Dear Editor and Reviewers,

We are thankful for the insightful comments on our 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:

The journal article on "Concurrent photochemical whitening and darkening of brown carbon" by Li et al., describes the behavior of primary and secondary brown carbon (BrC) in a sub-urban site near Beijing, China. By apportioning the total aerosol absorption between black carbon (BC), primary BrC and secondary BrC, they identify that traffic and biomass burning are main sources of primary BrC and that nitrogen-containing moderately oxygenated organic aerosol are the main source of secondary BrC. Further, a percentage decrease in primary BrC is observed together with a percentage increase in absorbance by secondary BrC from photooxidation, which is considered to offer field evidence of the concurrent of whitening and darkening of BrC.

Overall, there are some interesting methodologies used to separate primary and secondary BrC and use their diurnal variation to illustrate the dynamic behavior of BrC in the atmosphere. However, there is a significant lack of discussion on the various possible interpretations of the results, other than the authors' main conclusions. There is also a serious lack of discussion on uncertainties associated with the measurements/calculations. Furthermore, a language revision may be required to express the main findings in a more clear and concise manner. However, as extensive measurements from various instruments are available to them, a revised version of this manuscript that addresses these issues may be considered after review.

Main Comments:

1. The method used to apportion BrC absorbance to primary and secondary BrC, described by Wang et al. (2019), uses the assumption of a constant $(\sigma_{abs,total}/[rBC])_{pri}$ *.Previous reviewers have also raised their concerns regarding the validity of this assumption. While the authors have said that there are no pollution events that may result in a change in these values, the Figures 1 and 2 show that there may have been a few instances of such events. The authors also discuss this possibility in Lines 219-220 when discussing the changes observed for BC coating thickness during high pollution events. While it may not be straightforward to use a* $(\sigma_{abs,total}/[rBC])_{pri}$ *that is composition dependent, it is worth to mention the uncertainty associated with the assumption. For example, is it possible to discuss how the range of values for this ratio can affect the final BrC calculations?*

I believe a thorough investigation on the uncertainties associated with this ratio and the other components used equations are necessary. Also, a propagated error calculation can add value to the final output of these calculations.

Reply: We thank reviewer to point this out. We have calculated $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ for the high pollution period, which is 19.1% difference with the experiment mean. The uncertainty of this

parameter is mainly associated with the datapoints used according to Wang et al. (2019). According to reviewer's suggestion, we have gone through the uncertainties of each input parameter and output parameter using error propagation, which is now added in Table S1. The following is now added to discuss the uncertainties of each parameter.

"The uncertainty of $\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$ is 4% for the data points over 1.5 according to (Wang et al., 2019). The measurement of rBC mass from the SP2 had uncertainty of 20% (Schwarz et al., 2008), with relative coating thickness having uncertainty of 23% (Taylor et al., 2015), hereby resulting in a uncertainty of 27% for calculated MAC_{BC}. The above results in uncertainties of 31% and 20% for $\sigma_{abs,BC}$ and $\sigma_{abs,pri}$, respectively. The absorption measurement by MA200 had uncertainty of 25% ((Drinovec et al., 2015b; Duesing et al., 2019). All these uncertainties propagates the uncertainties of $\sigma_{abs,BrC}$, $\sigma_{abs,priBrC}$ and $\sigma_{abs,secBrC}$ as 40%, 37% and 32% respectively. These are summarized in Table S1."
L223-229

Table S1. Estimated uncertainties of input and output parameters.

Input Parameter	Uncertainty (%)	Output Parameter	Uncertainty (%)
$\left(\frac{\sigma_{abs,total}}{[rBC]}\right)_{pri}$	4[(a)]	$\sigma_{abs,BrC}$	40
BC mass concentration	20[(b)]	$\sigma_{abs,priBrC}$	37
MAC	27[(c)]	$\sigma_{abs,secBrC}$	32
$\sigma_{abs,BC}$	31		
$\sigma_{abs,pri}$	20		
$\sigma_{abs,total}$	25[(d-e)]		

(a) Wang et al. (2019)

(b) Schwarz et al. (2008)

(c) Taylor et al. (2015)

(d) Duesing et al. (2019)

(e) (Drinovec et al., 2015)

2. As the Micro Aethalometer gives absorbance measurements in three other wavelengths where BrC absorbance may be observed (i.e. 470,528 and 635nm), have the authors observed the same behavior of BrC in these wavelengths as well? Is the relative contribution or diurnal profile of primary and secondary BrC any different? Furthermore, including calculations of wavelength dependence, which is another important parameter that can describe the absorbing properties, can enrich the discussion.

