

**General Comments:** BrC aerosols are short-lived climate forcers and contribute substantially to anthropogenic radiative forcing. Their sources and evolution pathways need to be elucidated. This manuscript titled "Concurrent photochemical whitening and darkening of ambient brown carbon" explores these research questions using diurnal measurements of microphysical (SP2), light absorption (Aethalometer) and chemical characteristics (HR-Tof-AMS and FTIR) at a sub-urban site in Beijing. The manuscript assessed diurnal variation of AMS based PMS source factors, apportioned absorption coefficient at 375 nm for BC, primary BrC and secondary BrC and multiple linear regression between absorption and PMF factors. Overall, the study has some interesting findings about bleaching and darkening of BrC during night time, daytime (photochemical oxidation) and role of nitration in governing these BrC behaviours. However, the manuscript has many shortcomings in its current version. It needs through language editing and clarifications at many places throughout the manuscript. The study has relevance to the atmospheric research community and can be accepted for publication in the journal after major revision. The detailed comments are given below:

### Major comments

**1. Introduction** Motivation is weak and objectives of study are not clear? Many studies (some of them carried out in Asia are given below) have assessed diurnal profile of BrC absorption and role of nitrogen in governing them. You can cite these paper and please explicitly state how your study is different from these.

*R Satish, N Rastogi On the use of brown carbon spectra as a tool to understand their broader composition and characteristics: a case study from crop-residue burning samples. - ACS omega, 2019. <https://doi.org/10.1021/acsomega.8b02637>*

*R Satish, P Shamjad, N Thamban, S Tripathi, N Rastogi Temporal characteristics of brown carbon over the central Indo-Gangetic Plain. - Environmental science & technology, 2017. <https://doi.org/10.1021/acs.est.7b00734>*

2. Section 2.3 Citation for equation 3 and 4 missing? Many previous studies have used primary species, e.g., EC, K<sup>+</sup> etc. for quantifying primary and secondary OC. The author can cite those papers. Moreover, relevance or applicability of assumptions taken in eq. 3 and 4 for the site are missing. Please add a brief discussion about all these aspects.

Further, BrC and BC emissions from different sources are very different. For e.g., vehicular emissions are highly rich in BC, but not in BrC. For biomass burning, its vice-versa. How these scenarios will impact the  $[\sigma_{\text{abs}}/r_{\text{BC}}]_{\text{pri}}$  ratio and  $\sigma_{\text{abs}}\text{-SOA}$  estimation. The cluster analysis (Fig S1) and AMS results indicate that scenario is likely (Fig. 1) at the sampling site. How this will impact the overall findings of this study.

3. Line 104-105 How did the authors account for the effect of coating thickness while calculating  $[\sigma_{\text{abs}}/r_{\text{BC}}]_{\text{pri}}$  at different wavelengths?

4. Section 3.1. (Lines 162-167): The authors reported that "Both OOA1 and OOA2 showed nighttime peak due to the dark oxidation chemistry under high relative humidity." But this may or may not be true as boundary layer height is also lower during night compared to daytime. Moreover, nitrate radicals govern the dark oxidation chemistry. Thus, nitration of organics

during nighttime is a possibility, but that was not the case for OOA1 (N/C remain unchanged). Therefore, how can you attribute increase in OOA1 during night to dark oxidation chemistry? Please elaborate.

5. Line 190-191. How did you come with these numbers? Please mention it probably in methodology

If these are based on  $\sigma_{\text{abs}}$  values, then don't use words such as "mean contribution of absorption for BC, primary BrC and secondary BrC" as  $\sigma_{\text{abs}}$  values were not weighted with corresponding solar flux values. Instead, you can use words such as "mean contribution of absorption coefficient for BC, primary BrC and secondary BrC". Please keep this point in mind throughout the manuscript.

6. Discussion about some figures is missing in text, e.g, Fig. 4a

7. Line 229-230 and elsewhere: It is mentioned that "photobleaching process causing the decreased absorption efficiency per unit mass for primary BrC." But authors have not provided any discussion about MAC or absorptivity of BrC throughout the manuscript. It is absorption coefficient they are talking about. Please careful look into it.

8. Line 250 "Overall, by apportioning the absorption of primary and secondary BrC, we found the photooxidation led to an enhanced 251 contribution of secondary BrC by 30% but reduced contribution of primary BrC about 20% in the semi-urban environment." How did you come up with these numbers, discuss in either methodology or supplementary.

