Atmospheric Environment 125 (2016) 360–370

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Mass absorption efficiency of light absorbing organic aerosols from source region of paddy-residue burning emissions in the Indo-Gangetic Plain

B. Srinivas [a], N. Rastogi [a,*], M.M. Sarin [a], A. Singh [b], D. Singh [b]

[a] Physical Research Laboratory, Ahmedabad, India
[b] Punjabi University, Patiala, India

HIGHLIGHTS

- Atmospheric brown carbon (BrC) from paddy-crop residue burning has been studied.
- Temporal variability of mass absorption coefficient of BrC and K^+ are similar.
- MAE of BrC decreases from source region of emission to downwind oceanic region.
- Atmospheric radiative forcing due to BrC accounts for ~40% of that due to BC.

ARTICLE INFO

Article history:
Received 12 February 2015
Received in revised form 7 July 2015
Accepted 11 July 2015
Available online 13 July 2015

Keywords:
Brown carbon
Biomass burning
WSOC
Carbonaceous aerosols
India
South Asia

ABSTRACT

The mass absorption efficiency (MAE) of light absorbing water-soluble organics, representing a significant fraction of brown carbon (BrC), has been studied in fine mode aerosols ($PM_{2.5}$) from a source region (Patiala: 30.2 °N, 76.3 °E) of biomass burning emissions (BBEs) in the Indo-Gangetic Plain (IGP). The mass absorption coefficient of BrC at 365 nm ($b_{abs\text{-}365}$), assessed from absorption spectra of aqueous extracts, exhibits significant linear relationship with water-soluble organic carbon (WSOC) for day ($R^2 = 0.37$) and night time ($R^2 = 0.77$) samples; and slope of regression lines provides a measure of MAE of BrC (daytime: $\sim 0.75\ m^2\ g^{-1}$ and night time: $1.13\ m^2\ g^{-1}$). A close similarity in the temporal variability of $b_{abs\text{-}365}$ (for BrC) and K^+ in all samples suggests their common source from BBEs. The $b_{abs\text{-}365}$ of BrC follows a power law ($b_{abs\text{-}\lambda} \approx \lambda^{-\alpha}$; where α = angstrom exponent) and averages around $5.2 \pm 2.0\ M\ m^{-1}$ (where $M = 10^{-6}$). A significant decrease in the MAE of BrC from the source region (this study) to the downwind oceanic region (over Bay of Bengal, Srinivas and Sarin, 2013) could be attributed to relative increase in the contribution of non-absorbing WSOC and/or photo-bleaching of BrC during long-range atmospheric transport. The atmospheric radiative forcing due to BrC over the study site accounts for ~40% of that from elemental carbon (EC).

1. Introduction

In the present-day scenario of climate change, rapidly increasing anthropogenic emissions over south and south-east Asia have been a matter of debate among the atmospheric science community. Recent studies have suggested that carbonaceous species contribute significantly (~40–70%) to the ambient particulate matter over South Asia (Kanakidou et al., 2005; Rastogi et al., in press a). The seasonal emissions of organic aerosols from bio-fuel/biomass burning and fossil-fuel combustion are potential sources for the persistence of atmospheric brown clouds (Ramanathan et al., 2001 and references therein). In addition, emission of carbonaceous species could significantly influence the regional atmospheric radiative forcing estimates (Lawrence and Lelieveld, 2010 and references therein). Furthermore, it has been documented that a significant fraction of organic aerosols are water-soluble and could contribute to the CCN abundance on a regional scale. A number of studies conducted in South Asia emphasize that atmospheric water-soluble organics constitute a significant fraction (20–80 %)

---

* Corresponding author. Geosciences Division Physical Research Laboratory Navrangpura, Ahmedabad 380009, India

E-mail address: nrastogi@prl.res.in, neeraj6676@gmail.com (N. Rastogi).

http://dx.doi.org/10.1016/j.atmosenv.2015.07.017
1352-2310/

of total aerosol organic matter (Kirillova et al., 2013; Lawrence and Lelieveld, 2010; Miyazaki et al., 2009; Pavuluri et al., 2011; Rastogi et al., in press b; Srinivas and Sarin, 2014b).

Contrary to the role of elemental or black carbon (EC or BC) which absorbs solar radiation in the entire UV/Visible region, some of the water-soluble organics (referred as brown carbon, BrC) exhibit absorption characteristics in the near UV-region (Andreae and Gelencsér, 2006; Cheng et al., 2011; Hecobian et al., 2010; Zhang et al., 2013, 2011). Due to its dependence on the wavelength, the absorption angstrom exponent of BrC can be greater than unity (Yang et al., 2009). It has been also documented that absorption by water-soluble organics overlaps with another class of organic compounds, referred as humic like substances (HULIS) (Lukacs et al., 2007).

Their ubiquitous presence over rural, urban, remote continental and over marine regions (Graber and Rudich, 2006; Liu et al., 2014) demand systematic studies on characterization of light absorbing organic aerosols (their sources, transport and transformation pathways). It is noteworthy that biomass burning aerosols, collected from different geographic locations, show pronounced UV absorption suggesting their role as a possible source of BrC (Desyaterik et al., 2013; Hecobian et al., 2010; Lack et al., 2013; Saleh et al., 2013). A recent study has documented significant linear relationship between levuglucosan abundance (a specific biomass burning tracer, assessed through characteristic mass fragment ion which has an $m/z = 60$) and the particulate absorption at 404 nm (Lack et al., 2013).

