Response to Reviewer #1

Review of 'Chemical composition, optical properties, and oxidative potential of water and methanol-soluble organic compounds emitted from the combustion of biomass materials and coal' by Cao et al.

The manuscript describes the experimental data of aerosol particles generated by laboratory combustion of coal and biomass. The study mainly focuses on chemical characteristics of organic aerosols. The authors separated organic aerosol to three categories (water soluble, HULIS, and methanol soluble). The segregated samples were measured for UV-VIS, EEM, NMR, and DTT assay. It seems to the reviewer that the measurements were carefully conducted. Compared with the previous studies from the group, the major novelty of the manuscript seems to be the addition of DTT assay. However, the novelty was not clear without checking the references from the group. The importance/significance/novelty of the DTT assay data of the study was not clearly discussed. The reason why UV-VIS, EEM, and NMR measurements need to be concurrently conducted with the DTT assay was not shown. As a result, the manuscript looks like a collection of data, rather than a document which provides a coherent story. A significant improvement will be needed for the manuscript to be accepted by the journal.

Re: We appreciated the reviewer for the valuable criticisms and comments, which are of great help for improving the quality of the manuscript. We have revised the manuscript based on the comments and provided a point-by-point response to all the comments and explained how the comments and suggestions by the reviewer were addressed in the current version of the manuscript.

The introduction starts with the general importance of brown carbon. Subsequently, the authors describe recent studies on brown carbon from biomass burning and coal combustion, especially those from China. However, it was not clearly discussed what the current knowledge gap is.

Re: Thanks for your comments. In our manuscript, the introduction starts with the general importance of brown carbon (BrC) and then described recent studies on BrC from biomass burning and coal combustion. As reviewed by the literatures, most of these studies only focused on the relative abundances, chemical compositions, and optical properties of water-soluble BrC (e.g., HULIS) emitted from the combustion of various fuels (e.g., biomass material and coal) and different combustion conditions (e.g., smoldering, flaming) (Huo et al., 2018; Park et al., 2016; Fan et al., 2016). It is noted that water-insoluble BrC even exhibits a higher light absorption than water-soluble BrC in atmospheric aerosols (Chen et al., 2016, 2017, Bai et al., 2020, Huang et al., 2020, Li et al., 2018). However, knowledge on the chemical and optical properties of water-insoluble BrC from combustion sources are still lacking. Moreover, the association of chemical compositions responsible for light absorption of BrC from combustion sources is still constrained. Therefore, to gain more detailed information on BrC from combustion sources, a comprehensive characterization, including chemical, optical characteristics of the BrC fractions (include both water-soluble and water-insoluble BrC) from the combustion of biomass materials and coals, is required. We have revised that in the present manuscript. Please refer to Lines 80-92.

References:

Bai, Z., Zhang, L., Cheng, Y., Zhang, W., Mao, J., Chen, H., Li, L., Wang, L., and Chen, J.: Water/Methanol-Insoluble Brown Carbon Can Dominate Aerosol-Enhanced Light Absorption in Port Cities, Environmental science & technology, 54, 14889-14898, 10.1021/acs.est.0c03844, 2020.

Chen, Q., Miyazaki, Y., Kawamura, K., Matsumoto, K., Coburn, S., Volkamer, R., Iwamoto, Y., Kagami, S., Deng, Y., Ogawa, S., Ramasamy, S., Kato, S., Ida, A., Kajii, Y., and Mochida, M.: Characterization of Chromophoric Water-Soluble Organic Matter in Urban, Forest, and Marine Aerosols by HR-ToF-AMS Analysis and Excitation-Emission Matrix Spectroscopy, Environmental science & technology, 50, 10351-10360, 10.1021/acs.est.6b01643, 2016.

Chen, Q., Ikemori, F., Nakamura, Y., Vodicka, P., Kawamura, K., and Mochida, M.: Structural and Light-Absorption Characteristics of Complex Water-Insoluble Organic Mixtures in Urban Submicrometer Aerosols, Environmental science & technology, 51, 8293-8303, 10.1021/acs.est.7b01630, 2017.

