Concurrent photochemical whitening and darkening of ambient brown carbon

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Abstract. The light-absorbing organic aerosol (OA), known as brown carbon (BrC), has important radiative impacts, however its sources and evolution after emission remain to be elucidated. In this study, the light absorption at multiple wavelengths, mass spectra of OA and microphysical properties of black carbon (BC) were characterized at a typical sub-urban environment in Beijing. The absorption of BC is constrained by its size distribution and mixing state, being subtracted from total absorption to obtain the absorption of BrC, then by applying the least-correlation of BC absorption with secondary BrC, the absorption contributed by BC, primary BrC and secondary BrC was apportioned. The multi-linear regression analysis on the factorized OA mass spectra indicated the OA from traffic and biomass burning emission contributed to primary BrC. Importantly, the moderately oxygenated OA (O/C=0.62) was revealed to highly correlate with secondary BrC. These OA had higher nitrogen content, in line with the nitrogen-containing functional groups detected by the Fourier transform infrared spectrometer. The photooxidation was found to result in reduced contribution of primary BrC about 20% but enhanced contribution of secondary BrC by 30%, implying the concurrent whitening and darkening of BrC. This provides field evidence that the photochemically produced secondary nitrogen-containing OA can considerably compensate some bleaching effect on the primary BrC, hereby causing radiative impacts.

1. Introduction

Atmospheric absorbing organic aerosol (OA), known as brown carbon (BrC), is important contributor to anthropogenic absorption besides black carbon (BC) (Laskin et al., 2015; Liu et al., 2020), particularly at shorter visible wavelengths (Bahadur et al., 2012). Due to complex compositions of OA, the primary sources and subsequent evolution of BrC in the atmosphere remains to be explicitly understood and causes uncertainties in evaluating the radiative impacts of BrC (Liu et al., 2020).

The chromophores of BrC are mainly aromatic compounds associated with certain functional groups (Liu et al., 2015c). Particularly, compounds containing nitro, nitrated or other forms of nitrogen-containing functional groups are more absorbing (Nakayama et al., 2013; Jacobson, 1999). It is well established that primary OA, especially from biomass burning, contains a large fraction of BrC (Andreae and Crutzen, 1997; Rizzo et al., 2013; Bond, 2001). These primary BrC had a range of absorptivity, which was found to be controlled by burning phases, with OA co-emitting with BC (the flaming phase) exhibiting a higher absorptivity than OA-dominated smoldering phase (Liu et al., 2021). BrC can experience reactions with atmospheric oxidants after emission. Previous studies (Satish et al., 2017; Satish and Rastogi, 2019) found nitrogenous compounds from biomass burning were responsible for brown carbon over South Asia and the chromophores were photobleached in the afternoon. Numerous field and laboratory studies found the decease of BrC absorptivity due to photobleaching on chromophores, with lifetime ranging from a few hours (Zhao et al., 2015; Liu et al., 2021) to a few days (Forrister et al., 2015), which may depend on the concentration of ambient hydroxyl radical (Wang et al., 2014), also influenced by relative humidity and particle volatility (Schnitzler et al., 2020). The absorptivity of BrC could be also enhanced due to addition of functional groups by forming conjugated structure with aromatics. This was supported by a number of laboratory studies that BrC absorptivity could be enhanced when forming nitrogen-containing organic compounds, such as the formation of nitro-aromatics when aromatics reacted with NO_x (Nakayama et al., 2013), or produced organic amine after reacting with ammonia (Updyke et al., 2012). The enhancement of BrC absorptivity could occur either through nitration of exiting chromophores, or formation of new secondary organic aerosol (SOA) chromophores through gas-phase oxidation.

The above findings mean the enhancement or bleaching of BrC absorptivity via photooxidation will coexist. The time scale between both competing processes will ultimately determine the lifetime of BrC in the atmosphere. However, both processes have been rarely investigated in the field to explicitly determine the BrC components which principally determine the respective enhancement or decrease of its absorptivity, particularly in regions influenced by combined anthropogenic sources. In this study, by measurements using multiple-wavelength absorption and microphysical properties of BC in a sub-urban region, the absorption of BC, primary and secondary BrC was discriminated. In conjunction with source attribution via OA mass spectra, we are able to link the segregated absorption with certain sources and investigate their primary information and subsequent evolution. The competition between photobleaching and secondary formation of BrC was investigated in real world.

2. Experimental and instrumentation

2.1 Site description and meteorology

The experiment was conducted during springtime at the Beijing Cloud Laboratory and Observational Utilities Deployment Base (117.12°E, 40.14°N), which is located in the northeast suburban area in Beijing (Fig S1a). The site is surrounded by the northwest mountain ridge, without significant local primary anthropogenic emissions (Hu et al., 2021). The 72-h backward trajectories with every 3 hours initializing from the site are analyzed by the HYSPLIT model (Draxier and Hess, 1998) using the 3-hourly 1°×1° meteorological field from the GDAS reanalysis product. The obtained backward trajectories were further clustered to group the similar transport pathways (Makra et al., 2011). The meteorological parameters, including the temperature (T), ambient relative humidity (RH), wind speed (WS) and wind direction (WD) were measured by a monitoring station on the site.

2.2 Measurements of BC microphysics and absorption coefficient

In this study, the ambient aerosols were sampled by a large-flow (1.05 m^3 min^{-1}) air particle sampler (TH-1000C Ⅱ) with a $PM_{2.5}$ impactor (BGI SCC 1.829) and dried by a silica drier before measurement. The single particle soot photometer (SP2, DMT., USA) used continuous laser at λ=1064nm to incandesce light-absorbing aerosols (such as BC) for irradiating detectable visible light. The incandescence signal was used to measure the refractory black carbon (rBC) mass. The SP2 incandescence signal was calibrated using the Aquadag standard (Acheson Inc., USA), and a factor of 0.75 was applied to correct for ambient BC (Laborde et al., 2012). The scattering signal was calibrated by monodispersed polystyrene latex spheres (PSL). The BC core diameter (D_c) was calculated from the measured BC mass by assuming a BC density of 1.8 g cm^{-3} (Bond and Bergstrom, 2006). The leading edge only (LEO) method was applied to reconstruct the scattering signal of BC, which was used to determine the coated particle diameter (D_p) by a Mie-lookup table with the inputs of scattering and incandescence signal of each BC particle (Liu et al., 2014; Taylor et al., 2015). The mass median diameter (MMD) is derived from the D_c distribution, which is determined as below and above MMD the rBC mass concentration is equal (Liu et al., 2019a). The bulk coating thickness (D_p/D_c) is calculated as the cubic root of ratio of the total coated BC volume divided by the total volume of rBC.

