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 titled "Concurrent photochemical whitening and darkening of brown carbon" by Li et al. describes the behavior of primary and secondary brown carbon (BrC) from field observation in a sub-urban site near Beijing, China. The main finding of this work is that it is offering field evidence of concurrent whitening and darkening of ambient BrC.

The reviewers and editor have raised several concerns and have given suggestions for improvement, most of which have been addressed by the authors. However, it appears that the authors' have not fully grasped the reasoning for these comments and have failed to modify the manuscript in a significant way. Some of the comments have been addressed by adding one or two sentences in the suggested paragraph and the changes are not reflected anywhere else in the manuscript, even if it changes some of the main messaging. Take for example the comment by editor that additional evidence to justify the main claim of concurrent whitening and darkening, other than the percentage difference in primary and secondary BrC absorption, is needed. This has only been addressed in one line in the accompanying text, suggesting the enhancement in MAC of SOA, but not addressed in the abstract, where it only describes the percentage difference.

Reply: We have now added more discussions in the abstract and expanded discussions in the main texts.

In the abstract:

"The photochemical processes were found to reduce the mass absorption cross section (MAC) of primary OA but enhancement for secondary OA, resulting in the contribution of primary BrC to total absorbance decreased about 20% but enhanced contribution of secondary BrC by 30%, implying the concurrent whitening and darkening of BrC."

L22-23

In the main texts:

"This factor is obtained using the minimum R-squared (MRS) approach (Wu and Yu, 2016), by adjusting the factor until a minimum correlation between $\sigma_{abs,secBrC}$ and [rBC] is reached because the absorption from secondary sources are least likely to covary with that from primary sources (Wang et al., 2019a). This method has been used in urban and sub-urban environment to obtain the primary BrC associated with combustion sources. Being different from previous studies, an auxiliary characterization of rBC mass measured by the SP2 is used here to avoid the possible interference from absorption measured by the same instrument. There may be different $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ ratio between traffic and biomass burning sources and this may lead to bias in deriving the subsequent results. We have more carefully investigated the diurnal pattern of hydrocarbon-like OA (HOA) and biomass burning OA (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 in Fig. S8. 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 $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ in this environment during the experimental period. Previous studies using this method also derived the mean value of $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ for the urban environment influenced by multiple sources including traffic, coal combustion and biomass burning (Wang et al., 2019c; Wang et al., 2020; Gao et al., 2022). The $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ ratio at λ=375 nm, 470 nm, 528 nm, 635 nm and 880 nm is calculated to be 20.7, 17.0, 14.4, 11.7 and 5, respectively (Fig. S2), which falls within the reported values from previous studies 11-50 (Zhang et al., 2020; Wang et al., 2019a)."

L114-123

"Besides the morning rush-hour peak, there was an early afternoon peak for the absorption coefficient of secondary BrC, prevailing the dilution effect of daytime boundary layer (Fig. 4c-S5). The night and morning peak of OOA2 and the morning peak of $\sigma_{abs,secBrC}$ may result from primarily emitted moderately oxygenated OA, which was reported from some diesel sources (Dewitt et al., 2015; Gentner et al., 2012). The fraction of secondary BrC thus had a pronounced early afternoon peak soon after the peak solar radiation (Fig. 4f) and a peak after midnight soon after the nighttime peak of primary BrC (Fig. 4e). Fig. 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. This means the photochemistry caused the absorptivity of POA decreased but the absorptivity of SOA increased. Fig 4e-f shows 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 the other process such as aqueous reactions at nighttime may also contribute the change of MAC for BrC, the apparent change in the daytime was indeed observed in this study, and the absorption of aerosols plays a more important role on the radiative impacts in the daytime when intensive solar radiation."

L318-321, L324-326

"Overall, by apportioning the absorption of primary and secondary BrC, the BBOA was found to have the highest MAC and the other POA factors generally have a higher MAC than SOA, the OOA2 has a relatively high MAC which is likely to result from the production of secondary BrC. 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 photooxidation may compensate some bleaching effect of primary BrC."

