to understand the seasonal characteristics and chemistry of OA at this location, hitherto unknown for the IGP. This study is reporting for the first time the post monsoonal characteristics and sources of OA via real time measurements. A comparison with monsoon and winter time aerosol characteristics also provides some much needed insight into the changes in OA composition and characteristics from one season to another.

2. Materials and methods

2.1. Sampling site and sampling protocols

The sampling site (Fig. 1) is in the campus of Indian Institute of Technology (IIT), located at Kanpur (26.30 °N; 80.14 °E, 142 m above mean sea level: amsl) in the state of Uttar Pradesh (central part of IGP). The sampling site is located away from city center but within city limits. It's an academic campus with lots of greenery and away from industrial areas. Majority of the campus residents' use bicycles although a low volume traffic coming from outside is mainly comprised of two and four wheelers. Both, online and offline sampling was carried out during September–October. Ambient temperature during sampling period varied from 16 to 36 °C and relative humidity was ~50% at the sampling site. Real time AMS measurements of non-refractory submicron aerosols (NR-PM$_1$) have been carried out with a 2 min time resolution in high sensitivity V mode. Briefly, the AMS samples ambient air through a 100 μm diameter critical orifice and then focus particles through a series of aerodynamic lenses. A chopper wheel then delivers a slug of particles into the vacuum region of time of flight segment, wherein they attain distinct velocity proportional to their size. Subsequently, focused particles are subjected to vaporization using heated tungsten surface maintained at 600 °C in high vacuum (pressure around 10^{-8} Torr). Once in contact with the vaporizer, volatile and semi-volatile contents of the aerosol are flash vaporized (within a few seconds) followed by ionization via electron bombardment from AMS filament. This is a hard ionization process called hard electron impact (ionization energy = 70 eV). Ionized

molecules are then analyzed by Time of Flight mass spectrometry. Transmission efficiency of aerodynamic lenses is almost 100% for spherical particles with vacuum aerodynamic diameters (D$_{va}$) between 60 nm and 700 nm. More details about AMS working principles and uncertainties can be found elsewhere (Canagaratna et al., 2007; DeCarlo et al., 2006; Drewnick et al., 2005).

AMS can measure non-refractory submicron aerosol species like organics, sulfate, nitrate, chloride, and ammonium in real time. High resolution data of AMS can provide even more detailed information on OA chemistry and composition. High resolution (HR) data is processed using PIKA (v1.10H) in IgorPro. Although AMS allows real time aerosol characterization, it has some limitations. Due to hard ionization, molecular identities of organic components are completely lost. AMS can only detect non-refractory part of submicron aerosols due to 600 °C vaporization temperature. Thus, important refractory organic materials such as EC can't be characterized via AMS. AMS also can't perform single particle analysis and it is essentially a bulk characterization instrument. Quantitative data accuracy of AMS depends on chosen collection efficiency (CE) value, which accounts for the aerosol loss during transmission through aerodynamic lenses and bouncing off from vaporizer. CE value is calculated using a literature (Middlebrook et al., 2012) based formulation which takes aerosol chemical composition in consideration. The calculation revealed a value of 0.5, which has been previously used in the majority of the field campaigns around the world, and this value has also been found satisfactory for this location in our previous AMS based studies (Bhattu and Tripathi, 2015; Chakraborty et al., 2015). Choice of CE value is further justified by the good correlation obtained between offline OC and AMS OM values (Fig. S1), with a slope almost equal to the OM/OC ratio determined from AMS HR analysis (described in the next section).

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model developed by NOAA/Air Resources Laboratory (ARL) (Draxler and Rolph, 2003) was used to perform back trajectory (BT) analysis. The meteorological data required for the trajectory computation come from the Global Data Assimilation System archive maintained by ARL (available online at http://ready.arl.noaa.gov/archives.php). First, 78 h back trajectories were calculated at 500 m above the ground at every hour throughout the study period. Next, clustering of the trajectories were done as per spatial distributions using HYSPLIT4 software. The principles and processes associated with clustering are described in the software user guide (Draxler et al., 2014). Potential Source Contribution Function (PSCF) analysis was carried out utilizing BT analysis and using a tool called Zefir (V 3.321). Detail description of this tool can be found in previous studies (Petit et al., 2017; Zhang et al., 2017).

Offline PM$_1$ (particulate matter with aerodynamic diameter ≤ 1 μm) sampling has been carried out using a medium-volume air-sampler (calibrated flow-rate 175 l/min) (Kumar and Gupta, 2015). The samples were collected during day time for 45 min each (n = 119 and 10 blanks) onto pre-baked (at 600 °C for 8 h) quartz fiber filters (Whatman™; 47 mm Dia). Quartz filters were used as characterization of organic aerosols was the focus of this study, and in future, we intend to carry out a detail offline characterization study of the organics in collected filters. The short duration of the sampling was chosen to have some parity with the high time resolved sampling of AMS. Also, shorter duration sampling enabled us to have more number of filters and reduce the influence of sampling artifacts (like flow fluctuations, absorption of gas phase organics by filters) on observed concentrations. However, this high frequency sampling schedule demanded constant availability of alert manpower and a huge number of costly filters. Night time sampling was difficult due to limited availability of manpower and some short lasting but relatively frequent power cuts. So, considering logistical and economic aspects, only daytime high