The mass absorption cross section (MAC) (in m^2 g^{-1}) of each BC particle can be calculated using the measured coated and uncoated BC sizes by applying the Mie core-shell calculation. The absorption coefficient of BC at certain wavelength, $\sigma_{abs,BC}$ (λ) is determined by multiplying the calculated MAC and rBC mass concentration at each size:

$$\sigma_{abs,BC}(\lambda)=\sum_i MAC(\lambda, D_{p,i}, D_{c,i}) m(logD_{c,i}) \Delta logD_{c,i} \quad (1)$$

where m ($logD_{c,i}$) denotes the BC mass concentration at each logarithmic bin of D_c. The SP2 measurement at λ=1064nm longer than mostly populated BC size means the derived coatings and subsequent calculation of MAC is relatively independent of particle shape within uncertainty of 21% (Liu et al., 2014; Hu et al., 2021).

The absorption coefficients at wavelengths λ= 375, 470, 528, 635 and 880 nm were measured by a Micro-Aethalometer (MA200, Aethlabs, San Francisco, CA, USA). Aerosol particles were collected on filter tapes, on which the light attenuation was measured continuously with a time resolution of 30 s. The loading effect of filters was automatically corrected by

measuring attenuation at two different sampling flow rates on two spots in parallel (Drinovec et al., 2015). Moreover, a multi-scattering correction factor (C-value) of 3.5, 3.2 and 2.4 at the wavelengths 370 nm, 528 nm and 880 nm, respectively were utilized to correct attenuation for the multiple light scattering effect. It was obtained by comparing the absorption coefficient with a photoacoustic soot spectrometer (PASS-3, DMT) (Hu et al., 2021).

2.3 Attribution of primary and secondary BrC absorption coefficient

The absorption coefficient of BC at different λ is calculated using the measured uncoated core and coated size as mentioned above. The absorption coefficient of total BrC is obtained by subtracting the BC absorption coefficient from the total absorption at certain wavelength, expressed as:

$$\sigma_{abs,\,BrC}(\lambda) = \sigma_{abs,total}(\lambda) - \sigma_{abs,BC}(\lambda) \quad (2)$$

where the absorption coefficient of BC ($\sigma_{abs,BC}$) is obtained from the SP2 measurement, $\sigma_{abs,total}(\lambda)$ is the total light absorption of aerosols measured by the MA200. The absorption coefficient of secondary BrC, the absorption not contributed by primary sources, is obtained by subtracting the absorption of all primary sources from the total absorption (Crilley et al., 2015), expressed as:

$$\sigma_{abs,secBrC}(\lambda) = \sigma_{abs,total}(\lambda) - \sigma_{abs,pri}(\lambda) \quad (3)$$

where $\sigma_{abs,pri}(\lambda)$ is the light absorption from primary sources. Here an assumption is made that light absorption from primary aerosols is all from combustion sources, and these sources necessarily contain BC (Wang et al., 2018). Therefore, the total absorption from primary sources can be obtained by scaling a factor from the mass concentration of BC, expressed as:

$$\sigma_{abs,pri}(\lambda) = \left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri} \bullet [rBC] \quad (4)$$

where [rBC] is the mass concentration of rBC measured by the SP2, $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ is the scaling factor to derive the absorption of primary combustion sources from [rBC]. This factor is obtained using the minimum R-squared (MRS) approach (Wu and Yu, 2016), by adjusting the factor until a minimum correlation between $\sigma_{abs,secBrC}$ and [rBC] is reached because the absorption from secondary sources are least likely to covary with that from primary sources (Wang et al., 2019a). This method has been used in urban and sub-urban environment to obtain the primary BrC associated with combustion sources. Different sources may exhibit different ratios of $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$, however there were no sporadic pollution events during the experimental period, uniform sources are therefore considered, and this ratio tends to represent a mean for the experiment. Being different from previous studies, an auxiliary characterization of rBC mass measured by the SP2 is used here to avoid the possible interference from absorption measured by the same instrument. The $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ ratio at λ=375 nm, 470 nm, 528 nm, 635 nm and 880 nm is calculated to be 20.7, 17.0, 14.4, 11.7 and 5, respectively (Fig. S2), which falls within the reported values from previous studies 11-50 (Zhang et al., 2020; Wang et al., 2019a). This scenario assumes a relatively consistent absorption

relative to BC mass concentration from sources during experiment. This however may not include some sporadic events when sources with distinct OA or BC mass fraction may be introduced and alter the single $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ ratio. The $\sigma_{abs,secBrC}$ therefore represents the overall mean value during the experimental period but this ratio will vary with seasons and locations. The σ_{abs} of primary BrC can then be calculated as:

$$\sigma_{abs,priBrC}(\lambda) = \sigma_{abs,BrC}(\lambda) - \sigma_{abs,secBrC}(\lambda) \quad (5)$$

where $\sigma_{abs,BrC}$ and $\sigma_{abs,secBrC}$ is calculated from Equation (2) and (3), respectively. When evaluated the contribution of photooxidation to the absorption coefficient, the absorption coefficient during photooxidation (12:00-17:00) was divided by the respective average absorption coefficients of primary and secondary BrC.

2.4 Composition measurement

The mass concentration and chemical composition of non-refractory sub-micron PM ($NR\text{-}PM_1$) including organic aerosols (OA), nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-) and ammonium (NH_4^+) were determined with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., USA). The setup, operation, and calibration procedures of the AMS have been described elsewhere (Canagaratna et al., 2007). During this field observation, the AMS was operated in V-mode for the quantification of mass concentrations. The composition-dependent collection efficiencies were applied (Middlebrook et al., 2012), and the ionization efficiency was calibrated using 300 nm pure ammonium nitrate (Jayne et al., 2000). Elemental ratios of OA including oxygen-to-carbon (O/C), hydrogen-to-carbon (H/C) and nitrogen-to-carbon (N/C) were determined to the improved-ambient method (Canagaratna et al., 2015).

Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) was performed on the inorganic and organic high-resolution mass spectra to distinguish OA components from different sources (Zhang et al., 2011; Ulbrich et al., 2009; Decarlo et al., 2010). The mass spectra of the combined matrix for m/z <120 were excluded in PMF analysis. Five OA factors were identified. The diagnostics of PMF is summarized in Text S1and Fig. S6.

2.5 Offline Fourier transform infrared spectrometer (FTIR) analysis

Particulate Matter (PM) samples were collected once a day onto prebaked (600℃， 4h) quartz fiber filters (Whatman, QMA, USA) using a large-flow (1.05 m^3 min^{-1}) air particle sampler (TH-1000C II). The collected filter samples were stored in the refrigerator at -20℃ before analysis. The infrared spectra of collected samples were measured by a Fourier transform infrared spectrometer (FTIR, Thermo Scientific, USA) equipped with an iD5 attenuated total reflectance accessory (diamond crystal) to quantify the chemical functional groups over the wavenumbers range of 550-4000 cm^{-1} with a resolution of 0.5 cm^{-1}. The NO and NO_2 symmetric stretch in the FTIR spectra can characterize the functional groups associated with nitrogen-containing organics (Coury and Dillner, 2008). Fig. S3 shows typical examples of FTIR spectra and the assigned functional groups for the three pollution levels during experiment. The peak at 1110 cm^{-1} corresponds to the background of the quartz fiber filter overlapped with some X-H bending vibrations, which is subtracted for the following analysis. The characteristic organic nitrate

spectra appear at wavenumbers 860 cm^{-1} (NO symmetric stretch), 1280 cm^{-1} (NO_2 symmetric stretch) and 1630-1640cm^{-1} (NO_2 asymmetric stretch) (Bruns et al., 2010). After baseline calibration, The FTIR peaks of 1630cm^{-1} and 860cm^{-1} are integrated the absorption areas above the baseline. The summed integrated area of -NO and -NO_2 are hereby used to indicate the nitrogen-containing organics. There was no discernable peak of carbonyl group for our infrared spectrum, and the peak of OH at 2500 cm^{-1} - 3400 cm^{-1} for the carboxylic acid is not discernable neither, thus the influence of ketone and carboxylic acid may be of less importance for our dataset.

3. Results and Discussion

3.1 Source attributed OA

The overview results are shown in Fig. S1. The organics dominated the aerosol compositions for most time, but occasionally nitrate was the most abundant component (Fig. S1g). Note that the nitrate here may also include components containing in organics besides ammonium nitrate. Backward trajectories (Fig. S1a-d) showed that the most abundant PM_1 concentration was associated with air masses transported in shorter distance from southern regions (C1), but the longer and faster northerly transported air mass from cleaner north (C2) could dilute the concentrations.

The resolved OA factors by the PMF analysis are shown in Fig. 1, including the mass spectra, time series and diurnal profiles of each PMF factor with corresponded external and internal tracers. Three primary OA (POA) were identified as hydrocarbon-like OA (HOA), cooking-related OA (COA), biomass burning OA (BBOA), with O/C of 0.31, 0.18 and 0.39 respectively. These POA had considerable fraction of hydrocarbon fragments (C_xH_y), indicating their less aged status. The HOA profile was characterized by higher contributions of aliphatic hydrocarbons and has dominated ion tracers such as *m/z* 41 ($C_3H_5^+$), 43 ($C_3H_7^+$), 55 ($C_4H_7^+$) and 57 ($C_4H_9^+$). The HOA concentration correlated with BC (*r*=0.62), which emits from traffic emissions. The diurnal variation exhibited strong morning and afternoon rush-hour peaks of mass concentration. This factor was consistent with the mass spectra of previously measured HOA from on-road vehicle emissions in urban cities (Zhang et al., 2005; Aiken et al., 2009; Sun et al., 2016; Hu et al., 2017), which has m/z peaks characteristic of hydrocarbon fragments in series of $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$. The mass spectrum of HOA shows overall similarity to those of primary OA emitted from gasoline and diesel combustion sources (*r*=0.68) (Elser et al., 2016).

The OA from cooking sources (COA) is also characterized by prominent hydrocarbon ion series, however, with higher signal at $C_nH_{2n-1}^+$ than $C_nH_{2n+1}^+$. COA had apparent fragments of both $C_4H_9^+$ and $C_3H_3O^+$, and has a higher ratio of $C_3H_3O^+/C_3H_5O^+$ (3.1), $C_4H_7^+/ C_4H_9^+$ (2.2) than HOA (0.9–1.1), with cooking-related fragments of $C_5H_8O^+$ (m/z 84), $C_6H_{10}O^+$ (m/z 98) and $C_7H_{12}O^+$ (m/z 112) (Sun et al., 2011b; Mohr et al., 2012). The COA shows overall similar spectral pattern to the reference spectra of COA (*r*=0.92) (Elser et al., 2016). Its minor peak at noon and larger peak in the evening (Fig. 1l) also corresponded with the lunch and dinner time respectively. There was only a minor peak at noon for COA, which may be due to the sub-urban nature of the site where the major aerosols from cooking sources may have been processed and lost the signature near source.

The feature of this factor was also observed in sub-urban environment (Huang et al., 2021).

