Supplementary Information

Refractive Index and Absorption Attribution of Highly Absorbing Brown Carbon Aerosols from an Urban Indian City-Kanpur

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1. Instrumentation

A suit of high-end instruments was deployed for the measurement of optical, chemical and physical properties of atmospheric aerosols in the campaign. A brief description of each instrument is given below.

a. Liquid Waveguide Capillary Cell (LWCC)

LWCC-3250 (World Precision Instrument, Sarasota, FL, USA) is used to measure the light absorption spectra of filter extracts. LWCC has a 500 µL internal sample volume and wavelength range of 250 to 730 nm. The liquid absorption measurement system also includes a light source comprising dual deuterium and tungsten halogen light source (DT-Mini-2, Ocean Optics, Dunedin, FL). The spectrometer used to measure absorption is designated as USB4000 (Ocean Optics, Dunedin, FL). Two optical fiber cables (QP400-2-SR, Ocean Optics, Dunedin, FL) is used to couple the individual parts. Ocean Optics Spectra-Suite software is used to record the absorption at individual wavelengths. More details on LWCC setup and operation is available elsewhere[1].

b. Photo Acoustic Soot Spectrometer (PASS-3)

PASS 3 (Droplet Measurement Technology, CO, USA) is used to measure absorption and scattering coefficients of aerosols[2]. Coefficients were measured with a frequency of 0.5 Hz at three wavelengths as 405 and 781 nm using a flow rate of 1 L min^{-1}. Calibrations were performed on PASS 3 before and midway between the campaign.

c. High-Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS)

HR-ToF-AMS (Aerodyne Inc., USA) is used to measure the mass concentrations and mass size distributions of organic matter[3]. It also measures the same for inorganic species like ammonium, sulfate, nitrate, and chloride. Aerosols were taken as a flow rate of 1.35 cm^3 s^{-1} and get heated at ~ 600 °C. Heated aerosols were ionized using electron ionization technique (70 eV) and then individual mass to charge (m/z) species were measured in V mode of the mass spectrometer. An average spectrum in every 2 minutes is collected. Ionization efficiency calibrations were performed on HR-ToF-AMS before and after the campaign.

d. Single Particle Soot Photometer (SP 2)

SP 2 (Droplet Measurement Technology, CO, USA) is used to measure BC mass and number size distribution parameters[4,5]. SP 2 measures individual BC particle incandescence for mass and size distribution assuming a density of 1.8 g cm^{-3}. SP 2 has a lower and higher detection limits of 70 nm and 500 nm respectively. To include particles outside this limit, a lognormal fit (from 1 nm to 1000 nm) is applied. Calibration of SP 2 is done using aquadag according to standard procedure.

e. Thermal Denuder

Thermal denuder used in this study is custom made with a steel tube of 2.5 cm inner diameter and 120 cm in length. A heating coil controlled by an external temperature controller is wrapped around the periphery of the tube. Throughout the campaign thermal denuder is operated at a constant temperature of 300 ºC. Loss of particle in thermal denuder is characterized by the method given in Cappa et al[6]. Loss of aerosols was calculated using SP 2 were BC mass is measured in both atmospheric and denuded conditions. Since BC is a refractory material, ideally both cases should produce same mass. But due to the loss in thermal denuder, BC measured under thermally denuded conditions will be less than that of atmospheric conditions. So the thermal denuder correction factor is determined by the ratio of thermally denuded BC mass to atmospheric BC mass. The correction factor used in this study is 0.92.

2. Experimental setup

Fig. S1 shows the online experimental setup for measuring atmospheric and thermally denuded optical and physical aerosol properties. SP2 measured aerosols directly from the atmosphere. Aerosols were dried (RH <10%) by passing through a silica gel dryer before sending to other instruments. Drying of aerosols is required to avoid high RH condition errors in PASS 3[2] and to apply a uniform collection efficiency to HR-ToF-AMS[7]. An automatically controlled solenoidal valve is used to switch aerosol flow between the atmosphere and thermal denuder lines with a frequency of 10 minutes. Stainless steel and conducting polyurethane tube were used for connecting different instruments. A zero filter is used to check possible leaks in sampling line.

