

Responses to anonymous referee #2

General comments:

Comment: In this manuscript, the authors present evidence from field measurements that the nighttime formation of light-absorbing secondary organic aerosol from biomass burning emissions may involve coordinated gas- and aqueous-phase chemistry. This focus on nighttime formation of secondary brown carbon is a real strength of the work. The field measurements are extensive and appear sound, largely validated in previous reports from the same campaign. The results are presented in clear figures, and the paper is well structured at the paragraph and section levels for the most part. I do strongly recommend a revision for structure at the sentence level (grammar, etc.). The scope and implications of the manuscript are suitable for ACP. I have only minor comments for the authors to consider.

Response: Many thanks for your comments. We really appreciated your helpful comments and suggestions. We have scrutinized the manuscript at the sentence level and revised long sentences of different sections. We also revised the language according to editorial comments of reviewer#1.

Comment: 180 - This paragraph includes a lot of rationale, which I usually associate with Results and Discussion, rather than Materials and Methods - should this passage be the first sub-section in the Results and Discussion?

Response: We agree, and moved this paragraph to Sect 3.1 to make this section more consistent with the section title “Highly absorptive SOA formed during nighttime”.

Comment: 218 - Replace "philosophy" for clarity.

Response: we replaced "philosophy" with the word “framework”

Comment: 278 - I think the observation that the contribution of Night-OA is briefly higher than that of BBOA is overstated here - in Figure 3b, the points at hour six are almost perfectly overlapping, surely within the experimental uncertainty. Of course, the observation that the peak in the Night-OA

contribution coincides with the trough in the BBOA contribution is compelling evidence, regardless of the wording here.

Response: We agree, and revised this part as:

“and even approaches the contribution of BBOA near local time 06:00”

Comment: Figure 3 - Can error bars be incorporated into panels a, b, and d, like they are in panel c?

Response: We added error bars into Figure 3a. However, it would be a mess for b if error bars of all 4 lines are added without additionally necessary information to the discussion. Therefore, the error bars are not added in b. In Figure 3d, only one single value was retrieved for each wavelength, thus no error bars. We could not quantify the uncertainty arisen from the multilinear regression which is affected by many factors. The following sentence is added in the discussions:

“Note that the MAE retrieval using the multilinear regression bears uncertainties which is affected by many factors, for example, not completely independent of factors.”

Comment: 298 - I think more detail here would be helpful, e.g., what specific values are being compared? Also, the change in wavelength dependence upon oxidative aging can be compared to trends reported in the literature, e.g., for laboratory studies of aging.

Response: Agree. This sentence is revised as the following:

“The retrieved $AAE_{470-590}$ for BBOA and Night OA are in general consistent with the AAE of bulk BrC solutions ($AAE_{300-600}$ of near 6) extracted using different solvents which were sampled during and after a nighttime nationwide biomass burning event (Lin et al., 2017).”

As mentioned in the text, the direct quantification of $AAE_{370-470}$, $AAE_{470-590}$ for BBOA is difficult due to the entanglement of BC absorption and thus rarely reported. We didn't find other studies that have reported AAE value changes during BBOA aging.

Comment: 304 - This statement implies that evaporation is the only loss mechanism for the light absorption, although photodegradation is mentioned later on line 360. I recommend introducing photodegradation here or replacing evaporation with, more generally, decay or loss.

Response: Thank you very much for this helpful suggestion. We agree that using evaporation might be misleading, we revised this sentence as:

“and quick daytime loss (through such as repartitioning, photodegradation, etc.)”

Comment: 308 - I think a few representative past studies of aqSOA should be cited here.

Response: Agree. Representative references were added.

“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 (Odum et al., 1996) 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 (Blando and Turpin, 2000;Ervens et al., 2011), with the former referred to as gasSOA and the latter referred to as aqSOA (Kuang et al., 2020a).”

Comment: 311 - Rephrase this sentence for clarity.

Response: This sentence is revised as:

“Considering the highly absorptive characteristics of secondarily formed Night-OA, exploring the sources and formation pathways of Night-OA is of great importance in meriting the importance of Night-OA formations in global atmosphere.”

Comment: 319 - Capitalize Lagrangian.

Response: Revised.

Comment: 338 - Similarly, I think a few representative past studies of gas-particle partitioning should be cited here.

Response: References added.

“The gasSOA forms through condensation following partitioning theory thus adding mass mainly to condensation mode which contributes most to aerosol surface area concentrations (Kuang et al., 2020a;Zhai et al., 2023)”

Comment: 344 - The discussion of these two size ranges could be clarified by adding a vertical dashed line or grey band, etc., at 300 nm in Figure 4b.