Fan, X. J., Wei, S. Y., Zhu, M. B., Song, J. Z., and Peng, P. A.: Comprehensive characterization of humic-like substances in smoke PM2.5 emitted from the combustion of biomass materials and fossil fuels, Atmospheric Chemistry and Physics, 16, 13321-13340, 10.5194/acp-16-13321-2016, 2016.

Huang, R. J., Yang, L., Shen, J., Yuan, W., Gong, Y., Guo, J., Cao, W., Duan, J., Ni, H., Zhu, C., Dai, W., Li, Y., Chen, Y., Chen, Q., Wu, Y., Zhang, R., Dusek, U., O'Dowd, C., and Hoffmann, T.: Water-Insoluble Organics Dominate Brown Carbon in Wintertime Urban Aerosol of China: Chemical Characteristics and Optical Properties, Environmental science & technology, 54, 7836-7847, 10.1021/acs.est.0c01149, 2020.

Huo, Y. Q., Li, M., Jiang, M. H., and Qi, W. M.: Light absorption properties of HULIS in primary particulate matter produced by crop straw combustion under different moisture contents and stacking modes, Atmospheric Environment, 191, 490-499, 10.1016/j.atmosenv.2018.08.038, 2018.

Li, M., Fan, X., Zhu, M., Zou, C., Song, J., Wei, S., Jia, W., and Peng, P.: Abundances and light absorption properties of brown carbon emitted from residential coal combustion in China, Environmental science & technology, 10.1021/acs.est.8b05630, 2018.

Park, S. S., and Yu, J.: Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiments, Atmospheric Environment, 136, 114-122, 10.1016/j.atmosenv.2016.04.022, 2016.

The authors mention that ‘However, few studies have directly investigated the oxidative potential (OP) of BrC emitted from combustion processes.’ If there are already some studies on the topic, it would have been better to discuss the contributions/limitations of the previous research explicitly.

Re: Thank for your comments. In recently years, several studies had been conducted to directly or indirectly investigate the oxidative potential (OP) of BrC emitted from combustion processes and obtained some achievements (Ma et al., 2018, Chen et al., 2019). According to your comments, we have added some detailed information to discuss the contributions/limitations of these previous studies in the present manuscript. Please refer to Lines 98-115.

"As important contributors of ambient BrC, combustion-derived BrC is expected to have a strong ROS generation capacity and be harmful to human health. Verma et al (2014) analyzed the potential of the water-soluble fraction of atmospheric fine aerosols in the southeastern United States to generate ROS and revealed that biomass burning dominates the ROS-generation potential in winter, contributing more than 46% to DTT activities. In addition, study on the oxidative potential of water-soluble HULIS in fine aerosols in Beijing also indicated that combustion sources contributed high proportion to the oxidative stress of water-soluble HULIS fractions (Ma et al., 2018,). However, these results were mainly obtained based on the source apportionment receptor models (positive matrix factorization (PMF) and chemical mass balance (CMB)). Recently, the water extracts and HULIS from biomass burning were directly investigated and present significant oxidative potential to generate reactive oxygen species (e.g., 6.6–10.7 pmol/min/μg for HULIS) (Fan et al., 2018). However, the limited studies only focused on the water-soluble BrC fraction from biomass burning; and knowledge on the oxidative potential of water-insoluble BB BrC and BrC fractions emitted from other combustion processes such as coal combustion, is still lacking. In addition, the DTT activities of BrC from different combustion sources were generally different, but the key components or functional groups that responsible for the ROS generation capacity of combustion-derived BrC are unclear."

References:

Chen, Q., Wang, M., Wang, Y., Zhang, L., Li, Y., and Han, Y.: Oxidative Potential of Water-Soluble Matter Associated with Chromophoric Substances in PM2.5 over Xi'an, China, Environmental science & technology, 53, 8574-8584, 10.1021/acs.est.9b01976, 2019.

