Contribution of Particulate Brown Carbon to Light Absorption in the Rural and Urban Southeast US

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Abstract:

Measurements of wavelength dependent aerosol light absorption coefficients were carried out as part of the Southern Oxidant and Aerosol Study (SOAS) during the summer of 2013 to determine the contribution of light absorbing organic carbon (BrC) to total aerosol light absorption in a rural location (Centreville, Al) and an urban area (Atlanta, GA). The light absorption coefficients in the near UV and visible wavelengths were measured for both ambient air, as well as ambient air heated in a thermal denuder to 200 °C to remove the semi-volatile organic compounds. Atlanta measurements show dominance of semi-volatile brown carbon with an average absorption angstrom exponent (AAE) of 1.4 before heating and about 1.0 after heating. In urban Atlanta, a decrease of about ~35 % in the light absorption

coefficient at 370 nm after heating indicates that light absorbing organic compounds are a substantial fraction of the light absorption budget. Furthermore, a considerable increase in the fraction of light absorption by the semi-volatile aerosol occurs during the daytime, likely linked with photochemistry. Measurements at rural Centerville, on the other hand, do not show any major change in AAE with values before and after heating of 0.99 and 0.98, respectively. Overall the results suggest that photochemical aged urban emissions result in the presence of light absorbing BrC, while at rural locations which are dominated by aged aerosol and local biogenic emissions (based on measurements of Angstrom exponents) BrC does not significantly contribute to light absorption.

1 Introduction

Fine aerosols comprise a significant fraction of light absorbing particulate matter that influences the radiative balance of the atmosphere. The quantification of such effects depends on the accuracy of the scattering and absorption properties of aerosols. Light absorbing aerosol is a broad term that includes two optically and chemically distinct groups of carbonaceous species. Black carbon (BC) that typically has morphological and chemical properties similar to that of soot particles shows strong absorption at all visible wavelengths (Andreae and Geleneser, 2006). On the other hand, brown carbon (BrC) is the light absorbing organic matter that prominently absorbs light at shorter wavelengths. Both black and brown carbon tend to absorb light at overlapping wavelengths of solar radiation that makes it more difficult to quantify them using optical properties (Bergstrom et al., 2007; Bond and Bergstrom, 2006). Absorption by individual species is needed to reduce the uncertainties in forcing estimates (Forster et al., 2007). Different sources of absorbing aerosols include vehicular emissions, biomass burning, industrial emissions, humic and humic-like substances (HULIS), tarry materials from combustion and bioaerosols (Andreae and Crutzen, 1997;

Bond, 2007). They are present as a mixture in the atmosphere in unknown proportions depending on the type of sources, and secondary processing.

The absorption by aerosols at visible wavelengths usually follows a power law dependence. This spectral dependence of absorption can be approximated by the Absorption Angstrom Exponent (AAE) (e.g., Absorption is proportional to λ^{-AAE} , where λ is the wavelength)

$$B_{abs} = K\lambda^{-AAE} \quad \text{----- (1)}$$

where $babs_{\lambda}$ is the absorption coefficient at a wavelength of λ . Pure uncoated black carbon has an AAE of about 1 (Bergstrom et al., 2002; Bond and Bergstrom, 2006; Horvath, 1997; Lawless et al., 2004; Rosen et al., 1978) while brown carbon, which preferentially absorbs at shorter wavelengths, can have an AAE significantly greater than 2 (Hoffer et al., 2006; Kirchstetter et al., 2004).

