Dear Editor and Reviewer,

We are thankful for the comprehensive comments from Reviewer and Editor for the manuscript. We have now addressed all of the comments as below. The corresponding changes in the texts are highlighted in yellow.

Reviewer 3:

The manuscript by Li et al. titled "Concurrent photochemical whitening and darkening of brown carbon" describes the behavior of primary and secondary brown carbon (BrC) from field observation in a sub-urban site near Beijing, China. The total aerosol absorption is apportioned between black carbon (BC), primary BrC and secondary BrC. Traffic and biomass burning are identified as main sources of primary BrC and nitrogen-containing oxygenated organic aerosol are identified as the main source of secondary BrC. A reduction is observed in primary BrC absorbance/total absorbance during the day time with a simultaneous increase in secondary BrC absorbance/total absorbance. Their main finding that there is field evidence of concurrent whitening and darkening of BrC due to photochemical processes, is primarily based on this observed diurnal variation.

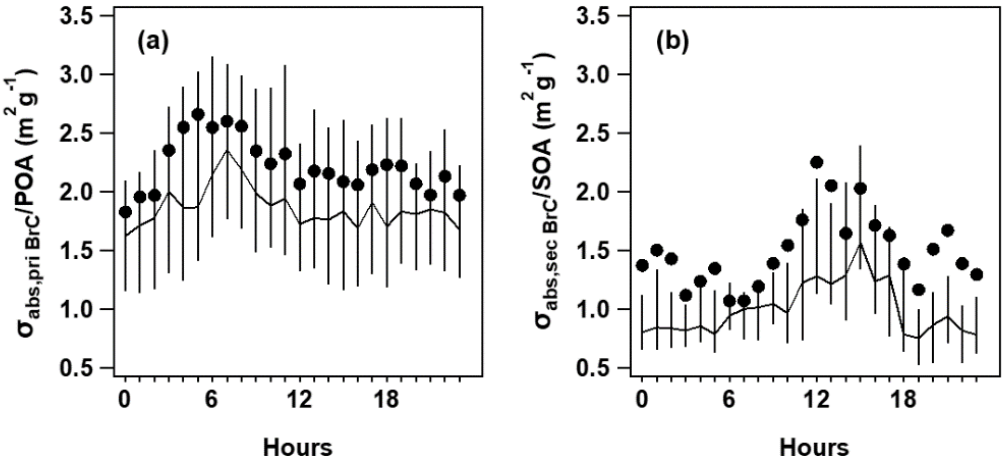
While there is some improvement from the previous version with the inclusion of other possible explanations for the observations and in acknowledging the uncertainties in the used method, it is questionable whether the authors have provided sufficient evidence that justify their main findings are indeed evidence of whitening and darkening of BrC, rather than formation and degradation of BrC.

Main Comments:

1. In Figure 4b), authors have shown the reduction in absorption coefficient of primary BrC/POA (i.e. the MAC of POA) as evidence for the whitening of primary BrC. While there are many uncertainties and other possibilities for this, it is offering some level of evidence for the "whitening" (a better term may be degradation) of primary BrC. However, the same is not shown for secondary BrC. The term "darkening" indicates that the formed secondary BrC increased their absorbance. The increase in secondary BrC abs/total abs only indicates that the absorbance from secondary BrC increased during this time. Due to the very obvious formation of SOA from photochemical processes will indeed result in this. However, it does not indicate that there was a "darkening" process. What does the diurnal variation of MAC of SOA look like? Are you able to see an increase in MACSOA? As OA factors from PMS and BrC absorbance (and primary and secondary BrC absorbance) is available, is it possible to investigate the MAC of the individual OA factor? Do their diurnal variations offer additional information of the "whitening and darkening" effect.

Reply: We thank reviewer to point this out. According to reviewer's suggestion, we have now also calculated the MAC of SOA, as shown below. We can derive the absorption of primary and secondary OA using the method here, but it is unable to derive the absorption or MAC for each PMF factor (only for total POA and SOA). The enhancement of MAC_{SOA} was found to peak in the afternoon. We agree with reviewer that the enhancement of SOA absorptivity may be from the production of BrC rather than only darkening the exiting BrC, we therefore have

changed the term from darkening to enhancement when necessary in the revision. Fig. 4 is now incorporated with MAC_{SOA}.