Response: Agree. A grey area is added, and the replotted figure is as the following:

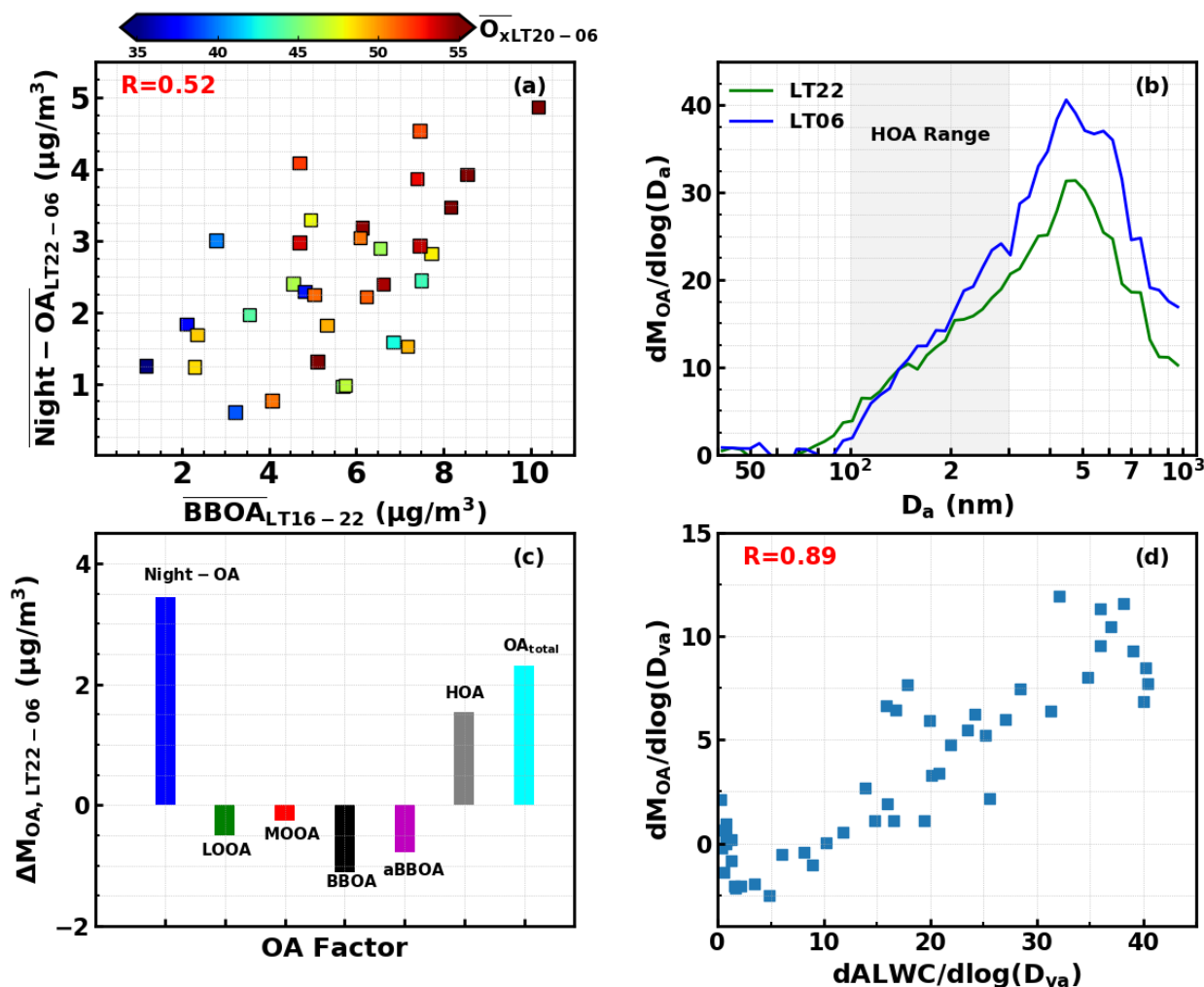


Figure 1. (a) Correlations between average nighttime Night-OA mass concentrations and average BBOA mass concentrations over LT16-22, colors corresponding to the average Ox ($\text{NO}_2 + \text{O}_3$) mixing ratio (ppb) during the night; (b) Average evolutions of organic aerosol mass size distributions from local time 22:00 (20th, 21st October) to 06:00 (21st, 22nd October), the grey band showing the size range of 100 nm – 300 nm; (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).

Comment: Figure 5 - The x-axis in these panels is shifted from that in Figure 3. Reformatting the time scale either here or there may help readers more quickly compare between the two figures.

Response: Agree. To show the continuous evolution of BBOA and Night-OA as well as corresponding optical properties, we revised Figure 3 (now Figure 2 in the revised version) as the following:

