Environmental Issues: Approaches and Practices (2019), 1:32-39
ISBN: 978-81-939266-1-1

First Measurements of Aerosol Climate Forcing Agents in Rural West Bengal

Archita Rana • Sayantan Sarkar*

Abstract This study reports the first measurements of aerosol climate forcing agents (black and brown carbon; BC and BrC) from a rural location in West Bengal. To this end, time-resolved measurements of aerosol optical properties were carried out at Mohanpur, West Bengal using a 7-wavelength Aethalometer during summer 2018. These were supplemented by time-integrated fine-mode aerosol ($PM_{2.5}$) samples, and analysis of optical properties of their aqueous and organic extracts. The daily averaged BC varied from 0.9-7.5 μg m^{-3} (mean: 3.6±2.0 μg m^{-3}), and its diurnal profile exhibited early morning (0700-0800 h) peaks characterized by high fossil fuel BC, and late evening (1900-2100 h) peaks from residential fuel use reflected by enhanced biomass burning (BB-BC). The contribution of BB-BC to BC_{total} was 17% for the study period. The diurnal profile of BrC absorption ($b_{abs(BrC)}$) tracked the BC-BB fraction with a concurrent peak during 1900-2100 h, suggesting co-emission. Overall, BrC contributed 15% and 18%, respectively, to total and BC-associated light absorption at 370 nm. Aqueous and organic extracts of summertime aerosol showed strong wavelength-dependence with averaged BrC_{AE} values of 7.2 and 6.2, respectively, confirming a substantial presence of both aqueous- and organic-soluble BrC chromophores. Fluorescence spectra for aqueous extracts showed a strong peak at ~420 nm, possibly indicating the presence of poly-conjugated humic-like substances (HULIS), while that for organic extracts exhibited a broader and more intense peak suggesting water-insoluble BrC chromophores. Overall, this study established for the first time that BrC is a significant component of light absorbing aerosol in rural West Bengal.

Keywords Angstrom exponent, Carbonaceous aerosols, Concentration-weighted trajectory (CWT), India, Optical properties

✉ **Sayantan Sarkar**[1, 2]
sayantan101@gmail.com
sayantan.sarkar@iiserkol.ac.in
Archita Rana[1]
[1]Department of Earth Sciences
[2]Centre for Climate and Environmental Studies
Indian Institute of Science Education and Research (IISER) - Kolkata, India

INTRODUCTION

Among aerosol chemical constituents, black carbon (BC) is the most potent climate forcing agent (radiative forcing estimate: +1.1 W m^{-2}; Bond et al., 2013) with pronounced effects on atmospheric stability, large scale circulation, monsoon patterns and snow albedo (Tiwari et al., 2013 and references therein). In India, large internal heterogeneities exist for BC

emission inventories, which translate into uncertainties in model-predicted atmospheric BC concentrations and corresponding climate effects on regional scales. Field-based measurements of BC aerosol concentrations, diurnal and seasonal variations, sources, and optical properties are therefore vital to constrain regional model predictions. Another fraction of carbonaceous aerosols, termed brown carbon (BrC), has emerged recently as a possibly significant contributor to aerosol climate forcing. BrC refers to the light-absorbing fraction of atmospheric organic carbon (OC), and is associated with both primary (biomass/bio-fuel combustion) and secondary (atmospheric photooxidation) sources, with effects on the surface UV budget and tropospheric chemistry (Mok et al., 2016). However, field studies on BrC optical properties and sources are highly scattered globally and are rare in India, which demands concerted efforts in this direction.