Reply: The parameters at other longer wavelengths (470, 528 and 635nm) also showed similar results with that at 375nm but with decreased fraction of BrC absorption with increased wavelength. We have also calculated and discussed AAE, which is the parameter to reflect the

wavelength dependence of absorption. Due to the relatively high contribution of BC to total absorption, we have not found apparent variation of AAE from the bulk measurement.

The related discussions are now added.

"The relative contribution and diurnal variation of primary and secondary BrC measured by MA200 at 470, 528 and 635nm wavelengths are similar to those at 375nm wavelengths, but with decreased fraction of BrC absorption with increased wavelength. Due to the high contribution of BC to total absorption (>50% even at shortest wavelength), the spectral dependence of absorption in bulk has not shown apparent diurnal variation."

L269-272

3. Line 248- is r>0.4 considered as a high correlation?

Reply: We use r=0.4 to distinguish the factors with relatively higher correction with BrC absorption within the five factors. It is changed as:

"MLR on the total BrC shows relatively higher correction (r>0.4) with the factors of HOA, BBOA and OOA2, suggesting the potential importance of the primary biomass burning and traffic source along with OOA2 in governing absorption of BrC."

L251

4. Line 226 - Do the MAC values of BC match well with those in literature?

Reply: We have added related discussions.

"MAC of BC at λ=375nm showed to be at 8.4 -16.6 $m^2 g^{-1}$ with enhanced absorption when high coatings, which was consistent with previous studies which reported MAC_{BC} of 8-10 $m^2 g^{-1}$, and higher value of 9.7 -17.2 $m^2 g^{-1}$ under polluted condition (Ding et al., 2019; Hu et al., 2021)."

L222-223

5. Lines 277-278 – The authors use the comparison of diurnal profiles, the reduction in the absorbance and the absorption coefficient per unit POA mass, as strong evidence of photobleaching of primary BrC. While photobleaching maybe one of the reasons for the observed reduction, the given evidence is not strong enough to make this an absolute conclusion. It is important to discuss if there are other possibilities for this. For an example, it possible that some primary species transformed into less absorbing secondary BrC species, and this could be via other reaction pathways. The type of HOA/BBOA contributing to the absorption during this period may have lower absorptivity. While it may be difficult to provide solid evidence for all the claims, it is important to discuss the possible reasons for such observations.

Reply: We thank reviewer to point this out. The suggestion about the conversion of primary OA to secondary OA with weaker absorption can indeed support our conclusion. We have added the suggested related discussions in the revision.

"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."

L288-289

Also, considering that BBOA is more absorbing per unit mass than traffic-related OA and has a corresponding peak at night, it is surprising to see the low, almost constant levels of abs/POA from 6-9pm. I believe the reasons for this have not been discussed in the manuscript.

Reply: We have added related discussions in the revision.

"Both HOA and BBOA had night peaks at 6-9pm with HOA having a higher concentration than BBOA. The HOA/BBOA ratio almost unvaried in the diurnal pattern, thus had not resulted in a significant variation of $\sigma_{abs,priBrC}$/POA (Fig. 1m, Fig. 1o and Fig. 4b.). "

L291-293

Furthermore, while the method used to apportion primary and secondary BrC has been previously used, it may be important to point out that it may not be as straightforward to separate primary and secondary sources of BrC by assuming that all primary BrC are from combustion sources and that there is no cooccurrence of primary and secondary BrC from these. In fact, authors themselves mention that their study and those previously do observe a cooccurrence of these emissions (Lines 272-273). Therefore, it is possible that some of the primary sources are being attributed to secondary sources and vice versa. This maybe a possible reason for the simultaneous peak observed for primary and secondary BrC during morning rush hour.