### Minor Comments

1. Line 27. This sentence looks confusing. I will suggest to replace the word "shortwave absorption" to "anthropogenic absorption" or "anthropogenic radiative forcing"

2. Line 37: Replace "A range" to "Numerous"

3. Line 39-40: "which may depend on the concentration of ambient hydroxyl radical (Wang et al., 2014)". This is only partially correct. Recently, some studies have reported substantial role of atmospheric condition (RH and temperature, viscosity etc.) on photochemical oxidation. For example.

*Emerging investigator series: heterogeneous OH oxidation of primary brown carbon aerosol: effects of relative humidity and volatility, 10.1039/D0EM00311E, Environ. Sci.: Processes Impacts, 2020, 22, 2162-2171*

Please modify the sentence and cite them properly

4. Line 36-40: The references cited didn't use absorptivity for half-life calculation. All these studies used BrC absorbance to indicate bleaching and BrC lifetime calculation. Please modify your sentence accordingly

5. Line 43-45: revise it to something like "The enhancement of BrC absorptivity could occur either through nitration of existing chromophores, or formation of new secondary organic aerosol (SOA) chromophores through gas-phase oxidation"

6. Line 48 "rule out" doesn't suit here. Replace it

7. Line 64 Grammatical error, should be "ambient aerosols were"

8. Line 64-65 sentence not clear, revise it.
9. Line 65 should be “.....refractory black carbon (rBC) mass.”
10. Line 66-68 Add a little bit more detail in this context.
11. Line 71-72 “The mass median diameter (MMD) is derived from the  $D_c$  distribution, below and above which size the rBC mass concentration is equal (Liu et al., 2019b).” sentence not clear, modify it.
12. Line 72-73 “The bulk coating thickness ( $D_p/D_c$ ) was calculated as the cubic root of the total coated BC volume weighted by the total volume of rBC.” Are you sure, it is weighted? I think coating thickness is ratio of cubic root of both volume (coated and core).
13. Line 74 should be “.....each BC particle....”
14. Line 82-83 the use of word “excluded” here doesn’t seem right. Modify it to something like “Moreover, a multi-scattering correction factor (C-value) of 3.5, 3.2 and 2.4 at the wavelengths 370 nm, 528 nm and 880 nm, respectively were utilized to correct attenuation for the multiple light scattering effect.”
15. **Section 2.3** In equation 4, Is ( $\sigma_{\text{abs}}/[\text{rBC}]_{\text{pri}}$ ) is based to  $\sigma_{\text{abs-tot}}$ . If yes, pls correct it to ( $\sigma_{\text{abs-tot}}/[\text{rBC}]_{\text{pri}}$ ) throughout the manuscript. If not, then mention what is  $\sigma_{\text{abs}}$  (It can’t be  $\sigma_{\text{abs-BC}}$  as it doesn’t not include contribution of BrC)?
16. Line 102-104 not clear, modify
17. Line 136-137 The sentence not clear  
“The FTIR peaks of  $1630\text{cm}^{-1}$  and  $860\text{cm}^{-1}$  are integrated the absorption areas above the baseline.”
18. Line 148-149 conjunction missing.
19. Line 149-150 “The diurnal variation exhibited strong morning and afternoon rush-hour peaks.” Peaks of what? Mention it in the sentence.
20. Line 156 Grammatical error “This off-road combustion sources...”
21. Line 180-181 Difficult to understand. Revise the sentence “It will introduce considerable uncertainties to use consistent MAC or AAE to derive the absorption of BC at multiple wavelengths.”
22. Line 181-182 revise it to “The MAC estimated using the measured BC core size and coatings (Fig. 2c) is thus used to derive the  $\sigma_{\text{abs,BC}}$  (section 2.2, shown in Fig. 2d).”
23. Line 183. Grammatical error “is showed”. And add a sentence mentioning variability in  $\sigma_{\text{abs-BC}}$  during study period (similar to variability for MACBC).
24. Line 187-192 this whole paragraph is very confusing and hard to understand. Revise it.
25. Line 202 it should be “where  $a_1$  to  $a_5$  represents the regression coefficients for each factor.”  $a_0$  is intercept. Modify accordingly.
26. Line 205-206 replace to “.....along with OOA2 in governing absorption of BrC.”
27. Lines 206 and 207 replace the “high” to “substantial”
28. Line 207-209 Sentence not clear, revise it.

29. Line 230-231 revise to “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).”

30. Line 238 you can modify it to something like “This ageing or oxidation likely occurred through photooxidation during early afternoon and aqueous processes (high RH conditions prevail during nighttime) during nighttime (Fig. 4h).”

31. Line 246 “NO<sub>3</sub> radical formed”?

32. Line 252 “This revealed that the whitening and darkening of BrC occurred simultaneously,”

33. Line 254 “location in the atmosphere.” you mean geographical location or altitude, please clarify?