The BBOA factor was identified based on the prominent signals of *m/z* 60 ($C_2H_4O_2^+$) and 73($C_3H_5O_2^+$), which are known fragments of levoglucosan (Cubison et al., 2011). And BBOA also correlated with potassium (K^+, $r = 0.80$), which are indicator of biomass burning (Pachon et al., 2013; Brown et al., 2016). The *m/z* 60 and 73 together with a unique diurnal variation have been shown to be a robust marker for the presence of aerosols from biomass burning emissions in many urban locations (Sun et al., 2016). The BBOA shows very similar mass spectral patterns to previously reported reference spectra of biomass burning (r=0.94) (Elser et al., 2016). The BBOA factor that was identified in spring accounted for 12.8% of the total OA in Beijing, similar to previous reports (Hu et al., 2017). Biomass (Cheng et al., 2013) and solid fuel burning emissions (Sun et al., 2014) have been widely observed to importantly contribute to the primary OA in this region. This off-road combustion source was particularly abundant during wintertime for residential heating activities (Shen et al., 2019; Yang et al., 2018; Liu et al., 2016), while boiler for industry use (mostly using coal as fuel) was in operation throughout the year (Liu et al., 2015b). During the springtime of the experiment, the residential heating activities dropped due to increased ambient temperature thus the BBOA may be mainly contributed by the industry sector.

Two types of oxygenated organic aerosols (OOA) were identified, in moderate (OOA2, O/C=0.62) and high oxidation state (OOA1, O/C=0.95), respectively, which is very similar to the spectra of OOA factors resolved in other cities (Hayes et al., 2013; Ulbrich et al., 2009). The average mass spectrum of OOA2 in this study is characterized by *m/z* 29 (mainly CHO^+), 43 (mainly $C_2H_3O^+$) and *m/z* 44 (CO_2^+), similar to the semi-volatile OOA spectrum identified in other locations (Sun et al., 2011a; Zhou et al., 2016). On average, OOA2 accounts for 42% and 18% of $C_xH_yO^+$ and $C_xH_yO_2^+$ ions, respectively (Fig. 1b). These results clearly indicate that OOA2 was primarily composed of less oxygenated, possibly freshly oxidized organics. Notably, OOA2 had a substantially higher N/C than other factors (N/C=0.037), and had highest correlation with nitrate (r=0.77) and with $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments (r=0.83). This factor therefore tends to largely result from nitrogen-containing OA and its elevation at night may be also associated with dark oxidation by nitrate radical.

The mass spectrum of OOA1, which was characterized by a dominant peak at *m/z* 44 (mainly CO_2^+), a highest O/C (0.95). On average, OOA1 contributes 51% of the $C_xH_yO^+$ signal and 23% of the $C_xH_yO_2^+$ signal (Fig. 1a). OOA1 showed particularly high correlation with sulfate (r=0.40) because of their similar volatilities (Huffman et al., 2009; Jimenez et al., 2009). The slight enhancement at noon for OOA1 (also for OOA2) soon after morning rush-hour indicated the likely rapid formation of SOA through photooxidation. This significantly higher mean OOA2 than median value in the diurnal pattern indicated that this OA type was largely associated with pollution events. Both OOA1 and OOA2 showed nighttime peak maybe due to reduced boundary layer.

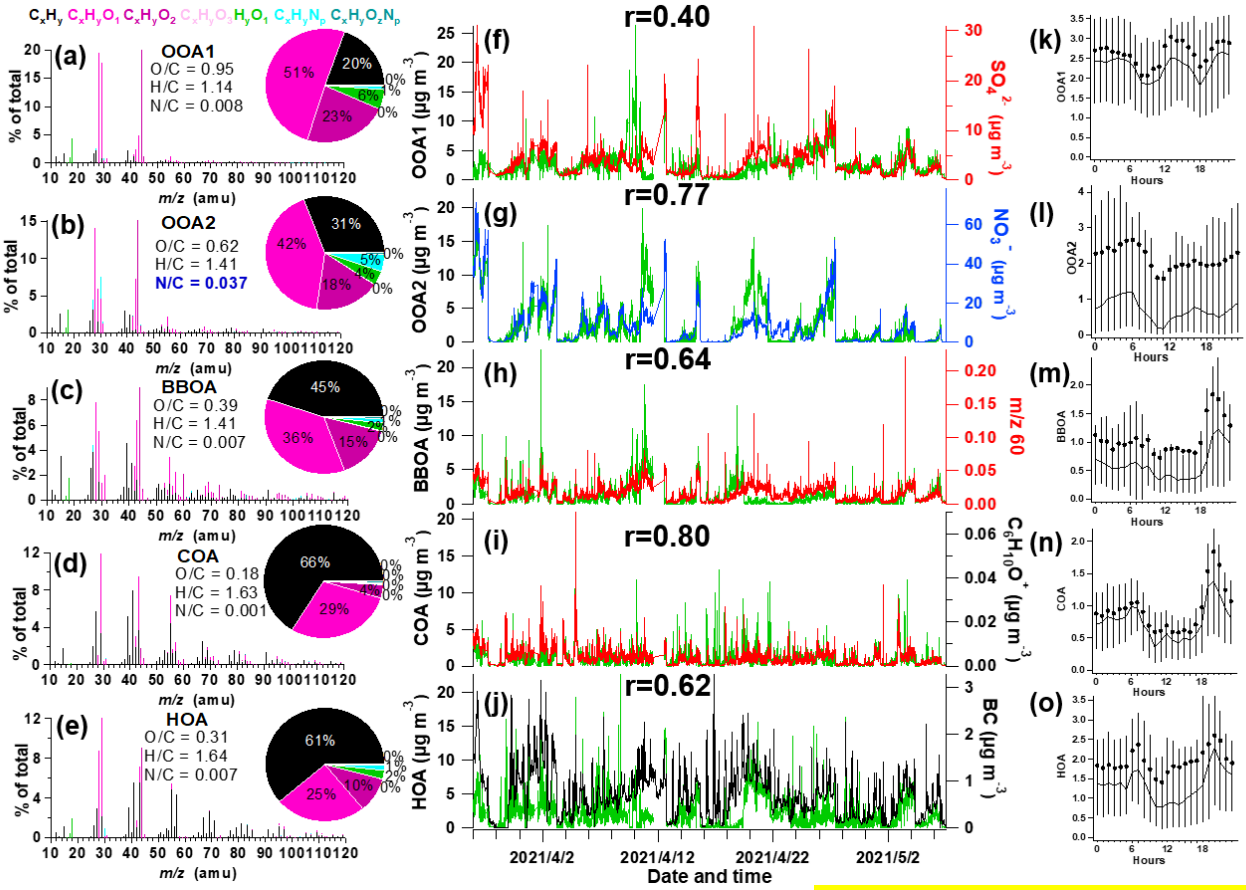

Figure 1. Information of source-apportioned organic aerosols by the PMF analysis. Mass spectra of (a) oxygenated OA1 (OOA1), (b) oxygenated OA2 (OOA2), (c) biomass burning OA (BBOA), (d) cooking-related OA (COA), (e). hydrocarbon-like OA (HOA), (f-j) Temporal variations of each PMF factor and the corresponding marker species. (k-o) Diurnal profiles of each factor. The lines, dots and whiskers denote the median, mean and the 25th/75th percentiles at each hour respectively.