The Indo-Gangetic Plain (IGP) is considered to be the predominant area source of BC in India and recent estimates show that West Bengal, located in the eastern IGP, is the second largest BC emitter nationally (Paliwal et al., 2016). Increased emission from this region is possibly from the use of biomass fuels and kerosene lamps for domestic energy production in rural areas, open crop residue burning, and outflows from the megacity Kolkata and population centers in the central and northwestern IGP. Despite such high emissions, field-based studies investigating BC distribution, sources and optical properties in this region are rare while those on BrC are non-existent. This limits our understanding of the impact of regionally transported (and photochemically aged) emissions on aerosol optical properties in rural West Bengal. This lack of surface measurement data also signifies that regional model estimates of BC cannot be validated for this region. In view of the above, we present here the first measurements of summertime BC and BrC, corresponding light absorption parameters, and potential source sectors at a rural site affected by regional emissions in West Bengal.

METHODS

Study area

The study was carried out at Mohanpur (22º96'N, 88º56'E), a rural area in Nadia district, West Bengal, characterized by agricultural fields and village settlements, with reduced vehicular traffic. The nearest town is Kalyani (population: 0.1 million) around 10 km to the W and the megacity Kolkata (population: 4.9 million) lies ~50 km to the S-SW. A cluster of small- and medium-scale industrial units are located ~10 km to the W, and the 450 MW Bandel coal-fired power station is situated ~15 km to the NW of the site. On a regional scale, clusters of large thermal power plants and steel industrial complexes in West Bengal, Odisha, Bihar, Jharkhand and Chhattisgarh are located within 500 km of the study area.

SAMPLING AND ANALYSIS

1) Time-resolved measurements of BC and BrC

A 7-wavelength (370-950 nm) Aethalometer (AE-33, Magee Scientific) was employed during late summer (May-July) 2018 to collect BC concentration and aerosol light

absorption data at a time resolution of 1 min. Aerosol light absorption coefficients (b_{abs}) were determined from wavelength-dependent BC mass absorption efficiencies (MAE) and BC mass density data. Assuming a BC Angstrom exponent (AE) of 1, a power law equation was used to estimate BC absorption across the entire wavelength range, followed by the determination of residual absorption by BrC ($b_{abs(BrC)}$). Subsequently, the wavelength dependence of BrC light absorption (AE_{BrC}) was calculated from a fit of $b_{abs(BrC)}$ vs wavelength. Diurnal variations of BC, b_{abs}, $b_{abs(BrC)}$ and AE_{BrC} were also studied. Finally, a two-component mixing model was employed for a preliminary assessment of fossil fuel vs biomass burning sources of BC.

2) Time-integrated optical measurements of Aerosol Aqueous and Organic Extracts

A low-volume $PM_{2.5}$ sampler (APM550 MFC, Envirotech) was deployed to collect 24 h $PM_{2.5}$ during April-July 2018 (n=29) using pre-combusted 47 mm quartz filters (QMA, Whatman). $PM_{2.5}$ loads were determined using a microbalance (Mettler-Toldeo, sensitivity: 0.01 mg) after conditioning in a constant temperature and RH chamber. A fraction of these samples (n=5) were extracted separately with 20 ml ultrapure water and 10 ml methanol for 30 min in an ultrasonicator to get water- and organic-extractable fractions of $PM_{2.5}$, respectively. The extracts were filtered through 0.22 µm PVDF syringe filters (Rankem), and were analyzed for optical characteristics of organic aerosol chromophores using UV-Vis (Evolution 201, Thermo-Fisher) and fluorescence (FluoroMax-3, Horiba) spectrometers. Corresponding b_{abs} were calculated and were used to estimate AE values of water- and organic-extractable fractions (Hecobian et al., 2010), and to comment on potential BrC sources.

3) Air mass trajectory clusters and Concentration Weighted Trajectories (CWTS)

To identify aerosol transport pathways and potential source sectors over this region, we calculated daily wind backward trajectories using GDAS meteorological data and the HYSPLIT transport and dispersion model (https://www.ready.noaa.gov/HYSPLIT.php). HYSPLIT was run for 96 hours backward at a starting height of 100 m to calculate daily trajectories followed by clustering based on standard protocol. Subsequently, BC, b_{abs}, $b_{abs(BrC)}$ and AE_{BrC} values were apportioned to each cluster. Directional gradients of source contributions were established by calculating concentration weighted trajectories (CWTs) for BC, b_{abs}, $b_{abs(BrC)}$ and AE_{BrC} (TrajStat; http://www.meteothinker.com/).