Brown carbon generally is believed to have negligible absorption, particularly with respect to that of BC, at NIR wavelengths. Wang et al. (2011) used this property to quantify the enhancement in absorption due to organic components emitted from wood burning by using a factor, Delta-C which is the difference between BC mass concentrations measured by Aethalometer at 370 nm ($BC_{Aeth,370}$) and 880 nm ($BC_{Aeth,880}$). The brown carbon concentration can also be estimated by subtracting black carbon absorption at near UV wavelengths after assuming an AAE of 1 for black carbon (Kirchstetter et al., 2004). However, this may not be true for internally mixed aerosols. The internal mixing of aerosols can have an AAE from 1 to 1.7 (Gyawali et al., 2009; Lack and Cappa, 2010). Estimation of BrC assuming an Angstrom Exponent of 1 for internally mixed aerosols may lead to its underestimation (Lack and Langridge, 2013). Recent studies on internal mixing of aerosols observed that black carbon aerosol coated with transparent organic or inorganic aerosol components show enhancement in absorption at all visible wavelengths (Schnaiter et al.,

2005; Zheng et al., 2002). This enhancement is caused by the shell acting as a lens that focuses more photons towards the absorbing core than that under external mixing conditions. The lensing effect has also been confirmed by several theoretical and laboratory studies. Lack and Cappa (2010) showed that the lensing effects also depend on the type of coating. A coating by BrC may reduce the lensing effect, i.e. absorption by BC core, compared to a clear coating. Liu et al. (2015) showed enhancement in absorption is a function of morphology, mixing state, coating thickness and the amount of low-volatility and semi-volatile brown carbon. More recent work by Zhang et al. (2016) looking at biomass burning aerosols in Fresno, Ca suggest that BrC plays a more important role in the light absorption budget, although the lensing effect is not entirely negligible (Zhang et al., 2016). It has been suggested that the lensing enhancement could range from 50% to 100% for typical atmospheric conditions (Bond and Bergstrom, 2006). Thus mixing state of absorbing aerosols effects absorption measurements and BC concentrations leading to an exaggeration or understatement in the estimation of radiative forcing from BC. It is also interesting to note that absorption is not always enhanced due to mixing state. When the aerosols are internally mixed, there is an enhancement in absorption. On the contrary, for externally mixed aerosols may have a cooling effect (Raatikainen et al. 2015). However, the effect of mixing state on enhancement is beyond the scope of this paper.

BrC are light absorbing organic compounds. Several studies have been carried out on the role of non-black carbon components in absorption measurements using a photoacoustic soot spectrometer. Cappa et al. (2012) showed enhancement in absorption by urban air masses due to photochemical ageing. They estimated the contribution of brown carbon in absorption using the absorptions at 406 nm and 530 nm. Nakayama et al. (2014), using similar instrument, showed the enhancement in absorption due to lensing effect and BrC. Lack and

Langridge (2013) gave a method to attribute absorption to BC and BrC using AAE by removing the volatile fraction (200 °C) during a biomass burning episode. They showed internal mixing of BC does not alter AAE, but causes a uniform enhancement at all wavelengths. The objective of this paper is to study the role of semi-volatile fraction of absorbing compounds in ambient aerosols on the wavelength dependence of absorption with very different source profiles using a filter-based technique at two locations in the Southeast US. An attempt has been made to quantify the enhancement in absorption by volatile BrC aerosols for these sites.

2 Experimental

2.1 Site Selection:

Absorption caused by the presence of semi-volatile BrC in ambient aerosols can be estimated by heating the ambient aerosols to a temperature high enough to remove the entire semi-volatile fraction. This will remove externally mixed light absorbing organic compounds as well as internally mixed organic compounds present in the form of shells on BC. Experiments were carried out to simultaneously measure BrC absorption by heated (using a thermodenuder at 200 °C) and non-heated aerosols at seven wavelengths ranging from UV to IR at two sites in Southeast USA- Atlanta, GA and Centreville, AL.

2.1.1 Urban- Atlanta, GA

Atlanta is an urban location in Southeast USA. The major sources of absorbing aerosols in Atlanta are dominated by local emissions from mobile sources, power plant emissions, and secondary organic aerosols (SOA) (Blanchard et al., 2011; Kim et al., 2003; Zhang et al., 2011). This study was carried out from May 23-30, 2013. The sampling was carried out in the Ford Environmental Science and Technology (Ford EST) building of Georgia Institute of

Technology located at 33.8 °N, 84.4 °W. The sampling site is 10 m above ground level and about 300 m away from nearest highway.

