https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

Formation of Highly Absorptive Secondary Brown Carbon Through Nighttime Multiphase Chemistry of Biomass Burning Emissions

Ye Kuang[1,*], Biao Luo[1], Shan Huang[1*], Junwen Liu[1], Weiwei Hu[2], Yuwen Peng[1], Duohong Chen[3], Dingli Yue[3], Wanyun Xu[4], Bin Yuan[1], Min Shao[1]

[1] Institute for Environmental and Climate Research, College of Environment and Climate, Jinan University, Guangzhou, China.

[2] State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[3] Guangdong Ecological and Environmental Monitoring Center, State Environmental Protection Key Laboratory of Regional Air Quality Monitoring, Guangzhou 510308, China

[4] State Key Laboratory of Severe Weather, Key Laboratory for Atmospheric Chemistry, Institute of Atmospheric Composition, Chinese Academy of Meteorological Sciences, Beijing, China

Corresponding author: Ye Kuang (kuangye@jnu.edu.cn) and Shan Huang (shanhuang_eci@jnu.edu.cn)

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

Abstract

Biomass burning is a major global source of both primary brown carbon (BrC) and reactive trace gases in the atmosphere, thus exerts significant impacts on global climate and regional atmospheric chemistry. However, a substantial gap remains in our understanding of the nighttime evolution of biomass burning emissions. Here we present prominent nighttime formation of secondary organic aerosol (Night-OA) with strong absorptivity but markedly different spectral dependence from that of primary biomass burning organic aerosols, which was observed during autumn of the Pearl River Delta region of China when biomass burning plumes prevailed. Our results demonstrate that the formation of Night-OA appeared high dependence on both magnitudes of afternoon biomass burning emissions and available oxidants of NO_2 and O_3. Active nighttime NO_3 radical chemistry was characterized by quick O_3 depletion and almost zero concentration of NO, and the rapid decrease of NO_2 coincident with the quick nitrate formation suggests that the rapid NO_2 consumption supplied the NO_3 and N_2O_5 reaction chains. However, the quickest Night-OA formation occurred when nitrate formation ceased and relative humidity reached maximum, and mainly added mass to aerosol water abundant diameter ranges. This co-variation demonstrates that gas-phase and aqueous-phase chemistry of biomass burning precursors likely coordinated to promote the quick nighttime formation of Night-OA. Findings of this study highlight the nighttime darkening of biomass burning plumes through multiphase reactions and the proposed secondary BrC formation mechanisms may have broad implications in climate and air quality effects of biomass burning, such as the interaction between biomass burning plumes with water abundant pyroconvection cloud.

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

1 Introduction

Light absorbing organic aerosols termed as brown carbon (BrC) (Andreae and Gelencsér, 2006), absorbs solar radiation and warms the atmosphere, acts as potential photosensitizers and alters atmospheric oxidation capacity (Liu et al., 2020), thus impacting profoundly on atmospheric chemistry, air quality and climate (Jo et al., 2016). Biomass burning activities happen frequently across the globe due to natural and anthropogenic activities, injecting large amounts of fine organic aerosols (known as biomass burning organic aerosol, BBOA) and trace gases into the global atmosphere, thereby acting as a major global source of atmospheric primary organic aerosols and non-methane volatile organic compounds (Andreae and Merlet, 2001;Akagi et al., 2011;Andreae, 2019;van der Werf et al., 2017), thus exerting significant impacts on global climate (Liu et al., 2021;Yu et al., 2019;Yu et al., 2021). The freshly emitted BBOA is highly absorptive near ultraviolet wavelengths and considered as a major contributor to atmospheric BrC (Wang et al., 2016). A number of laboratory studies revealed that secondary organic aerosol (SOA) formed from the oxidation of biomass burning precursors (BBSOA) is also absorptive (Saleh et al., 2013), however, the importance of secondary BrC formed from biomass burning precursors remains uncertain.

Both daytime and nighttime chemistry play significant roles in aging biomass burning plumes and associated secondary SOA and BrC formation. Daytime aging of biomass burning emissions and its impacts on SOA formations have previously been extensively investigated (Hodshire et al., 2019) , which found that the formed SOA contributed substantially to BrC (Kumar et al., 2018;Saleh, 2020) and confirmed by field measurements. For example, Palm et al. (2020) observed that daytime oxidation of emitted phenolic compounds contributed a majority to BBSOA formation, with products being highly absorptive. Compared with daytime aging experiments of biomass burning emissions, laboratory studies representative of night chemistry are scarce. At night, the consumptions of O_3 and OH is much faster than their formation rates due to the absence of photochemical reactions, thus atmospheric concentration of these two oxidants reduce rapidly after sunset. The depletion of O_3 through NO_2 oxidation generates NO_3 radical that act as a major oxidant during nighttime periods and drives the tropospheric nighttime chemistry. Decker et al. (2019) investigated the nighttime chemical transformation in biomass burning plumes using a box model, which was initialized by aircraft observations, with results demonstrating NO_3 radical loss mostly due to reactions with biomass

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

burning volatile organic compounds (VOCs). In recent years, a number of laboratory studies using NO_3 as oxidant were carried out to explore influences of nighttime aging on biomass burning emissions related SOA formations and associated BrC evolutions (Cheng et al., 2020;Li et al., 2020a;Jiang et al., 2019;Tiitta et al., 2016;Hartikainen et al., 2018). Their results demonstrated that both nighttime aging of BBOA aerosols and biomass burning VOC precursors such as pyrrole can potentially act as important sources of SOA and BrC. However, contributions derived from laboratories studies cannot be directly linked with SOA and BrC contribution magnitudes within ambient nighttime atmosphere. Kodros et al. (2020) further highlighted the importance of nighttime processing of biomass burning emissions as an important global source of SOA based on combined results from laboratory and field observations. Nevertheless, field measurements that observed nighttime evolutions of biomass burning plumes and directly confirmed significant contributions of SOA and BrC from nighttime aging of biomass burning emissions are highly in lack. Only one field measurement study has observed substantial increase of BrC light absorption during a night-long biomass burning event and identified nitroaromatics in abundance within aged BBOA aerosols, contributing greatly to light absorption (Lin et al., 2017;Bluvshtein et al., 2017), based on which it was hypothesized that nighttime chemistry involving NO_3 radical oxidation of primary BBOA might play significant roles in BrC transformation. Nighttime conditions are typically characterized by high atmospheric relative humidity (RH) caused by temperature decreases, therefore likely result in abundant aerosol water, which might favor aqueous SOA and BrC formation (Wang et al., 2019b). However, most of previous laboratory studies have not investigated the role of RH or aqueous phase chemistry in nighttime aging of biomass burning plumes. Kodros et al. (2022) found that nighttime oxidation of biomass burning emissions were sensitive to RH, however, could not conclude what roles RH was. Their results demonstrated that homogenous gas-phase oxidation and subsequent condensation of lower-volatility vapors was probably the dominant process, however, they could not rule out the possible role of heterogeneous oxidation processes. Therefore, how nighttime NO_3 radical chemistry coordinates with aerosol aqueous or heterogenous reactions under high nighttime RH conditions to affect SOA and BrC formations remains unexplored, which is a substantial knowledge gap in the research field of nighttime chemical transformation of biomass burning emissions and its role in SOA and secondary BrC formations.

In this study, we report substantial amounts of highly absorptive SOA likely formed during nighttime mainly from biomass burning emissions. The potential formation mechanisms of nighttime

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

SOA formation are investigated based on real-time measurements of parameters such as gaseous pollutants, aerosol physical and chemical properties and meteorological factors. Our results revealed that coordinated nighttime multiphase chemistry of biomass burning emissions likely formed highly absorptive SOA, which improved our current understanding on nighttime aging of biomass burning emissions and might also have significant implications for cloud processing of biomass burning. Additionally, this study is a companion paper to Luo et al. (2022), where we proposed an improved absorption Ångström exponent (AAE) ratio method for deriving multiwavelength BrC absorptions from multiwavelength aerosol absorption measurements using an aethalometer, and investigated comprehensively size distribution, absorption and scattering as well refractive index of primary BBOA.

2 Materials and Methods

2.1 Field measurements

A field campaign was conducted from 30 September to 17 November 2019 at a regional background site of the Peral River Delta region. This site locates at the country side of Heshan county, about 55 km away from the megacity Guangzhou and at the top of hill with surroundings are small villages and residential towns. Routine observations of air pollutants such as carbon monoxide, ozone nitrogen dioxides and $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 μm), and meteorological parameters such as air relative humidity (RH), temperature, wind speeds and directions were managed by the provincial environmental monitoring authority and this site is authorized as a regional background supersite. During the observation period, intensive aerosol measurements including aerosol optical properties, aerosol size distributions as well as aerosol chemical compositions were also performed to investigate relationships between aerosol physical properties and aerosol chemical compositions. The aerosol scattering properties and aerosol hygroscopicity were measured using a humidified nephelometer (Aurora 3000) system (Kuang et al., 2021). Aerosol absorptions of multiple wavelengths were measured using an aethalometer (Magee AE33, (Drinovec et al., 2015)). Aerosol size distributions were measured jointly by using a scanning mobility particle sizer (SMPS, TSI 3080) and an aerodynamic particle sizer (APS; TSI Inc., Model 3321). More details on the site and set-up of instruments please refer to Kuang et al. (2021) and Luo et al. (2022).

