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Internally mixed black carbon in the Indo-Gangetic Plain and its effect on absorption enhancement

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ABSTRACT

We present the systematic analysis of individual black carbon (BC) mixing state and its impact on radiative forcing from an urban Indian city, Kanpur, located in Indo-Gangetic Plain (IGP). Simultaneous measurements using Single Particle Soot Photometer (SP2), Photo-Acoustic Soot Spectrometer (PASS-3) and High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) were conducted from 8 January 2015 to 28 February 2015 at Kanpur. BC mass and number concentrations varied between 0.7 and 17 μg/m^3 and 277–5866 #/cm^3 with a mean of 4.06 μg/m^3 and 1314 #/cm^3, respectively. The diurnal variation of BC mass concentration showed a traffic hour peak during both the morning and late night. The mean fraction of "thickly coated BC" particles (fTC_{BC}) was found to be 61.6%, indicating that a large fraction of BC particles was internally mixed. The fTC_{BC} increased after sunrise with a peak at about noontime, indicating that the formation of secondary organic aerosol under active photochemistry can enhance organic coating on a core of black carbon. High-resolution positive matrix factorization (HR-PMF) factors showed distinct characteristics with fTC_{BC}. While primary organic aerosols like cooking organic aerosols (COA) and biomass burning organic aerosols (BBOA) were negatively correlated with fTC_{BC} ($r = -0.78$ and -0.51, respectively), aged low volatile oxygenated organic aerosol (LVOOA) was forming a coating over BC ($r = 0.6$). Similar positive correlation of fTC_{BC} with inorganic species like ammonium ($r = 0.58$) and nitrate ($r = 0.47$) further suggested that BC appears to be largely coated with LVOOA, ammonium, and nitrate. A positive correlation between the fTC_{BC} and the mass absorption cross-section at 781 nm (MAC_{781}) was also observed ($r = 0.58$). Our results suggest that the observed fTC_{BC} could amplify the MAC_{781} approximately by a factor of 1.8, which may catalyze the positive radiative forcing in the IGP.

1. Introduction

Black carbon (BC) is emitted into the atmosphere by incomplete combustion of fossil fuels and biomass burning (Bond et al., 2013; Chen et al., 2015; Novakov et al., 2000; Oshima et al., 2009; Talukdar et al., 2015; Tiwari et al., 2016; Vaishya et al., 2017; Verma et al., 2017). In spite of its short atmospheric lifetime of about 4 to 12 days (Cape et al., 2012; Schwarz et al., 2006), it plays an important role in radiative forcing (Jacobson, 2001) by strongly absorbing solar radiation and lowering the fraction of the extinction due to scattering (Penner et al., 1998; Ram et al., 2012b; Ramanathan et al., 2001). While BC aerosols are generally externally mixed and hydrophobic when they are freshly emitted (Willis et al., 2016; Zhang et al., 2016), atmospheric aging leads to internally mixed BC with hydrophilic compounds (e.g. organic acids and ammonium sulfate) (Zhang et al., 2015) through condensation and coagulation which increases its hygroscopicity and size (Liu et al., 2010; Moteki et al., 2007). These hydrophilic internally mixed BC can act as condensation nuclei (CCN) (McMeeking et al., 2011a; Shiraiwa et al., 2007) which can affect the climate (Cappa et al., 2012) by changing its wet scavenging efficiency and atmospheric lifetime (Oshima et al., 2009).

Kanpur is an industrial city located in the Indo-Gangetic Plain (IGP) which is one of the most populated and polluted regions in northern India (Ram et al., 2010). While the BC concentration in Kanpur is found to be comparable to other developing nations like China, it is much higher than that of developed nations like Europe and United States (Ramachandran and Rajesh, 2007; Tripathi et al., 2005a). BC concentrations in Kanpur reach significantly high levels (17 μg/m^3) in winter period, perhaps due to the combined effect of the shallow boundary layer height (Baxla, 2009; Tripathi et al.,2007) and increased

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anthropogenic emissions (biomass/trash burning) (Kanawade et al., 2014; Nair et al., 2007). These anthropogenic emissions also generate hygroscopic organic and inorganic aerosols along with BC. Furthermore, the high relative humidity (RH) in winter period promotes the internal mixing of these hygroscopic aerosols with BC, where they assume to form a core-shell structure with a BC core (Bond and Bergstrom, 2006). Previous studies indicate that the coating of these non-absorbing organic and inorganic aerosols on BC can enhance the magnitude of solar radiation absorption and this is generally termed as the lensing effect (Liu et al., 2015; Schwarz et al., 2008; Shamjad et al., 2012). This enhancement in absorption depends upon the type of coating material, the thickness of the coating on BC and the morphology of BC (Andreae and Gelencsér, 2006; Laborde et al., 2013; Liu et al., 2015).

Most of the previous studies in IGP used photoacoustic techniques, filter-based measurements, modelled algorithms and thermal optical measurements to measure the BC mass and its mixing state (Dey et al., 2008; Kaul et al., 2011; Raju et al., 2016; Ram et al., 2016; Shamjad et al., 2015, 2012; Tripathi et al., 2005b). But traditional filter based BC measurements (e.g. Aethalometer) are prone to limitations which overestimate the light absorption due to multiple scattering substrates (Arnott et al., 2005), whereas at higher RH photo-acoustic methods underestimate absorption and affect the indirect estimation of BC (Arnott, 2003). Moreover, these bulk techniques cannot provide the information on mixing state of individual BC particles (Li et al., 2016) which is very important in the BC radiative forcing calculation as the internally mixed BC particles can increase the positive radiative forcing (Jacobson, 2001).