Fan, X., Li, M., Cao, T., Cheng, C., Li, F., Xie, Y., Wei, S., Song, J., and Peng, P. a.: Optical properties and oxidative potential of water-and alkaline-soluble brown carbon in smoke particles emitted from laboratory simulated biomass burning, Atmospheric Environment, 194, 48-57, 10.1016/j.atmosenv.2018.09.025, 2018.

Ma, Y., Cheng, Y., Qiu, X., Cao, G., Fang, Y., Wang, J., Zhu, T., Yu, J., and Hu, D.: Sources and oxidative potential of water-soluble humic-like substances ($HULIS_{WS}$) in fine particulate matter ($PM_{2.5}$) in Beijing, Atmospheric Chemistry and Physics, 18, 5607-5617, 10.5194/acp-18-5607-2018, 2018.

Verma, V., Fang, T., Guo, H., King, L., Bates, J. T., Peltier, R. E., Edgerton, E., Russell, A. G., and Weber, R. J.: Reactive oxygen species associated with water-soluble $PM_{2.5}$; in the southeastern United States: spatiotemporal trends and source apportionment, Atmospheric Chemistry and Physics, 14, 12915-12930, 10.5194/acp-14-12915-2014, 2014.

Section 3 (results and discussion) describes the measurement results, and demonstrates that the values were comparable to the previous studies. Although it is always good to see the agreements of the present data with previous studies, the novelty/uniqueness of the present study was unclear. In addition, the section does not discuss the data deeply, although the data obtained by the authors were compared with that from previous studies.

Re: Thanks. In the present manuscript, we conducted a major revision to improve the results interpretation and discussion, and clearly present the novelty of the present study (Please refer to Lines 286-292; 314-317; 386-396; 464-470; 560-575; 579-594 and section 3.6). In addition, this is a direct analysis of oxidative potential of BrC fractions (include water-soluble and water-insoluble BrC) emitted from biomass burning and coal combustion, that are rarely reported in previous studies. The DTT activities of different BrC fractions derived from the combustion of six biomass fuels and five coals were shown and compared with those in ambient aerosols, and the key components and functional groups contribute to the DTT activities were discussed. More importantly, we also used the Principal component analysis and Pearson correlation coefficient to investigate the relationship between the DTT activities and the chemical and optical characteristics (e.g., fluorophores, proton functional groups) for these combustion-derived BrC fractions. Our results indicated that humic-like fluorophore component (C4) has stronger ability to produce ROS species. The detailed revision please refer to Lines 617-663.

The manuscript contains grammatical issues. It would have been better if a native speaker of English checked it.

Re: We have asked an English expert from the ***ACS Authoring Services*** (http://es.acschemworx.acs.org) to edit English in our manuscript.

ACS Authoring Services

Editing Certificate

This document certifies that the manuscript

Chemical composition, optical properties, and oxidative potential of water- and methanol-soluble organic compounds emitted from the combustion of biomass materials and coal

prepared by the authors

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Specific comments

L184 'Approximately 5 mg of the BrC fractions (i.e., HULIS, WSOC, and MSOC) derived from BB and CC were dissolved in 500 μL deuterium oxide and then transferred to a 5 mm NMR tube'

MSOC should contain some water-insoluble fraction. I wonder if all the components of the sample have successfully been measured.

Re: We are so sorry for this wrong sentence. After checking the experimental records, we confirmed that this is a clerical error. In this study, for the ^{1}H NMR measurement, water-soluble BrC fractions (WSOC and HULIS) were redissolved in 500 μL deuterium oxide, but MSOC were redissolved in 500 μL deuterated methanol. Therefore, all the components of MSOC fraction have been successfully measured in our study. Accordingly, we have corrected that in the present manuscript. Please refer to Lines 220-222.