2.1.2 Clean Rural-Centreville, AL

Sampling was carried out in Centreville, AL, a rural location, from June 4 to July 16, 2013 as a part of Southern Oxidant and Aerosol Study (SOAS). The site is located at 32.9 °N, 87.2 °W and altitude 126 m above MSL. This is surrounded by mixed deciduous (oak-hickory) and loblolly pine trees and is about 50 km south-east of Tuscaloosa. The major sources of emissions are natural biogenic emissions and located far away from anthropogenic sources (Hidy et al., 2014).

2.2 Volatility Measurements:

To study the impact of BrC aerosols on light absorption by filter transmittance-based measurement methods in Southeastern U.S., aerosol volatility measurements were carried out using a themodenuder (Dekati[®]) set at 200 °C. Two Aethalometers (Magee Scientific Inc.) with flow rates of 3 LPM each were connected upstream and downstream of the TD to measure the change in filter transmittance and associated wavelength dependent light absorption, before and after heating to 200°C, respectively. The themodenuder (TD) consists of a 95 cm long heater section with a maximum operating temperature of 300 °C followed by a denuder (adsorber) section. The denuder section removes the vaporized volatile and semi-volatile compounds by adsorption on to the activated charcoal. The sample is then cooled using air or water as the medium. The estimated residence time based on the dimensions of the themodenuder at the operated flowrate was 1.4 s.

Measurement of absorption by suspended particles is becoming more common, however, the

method of inferring BC absorption using filter based techniques, such as with an Aethalometer, is more widespread as they are inexpensive, easy to operate and can run unattended for long periods of time. One drawback to point out is that the Aethalometer collects particles on a filter, and therefore it is likely that particle morphology is not maintained after deposition. Therefore, coatings that may enhance light absorption (i.e. the lensing effect) may be compromised and do not enhance absorption as under atmospheric conditions. Hence ambient measurements of light absorption coefficient can be viewed as lower limit estimates. The Aethalometer estimates the wavelength dependent absorption coefficients at seven wavelengths ranging from UV (370 nm) to near Infrared (950 nm) of light absorbing species by measuring the attenuation using the Lambert-Beer law for the particles deposited on a quartz filter (Hansen et al., 1984). The mass concentration of optically absorbing species (BC_{Aeth}) is later derived from absorption coefficients using wavelength specific mass attenuation cross sections. This wide range of wavelengths can be used to estimate the source contribution of light absorbing carbon (Lack and Langridge, 2013; Wang et al., 2011).

It is worth noting that these filter-based techniques may introduce significant bias in the abundance of organic aerosols and light absorbing carbon. Bias was seen both for laboratory and ambient aerosols (Lack et al 2008, Cappa et al. 2008). These studies indicate that filter based measurements overestimate light absorption by aerosols when the organic loading is large. For urban locations, a positive bias of up to 50% may be expected (Lack et al. 2008). This has been considered to evaluate the possible uncertainty in the data analysis for this study.

Data analysis:

BC_{Aeth} derived from the Aethalometer needs to be corrected for systematic errors. The most

common errors in BC_{Aeth} estimation are due to filter loading (noted above) and multiple scattering by filter fibers (Weingartner et al., 2003). The measured BC_{Aeth} were corrected for loading effects using Virkkula et al. (2007). A correction factor was calculated for each filter spot so that the BC_{Aeth} become continuous over the spot change.

$$k_i = \frac{BC_{Aeth,0}(t_{i+1,first}) - BC_{Aeth,0}(t_{i,last})}{ATN(t_{i,last}).BC_{Aeth,0}(t_{i,last}) - ATN(t_{i+1,first}).BC_{Aeth,0}(t_{i+1,first})} \quad \text{---- (2)}$$

$$BC_{Aeth,corrected} = (1 + k.ATN)BC_{Aeth,0}^{183} \quad \text{---- (3)}$$

Where $t_{i,last}$ is the last data of measurement for the filter spot i and $t_{i+1,first}$ is the first data of measurement for the next filter spot $i+1$. The values of k_i obtained from equation (2) will be different for each filter spot. $BC_{Aeth,0}$ and $BC_{Aeth,corrected}$ are the measured BC values before and after correction. The average change from measured BC_{Aeth} after correction obtained from equation (3) for Atlanta and Centreville are 35% and 18%, respectively.

