Chemical characteristics of brown carbon in atmospheric particles at a suburban site near Guangzhou, China

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Abstract:
Light-absorbing organic carbon (or brown carbon, BrC) in atmospheric particles has received much attention for its potential role in global radiative forcing. While a number of field measurement campaigns have differentiated light absorption by black carbon (BC) and BrC, the chemical characteristics of BrC are not well understood. In this study, we present co-located real-time light absorption and chemical composition measurements of atmospheric particles to explore the relationship between the chemical and optical characteristics of BrC at a suburban site downwind of Guangzhou, China from November to December 2014. BrC and BC contributions to light absorption were estimated using measurements from a seven-wavelength aethalometer, while the chemical composition of non-refractory PM$_1$ was measured with a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Using the Absorption Angstrom Exponent (AAE) method, we estimated that BrC contributed 23.6% to the total aerosol absorption at 370 nm, 18.1% at 470 nm, 10.7% at 520 nm, 10.7% at 590 nm, and 10.5% at 660 nm. Biomass burning organic aerosol (BBOA) has the highest mass absorption coefficient among sources of organic aerosols. Its contribution to total brown carbon absorption coefficient decreased but that of low-volatility oxygenated organic aerosol (LVOOA) increased with increasing wavelength, suggesting the need for wavelength-dependent light absorption analysis for BrC in association with its chemical makeup. Clear correlations of N-containing ion fragments with absorption coefficient were observed. These correlations also depended on their degrees of unsaturation/cyclization and oxygenation. While the current study relates light absorption by BrC to ion fragments, more detailed chemical characterization is warranted to constrain this relationship.
Introduction:

Atmospheric particles participate considerably in the global climate direct effect via their light-scattering (e.g., sulfate) and/or light-absorbing components (e.g., black carbon, BC). BC is the major contributor to light absorption that increases the atmospheric energy budget, but the contribution of brown carbon (BrC) cannot be ignored. The BrC absorption contribution to total aerosol forcing can reach 20–50% over regions dominated by seasonal biomass burning and biofuel combustion (Feng et al., 2013). BrC absorbs light primarily at UV and short visible wavelengths, absorbing negligible amounts at long visible wavelengths, while BC absorbs strongly throughout the visible spectrum (Andreae and Gelencsér, 2006; Bergstrom et al., 2007; Bond and Bergstrom, 2006). In global climate models, the direct radiative forcing of organic aerosols at the top of atmosphere can shift from cooling (−0.08 W m⁻²) to warming (+0.025 W m⁻²) when strong BrC absorption is included (Feng et al., 2013). However, uncertainties in the sources, formation, chemical composition, and absorption properties of BrC hinder more accurate estimations of radiative forcing induced by atmospheric particles.

BrC is operationally defined and has many chemical constituents, which makes chemical characterization quite challenging. Both primary and secondary organic aerosols can act as BrC (Laskin et al., 2015). For example, biomass burning organic aerosol (BBOA) has been identified as a contributor to BrC in rural areas in the southern United States (Di Lorenzo et al., 2017; Washenfelder et al., 2015), while coal combustion organic aerosol (CCOA) contributes substantially to BrC during winter in Beijing (Yan et al., 2017). Species from secondary formation processes, such as humic-like substances (HULIS) formed by in-cloud processing (Rinco et al., 2009), species from gas-phase photo-oxidation of volatile organic compounds (VOCs) in the presence of NOₓ, and species from reactions between carbonyl compounds and ammonia in the aqueous film at the particle surface, can also contribute to BrC (Gen et al., 2018; Laskin et al., 2010; Liu et al., 2015). Highly conjugated organics, nitro-aromatic compounds, imidazoles, and other N-heterocyclic compounds have been found in BrC (Laskin et al., 2015; Lin et al., 2016). Sun et al. (2007) also found that light-absorbing organic molecules in BrC are likely large (i.e., possessing > 18 carbon atoms); these molecules are generally highly unsaturated and contain three or more oxygen atoms and/or one or more nitrogen atoms.

