

Dear Editor and Reviewers,

We are thankful for the comprehensive comments from Reviewer and Editor for the manuscript. We have now addressed all comments and revised our previous manuscript accordingly. The corresponding changes in the texts are **highlighted in yellow**.

**Reviewer 3:**

*Referee report on ACP-2022-483 - Concurrent photochemical whitening and darkening of ambient brown carbon*

*Appreciate the effort of the authors to address the comments in detail and incorporate them in the necessary content throughout the manuscript. I believe the manuscript is suitable for publication after the following minor comments are addressed. Overall, as there are several instances of long sentences and grammatical errors that cloud the important messaging, a thorough language revision may be considered.*

We thank reviewer for the generally positive comments for the current version of the manuscript. We have now addressed all the comments raised.

**Minor Comments:**

*1. Lines 22-25-MAC and contribution to total absorbance of POA and SOA could be discussed for POA and SOA separately to make the message clearer. For example. “Photochemical processes were found to reduce the mass absorption cross section (MAC) of primary OA, reducing its contribution to total absorption by 20%, at the same time increasing MAC for secondary OA, which showed a 30% enhancement in contribution to total absorbance.....”*

**Reply:** This is revised.

**“The photochemical processes were found to reduce the mass absorption cross section (MAC) of primary OA, reducing its contribution to total absorption by 20%, at the same time increasing MAC for secondary OA, which showed a 30% enhancement in contribution to total absorbance, implying the concurrent whitening and darkening of BrC.”**

L23-25

*2. Line 25-26-“The study provides.....nitrogen-containing secondary OA can compensate for some effects of bleaching of primary BrC.”*

*In some text, the authors have implied that photooxidation was responsible for the observed changes while in other instances photochemical processes are mentioned. As the study cannot isolate what type of reactions may have caused the increase or decrease in absorptivity, maybe it is safer to use the term photochemical processes. Please read through and keep the message consistent.*

**Reply:** We agree with reviewer that the study is unable to isolate what type of reactions may have caused the increase or decrease in absorptivity. We have therefore changed the term

photooxidation as photochemical processes. Related discussions are revised.

“The above findings mean the enhancement or bleaching of BrC absorptivity via **photochemical processes** will coexist.”

“The slight enhancement at noon for OOA1 (also for OOA2) soon after morning rush-hour indicated the likely rapid formation of SOA through **photochemical processes**.”

“This aging or oxidation likely occurred through **photochemical processes** during early afternoon and aqueous processes (high RH conditions) during nighttime.”

“The high NO<sub>x</sub> emission of traffic VOCs may have largely involved nitrogen chemistry **in the photochemical processes**.”

“The daytime formation of organic nitrate may follow the gas-phase **photochemical processes** in which the excess NO could add to the peroxy radical to produce organic nitrate (Liebmann et al., 2019).”

“We found the **photochemical processes** decreased the MAC of POA but increased the MAC of SOA, resulting in an enhanced contribution of secondary BrC to total absorbance by 30% but reduced contribution of primary BrC about 20% in the semi-urban environment. This revealed that the whitening and darkening of BrC occurred simultaneously, and the secondary BrC produced by **photochemical processes** may compensate some bleaching effect of primary BrC.”

L50, L214, L332, L335, L337, L354, L357

3. Line 318-321 -The sentences are not well combined. Re-writing these sentences combining the messages maybe clearer.

4. Line 321- Needs revision for grammatical errors and plain language.

**Reply:** This is revised.

“Fig. 4b-c showed that the MAC of POA decreased after the morning peak, but the MAC of SOA had an afternoon peak. This indicated the enhancement of absorptivity of secondary BrC, which occurred in a few hours after the peak solar radiation. These results implied the **photochemical processes** decreased the absorptivity of POA but increase for of SOA.”

L322-324

5. Line 324- Can be considered to be revised as “Though other processes such as aqueous-phase reactions may cause changes to MAC of BrC at nighttime, the apparent change in aerosol absorption observed in this study during daytime can play an important role on the radiative impacts due to intensive solar radiation during daytime”?