RESULTS AND DISCUSSIONS

1) Diurnal variations of BC and relative contributions of Fossil Fuel vs Biomass burning

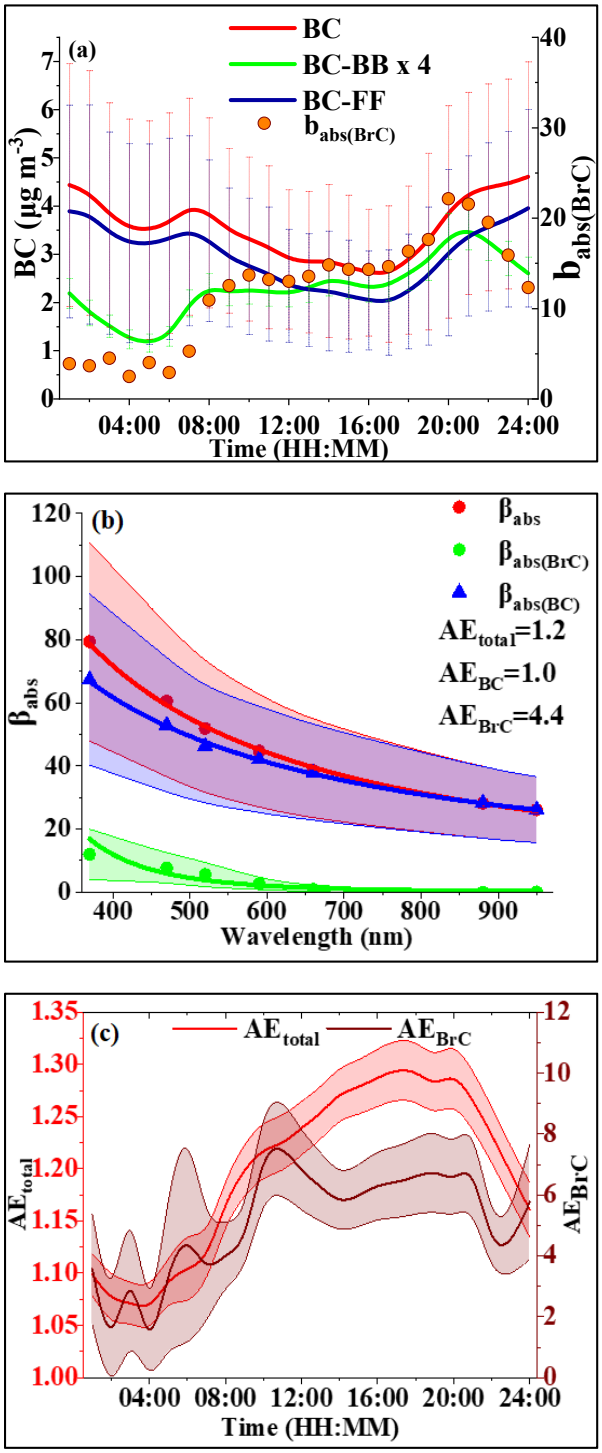
Daily averaged BC concentration for the study period varied from 0.9-7.5 µg m^{-3}, with an overall mean of 3.6 ± 2.0 µg m^{-3}. BC levels were significantly higher (p<0.01) during nighttime (mean: 4.1 ± 1.9 µg m^{-3}) compared to daytime (mean: 3.1 ± 1.3 µg m^{-3}), possibly due to increased residential fuel use emissions, and accumulation resulting from lower nocturnal mixing depths. The diurnal

profile of BC (Fig. 1a) shows an increasing trend after 1700 h lasting till 0200 h, and a secondary peak at 0700-0800 h. Based on results of the two-component mixing model, fossil fuel use is responsible for the overwhelming majority (83%) of the observed BC levels, and this component (BC-FF) tracks the total BC profile very well. It therefore appears that the secondary BC peak at 0700-0800 h is related to morning traffic even though the site is well away from major roads. The post-evening increasing trend of BC is also reproduced by the BC-FF component, possible due to increased nighttime movement of diesel trucks on the National Highway around 1.5 km away. The biomass burning component (BC-BB), on the other hand, contributes 17% to total BC, and shows a distinctly different diurnal profile. There is a notable rise in BC-BB during 0600-0800 h, possible from morning cooking activities, and a much larger peak at 2100 h followed by a decline, suggesting enhanced residential fuel use during the evening.