Diurnal variation of MAC for POA and SOA.

The related discussions are revised: "Fig. 4b showed that the MAC of POA decreased after the morning peak. The MAC of SOA showed an afternoon peak (Fig. 4c), indicating the enhancement of absorption efficiency of secondary BrC, which occurred in a few hours after the peak solar radiation."

L321-323

2. Lines 269-271-While the overall AAE of total absorbance may be highly influenced by BC absorbance, the AAE of total BrC, primary BrC and secondary BrC can be individually calculated as the total absorbance has already been apportioned.

Reply: The mean AAE during the experiment is now obtained through a power fitting on the average absorption coefficient at different wavelengths for total BrC, primary BrC and secondary BrC. We have added related discussions.

"The mean AAE of total BrC, primary BrC and secondary BrC is obtained by power fitting on the mean absorption coefficient during the experiment (Fig.S7), which is 6.2, 5.7 and 6.4 respectively. This is consistent with other studies that SOA usually had a higher AAE than POA (Gilardoni et al., 2016; Jiang et al., 2022)."

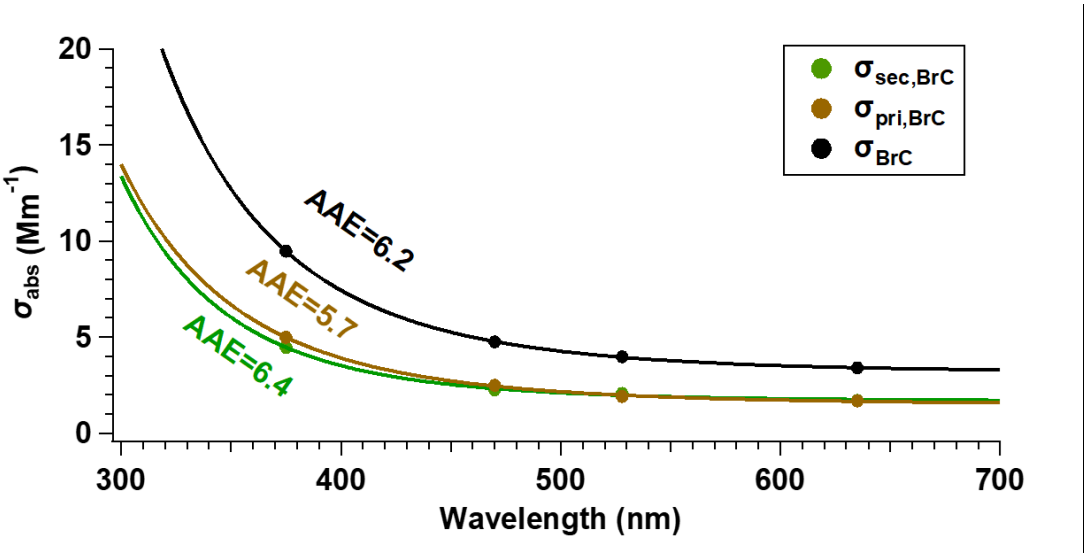


Figure S7. Absorption coefficient at λ=375, 470, 528 and 635 nm for total BrC, primary BrC and secondary BrC. The AAE is obtained by power fitting on the spectra of absorption coefficient.

L270-272

3. Line 291-293 – The meaning is very unclear.

Reply: This sentence is now removed.

4. Line 22 and line 316- "fraction of total absorbance of secondary BrC" is unclear. Do you mean fraction of absorbance of secondary BrC to total absorbance?

Reply: We have now clarified this point according to reviewer's suggestion.

"The photochemical processes were found to result in reduced contribution of fraction of absorbance of primary BrC to total absorbance about 20% but enhanced contribution of secondary BrC by 30%, implying the concurrent whitening and darkening of BrC."

"Overall, by apportioning the absorption of primary and secondary BrC, we found the photochemical processes led to an enhanced contribution of fraction of absorbance of secondary BrC to total absorbance by 30% but reduced contribution of primary BrC about 20% in the semi-urban environment."

L22-23, L320

5. Lines 327-336 - As the primary focus of the paper is the "whitening and darkening" of BrC, a more detailed analysis with further evidence is required to make a strong conclusion on this. The 4. Conclusions section does not even include this main point and does not offer any atmospheric implication of the major observations from this manuscript.