This correction is somewhat similar to the algorithm applied in the ‘dual spot’ aethalometer (Drinovec et al. 2015, Virkkula et al. 2015). The correction factor ‘ k ’ has been shown to depend on single scattering albedo (SSA) and backscatter fraction (Virkkula et al., 2015). A larger backscatter function results in a larger correction factor, and the other way for SSA.

The corrected BC_{Aeth} values at all measured wavelengths were used for the calculation of AAE. Each set of data was checked for wavelength dependence by plotting $\log(\lambda)$ vs $\log(B_{abs})$. Datasets with a linear regression R^2 less than 0.9 were discarded. Such discarded points accounted for less than 5% of the entire dataset. The remaining data was used to calculate real time AAE using equation 1. The standard error of slope (i.e. AAE) was

estimated that was later expressed in terms of percentage. The estimated uncertainty in AAE was 8%. The uncertainty in the black carbon measurement was 10% (Babu and Moorthy, 2002) and an assumed positive bias of 50 % due to multiple scattering (Lack et al., 2008)

3 Results:

3.1 Estimation of Thermodenuder Particle Losses:

Two collocated seven-wavelength Aethalometers (Magee Scientific, Inc.) sampling ambient fine aerosol were compared against each other for BC_{Aeth} . This wavelength spectrum includes the near UV wavelength ranges where BrC absorbs and also the red and IR wavelengths at which BrC does not absorb. The sampling was carried out continuously for about 10 days from May 10-20, 2013 on the roof of the Ford EST building, Atlanta, GA. The time series of BC_{Aeth} measured at two extreme wavelengths- 370 nm (UV) and 880 nm (Near IR) are shown in Figure 1(a) and Figure 1(c), respectively. The BC mass concentrations were within 10% for both Aethalometers at both wavelengths, as also seen in the scatter plots in Figure 1(b) and 1(d). There was no statistically significant difference between the BC_{Aeth} from the aethalometers (two tailed paired t-test, $p=0.49$ at 370 nm and $p=0.51$ at 880 nm).

When the thermodenuder (TD) is connected in line before the Aethalometer, there could be losses in absorption due to wall deposition as a result of diffusion, sedimentation and thermophoresis (Lee et al., 2010; Stevanovic et al., 2013). To determine the losses of absorbing aerosols due to diffusion and sedimentation inside the thermodenuder under ambient conditions (i.e., denuder was not heated), BC_{Aeth} were measured upstream and downstream of the thermodenuder for 3 days from May 21-24, 2013 and compared. Figure 2 (a and b) show the time series of Aethalometer estimated BC_{Aeth} at two wavelengths; 370 nm and 880 nm. The losses in absorption were found to be $32\pm3\%$ at 370 nm and $24\pm6\%$ at 880

nm. These loss estimates were used for the correction of absorption data measured for the heated aerosol experiment. The corrected BC_{Aeth} after the TD agree within $10\pm6\%$ to the ambient concentrations under TD off conditions. Statistically, there was no significant difference between the BC_{Aeth} measured from the aethalometers after correcting for losses (two tailed paired t-test, $p=0.08$ at 370 nm and $p=0.24$ at 880 nm).

Thermophoretic losses may occur inside the heated thermodenuder. These losses are more dependent on temperature than aerosol size. To estimate the losses in the heated thermodenuder, laboratory generated NaCl aerosol was passed through it keeping the temperature of TD as 100 °C. The size distributions before and after heating were measured using a Scanning Mobility Particle Sizer (SMPS) as shown in Figure 3. The total particle losses were estimated to be about 25% at 100 °C. This figure gives the combined losses due to sedimentation, wall deposition and thermophoretic losses inside the TD. Olson et al. (2015) using the same thermodenuder estimated combined losses of around 25% at 200 °C for NaCl particles. Therefore, the combined losses (i.e., denuder heated) were similar to losses when not heated, indicating thermophoretic losses were negligible.

