Authors' response to reviewer' comments

We would like to thank the reviewer for the thoughtful comments and suggestions to improve the manuscript. We address each comment individually below, with the reviewer' comment **in black** and our responses **in blue** and the revised text **in green**.

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Response to Reviewer #2:

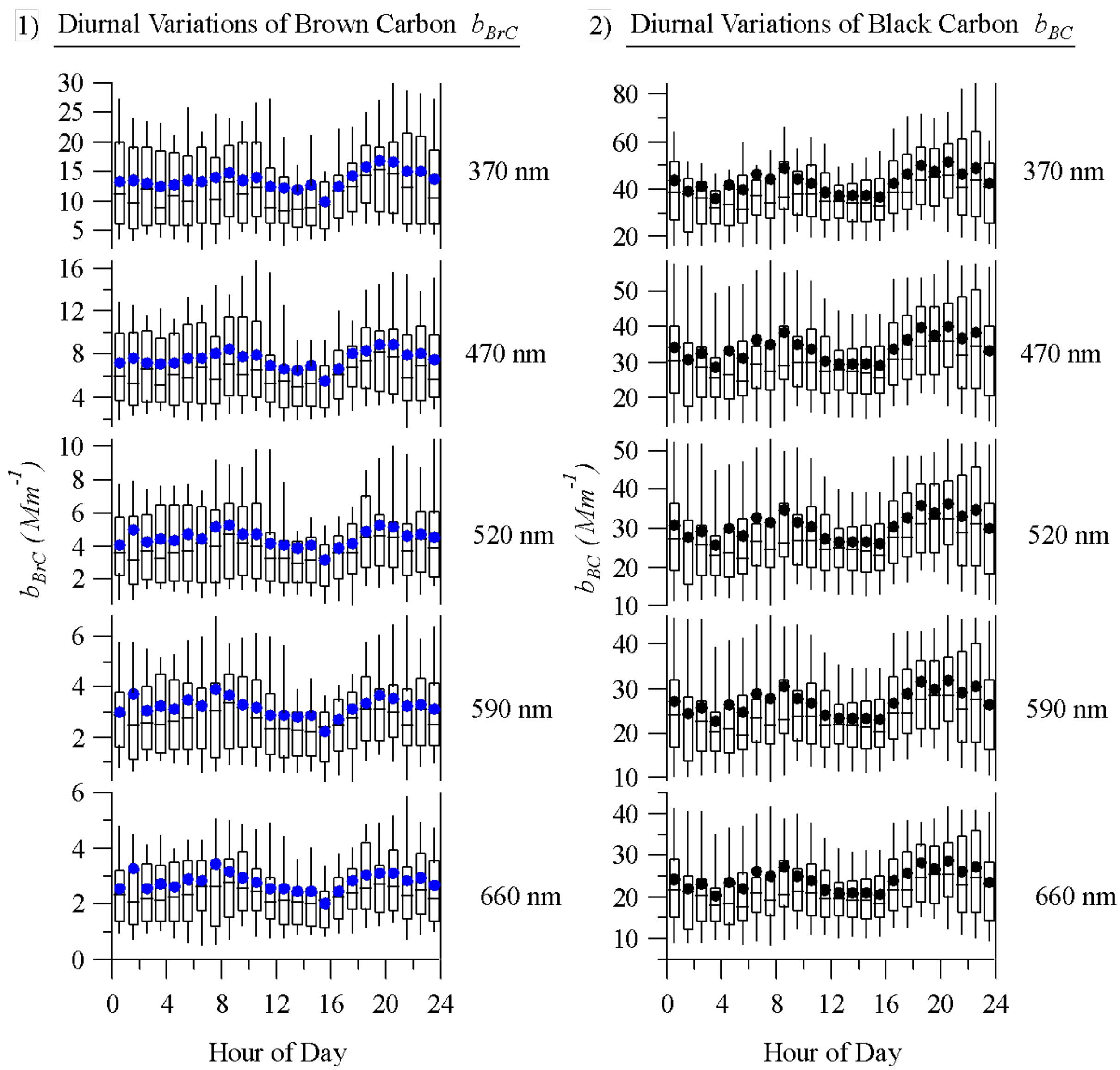
Using a combination of light-absorption measurements (7-wavelength Aethalometer) and chemical-speciation measurements (HR-ToF-AMS) performed in Guangzhou, Qin et al. report 1) contributions of brown carbon to aerosol light absorption, 2) temporal variability of brown-carbon absorption, and 3) correlations between brown-carbon absorption and OA constituents. The manuscript is well written and the topic (sources and speciation of brown carbon) is timely. I believe that this manuscript is suitable for publication in ACP after the following comments are addressed:

General comments:
I believe that the observations could be interrogated further to gain more insight on BrC sources and optical properties of the various components:

1. How do the diurnal cycles of b_BrC compare to b_BC? This comparison could shed light on how similar the sources of BC and BrC are, and also on the relative contributions of primary versus secondary OA to BrC.

Reply:
The reviewer raised an important point. We have replaced the original Figure 4 showing the diurnal cycles of b_{BrC} to a revised Figure 4 showing the diurnal cycles of b_{BrC} and b_{BC}.

Revised text:
Figure 4 shows the diurnal variations of both b_{BrC} and b_{BC} at 370, 470, 520, 590, and 660 m respectively. In general, the diurnal cycles of b_{BrC} and b_{BC} share similar patterns, indicating that they may have similar sources. However, it should be noted that some OA factors, such as BBOA and HOA, also share similar patterns (Qin et al., 2017). Overall, there were two peaks at each wavelength. The first peak appeared in the morning at around 8:00 LT, with a peak before 8:00 LT for longer wavelength and after 8:00 LT for shorter wavelength. The second peak appeared at 21:00 LT and its intensity decreased until 24:00 LT. These changes may be attributed to diurnal changes in particle source, which most likely originated from crop residue burning in the fall and winter in nearby regions (Wang et al., 2017)

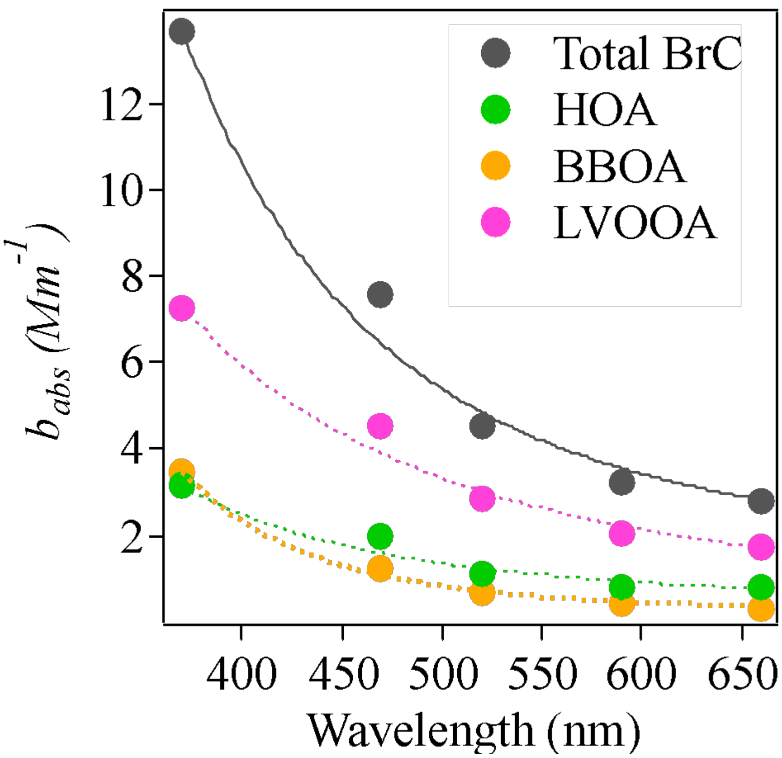


2. As the authors allude to in the Abstract and the Introduction, the light-absorption properties of different BrC species exhibit different wavelength dependence. The data presented in this manuscript could be utilized to further investigate/highlight this.

Reply:
We thank the reviewer for this thoughtful suggestion. Below is the response to each suggestion.