Reply: The MAC of secondary BrC is now added to aid the conclusion. The conclusion is also revised to indicate the atmospheric implication about the concurrent bleaching and formation

of BrC.

"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 by photochemistry. The production of secondary BrC should be considered when assessing the environment and climate impacts of light-absorbing aerosols."

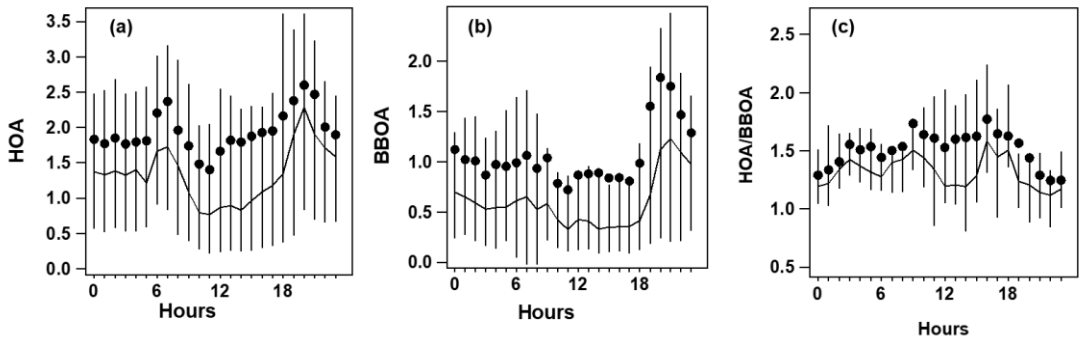
L338-339, L342-344

Editor:

There are still a couple major concerns from the reviewer regarding the results interpretation that requires further improvement/clarification. In addition, I would like to include a few additional major comments as listed below.

1) Further justification is required for the use of a single value of Sigma(abs,pri) (i.e. determined by equation 4) as two primary BrC sources (i.e., traffic and biomass burning) are identified in this work. The OA from these two primary emissions likely have different BrC absorption and characteristics. Although the argument is provided (lines 291-293) to claim that the HOA/BBOA ratio almost unvaried in the diurnal pattern, Figure 1 clearly shows that the HOA/BBOA ratios are different between the morning rush hour and the night-time peak. This is very important to provide stronger justification here as the subsequent calculation can have significant impact on the arguments for photobleaching of primary BrC and formation of secondary BrC associated with the primary emissions in page 12.

Reply: We thank editor to point this out. We agree with editor that there may be different primary BrC/BC ratio between HOA and BBOA sources and this may lead to bias in deriving the subsequent results. We have more carefully investigated the diurnal pattern of HOA and BBOA, and found only a slight morning rush-hour peak for HOA (though bearing considerable variation). A further investigation on the HOA/BBOA ratio found no apparent diurnal pattern (bearing large variation), shown as below. The source difference is therefore not considered to have significantly influenced the diurnal pattern of derived parameters. In addition, this method is only valid with sufficient data points thus we may only obtain a single mean value for the entire experiment, which represents the mean BrC_{pri}/BC in this environment during the experimental period.



Diurnal variation of HOA, BBOA and HOA/BBOA.

Other literatures using this method also derived the mean value of BrC_{pri}/BC for the urban environment influenced by multiple sources including traffic, coal combustion and biomass burning (Wang et al., 2019; Wang et al., 2020; Gao et al., 2022).

2) Lines 285-287: More detail interpretation is required for assigning photobleaching as a key aging process of primary BrC peak observed at nighttime. Why the key aging process involved

has to be photobleaching? The logic flow of the discussion implies that the changes in primary BrC absorption occurred locally or in short time scale. If so, please provide more detail clarification. Can the observation cause by regional transport of aged BBOA as well for example? What are the implications in terms of BrC chemistry/characteristics if the BrC absorptivity deceased faster than the HOA and BBOA mass?

Reply: We thank editor to point out these important points. More clarification is now added to explain the decreased absorptivity of primary BrC. In the daytime, the BrC may react with OH radical in aerosol phase, or by enhanced evaporation and reaction in gas phase, and maybe further decreased by aqueous reaction when higher RH at night. All these may contribute to the decrease of chromophores. We agree with editor that some more aged BBOA source could be mixed with fresher HOA source, though there may be also some aged HOA. The aging scale of these sources is unable to be resolved in this study, but this is not likely to affect the diurnal pattern (which tends to be more influenced by local sources) we investigated, thus not affecting the conclusion.