The Pearl River Delta (PRD) region, one of the most economically developed regions in China, suffers under air pollution from a variety of sources (Chan and Yao, 2008; Li et al., 2017). Source
apportionment using positive matrix factorization (PMF) analysis of mass spectral data sets from high resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS) has revealed that the organic aerosol (OA) in this region arises from traffic emissions (i.e., hydrocarbon-like organic aerosol, or HOA), biomass burning (BBOA), cooking (COA), and secondary formation (i.e., oxygenated organic aerosols, or OOAs). In the PRD, HOA is often the largest contributor to OA at urban sites (He et al., 2011), while SOA plays a more important role at rural sites (Gong et al., 2012; Huang et al., 2011). BBOA has also been found to contribute significantly to total OA in the PRD region, with contributions of 24% at an urban site in Shenzhen (He et al., 2011) and 14% and 25% at rural sites in Heshan and Kaiping, respectively (Gong et al., 2012; Huang et al., 2011). Yuan et al. (2016) attributed 6-12% of the total aerosol absorption at 405 nm at a rural site in the PRD to BrC; the authors found higher BrC contributions during fall, which they ascribed to biomass burning (BBOA) activities nearby. However, the BrC components responsible for light absorption remain relatively unknown; this hinders a thorough understanding of the relationships between optical properties and chemical characteristics and, in turn, the realization of a generalized framework that can be extended to other sources and regions.

In this work, we present simultaneous measurements of aerosol chemical composition and light absorption of aerosol particles at a suburban site downwind of Guangzhou in the PRD, China. Contributions of BC and BrC to total aerosol light absorption were differentiated and quantified using measurements from a seven-wavelength aethalometer. Sources of OA, which were determined using PMF analysis, were correlated to BrC light absorption to identify the major contributor(s) to short-wavelength light absorption. More detailed chemical characteristics, such as N-containing ion fragments, the degree of unsaturation (indicated by the ion double bond equivalent, or ion DBE), and the degree of oxygenation (indicated by the number of oxygen atoms in ions), were also used to investigate the structural characteristics of BrC related to light absorption.

Methodology

1. Sampling site

We conducted field measurements at the Guangzhou Panyu Atmospheric Composition Station (GPACS, 23°00’ N, 113°21’ E), on the periphery of Guangzhou, China, from November 7, 2014
to January 3, 2015. The GPACS is located on top of a hill with an altitude of approximately 150 m a.s.l. (Cheung et al., 2016; Tan et al., 2013; Zou et al., 2015); it is approximately 15 km south of the city center and was downwind of the central city throughout the sampling period, during which north winds prevailed (Qin et al., 2017).

2. Measurements and data analysis

Aerosol light absorption was measured with a seven-wavelength aethalometer (Magee Scientific, model AE33) at 370, 470, 520, 590, 660, 880, and 950 nm. Ambient air was drawn through a 2.5-µm cut-off inlet at 2 L/min before entering the aethalometer; particles were collected on the filter substrate, and light attenuation at the wavelengths above was recorded continuously. The optical properties of the collected particles were determined by comparing light attenuation in particle-laden and particle-free filter areas (Weingartner et al., 2003). To convert aerosol particles light attenuation coefficients at the filter substrate to the light absorption coefficients suspended in the air, a real-time compensation parameter $k$ and a fixed multiple scattering parameter $C$ were used. The real-time loading effect correction was performed using two parallel measurements of optical attenuations at different accumulation rates. $C_{\text{ref}}=2.14$ for quartz filter and $C_{\text{ref}}=1.57$ for tetrafluoroethylene (TFE)-coated glass filter were recommended from previously studies for the fresh soot particles (Drinovec et al., 2015; Weingartner et al., 2003). However, with the presence of semi-volatile oxidation products, significantly higher values ($C=3.6\pm0.6$) were observed in the organic coating experiment using a quartz filter (Weingartner et al., 2003). Wavelength dependence of $C$ has also been reported in the literature (Arnott et al., 2005; Schmid et al., 2006; Segura et al., 2014). A broad range of $C$ (from 2.8 to 7.8) at several sites was also used by Collaud Coen et al. (2010). As the multiple scattering parameter ($C$) may be site specific, we further compared the absorption from AE33 with the co-located measurements. Here, we extracted the light absorption based on extinction and scattering measurements from cavity ring-down spectroscopy (CRD, Hexin XG-1000) and Nephelometer (TSI, 3563), respectively, as below.