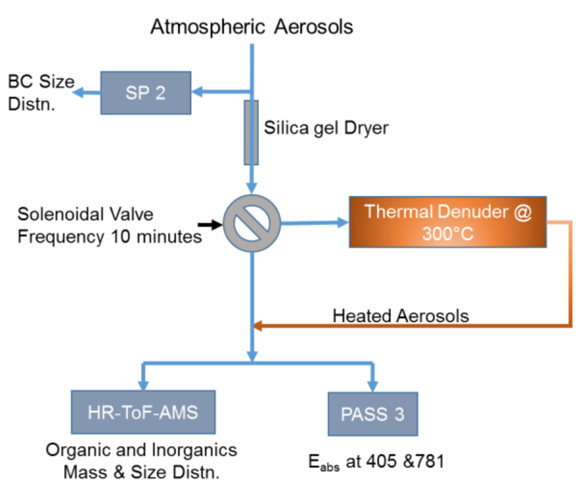

Figure S1. Experiment Setup

3. Modeling methodology

In flow chart diagrams green shade boxes indicate directly measured values, and red shades indicate modeled or calculated values. B_{abs} is the absorption coefficient in (Mm^{-1}) at a particular wavelength. Values in brackets inside boxes indicate the Mie code inputs.

a. Coating Factor (CF) Determination

Procedure followed to determine CF is explained below:

1. Calculate measured enhancement in absorption at 781 nm ($E_{abs\ measured\ 781}$)

$$E_{abs\ measured\ 781} = \frac{B_{abs\ Atm\ 781}}{B_{abs\ TD\ 781}}$$

2. Calculate absorption due to all BC core at 781 nm ($B_{abs\ All\ BC\ core\ 781}$) using Mie theory (Inputs: hourly average all BC size distribution, BC refractive index at 781 nm)
3. Calculate absorption due to externally mixed BC core at 781 nm ($B_{abs\ Externally\ Mixed\ BC\ 781}$) using Mie theory (Inputs: hourly average externally mixed BC size distribution, BC refractive index at 781 nm)
4. Calculate absorption due to internally mixed BC core+shell at 781 nm ($B_{abs\ core+shell\ 781}$) using Mie theory (Inputs: hourly average internally mixed BC size distribution, BC refractive index at 781 nm, CF=1, shell refractive index)
5. Calculate $E_{abs\ model\ 781}$ as $\frac{B_{abs\ core+shell\ 781}}{B_{abs\ core\ 781}}$
6. Iterate CF until $E_{abs\ model\ 781} = E_{abs\ measured\ 781}$
7. Select CF matching the condition in step 6