2) Time-resolved BrC light absorption characteristics

The overall aerosol b_{abs} shows a similar wavelength dependence (AE =1.2, Fig. 1b) as pure BC (AE = 1). Extrapolating b_{abs} for BC to lower wavelengths gives an estimate of BrC absorption in the UV-Vis region. The $b_{abs(BrC)}$ at 370 nm is used as a proxy of total BrC absorption, and its diurnal variation is shown in Fig. 1a. It is clear that $b_{abs(BrC)}$ follows a similar hourly profile as BC-BB, suggesting co-emission. The high overall mean AE_{BrC} (4.4, Fig. 1b) with notable peaks (AE_{BrC} = 4-6.5) during 0600 and 2100 h (Fig. 1c) also strongly support a biomass burning

Figure 1: Diurnal variation of BC, fossil-fuel and biomass burning (×4) BC, and babs(BrC) (a); wavelength dependence of total, BC and BrC absorption (b); total and BrC AE (AEtotal, AEBrC) (c).

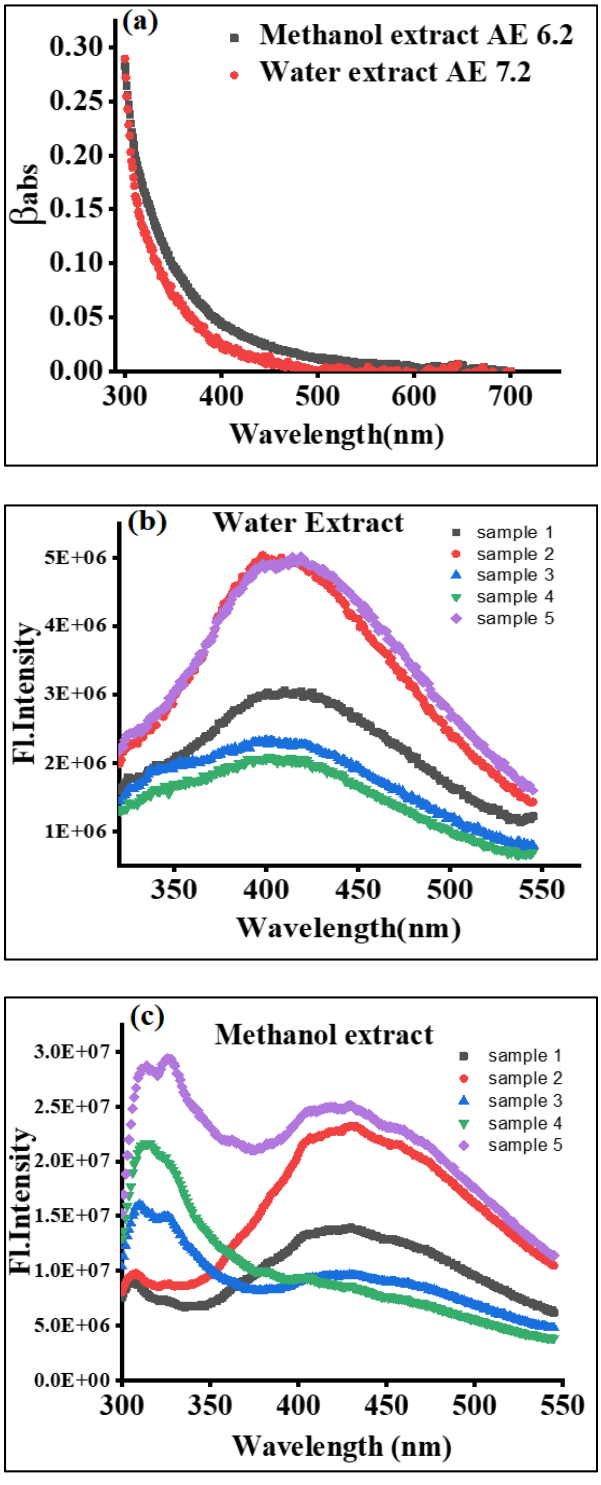


source (Hecobian et al., 2010). This might indicate that smoldering combustion of biofuels in the residential sector produce substantial amounts of BrC chromophores along with BC. Interestingly, the hourly $b_{abs(BrC)}$ profile shows a slowly increasing trend during afternoon hours, which is mirrored by a AE_{BrC} peak of ~7.5 at 1100-1200 h. This possibly suggests secondary BrC formation from atmospheric processes in the afternoon as a consequence of increased emissions of biogenic volatile organic