The submicron aerosol chemical compositions were measured using a soot particle high-resolution time of flight aerosol mass spectrometer (SP-AMS, Aerodyne Research, Inc., Billerica, MA,

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

USA). The set-up and validation of SP-AMS measurements were performed and discussed in Kuang, et al. (Kuang et al., 2021), thus not detailed here. Source identification of organic aerosols was performed using the commonly used positive matrix factorization (PMF), two primary OA factors and four secondary OA factors are identified, and the determination of PMF factors are thoroughly discussed in Luo et al. (2022). The two primary OA factors include biomass burning organic aerosols (BBOA) and a hydrocarbon-like organic aerosols (HOA). The biomass burning emissions represent the most important primary sources during the observations as discussed in Luo et al. (2022), and its most prominent activities were usually observed near sunset (Fig.1a).The four SOA factors including more oxygenated organic aerosols (MOOA, O/C=1), less oxygenated organic aerosols (LOOA, O/C=0.72), nighttime-formed organic aerosols (Night-OA, O/C=0.32) and aged BBOA (aBBOA, O/C=0.39). The Night-OA factor was characterized by its obvious correlation with nitrate and they both exhibited obvious increase after sunset (Fig.1a). The name of aBBOA was originally because of its correlation with $C_6H_2NO_4^+$ which is a typical fragment of the aged BBOA component nitrocatechol (Bertrand et al., 2018). The mass spectral profiles and time series of these organic aerosol factors were shown in supplement of Luo et al. (2022), and details about the determination of these factors are introduced in supplement of Luo et al. (2022). Note that the AE33 measurements were only available until 1th of November, while SP-AMS measurements were available until 18th of November, resulting in different time frames of different timeseries.

Given that PMF analysis is fundamental to our study, the mass spectral profiles of factors are provided in Fig. S1, and key aspects of the resolved results are explained here, particularly concerning the O/C characteristics and the naming of aBBOA and Night-OA. In previous studies (Kuang et al., 2021;Luo et al., 2022), we already realized that the correlation between aBBOA and $C_6H_2NO_4^+$ was actually weak (R=0.31), suggesting that it might not fully be constituted of aging products of primary BBOA considering its O/C was even lower than that of BBOA. However, aBBOA exhibited similar diurnal behavior to LOOA showing clear daytime photochemical production plus an evening peak around 19:00 (local time) just after the peak hour of BBOA as shown in Fig.S1. Also, the evening peak value of aBBOA between 19:00 and 22:00 of each day was found to be moderately correlated with the noon peak in the next day (R =0.55; (Wu et al., 2024)). This tells that aBBOA could be emitted from biomass burning. However, it could be speculated that only a small portion (aBBOA accounts for an average of 8% of the mass increase during identified biomass burning events, Fig. 3 of Luo et al.

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

(2022)) is directly emitted. Most of it likely originated from the gas-phase oxidation of biomass burning emitted VOC precursors considering that aBBOA mainly added mass to diameters of condensation mode (see discussions about size distributions of OA factors in supplement of Luo et al. (2022)), which could have a low O/C during short oxidation periods, as demonstrated in previous indoor experiments on biomass burning emissions (Yee et al., 2013; Ahern et al., 2019). This hypothesis is further supported by the fact that increases in aBBOA loading enhance organic aerosol hygroscopicity despite its low O/C, as demonstrated by Kuang et al. (2021), whereas primary organic aerosols have not been observed to enhance overall organic aerosol hygroscopicity (Kuang et al., 2020).

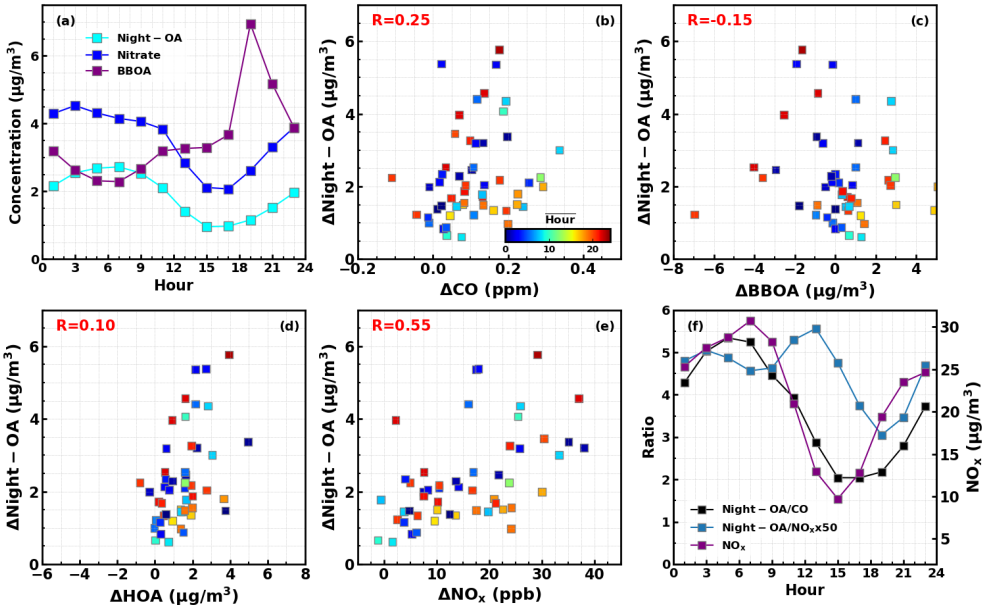

Figure 1. (a) Diurnal variations of nitrate, Night-OA and BBOA; **(b-e)** Relations between increases of Night-OA and increases of CO, BBOA, HOA and NOx for identified Night-OA increase cases, colors of scatter plots represent the average time of Night-OA increase cases; **(f)** Diurnal variations of ratios Night-OA/CO, Night-OA/NOx in the left axis and NOx in the right axis.

The Night-OA factor has a relatively low O/C ratio of 0.32, raising the question of whether it originates from primary emissions or secondary formation. As discussed in Luo et al. (2022), traffic, cooking (The HOA and COA and were not separated in the PMF results although the hydrocarbon factor was named HOA as discussed in Kuang et al. (2021)), and biomass burning are likely the dominant primary sources during this campaign. If Night-OA were a primary source, it would be expected to increase alongside other primary sources. We identified most Night-OA increase events

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

and examined their correlation with variations in other primary sources, as shown in Fig. 1b-e. This analysis reveals that Night-OA increases were typically observed after sunset, though occasionally during the daytime. Night-OA increases showed weak correlations with changes of CO (R=0.25), HOA (R=0.1), and BBOA (R=-0.15), but a moderate correlation with NOx (R=0.55). During significant biomass burning events (indicated by substantial BBOA increases), the concentration of Night-OA actually decreased on average (Fig. 3 of Luo et al. (2022)), suggesting that Night-OA is unlikely to be emitted from biomass burning. We also identified all significant HOA increase events that did not coincide with biomass burning and analyzed the average HOA increase and variations in other aerosol components (Fig. S2). It shows that, despite significant HOA increases, the average mass concentration of Night-OA remained almost unchanged, indicating that Night-OA is also unlikely to originate from HOA-associated emissions. Therefore, the weak but positive correlations between Night-OA and HOA as well as CO are likely associated with the accumulation characteristics of primary emissions after sunset. The higher correlations between Night-OA and NOx may also result from the accumulation of NOx starting in the afternoon when photochemical depletion is weaker. Another possibility to consider is whether Night-OA increases could be associated with plumes containing higher NOx transported from other regions. We investigated the diurnal variations of the Night-OA/CO and Night-OA/NOx ratios, observing persistent increases in Night-OA/CO and Night-OA/NOx ratios when significant Night-OA formation began. This suggests that Night-OA is likely formed through secondary processes, consistent with that it was also correlated with nitrate (R=0.67). The low O/C of Night-OA, still higher than that of the primary factor HOA, was determined by a high amount of $C_xH_y^+$ ions in spite of significant intensity of oxidation tracers $C_2H_3O^+$ and CO_2^+, suggesting that Night-OA was oxidation products with low oxidation state during the nighttime. Similar situation was previously found in study at Bakersfield of USA in which Liu et al. (2012) identified SOA factors as alkane-SOA and aromatic-SOA with moderate O/C (0.27-0.36). Meanwhile, NOx potentially promoted its formation, given the highest N/C ratio of Night-OA among all resolved factors. This will be discussed further in Sect 3.2.

In summary, both aBBOA and Night-OA are not likely primary, while the naming of aBBOA and Night-OA factors might not be perfect, we retain these terms in this study for consistency with our previous work (Kuang et al., 2021;Luo et al., 2022;Wu et al., 2024).

2.2 Quantification of BrC absorptions

In Luo et al. (2022), we proposed an improved AAE ratio method to subtract brown carbon (BrC)

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

absorptions from measured total aerosol absorptions during this field campaign. Therefore, the details about discussions of this method please refer to Luo et al. (2022), and we only introduce briefly the philosophy of the new method here. The essential part of deconvolving BrC absorptions from total aerosol absorptions is the adequate representation of black carbon (BC) spectral absorptions using the Ångström exponent law. Results of previous studies (Wang et al., 2018a;Li et al., 2019a) demonstrated that significant wavelength dependence of AAE_{BC} and constant assumption of AAE_{BC} in BrC absorption retrievals might lead to significant bias. Thus, the AAE ratio defined as $R_{AAE}(\lambda)=AAE_{BC,\lambda-880}/AAE_{BC,950-880}$ was proposed to tackle spectral AAE_{BC} variations, and on-line measurement data of $AAE_{950-880}$ were used as $AAE_{BC,950-880}$ due to negligible absorption contributions of BrC at wavelengths of 880 nm and 950 nm. Thus, BrC absorptions (σ_{BrC}) at different wavelength (λ) including 370 nm, 470 nm, 530 nm, 590 nm and 660 nm can be derived using the following formula, where σ_a is measured aerosol absorption:

$$\sigma_{BrC}(\lambda) = \sigma_a(\lambda) - \sigma_{BC}(880\ nm) \times \left(\frac{880}{\lambda}\right)^{AAE_{BC,950-880} \times R_{AAE}(\lambda)} \quad (1)$$

As the sophisticated discussions presented in Luo et al. (2022), variations of many factors such as BC refractive index, coating shell refractive index as well as BC mixing state, and BC mass size distributions (Li et al., 2019b) might influences the magnitudes of $R_{AAE}(\lambda)$. However, sensitivity tests shown in Luo et al. (2022) clearly concluded that BC mass size distributions dominated R_{AAE} (λ) variations. In Heshan campaign, the BC calibration for SP-AMS was not available, so, the carbon signals were used to retrieve shape of BC mass size distribution, and the total mass was constrained by the ratio between integrated C_x (C_1-C_9) signals and BC mass concentrations provided by the AE33. The real-time measured carbon fragments (C_x) distributions by the SP-AMS were therefore used to distribute the total BC mass to different diameter bins to calculate R_{AAE} (λ) as introduced in Luo et al. (2022). Details of the calculation can be found in its supplement. The average and standard deviations of R_{AAE} (370), R_{AAE} (470), R_{AAE} (520), R_{AAE} (590) and R_{AAE} (660) are 0.79(±0.044), 0.85(±0.038), 0.88(±0.035), 0.9(±0.035) and 0.93(±0.031) during the observation period.