3.2 Estimated BC_{Aeth} Mass Concentrations at UV and NIR wavelengths:

Semi-volatile organic aerosols and their mixing with light absorbing aerosols affect the absorption measurements by filter transmittance based techniques. To study this effect, one Aethalometer directly measured the wavelength dependent light absorption coefficient of ambient $PM_{2.5}$ aerosols and the second Aethalometer measured the absorption after the same $PM_{2.5}$ aerosols were heated to remove the semi-volatile components. Therefore, the estimated light absorption coefficients and associated BC_{Aeth} measured after heating can be attributed to

light absorbing black carbon during the period. This section discusses the absorption properties of aerosols before and after heating for two locations representing different particulate source characteristics.

The study was carried out on the roof of Ford EST from May 24-30, 2013 in Atlanta and from June 4-July 16, 2013 in Centreville, AL. Past studies show that major sources of fine fraction of aerosols in Atlanta are sulfate-rich secondary aerosol, vehicle emissions, secondary aerosols from biogenic VOCs and wood smoke (Kim et al., 2003). Absorbing aerosols from these sources comprise both BrC and BC (Liu et al., 2013; Zhang et al., 2011).

3.2.1 Atlanta, GA:

Simultaneous measurements of BC were carried out before (Labeled as ‘Ambient’) and after heating to 200 °C (Labeled as ‘TD’). Time series of BC_{Aeth} measured before and after heating by two extreme wavelengths- 370 nm and 880 nm are shown in Figure 4(a) and 4(b), respectively. Losses in absorption are seen at both wavelengths after heating. The losses are more pronounced at 370 nm indicating the loss of semi-volatile compounds. The ratio of absorption at 370 nm by ambient aerosol to absorption by TD aerosol gives the contribution in absorption due to semi-volatile compounds ($Ratio_{Amb/TD}$). These compounds could be BrC or possibly non-absorbing transparent semi-volatile coatings on BC. The mixing state of these compounds with BC is not known during this study. Figure 4(c) shows the time series of $Ratio_{Amb/TD}$ for 200 °C. $Ratio_{Amb/TD}$ close to 1 indicates no decrease in absorption values after heating and therefore, indicates lack of semi-volatile absorbing aerosols. Furthermore, $Ratio_{Amb/TD}$ greater than 1 indicates the presence of semi-volatile light absorbing compounds that are removed by the thermo-denuder. Figure 4(d) shows histograms of $Ratio_{Amb/TD}$ at 370 nm and 880 nm. Histograms of $Ratio_{Amb/TD}$ at 370 nm show a clear shift towards higher

values compared to the $\text{Ratio}_{\text{Amb/TD}}$ at 880 nm, consistent with contributions from BrC which only absorbs at 370 nm. The $\text{Ratio}_{\text{Amb/TD}}$ greater than 1 at 880 nm could be attributed to the losses inside TD at 200 °C. Internal mixing of aerosols amplifies the absorption at all measured wavelengths. A BC core with a semi-volatile and transparent shell could amplify the measured absorption uniformly across all wavelengths. Volatilization of the shell could lead to a drop in BC_{Aeth} at all measured wavelengths leading to $\text{Ratio}_{\text{Amb/TD}}$ greater than 1 at $\text{BC}_{\text{Aeth},880}$. Schnaiter et al. (2005) showed that the amplification factors ($\text{Ratio}_{\text{Amb/TD}}$) for internally mixed aerosols range from 1.8 to 2.1. This depends on several factors including core and shell thickness. Bueno et al. (2011) showed this dependence of $\text{Ratio}_{\text{Amb/TD}}$ as a function of shell thickness. This could also be due to the losses inside the thermodenuder due to wall losses or thermophoretic losses. So the losses at 880 nm, even though a very small fraction, should be used with caution.

