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 1:

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:

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+ 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 $\sigma_{abs,secBrC}$ 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 [σabs/[rBC]pri ratio and σabs-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 $\left(\frac{\sigma_{abs}}{[rBC]}\right)_{pri}$, 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 [σabs/[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 σabs values, then don't use words such as "mean contribution of absorption for BC, primary BrC and secondary BrC" as σabs 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

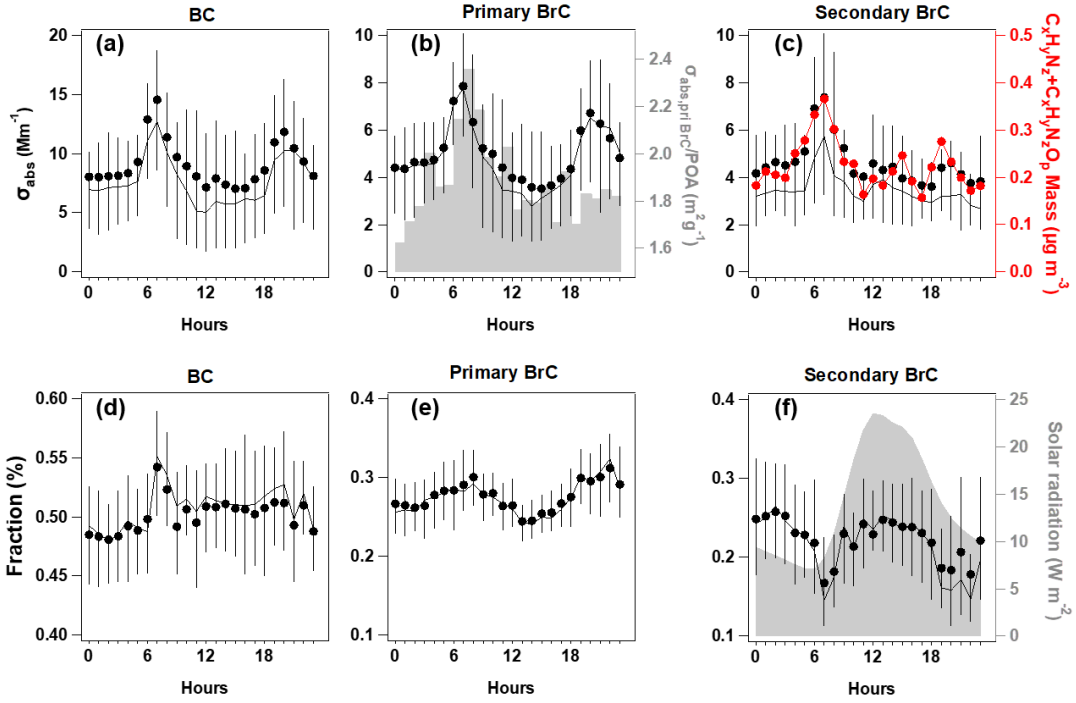

Figure 4. Diurnal variations of absorption coefficient at λ=375nm ($\sigma_{abs,375}$) for BC (a), primary BrC and the absorption efficiency of primary BrC ($\sigma_{abs,priBrC}$)/POA is shown in shade (b), and secondary BrC, along with the $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments (c); the respective 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.

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 40 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 exiting 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 exiting 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 m^3 min^{-1}) air particle sampler (TH-1000C II) with a $PM_{2.5}$ 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 λ=1064nm 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 Dc 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 Dc 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 (Dp/Dc) 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 (*Dp/Dc*) 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 (σabs/[rBC]pri) is based to σabs-tot. If yes, pls correct it to (σabs-tot/[rBC]pri) throughout the manuscript. If not, then mention what is σabs (It can't be σ abs-BC as it doesn't not include contribution of BrC)?

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

16. Line 102-104 not clear, modify

17. Line 136-137 The sentence not clear "The FTIR peaks of 1630cm-1 and 860cm-1 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 σabs,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 σ abs-BC during study period (similar to variability for MACBC).

Reply: Revised.

The $\sigma_{abs,BC}$ was 9.1±7.3 Mm^{-1} during experimental period. MAC of BC at λ=375nm showed to be at 8.4 -16.6 m^2 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 ($\sigma_{abs,total}$) and attributed absorption of BC ($\sigma_{abs,BC}$), primary ($\sigma_{abs,priBrC}$) and secondary BrC ($\sigma_{abs,secBrC}$) at λ=375nm 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), $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments, and the FTIR measured -NO + $-NO_2$, are also shown in Fig. 3d-e."