$$b_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{sp}}$$

(1)

where $b_{\text{abs}}$, $\sigma_{\text{ext}}$ and $\sigma_{\text{sp}}$ are absorption coefficient, extinction coefficient and scattering coefficient.

The scatter plot of absorption at 532 nm from measurement from the aethalometer (AE33) and that calculated from CRD and Nephelometer (CRD-Neph) is displayed in Figure 1. AE 33 absorption
coefficient was higher than the absorption estimated from Eq. 1. by a factor of 2.10. Therefore, the final multiple scattering parameter (C) was set to \( C_{\text{final}} = C_{\text{ref}} \times 2.10 = 3.29 \). This value is comparable with previous aethalometer measurements (C=3.48) in the PRD region (Wu et al., 2009, 2013).

The non-refractory chemical composition of submicron aerosols was measured with an Aerodyne HR-ToF-AMS (Aerodyne Research Inc., Billerica, MA, USA). Briefly, the AMS collected five-minute-average particle mass spectra for the high-sensitivity V plus particle time-of-flight (PtToF) mode and the high-resolution W mode. AMS data analysis was performed using the SQUIRREL (v1.56D) and PIKA (v1.15D) toolkits in Igor Pro (WaveMetrics Inc., Lake Oswego, OR). Source apportionment was performed via PMF analysis with Multilinear Engine 2 (ME-2) via the SoFi interface (Canonaco et al., 2013). Five factors, including HOA, COA, BBOA, semi-volatile oxygenated organic aerosol (SVOOA), and low-volatility oxygenated organic aerosol (LVOOA), were resolved (Qin et al., 2017). The campaign average OA composition was dominated by surrogates of SOA (SVOOA + LVOOA). However, freshly-emitted hydrocarbon-like organic aerosols (HOA) contributed up to 40.0% of OA during high-OA periods; during nighttime, HOA contributed 23.8% to 28.4% on average. BBOA contributed 9.6% (1.87 µg/m³) of total OA in November and 6.5% (1.38 µg/m³) in December. AMS data treatment was discussed in detail in Qin et al. (2017). Data from a thermo-optical elemental carbon and organic carbon (ECOC) analyzer (Sunset Laboratory Inc.) were also used for comparison.

Results and discussion

1. Aerosol absorption

Figure 2a shows the box-whisker plot of aerosol absorption coefficients \( (b_{abs}) \) from 370 nm to 950 nm from the aethalometer measurements during the campaign. The campaign-average absorption coefficients were 56.00 Mm\(^{-1}\) at 370 nm, 40.99 Mm\(^{-1}\) at 470 nm, 34.76 Mm\(^{-1}\) at 520 nm, 29.91 Mm\(^{-1}\) at 590 nm, 26.69 Mm\(^{-1}\) at 660 nm, 18.06 Mm\(^{-1}\) at 880 nm, and 16.71 Mm\(^{-1}\) at 950 nm.

In multi-wavelength absorption measurements, the total absorption Ångström exponent (AAE) can be calculated by a power-law fitting of the absorption coefficient over all available wavelengths. AAE of unity has been widely used for pure black carbon, while a shift to higher AAE value has been observed with the presence of brown carbon. The reason behind is that BrC has a much stronger absorption at UV and short visible wavelengths than at long visible wavelengths, which
yields a steeper curve (Andreae and Gelencsér, 2006; Bergstrom et al., 2007; Bond and Bergstrom, 2006). The presence of non-absorbing OA shells over BC cores may also lead to a shift of AAE (Gyawali et al., 2009). This latter possibility is analyzed in a separated manuscript (Li et al., in preparation). As shown in Figure 2b, the AAE values, which average at 1.43, are almost always higher than 1, indicating appreciable contributions from BrC to particle light absorption at this site.