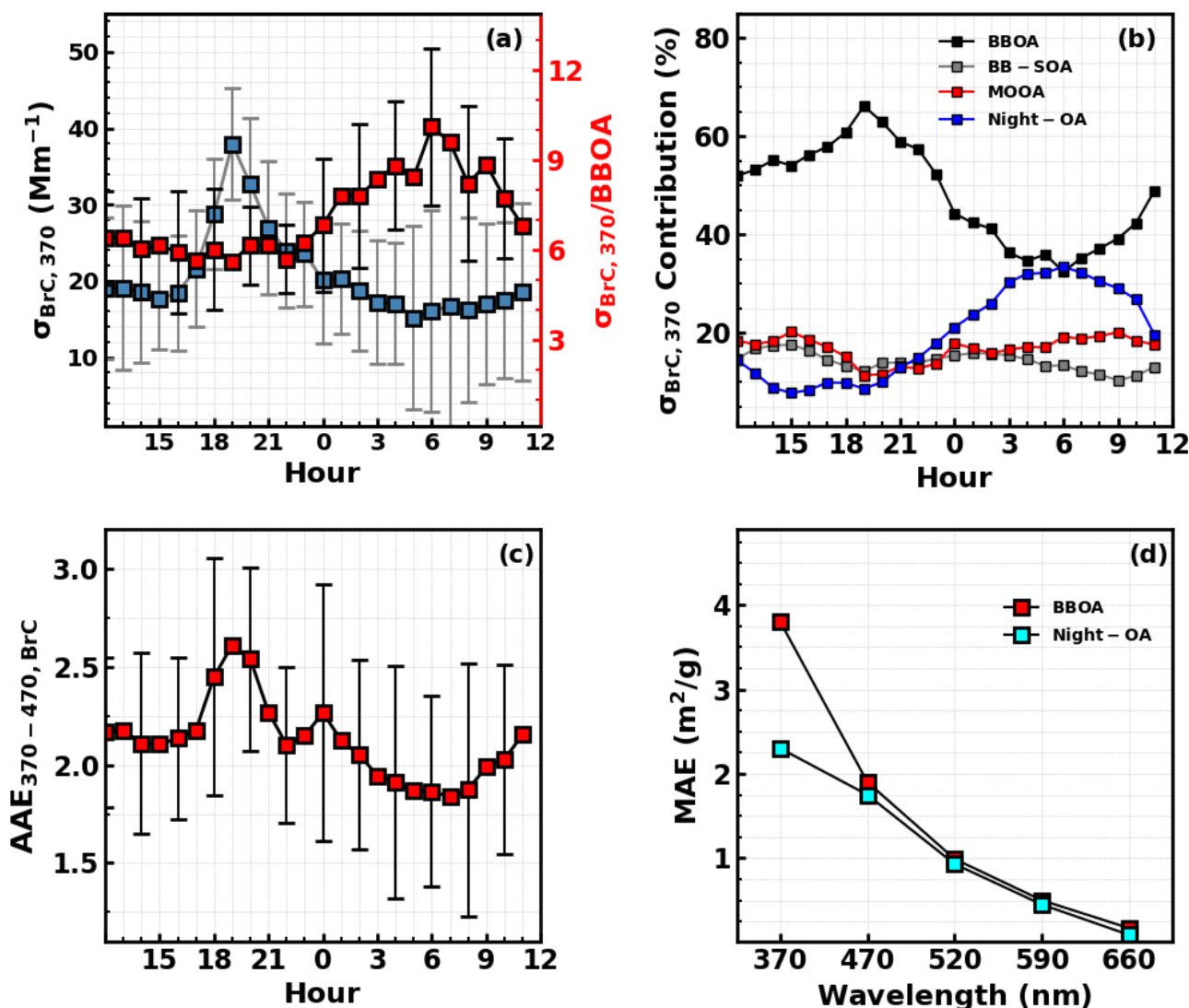


Figure 2. (a) Diurnal variations of $\sigma_{BrC,370}$ and the ratio $\sigma_{BrC,370}/BBOA$; (b) Diurnal variations of contributions of different OA factors to $\sigma_{BrC,370}$; (c) Average diurnal variations of brown carbon absorption angstrom exponent between 370 nm and 470 nm; (d) Retrieved mass absorption efficiencies (MAE) of BBOA and Night-OA at multi-wavelengths using the multilinear regression model.

Comment: 391 - I recommend including a reaction scheme of this and the other gas-phase reactions

discussed throughout this paragraph.

Response: These reactions of N_2O_5 formation through NO_3 chemistry are common reactions in atmospheric chemistry. We added references when reactions were mentioned.

“The hydrolysis of N_2O_5 (Evans and Jacob, 2005; Bertram and Thornton, 2009; Wang et al., 2017; Chen et al., 2018; Wang et al., 2020) that is formed from NO_2 addition of NO_3 radicals (Seinfeld and Pandis, 2016; Fan et al., 2021), represents an important pathway of nitrate formation during nighttime period.”

Comment: 393 - From here to the end of the paragraph, additional references to specific features in Figure 5 would help.

Response: Revised. References are added:

“The hydrolysis of N_2O_5 (Evans and Jacob, 2005; Bertram and Thornton, 2009; Wang et al., 2017; Chen et al., 2018; Wang et al., 2020) that is formed from NO_2 addition of NO_3 radicals (Seinfeld and Pandis, 2016; Fan et al., 2021), 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 (Yang et al., 2022; Wang et al., 2023a), providing abundant NO_3 radical during the initial stage of Night-OA formation and likely initialized the Night-OA formation (Rollins et al., 2012; Kiendler-Scharr et al., 2016; Decker et al., 2019). 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 (Yang et al., 2022). 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 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 NO₂ formation to O₃ depletion ([Wang et al., 2023a](#)) during the quick Night-OA increase stage, and the NO₃ radical chemistry have ceased and likely did not directly participate in the succeeding quick aqueous-phase Night-OA formation.”