

## Response to anonymous referee #1:

### **Main 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>

**Reply:** We thank reviewer to point this out. The mentioned references are added and discussed.

“Previous studies (Satish et al., 2017; Satish and Rastogi, 2019) found nitrogenous compounds from biomass burning were responsible for brown carbon over South Asia and the chromophores were photobleached in the afternoon.”

L37-38

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.

**Reply:** The references are now added to explain the application of the minimum-R squared approach to derive the absorption of primary OA associated with BC. This method has been used in urban or sub-urban environment thus is applicable for our study.

“Here an assumption is made that light absorption from primary aerosols is all from combustion sources, and these sources necessarily contain BC (Wang et al., 2018). This factor is obtained using the minimum R-squared (MRS) approach (Wu and Yu, 2016), by adjusting the factor until a minimum correlation between  $\sigma_{\text{abs,secBrC}}$  and [rBC] is reached because the absorption from secondary sources are least likely to covary with that from primary sources (Wang et al., 2019). This method has been used in urban and sub-urban environment to obtain the primary BrC associated with combustion sources.”

L103-104, L111-112

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  $[\sigma_{\text{abs}}/[\text{rBC}]]_{\text{pri}}$  ratio and  $\sigma_{\text{abs-SOA}}$  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.*

**Reply:** We thank reviewer to point this out. We agree with reviewer that different sources will have different ratios of POA/BC. However, after careful examination, there was no sporadic event such biomass burning or local pollution events during the experimental period (as indicated by the temporal evolution of attributed OA sources in Fig, 1), we therefore consider, the sources were uniform and this ratio had not significantly varied during the one-month experimental period. The ratio obtained here therefore represents the average ratio throughout the experiment. Related discussions are added.

“Different sources may exhibit different ratios of  $\left(\frac{\sigma_{abs}}{[rBC]_{pri}}\right)$ , however there were no sporadic pollution events during the experimental period, uniform sources are therefore considered, and this ratio tends to represent a mean for the experiment.”

L112-114

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

**Reply:** The MA200 directly measures absorption, and the influence of BC coating thickness on the absorption of BC is considered in section 3.2 (Fig. 2).

*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.*

**Reply:** We thank reviewer to point this out and have revised related discussions.

“Notably, OOA2 had a substantially higher N/C than other factors (N/C=0.037), and had highest correlation with nitrate ( $r=0.77$ ) and with  $C_xH_yN_z$  and  $C_xH_yN_zO_p$  fragments ( $r=0.83$ ). This factor therefore tends to largely result from nitrogen-containing OA and its elevation at night may be also associated with dark oxidation by nitrate radical.”

“The slight enhancement at noon for OOA1 (also for OOA2) soon after morning rush-hour indicated the likely rapid formation of SOA through photooxidation. This significantly higher mean OOA2 than median value in the diurnal pattern indicated that this OA type was largely associated with pollution events. Both OOA1 and OOA2 showed nighttime peak maybe due to reduced boundary layer.”

L201-202, L208-209

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

*Methodology. If these are based on  $\sigma_{abs}$  values, then don't use words such as “mean*

*contribution of absorption for BC, primary BrC and secondary BrC” as  $\sigma_{abs}$  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.*

**Reply:** We have rephased the absorption as absorption coefficient at appropriate places throughout the texts.

“The mean contribution of absorption coefficient for BC, primary BrC and secondary BrC is 51%, 27% and 22% in this study.”

“The absorption coefficient of secondary BrC, the absorption not contributed by primary sources, is obtained by subtracting the absorption of all primary sources from the total absorption (Crilley et al., 2015)”