To further explore the importance of BrC at this site, BrC absorption at a short wavelength $\lambda_1$ ($b_{\text{BrC},1}$) can be derived by subtracting BC absorption ($b_{\text{BC},1}$) from the total aerosol absorption (Lack and Langridge, 2013) via:

$$b_{\text{BrC},1} = b_{\lambda_1} - b_{\text{BC},1}$$

where absorption $b_{\lambda_1}$ is the measured absorption at the short wavelength $\lambda_1$. BC absorption at $\lambda_1$ ($b_{\text{BC},1}$) can be obtained from the AAE value of BC ($\text{AAE}_{\text{BC}}$) via:

$$b_{\text{BC},1} = b_{\lambda_2} \times (\lambda_2/\lambda_1)^{\text{AAE}_{\text{BC}}}$$

where $b_{\lambda_2}$ is the absorption at a longer wavelength $\lambda_2$ (880 nm), which is assumed to have no contributions from BrC or dust (Drinovec et al., 2015; Zhu et al., 2017). The uncertainty involved in attributing BrC and BC absorption at short wavelengths has been explored explicitly by Lack and Langridge (2013).

Figure 3 shows the $b_{\text{abs}}$ attributed to BC and BrC ($b_{\text{BC}}$ and $b_{\text{BrC}}$) at different wavelengths. Aerosol light absorption coefficients were dominated by BC, but $b_{\text{BrC}}$ was not negligible, especially at short wavelengths. The campaign-average $b_{\text{BrC}}$ values were 13.67, 7.56, 4.49, 3.22, and 2.81 Mm$^{-1}$ at 370, 470, 520, 590, and 660 nm, respectively; BrC absorption contributed 23.6%, 18.1%, 10.7%, 10.7%, and 10.5% of the total absorption at the corresponding wavelengths. The proportions of BrC and BC in our campaign were slightly higher than those reported an earlier study in the PRD by Yuan et al. (2016). In their study, the average light absorption contributions of BrC during Shenzhen winter, Shenzhen fall, and Heshan fall campaigns were 11.7%, 6.3%, and 12.1% at 405 nm and 10.0%, 4.1%, and 5.5% at 532 nm, respectively.

Figure 4 shows the diurnal variations of $b_{\text{BrC}}$ at 370, 470, 520, 590, and 660 nm. At all wavelengths, $b_{\text{BrC}}$ was relatively constant from 00:00 LT to 16:00 LT, at which time it began to increase, peaking
at 21:00 LT and then decreasing until 24:00 LT. These changes may be attributed to diurnal
changes in BrC sources, which most likely originated from crop residual burning in fall and winter
in nearby regions (Wang et al., 2017). The diurnal variations of the different wavelengths were not
significantly different, although short wavelengths exhibited more obvious diurnal variations.

2. Correlation of light absorption by BrC with OA components

To explore the possible sources of BrC, correlations were determined between \( b_{\text{BrC}} \) at 370 nm
\( (b_{\text{BrC,370}}) \) and various OA types. Data at 370 nm were chosen (over data at longer wavelengths) for
their higher signal-to-noise ratios and larger contributions of BrC to light absorption. Figure 5
shows that BBOA concentrations and \( b_{\text{BrC,370}} \) were well correlated (Pearson’s correlation
coefficient, \( R_p = 0.58 \)). More interestingly, a moderate correlation (\( R_p = 0.40 \)) was also found
between \( b_{\text{BrC,370}} \) and the LVOOA mass concentration. Although the LVOOA factor was not further
resolved into OOA factors with biomass origins, it is likely that a portion of LVOOA was formed
from biomass burning precursors through either gas-phase oxidation or heterogeneous reactions.
Satish et al. (2017) found correlations between BrC absorption and both primary BBOA and
BBOA-related SVOOA factors. They also reported that the slope of the correlation between
\( b_{\text{BrC,370}} \) and BBOA (slope = 1.35) was 4.8 times higher than that between \( b_{\text{BrC,370}} \) and one of the
biomass burning SVOOA factors (slope = 0.28), indicating that aging may have reduced the
absorption capacity of biomass-related OA.