3.2 Segregated aerosol absorption

Fig. 2 shows the time series of BC properties, including the BC mass concentration, D_p/D_c, D_c, MAC and light absorption coefficient of BC (section 2.2). The MMD of BC core varied between 93 – 274 nm which may correspond to the source-specific information (Liu et al., 2019b) or coagulation process during ageing. The coating of BC (indicated by D_p/D_c) showed sporadic enhancement which was closely associated with enhanced PM concentration (Fig. 2a). This was consistent with previous studies that high coatings of BC occurred during heavier pollution due to the enhanced secondary formation of condensable materials to particle phase (Ding et al., 2019; Zhang et al., 2018). This clearly indicates the variation of mixing state of BC and this will potentially influence its MAC and absorption Ångström exponent (AAE) (Liu et al., 2015a). It will introduce considerable uncertainties to use constant MAC or AAE to derive the absorption coefficient of BC at multiple wavelengths. The MAC estimated using the measured BC core size and coatings (Fig. 2c) is thus used to derive the $\sigma_{abs,BC}$ (section 2.2, shown in Fig. 2d). The $\sigma_{abs,BC}$ was 9.1±7.3 Mm^{-1} during experimental period. MAC of BC at λ=375nm showed to

be at 8.4 -16.6 m^2 g^{-1} with enhanced absorption when high coatings.

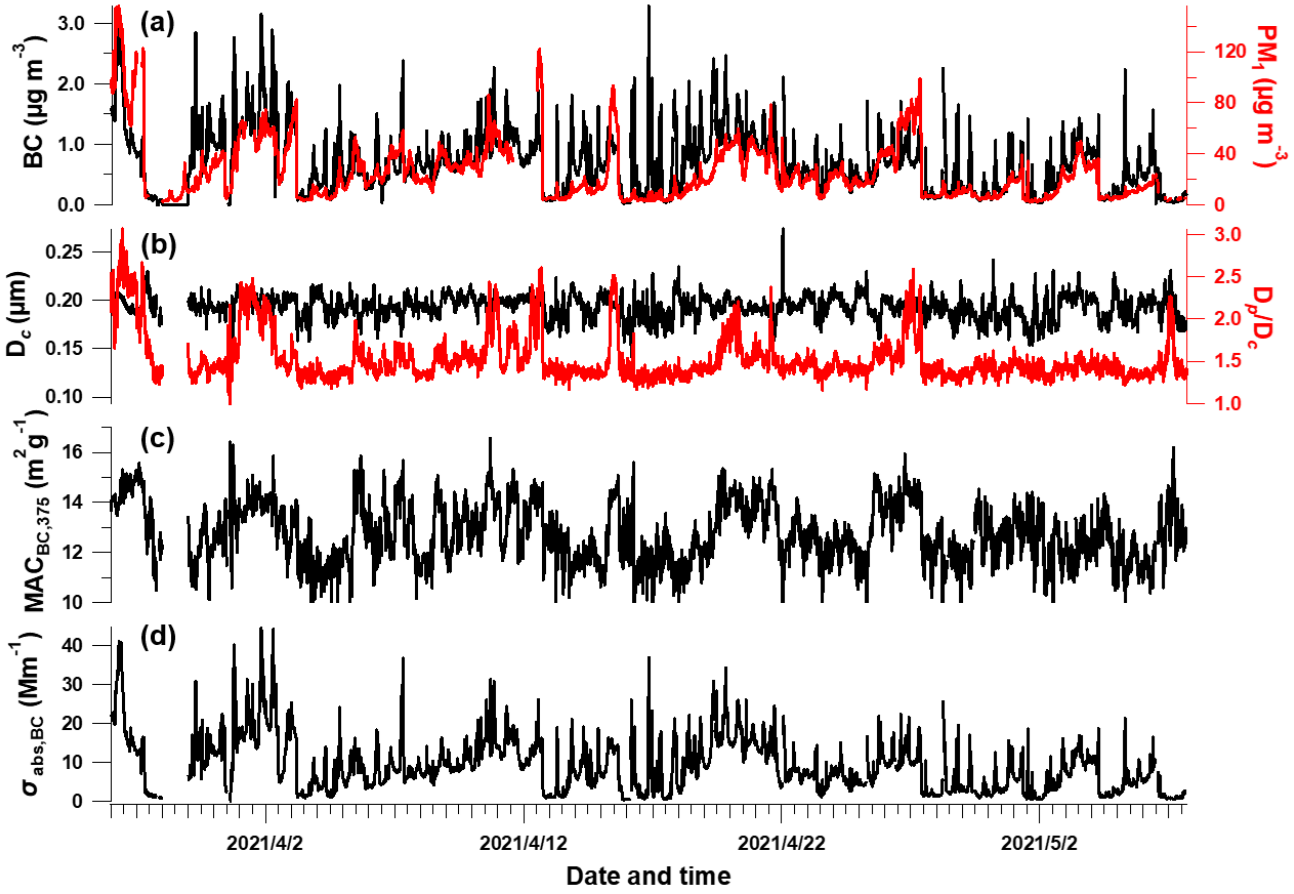

Figure 2. Temporal evolution of BC-related properties. (a) rBC and PM_1 mass concentration, (b) BC core diameter and bulk coating thickness (D_p/D_c), (c) calculated mass absorption cross section (MAC) at λ=375nm, (d) absorption coefficient of BC.