L529 'These results suggested that the primary smoke from BB and CC in this study had a weaker ROS generation capacity than ambient aerosols, which was likely due to the differences in the chemical composition of WSOC in BB and CC smoke particles and ambient aerosols'

I think that it is an important point. Do the authors have any ideas/hypothesis on how the NMR or EEM data could contribute to discussing this point?

Re: Thanks. This is good comment. In this study, The DTT_m value of WSOC ranged from 0.5 pmol/min/μg (B-3) to 7.4 pmol/min/μg (CS), with a mean of 3.8±2.5 pmol/min/μg. These DTT_m values were lower than those in ambient aerosols in some regions of USA and China (Verma et al., 2012; Chen et al., 2019; Yu et al., 2019). These results suggested that the primary water-soluble organic fraction from BB and CC had a weaker ROS generation capacity than that in ambient aerosols, which was likely due to the differences in the chemical composition (e.g., functional groups) of WSOC in BB and CC smoke particles and ambient aerosols (Lin and Yu, 2011; Dou et al., 2015; Wong et al., 2019; Lin and Yu, 2019).

We agreed with your comments that it is an important point and the data obtained by NMR or EEM measurements could be useful to explain the DTT activities. In the revised manuscript, we have added the PCA and Pearson correlation coefficient analysis to explore how to use the EEM or NMR data to explain the differences of DTT activities of BrC fractions emitted from combustion sources (see new section 3.6). The results indicated that the humic-like fluorophore (C4) may mainly comprised with chemical species with a conjugated system and highly oxygenated species, such as quinones or aromatic acids and may be the key components for the enhancement of the ability of BrC to produce ROS species. The detailed revision please refer to Lines 617-663.

References:

Chen, Q., Wang, M., Wang, Y., Zhang, L., Li, Y., and Han, Y.: Oxidative Potential of Water-Soluble Matter Associated with Chromophoric Substances in PM2.5 over Xi'an, China, Environmental science & technology, 53, 8574-8584, 10.1021/acs.est.9b01976, 2019.

Dou, J., Lin, P., Kuang, B. Y., and Yu, J. Z.: Reactive Oxygen Species Production Mediated by Humic-like Substances in Atmospheric Aerosols: Enhancement Effects by Pyridine, Imidazole, and Their Derivatives, Environmental science & technology, 49, 6457-6465, 10.1021/es5059378, 2015.

Lin, M., and Yu, J. Z.: Dithiothreitol (DTT) concentration effect and its implications on the applicability of DTT assay to evaluate the oxidative potential of atmospheric aerosol samples, Environmental pollution, 251, 938-944, 10.1016/j.envpol.2019.05.074, 2019.

Lin, P., and Yu, J. Z.: Generation of reactive oxygen species mediated by humic-like substances in atmospheric aerosols, Environmental science & technology, 45, 10362-10368, 10.1021/es2028229, 2011.

Verma, V., Rico-Martinez, R., Kotra, N., King, L., Liu, J., Snell, T. W., and Weber, R. J.: Contribution of water-soluble and insoluble components and their hydrophobic/hydrophilic subfractions to the reactive oxygen species-generating potential of fine ambient aerosols, Environmental science & technology, 46, 11384-11392, 10.1021/es302484r, 2012.

Wong, J. P. S., Tsagkaraki, M., Tsiodra, I., Mihalopoulos, N., Violaki, K., Kanakidou, M., Sciare, J., Nenes, A., and Weber, R. J.: Effects of Atmospheric Processing on the Oxidative Potential of Biomass Burning Organic Aerosols, Environmental science & technology, 53, 6747-6756, 10.1021/acs.est.9b01034, 2019.

Yu, S., Liu, W., Xu, Y., Yi, K., Zhou, M., Tao, S., and Liu, W.: Characteristics and oxidative potential of atmospheric PM2.5 in Beijing: Source apportionment and seasonal variation, The Science of the total environment, 650, 277-287, 10.1016/j.scitotenv.2018.09.021, 2019.