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Aerosol chemical characterization and role of carbonaceous aerosol on radiative effect over Varanasi in central Indo-Gangetic Plain

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HIGHLIGHTS

- Carbonaceous aerosols account for 14% (6%–26%) of PM_{10} mass at Varanasi.
- Relatively lower OC/EC suggests higher contribution from fossil-fuel combustion.
- Relatively low secondary organic aerosol formation.
- Ratios between organic and inorganic species help in understanding aerosol source.
- EC contributes to the surface (37–63%) and atmospheric (54–77%) radiative effect.

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ABSTRACT

This study investigates the chemical composition of PM_{10} aerosols at Varanasi, in the central Indo-Gangetic Plain (IGP) during April to July 2011, with emphasis on examining the contribution of elemental carbon (EC) to the estimates of direct aerosol radiative effect (DARE). PM_{10} samples are analysed for carbonaceous aerosols (Organic Carbon, OC and EC) and water-soluble ionic species (WSIS: Cl^-, SO_4^{2-}, NO_3^-, PO_4^{2-} NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) and several diagnostic ratios (OC/EC, K^+/EC, etc) have been also used for studying the aerosol sources at Varanasi. PM_{10} mass concentration varies between 53 and 310 $\mu g\, m^{-3}$ (mean of 168 ± 73 $\mu g\, m^{-3}$), which is much higher than the National and International air quality standards. The OC mass concentration varies from 6 $\mu g\ m^{-3}$ to 24 $\mu g\ m^{-3}$ (mean of 12 ± 5 $\mu g\ m^{-3}$; 7% of PM_{10} mass), whereas EC ranges between 1.0 and 14.3 $\mu g\ m^{-3}$ (4.4 ± 3.9 $\mu g\ m^{-3}$; ~3% of PM_{10} mass). The relative low OC/EC of 3.9 ± 2.0 and strong correlation ($R^2 = 0.82$) between them suggest the dominance of primary carbonaceous aerosols. The contribution of WSIS to PM_{10} is found to be ~12%, out of which ~57% and 43% are anions and cations, respectively. The composite DARE estimates via SBDART model reveal significant radiative effect and atmospheric heating rates (0.9–2.3 K day^{-1}). Although the EC contributes only ~3% to the PM_{10} mass, its contribution to the surface and atmospheric forcing is significantly high (37–63% and 54–77%, respectively), thus playing a major role in climate implications over Varanasi.

1. Introduction

Carbonaceous aerosols (including organic carbon, OC and elemental carbon, EC) and particulate matter (PM) have gain significant importance in aerosol research due to adverse effects on human health, environmental issues and climate change (Novakov et al., 2005; Kassomenos et al., 2014; Salameh et al., 2015). Several

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studies over the globe reported that both short and long-term exposures to high PM concentrations are associated with respiratory diseases, lung cancer, asthma and heart attacks (Pope and Dockery, 2006; Putaud et al., 2010). The effects of these aerosols depend on particle size and chemical composition, with the finer and toxic particles to be the most hazardous as they can go deeper in the lungs (Pöschl, 2005). In order to reduce the adverse impacts and to develop the mitigation strategies for air quality control, the knowledge of PM and its chemical composition is very essential, especially over the developing countries in South and East Asia with the highest emissions (Bond et al., 2013).

Carbonaceous aerosols constitute a significant part (~10–70%) of the fine aerosol mass ($PM_{2.5}$) (Yu et al., 2004; Kanakidou et al., 2005; Fuzzi et al., 2006; Tiwari et al., 2009, 2013a) and play a crucial role in atmospheric chemistry, radiative transfer and precipitation (Rosenfeld, 2002; Zhang et al., 2009). These aerosols exist mainly in the form of OC, which is a complex mixture of thousands of different organic compounds (primary emissions and secondary formation) containing polycyclic aromatic hydrocarbons. OC is considered as mostly scattering aerosol type, though a fraction of OC (called as Humic Like Substances, HULIS) shows some absorption in the UV region (Kirchstetter et al., 2004; Andreae, and Gelencser, 2006; Dinar et al., 2008). On the other hand, EC is a mixture of graphite-like particles and is primarily absorbing particulate species in the atmosphere (Cao et al., 2005).

The Indo-Gangetic Plain (IGP) is one of the most densely populated regions over the globe where aerosols are composed of mixtures of anthropogenic and natural emissions with distinct seasonal characteristics (Ramanathan and Ramana, 2005; Dey and Di Girolamo, 2010; Srivastava and Ramachandran, 2013; Tiwari et al., 2014a, 2014b). During the pre-monsoon and early-monsoon period, the region experiences high aerosol loading, which is of particular research interest due to large heterogeneity in aerosol characteristics and their impacts on radiative forcing and monsoon rainfall (Gautam et al., 2009, 2011; Srivastava et al., 2011, 2012; Kaskaoutis et al., 2013). Forest fires in Himalayan foothills (Vadrevu et al., 2012), agricultural burning of wheat crop residue in northwestern India (Kumar et al., 2011), urban and industrial fossil-fuel combustion (Ram and Sarin, 2011), biomass and bio-fuels burning (Ram et al., 2012), along with dust plumes originating from Thar desert, southwest Asia and Arabia (Bhattacharjee et al., 2007; Pandithurai et al., 2008; Rashki et al., 2015) synthesize a thick brownish aerosol cloud covering entire northern India and southern Himalayan foothills with significant effects on clouds, monsoon and climate (Ramanathan et al., 2005; Lau and Kim, 2006; Lal et al., 2013; Das et al., 2014; Wonsick et al., 2014).