L230-234

25. Line 202 it should be "where a1 to a5 represents the regression coefficients for each factor." ao 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 "NO3 radical formed"?

Reply: This is revised.

"The nighttime chemistry involving NO_3 radical through the oxidation of NO_2 by O_3,"

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.

Reviewer 2:

The manuscript entitled "Concurrent photochemical whitening and darkening of ambient brown carbon" investigates the contribution of BC and BrC to aerosol absorption, deploying up-to-date chemical and microphysical aerosol characterization techniques in a suburban area of Beijing. The analysis of primary and secondary BrC absorption daily variability is used to derive conclusion on aerosol darkening and bleaching processes, but this part of the analysis is only weakly supported by experimental results.

Main Comments:

1.The identification of OA sources with PMF analysis could be improved. The authors could analyze how the factor mass spectra identified in the present study correlate with previous results. A library with existing profiles can be found here: https://cires1.colorado.edu/jimenez-group/HRAMSsd/.

In addition the mass spectra can be compared to unit mass resolution reference spectra from https://cires1.colorado.edu/jimenez-group/AMSsd/.

Reply: We thank reviewer to point this out. All resolved factors are now compared with literatures and the library reviewer suggested. Related discussions are now added.

"These POA had considerable fraction of hydrocarbon fragments (C_xH_y), indicating their less aged status. The HOA profile was characterized by higher contributions of aliphatic hydrocarbons and has dominated ion tracers such as *m/z* 41 ($C_3H_5^+$), 43 ($C_3H_7^+$), 55 ($C_4H_7^+$) and 57 ($C_4H_9^+$). The HOA concentration correlated with BC (r=0.62), which emits from traffic emissions. The diurnal variation exhibited strong morning and afternoon rush-hour peaks of mass concentration. This factor was consistent with the mass spectra of previously measured HOA from on-road vehicle emissions in urban cities (Zhang et al., 2005; Aiken et al., 2009; Sun et al., 2016; Hu et al., 2017), which has m/z peaks characteristic of hydrocarbon fragments in series of $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$. The mass spectrum of HOA shows overall similarity to those of primary OA emitted from gasoline and diesel combustion sources (r=0.68) (Elser et al., 2016).

The OA from cooking sources (COA) is also characterized by prominent hydrocarbon ion series, however, with higher signal at $C_nH_{2n-1}^+$ than $C_nH_{2n+1}^+$. COA had apparent fragments of both $C_4H_9^+$ and $C_3H_3O^+$, and has a higher ratio of $C_3H_3O^+/C_3H_5O^+$ (3.1), $C_4H_7^+/C_4H_9^+$ (2.2) than HOA (0.9–1.1), with cooking-related fragments of $C_5H_8O^+$ (m/z 84), $C_6H_{10}O^+$ (m/z 98) and $C_7H_{12}O^+$ (m/z 112) (Sun et al., 2011b; Mohr et al., 2012). The COA shows overall similar spectral pattern to the reference spectra of COA (r=0.92) (Elser et al., 2016). Its minor peak at noon and larger peak in the evening (Fig. 1l) also corresponded with the lunch and dinner time respectively."

"The BBOA factor was identified based on the prominent signals of *m/z* 60 ($C_2H_4O_2^+$) and 73($C_3H_5O_2^+$), which are known fragments of levoglucosan (Cubison et al., 2011). And BBOA also correlated with potassium (K^+, r = 0.80), which are indicator of biomass burning (Pachon et al., 2013; Brown et al., 2016). The *m/z* 60 and 73 together with a unique diurnal variation have been shown to be a robust marker for the presence of aerosols from biomass burning emissions in many urban locations (Sun et al., 2016). The BBOA shows very similar mass

spectral patterns to previously reported reference spectra of biomass burning (r=0.94) (Elser et al., 2016). The BBOA factor that was identified in spring accounted for 12.8% of the total OA in Beijing, similar to previous reports (Hu et al., 2017). Biomass (Cheng et al., 2013) and solid fuel burning emissions (Sun et al., 2014) have been widely observed to importantly contribute to the primary OA in this region."