L340-343

Furthermore, comments have been made regarding calculating the MAC of individual OA factors, and has not been addressed. With source-apportioned OA factors and total OA absorbance, several studies have used methods such as multiple linear regression analysis (Qin et al. "Chemical characteristics of brown carbon in atmospheric particles at a suburban site near Guangzhou, China." ACP 18.22 (2018): 16409-16418. Wang et al. "Wintertime optical properties of primary and secondary brown carbon at a regional site in the North China Plain." ES&T 53.21 (2019): 12389-12397. Kasthuriarachchi et al. "Light absorbing properties of primary and secondary brown carbon in a tropical urban environment." ES&T 54.17 (2020): 10808-10819. Wang et al. "Aqueous production of secondary organic aerosol from fossil-fuel emissions in winter Beijing haze." PNAS 118.8 (2021): e2022179118 and latest studies with ridge regression models (Zhang et al. "Impact of COVID-19 lockdown on the optical properties and radiative effects of urban brown carbon aerosol." Geo. Front. 13.6 (2022): 101320.) to obtain MAC of individual OA factors. The fact that authors have failed to do the same is questionable. The addition of this information has the potential to offer supporting evidence to the main claim of this work as it will help to identify how the MAC of each OA factor changed during the day.

A complete revision of this work, including MAC of individual factors and addressing the uncertainties of the calculation, assumptions etc., with more focus on the light absorbing properties in the Results and Discussion section (more than half is attributed to OA source discussion), with a thorough language revision may be re-submitted for revision.

Reply: We thank reviewer to point this out. By rechecking the manuscript, we found we have actually performed the multiple linear regression in the previous version, as reviewer suggested. We have now reemphasized this point and added related discussions.

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

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

where a_1 to a_5 represents the regression coefficients for each factor. These coefficients can be associated with the absorptivity of each factor, i.e., a larger coefficient implies a higher MAC for the source associated with that OA factor (Kasthuriarachchi et al., 2020; Wang et al., 2021). The BBOA was found to have the highest MAC at 2.59 $m^2\ g^{-1}$, consistent with previous studies which also found significantly higher absorption for biomass burning source (Qin et al., 2018; Wang et al., 2019b; Zhang et al., 2022). The other POA factors generally have a higher MAC than SOA (the MAC of HOA and COA are is 1.70 $m^2\ g^{-1}$ and 1.30 $m^2\ g^{-1}$, respectively). Particularly, the OOA2 has a relatively high MAC of 1.22 $m^2\ g^{-1}$, which is likely to result from the production of secondary BrC as discussed below. The contribution of each source-specific OA factor to $\sigma_{abs,BrC}$ can also be obtained. This analysis is performed for the total BrC, primary and secondary BrC respectively. The results are shown in Table 1."

L258-265

Editor:

Thanks for your detail responses to my comments for your last version, and I think you have addressed my questions appropriately. For the next revision, I suggest to add the diurnal variation of HOA/BBOA and related justification in SI so that reader can closely follow the detail of your data analysis approach. The updated Figure 4 certainly enhance the supporting argument for the main message of this work.

Reply: We are thankful to Editor for the comprehensive comments to our manuscript. The diurnal variation of HOA/BBOA is now added in Figure S8.

However, the reviewer#3 still have some major concerns in terms of presentation quality and data analysis as outlined in the reviewer's report. Although the reviewer recommends to reject this work, I think this work can be potentially important to advance our understanding of BrC sources and formation in the atmosphere if the reviewer's comment can be addressed appropriately.

We thank Editor for the opportunity to revise our manuscript, and we believe in this version we will fully address all of the issues reviewer#3 raised.

In my point of view, there are still two major actions/justification requested by the reviewer#3 to enhance the quality of this manuscript.

1) The reviewer requests to check all the scientific arguments are consistently presented throughout the manuscript as some of the conclusion and details might be changed along the review process.