Diurnal variations of BC_{Aeth} mass concentration at 370 nm and 880 nm at ambient conditions and after the TD at 200 °C are shown in Figure 5. The hourly standard errors in the BC_{Aeth} concentrations are shown as error bars. A peak in BC_{Aeth} at both 370 nm and 880 nm is seen around 0800 hrs and coincides with the morning peak traffic. Average BC_{Aeth} mass concentration measured at 370 nm is about 20% higher than that measured at 880 nm. Interestingly, the difference between $\text{BC}_{\text{Aeth},370}$ and $\text{BC}_{\text{Aeth},880}$, may be caused by BrC absorption (Wang et al., 2011) that is higher during the daytime compared to that at night. The higher $\text{BC}_{\text{Aeth},370}$, during daytime during the summer likely occurs due to the presence of secondary compounds formed due to photochemical reactions (Kim et al., 2003). The formation of secondary BrC could be due to multiphase reactions involving gas, particulate and aqueous phases. There have been several studies on the formation mechanisms of secondary brown carbon aerosols and their reaction timescales (Bones et al., 2010; Casale et

al., 2007; Esteve and Nozière, 2005; Jacobson, 1999; Laskin et al., 2010; Limbeck et al., 2003; Nguyen et al., 2012; Powelson et al., 2013). Some of these reactions are driven by photochemistry and elevated concentrations of $\text{NH}_3/\text{NH}_4^+$ and secondary organic aerosols (SOA), attributed to anthropogenic emissions (Updyke et al., 2012). This increase in photochemical SOA was also observed over several urban locations in Southeastern US including Atlanta (Hecobian et al., 2010; Hennigan et al., 2009). After heating, BC_{Aeth} mass concentrations at both the wavelengths are similar. This indicates that the absorbing BrC aerosols mixed internally or externally, that tend to amplify the measured BC_{Aeth} concentration at 370 nm are removed after heating to 200 °C

Diurnal variation of AAE for Atlanta is shown in Figure 5(c) along with error bars that represent the hourly standard errors. AAE ranged between 1.1 and 1.5 for ambient aerosols during the period of study. AAE above 1 indicates the presence of UV absorbing BrC aerosols. After heating to 200 °C, the light absorbing semi-volatile fraction of the aerosols was removed bringing the AAE near to 1 (Figure 5(c)), similar to the theoretical value for BC (Russell et al., 2010). When the BC aerosols are coated with non-absorbing transparent shell, there is enhancement in BC_{Aeth} measurements at all measured wavelengths (Bond 2006). This keeps the AAE similar to the actual AE of BC but may overestimate the BC_{Aeth} values in ambient aerosols. However, if the shell is of BrC, the enhancement might be reduced leading to a decrease in enhancement of absorption depending on the wavelength of absorption, thickness of wavelength and imaginary refractive index (Lack and Cappa, 2010).

3.2.2 Centerville, AL:

Figure 6 shows the time series of BC mass concentration measured at 370 nm (Figure 6a) and 880 nm (Figure 6b) at Centerville, AL. The BC_{Aeth} concentrations remained similar before