Another important issue relates to climatic significance of BrC through direct radiative forcing by the absorption of incoming solar radiation (Bahadur et al., 2012; Chung et al., 2012; Feng et al., 2013; Jacobson, 2012) and semi-direct effect that involves significant warming/heating of cloud water followed by evaporation (Jacobson, 2012). Based on global simulations, accounting for the atmospheric abundances of BrC, radiative forcing by organic aerosols changes sign (from -0.08 W m^{-2} to $+\ 0.025$ W m^{-2}) at the top of the atmosphere (Feng et al., 2013).

The Indo-Gangetic Plain (IGP) in northern India is dominated by bio-fuel and biomass burning emissions (BBEs) and fossil-fuel combustion sources (FF-comb). The carbonaceous aerosols injected from anthropogenic sources are of considerable significance in the regional atmospheric chemistry and climate change scenario (Indo-Asian haze, Atmospheric brown clouds etc). The increase in atmospheric abundances of carbonaceous species such as black carbon and WSOC are suggested to be the significant factors for the Atmopsheric Brown Cloud over the IGP. More recently, light absorbing water-soluble organics have received considerable attention due to their impact on regional to global scale climate forcing (Bahadur et al., 2012; Feng et al., 2013). In spite of their climatic significance, lack of ground-based observations and poor characterization of organic aerosols limits our ability to assess climate forcing feedbacks (Kirillova et al., 2014b; Srinivas and Sarin, 2013, 2014a).

In this manuscript, we report on the mass absorption efficiency of BrC in fine mode aerosols ($PM_{2.5}$) collected from a source region (Patiala: 30.2 °N, 76.3 °E) of BBEs in the IGP during October–December, 2011 (a period characterized by large scale paddy-residue burning).

2. Methodology

2.1. Analytical scheme

The sampling site at Patiala (30.2 °N, 76.3 °E) has been selected for characterization of rice-straw burning emissions during mid-October to mid-November soon after the crop harvesting season. A detailed description regarding the sampling site and the prevailing meteorology are presented in our earlier publication (Rajput et al., 2011; Rastogi et al., 2014). In this study, particulate matter <2.5 μm aerodynamic diameter ($PM_{2.5}$) samples ($n = 47$) were collected from the site during October to December (2011). For sample collection, a high volume air sampler (Thermo-Anderson, HVS) with a flow rate of ~1.13 m^3 min^{-1} was set up on the terrace of Physics Department at Punjabi University, Patiala. On an average, aerosol samples were collected for ~8 h (separately during day and night) and volume of air filtered was ~540 m^3. The flow rate of the air sampler was frequently calibrated to ascertain the variability, if any, and found to be within the uncertainty of 5%. All samples were collected on pre-combusted (at 450 °C for 10–12 h) tissuquartz (PALLFLEX$^{®TM}$) filters (25 × 20 cm^2). Soon after their collection, filters were wrapped in Aluminium foils and sealed in plastic zip-lock bags and stored in the deep freezer at −19 °C until the time of analysis.

The $PM_{2.5}$ mass concentrations were assessed gravimetrically from the tare weights of the filters before and after the particulate collection on an electronic balance (Saratorius, Model LA130S-F). Prior to their weighing, aerosol filters were equilibrated to ambient room temperature (~22 °C) under constant relative humidity (~37–42 %). Subsequently, samples were analyzed for inorganic constituents and carbonaceous species (EC, OC and WSOC).

An aliquot of aerosol filter was extracted with ultra pure deionized water (Milli-Q water; specific resistivity: 18.2 MΩ cm^{-1}). Subsequently, filter extracts were analyzed for concentrations of water-soluble inorganic constituents (WSIC) on Ion Chromatograph (DIONEX, Model: ICS-5000) equipped with dual columns and suppressors for the simultaneous analysis of both anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, $NH_4{}^+$, K^+, Mg^{2+} and Ca^{2+}). Another filter aliquot, 1.5 cm^2 punch was used to assess the concentrations of elemental and organic carbon (EC and OC) on Sunset EC-OC analyzer using the NIOSH protocol (Birch and Cary, 1996). The analytical accuracy of the measurement of organic carbon on EC-OC analyzer was ascertained by analyzing working standard solutions, prepared from suitable dilution of potassium hydrogen phthalate (KHP) and sucrose solutions (1000 ppm). The precision of measured OC and EC concentrations was ascertained based on repeat analyses of several samples and found to be within ±3% for OC and ±5% for EC. Another portion of filter aliquot is (18 cm^2) was extracted with Milli-Q and filtered through precombusted (at 450 °C for 4 h) glass fiber filter (GF/F, Whatman, pore size: 0.7 μm). Subsequently, filtered aqueous extracts were analyzed for water-soluble organic carbon (WSOC) on Total Organic Carbon analyzer (Shimadzu, Model: TOC-5000a). Further details regarding analytical protocol and uncertainties, reference is made to Rajput et al. (2011) and Rastogi et al. (2014). The mass concentration of EC, OC, and WSOC and other water-soluble inorganic ions (K^+, SO_4^{2-}, NO_3^-, and Ca^{2+}) are obtained from Rastogi et al. (2014).

2.2. Absorption coefficient, mass absorption efficiency & angstrom exponent of BrC

For these parameters, an aliquot of aqueous extract of $PM_{2.5}$ was analyzed for absorption signal (scan taken from 300 to 700 nm) using 2 m long liquidcore wave-guide capillary cell (LWCC, World Precision Instruments Inc.) coupled to a USB-4000 spectrophotometer, and D_2-lamp (Ocean optics) was used as light source. The absorption coefficient (b_{abs}) of BrC is assessed from absorption by WSOC at 365 nm relative to 700 nm. The detailed analytical protocol and uncertainty in the assessment of optical properties of WSOC are described in our earlier publications (Srinivas and Sarin, 2013, 2014a). Breifly, the b_{abs} of BrC is