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

**Reply:** Related discussions are now added in section 3.4:

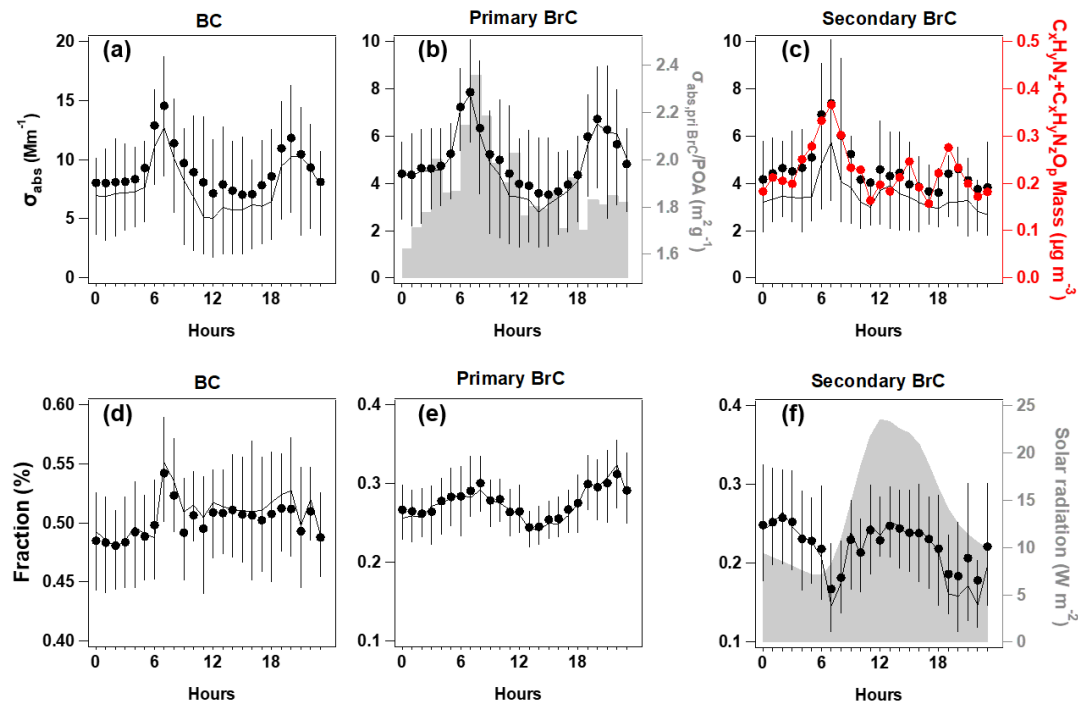
“The diurnal variation of  $\sigma_{abs,375}$  for BC and primary BrC and their fractions showed consistent morning rush-hour peaks at 6:00-8:00 and the night-time enhancement due to reduced boundary layer (Fig. 4a-b).”

*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.*

**Reply:** We have added a new plot about absorption coefficient per unit mass of POA, to indicate the daytime photobleaching process.

“Fig. 4b showed the decrease of primary BrC absorption tended to be more rapid than the HOA and BBOA mass (even a slight increase for HOA, Fig. 1m and Fig. 1o), leading to decreased absorption coefficient per unit mass of primary BrC (shade in Fig. 4b), which indicates the photobleaching process.”

L277-278



**Figure 4. Diurnal variations of absorption coefficient at  $\lambda=375\text{nm}$  ( $\sigma_{\text{abs},375}$ ) for BC (a), primary BrC and the absorption efficiency of primary BrC ( $\sigma_{\text{abs,priBrC}}/\text{POA}$ ) is shown in shade (b), and secondary BrC, along with the  $\text{C}_x\text{H}_y\text{N}_z$  and  $\text{C}_x\text{H}_y\text{N}_z\text{O}_p$  fragments (c); the respective fraction in total for the segregated  $\sigma_{\text{abs},375}$  (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.**

8. Line 250 “Overall, by apportioning the absorption of primary and secondary BrC, we found the photooxidation led to an enhanced 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.

**Reply:** The related discussions are added.

“Fig 4e-f shows the photooxidation led to an enhanced contribution of secondary BrC by 30% but reduced contribution of primary BrC about 20%.”

L284-286

**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”

**Reply:** These are revised,

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.

**Reply:** This is now revised.

“which may depend on the concentration of ambient hydroxyl radical (Wang et al., 2014), also influenced by relative humidity and particle volatility (Schnitzler et al., 2020).”

L41-42

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

**Reply:**

“with lifetime ranging from a few hours (Zhao et al., 2015; Liu et al., 2021) to a few days (Forrister et al., 2015)”

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”

**Reply:** This is revised.

“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.”

L45-47

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

**Reply:**

“However, both processes have been rarely investigated in the field to explicitly determine the BrC components which principally determine the respective enhancement or decrease of its absorptivity, particularly in regions influenced by combined anthropogenic sources.”

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

**Reply:** Revised.

8. Line 64-65 sentence not clear, revise it.

**Reply:** We thank reviewer to point this out and we have revised:

“In this study, the ambient aerosols were sampled by a large-flow ( $1.05 \text{ m}^3 \text{ min}^{-1}$ ) air particle sampler (TH-1000C II) with a  $\text{PM}_{2.5}$  impactor (BGI SCC 1.829) and dried by a silica drier before measurement.”