**Reply:** Thanks for the suggestion. This is revised.

“**Though other processes such as aqueous-phase reactions may cause changes to the MAC of BrC at nighttime, the apparent change in aerosol absorption observed in this study can play an important role on the radiative impacts due to intensive solar radiation during daytime.**”

6. Lines 314-339 – *If possible, it may be better to revise this paragraph and re-organise the important information mentioned. The current layout appears to be jumping back and forth between MAC, relative contribution of POA and SOA and SOA formation pathways.*

**Reply:** This paragraph is now reorganized.

“The night and morning peak of OOA2 and the morning peak of the absorption coefficient of secondary BrC ( $\sigma_{\text{abs,secBrC}}$ ) may result from primarily emitted moderately oxygenated OA, which was reported from some diesel sources (Dewitt et al., 2015; Gentner et al., 2012). Besides the morning rush-hour peak, there was an early afternoon peak for  $\sigma_{\text{abs,secBrC}}$  prevailing the dilution effect of daytime boundary layer (Fig. 4c-S5). The fraction of  $\sigma_{\text{abs,secBrC}}$  in total  $\sigma_{\text{abs}}$  thus had a pronounced early afternoon peak soon after the peak solar radiation (Fig. 4f), and a peak after midnight soon after the nighttime peak of primary BrC (Fig. 4e).

Fig. 4b-c showed that the MAC of POA decreased after the morning peak, but the MAC of SOA had an afternoon peak. This indicated the enhancement of absorptivity of secondary BrC, which occurred in a few hours after the peak solar radiation. These results implied the photochemical processes decreased the absorptivity of POA but increase for of SOA. Fig 4e-f showed the photochemical processes led to an enhanced contribution of secondary BrC to the total absorption by 30% from the morning rush-hour to midday, but during the same time reduced the contribution of primary BrC to the total absorption about 20%. Though other processes such as aqueous-phase reactions may cause changes to the MAC of BrC at nighttime, the apparent change in aerosol absorption observed in this study can play an important role on the radiative impacts due to intensive solar radiation during daytime.

Table 1 showed the SOA compounds containing nitrogen (i.e., the OOA2) considerably contributed to the light absorption. The shift of peaking time from primary to secondary BrC demonstrates the possible processes of SOA formation, such as from gases. This aging or oxidation likely occurred through photochemical processes during early afternoon and aqueous processes (high RH conditions) during nighttime. The oxidized volatile organic compounds (VOCs) with nitrogen chemistry involved could condense to produce additional mass in particle phase (Ehn et al., 2014; Finewax et al., 2018). The high  $\text{NO}_x$  emission of traffic VOCs may have largely involved nitrogen chemistry in the photochemical processes. Previous studies found the  $\text{NO}_x$ -involved SOA could produce considerable chromophores containing nitroaromatics in hours (Wang et al., 2019d; Keyte et al., 2016). The daytime formation of organic nitrate may follow the gas-phase photochemical processes in which the excess NO could add to the peroxy radical to produce organic nitrate (Liebmann et al., 2019). The nighttime chemistry involves  $\text{NO}_3$  radical through the oxidation of  $\text{NO}_2$  by  $\text{O}_3$ , through which the organic nitrate could be produced by initializing the production of nitrooxy peroxy radicals (Ng et al., 2008; Rollins et al., 2012). Laboratory studies also widely observed the rapid production of nitrogen-containing OA through  $\text{NO}_x$  chemistry, which could contribute to light absorption of aerosols (Nakayama et al., 2013; Liu et al., 2015c).”

7. Line 340-342 – Sentence too long and unclear. Please re-write as two or more sentences.

8. Line 340-348 – Can be considered to be included in Conclusions section instead, as it is repeating some of the main messages that was described in the paragraph right above.

**Reply:** This paragraph is now moved to the conclusion section.

“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. Primary OA generally had a higher MAC than secondary OA. OA from biomass burning was found to have the highest MAC in POA factors. Secondary BrC was found to be associated with an oxygenated secondary OA factor with higher nitrogen content. We found the photochemical processes decreased the MAC of POA but increased the MAC of SOA, resulting in an enhanced contribution of secondary BrC to total absorbance by 30% but reduced contribution of primary BrC about 20% in the semi-urban environment. This revealed that the whitening and darkening of BrC occurred simultaneously, and the secondary BrC produced by photochemical processes may compensate some bleaching effect of primary BrC. The dominance of both competing processes may depend on the timescale and altitude in the atmosphere. For example, the enhanced BrC fraction observed above the planetary boundary layer may be explained by the enhanced secondary BrC (Tian et al., 2020), while further aging may bleach the produced chromophores of these SOA.

The results emphasize the importance of nitrogen-containing OA in contributing to BrC. The NO<sub>x</sub>-involved chemistry is prone to add nitrogen element to the existing OA and enhance the absorptivity of chromophores. The anthropogenic NO<sub>x</sub> 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.”

L350-365

9. Lines 360-361- “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.” - I am unclear of the relevance of this sentence.

**Reply:** This is removed.