3 Results and discussions

3.1 Highly absorptive SOA formed during nighttime.

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

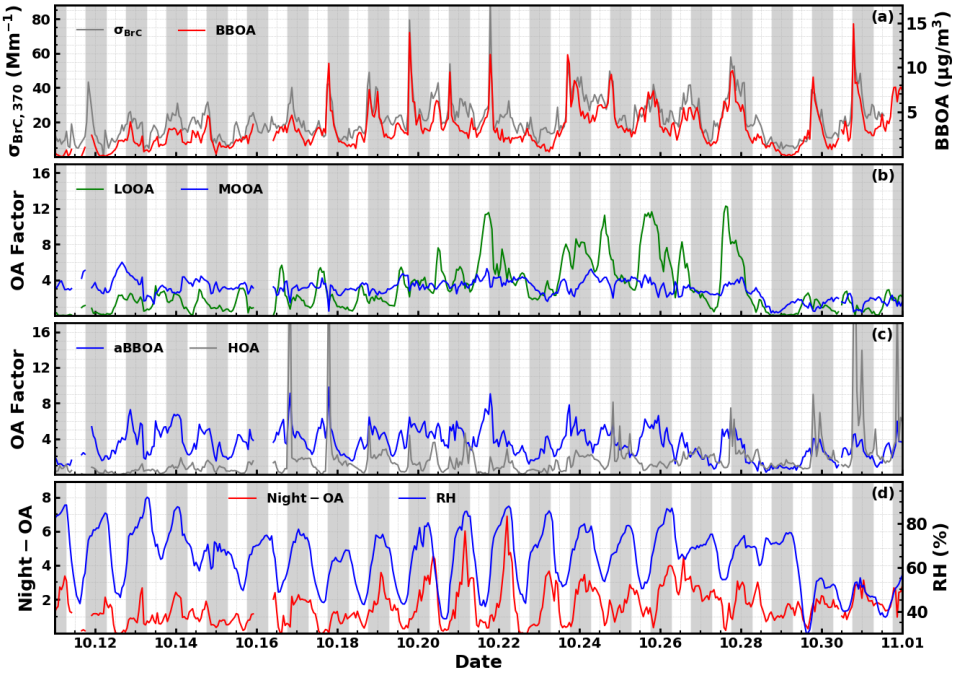

Figure 2. Timeseries of **(a)** brown carbon absorption at 370 nm ($\sigma_{BrC,370}$) in the left axis and BBOA in the right axis; **(b)** LOOA and MOOA; **(c)** aBBOA and HOA; **(d)** Night-OA in the left axis and RH in the right axis. Shaded areas represent nighttime periods.

As reported by Luo et al. (2022), biomass burning events happened frequently during the observation period and biomass burning was the dominant source of primary organic aerosols with the average BBOA/HOA ratio of 3.3. The dominant contribution of biomass burning to primary aerosol emissions together with the strong biomass burning emissions before dusk as well as sometimes daytime emission characteristics (Luo et al., 2022) provided a unique opportunity to explore the nighttime chemistry associated with biomass burning and its impacts on atmospheric BrC evolution in biomass burning plumes. Timeseries of retrieved $\sigma_{BrC,370}$ is shown in Fig.2a. It shows that BBOA varies quite consistently with $\sigma_{BrC,370}$ and they are highly correlated (R=0.88), demonstrating the dominant contribution of BBOA to BrC absorptions. However, the correlation coefficient between BBOA and σ_{BrC} decreases as the wavelength increases, i.e., the correlation coefficients between σ_{BrC} at 470 nm, 520 nm, 590 nm, 660 nm and BBOA are 0.83, 0.8, 0.76, 0.69. In addition, as shown in Fig.2a, coordinal variations between BBOA $\sigma_{BrC,370}$ are usually seen during daytime especially during the dusk BBOA spike periods, however, the $\sigma_{BrC,370}$ usually deviates substantially from BBOA

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

variations during the nighttime (gray areas in Fig.2). The average diurnal variations of both $\sigma_{BrC,370}$ and the ratio $\sigma_{BrC,370}$/BBOA is presented in Fig.3a, and quick $\sigma_{BrC,370}$/BBOA increase were observed during nighttime before 06:00 LT. These results demonstrate that organic aerosol components other than BBOA also contribute substantially to BrC absorption and differ much at different wavelengths.

The time series of OA factors other than BBOA are also shown in Fig.2b-d. As analyzed in Kuang et al. (2021), SOA contribute dominantly to total OA mass (SOA mass fraction>70% on average) during this field campaign. Most prominent features of SOA formations are the quick daytime formation of LOOA, aBBOA and nighttime formation of Night-OA, while MOOA exhibit almost no diurnal variations and are mostly associated with the regional airmass. The average mass absorption efficiencies (MAEs) (m^2/g) of different OA factors are retrieved using multivariate linear regression method (Fig.S3), and the deduced average MAEs values at 370 nm for BBOA, aBBOA, HOA, LOOA, MOOA and Night-OA are 3.8, 0.84, 0.24, 0, 1, 2.3 m^2/g respectively. Note that negative value of about -0.1 is retrieved if LOOA values were inputs of the multivariate linear regressions, demonstrating quite low absorptivity of LOOA, thus MAE of LOOA is treated as zero. As shown in Fig.2b, rapid LOOA formation episodes happened frequently during daytime but $\sigma_{BrC,370}$ still varies only with BBOA during that period, which confirms the white property of LOOA. The derived MAE of HOA is very small which is consistent with the low absorptivity of HOA during HOA spikes. The prominent BrC factors are identified as BBOA, Night-OA, MOOA and aBBOA. The most surprising part is the highly absorptive property of Night-OA whose absorptivity is only lower than that of BBOA but much higher than other OA factors. Based on derived MAE values for OA factors as well as their mass concentrations, contributions of OA factors to $\sigma_{BrC,370}$ are estimated and their diurnal variations are shown in Fig.3b. It reveals that Night-OA accounts for the second largest contribution to BrC absorption during nighttime and even reaches beyond the contribution of BBOA near local time 06:00 (>30%), which explains the observed substantial nighttime deviation of $\sigma_{BrC,370}$ from BBOA as shown in Fig.3a. The average contributions of BBOA, Night-OA, MOOA and aBBOA to $\sigma_{BrC,370}$ are 50%, 20%, 16%, 12%, respectively. The time series of estimated OA contributions to BrC absorption at 370 nm are shown in Fig.S4, it tells that Night-OA sometimes contribute dominantly (>50%) to $\sigma_{BrC,370}$ especially when rapid increase of Night-OA appeared due to nighttime secondary formation.

Different BrC components usually exhibit different absorption spectral dependences (Laskin et al., 2015). Diurnal variations of $AAE_{370\text{-}470,\ BrC}$ are investigated and shown in Fig.3c. The $AAE_{370\text{-}470,}$

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

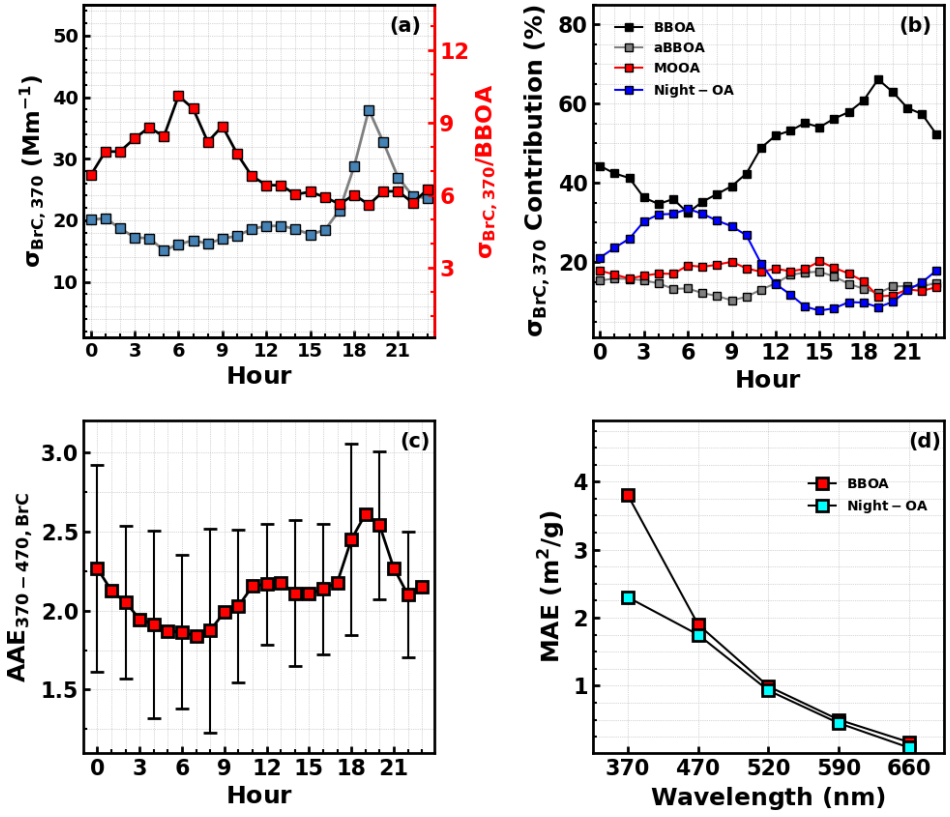

Figure 3. (a) Diurnal variations of $\sigma_{BrC,370}$ and the ratio $\sigma_{BrC,370}$/BBOA; **(b)** Diurnal variations of contributions of different OA factors to $\sigma_{BrC,370}$; **(c)** Average diurnal variations of brown carbon absorption angstrom exponent between 370 nm and 470 nm; **(d)** Retrieved mass absorption efficiencies (MAE,) of BBOA and Night-OA at multi-wavelengths.