and after heating to 200 °C, unlike Atlanta. This indicates that light absorbing aerosols in the rural southeast have low volatility, and/or the semi-volatile organic compounds present are non-absorbing. The ratio of non-heated (ambient) to heated BC_{Aeth} mass concentrations stayed around 1 throughout the sampling duration except for a few peaks as seen in Figure 6(c). More than two-thirds of these ratios at 370 nm lie between 1 and 1.3 for both wavelengths, as seen from the histogram in Figure 6(d). Unlike Atlanta, Centerville data shows weak enhancement in BC_{Aeth} mass concentration $\pm$ standard errors during nighttime at both the wavelengths (Figure 7a and 7b). This could also be seen as a decrease in BC concentrations during daytime expansion of the planetary boundary layer. Xu et al. (2015) showed after adjusting the organic aerosol concentration for boundary layer height, a profound increase in the concentrations of organic aerosols during noon indicated the role of photochemical reactions in their formation. Hidy et al. (2014) showed a peak in organic carbon mass concentrations around 9 am in Centerville during the same period of sampling as this study. A dip in absorption values at that hour of day indicates that the organic carbon in Centerville does not contribute much towards absorption. An average Angstrom exponent of 1 before and after heating (Figure 7c) indicates the absence or very low concentrations of absorbing brown aerosols. The diurnal plot for the $Ratio_{Amb/TD}$ also shows a flat trend as seen in Figure 7d. Low levels of BrC at Centerville agree with the findings of Washenfelter et al. (2015). For the same study, they found the BrC contributed $9 \pm 9\%$ to the light absorption coefficient at 365 nm. In that study, a direct measurement of BrC in aerosol liquid extracts was used, instead of inferring BrC from Angstrom exponents.

3.3 Contribution of Brown carbon to light absorption:

Absorption attributed to semi-volatile light absorbing BrC can also be ascertained by using the wavelength dependence curve of the light absorption coefficient (Lack and Langridge,

2013). Figure 8 shows the absorption coefficient as a function of wavelength for Ambient and TD conditions for Atlanta (8a) and Centreville (8b). Both curves follow a power law dependence of absorption coefficient with wavelength with a R^2 around 1. The estimated average AAE for ambient aerosols is 1.4 and that of the TD is 1.06 for Atlanta. The error bars in the plots are the standard errors of absorption estimated for the entire duration of the study. Power law fits for ambient and TD wavelength dependent absorption values give the AAE greater than 1 for ambient due to the presence of semi-volatile BrC that was removed after heating, bringing the AAE to 1. The enhancement in absorption due to the presence of semi-volatile BrC can be quantified using the absorption measured before and after the removal of semi-volatile BrC. Effective absorption by BrC can be quantified by subtracting the absorption due to black carbon and internal mixing, if any, from the total absorption at 370 nm after adjusting for the losses in absorption at 880 nm due to thermophoresis or the removal of transparent semi-volatile shells in the BC after heating. AAE values range from 0.8 to 1.4 can be due to internal mixing of organic compounds and freshly emitted absorbing aerosols (Lack and Langridge, 2013). However, in this study BrC absorption at 370 nm led to an AAE of 1.4 in Atlanta, as seen from Figure 8.

Heating the aerosols to 200 °C removed most of the semi-volatile compounds that enhance absorption at lower wavelengths. Losses in absorption were seen at both extremes of the wavelengths measured. Losses observed in 880 nm could be due to the removal of an organic shell coating that contains light absorbing organic compounds as well as other light scattering compounds (i.e. major ions).

The real time quantification of absorption by BrC using the above technique is shown for Atlanta in Figure 9. The estimated BrC absorption at 370 nm is the total absorption at 370 nm

(before TD) less the absorption caused by BC, after TD, at 370 nm, which is the absorption obtained after heating to 200 °C. The losses in absorption at 880 nm are also accounted for during these calculations. (Please refer to Figure 8a for pictorial explanation). The time series (Figure 9a) and diurnal variation (Figure 9b) shows the absorption attribution to BrC. The amount of absorption by black carbon aerosols is shown in black as 'BC abs at 370 nm'. This is the absorption measured after removing the semi-volatile aerosols using a TD. BrC absorption is shown in grey, color which is the absorption caused only due to brown carbon absorption at 370 nm. The diurnal variation of these data in Figure 9b shows a significant fraction of BrC throughout the day. For the sampling during the fraction of BrC to BC absorption at 360nm varied between 0.24 and 0.83 in Atlanta. Episodes of high absorption due to BrC are seen on May 27 and May 28, 2013. For Centerville, the AAE before and after heating were similar. Therefore, estimation of BrC using their optical and volatility properties is not carried out for Centerville as BrC levels appear to be too low to quantify with this method (Lack et al., 2013).