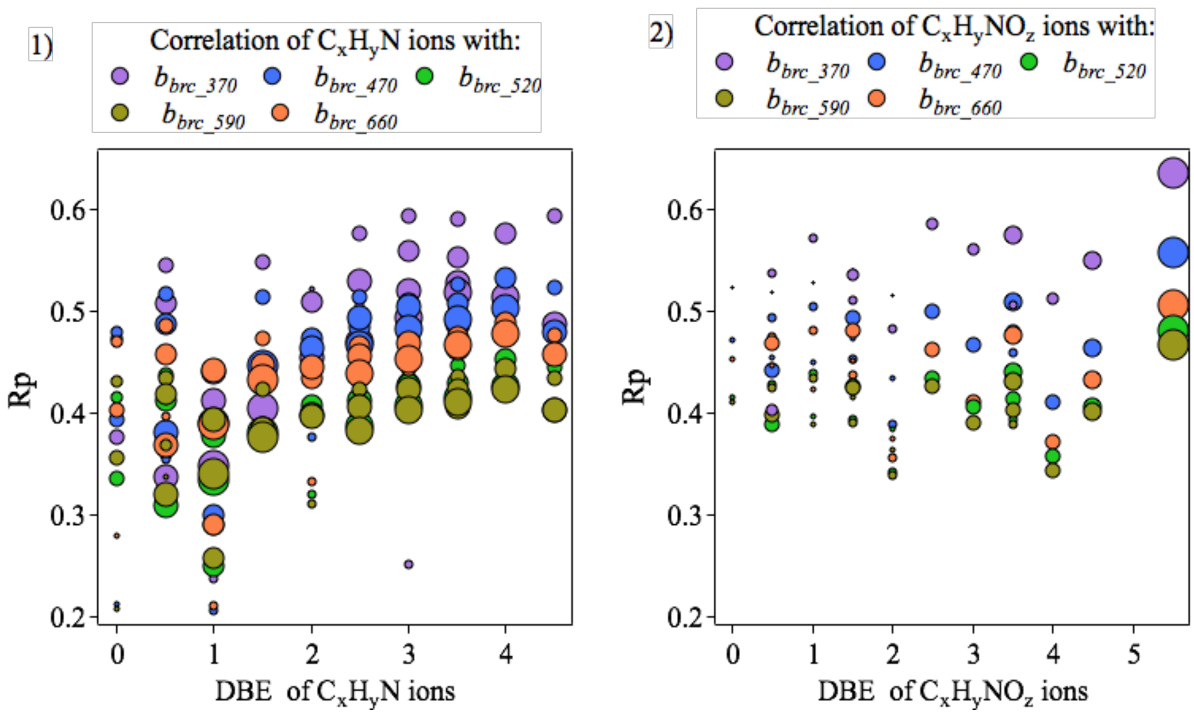
Specifically, I suggest:
Extending the analysis in section 2 to present not only MAC values, but also AAE values of the different BrC components.

Reply:
The figure below shows the exponential decay of b_{abs} for different light-absorbing components. The fitted AAE values for those components are 3.52, 3.28, 5.50 and 2.67 for total BrC, HOA, BBOA and LVOOA respectively. These results indicate that variability of AAE values ranging from different sources which is likely inherent to the chemical variability of BrC constituents. We have now included them in Figure 7 in main text and discuss this point in Line 220-224 on Page 9.



Extending the analysis in section 3 to present the correlations with N-containing ions at longer wavelengths as well, and discuss any differences between different wavelengths.

Reply:
Figure below shows more correlation analysis between b_{Brc} at different wavelength and DBE of C_xH_yN and $C_xH_yNO_z$ ions. The Pearson's R (R_p) values are in general consistent with what we have shown in Figure 8 in the original main text.



Revised text:

Figure 8 shows the correlation coefficients between b_{BrC} at all available wavelengths and the mass loadings of each ion in $C_xH_yN^+$ and $C_xH_yNO_z^+$ families at different DBE values. For the $C_xH_yN^+$ family, R_p increased as DBE increased across all wavelength, suggesting that b_{BrC} was better correlated with fragments with higher degrees of unsaturation or cyclization. And increasing trend of R_p as DBE increased is more obvious for short wavelengths (e.g. λ at 370 nm and 470 nm), suggesting that the absorption at short wavelengths are more associated with the unsaturation or cyclization. Indeed, in saturated organics, light absorption involves excitation of n electrons, which requires more energy and, therefore, shorter incident wavelengths (e.g., short UV). In unsaturated organics, the delocalized π electrons are in clusters of sp2 hybrid bonds and in longer conjugated systems, such that the energy difference between the excited state and the ground state goes down, which makes the absorption band shift to longer wavelengths. These structural features may explain in part the increased correlation between mass loadings of the $C_xH_yN^+$ family and light absorption with decreasing ion saturation. For the $C_xH_yO_zN^+$ family, we did not observe obvious trends in the correlation coefficient with changing degree of saturation/cyclization (Figure 8b). This phenomenon is consistent across different wavelength. However, the overall Pearson's Rs of b_{BrC} with $C_xH_yO_zN^+$ were higher than those with $C_xH_yN^+$. The R_p for each group of ions is higher at short wavelengths (λ at 370 nm and 470 nm).

