Response to Reviewers

We appreciate the reviewers for their constructive criticisms and valuable comments, which were of great help in improving the quality of the manuscript. We have updated the manuscript based on their comments and provided a detailed response below. Reviewer comments are in regular black, our responses are in blue, and the additions/updated text from the manuscript are in red.

Interactive comment on "The evolutionary behavior of chromophoric brown carbon during ozone aging of fine particles from biomass burning" by Xingjun Fan et al.

Anonymous Referee #1

This manuscript, titled "The evolutionary behavior of chromophoric brown carbon during ozone aging of fine particles from biomass burning", communicates an in-depth study of brown carbon particulate matter from three fuels, and the consequences of ozone aging. I am impressed by the depth of the study and the thoughtful discussion in the results section. I believe this work is well-suited for publication in Atmospheric Chemistry and Physics, however, I have three concerns that should be addressed before the manuscript be accepted for publication.

Re: We thank the referee for the positive comments and constructive suggestions, we have revised the manuscript according to the comments point by point.

Major criticisms and questions

1. The ozone aging experiments are described as taking place for a set of "designed exposure times" (page 5, line 20). In the context of atmospheric aerosol aging, it is desirable (if not necessary) to equate reactor times to equivalent atmospheric aging. This is essential to drawing conclusions between laboratory results and in situ, real world observations. I am concerned that exposing the filters to 70 ppm of ozone is not

strictly applicable to the real-world atmosphere, where concentrations exceeding 8 ppm are rare, and only found in the upper stratosphere. Some analogy between time spent in the reactor to time spent in the atmosphere would greatly strengthen this manuscript. Can this information be provided, along with the methodology used to derive it? The specific methodology may be relegated to the supporting information.

Re: Thanks. We agreed with your comments "it is desirable to equate reactor conditions and times to equivalent atmospheric aging, which is essential to drawing conclusions between laboratory results and in situ, real world observations". In fact, many O_3 oxidation simulation experiments have been conducted to investigate the aging of carbonaceous compounds under different O_3 concentration (20 ppb – 12,200 ppm) (Baduel et al., 2011; D'Anna et al., 2009; Pillar et al., 2014, 2017). For example, low O_3 concentrations (20 ppb - 6 ppm) had been used for oxidizing the thin films of humic matter (Baduel et al., 2011; D'Anna et al., 2009) and oxy-aromatics (i.e. catechol and its substituted ones) (Pillar et al., 2014, 2017), in which the changes of the uptake coefficient of O_3 and the early aging mechanism occurred in air-particle interface had been explored. In addition, to explore the changes of physicochemical properties of particulate samples from combustion process, or to investigate the optical properties of newly formed light absorbing organic compounds during O_3 aging process, a relatively high O_3 concentrations (20 ppm-12,200 ppm) were commonly used in the simulation experiments (Li et al., 2013, 2015; Decesari et al., 2002; Gallimore et al., 2011; Pillar et al., 2015; Zhu et al., 2019). Importantly, some studies have revealed that the oxidation mechanism at higher O_3 concentration is similar to that done at much lower O_3 concentration (Pillar et al., 2015; Gallimore et al., 2011). In this study, the main objective is to investigate the evolutionary behavior of chromophoric BrC compounds during O_3 aging of BB smoke samples, thus the aging simulation experiment was conducted at a relative higher O_3 concentration (70 ppm). The detailed explanation for high O_3 concentration used in this study have been provided in "S1. Ozone aging reactor and operation" in the revised supporting information (SI). (see Page 1, lines 13-34 in revised SI)

Moreover, we also agreed with the comments that some analogy between time spent in the reactor to time spent in the atmosphere would greatly strengthen this manuscript. In this study, the O_3 exposure amounts for 1 h in reactor were ~1.7×10^{15} molec cm^{-3} h. For a highly O_3 polluted (~120 ppb) area (Chen et al., 2020), 24 h-average atmospheric O_3 exposure amount were ~7.1×10^{13} molec cm^{-3} h. In this case, the oxidation for 1 h in our reactor was approximately equivalent to 260 d of oxidation at polluted atmosphere. However, the smoke samples of this study were highly condensed and coagulated on the filter, so the exposure area of particles were greatly reduced. As a result, the equivalent day for O_3 oxidation should be highly shortened. Moreover, our results demonstrated many similar oxidation behaviors of organic chromophores to those of atmospheric humic substances and BB-derived oxy-aromatics under low O_3 concentration (20 ppb- 6 ppm) (Baduel et al., 2011; D'Anna et al., 2009; Pillar et al., 2014, 2017). Therefore, we believed that the evolutionary behaviors of BB-BrC revealed here should be similar to those occurred under atmospheric relevant O_3 concentrations during their lifetime in atmosphere. Some descriptions have been added in section S1 in revised supporting information. (See Page 1, line 37 to Page 2, line 12 in revised SI).

References:

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[3] D'Anna, B.; Jammoul, A.; George, C.; Stemmler, K.; Fahrni, S.; Ammann, M.; Wisthaler, A., Light-induced ozone depletion by humic acid films and submicron aerosol particles. Journal of Geophysical Research 2009, 114, (D12).

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[5] Gallimore, P. J.; Achakulwisut, P.; Pope, F. D.; Davies, J. F.; Spring, D. R.; Kalberer, M., Importance of relative humidity in the oxidative ageing of organic aerosols: case study of the ozonolysis of maleic acid aerosol. Atmos. Chem. Phys. 2011, 11, (23), 12181-12195.

[6] Li, Q.; Shang, J.; Zhu, T., Physicochemical characteristics and toxic effects of ozone-oxidized black carbon particles. Atmospheric Environment 2013, 81, 68-75.