"Two types of oxygenated organic aerosols (OOA) were identified, in moderate (OOA2, O/C=0.62) and high oxidation state (OOA1, O/C=0.95), respectively, which is very similar to the spectra of OOA factors resolved in other cities (Hayes et al., 2013; Ulbrich et al., 2009). The average mass spectrum of OOA2 in this study is characterized by *m/z* 29 (mainly CHO^+), 43 (mainly $C_2H_3O^+$) and *m/z* 44 (CO_2^+), similar to the semi-volatile OOA spectrum identified in other locations (Sun et al., 2011a; Zhou et al., 2016). On average, OOA2 accounts for 42% and 18% of $C_xH_yO^+$ and $C_xH_yO_2^+$ ions, respectively (Fig. 1b). These results clearly indicate that OOA2 was primarily composed of less oxygenated, possibly freshly oxidized organics. 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 mass spectrum of OOA1, which was characterized by a dominant peak at *m/z* 44 (mainly CO_2^+), a highest O/C (0.95). On average, OOA1 contributes 51% of the $C_xH_yO^+$ signal and 23% of the $C_xH_yO_2^+$ signal (Fig. 1a). OOA1 showed particularly high correlation with sulfate (r=0.40) because of their similar volatilities (Huffman et al., 2009; Jimenez et al., 2009)."

L166-168, L169-175, L176-178, L182-188, L195-199, L203-204

In addition, COA in previous works usually shows a peak at noon, while in this study the lunch peak is barely visible. The author should discuss this discrepancy.

Reply: The was only a minor peak at noon for COA, which may be due to the sub-urban nature of the site where the major aerosols from cooking sources may have been processed and lost the signature near source. Related discussions are now added:

"The was only a minor peak at noon for COA, which may be due to the sub-urban nature of the site where the major aerosols from cooking sources may have been processed and lost the signature near source. The feature of this factor was also observed in sub-urban environment (Huang et al., 2021)."

L179-181

Finally, the authors claim the use of external tracers to identify the PMF factors, but for COA an internal tracer was used instead, which makes the attribution risky, especially considering the correlation in time with HOA factors (based on the diurnal profile).

Reply: Previous literatures have widely used $C_6H_{10}O^+$ is considered a signature fragment mainly from cooking emission rather than from traffic (Sun et al., 2011b), but an unambiguous external tracer for cooking source is difficult to find. We have tested $C_6H_{10}O^+$ had a much weaker correlation with HOA (r = 0.48) than COA (r = 0.80), thus this factor is likely COA rather than HOA. In addition, the correlation between HOA and COA is 0.31 for time series,

and 0.42 for mass spectra, therefore these factors can be discriminated.

2.This study identifies organic nitrate using ATR-FT-IR, integrating the spectra area around the characteristic absorption peaks at 860 cm^{-1} and 1640 cm^{-1}, in agreement with Liu et al. (2012). Nevertheless previous studies showed that the region between 1600 and 1700 cm^{-1} shows typically a strong absorption signal due to the carbonyl group of ketones and carboxylic acid (Maria et al., 2002; Russell et al., 2009), which would lead to an overestimation of the NO_2 absorption at 1640 cm^{-1}.

Reply: We thank reviewer to point this out. Although the carbonyl group has absorption at 1640 cm^{-1}- 1850 cm^{-1} (Russell et al., 2009), and Maria et al. (2003) pointed out the absorption peak of carbonyl group was around 1720 cm^{-1}. However there was no discernable peak of carbonyl group for our infrared spectrum, and the peak of OH at 2500 cm^{-1} - 3400 cm^{-1} for the carboxylic acid is not discernable neither, thus the influence of ketone and carboxylic acid may be of less importance for our dataset. The related discussions are added.

"There was no discernable peak of carbonyl group for our infrared spectrum, and the peak of OH at 2500 cm^{-1} - 3400 cm^{-1} for the carboxylic acid is not discernable neither, thus the influence of ketone and carboxylic acid may be of less importance for our dataset."

L153-155

3.The discussion about the bleaching and darkening of BrC is based on the analysis of

diurnal profiles of primary and secondary BrC , both absolute absorption coefficient and fractional contribution in figure 4. The text reports: "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), which indicated the likely photobleaching process", but this decrease is difficult to discern in the figure.