Specific comments:

3. Line 6: I see what the authors are trying to say, but the statement that absorption "increases the atmospheric energy budget"is not accurate. The atmosphere does not store energy, but re-emits it back as IR radiation to space. Absorption increases the average temperature of the atmosphere.

Reply:

We thank the reviewer to point out the ambiguous sentence. We clarified the sentence in the revised text.

Revised text:
BC is a major contributor to light absorption that leads to positive radiative forcing, increasing the average temperature of the atmosphere.

4. Line 7-8: Do you mean 20%-50% of the total aerosol warming (i.e. positive forcing)?

Reply:
Thanks for pointing out the ambiguous sentence. We meant the 20%-50% of total aerosol light absorption. We have revised the sentence as follow:

Revised text:
The BrC absorption contribution to total aerosol light absorption can reach 20–50% over regions dominated by seasonal biomass burning and biofuel combustion (Feng et al., 2013).

5. Line 10: Several studies have shown that BrC absorption in the long-visible wavelengths is not negligible (e.g.1–3)

Reply:
Thanks for pointing out the misleading sentence. Yes, we agree that BrC absorption in the long-visible wavelengths is not negligible. We were trying to distinguish the absorption properties of BrC and BC which makes the AAE attribution method possible. A revised text have been added.

Revised text:
A significant difference in optical feature of BrC and BC is that BrC absorbs light primarily at UV and short-visible wavelengths with the absorption decreasing significantly at long wavelengths, while BC absorbs strongly and constantly throughout the UV to visible spectrum (Andreae and Gelencsér, 2006; Bergstrom et al., 2007; Bond and Bergstrom, 2006).

6. Line 24-27: The authors state that they deal with the effect of coating on AAE in another manuscript, but this should be discussed here as well because it is central to the observations, especially that the average AAE value of 1.43 is at the edge of what has been argued to be just coated BC or BC+BrC.

Reply:
The reviewer raised an important point. A Mie theory model was used to estimate the AAE for BC-containing particles (AAE_{BC}) at core-shell scenarios with different refractive indexes. A detailed discussion is presented in another manuscript. Briefly, AAE_{BC} is sensitive to specific refractive index of core and shell of the particles and the size of the particle. The size distribution is from scanning mobility particle sizer and aerodynamic particle sizer measurement, and we vary the refractive index of the core and shell in the model. The method is adopted from a previous publication from the group (Tan et al., 2016). In general, AAE_{BC} increases as the real part refractive index of the core increases or the imaginary decreases, or alternatively real part of the shell

increases. The AAE_{BC} ranges from 0.67-1.03 across the different scenario. Table S1 is added in the revised manuscript.