286 BrC exhibits distinct diurnal variations, with one peak at dusk when BBOA reaches its highest mass
287 concentration and a trough at the time when Night-OA contributes most to and BBOA contribute the
288 least to $\sigma_{BrC,370}$. This phenomenon suggests that spectral dependence of Night-OA absorptivity differs
289 much with that of BBOA. The multivariate linear regression method is thus also used for retrieving
290 MAEs of BBOA and Night-OA at wavelengths of 470 nm, 520 nm, 590 nm and 660 nm (the
291 performance of using retrieved MAE values at multiple wavelengths are shown in Fig.S3), and the
292 retrieved spectral dependence of BBOA and Night-OA absorptivity are shown in Fig.3d. The results
293 show that Night-OA absorbs as strong as that of BBOA at visible wavelength ranges, highlighting a
294 more important role of Night-OA in BrC absorption than expected from the retrieval of $\sigma_{BrC,370}$. The

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

retrieved $AAE_{370\text{-}470}$, $AAE_{470\text{-}590}$ for BBOA and Night-OA are 3 and 5.9, 1.3 and 6, respectively, which explains the observed quick decrease of $AAE_{370\text{-}470,\ BrC}$ during nighttime. The direct quantification of $AAE_{370\text{-}470}$, $AAE_{470\text{-}590}$ for BBOA is difficult due to the entanglement of BC absorption and thus rarely reported. The retrieved $AAE_{470\text{-}590}$ for BBOA and Night OA are in general consistent with the AAE of bulk BrC solutions extracted using different solvents which were sampled during and after a nighttime nationwide biomass burning event (Lin et al., 2017).

3.2 Precursors and Possible Mechanisms of the Night-OA formation.

As shown in Fig.1a and Fig.2d, the Night-OA concentration increased during the nighttime, while usually decreased and reached near zero in the afternoon, so the Night-OA factor is characterized by its rapid nighttime formation and quick daytime evaporation. In general, SOA can either be formed through condensation of gas-phase chemically aged low- or semi-volatile VOC precursors following the gas-particle partitioning theory or formed in the aqueous phase through further oxidation of water-soluble primary VOCs as well as secondary products of gas-phase VOC aging processes, with the former referred to as gasSOA and the latter referred to as aqSOA. Several recent researches reveal that SOA can also be formed through oxidation of semi-volatile components evaporated from emitted primary organic aerosols in gas phase (Palm et al., 2020) or in the aqueous phase (Wang et al., 2021). The sources and formation pathways of Night-OA is of great concern in meriting the importance of Night-OA formations in global atmosphere and paving the way for designing targeted laboratory experiments in future.

The VOC profiles of this observation site are quite complex as mixtures of both different anthropogenic sources and natural sources (Song et al., 2019). However, prominent and continuous Night-OA formation events observed from 19 to 22 October which are accompanied with frequently observed sharp increase of BBOA mass concentrations before the fall of night bring hints that Night-OA formation might be associated with biomass burning emissions. Indeed, the air is always moving and to be lagrangian, the air after midnight might differ with those before midnight. However, the relations between Night-OA signals after midnight and emission signals before midnight might still deliver some clues. The average nighttime mass concentrations of Night-OA from 22:00 LT to 06:00 LT (the next day) are plotted against the average BBOA mass concentrations from 16:00 LT to 22:00 LT of this campaign and the results are shown in Fig.4a. It shows that Night-OA formation is positively correlated with BBOA before the night which supports the speculation that Night-OA formation is a

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

result of the nighttime chemistry of biomass burning emissions. The nighttime oxidant levels indicated by the concentrations of Ox (NO_2+O_3) represented by colors in Fig.4a demonstrates that the highest Night-OA formation was accompanied with strongest biomass burning emissions and most abundant oxidants, suggesting that the importance of nighttime aging processes in Night-OA formation. Following evidences show that gas-phase and aqueous-phase chemistry of biomass burning precursors likely have coordinated to promote the quick nighttime formation of Night-OA.

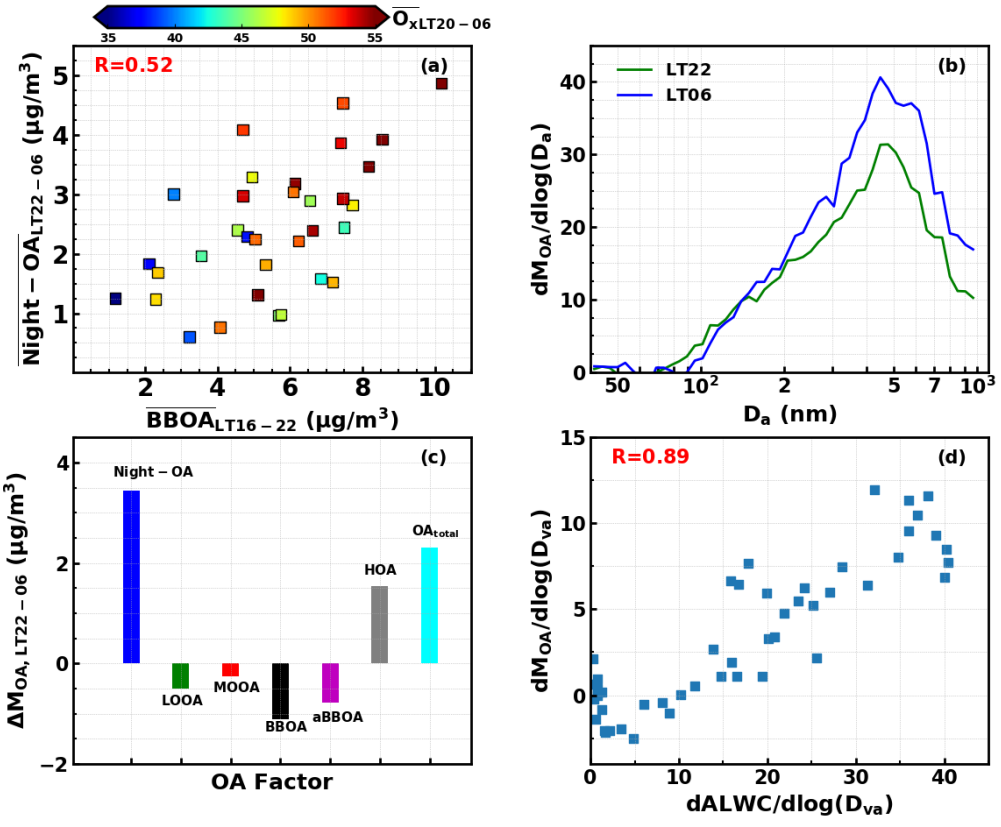

Figure 4. **(a)** Correlations between average nighttime Night-OA mass concentrations and average BBOA mass concentrations over LT16-22, colors corresponding to the average Ox (NO_2+O_3) mixing ratio (ppb) during the night; **(b)** Average evolutions of organic aerosol mass size distributions from local time 22:00 (20, 21 October) to 06:00 (21, 22 October); (c) Average differences for organic aerosol (OA) mass concentration corresponding to (b); **(d)** The correlations between increase of size-resolved organic mass concentrations in (c) (LT06 minus LT22) with average size-resolved aerosol liquid water content (ALWC).

Three obvious Night-OA formation episodes which lasted more than three days, as shown in Fig.S5, were observed during the entire field campaign. The peak Night-OA mass concentration of

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

each night increased during these episodes and were accompanied with the increase of nighttime peak RH during each episode, suggesting that abundant nighttime aerosol water might play significant roles in Night-OA formation. More solid clues could be found from different behaviors of gasSOA and aqSOA formations in modifying the aerosol size distribution. The gasSOA forms through condensation following partitioning theory thus adding mass mainly to condensation mode which contributes most to aerosol surface area concentrations. Whereas, aqSOA formation depends on amounts of liquid water content thus adding mass mainly to the mode where most aerosol water resides. The evolution of average OA size distribution during the night of 20 and 21 October when most prominent Night-OA formation occurred is illustrated in Fig.4b. During the two nights from 22:00 LT to 06:00 LT, Night-OA formations contributed most to the mass concentration increase of the entire OA and HOA contributed less, while mass concentrations of all other OA factors have decreased and partially balanced out the OA increase (Fig.4c). HOA emissions mainly added mass to diameter ranges of 100-300 nm as demonstrated by Luo et al. (2022). However, as shown in Fig.4b, substantial increase of mass concentrations at diameter range of > 300 nm occurred even all other SOA factors showed a decreasing trend for the case shown in Fig.4c, suggesting the substantial OA mass increase of larger than 300 nm are contributed by the Night-OA increase. The results shown in Fig.4d showed that the size-resolved increase of OA mass for abovementioned cases (Fig.4b and c) was highly correlated with size-resolved aerosol liquid water content (details about the size resolved aerosol water content calculation are presented in Sect 1.2 of the supplement), demonstrating that the Night-OA formation added mass mainly to aerosol water abundant diameter ranges. The average RH of the cases shown in Fig.4b-d is around 80%, with a corresponding average hygroscopicity parameter κ of 0.26 measured by the humidified nephelometer system, demonstrating a growth factor of ~ 1.27 (water thickness of ~81 nm for aerosol diameter of about 300 nm), thus not a thin film of water for heterogeneous reactions, but more likely formed through dark aqueous reactions.