Using the method above, the total ($\sigma_{abs,total}$) and attributed absorption of BC ($\sigma_{abs,BC}$), primary ($\sigma_{abs,priBrC}$) and secondary BrC ($\sigma_{abs,secBrC}$) at λ=375nm are shown in Fig. 3a-c. In Fig. 3b, the brown and green shades above the adjacent tracer indicate the absorption coefficient of primary and secondary BrC, respectively. Fig. 3c shows that the absorption coefficient of primary BrC was higher than secondary BrC for most time, but for certain periods they were equivalent or secondary BrC occasionally exceeds primary BrC. The mean contribution of absorption coefficient for BC, primary BrC and secondary BrC is 51%, 27% and 22% in this study. The tracers associated with nitrogen-containing organics, such as OOA2 (with highest N/C), $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments, and the FTIR measured -NO + $-NO_2$, are also shown in Fig. 3d-e.

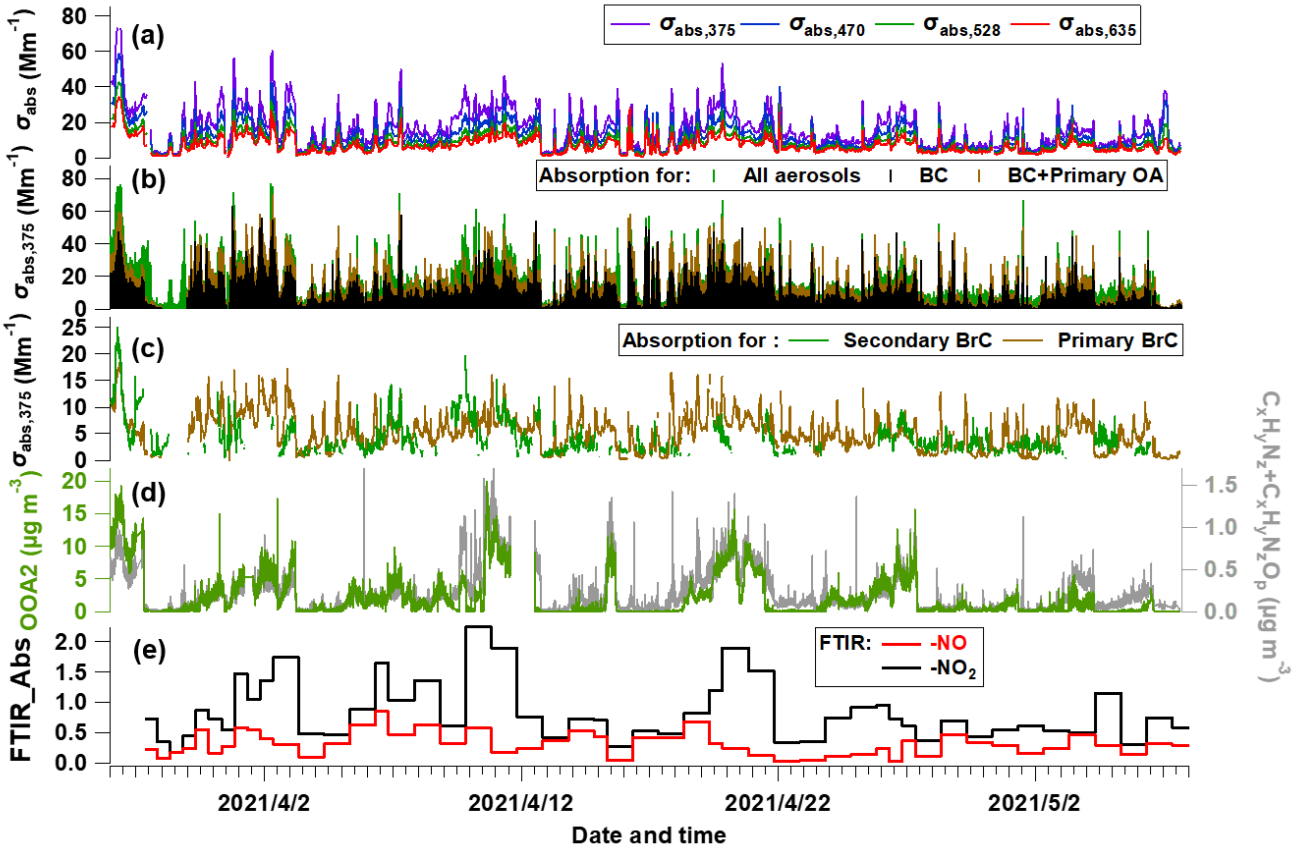

Figure 3. Temporal evolution of segregated absorbing properties. (a) Absorbing coefficients (σ_{abs}) at multiple wavelengths measured by the aethalometer, (b) σ_{abs} at λ=375nm ($\sigma_{abs,375}$) for all aerosols, primary OA and BC, (c) $\sigma_{abs,375}$ for primary BrC and secondary BrC. (d) mass concentration of OOA2 and the $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments measured by the AMS. (e) FTIR-measured absorption of -NO and -NO_2 bonds.

3.3 Source attribution of BrC absorption

A multiple linear regression (MLR) analysis is performed to apportion the absorption coefficient of BrC with the PMF attributed OA factors, expressed as:

$$\sigma_{abs,BrC}=a_0+a_1\bullet[OOA1]+a_2\bullet[OOA2]+a_3\bullet[BBOA]+a_4\bullet[COA]+a_5\bullet[HOA] \quad (6)$$

where a_1 to a_5 represents the regression coefficients for each factor. The contribution of each source-specific OA factor to $\sigma_{abs,BrC}$ can be obtained. This analysis is performed for the total BrC, primary and secondary BrC respectively. The results are shown in Table 1. MLR on the total BrC shows high correlation (r>0.4) with the factors of HOA, BBOA and OOA2, suggesting the potential importance of the primary biomass burning and traffic source along with OOA2 in governing absorption of BrC. MLR analysis on the primary BrC distinguishes its substantial correlation with BBOA (r=0.40) and HOA (r=0.46), while MRL on the secondary BrC has a high correlation with OOA2 only (r=0.44). The MRL analysis links the apportioned absorption of physical properties with source-attributed chemical compositions, therefore validating and identifying the sources of primary

and secondary BrC.