compounds in response to heat stress followed by photochemical oxidation in the presence of oxidants (OH, O_3, etc.). Overall, the relative contributions of BrC to total and BC-associated light absorption were considerable (15% and 18%, respectively, at 370 nm), which establishes that BrC is a significant component of light absorbing aerosol in the eastern IGP.

3) Optical properties of aerosol extracts

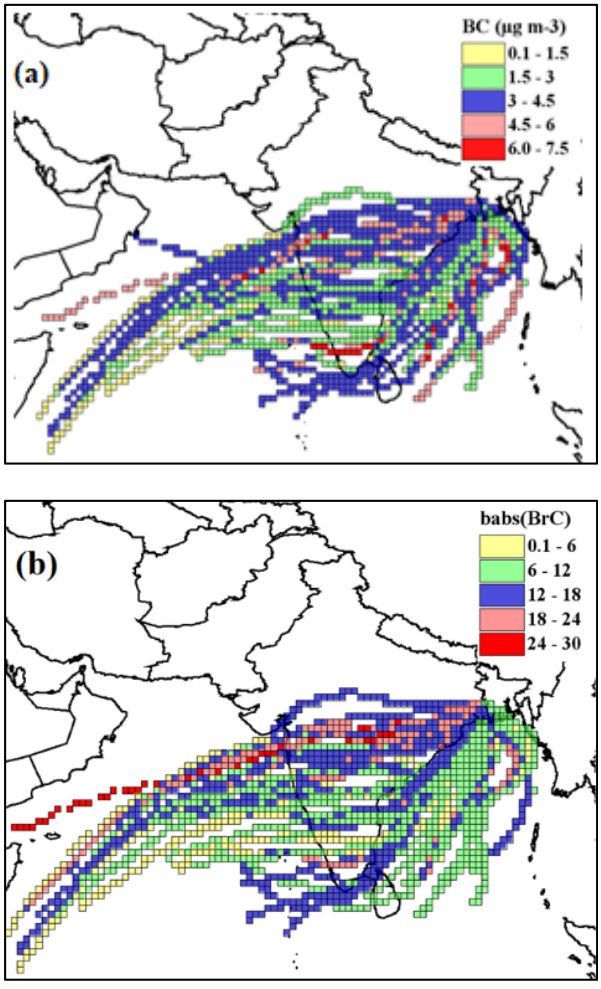
UV-Vis absorption for water and organic extracts were converted to corresponding b_{abs}, and were used to estimate corresponding AE (Fig. 2a). The averaged AE for the water extracts was 7.2, which confirms the presence of water soluble BrC chromophores. Previous studies have reported AE values of ~7 for aqueous extracts of water-soluble humic like substances (HULIS) from biomass burning plumes and fresh secondary organic aerosol (SOA) (Hecobian et al., 2010 and references therein). In comparison, methanol extracts showed an averaged AE of 6.2. Fluorescence spectra for the aqueous extracts (Fig. 2b) showed a strong peak at ~420 nm, similar to that observed for aqueous extracts of HULIS with poly-conjugated structures (Varga et al.,

Figure 2: Optical characteristics of aqueous and organic extracts of PM2.5: a) babs-λ relationship for UV-Vis; b) fluorescence spectra of water extract; c) fluorescence spectra of methanol extract.