Reply: A new plot about absorbing efficiency (absorption coefficient divided by mass) is now added in Fig. 4b to aid this conclusion. The related discussions are revised.

"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 (the shade in Fig. 4b), which indicates the photobleaching process."

L277-278

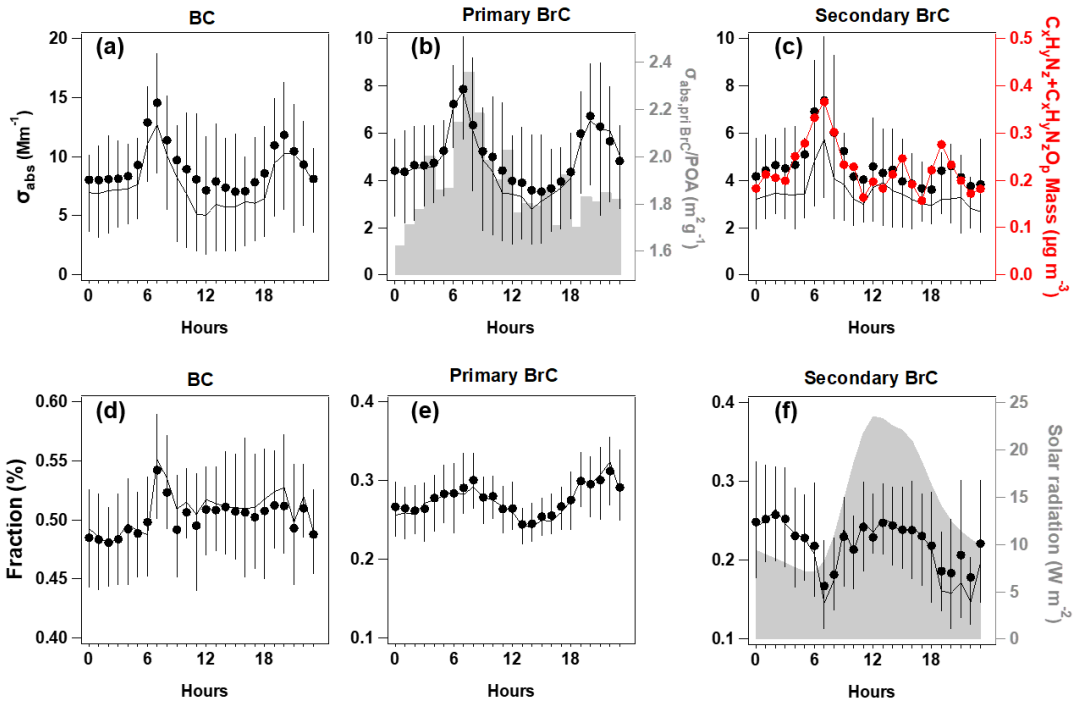

Figure 4. Diurnal variations of absorption coefficient at λ=375nm ($\sigma_{abs,375}$) for BC (a), primary BrC and the absorption efficiency of primary BrC ($\sigma_{abs,priBrC}$)/POA is shown in shade (b), and secondary BrC, along with the $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments (c); the respective 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.

In addition, the attribution of secondary BrC to local photochemical production is based on the comparison between the fraction of secondary BrC diurnal profile and solar radiation, but if local photochemistry triggered secondary BrC formation I would expect to see a correlation between secondary BrC absorption (reported in fig.4 c) and solar radiation. On the contrary, secondary BrC absorption shows a peak in the morning, when photochemistry is expected to be lower.

Reply: We have carefully considered the comments from reviewer. The morning peak coinciding with the primary BrC can be explained as the rapid formation of BrC from sources when emitted gases rapidly 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). In addition to the morning rush-hour peak, a peak after midday also observed for secondary BrC, and this small peak at noon was consistent with the peak of solar radiation, confirming that local photochemistry triggered the formation of secondary brown carbon. Related discussions are revised.

"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).”

L271-274

Minor Comments:

1.Line 34-36. Please revise this sentence. Saleh et al. 2014 reported that the OA to BC ratio is higher during the smoldering phase, but do not compare the absorption efficiency of BrC produced during smoldering and flaming. Similarly, Chakrabarty et al. observed an increase in the absorption angstrom exponent of aerosol particles during smoldering, due to the larger OA contribution, but did not report differences in the imaginary part of the BrC refractive index during smoldering and flaming.