Table 1. Results of the multilinear regression analysis (MLR) between $\sigma_{abs,375}$ and the five PMF-resolved OA factors, with $\sigma_{abs,375}$ of total BrC, primary and secondary BrC as dependent, respectively. All regression coefficients have passed the significance test with p<0.01. Partial correlations above 0.4 are marked in red. Since negative values appear when the COA participates, which is thus not included in the final regression but the values using COA factor are shown in brackets.

Dependent	$\sigma_{abs,BrC}$		$\sigma_{abs,pri\ BrC}$		$\sigma_{abs,sec\ BrC}$	
Model	Regression coefficient	Partial correlation	Regression coefficient	Partial correlation	Regression coefficient	Partial correlation
Constant	2.26		1.67		1.47 (1.52)	
OOA1	0.57	0.23	0.04	0.02	0.46(0.46)	0.24 (0.24)
OOA2	1.22	**0.53**	0.37	0.25	0.74 (0.74)	**0.44 (0.44)**
BBOA	2.59	**0.46**	1.22	**0.40**	1.14 (1.18)	0.29 (0.29)
COA	1.30	0.22	1.45	0.36	/ (-0.25)	/ (-0.05)
HOA	1.70	**0.47**	1.17	**0.46**	0.49 (0.52)	0.20 (0.21)
R^2	0.77		0.63		0.55 (0.55)	

Importantly, an oxygenated secondary OA factor (OOA2) is identified to significantly contribute to the secondary BrC. This OOA has a moderate O/C (0.62) and a highest N/C of 0.037 among all factors. The high N/C means this factor contains the most abundant nitrogen-containing fragments, implied as its high correlation with the $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments (r=0.83, Fig. 3d) and with the FTIR absorption for -NO_2 and -NO bonds (r=0.69, Fig. S4). The -NO bond is mostly related to the organic nitrates ($RONO_2$), and -NO_2 peak could result from both organic nitrates and nitro-organics (Bruns et al., 2010). There is no discernable peak for organic amines. These all consistently imply that the OOA2 factor contained substantial fraction of nitrogen-containing organics, and these compounds have contributed to the absorption of secondary BrC.

3.4 Simultaneous whitening and darkening process of BrC

The diurnal variation of $\sigma_{abs,375}$ for BC and primary BrC and their fractions showed consistent morning rush-hour peaks at 6:00-8:00 and the night-time enhancement due to reduced boundary layer (Fig. 4a-b). This was in line with the morning peak of HOA and night peak of BBOA. The traffic source in this region, in particular the diesel vehicles, was reported to emit considerable OA with certain chromophores, such as aromatics (Yao et al., 2015) and heterocyclic organic compounds (Gentner et al., 2017; Schuetzle, 1983). In the morning rush-hour, BC and primary BrC accounted for 51±4% and 29±4% in the total $\sigma_{abs,375}$ respectively, with the remaining 20±2% classified as secondary BrC. The morning peak coinciding with the primary BrC may result from the rapid formation of BrC from sources when emitted gases condensed and formed aerosols. These may lead to high cooccurrence between primary and secondary BrC. Previous studies in urban environment also observed

concurrent peaks of primary and secondary BrC, which usually occurred at morning rush hour (Zhang et al., 2020). The night had contributions from BC and primary BrC at 50±2% and 30±3% respectively, with 20±3% as secondary BrC. Fig. 4b showed the decrease of primary BrC absorption tended to be more rapid than the HOA and BBOA mass (even a slight increase for HOA Fig. 1m and Fig. 1o), leading to decreased absorption coefficient per unit mass of primary BrC (shade in Fig. 4b), which indicates the photobleaching process. In this context, a recent chamber study reported that the primary BrC from biomass burning plumes could be bleached to half of the initial absorptivity in 2-3 hours (Liu et al., 2021).

Besides the morning rush-hour peak, there was an early afternoon peak for the absorption coefficient of secondary BrC, prevailing the dilution effect of daytime boundary layer (Fig. 4c-S5). The night and morning peak of OOA2 and the morning peak of $\sigma_{abs,secBrC}$ may result from primarily emitted moderately oxygenated OA, which was reported from some diesel sources (Dewitt et al., 2015; Gentner et al., 2012). The fraction of secondary BrC thus had a pronounced early afternoon peak soon after the peak solar radiation (Fig. 4f) and a peak after midnight soon after the nighttime peak of primary BrC (Fig. 4e). Fig 4e-f shows the photooxidation led to an enhanced contribution of secondary BrC by 30% but reduced contribution of primary BrC about 20%. This shift of peaking time from primary to secondary BrC demonstrates the likely process of SOA formation from gases, and these SOA compounds containing nitrogen (i.e., the OOA2) considerably contributed to the light absorption. This ageing or oxidation likely occurred through photooxidation during early afternoon and aqueous processes (high RH conditions prevail during nighttime) during nighttime. The oxidized volatile organic compounds (VOCs) with nitrogen chemistry involved could condense to produce additional mass in particle phase (Ehn et al., 2014; Finewax et al., 2018). Due to the high NO_x emission, photooxidation of traffic VOCs may have largely involved nitrogen chemistry. Previous studies found the NO_x-involved SOA could produce considerable chromophores (Lin et al., 2015; Siemens et al., 2022), such as the traffic VOCs may produce SOA in a time scale of hours, containing nitro-aromatics (Wang et al., 2019b; Keyte et al., 2016). The daytime formation of organic nitrate may follow the gas-phase photooxidation mechanism, in which the excess NO could add to the peroxy radical to produce organic nitrate (Liebmann et al., 2019). The nighttime chemistry involving NO_3 radical through the oxidation of NO_2 by O_3, contributed to the important formation of organic nitrate by initializing the production of nitrooxy peroxy radicals (Ng et al., 2008; Rollins et al., 2012). Laboratory studies (Nakayama et al., 2013; Liu et al., 2015c) also widely observed the rapid production of nitrogen-containing OA involving NO_x chemistry could contribute to light absorption of aerosols.