2001). For organic extracts (Fig. 2c), the fluorescence intensity was elevated and the peak at ~420 nm was broader, suggesting that a substantial fraction of aerosol chromophores are water-insoluble. Overall, this chemical-optical characterization of aerosol liquid extracts confirm a substantial presence of organic chromophores, and supports the conclusions from *in situ* optical measurements presented in the previous section.

Figure 3: CWT plots of BC (a) and babs(BrC) (b) for the study period.



4) Potential source sectors and aerosol age

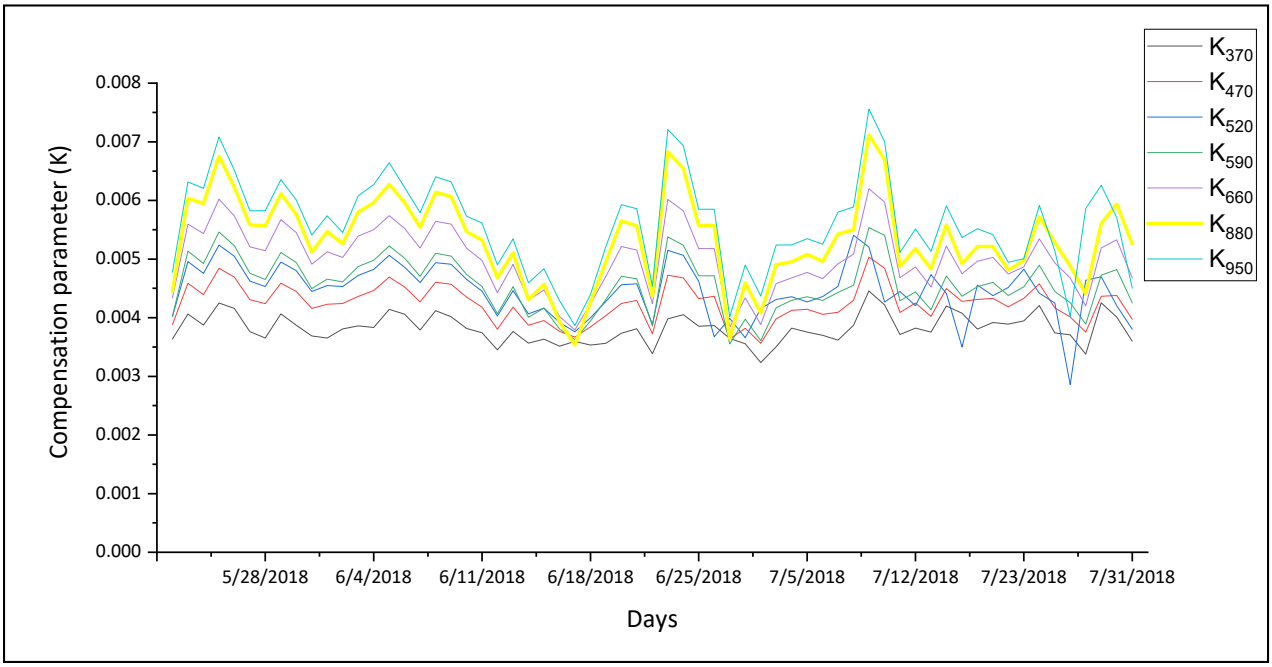
The majority of air masses arrived from the SW during the study period, and two trajectory clusters were identified: i) originating over Bay of Bengal; ii) originating over the Arabian Sea and travelling over central and peninsular India. A CWT plot of BC concentration (Fig. 3a) shows that small amounts of BC were transported across central India and the eastern coast to the study site, with scattered high values potentially associated with power plant clusters in Odisha and Chhattisgarh, industrial centers in peninsular India, and ship tracks over Bay of Bengal. On the other hand, $b_{abs(BrC)}$ showed relatively higher values associated with air mass transport over central India compared to other pathways. Summertime forest fires over central India (especially, Chhattisgarh and coastal Odisha) could potentially be responsible for the high $b_{abs(BrC)}$ (along with BC) observed here (Venkataraman et al., 2006).