Reply: We have revised this sentence according to reviewer’s suggestion:

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

L34-36

2.The authors classify the sampling period based on the analysis of back-trajectories (see figure S1). The sampling site is located in a suburban area of Beijing where local and nearby pollution sources are likely affecting the observed PM trend, rather than synoptic scale circulation. If the author wants to discriminate the sampling period into cluster, I would suggest to use local meteorology, including temperature, relative humidity, and wind speed/direction. For example, figure S1 shows an increase in the concentration and relative contribution of nitrate when relative humidity is higher, suggesting the relevance of local processes. Furthermore, wind speed and direction might help to spot the time when the impact of the urban Beijing area is higher.

Reply:

We thank reviewer to point this out. Local meteorology including wind and RH is also examined, which was found not to be the main driving factor to determine the pollution level, but the synoptic circulation of air mass is the major factor. This is because Beijing city acts strict environmental regulations but the air pollutants were synoptically transported from the polluted southern regions to the Beijing City, while the rapidly transported cleaner air from the north usually diluted the pollutants. The results here are consistent with a wide range of previous studies about the pollution conditions associated with synoptic patterns in Beijing region (Wu et al., 2022; Liu et al., 2019; Hu et al., 2020).

We have also included the local wind information in the revised figure S1.

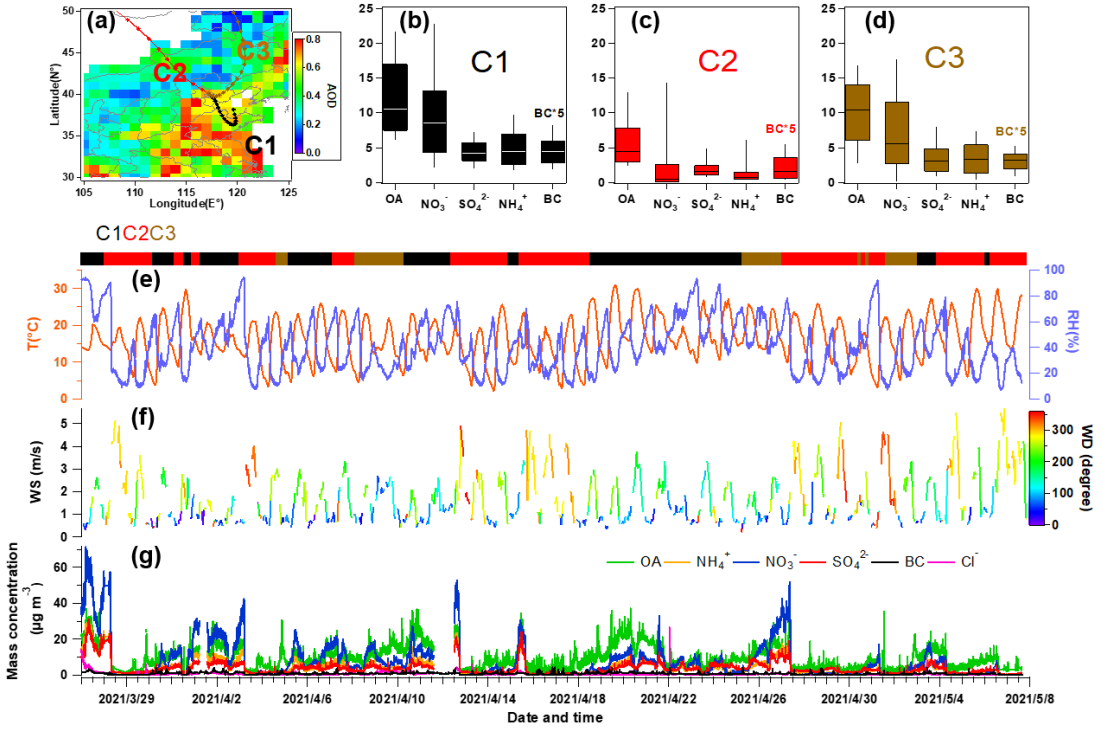

Figure S1. (a) Clustered back-trajectories for the past 72 hours during the experiment with markers denoting 12h intervals. (b-d) Statistics for the concentrations of key aerosol compositions from each cluster. The whiskers, box boundaries and lines in box denote the 10th/90th percentiles, 25th/75th percentiles and the median, respectively. (e) Time series of RH and T, (f) wind speed colored by wind direction, (g) mass concentrations of key aerosol compositions.