Multiple regression analysis was also used to resolve the correlation factors of each OA component
\( (\text{m}^2\text{g}^{-1}) \) at each wavelength.

\[
b_{\text{BrC}} = a\times[\text{HOA}]+b\times[\text{COA}]+c\times[\text{BBOA}]+d\times[\text{SVOOA}]+e\times[\text{LVOOA}] \tag{4}
\]

where a, b, c, d, e indicates the correlation factors of each OA component (\( \text{m}^2\text{g}^{-1} \)) and [..] indicates
the mass concentration of each OA component. These correlation factors obtained are equivalent
to MAC mass absorption coefficient (MAC) of each OA component. We will use these factors to
compare with MAC reported in the literature later.

Washenfelder et al. (2015) reported a MAC of 1.3 ± 0.06 \( \text{m}^2\text{g}^{-1} \) using the \( b_{\text{BrC}} \) at 365 nm for
BBOA in the rural southeastern United States, which was 40 to 135 times higher than the MAC
values reported for other OA factors. Di Lorenzo et al. (2017) found that both BBOA and more-
oxidized oxygenated organic aerosol (MO-OOA) were associated with water soluble BrC and that
the MAC of BBOA doubled that of MO-OOA. However, Forrister et al. (2015) observed that BrC in wildfire plumes had a lifetime of roughly 9 to 15 hours, probably due to conversion to SOA with lower light absorption capacity. In our study, the MAC (correlation factor in Table 1) of BBOA at 370 nm was 3.4 ± 0.41 m² g⁻¹, roughly 3.4 times that of LVOOA (1.04 ± 0.08 m² g⁻¹).

Like the studies listed above (Forrister et al., 2015; Di Lorenzo et al., 2017; Washenfelder et al., 2015), our results suggest that the absorption coefficient of nascent BBOA is higher than that of its aged counterpart at short wavelength. However, it should be noted that LVOOA might consist of some other non-absorbing SOA components with no biomass origin. It is therefore important to consider chromophore lifetimes when modeling light absorption by BrC. As noted in Laskin et al. (2015), the physicochemical properties of chromophores in BrC may exhibit dynamic changes that are not yet sufficiently understood. In addition, the difference between MAC values of BBOA and LVOOA decreased for longer wavelengths. The MAC values of BBOA were roughly 3.4, 1.8, 1.5, 1.48, and 0.80 times those of LVOOA at 370, 470, 520, 570, and 660 nm, respectively. The contribution to total absorption coefficient also varied with wavelengths. The contribution from BBOA decrease from 25.8% to 10.1% from 370 nm to 660 nm, while the contribution from LVOOA increase from 49.3% to 60.2 % from 370nm to 660nm. The contribution of HOA was more stable across different wavelengths but was also significant, likely due to the high mass concentration of HOA. Altogether, these observations indicate that the wavelength-dependent light absorption of different OAs must be considered in light absorption models.

3. Correlation of $b_{BrC}$ with N-containing organic ions

The chromophores in BrC that are responsible for OA light absorption are not well characterized. Structurally, light absorption depends on the extent of $sp^3$ hybridization, in which π electrons are usually found (Bond and Bergstrom, 2006). Of the elements commonly found in OA, both C and N have strong tendencies toward $sp^2$ hybridization. It has also been found that, despite their small OA mass fraction contributions, N-containing organic species in OA can be responsible for appreciable light absorption (Chen et al., 2016; Laskin et al., 2015). Thus, we examined the correlations between $b_{BrC}$ and N-containing ions from AMS measurements. These ion fragments, including the $C_3H_7N^+$ and $C_3H_7O_2N^+$families, likely originated from N-heterocyclic compounds.

