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Brown carbon in atmospheric outflow from the Indo-Gangetic Plain: Mass absorption efficiency and temporal variability

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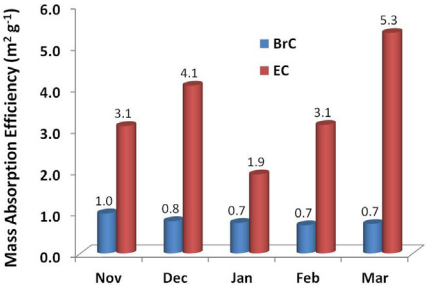
HIGHLIGHTS

- First data on atmospheric brown carbon (BrC) from northern India.
- BrC absorption shows linear increase with water-soluble organic carbon.
- Angstrom exponent of BrC is consistent with that for biomass burning emissions.
- Ratio of mass absorption efficiency of BrC relative to EC is as high as 0.72.
- Atmospheric radiative forcing by BrC and BC needs reassessment on regional scale.

GRAPHICAL ABSTRACT



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ABSTRACT

The simultaneous measurements of brown carbon (BrC) and elemental carbon (EC) are made in ambient aerosols ($PM_{2.5}$), collected from a site in north-east India during November'09–March'10, representing the atmospheric outflow from the Indo-Gangetic Plain (IGP) to the Bay of Bengal (BoB). The absorption coefficient of BrC (b_{abs}), assessed from water-soluble organic carbon (WSOC) at 365 nm, varies from 2 to 21 M m^{-1} and exhibits significant linear relationship ($P < 0.05$) with WSOC concentration (3–29 μg m^{-3}). The angstrom exponent (α: 8.3 ± 2.6, where $b_{abs} \approx \lambda^{-\alpha}$) is consistent with that reported for humic-like substances (HULIS) from biomass burning emissions (BBE). The impact of BBE is also discernible from mass ratios of nss-K^+/EC (0.2–1.4) and OC/EC (3.4–11.5). The mass fraction of WSOC (10–23%) in $PM_{2.5}$ and mass absorption efficiency of BrC ($\sigma_{abs\text{-}BrC}$: 0.5–1.2 m^2 g^{-1}) bring to focus the significance of brown carbon in atmospheric radiative forcing due to anthropogenic aerosols over the Indo-Gangetic Plain.

1. Introduction

The light absorbing species of atmospheric particulate matter are gaining considerable interest in recent years owing to their significant role in regional as well as global climate change (Fuzzi et al., 2006). Although several studies have evaluated their impact on the atmospheric environment, uncertainties associated with the regional scenario are still large and demand further detailed assessment. One of the possible sources of uncertainty could be attributed to poor characterization of organic aerosols in the atmospheric particulate matter (Huebert and Charlson, 2000). In this context, detailed information on sources, size-distribution and compositional changes during transport of carbonaceous aerosols is essential for assessing their atmospheric radiative forcing.

Among the carbonaceous species, two distinct forms of carbon [elemental or black carbon (EC or BC) and brown carbon (BrC)] are of particular interest due to their light absorbing properties. The EC

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absorbs solar radiation in the visible region (Bond, 2001; Bond et al., 2013), whereas BrC shows prominent absorption in the near UV-region (Alexander et al., 2008; Andreae and Gelencsér, 2006; Hecobian et al., 2010; Lack et al., 2012; Liu et al., 2014; Lukács et al., 2007; Yang et al., 2009). However, real time data on absorption properties of BrC are rather limited. The omnipresence of BrC in rural, urban and remote environments has been emphasized by Graber and Rudich, (2006) suggesting the need for its adequate representation in climate model simulations.

The presence of brown carbon is documented based on the absorption spectra of aqueous extracts of ambient aerosols (Havers et al., 1998; Kirchstetter et al., 2004; Zhang et al., 2013). Furthermore, its abundance has been studied using aerosol light absorption measurements near to the specific combustion sources (Bond, 2001). A significant overlap in the spectral proprieties of BrC (assessed from water-soluble organic carbon, WSOC) and humic-like substances (HULIS), derived from the biomass burning emissions, has been reported during the LBA-SMOCC (Large scale Biosphere atmosphere experiment in Amazonia-SMOke aerosols, Clouds, rainfall and Climate) Experiment (Hoffer et al., 2006). The emission from biomass burning is recognized as a primary source of HULIS and of brown carbon (Andreae and Gelencsér, 2006; Park et al., 2010). It has been also suggested that tar balls from smoldering combustion of bio-fuels (or biomass) are a significant source of atmospheric brown carbon (Chakrabarty et al., 2010). In addition to emissions from specific sources, formation of brown carbon through heterogeneous reactions of secondary organic aerosols (emitted from biogenic and anthropogenic precursors like terpenes) with ammonia is also documented by Updyke et al. (2012).