L67-68

9. Line 65 should be “.....refractory black carbon (rBC) mass.”

**Reply:** Revised.

10. Line 66-68 Add a little bit more detail in this context.

**Reply:**

The single particle soot photometer (SP2, DMT., USA) used continuous laser at  $\lambda=1064\text{nm}$  to incandesce light-absorbing aerosols (such as BC) for irradiating detectable visible light. The incandescence signal was used to measure the refractory black carbon (rBC) mass.”

L69-70

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.

**Reply:** This is revised.

“The mass median diameter (MMD) is derived from the  $D_c$  distribution, which is determined as below and above MMD the rBC mass concentration is equal (Liu et al., 2019b).”

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).

**Reply:** This is revised.

“The bulk coating thickness ( $D_p/D_c$ ) is calculated as the cubic root of ratio of the total coated BC volume divided by the total volume of rBC.”

L78

13. Line 74 should be “...each BC particle....”

**Reply:** Revised.

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.”

**Reply:** We thank reviewer to point this out and we have revised:

“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.”

L89-91

15. Section 2.3 In equation 4, Is  $(\sigma_{abs}/[rBC]_{pri})$  is based to  $\sigma_{abs-tot}$ . If yes, pls correct it to  $(\sigma_{abs-tot}/[rBC]_{pri})$  throughout the manuscript. If not, then mention what is  $\sigma_{abs}$  (It can’t be  $\sigma_{abs-BC}$  as it doesn’t not include contribution of BrC)?

**Reply:** We thank reviewer to point this out.  $\sigma_{abs}$  is now revised  $\sigma_{abs-total}$ .

16. Line 102-104 not clear; modify

17. Line 136-137 The sentence not clear “The FTIR peaks of 1630cm<sup>-1</sup> and 860cm<sup>-1</sup> are integrated the absorption areas above the baseline.”

18. Line 148-149 conjunction missing.

**Reply:** These are revised.

19. Line 149-150 “The diurnal variation exhibited strong morning and afternoon rush-hour peaks.” Peaks of what? Mention it in the sentence.

**Reply:** Revised.

“The diurnal variation exhibited strong morning and afternoon rush-hour peaks of mass concentration.”

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).”

**Reply:** These are revised.

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).

**Reply:** Revised.

The  $\sigma_{\text{abs,BC}}$  was  $9.1 \pm 7.3 \text{ Mm}^{-1}$  during experimental period. MAC of BC at  $\lambda=375\text{nm}$  showed to be at  $8.4 - 16.6 \text{ m}^2 \text{ g}^{-1}$  with enhanced absorption when high coatings.”

L225

24. Line 187-192 this whole paragraph is very confusing and hard to understand. Revise it.

**Reply:** We thank reviewer to point this out and we have revised:

“Using the method above, the total ( $\sigma_{\text{abs,total}}$ ) and attributed absorption of BC ( $\sigma_{\text{abs,BC}}$ ), primary ( $\sigma_{\text{abs,priBrC}}$ ) and secondary BrC ( $\sigma_{\text{abs,secBrC}}$ ) at  $\lambda=375\text{nm}$  are shown in Fig. 3a-c. In Fig. 3b, the brown and green shades above the adjacent tracer indicate the absorption coefficient of primary and secondary BrC, respectively. Fig. 3c shows that the absorption coefficient of primary BrC was higher than secondary BrC for most time, but for certain periods they were equivalent or secondary BrC occasionally exceeds primary BrC. The mean contribution of absorption coefficient for BC, primary BrC and secondary BrC is 51%, 27% and 22% in this study. The tracers associated with nitrogen-containing organics, such as OOA2 (with highest N/C),  $\text{C}_x\text{H}_y\text{N}_z$  and  $\text{C}_x\text{H}_y\text{N}_z\text{O}_p$  fragments, and the FTIR measured  $-\text{NO} + -\text{NO}_2$ , are also shown in Fig. 3d-e.”

L230-234

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).”

**Reply:** These are revised.



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

**Reply:** This is revised.

“The nighttime chemistry involving NO<sub>3</sub> radical through the oxidation of NO<sub>2</sub> by O<sub>3</sub>,”

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?

**Reply:** These are revised.