In addition, as shown in Fig.S6, the Night-OA decreased quickly during daytime, which is beyond the dilution effect of boundary layer development (indicated by rapid decrease of Night-OA/CO as shown in Fig.S6) thus implying the substantial daytime loss of Night-OA which might be caused by several processes, such as partitioning and photodegradation (Wang et al., 2023). The partitioning dynamics of gasSOA and aqSOA also differ much, which might add more information in looking into the Night-OA formation pathway. Following the rule of partitioning theory, evaporation equilibrium

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

of the condensation of gasSOA is tightly associated with air temperature. Equilibrium of the reversible aqSOA formation greatly depends on aerosol water changes, while evaporation of irreversible SOA production through aqueous pathways are quite sophisticated (Tong et al., 2021). It was found that the percentile of Night-OA mass loss during the daytime (07:00 to 16:00 LT) are more tightly correlated with RH decrease compared with temperature increase (Fig.S7). HOA also exhibits obvious evaporation during daytime (indicated by rapid decrease of HOA/CO Fig.S6), however, the daytime loss of HOA seems more tightly correlated with temperature increase as shown in Fig.S8. The phenomenon that Night-OA daytime loss is more correlated with RH decrease implied that Night-OA possibly co-evaporated with water vapor as RH decrease. This might serve weakly but still another supporting clue for that Night-OA were likely formed through aqueous pathways and maybe reversible.

As revealed by Fig.4a that nighttime oxidation levels play significant roles in Night-OA formation, the question leaves what's the role of nighttime gas-phase chemistry in promoting the Night-OA formation.

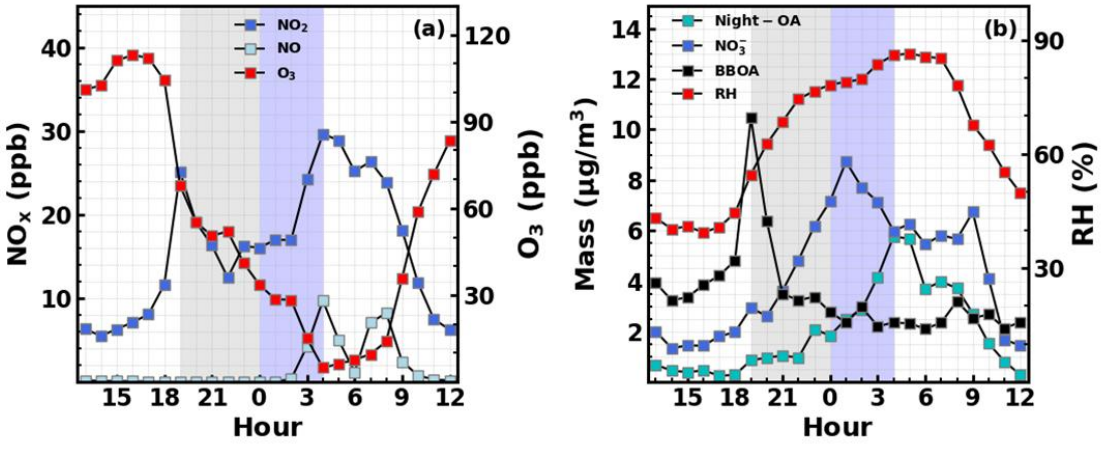

Figure 5. Average diurnal variations of **(a)** NO_2, NO, O_3; **(b)**Night-OA, nitrate, BBOA and RH during the two nights: 20 to 21 October when most prominent Night-OA formation occurred. Shaded areas represent periods of Night-OA increased, and blue parts correspond to remarkable increase period of Night-OA.

The average diurnal variations of gas pollutants and meteorological parameters typical of nighttime chemistry including NO, NO_2, O_3, Night-OA, nitrate, RH as well as BBOA for the most prominent Night-OA formation case (20 to 21, October, consistent with Fig.4b) are shown in Fig.5. At night, NO_2 and NO_3 radical do not photolyze, NO reacts rapidly with O_3 and as a result almost all NOx

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

is concerted to NO_2 (Fig.5a). NO_2 will further react with O_3 to form NO_3 radical which is the most important gas-phase oxidant during the nighttime (Chapleski et al., 2016). In this case, NO_2 concentration increased substantially before the sunset but the trend ended and shifted suddenly to decrease when BBOA emissions were highest and then decreased rapidly along with the dropping BBOA mass concentration. The reduction of BBOA mass concentration mainly attributed to the end of local combustion events might also be associated with BBOA evaporation after its strong emissions due to the mix of biomass burning plumes with background airmass, and this dilution effects shall deliver semi-volatile VOCs such as phenolic compounds from particle phase to gas phase (Palm et al., 2020). The Night-OA increased slowly during the rapid NO_2 decrease phase but nitrate concentration increased substantially with decreasing O_3 concentration (still higher than 30 ppb as shown in gray shaded areas). The hydrolysis of N_2O_5, which is formed from NO_2 addition of NO_3 radicals, represents an important pathway of nitrate formation during nighttime period. The rapid decrease of NO_2 coincident with the quick nitrate formation implies that the rapid NO_2 consumption supplied the NO_3 and N_2O_5 reaction chains, providing abundant NO_3 radical during the initial stage of Night-OA formation. The active nighttime NO_3 chemistry and its impacts on nitrate formations during the observation periods were further confirmed by Yang et al. (2022) who conducted box model simulations. In addition, Li, et al. (2020a) demonstrated that night NO_3 radical darkened the BBOA with the MAE enhancement ratio range from 1.3 to 3.2 for optical wavelength of less than 650 nm. The retrieved average MAE of BBOA through multilinear fitting was higher than the average MAE of freshly emitted BBOA during BBOA spikes as reported by Luo et al. (2022) (3.8 vs 2.6 m^2/g), suggesting the darkening of primary BBOA which is consistent with the prevailing nighttime NO_3 chemistry processes during the observations. The highest Night-OA production rate occurred when both NO_2 and NO began to increase (O_3 still decreased rapidly and reached below 30 ppb, shown as the blue shaded area) and the RH reached near the its maximum, which further highlights the crucial role of aerosol liquid water content in Night-OA formation. However, the quick increase of NO_2 and NO implies that the dominant contribution of NO_2 formation to O_3 depletion, and the NO_3 radical chemistry have ceased and likely did not directly participate in the succeeding quick aqueous-phase Night-OA formation. Nevertheless, quick depletion of O_3 and increase of NO_2 with the quickest Night-OA formation occurred demonstrates that the NO_2 might play significant roles in the subsequent quick Night-OA formation. These results demonstrate that the aqueous-phase processing of biomass burning

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

emissions with abundant NO_2 could likely form highly absorptive SOA, while the nighttime gas-phase chemistry with typically high NO_2, NO_3 radical and RH could likely magnify the Night-OA formation.

A previous field study (Lin et al., 2017) demonstrated that most chromophores were nitroaromatic compounds (NAC) during the observed nighttime bonfire event with the major contribution to the solvent extractable BrC, and the NAC contribution to BrC absorption increased towards near visible wavelengths, and this characteristics is consistent with the aforementioned BrC absorption spectral dependence characteristics in Sect 3.1. Actually, the relatively low O/C of Night-OA while high N/C and H/C ratios (0.04 and 1.89, even higher than those of BBOA which are known composed of complex nitrogen containing compounds) was consistent with the features (low O/C, high N/C (ring- and N-containing structures of NACs) and low hygroscopicity) of aerosols that involved such as nitro-phenolic compounds (Chen et al., 2022) secondarily formed from reactions of cyclic aromatics that involve NO_3 radical chemistry (Rana and Guzman, 2022;Mayorga et al., 2021) during nighttime which likely have larger molecular weight and thereby lower hygroscopicity (Wang et al., 2019a;Price et al., 2022;Petters et al., 2009). The increased loading of Night-OA would lower organic aerosol hygroscopicity, which was confirmed previously by Kuang et al. (2021). However, the high N/C of Night-OA was consistent with its strong absorptivity considering that aerosol absorptions are generally linked with N-containing components (Qin et al., 2018;Kasthuriarachchi et al., 2020), however, N/C of 0.04 implies the complex structures of Night-OA components. These results also demonstrate that NAC are probably key components of the Night-OA factor, considering that biomass burning was indeed important sources of precursors (Li et al., 2020b;Decker et al., 2019) to form NACs, consistent with the inference that precursors of Night-OA came from biomass burning. On the basis of limited existing literatures, Wang et al. (2019c) have summarized the secondary NAC formation pathways of benzene, toluene, phenol and methylcatechol which represented a significant fraction of biomass burning VOC emissions (Stockwell et al., 2015), and emphasized that the NO_3 radical does not directly participate in the aqueous phase reactions in NAC formation reaction chains, but first oxidizes these precursors into intermediate products which then react with NO_2 to form nitrophenols and nitrocatechols that are further oxidized in the particle phase to generate NAC. This gas-phase oxidation and subsequent particle-phase reaction chains of NAC production may explain the observed Night-OA formation characteristics that the most-prominent Night-OA formation occurred after the strongest NO_3 radical chemistry when the aerosol liquid water content was abundant, highlighting the great

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

importance of nighttime multiphase chemistry in Night-OA formation. Aside from the case shown in Fig.5, much higher correlation coefficient between nighttime average Night-OA mass concentration and nighttime average O_x concentrations than that of NO_2 shown in Fig.S9 for the entire campaign (0.58 versus 0.39) further stresses that the coordination of night-time gas-phase and aqueous-phase was responsible for the quick Night-OA formation. In addition, obvious daytime increase in Night-OA was occasionally observed (Fig.S10 and Fig.S11) as mentioned in Sect.2 when the RH remain high and NO_2 as well as biomass burning emissions increased substantially. This results further emphasizes that NO_2 might play significant roles in aqueous phase reactions of oxidized biomass burning precursors which might be directly emitted or transformed through active nighttime NO_3 chemistry (Decker et al., 2019).