Overall, by apportioning the absorption of primary and secondary BrC, we found the photooxidation led to an enhanced contribution of secondary BrC by 30% but reduced contribution of primary BrC about 20% in the semi-urban environment. This revealed that the whitening and darkening of BrC occurred simultaneously, and the secondary BrC produced by photooxidation may compensate some bleaching effect of primary BrC. The dominance of both competing processes may depend on the timescale and altitude in the atmosphere. For example, the enhanced BrC fraction observed above the planetary boundary layer may be explained by the enhanced secondary BrC (Tian et al., 2020), while further ageing may bleach the produced chromophores of these SOA.

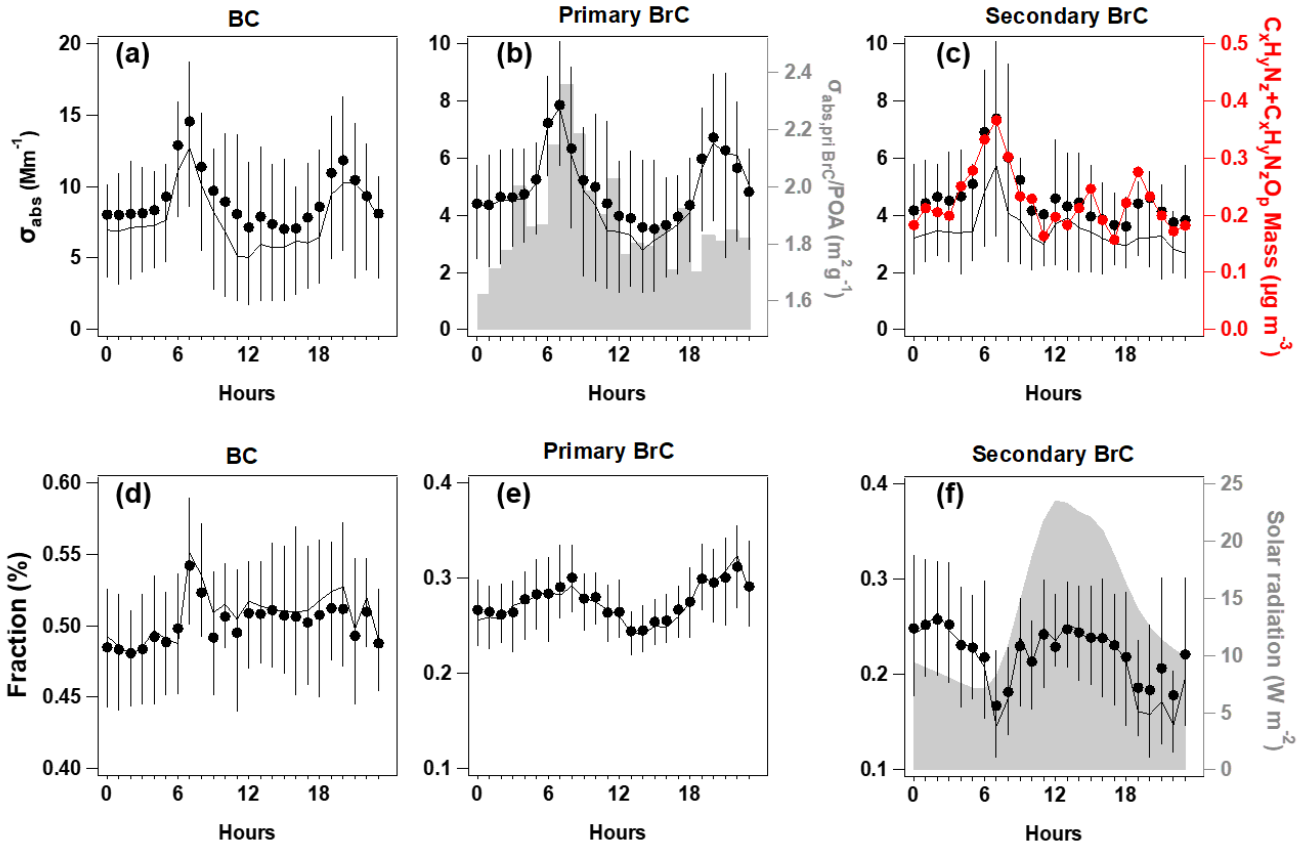

Figure 4. Diurnal variations of absorption coefficient at λ=375nm ($\sigma_{abs,375}$) for BC (a), primary BrC and absorption efficiency of primary BrC ($\sigma_{abs,priBrC}$)/POA is shown in shade (b), and secondary BrC, along with the $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments (c); the respective fraction in total for the segregated $\sigma_{abs,375}$ (d-f), with direct radiation shown in shade. In each plot, the lines, dots and whiskers denote the median, mean and the 25th/75th percentiles at each hour respectively.

4. Conclusion

This study apportioned the shortwave absorption of BC, primary and secondary BrC, through concurrent measurements of BC microphysical properties and OA mass spectra. The apportioned primary BrC absorption was linked with traffic and biomass burning emissions, while secondary BrC was found to be associated with an oxygenated secondary OA factor with higher nitrogen content. The enhancement of secondary BrC and decease of primary BrC simultaneously occurred via daytime photooxidation. The results emphasize the importance of nitrogen-containing OA in contributing to BrC. These OA could primarily emit as aerosol phase, or in gas phase which requires further oxidation to be in aerosol phase to serve as BrC. The NO_x-involved chemistry is prone to add nitrogen element to the existing OA and enhance the absorptivity of chromophores. The anthropogenic NO_x emission could be therefore an important source in producing shortwave absorbing components in the atmosphere, which may offset some of the conventionally-thought photobleaching of BrC.

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Author contribution

D.L., X.J. and Qian L. prepared and designed the observation. D.L., Qian L., X.J and P.T. initiated the field campaign and conducted the measurements. Qian L., D.L. P.T., Y.W., S.L. and K.H. contributed to the data analysis. Quan L., H.M., L.R., B.K., D.D. and S.K. provided technical support and assistance. Qian L. and D.L. wrote the manuscript. All authors read and approved the final manuscript.

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