Despite the fact that the atmosphere over the IGP is dominated by coarse-mode dust aerosol during the pre-monsoon and early monsoon seasons (Singh et al., 2004; Srivastava et al., 2011), carbonaceous aerosols are of high importance for studying the radiative impact and, therefore, numerous studies have focused on examining their contribution to PM_{10} and $PM_{2.5}$ mass, as well as the ionic species over whole IGP (Karar and Gupta, 2006; Dubey and Pervez, 2008; Shukla and Sharma, 2008; Behera and Sharma, 2010a, 2010b; Ram et al., 2010a, 2010b; Rastogi et al., 2014; Srinivas and Sarin, 2014). These studies conclude moderate-to-high values (around 5 to 9) of OC/EC, significant variations in the aerosol chemical composition (soot, water soluble and insoluble components) due to changes in meteorology, influence of biomass burning and long-range aerosol transport to understand climate implications in view of atmospheric heating rates. Chemical analysis of $PM_{2.5}$ at Patiala northwestern India, during October 2011 to March 2012 (Rastogi et al., 2014) exhibited a pronounced variability in $PM_{2.5}$ concentrations, ionic (SO_4^{2-}, NO_3^-, NH_4^+, K^+, etc) and carbonaceous species (i.e. OC, EC and WSOC). NH_3 was found to play an important role in $PM_{2.5}$ ion chemistry for neutralization process and in the formation of secondary inorganic aerosols (SIA; NH_4^+, SO_4^{2-} and NO_3^-) at Kanpur (Sharma et al., 2007), where SIA formation accounted for 30% of $PM_{2.5}$ mass (Behera and Sharma, 2010a). More recently, Srinivas and Sarin (2014) studied $PM_{2.5}$ mass concentrations, carbonaceous aerosol and inorganic species in the polluted outflow from IGP to the Bay of Bengal (BoB) during November 2009–March 2010. The consistency in the aerosol chemical composition between a downwind IGP site (Kharagpur) and marine-cruise observations over BoB suggested that the IGP is the main source for aerosol-pollution over BoB. Despite the large EC concentrations over Ganges valley and Indian subcontinent (Nair et al., 2012), studies in evaluating the EC radiative effect and its contribution to the direct aerosol radiative effect (DARE; Myhre et al., 2013) are very sparse (Das and Jayaraman, 2011; Dumka et al., 2013).

Therefore, the chemical characterization of near-surface aerosol is of high scientific interest and essential to assess the impact of atmospheric chemistry on aerosol optical properties, radiation budget, monsoon and climate. The present study aims to examine the chemical composition and source apportionment of PM_{10} aerosols at Varanasi, an urban site located in the central IGP, during the period April to July 2011. Furthermore, we attempt to assess the role of primary emissions and secondary aerosol formation processes for source apportionment using organic and inorganic species and tracers. The composite DARE and contribution of EC radiative effect have also been investigated in order to understand the role of carbonaceous aerosols.

2. Sampling location, measurements and techniques

2.1. Observational site

PM_{10} (particulate matter with aerodynamic diameter < 10 μm) aerosol samples were collected at Varanasi (25.3°N, 83.0°E, 83 m amsl) located in the west bank of the Ganges river in the central IGP. Varanasi has a population of around 1.5 million, with high traffic density and anthropogenic pollution, while the surrounding region is very fertile for growing rice, wheat and major cereal crop production (Tiwari and Singh, 2013). During pre-monsoon the transported dust from arid regions of west India, Arabia and southwest Asia along with locally-produced dust from the Ganges banks and road re-suspension dominates, which is mixed with anthropogenic and industrial aerosol from fossil fuel, biofuel and biomass burning (Tiwari et al., 2013a). Monsoon rainfall usually starts in the first half of June and lasts till mid-end of September contributing in atmospheric cleansing. During the study period (April–July 2011), the ambient temperature ranged between 28.3 and 37.4 °C with a mean value of 33.0 ± 2.9 °C, while the relative humidity (RH) varied from 24.5 to 90.0 % (average: 53.6 ± 18.8). The wind speed was relatively low in the order of 1.0–3.0 m s^{-1} (average: 2.1 ± 0.7 m s^{-1}), which was progressively increased in June and July, with northwest dominance in April and May and southeast in July. During the study period the total rainfall was 36.3 mm.

2.2. Chemical analyses of aerosol samples

The sampling site was located at the terrace of the Department of Geophysics, Banaras Hindu University, ~20 m above ground level. All the PM_{10} samples were collected on a quartz filter (Whatman 1851-047QMA Microfiber 47 mm in diameter) using a medium volume sampler (APM 541 samplers; Envirotech Pvt. Ltd., India) with a flow rate of one cubic meter per hour. A total of 22