An independent estimate of aerosol aging is provided by the real-time calculation of the compensation parameter (k) in the AE-33 Aethalometer. A time series of k for the 7 seven selected wavelengths is presented in Fig. 4. The value of k at 880 nm (k_{880}) varies from 0.004 to 0.007 for summer 2018 in rural West Bengal, indicating an overall predominance of relatively fresh aerosols (Drinovec et al., 2016). This shows that although air masses arrived at the study location via long-range transport (thousands of km), BC aerosols were most likely sourced from the regional vicinity of the study site during summer.

CONCLUSIONS

This pilot study on summertime aerosol optical characteristics in rural West Bengal

Figure 4: Time series of the compensation parameter (k) for the study period.



found that BC in this region has a strong fossil-fuel derived signature mixed with a residential fuel use derived component. Aerosol BrC, predominantly sourced from smoldering biofuel combustion and secondary processes, makes a non-trivial contribution to total aerosol light extinction. Aqueous and organic aerosol extracts show a strong wavelength dependence of UV-Vis absorption, consistent with the presence of polyconjugated HULIS chromophores, in addition to broad fluorescence signatures. There also appears to be a small contribution from regional atmospheric transport to aerosol BC and BrC in rural West Bengal.

ACKNOWLEDGEMENT

Archita Rana and Sayantan Sarkar acknowledge IISER-Kolkata for provision of Integrated Ph.D. fellowship and Start-up Grant, respectively, for the duration of this work.

REFERENCES

- Bond TC, Doherty SJ, Fahey DW, Forster PM, Berntsen T et al. (2013) Bounding the role of black carbon in the climate system: A scientific assessment. J. Geophys. Res. Atmos. 118:5380–5552
- Drinovec L, Gregoric A, Zotter P, Wolf R, Bruns EA, Prevot ASH et al. (2016) Measuring aerosol black carbon age using aethalometers. Conference of the Indian Aerosol Science and Technology Association (IASTA-2016), Ahmedabad, India.
- Hecobian A, Zhang X, Zheng M, Frank N, Edgerton ES and Weber RJ (2010) Water-soluble organic aerosol material and the light-absorption characteristics of aqueous extracts measured over the Southeastern United States. Atmos. Chem. Phys. 10: 5965-5977.

- Mok J, Krotkov NA, Arola A, Torres O, Jethva H et al. (2016) Impacts of brown carbon from biomass burning on surface UV and ozone photochemistry in the Amazon Basin. Sci. Rep. 6, article no.36940.
- Paliwal U, Sharma M and Burkhart JF (2016) Monthly and spatially resolved black carbon emission inventory of India: uncertainty analysis. Atmos. Chem. Phys. 16: 12457-12476.
- Tiwari S, Srivastava AK, Bisht D, Parmita P, Srivastava MK and Attri SD (2013) Diurnal and seasonal variations of black carbon and $PM_{2.5}$ over New Delhi, India: Influence of meteorology. Atmos. Res. 125-126, 50-62.
- Varga B, Kiss G, Ganszky I, Gelencser A and Krivacsy Z (2001) Isolation of water-soluble organic matter from atmospheric aerosol. Talanta 55, 561-572.
- Venkataraman C, Habib G, Kadamba D, Shrivastava M, Leon JF et al. (2006) Emissions from open biomass burning in India: Integrating the inventory approach with high-resolution Moderate Resolution Imaging Spectroradiometer (MODIS) active-fire and land cover data. Global Biogeochem. Cycles 20, GB2013.