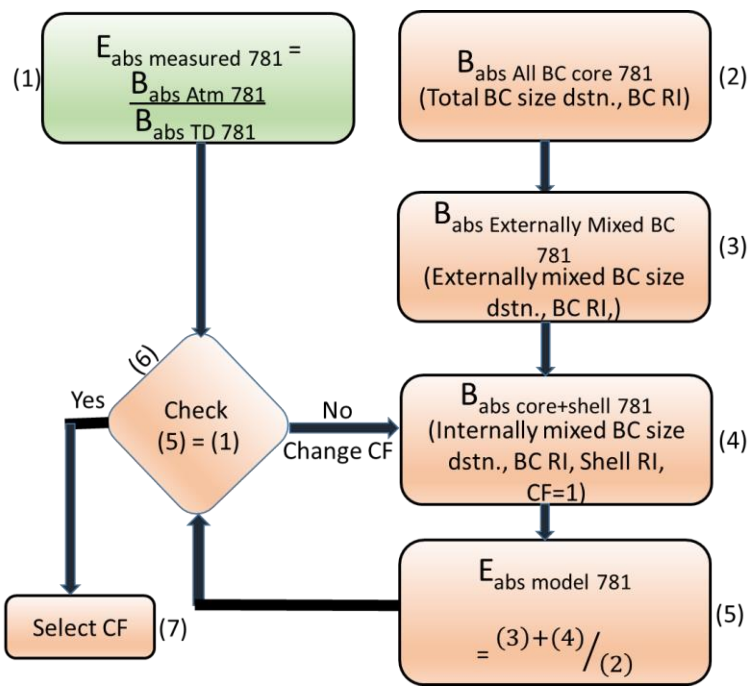

Figure S2a. Modelling Approach for CF determination

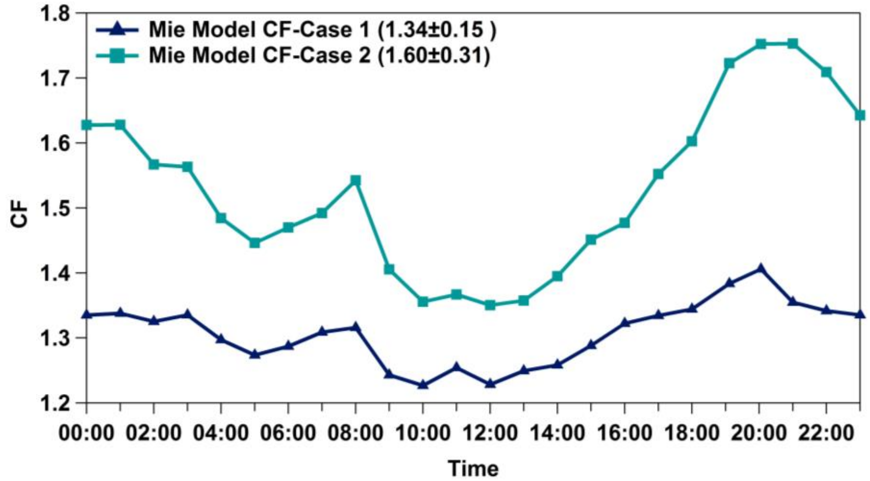

Figure S2b. CF Comparison between Mie Model cases

b. Mass of internally and externally mixed BrC

Once the CF is fixed, next step is to identify the composition of the shell. We assume the shell to be homogeneously mixed with organic and inorganic species having same volume fractions as they existed in the atmosphere. The steps involved in determining the shell composition and calculating the mass of externally mixed BrC is detailed in Fig. S3.

Procedure followed to calculate the mass of internally and externally mixed BrC is listed below.

1. Total aerosol mass = Mass of (BC + organics from AMS + inorganics from AMS)
2. Volume fraction of organics = $\frac{\text{(Mass of organics/density of organics)}}{\text{(Total aerosol mass /particle density)}}$
3. Volume fraction of inorganics = $\frac{\text{(Mass of inorganics/density of inorganics)}}{\text{(Total aerosol mass /particle density)}}$
4. Mass of total OC is calculated from AMS as $\frac{\text{Mass of organic matter (OM) from AMS}}{\left(\frac{OM}{OC}\right) from\ AMS}$
5. Volume fraction of core is calculated as $\frac{1}{(CF)^3}$
6. Mass fraction of core = $\frac{(core\ density)}{(particle\ density)}$ x (volume fraction of core)
7. Volume fraction of shell is calculated as 1- (volume fraction of core)
8. Mass fraction of shell = $\frac{(shell\ density)}{(particle\ density)}$ x (volume fraction of shell)
9. Mass of shell = $\left(\frac{\text{core mass}}{\text{mass fraction of core}}\right)$ x mass fraction of shell

This mass of shell mass contains both organics and inorganics. From this, the mass of OC alone needs to be calculated.

10. Assuming volume fraction of organics and inorganics remains same in atmosphere and shell composition,

$$\text{mass of organics in shell} = \frac{\text{Volume fraction of organics}}{\text{Total volume fraction of organics and inorganics}} \times Mass\ of\ shell$$

11. OC in the shell is calculated using OM/OC ratio from AMS- Same as step 1.
12. Mass of externally mixed OC = Total OC – Internally mixed OC.