Figure 6 shows that the mass loadings of $C_3H_7N^+$ and $C_3H_7O_2N^+$ families are correlated with $b_{BrC}$ at 370 nm and that correlations are stronger for fragments containing both N and O atoms. These results are consistent with Chen et al. (2016), who suggested that organic compounds with O and
N atoms might contribute substantially to total light absorption and fluorescence in OA components.

The effects of oxygenation (as indicated by the number of O atoms in an ion) and unsaturation/cyclization (as indicated by the ion double bond equivalent, or ion DBE) were also examined for each C,H,N and C,H,O,N ion family. Several studies found that species with high DBE values may have substantial network of conjugated double bonds and likely contribute to light absorption (Budisulistiorini et al., 2017; Laskin et al., 2014; Lin et al., 2016). The ion DBE represents the number of double bonds (unsaturation) or rings (cyclization) that an ion contains and is calculated on the basis of the elemental formula via the following equation:

\[
\text{DBE} = C + 1 - \frac{H}{2} - \frac{X}{2} + \frac{N}{2}
\]

where C, H, X, and N are the number of carbon, hydrogen, halogen (Cl, Br, I, and F), and nitrogen atoms present in the ion, respectively.

Figure 7a shows the correlation coefficients between \(b_{\text{BrC,370}}\) and the mass loadings of each of the C,H,N family at different DBE values. For the C,H,N family, \(R^2\) increased as DBE increased (except for ions with a DBE of 1), suggesting that \(b_{\text{BrC,370}}\) was better correlated with fragments with higher degrees of unsaturation or cyclization. Indeed, in saturated organics, light absorption involves excitation of \(n\) electrons, which requires more energy and, therefore, shorter incident wavelengths (e.g., short UV). In unsaturated organics, the delocalized \(\pi\) electrons in clusters of \(sp^2\) hybrid bonds, as well as those in large conjugated systems, can extend absorption from short UV to longer wavelengths into the near-visible spectrum. These structural features may explain in part the increased correlation between mass loadings of the C,H,N ion and light absorption with decreasing ion saturation. For the C,H,O,N family, we did not observe obvious trends in correlation coefficient with changing degree of saturation/cyclization (Figure 7b). However, the overall correlation was higher than those with C,H,N.

Conclusions

This paper presents collocated, real-time atmospheric particle light absorption and chemical composition measurements at a suburban site in PRD, China. While BC dominated aerosol light absorption, BrC also contributed to absorption at short wavelengths. The aerosol light absorption coefficients of BrC were 13.67, 7.56, 4.49, 3.22, and 2.81 \(\text{Mm}^{-1}\) at 370, 470, 520, 590, and 660 nm,
respectively, and BrC contributed 23.6%, 18.1%, 10.7%, 10.7%, and 10.5% of the total absorption at the corresponding wavelengths. Hydrocarbon-like organic aerosol (HOA), biomass burning organic aerosol (BBOA) and low-volatility oxygenated organic aerosol (LVOOA) were also substantial for the source of BrC. At short wavelength (370 nm), the mass absorption coefficient of BBOA was higher than those of HOA and LVOOA. However, the difference between the mass absorption coefficients of BBOA and other OA factors decreased with increasing wavelength. The contribution of different OA sources to total absorption coefficient also varied with wavelengths. Such a wavelength dependent trend is also observed for their contribution to total BrC absorption coefficients. C$_x$H$_y$N$^+$ and C$_x$H$_y$O$_z$N$^+$, were likely the chromophores responsible for the observed BrC light absorption. The mass loadings of C$_x$H$_y$N$^+$ and C$_x$H$_y$O$_z$N$^+$ ion families became better correlated with the BrC light absorption coefficient as their degrees of unsaturation/cyclization and oxygenation increased. This study shows wavelength-dependent light absorption by BrC is strongly influenced by moderately specific molecular characteristics such as degrees of unsaturation/ cyclization and oxygenation. An exploration of the absorptive properties of more specific molecular features, such as the chemical identities of BrC constituents, would require a more detailed chemical characterization of the highly complex OA composition.