4. Environmental and climate significance

Biomass burning emissions, as the largest sources of primary aerosols and the second largest sources of VOCs, exert increasingly greater impacts on the regional air quality and global climate under the context of global warming (Running, 2006). However, the lack of knowledge on the complex chemical aging of biomass burning plumes during its transport hinders the accurate representation of biomass burning VOCs and BBOA evolution in air quality and climate models. Kodros et al. (2022) concluded based on laboratory experiments that dark aging of biomass burning emissions was sensitive to RH, and their results suggested that the SOA was mainly formed through condensation of gas-phase oxidation products, however, not ruling out the possibility of heterogeneous oxidations. This study highlights that nighttime gas-phase chemistry of biomass burning VOC precursors in conjunction with further aqueous-phase reactions likely contributed substantially to ambient SOA that is highly absorptive. Although more comprehensive studies about detailed mechanisms are needed and the robustness of the conclusion in this study needs to be further examined as well as the exact types of fires during this campaign are not known, still, this finding has important implications for our understanding on nighttime evolution of biomass burning plumes. Field observations in this study revealed the abundant existence of highly hygroscopic inorganic components within ambient aerosols that contributed substantially to aerosol liquid water in ambient air, while aerosols produced in the chamber of Kodros et al. (2022) were dominated by organics (only with very small amounts of inorganic nitrate formed during the aging processes) which might have inhibited aqueous reaction

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

pathways. Inspired by this study, future laboratory studies investigating nighttime aging of biomass burning plumes should consider not only the high nighttime RH conditions, but also the complex mixture of background inorganic aerosols with biomass burning emissions when simulating aerosols within biomass burning plumes.

In addition, biomass burning plumes might form convective clouds under strong ground surface heating and moisture release (pyrocumulus clouds or pyrocumulonimbus clouds) (Andreae et al., 2004;Fromm et al., 2006;Cunningham and Reeder, 2009;Lareau and Clements, 2016), or interact with clouds/fogs during long-range transport (Engelhart et al., 2011). Clouds/fogs provide large amount of liquid water regardless of day or night, while active photochemistry in biomass burning plumes may increase O_3 and NO_2 production (Hecobian et al., 2011;Marufu et al., 2000;Ziemke et al., 2009) (biomass burning also emits NO_2 directly as shown in Fig.45, likely promoting NO_3 radical production (Selimovic et al., 2020) during nighttime. This suggests a potential formation of highly absorptive SOA in cloud droplets, which results in even browner cloud droplets, impacting cloud optical properties, cloud lifetime (e.g. promoting cloud burning off effect) and precipitation. Especially, since violent pyroconvection can penetrate into the stratosphere, darkening of clouds might have regional impacts on cloud properties as well as radiative balance. Moreover, the biomass burning plumes transported from remote areas can sometimes mix down into the boundary layer and exert significant impacts on regional air quality (Wang et al., 2018b). The top of the boundary layer is usually characterized by high RH conditions due to abundant water vapor but lower temperatures, as well as high O_x concentrations due to substantial anthropogenic NO_x emissions and active photochemistry, and thus potentially large amounts of highly absorptive SOA formation could be expected in this kind of biomass burning plumes.

Overall, results of this study provide important insights into nighttime evolutions of biomass burning and an uncovered potential secondary BrC formation mechanism that has broad implications for climate and air quality effects of biomass burning, especially the interaction between biomass burning plumes with clouds in the aging process during nighttime. However, much more efforts are still required to further disentangle the complex routes of gas-phase biomass burning VOC oxidation and subsequent aqueous-phase reactions.

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

Data availability. The data used in this study are available from the corresponding author upon request Ye Kuang (kuangye@jnu.edu.cn) and Shan Huang (shanhuang_eci@jnu.edu.cn)

Competing interests. The authors declare no competing financial interest.

Author Contributions. YK conceived this research and wrote the manuscript. SH conducted the SPAMS measurements and performed the PMF analysis. BL performed the AE33 measurements. MS and BY planned this campaign. JL, WH, YP, DC, and DY participated this campaign and provided full support for the campaign. WX provided insights into reaction mechanism analysis.

Financial supports. This work is supported by the National Natural Science Foundation of China (grant No. 41805109, 41807302), National Key Research and Development Program of China (grant No. 2017YFC0212803, 2016YFC0202206), Key-Area Research and Development Program of Guangdong Province (grant No. 2019B110206001), Special Fund Project for Science and Technology Innovation Strategy of Guangdong Province (grant No.2019B121205004), Guangdong Natural Science Funds for Distinguished Young Scholar (grant No. 2018B030306037).

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

References

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, 10.5194/acp-11-4039-2011, 2011.

Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochemical Cycles, 15, 955-966, https://doi.org/10.1029/2000GB001382, 2001.

Andreae, M. O., Rosenfeld, D., Artaxo, P., Costa, A. A., Frank, G. P., Longo, K. M., and Silva-Dias, M. A. F.: Smoking Rain Clouds over the Amazon, Science, 303, 1337-1342, doi:10.1126/science.1092779, 2004.

Andreae, M. O., and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131-3148, 10.5194/acp-6-3131-2006, 2006.

Andreae, M. O.: Emission of trace gases and aerosols from biomass burning – an updated assessment, Atmos. Chem. Phys., 19, 8523-8546, 10.5194/acp-19-8523-2019, 2019.

Bertrand, A., Stefenelli, G., Jen, C. N., Pieber, S. M., Bruns, E. A., Ni, H., Temime-Roussel, B., Slowik, J. G., Goldstein, A. H., El Haddad, I., Baltensperger, U., Prévôt, A. S. H., Wortham, H., and Marchand, N.: Evolution of the chemical fingerprint of biomass burning organic aerosol during aging, Atmospheric Chemistry and Physics, 18, 7607-7624, 10.5194/acp-18-7607-2018, 2018.

Bluvshtein, N., Lin, P., Flores, J. M., Segev, L., Mazar, Y., Tas, E., Snider, G., Weagle, C., Brown, S. S., Laskin, A., and Rudich, Y.: Broadband optical properties of biomass-burning aerosol and identification of brown carbon chromophores, Journal of Geophysical Research: Atmospheres, 122, 5441-5456, https://doi.org/10.1002/2016JD026230, 2017.

Chapleski, R. C., Zhang, Y., Troya, D., and Morris, J. R.: Heterogeneous chemistry and reaction dynamics of the atmospheric oxidants, O3, NO3, and OH, on organic surfaces, Chem Soc Rev, 45, 3731-3746, 10.1039/c5cs00375j, 2016.

Chen, Y., Zheng, P., Wang, Z., Pu, W., Tan, Y., Yu, C., Xia, M., Wang, W., Guo, J., Huang, D., Yan, C., Nie, W., Ling, Z., Chen, Q., Lee, S., and Wang, T.: Secondary Formation and Impacts of Gaseous Nitro-Phenolic Compounds in the Continental Outflow Observed at a Background Site in South China, Environmental science & technology, 56, 6933-6943, 10.1021/acs.est.1c04596, 2022.

Cheng, Z., Atwi, K. M., Yu, Z., Avery, A., Fortner, E. C., Williams, L., Majluf, F., Krechmer, J. E., Lambe, A. T., and Saleh, R.: Evolution of the light-absorption properties of combustion brown carbon aerosols following reaction with nitrate radicals, Aerosol Science and Technology, 1-15, 10.1080/02786826.2020.1726867, 2020.

Cunningham, P., and Reeder, M. J.: Severe convective storms initiated by intense wildfires: Numerical simulations of pyro-convection and pyro-tornadogenesis, Geophysical Research Letters, 36, https://doi.org/10.1029/2009GL039262, 2009.

Decker, Z. C. J., Zarzana, K. J., Coggon, M., Min, K.-E., Pollack, I., Ryerson, T. B., Peischl, J., Edwards, P., Dubé, W. P., Markovic, M. Z., Roberts, J. M., Veres, P. R., Graus, M., Warneke, C., de Gouw, J., Hatch, L. E., Barsanti, K. C., and Brown, S. S.: Nighttime Chemical Transformation in Biomass Burning Plumes: A Box Model Analysis Initialized with Aircraft Observations, Environmental science & technology, 53, 2529-2538, 10.1021/acs.est.8b05359, 2019.

Drinovec, L., Močnik, G., Zotter, P., Prévôt, A. S. H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A., and Hansen, A. D. A.: The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation, Atmospheric Measurement Techniques, 8, 1965-1979, 10.5194/amt-8-1965-2015, 2015.

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

562 Engelhart, G. J., Moore, R. H., Nenes, A., and Pandis, S. N.: Cloud condensation nuclei activity of isoprene secondary
563 organic aerosol, Journal of Geophysical Research: Atmospheres, 116, 10.1029/2010jd014706, 2011.

564 Fromm, M., Tupper, A., Rosenfeld, D., Servranckx, R., and McRae, R.: Violent pyro-convective storm devastates Australia's
565 capital and pollutes the stratosphere, Geophysical Research Letters, 33, https://doi.org/10.1029/2005GL025161, 2006.

566 Hartikainen, A., Yli-Pirilä, P., Tiitta, P., Leskinen, A., Kortelainen, M., Orasche, J., Schnelle-Kreis, J., Lehtinen, K. E. J.,
567 Zimmermann, R., Jokiniemi, J., and Sippula, O.: Volatile Organic Compounds from Logwood Combustion: Emissions and
568 Transformation under Dark and Photochemical Aging Conditions in a Smog Chamber, Environmental science & technology,
569 52, 4979-4988, 10.1021/acs.est.7b06269, 2018.