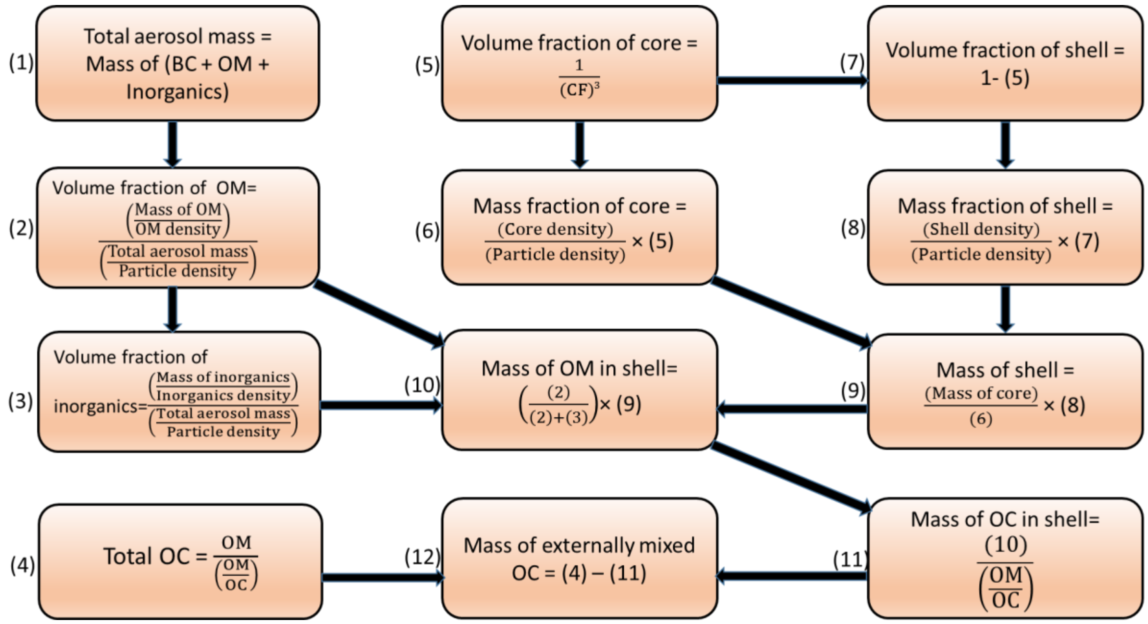

Figure S3. Procedure for Calculating Internal and External Mixing Composition

c. Fraction of absorption due to BC, shell and externally mixed BrC

Atmospheric and denuded absorption measured is used to get the fraction of absorption due to BC. A modeling approach as shown in Fig. S4 is used to further understand the contribution to absorption from lensing effect and externally mixed BrC. Since the shell is a homogeneous mixture of organics and inorganics the net refractive index of the mixture needs to be calculated. We used volume mixing rule to calculate the same.

Steps to calculate the fraction of absorption due to BC, shell and externally mixed BrC

1. Calculate absorption due to all BC core at 405 nm ($B_{abs\ All\ BC\ core\ 405}$) using Mie theory (Inputs: Hourly average all BC size distribution, BC refractive index at 405 nm)
2. Calculate absorption due to internally mixed BC core at 405 nm ($B_{abs\ Internal\ BC\ core\ 405}$) using Mie theory (Inputs: Hourly average internally mixed BC size distribution, BC refractive index at 405)
3. Calculate net refractive index of the shell. Since shell contains both organics and inorganics net refractive index of the shell is calculated using volume mixing rule.
4. Calculate absorption due to internally mixed core+shell at 405 nm ($B_{abs\ BC\ core+shell\ 405}$) using Mie theory (Inputs: Hourly average internally mixed BC size distribution, BC refractive index at 405, CF, net shell refractive index at 405 nm).