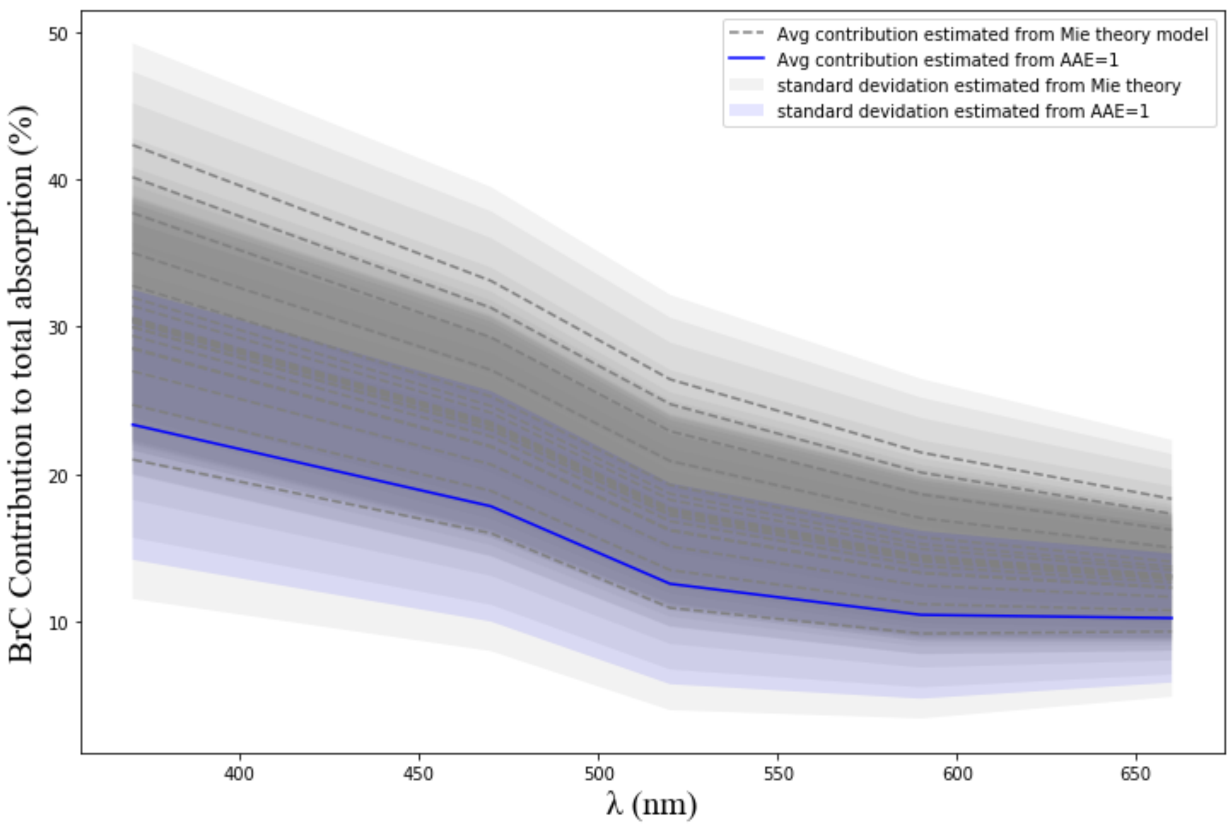
Table S1. AAE_{BC} estimation from Mie theory model

Model run number	Refractive index				AAE
	Core		Shell		
	Real part	Imaginary part	Real part	Imaginary part	
1	1.6	0.54i	1.55	0.0000001i	0.848518188
2	1.7	0.54i	1.55	0.0000001i	0.871846684
3	1.8	0.54i	1.55	0.0000001i	0.89561921
4	1.9	0.54i	1.55	0.0000001i	0.919776955
5	2	0.54i	1.55	0.0000001i	0.943934591
6	1.8	0.4i	1.55	0.0000001i	0.979578577
7	1.8	0.5i	1.55	0.0000001i	0.91879886
8	1.8	0.6i	1.55	0.0000001i	0.862171196
9	1.8	0.7i	1.55	0.0000001i	0.809566808
10	1.8	0.8i	1.55	0.0000001i	0.760456075
11	1.8	0.9i	1.55	0.0000001i	0.714608394
12	1.8	1.0i	1.55	0.0000001i	0.671630187
13	1.8	0.54i	1.35	0.0000001i	0.885192669
14	1.8	0.54i	1.4	0.0000001i	0.887286337
15	1.8	0.54i	1.45	0.0000001i	0.8885085
16	1.8	0.54i	1.5	0.0000001i	0.890599011
17	1.8	0.54i	1.55	0.0000001i	0.89561921
18	1.8	0.54i	1.6	0.0000001i	0.905391588
19	2	0.4i	1.6	0.0000001i	1.035139318

7. Line 137-140: The authors reference Lack and Langridge (2013) for the uncertainty in the AAE attribution method, but this is not adequate. The uncertainty should be addressed in this manuscript as well.

Reply:
Uncertainty of the BrC light absorption from the AAE attribution method is primarily from uncertainty of choice of AAE_{BC}. Sensitivity analysis of BrC contribution to total light absorption is added based on the AAE_{BC} from Mie theory model output. We have added the following discussion in the revised manuscript in main text Line 171-173 and Figure S1.

Revised text:



Reference:
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