570 Hecobian, A., Liu, Z., Hennigan, C. J., Huey, L. G., Jimenez, J. L., Cubison, M. J., Vay, S., Diskin, G. S., Sachse, G. W., Wisthaler,
571 A., Mikoviny, T., Weinheimer, A. J., Liao, J., Knapp, D. J., Wennberg, P. O., Kürten, A., Crounse, J. D., Clair, J. S., Wang, Y., and
572 Weber, R. J.: Comparison of chemical characteristics of 495 biomass burning plumes intercepted by the NASA DC-8 aircraft
573 during the ARCTAS/CARB-2008 field campaign, Atmos. Chem. Phys., 11, 13325-13337, 10.5194/acp-11-13325-2011, 2011.

574 Hodshire, A. L., Akherati, A., Alvarado, M. J., Brown-Steiner, B., Jathar, S. H., Jimenez, J. L., Kreidenweis, S. M., Lonsdale, C.
575 R., Onasch, T. B., Ortega, A. M., and Pierce, J. R.: Aging Effects on Biomass Burning Aerosol Mass and Composition: A
576 Critical Review of Field and Laboratory Studies, Environmental science & technology, 53, 10007-10022,
577 10.1021/acs.est.9b02588, 2019.

578 Jiang, H., Frie, A. L., Lavi, A., Chen, J. Y., Zhang, H., Bahreini, R., and Lin, Y.-H.: Brown Carbon Formation from Nighttime
579 Chemistry of Unsaturated Heterocyclic Volatile Organic Compounds, Environmental Science & Technology Letters, 6, 184-
580 190, 10.1021/acs.estlett.9b00017, 2019.

581 Jo, D. S., Park, R. J., Lee, S., Kim, S. W., and Zhang, X.: A global simulation of brown carbon: implications for photochemistry
582 and direct radiative effect, Atmos. Chem. Phys., 16, 3413-3432, 10.5194/acp-16-3413-2016, 2016.

583 Kasthuriarachchi, N. Y., Rivellini, L.-H., Adam, M. G., and Lee, A. K. Y.: Light Absorbing Properties of Primary and Secondary
584 Brown Carbon in a Tropical Urban Environment, Environmental science & technology, 54, 10808-10819,
585 10.1021/acs.est.0c02414, 2020.

586 Kodros, J. K., Papanastasiou, D. K., Paglione, M., Masiol, M., Squizzato, S., Florou, K., Skyllakou, K., Kaltsonoudis, C., Nenes,
587 A., and Pandis, S. N.: Rapid dark aging of biomass burning as an overlooked source of oxidized organic aerosol, Proceedings
588 of the National Academy of Sciences, 117, 33028-33033, doi:10.1073/pnas.2010365117, 2020.

589 Kodros, J. K., Kaltsonoudis, C., Paglione, M., Florou, K., Jorga, S., Vasilakopoulou, C., Cirtog, M., Cazaunau, M., Picquet-
590 Varrault, B., Nenes, A., and Pandis, S. N.: Secondary aerosol formation during the dark oxidation of residential biomass
591 burning emissions, Environmental Science: Atmospheres, 2, 1221-1236, 10.1039/D2EA00031H, 2022.

592 Kuang, Y., Xu, W., Tao, J., Ma, N., Zhao, C., and Shao, M.: A Review on Laboratory Studies and Field Measurements of
593 Atmospheric Organic Aerosol Hygroscopicity and Its Parameterization Based on Oxidation Levels, Current Pollution
594 Reports, 10.1007/s40726-020-00164-2, 2020.

595 Kuang, Y., Huang, S., Xue, B., Luo, B., Song, Q., Chen, W., Hu, W., Li, W., Zhao, P., Cai, M., Peng, Y., Qi, J., Li, T., Wang, S.,
596 Chen, D., Yue, D., Yuan, B., and Shao, M.: Contrasting effects of secondary organic aerosol formations on organic aerosol
597 hygroscopicity, Atmos. Chem. Phys., 21, 10375-10391, 10.5194/acp-21-10375-2021, 2021.

598 Kumar, N. K., Corbin, J. C., Bruns, E. A., Massabó, D., Slowik, J. G., Drinovec, L., Močnik, G., Prati, P., Vlachou, A.,
599 Baltensperger, U., Gysel, M., El-Haddad, I., and Prévôt, A. S. H.: Production of particulate brown carbon during

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

atmospheric aging of residential wood-burning emissions, Atmos. Chem. Phys., 18, 17843-17861, 10.5194/acp-18-17843-2018, 2018.

Lareau, N. P., and Clements, C. B.: Environmental controls on pyrocumulus and pyrocumulonimbus initiation and development, Atmos. Chem. Phys., 16, 4005-4022, 10.5194/acp-16-4005-2016, 2016.

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, Chemical Reviews, 115, 4335-4382, 10.1021/cr5006167, 2015.

Li, C., He, Q., Hettiyadura, A. P. S., Käfer, U., Shmul, G., Meidan, D., Zimmermann, R., Brown, S. S., George, C., Laskin, A., and Rudich, Y.: Formation of Secondary Brown Carbon in Biomass Burning Aerosol Proxies through NO3 Radical Reactions, Environmental science & technology, 54, 1395-1405, 10.1021/acs.est.9b05641, 2020a.

Li, M., Wang, X., Lu, C., Li, R., Zhang, J., Dong, S., Yang, L., Xue, L., Chen, J., and Wang, W.: Nitrated phenols and the phenolic precursors in the atmosphere in urban Jinan, China, Science of The Total Environment, 714, 136760, https://doi.org/10.1016/j.scitotenv.2020.136760, 2020b.

Li, Z., Tan, H., Zheng, J., Liu, L., Qin, Y., Wang, N., Li, F., Li, Y., Cai, M., Ma, Y., and Chan, C. K.: Light absorption properties and potential sources of particulate brown carbon in the Pearl River Delta region of China, Atmos. Chem. Phys., 19, 11669-11685, 10.5194/acp-19-11669-2019, 2019a.

Li, Z. J., Tan, H. B., Zheng, J., Liu, L., Qin, Y. M., Wang, N., Li, F., Li, Y. J., Cai, M. F., Ma, Y., and Chan, C. K.: Light absorption properties and potential sources of particulate brown carbon in the Pearl River Delta region of China, Atmospheric Chemistry and Physics, 19, 11669-11685, 10.5194/acp-19-11669-2019, 2019b.

Lin, P., Bluvshtein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass Burning Event, Environmental science & technology, 51, 11561-11570, 10.1021/acs.est.7b02276, 2017.

Liu, P., Kaplan, J. O., Mickley, L. J., Li, Y., Chellman, N. J., Arienzo, M. M., Kodros, J. K., Pierce, J. R., Sigl, M., Freitag, J., Mulvaney, R., Curran, M. A. J., and McConnell, J. R.: Improved estimates of preindustrial biomass burning reduce the magnitude of aerosol climate forcing in the Southern Hemisphere, Science Advances, 7, 10.1126/sciadv.abc1379, 2021.

Liu, S., Ahlm, L., Day, D. A., Russell, L. M., Zhao, Y., Gentner, D. R., Weber, R. J., Goldstein, A. H., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Rubitschun, C., Surratt, J. D., Sheesley, R. J., and Scheller, S.: Secondary organic aerosol formation from fossil fuel sources contribute majority of summertime organic mass at Bakersfield, J. Geophys. Res. - Atmos., 117, https://doi.org/10.1029/2012JD018170, 2012.

Liu, Y., Wang, T., Fang, X., Deng, Y., Cheng, H., Bacha, A. U., Nabi, I., and Zhang, L.: Brown carbon: An underlying driving force for rapid atmospheric sulfate formation and haze event, The Science of the total environment, 734, 139415, 10.1016/j.scitotenv.2020.139415, 2020.

Luo, B., Kuang, Y., Huang, S., Song, Q., Hu, W., Li, W., Peng, Y., Chen, D., Yue, D., Yuan, B., and Shao, M.: Parameterizations of size distribution and refractive index of biomass burning organic aerosol with black carbon content, Atmos. Chem. Phys., 22, 12401-12415, 10.5194/acp-22-12401-2022, 2022.

Marufu, L., Dentener, F., Lelieveld, J., Andreae, M. O., and Helas, G.: Photochemistry of the African troposphere: Influence of biomass-burning emissions, Journal of Geophysical Research: Atmospheres, 105, 14513-14530, https://doi.org/10.1029/1999JD901055, 2000.

Mayorga, R. J., Zhao, Z., and Zhang, H.: Formation of secondary organic aerosol from nitrate radical oxidation of phenolic

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

VOCs: Implications for nitration mechanisms and brown carbon formation, Atmospheric Environment, 244, 117910, https://doi.org/10.1016/j.atmosenv.2020.117910, 2021.

Palm, B. B., Peng, Q., Fredrickson, C. D., Lee, B. H., Garofalo, L. A., Pothier, M. A., Kreidenweis, S. M., Farmer, D. K., Pokhrel, R. P., Shen, Y., Murphy, S. M., Permar, W., Hu, L., Campos, T. L., Hall, S. R., Ullmann, K., Zhang, X., Flocke, F., Fischer, E. V., and Thornton, J. A.: Quantification of organic aerosol and brown carbon evolution in fresh wildfire plumes, Proceedings of the National Academy of Sciences, 202012218, 10.1073/pnas.2012218117, 2020.

Petters, M. D., Carrico, C. M., Kreidenweis, S. M., Prenni, A. J., DeMott, P. J., Collett Jr., J. L., and Moosmüller, H.: Cloud condensation nucleation activity of biomass burning aerosol, Journal of Geophysical Research: Atmospheres, 114, https://doi.org/10.1029/2009JD012353, 2009.

Price, C. L., Preston, T. C., and Davies, J. F.: Hygroscopic Growth, Phase Morphology, and Optical Properties of Model Aqueous Brown Carbon Aerosol, Environmental science & technology, 56, 3941-3951, 10.1021/acs.est.1c07356, 2022.