Acknowledgements

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References


Feng, Y., Ramanathan, V. and Kotamarthi, V. R.: Brown carbon: A significant atmospheric...


Table 1. Multilinear regression analyses between $b_{BrC}$ at each wavelength and mass loading of different OA factors from AMS-PMF/ME-2.

<table>
<thead>
<tr>
<th></th>
<th>370 nm</th>
<th></th>
<th>470 nm</th>
<th></th>
<th>520 nm</th>
<th></th>
<th>590 nm</th>
<th></th>
<th>660 nm</th>
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<tbody>
<tr>
<td></td>
<td>Correlation factor ($m^2 g^{-1}$)</td>
<td>Contribution to $b_{BrC}$</td>
<td>Correlation factor ($m^2 g^{-1}$)</td>
<td>Contribution to $b_{BrC}$</td>
<td>Correlation factor ($m^2 g^{-1}$)</td>
<td>Contribution to $b_{BrC}$</td>
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<td>Contribution to $b_{BrC}$</td>
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</tr>
<tr>
<td>HOA</td>
<td>0.61±</td>
<td>0.38±</td>
<td>0.22±</td>
<td>0.16±</td>
<td>0.16±</td>
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<tr>
<td></td>
<td>0.05</td>
<td>22.7%</td>
<td>0.03</td>
<td>25.4%</td>
<td>0.02</td>
<td>24.5%</td>
<td>0.02</td>
<td>25.1%</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>3.4±</td>
<td>1.2±</td>
<td>0.63±</td>
<td>0.43±</td>
<td>0.21±</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>BBOA</td>
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<td>25.2%</td>
<td>0.26</td>
<td>15.9%</td>
<td>0.18</td>
<td>13.9%</td>
<td>0.14</td>
<td>13.4%</td>
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<tr>
<td></td>
<td>1.04±</td>
<td>0.65±</td>
<td>0.41±</td>
<td>0.29±</td>
<td>0.26±</td>
<td></td>
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<tr>
<td>LVOOA</td>
<td>0.08</td>
<td>52.2%</td>
<td>0.05</td>
<td>58.7%</td>
<td>0.04</td>
<td>61.5%</td>
<td>0.03</td>
<td>61.5%</td>
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Notes: 1) Correlation coefficient (R) for each regression analysis: 0.65 at 370 nm, 0.58 at 470 nm, 0.51 at 520 nm, 0.51 at 570 nm and 0.54 at 660 nm; 2) The correlation factors for COA and SVOOA are near zero at all wavelength, indicating a negligible contribution from these factors. So only the correlation factors for HOA, BBOA and LVOOA are listed in the table.
Figures

Figure 1. Scatter plot of absorption coefficients at 532 nm measured with aethalometer (AE33) and those estimated from cavity ring-down spectroscopy (CRD) and Nephelometer measurements.
Figure 2. a) Box-whisker plot of absorption coefficient at seven wavelengths as measured with the AE33; b) Histogram of AAE values over the measurement campaign.
Figure 3. a) Fractions of BC and BrC contributions to aerosol particle light absorption at different wavelengths; b) Contributions of BC and BrC to the total light absorption coefficient at different wavelengths.
Figure 4. Diurnal variations of BrC light absorption coefficients ($b_{BrC}$) at different wavelengths.
Figure 5. Correlations between the BrC absorption coefficients at 370 nm and the mass loadings of OA factors resolved by AMS-PMF/ME-2.

![Correlation Chart]

- Slope = 0.68, $R_p = 0.46$
- Slope = 0.38, $R_p = 0.054$
- Slope = 0.58, $R_p = 0.27$
- Slope = 1.30, $R_p = 0.40$
Figure 6. Correlations between BrC absorption coefficients at 370 nm and mass concentrations of N-containing organic ion families.
Figure 7. Correlation coefficients between BrC absorption coefficient at 370 nm and N-containing organic ion fragments grouped by double bond equivalence (panels a and b) and number of oxygen atoms (panel c). Larger grey dots correspond to higher carbon numbers.