Reply: We have now very carefully revisited the manuscript once again to make sure all the related discussions have been adapted for the updated figures and data analysis. The revisions are listed as below:

"The photochemical processes were found to reduce the mass absorption cross section (MAC) of primary OA but enhancement for secondary OA, resulting in the contribution of primary BrC to total absorbance decreased about 20% but enhanced contribution of secondary BrC by 30%, implying the concurrent whitening and darkening of BrC."

L22-23

"This factor is obtained using the minimum R-squared (MRS) approach (Wu and Yu, 2016), by adjusting the factor until a minimum correlation between $\sigma_{abs,secBrC}$ and [rBC] is reached because the absorption from secondary sources are least likely to covary with that from primary sources (Wang et al., 2019a). This method has been used in urban and sub-urban environment to obtain the primary BrC associated with combustion sources. Being different from previous studies, an auxiliary characterization of rBC mass measured by the SP2 is used here to avoid the possible interference from absorption measured by the same instrument. There may be different

$\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ ratio between traffic and biomass burning sources and this may lead to bias in deriving the subsequent results. We have more carefully investigated the diurnal pattern of hydrocarbon-like OA (HOA) and biomass burning OA (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 in Fig. S8. 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 $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ in this environment during the experimental period. Previous studies using this method also derived the mean value of $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ for the urban environment influenced by multiple sources including traffic, coal combustion and biomass burning (Wang et al., 2019c; Wang et al., 2020; Gao et al., 2022). The $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ ratio at λ=375 nm, 470 nm, 528 nm, 635 nm and 880 nm is calculated to be 20.7, 17.0, 14.4, 11.7 and 5, respectively (Fig. S2), which falls within the reported values from previous studies 11-50 (Zhang et al., 2020; Wang et al., 2019a)."

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"Besides the morning rush-hour peak, there was an early afternoon peak for the absorption coefficient of secondary BrC, prevailing the dilution effect of daytime boundary layer (Fig. 4c-S5). The night and morning peak of OOA2 and the morning peak of $\sigma_{abs,secBrC}$ may result from primarily emitted moderately oxygenated OA, which was reported from some diesel sources (Dewitt et al., 2015; Gentner et al., 2012). The fraction of secondary BrC thus had a pronounced early afternoon peak soon after the peak solar radiation (Fig. 4f) and a peak after midnight soon after the nighttime peak of primary BrC (Fig. 4e). Fig. 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. This means the photochemistry caused the absorptivity of POA decreased but the absorptivity of SOA increased. Fig 4e-f shows 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 the other process such as aqueous reactions at nighttime may also contribute the change of MAC for BrC, the apparent change in the daytime was indeed observed in this study, and the absorption of aerosols plays a more important role on the radiative impacts in the daytime when intensive solar radiation."

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"Overall, by apportioning the absorption of primary and secondary BrC, the BBOA was found to have the highest MAC and the other POA factors generally have a higher MAC than SOA, the OOA2 has a relatively high MAC which is likely to result from the production of secondary BrC. 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 photooxidation may compensate some bleaching effect of primary BrC."

L340-343

2) The reviewer requests to obtain MAC values for individual OA factor. The authors response to my previous comment that it is unable to derive the MAC values for each OA factor, and I suggest the authors to provide a more clear explanation on this. Nevertheless, my understanding is that the results presented in Table 1 were actually obtained by MLR analysis between total BrC absorption and PMF-OA factors, which is similar to the approach used by other studies (see the reference list from the reviewer). The regression coefficient is likely relevant to the MAC values, which at least can be used to compare the light absorption properties of HOA, BBOA and OOA-2 observed in this study (e.g., BBOA > HOA ~OOA-2), and perhaps those derived in other previous studies.

Reply: We thank Editor to point this out. By rechecking the manuscript, we found we have actually performed the multiple linear regression in the previous version, as Editor suggested. We have now reemphasized this point and added related discussions.

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

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

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L258-265