Qin, Y. M., Tan, H. B., Li, Y. J., Li, Z. J., Schurman, M. I., Liu, L., Wu, C., and Chan, C. K.: Chemical characteristics of brown carbon in atmospheric particles at a suburban site near Guangzhou, China, Atmos. Chem. Phys., 18, 16409-16418, 10.5194/acp-18-16409-2018, 2018.

Rana, M. S., and Guzman, M. I.: Oxidation of Catechols at the Air–Water Interface by Nitrate Radicals, Environmental science & technology, 56, 15437-15448, 10.1021/acs.est.2c05640, 2022.

Running, S. W.: Is Global Warming Causing More, Larger Wildfires?, Science, 313, 927, 10.1126/science.1130370, 2006.

Saleh, R., Hennigan, C. J., McMeeking, G. R., Chuang, W. K., Robinson, E. S., Coe, H., Donahue, N. M., and Robinson, A. L.: Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions, Atmos. Chem. Phys., 13, 7683-7693, 10.5194/acp-13-7683-2013, 2013.

Saleh, R.: From Measurements to Models: Toward Accurate Representation of Brown Carbon in Climate Calculations, Current Pollution Reports, 6, 90-104, 10.1007/s40726-020-00139-3, 2020.

Selimovic, V., Yokelson, R. J., McMeeking, G. R., and Coefield, S.: Aerosol Mass and Optical Properties, Smoke Influence on O3, and High NO3 Production Rates in a Western U.S. City Impacted by Wildfires, Journal of Geophysical Research: Atmospheres, 125, e2020JD032791, https://doi.org/10.1029/2020JD032791, 2020.

Song, M., Liu, X., Zhang, Y., Shao, M., Lu, K., Tan, Q., Feng, M., and Qu, Y.: Sources and abatement mechanisms of VOCs in southern China, Atmospheric Environment, 201, 28-40, https://doi.org/10.1016/j.atmosenv.2018.12.019, 2019.

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, Atmos. Chem. Phys., 15, 845-865, 10.5194/acp-15-845-2015, 2015.

Tiitta, P., Leskinen, A., Hao, L., Yli-Pirilä, P., Kortelainen, M., Grigonyte, J., Tissari, J., Lamberg, H., Hartikainen, A., Kuuspalo, K., Kortelainen, A. M., Virtanen, A., Lehtinen, K. E. J., Komppula, M., Pieber, S., Prévôt, A. S. H., Onasch, T. B., Worsnop, D. R., Czech, H., Zimmermann, R., Jokiniemi, J., and Sippula, O.: Transformation of logwood combustion emissions in a smog chamber: formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging, Atmos. Chem. Phys., 16, 13251-13269, 10.5194/acp-16-13251-2016, 2016.

Tong, Y., Pospisilova, V., Qi, L., Duan, J., Gu, Y., Kumar, V., Rai, P., Stefenelli, G., Wang, L., Wang, Y., Zhong, H., Baltensperger, U., Cao, J., Huang, R. J., Prévôt, A. S. H., and Slowik, J. G.: Quantification of solid fuel combustion and aqueous chemistry contributions to secondary organic aerosol during wintertime haze events in Beijing, Atmos. Chem. Phys., 21, 9859-9886,

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

10.5194/acp-21-9859-2021, 2021.

van der Werf, G. R., Randerson, J. T., Giglio, L., van Leeuwen, T. T., Chen, Y., Rogers, B. M., Mu, M., van Marle, M. J. E., Morton, D. C., Collatz, G. J., Yokelson, R. J., and Kasibhatla, P. S.: Global fire emissions estimates during 1997–2016, Earth Syst. Sci. Data, 9, 697-720, 10.5194/essd-9-697-2017, 2017.

Wang, J., Nie, W., Cheng, Y., Shen, Y., Chi, X., Wang, J., Huang, X., Xie, Y., Sun, P., Xu, Z., Qi, X., Su, H., and Ding, A.: Light absorption of brown carbon in eastern China based on 3-year multi-wavelength aerosol optical property observations and an improved absorption Ångström exponent segregation method, Atmos. Chem. Phys., 18, 9061-9074, 10.5194/acp-18-9061-2018, 2018a.

Wang, J., Shilling, J. E., Liu, J., Zelenyuk, A., Bell, D. M., Petters, M. D., Thalman, R., Mei, F., Zaveri, R. A., and Zheng, G.: Cloud droplet activation of secondary organic aerosol is mainly controlled by molecular weight, not water solubility, Atmos. Chem. Phys., 19, 941-954, 10.5194/acp-19-941-2019, 2019a.

Wang, J., Ye, J., Zhang, Q., Zhao, J., Wu, Y., Li, J., Liu, D., Li, W., Zhang, Y., Wu, C., Xie, C., Qin, Y., Lei, Y., Huang, X., Guo, J., Liu, P., Fu, P., Li, Y., Lee, H. C., Choi, H., Zhang, J., Liao, H., Chen, M., Sun, Y., Ge, X., Martin, S. T., and Jacob, D. J.: Aqueous production of secondary organic aerosol from fossil-fuel emissions in winter Beijing haze, Proceedings of the National Academy of Sciences, 118, e2022179118, 10.1073/pnas.2022179118, 2021.

Wang, Q., Saturno, J., Chi, X., Walter, D., Lavric, J. V., Moran-Zuloaga, D., Ditas, F., Pöhlker, C., Brito, J., Carbone, S., Artaxo, P., and Andreae, M. O.: Modeling investigation of light-absorbing aerosols in the Amazon Basin during the wet season, Atmos. Chem. Phys., 16, 14775-14794, 10.5194/acp-16-14775-2016, 2016.

Wang, Q., Ye, J., Wang, Y., Zhang, T., Ran, W., Wu, Y., Tian, J., Li, L., Zhou, Y., Hang Ho, S. S., Dang, B., Zhang, Q., Zhang, R., Chen, Y., Zhu, C., and Cao, J.: Wintertime Optical Properties of Primary and Secondary Brown Carbon at a Regional Site in the North China Plain, Environmental science & technology, 53, 12389-12397, 10.1021/acs.est.9b03406, 2019b.

Wang, S.-C., Wang, Y., Estes, M., Lei, R., Talbot, R., Zhu, L., and Hou, P.: Transport of Central American Fire Emissions to the U.S. Gulf Coast: Climatological Pathways and Impacts on Ozone and PM2.5, Journal of Geophysical Research: Atmospheres, 123, 8344-8361, https://doi.org/10.1029/2018JD028684, 2018b.

Wang, Y., Hu, M., Wang, Y., Zheng, J., Shang, D., Yang, Y., Liu, Y., Li, X., Tang, R., Zhu, W., Du, Z., Wu, Y., Guo, S., Wu, Z., Lou, S., Hallquist, M., and Yu, J. Z.: The formation of nitro-aromatic compounds under high NO_{<i>x</i>} and anthropogenic VOC conditions in urban Beijing, China, Atmospheric Chemistry and Physics, 19, 7649-7665, 10.5194/acp-19-7649-2019, 2019c.

Wang, Y., Qiu, T., Zhang, C., Hao, T., Mabato, B. R. G., Zhang, R., Gen, M., Chan, M. N., Huang, D. D., Ge, X., Wang, J., Du, L., Huang, R.-J., Chen, Q., Hoi, K. I., Mok, K. M., Chan, C. K., and Li, Y. J.: Co-photolysis of mixed chromophores affects atmospheric lifetimes of brown carbon, Environmental Science: Atmospheres, 3, 1145-1158, 10.1039/D3EA00073G, 2023.

Wu, L., Huang, S., Liu, Y., Song, Q., Hu, W., Chen, W., Kuang, Y., Wang, X., Li, W., Peng, Y., Chen, D., Yue, D., Song, W., Yuan, B., Wang, X., and Shao, M.: Source, formation mechanism and inhalation deposition flux of organic aerosols in urban and rural areas of the Pearl River Delta, Acta Scientiae Circumstantiae, 44, 15-28, 10.13671/j.hjkxxb.2023.0194, 2024.

Yang, S., Yuan, B., Peng, Y., Huang, S., Chen, W., Hu, W., Pei, C., Zhou, J., Parrish, D. D., Wang, W., He, X., Cheng, C., Li, X. B., Yang, X., Song, Y., Wang, H., Qi, J., Wang, B., Wang, C., Wang, C., Wang, Z., Li, T., Zheng, E., Wang, S., Wu, C., Cai, M., Ye, C., Song, W., Cheng, P., Chen, D., Wang, X., Zhang, Z., Wang, X., Zheng, J., and Shao, M.: The formation and mitigation of nitrate pollution: comparison between urban and suburban environments, Atmos. Chem. Phys., 22, 4539-4556, 10.5194/acp-22-4539-2022, 2022.

https://doi.org/10.5194/egusphere-2024-2654
Preprint. Discussion started: 18 September 2024

715 Yu, P., Toon, O. B., Bardeen, C. G., Zhu, Y., Rosenlof, K. H., Portmann, R. W., Thornberry, T. D., Gao, R.-S., Davis, S. M., Wolf,
716 E. T., de Gouw, J., Peterson, D. A., Fromm, M. D., and Robock, A.: Black carbon lofts wildfire smoke high into the
717 stratosphere to form a persistent plume, Science, 365, 587, 10.1126/science.aax1748, 2019.

718 Yu, P., Davis, S. M., Toon, O. B., Portmann, R. W., Bardeen, C. G., Barnes, J. E., Telg, H., Maloney, C., and Rosenlof, K. H.:
719 Persistent Stratospheric Warming Due to 2019–2020 Australian Wildfire Smoke, Geophysical Research Letters, 48,
720 e2021GL092609, https://doi.org/10.1029/2021GL092609, 2021.

721 Ziemke, J. R., Chandra, S., Duncan, B. N., Schoeberl, M. R., Torres, O., Damon, M. R., and Bhartia, P. K.: Recent biomass
722 burning in the tropics and related changes in tropospheric ozone, Geophysical Research Letters, 36,
723 https://doi.org/10.1029/2009GL039303, 2009.

724