Reply: We agree with the reviewer that it is possible that some primary sources are attributed to secondary sources or vice versa, which may explain the simultaneous peak observed for primary and secondary BrC during morning rush hour. Related discussions are added.

"The morning peak coinciding with the primary BrC may result from the rapid formation of BrC from sources when emitted gases condensed and formed aerosols. These may lead to high cooccurrence between primary and secondary BrC. Previous studies in urban environment also observed concurrent peaks of primary and secondary BrC, which usually occurred at morning rush hour (Zhang et al., 2020). Furthermore, it is possible that some primary sources are attributed to secondary sources. This may explain the simultaneous peak observed for primary and secondary BrC during the morning rush hour."

L278-284

6. I am unable to follow how the authors determined that there is a 20% decrease in primary and 30% increase in secondary BrC absorbance due to photooxidation. If I understand correctly, it says in the methodology that this is compared to the overall average absorbance of primary and secondary BrC absorbance. If this is the case, how is it determined that photooxidation alone was responsible for the increase or decrease when there are various

processes taking place throughout the day that affect BrC absorbance. I notice that previous reviewers have also raised this concern, but I don't believe it has been properly addressed in the revised manuscript.

Reply: We agree with reviewer that there are multiple processes in the daytime such as photooxidation, photolysis or other photochemical processes may play roles on modifying the absorbance of brown carbon. We have therefore changed the term photooxidation as multiple photochemical processes for these discussions. In addition, we have more clearly demonstrated how the values are obtained. Related discussions are revised.

"The photochemical processes were found to result in reduced contribution of fraction of total absorbance of primary BrC about 20% but enhanced contribution of secondary BrC by 30%."

"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%."

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

L22, L298-301, L315-316

7. Figure 4 (d-e) –Authors may consider to use "Fraction of total absorbance" or a similar title that better describes what the axis represents

This is the case throughout the text where, when a fraction or a percentage is used. Ideally, the description should include the denominator. It may be particularly important to describe it properly when the percentage decrease and increase of primary and secondary BrC absorbance is used to describe the effect of photochemical reactions (Lines 22-23 and 300-301) as this is one of the primary claims.

Reply: We have revised the title of Figure 4 (d-e) and have revised related discussions.

"The photochemical processes were found to result in reduced contribution of fraction of total absorbance of primary BrC 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 total absorbance of secondary BrC by 30% but reduced contribution of primary BrC about 20% in the semi-urban environment."

