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

Qian Li[1], Dantong Liu[1*], Xiaotong Jiang[1], Ping Tian[2], Yangzhou Wu[1], Siyuan Li[1], Kang Hu[1], Quan Liu[3], Mengyu Huang[2], Ruijie Li[2], Kai Bi[2], Shaofei Kong[4], and Deping Ding[2]

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.

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.

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

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

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.

   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.

   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.

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.

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.

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.

(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

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

(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.

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