Uncertainties in atmospheric radiative forcing estimates continue to cause major debate (IPCC-2007), largely arising from the poor representation of the organic carbon fraction in atmospheric aerosols (Forster et al., 2007). More recently, Feng et al., (2013) have emphasized the importance of brown carbon absorption in aerosol radiative forcing ($\sim$0.25 W m^{-2}) using a general circulation model coupled to a chemical transport model. Their results suggest that atmospheric brown carbon could contribute nearly 19% of the total absorption by anthropogenic aerosols; whereas 71% is attributable to that from BC (or EC) and $\sim$9% is from sulphates and coatings of non absorbing organic compounds on soot carbon (Feng et al., 2013). Furthermore, their study also highlights an overall mismatch between observations and model results for the simulated aerosol radiative forcing and suggests the need to incorporate absorption due to brown carbon in the global models. In this study, we have made simultaneous measurements of BrC and EC in ambient aerosols ($PM_{2.5}$) collected from a downwind sampling site in the Indo-Gangetic Plain, representing the atmospheric outflow. We have also assessed the mass absorption efficiency of BrC from water-extracts of aerosols.

2. Materials and methods

2.1. Site description and meteorology

The Indo-Gangetic Plain (IGP), situated in the northern part of the Indian peninsula, generates a host of airborne pollutants. Fossil-fuel combustion, biomass burning (mainly agricultural crop-residue) and bio-fuel (wood) are some of the characteristic sources of pollutants. The impact of anthropogenic aerosols on oceanic regions located downwind of pollution sources in the Indo-Gangetic Plain has been well documented through field experiments such as INDOEX (Ramanathan et al., 2001; Lelieveld et al., 2001; Mayol-Bracero et al., 2002) and ICARB (Sudheer and Sarin, 2008; Sarin et al., 2010; Kumar et al., 2008; Srinivas and Sarin, 2012; Srinivas and Sarin, submitted for publication). Under favourable meteorological conditions (shallow boundary height and north-easterly/westerly winds), the downwind transport of pollutants from the IGP to the Bay of Bengal is a conspicuous feature during the wintertime (from December to March).

Ambient aerosols ($PM_{2.5}$ $\approx$ particulate matter whose aerodynamic diameter is less than 2.5 μm) were collected during November'09–March'10 from a downwind site (Kharagpur: 22.3 °N, 87.3 °E) in the Indo-Gangetic Plain (IGP). During the wintertime, the sampling site is influenced by long-range transport of pollutants from upwind sources in the IGP. Surface level meteorological parameters were obtained from NCEP (National Centre for Environmental Predictions)-NCAR reanalysis data sets. The winds were predominantly north-easterly (0.5–3.8 m s^{-1}), and relative humidity and surface temperature varied from 38 to 58% and 21.5 to 30.4 °C, respectively. The air mass back trajectories (7-day AMBTs), computed from the NOAA website using hybrid single particle Lagrangian integrated trajectory model (HYSPLIT, version 4.0; (Draxler, 2002)), suggest transport of pollutants from the upwind source regions.

2.2. Methodology

Aerosol samples ($PM_{2.5}$, N = 46) were collected on pre-combusted tissuquartz filters (PALLFLEX®™) using a high-volume ($\sim$1.13 m^3 min^{-1}) air sampler (HVS-$PM_{2.5}$, Thermo-Anderson Inc.). Most of the samples (N = 42) were collected over a period of $\sim$22 h. After collection, all samples were stored in a deep freezer at −19 °C until the time of their chemical analysis. For all chemical analyses, sample filters were handled under a clean laminar flow bench (Class − 1000). The absorption spectra of aqueous extracts of aerosols were measured on a UV–vis Spectrophotometer (Model: USB-4000) coupled to a 2 m long waveguide capillary column. Deuterium and tungsten halogen lamps (DT-Mini-2, Ocean Optics) are used as a light source. Liquid samples were injected via capillary injector into Liquid-core Waveguide Capillary Cell (LWCC from World Precision Instrument, Sarasota, FL), with an internal volume of 250 μL. Absorption spectra were recorded over a wavelength range of 300–800 nm with an Ocean Optics Spectra-Suite data acquisition software system (Ocean Optics, Dunedin, FL). Simultaneously, concentrations of organic and elemental carbon (OC and EC) were also measured by thermo-optical transmittance method using Sunset-Lab EC–OC Analyzer. Water-soluble organic carbon (WSOC) was measured on total organic carbon analyzer (model: Shimadzu, TOC-5000a). Along with the samples, filter (and field) blanks were also analyzed for OC and WSOC. The contribution from blank signals was found to vary from 4 to 29% and 0.1 to 14% of the maximum and minimum signals measured for OC and WSOC, respectively. Based on the repeat measurements, the overall analytical reproducibility was better than 5% for OC and WSOC, whereas it was less than 10% for EC. For further details regarding the experimental protocol and method detection limits for OC, EC and WSOC, reference is made to our earlier publications (Ram et al., 2010; Rengarajan et al., 2007).

2.3. Absorption coefficient

In this study, absorption spectra of water extracts of aerosols (representing bulk of the water-soluble organic carbon) have been used to assess the absorption coefficient (b_{abs}) similar to that described by Hecobian et al., (2010) and is expressed as:

$$b_{abs} = (A_{365} - A_{700}) \times (V_{ext} \times 8) \times \ln(10)/(V_{aero} \times L)$$

In this equation, A_{365} and A_{700} correspond to measured absorbance at 365 and 700 nm, respectively. V_{ext} refers to volume of the aqueous extract ($\sim$50 ml) in which 1/8th portion of aerosol filter is extracted and factor '8' is used to estimate the absorption signal for