L22, L315-316

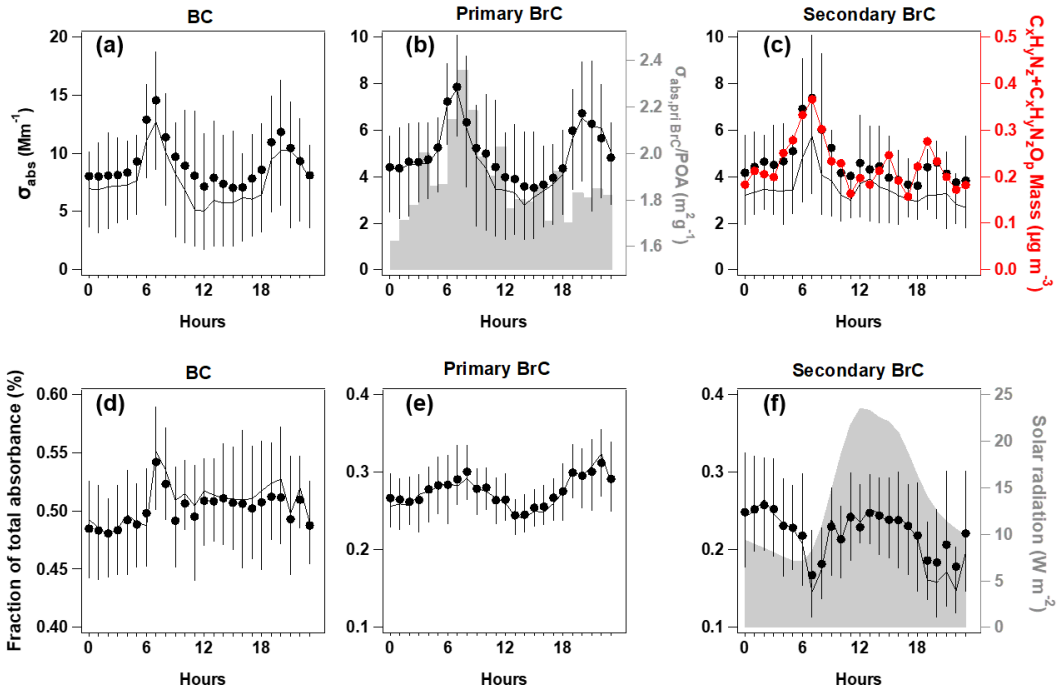

Figure 4. Diurnal variations of absorption coefficient at λ=375nm ($\sigma_{abs,375}$) for BC (a), primary BrC and absorption efficiency of primary BrC ($\sigma_{abs,priBrC}$)/POA is shown in shade (b), and secondary BrC, along with the $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments (c); the respective fraction in total for the segregated $\sigma_{abs,375}$ (d-f), with direct radiation shown in shade. In each plot, the lines, dots and whiskers denote the median, mean and the 25th/75th percentiles at each hour respectively.

Minor comments :

(i) The sentences in the abstract are too long and the message is confusing. Please rephrase. For example;

" The absorption of BC is constrained by its size distribution and mixing state, being subtracted from total absorption to obtain the absorption of BrC, then by applying the least-correlation of BC absorption with secondary BrC, the absorption contributed by BC, primary BrC and secondary BrC was apportioned" can be rephrased as;

"The absorption of BC is constrained by its size distribution and mixing state and the BrC absorption is obtained by subtracting the BC absorption from the total aerosol absorption. Aerosol absorption was further apportioned to BC, primary BrC and secondary BrC by applying the least-correlation between secondary BrC and BC."

Several other instances where the messaging is unclear due to long sentences can be found throughout the manuscript. Please try to write in clear and concise sentences to get the message across more clearly.

Reply: This is revised.

"The absorption of BC is constrained by its size distribution and mixing state and the BrC absorption is obtained by subtracting the BC absorption from the total aerosol absorption. Aerosol absorption was further apportioned to BC, primary BrC and secondary BrC by applying

the least-correlation between secondary BrC and BC."

"These primary BrC has a range of absorptivity, which was found to be controlled by burning phases. OA co-emitting with BC (the flaming phase) exhibited a higher absorptivity than OA-dominated smoldering phase (Liu et al., 2021)."

L16-18, L35-36

(ii) Several grammar, spelling mistakes and missing words can be found. Please read thoroughly to minimize the errors. I am only listing a few examples.

e.g.: Line 27 - Atmospheric absorbing organic aerosol (OA), known as brown carbon (BrC), is "a" important contributor to anthropogenic 28 absorption besides black carbon (BC)

Line 34 – These primary BrC "has" ….(again long sentence here and the message is unclear).

Line 46- "Existing" chromophores

Reply: This is revised.

L27, L34, L46

(iii) The word brown carbon used in the middle of text after acronym BrC is first introduced. Please be consistent.

Reply: This is revised.

L38

(iv) Line 37 - Dasari, Sanjeev, et al. "Photochemical degradation affects the light absorption of water-soluble brown carbon in the South Asian outflow." Science advances 5.1 (2019) also discuss photochemical degradation of South Asian outflow.

Reply: This is added.

L37

(v) Line 39 - "decease" should be changed to "decrease" ….and photobleaching "of"

Reply: This is revised.

L39

References

Wang, Q., Han, Y., Ye, J., Liu, S., Pongpiachan, S., Zhang, N., Han, Y., Tian, J., Wu, C., Long, X., Zhang, Q., Zhang, W., Zhao, Z., and Cao, J.: High Contribution of Secondary Brown Carbon to Aerosol Light Absorption in the Southeastern Margin of Tibetan Plateau, Geophysical Research Letters, 46, 4962-4970, 10.1029/2019gl082731, 2019.