4 Summary and conclusions:

Sampling for aerosol absorption was carried out in an urban setting (Atlanta, GA) and a rural location (Centerville, AL) during the summer of 2013 as a part of Southern Oxidant Aerosol Study (SOAS). Wavelength dependent absorption from 370 nm to 950 nm was obtained simultaneously for ambient aerosol as well as aerosol heated to 200 °C to determine the contribution of semi-volatile BrC to the total aerosol absorption. Absorption Angstrom Exponent (AAE) was estimated for the measured absorption from 370 nm to 880 nm. In Atlanta, AAE for ambient aerosol was found to be around 1.4 that decreased to 1.1 after heating. This decrease was due to the removal of semi-volatile light absorbing brown carbon inside the Thermodenuder (TD). Heating the aerosol to 200 °C led to a decrease in the

absorption coefficient by about 35% at 370 nm in Atlanta. Interestingly, there was a decrease in the absorption coefficient by ~20% at 880 nm after heating. This decrease could be due to removal of transparent coating in ambient aerosol. Considering black carbon to be same as TD absorption and adjusting for the losses in absorption at 880 nm, the real time variation of brown carbon for ambient aerosol is estimated. The ratio of estimate BrC to BC absorption at 370 nm varied between 0.24 and 0.83. A higher ratio was observed during the daytime due to urban emissions and secondary compounds formed due to photochemistry.

For Centreville, the AAE values before and after heating remained similar. But, a decrease in absorption was seen after heating by about 20% at both extremes thereby keeping the AAE similar under both conditions. This indicates that light absorbing aerosols in Centreville have low volatility, and/or the semi-volatile organic compounds present are largely non-absorbing.

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Figure

Figure 1: BC mass concentrations measured using Aethalometers sampling side-by-side at room temperature at (a) 370 nm and (b) 880 nm

Figure 2: BC mass concentrations measured using Aethalometers in the upstream and downstream of thermodenuder at room temperature at (a) 370 nm and (b) 880 nm

Figure 3: Number size distribution of aerosolized NaCl before and after heating to 100 °C to study the losses inside thermodenuder

Figure 4: Time series of BC mass concentrations measured before and after thermodenuder at 200 °C at (a) 370 and (b) 880 nm in Atlanta. (c) shows the time series of ratio of BC mass concentration before and after thermodenuder. (d) shows the normalized frequency of ratio at 370 nm and 880 nm.

Figure 5: Diurnal variation of BC mass concentration measured using Aethalometer before and after thermodenuder at 200 °C in Atlanta at (a) 370 nm and (b) 880 nm. (c) and (d) show the diurnal variations of Absorption angstrom exponent and ratio of BC mass concentration at ambient to thermodenuder for Atlanta respectively.

Figure 6: Time series of BC mass concentrations measured before and after thermodenuder at 200 °C at (a) 370 and (b) 880 nm in Centerville. (c) shows the time series of ratio of BC mass concentration before and after thermodenuder. (d) shows the normalized frequency of ratio at 370 nm and 880 nm.

Figure 7: Diurnal variation of BC mass concentration measured using Aethalometer before and after thermodenuder at 200 °C in Centerville at (a) 370 nm and (b) 880 nm. (c) and (d) show the diurnal variations of Absorption angstrom exponent and ratio of BC mass concentration at ambient to thermodenuder for Centerville respectively.

Figure 8: Wavelength dependence of average absorption over (a) Atlanta and (b) Centerville before (Ambient, shown as black line) and after (TD, shows as grey solid line) heating to 200 C. The enhanced absorption values at 370 nm in Atlanta are attributed to BrC absorption. The dashed line shows the corrected TD after adjusting for the losses at 880 nm.

Figure 9: (a) Time series of estimated absorption in brown carbon at 370 nm over Atlanta. Black line shows the absorption at 370 nm after heating and Grey line shows the estimated BrC absorption at 370 nm, which is the Ambient absorption less TD absorption at 370 nm (b) Diurnal variation of BrC absorption at 370 nm over Atlanta averaged for the entire study duration.