3.Line 77: the authors derived BC MAC based on the Mie theory. Liu et al 2018 showed that the Mie theory holds for spherical particles, but fails in reproducing the absorption of fractal particles. The author should discuss the uncertainty derived from it.

Reply: The coatings obtained by the SP2 measurement at λ=1064nm can be relatively independent of particle shape owing to the longer measurement wavelength, as discussed in previous studies (Liu et al., 2014; Hu et al., 2021). Related discussions are added.

"The SP2 measurement at λ=1064nm longer than mostly populated BC size means the derived coatings and subsequent calculation of MAC is relatively independent of particle shape within uncertainty of 21% (Liu et al., 2014; Hu et al., 2021)."

L83-85

4.Line 105: How do the primary absorption to rBC concentration ratios compared with previous studies?

Reply:

"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 (Wang et al., 2019; Zhang et al., 2020)."

L117-118

5.Line 141-142: Inorganic nitrate usually dominates nitrate signal in the AMS measurements (Farmer et al., 2010). Please, revise this sentence or estimate organic nitrate from AMS signal and compare it with inorganic nitrate.

Reply: This sentence has been removed.

Technical comments:

Line 83: corrected instead of excluded

Line 181: constant instead of consistent

Line 226: accounted for instead of occupied

Reply: These are now corrected.

Figure1: the author might want to change the order of factors in the figure and report

OOA1 before OOA2.

Reply: This is revised.

Figure 3: If possible, the author might want to use horizontal lines instead of circles as markers in fig 3e to clarify that the FTIR data correspond to a time range of 24 hours. The horizontal lines should start and end at the beginning and end of the corresponding sampling period.

Figure 3: panel b shows a day dominated by secondary BrC at the end of the field experiment (likely May 7), while in fig 3c the secondary BrC absorption during the same day is not reported.

Reply: We thank reviewer to point this out. In Fig. 3, the missing data is now corrected and markers are revised according to reviewer's suggestion.