[7] Li, Q.; Shang, J.; Liu, J.; Xu, W.; Feng, X.; Li, R.; Zhu, T., Physicochemical characteristics, oxidative capacities and cytotoxicities of sulfate-coated, 1,4-NQ-coated and ozone-aged black carbon particles. Atmospheric Research 2015, 153, 535-542.

[8] Pillar, E. A.; Camm, R. C.; Guzman, M. I., Catechol Oxidation by Ozone and Hydroxyl Radicals at the Air–Water Interface. Environmental Science & Technology 2014, 48, (24), 14352-14360.

[9] Pillar, E. A.; Guzman, M. I., Oxidation of Substituted Catechols at the Air-Water Interface: Production of Carboxylic Acids, Quinones, and Polyphenols. Environ Sci Technol 2017, 51, (9), 4951-4959.

[10] Pillar, E. A.; Zhou, R.; Guzman, M. I., Heterogeneous Oxidation of Catechol. The Journal of Physical Chemistry A 2015, 119, (41), 10349-10359.

[11] Zhu, J.; Chen, Y.; Shang, J.; Zhu, T., Effects of air/fuel ratio and ozone aging on physicochemical properties and oxidative potential of soot particles. Chemosphere 2019, 220, 883-891.

2. Quartz filters are known to collect some fraction of the gas phase (e.g., Parshintsev et al. 2011). Depending on how quickly the ozone aging was performed after filter gathering was performed (and the storage and handling methods of the filters), gas-phase artifacts (SVOCs and IVOCs especially) may be interacting with the

reactor environment in ways that aren't fully explored in the manuscript. The authors should discuss this and other sources of filter artifacts.

Re: Thanks. We agreed with your comments that the quartz filter could absorb some gas-phase organic artifacts (i.e. semivolatile and intermediate volatility organic compounds) during BB smoke particles sampling (Geller et al., 2006; Parshintsev et al. 2011). According to previous studies, the average adsorption organic artifacts (organic carbon, OC) amounts on quartz filters are very small (0.48-0.98 μgC/cm^2) (Arhami et al., 2006; Subramanian et al., 2004). In the current study, the OC contents on fresh BB smoke filters are in the range of ~250-750 μgC/cm^2, which are much higher than the possible artifacts. Therefore, the potential contributions from O_3 oxidation of possible artifacts on filters to bulk BB-BrC compounds can be neglected. We have added the relevant descriptions in the section 2.2 in revised manuscript. (see Page 4, lines 23-29)

References:

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and Undenuded Sampler Configurations Special Issue of Aerosol Science and Technology on Findings from the Fine Particulate Matter Supersites Program. Aerosol Science and Technology 2004, 38, (sup1), 27-48.

3. On page 13, line 20, the authors state "The present study has confirmed that the bleaching of chromophoric BB-BrC dominantly occurs during O3 aging..." While the authors have presented strong evidence that O3 aging can certainly bleach BB-BrC, they present no evidence that it is the dominant mechanism for bleaching. In fact, on page 8, they present contradictory evidence from Kumar et al. (2018) who showed that the MAE365 values decreased by up to 2.3 times under OH radical aging, whereas in this study they showed a maximum decrease of 2.2. The authors should address this discrepancy, and provide a thorough meta-analysis of bleaching results from literature investigating different pathways and oxidants.

Re: Thanks for the comments. We are sorry for this ambiguous sentence. In this study, the results indicated that the bleaching rather than the formation of BrC was the dominant reaction during O_3 aging process of BB smoke samples. Therefore, the O_3 aging can certainly bleach the BB-BrC compounds, but it didn't mean that the O_3 aging was the dominant mechanism for bleaching of BrC in ambient atmosphere. To avoid the misunderstanding, this sentence had been rewritten in revised manuscript. (see Page 13, lines 22-24)

In addition, we think that the results reported by Kumar et al. (2018) don't contradict our findings. The heterogenous aging of BB emission by OH radical simulated by Kumar et al. (2018) and O_3 aging in current study both are important reactions in ambient environment. They both indicate the occurrence of bleaching of BrC in the aging process. It is well known that the aging of BB smoke samples may happened with various activated species such as OH radical, O_3, or other oxidants in the complex atmospheric environments. The apparent aging changes of BB smoke samples in atmospheric environment should be resulted from complex atmospheric

processes. In this study, we mainly focused on the evolutionary behavior of chromophoric BrC during O_3 aging of BB smoke samples. To better understand the aging behaviors of BrC in ambient atmosphere, we have revised the manuscript based on a thorough meta-analysis of bleaching results from literatures investigating different pathways and oxidants in the revised manuscript. (see Page 2, line 39 to Page 3, line 2; Page 6, line 35-39; Page 7, lines 13-16; Page 7, lines 34-35; Page 11, lines 5-9, 14-18)

Minor technical corrections and clarifying questions

Page 5 Line 3 – I suggest re-writing the final sentence to "BB particles were obtained from each of the three fuels."

Re: Revised.

Line10 – I am unfamiliar with the term "glass garden". Please explain what this is, and its specific use in the ozone aging experiments.

Re: We are sorry for this ambiguous word. In this study, it refers to a glass dish. The filter samples were spread in this glass dish and then exposed in ozone environment. The term "glass garden" had been revised to "glass dish (Φ = 90 mm)" in the text. (see page 4, line 16)

Line 23 – replace "designed" with "designated".

Re: Revised.

Page 6 Line 19 – replace "series" with "type".

Re: Revised.

Line 30 – remove “It is obvious that”.

Re: Revised.

Page 7 Line 13 – remove “It is obvious that”.

Re: Revised.

Page 11 Line 2 – Change “Detail” to “Detailed”.

Re: Revised.