Studies also tried to depict mixing state and morphology of BC using single particle offline measurements using electron and X-ray microscopy. (China et al., 2013) identified that the biomass burning generates BC with varying morphologies and 50% of soot particles were embedded (heavily coated). In another study, (Adachi et al., 2014) found that 75% of BC was internally mixed with sulfate in Japan. Generally, BC was more internally mixed with sulfate and organics (Adachi and Buseck, 2008; Fu et al., 2012), spherical in shape once it is thickly coated (Ueda et al., 2016) and condensation of organics and inorganics over BC showed an increase in its particle size (Moffet et al., 2016).

The present study used the Droplet Measurement Technologies (DMT) Single Particle Soot Photometer (SP2), which has gained more attention in recent years because of its higher selectivity and specificity towards refractory BC measurement. BC measurements using SP2 are also free from most of the artifacts of the aforesaid previously used instruments. Here, we report the mixing state of individual BC particles at an urban site, Kanpur, in IGP during the winter of 2014–2015. Alongside SP2 measurements, optical properties of BC and non-refractory submicron concentration of aerosols were also measured simultaneously using the DMT Photo Acoustic Soot Spectrometer (PASS-3) and Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, hereafter referred to as AMS), respectively.

2. Experimental methods

2.1. Sampling site

Measurements were carried out at the Centre for Environmental Science and Engineering (CESE) building in the Indian Institute of Technology, Kanpur campus (26.46°N, 80.32°E, 142 m above mean sea level) from 8 January 2015 to 28 February 2015, characterized as winter season. Kanpur is an industrial hub of northern India, which is located in the central part of IGP where coal-based power plants, fossil fuel combustion, and biomass burning significantly contribute towards the total anthropogenic aerosol loading (Kanawade et al., 2014; Ram et al., 2010) and absorbing aerosols. Specifically, the winter season in northern India is characterized by the widespread biomass/trash burning, resulting in a high aerosol loading due to prevailing stable weather conditions (Dey et al., 2005; Singh et al., 2004) and also witnesses frequent occurrence of fog with high RH conditions (Kaul et al., 2011).

A high mass concentration of absorbing aerosols (Sanap and Pandithurai, 2015) and organics (Chakraborty et al., 2015), shallow boundary layer height (Nair et al., 2007) and frequent fog episodes (Kaul et al., 2011; Ram et al., 2012a) in the winter period mark IGP as one of the regional BC hotspot and an ideal location to study aerosols mixing state (Bhattu and Tripathi, 2015; Ram et al., 2014). These complex ambient characteristics and high aerosol loading can further interact with the climatology of downwind receptor sites. To understand the significance of BC loading in IGP to the downwind receptor sites, Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT 4) (Draxler et al., 2016) model forward trajectory analysis was performed for air mass originating from our site. The data was retrieved from Global Data Assimilation System (GDAS) and the model was run at the height of 50 m above ground at an interval of 5 days (starting at "6:30 UTC") from January 10 to February 25. The air mass forward trajectories show (Fig. 1) that the mixing state of BC in IGP can influence the radiative forcing calculation of both short range (east and south-east India) and also long range (Tibetan plateau and China) receptor sites.

2.2. Instrumentation

SP2, PASS-3, and AMS all were kept inside an air-conditioned laboratory with sampling lines extended towards the open atmosphere. These instruments were operated in parallel to analyze the real-time characteristics of BC and non-refractory organics and inorganics simultaneously. Ambient aerosols were dried by using a silica diffusion dryers to effectively reduce the RH to < 10% before passing to AMS and PASS-3. SP2, which can operate between an RH of 0–100%, was directly connected to the ambient air similar to the setup discussed elsewhere (Laborde et al., 2012; Liu et al., 2013; Shamjad et al., 2016).

2.2.1. Single Particle Soot Photometer (SP2)

SP2 was used to measure mass, number concentration and size distribution of BC particles. In SP2, an intracavity Nd: YAG laser beam of 1064 nm was used to quantify the mass of individual BC particles. The TEM00 mode laser beam intercepts the aerosol flow (which was taken as 30 Volumetric Cubic Centimeter per Minute (VCCM) for the present study) in a perpendicular plane. The Nd: YAG laser beam heats up the black carbon particle to its vaporization temperature. The emitted incandescent light was detected using avalanche photodiodes (Moteki and Kondo, 2010, 2007; Schwarz et al., 2006; Stephens et al.,

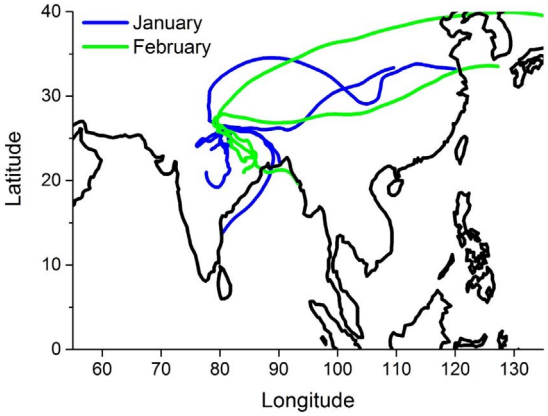

Fig. 1. HYSPLIT 5-day forward trajectory of air mass from January to February. The model was run at 50 m above from ground from January 10 to February 25 at an interval of 5 days, starting at "6:30 UTC".