5. Calculate Babs due to shell, $B_{abs\ shell\ 405} = B_{abs\ BC\ core+shell\ 405} - B_{abs\ Internal\ BC\ core\ 405}$
6. Calculate a lognormal mass size distribution of OC using standard lognormal equation (Input: Externally mixed OC mass concentration, Standard deviation (1.8 from AMS P-ToF), Diurnal Mass mode diameter (from AMS P-ToF)). Convert lognormal mass size distribution of OC to lognormal number size distribution.
7. Calculate $B_{abs\ Ext\text{-}BrC\ 405}$ using Mie theory (Inputs: OC number size distribution, k_{BrC} at 405).
8. Calculate total $B_{abs\ model\ 405} = B_{abs\ All\ BC\ core\ 405} + B_{abs\ shell\ 405} + B_{abs\ Ext\text{-}BrC\ 405}$
9. Fraction of absorption due to BC is calculated as the ratio of thermally denuded absorption ($B_{abs\ TD\ 405}$) to atmospheric absorption ($B_{abs\ Atm\ 405}$) at 405 nm.

   $f_{Babs\ BC\ 405} = \frac{B_{abs\ TD\ 405}}{B_{abs\ Atm\ 405}}$
10. Fraction of absorption due to shell = $f_{Babs\ shell\ 405} = \frac{B_{\text{abs shell 405}}}{B_{\text{abs model 405}}}$
11. Fraction of absorption due to externally mixed OC =

$$f_{Babs\ Ext-BrC\ 405} = 1 - f_{Babs\ BC\ 405} - f_{Babs\ shell\ 405}$$

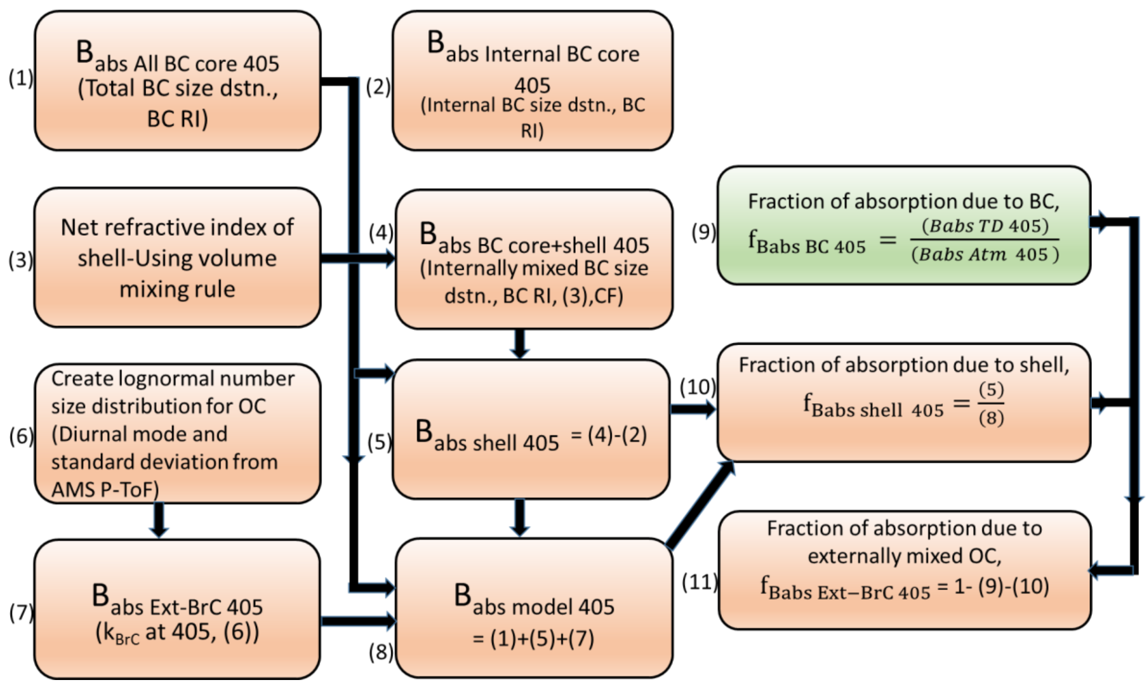

Figure S4. Modeling Methodology for Factorizing Total Absorption

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