More discussions about the implications of BrC absorptivity decrease are also added.

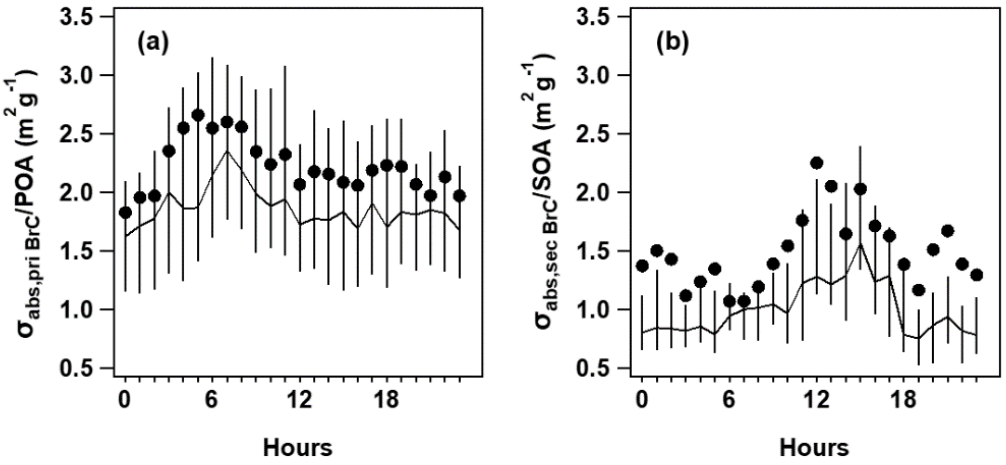
"The night had contributions from BC and primary BrC at 50±2% and 30±3% respectively, with 20±3% as secondary BrC. Fig. 4b showed the decrease of primary BrC absorption tended to be more rapid than the HOA and BBOA mass (even a slight increase for HOA Fig. 1m and Fig. 1o) in the midday, leading to decreased absorption coefficient per unit mass of primary BrC (shade in Fig. 4b), which indicates the decrease of BrC absorptivity likely due to photochemistry. This may involve the OH radical reaction with existing chromophores in aerosol phase (Schnitzler et al., 2020) or by enhanced evaporation of aerosols to gas phase (Palm et al., 2020) leading to further decrease of BrC absorptivity during midday. In addition to photobleaching, it possible that some primary species transformed into less absorbing secondary BrC species. During this period, the type of HOA or BBOA that contribute to absorption may also have a lower absorptivity. 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). The reaction of BrC with OH radical has been widely recognized as the main pathway for the loss of primary BrC absorptivity (Liu et al., 2020), and was parameterized as an exponential decrease with time at certain OH radical concentration in global scale (Wang et al., 2018b)."

L288-291, L295-297

3) Lines 315-321: As the key message of this work is concurrent photochemical whitening and darkening (or degradation and formation) of ambient BrC as reflected in the title of manuscript. However, the changes in the percentage contribution of primary and secondary BrC to the total absorbance would not be able to support this conclusion. Instead, absolute changes in BrC mass and/or absorbance (e.g. MAC of total OA or PMF factors) are likely required to support this conclusion and they should be clearly presented in the manuscript.

Reply: We thank editor to point this out. In addition to the changes in the percentage contribution of primary and secondary BrC to the total absorbance, we have also added the MAC (absorption per unit mass of OA) of POA and SOA to imply the change of their

absorptivity. We can derive the absorption of primary and secondary OA using the method here, but it is unable to derive the absorption for each PMF factor (only for total POA and SOA). The enhancement of MAC_{SOA} was found to peak in the afternoon. Fig. 4 is now incorporated with MAC_{SOA}.



Diurnal variation for MAC of POA and SOA.

These are now added in the revision: "Fig. 4b showed that the MAC of POA decreases after the morning peak. The MAC of SOA showed an afternoon peak (Fig. 4c), indicating the enhancement of absorption efficiency of secondary BrC, which occurred in a few hours after the peak solar radiation."

L321-323

References

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