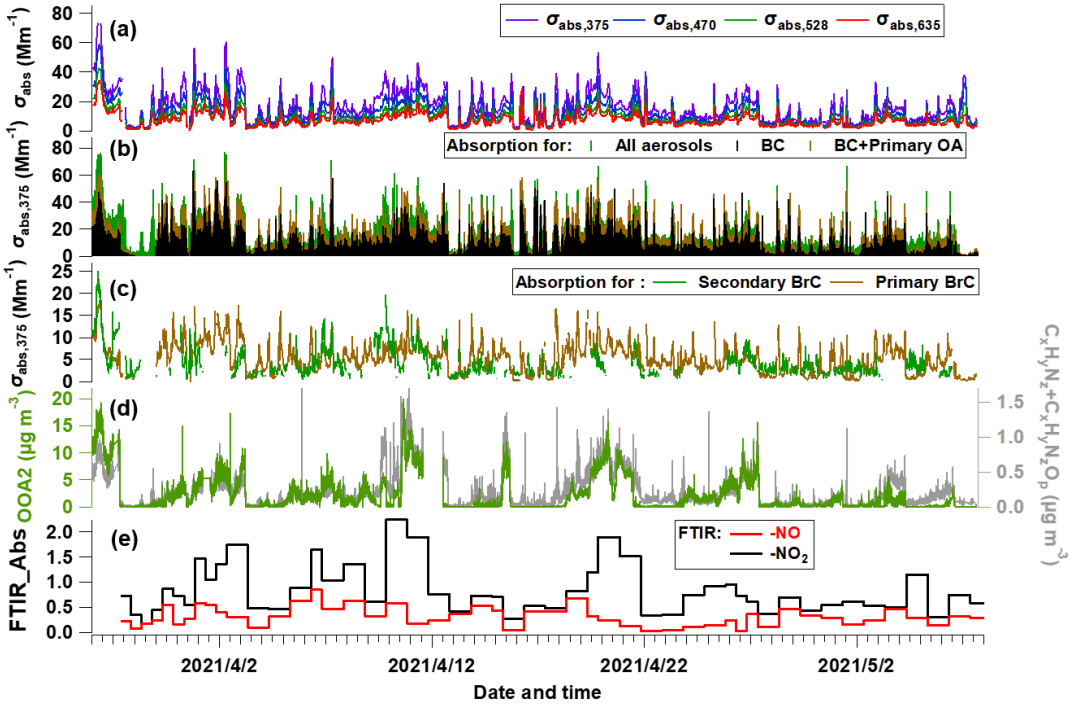

Figure 3. Temporal evolution of segregated absorbing properties. (a) Absorbing coefficients (σ_{abs}) at multiple wavelengths measured by the aethalometer, (b) σ_{abs} at λ=375nm ($\sigma_{abs,375}$) for all aerosols, primary OA and BC, (c) $\sigma_{abs,375}$ for primary BrC and secondary BrC. (d) mass concentration of OOA2 and the $C_xH_yN_z$ and $C_xH_yN_zO_p$ fragments measured by the AMS. (e) FTIR-measured absorption of -NO and -NO_2 bonds.

References

Hu, K., Zhao, D., Liu, D., Ding, S., Tian, P., Yu, C., Zhou, W., Huang, M., and Ding, D.: Estimating radiative impacts of black carbon associated with mixing state in the lower atmosphere over the northern North China Plain, Chemosphere, 252, 10.1016/j.chemosphere.2020.126455, 2020.

Hu, K., Liu, D., Tian, P., Wu, Y., Deng, Z., Wu, Y., Zhao, D., Li, R., Sheng, J., Huang, M., Ding, D., Li, W., Wang, Y., and Wu, Y.: Measurements of the Diversity of Shape and Mixing State for Ambient Black Carbon Particles, Geophysical Research Letters, 48, 10.1029/2021gl094522, 2021.

Liu, D., Allan, J. D., Young, D. E., Coe, H., Beddows, D., Fleming, Z. L., Flynn, M. J., Gallagher, M. W., Harrison, R. M., Lee, J., Prevot, A. S. H., Taylor, J. W., Yin, J., Williams, P. I., and Zotter, P.: Size distribution, mixing state and source apportionment of black carbon aerosol in London during wintertime, Atmos Chem Phys, 14, 10061-10084, 10.5194/acp-14-10061-2014, 2014.

Liu, D., Joshi, R., Wang, J., Yu, C., Allan, J. D., Coe, H., Flynn, M. J., Xie, C., Lee, J., Squires, F., Kotthaus, S., Grimmond, S., Ge, X., Sun, Y., and Fu, P.: Contrasting physical properties of black carbon in urban Beijing between winter and summer, Atmos Chem Phys, 19, 6749-6769, 10.5194/acp-19-6749-2019, 2019.

Maria, S. F., Russell, L. M., Turpin, B. J., Porcja, R. J., Campos, T. L., Weber, R. J., and Huebert, B. J.: Source signatures of carbon monoxide and organic functional groups in Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) submicron aerosol types, Journal of Geophysical Research-Atmospheres, 108, 10.1029/2003jd003703, 2003.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S.: Oxygenated fraction and mass of organic aerosol from direct emission and atmospheric processing measured on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, Journal of Geophysical Research-Atmospheres, 114, 10.1029/2008jd011275, 2009.

Sun, Y. L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W. N., Bae, M. S., Hung, H. M., Hogrefe, O., Frank, B., Rattigan, O. V., and Lin, Y. C.: Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution time-of-flight aerosol mass apectrometer, Atmospheric Chemistry and Physics, 11, 1581-1602, doi:10.5194/acp-11-1581-2011, 2011b.

Wu, Y., Liu, D., Tian, P., Sheng, J., Liu, Q., Li, R., Hu, K., Jiang, X., Li, S., Bi, K., Zhao, D., Huang, M., Ding, D., and Wang, J.: Tracing the Formation of Secondary Aerosols Influenced by Solar Radiation and Relative Humidity in Suburban Environment, Journal of Geophysical Research-Atmospheres, 127,

10.1029/2022jd036913, 2022.

Zhang, Q., Shen, Z., Zhang, L., Zeng, Y., Ning, Z., Zhang, T., Lei, Y., Wang, Q., Li, G., Sun, J., Westerdahl, D., Xu, H., and Cao, J.: Investigation of Primary and Secondary Particulate Brown Carbon in Two Chinese Cities of Xi'an and Hong Kong in Wintertime, Environmental Science & Technology, 54, 3803-3813, 10.1021/acs.est.9b05332, 2020.