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Reply on RC2

Jiao Tang et al.

Author comment on "Measurement report: Long-emission-wavelength chromophores dominate the light absorption of brown carbon in aerosols over Bangkok: impact from biomass burning" by Jiao Tang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-175-AC2, 2021

RC- Reviewer's Comments; AC – Authors' Response Comments

Response to Anonymous Referee #2

RC1: In this manuscript, the authors present a comprehensive study of water- and methanol-soluble chromophores and fluorophores in brown carbon (BrC) from aerosol samples collected year-round in Bangkok, using absorption and excitation-emission matrix (EEM) spectroscopies and numerical methods, including both parallel factor analysis (PMA) and positive matrix factorization (PMF). The selection and preparation of samples and the spectral and factor analyses are all well designed and carefully executed. The observations of chromophores and fluorophores together provide insights into the origin and fate of BrC in the atmosphere. For example, the PMA analysis of EEM observations indicates that atmospheric aging shifts the wavelengths of emission from fluorophores, as primary species react and secondary species form. The PMF analysis indicates that components most associated with absorption at 365 nm are largely emitted from biomass burning. These components are also characterized by long emission wavelengths, suggesting that the constituent molecules incorporate extended conjugated systems or charge-transfer interactions. With these and other impactful implications, the manuscript is suitable for publication in ACP. I have only technical and minor comments for the authors to consider.

AC1: We greatly appreciate the reviewer for recognizing the merits of this work and for providing valuable suggestions. These suggestions would help us improve the manuscript.

RC2: Line 31 - Please reword "these inferences exhibited a refutation".

AC2: Thanks for your suggestions, we have revised it as follows: which exhibited a different characteristic from primary biomass burning and coal combustion results. Please see line 31-32 in the revised manuscript.

RC3: Line 80 - Here and throughout the use of chromophore versus fluorophore is sometimes ambiguous. I would argue the claim in this sentence is not true, since many previous studies have explored the relationship between chromophores (i.e., the species that give a material its color) and BrC. If chromophores were to be replaced with fluorophores, or "fluorescent chromophores" as in line 94, the claim is not so problematic.

AC3: Thanks for your suggestions. We did confuse “fluorophore” and “chromophore”. In the previous studies, for example, Lin et al. (2016, 2017, 2018) have investigated the relationship between chromophores and BrC using the combination of high-performance liquid chromatography (HPLC), photodiode array (PDA) spectrophotometry, and high-resolution mass spectrometry (HRMS). They identified BrC chromophores like polycyclic aromatic hydrocarbons (PAHs), heterocyclic O-PAHs and N-PAHs, nitro-phenols, et. The compounds can regard as chromophores. However, not all chromophores were fluorophores. In the study of Chen et al. (2019), they separately measured the light absorption and fluorescence properties of several nitrophenol standards, and the results showed strong light absorption properties, but no strong fluorescence signal was observed. Thus, we have replaced chromophores with “fluorescent chromophores” throughout the revised manuscript.

References:

Chen, Q., Mu, Z., Song, W., Wang, Y., Yang, Z., Zhang, L., and Zhang, Y. L.: Size□Resolved Characterization of the Chromophores in Atmospheric Particulate Matter From a Typical Coal□Burning City in China, J. Geophys. Res.-Atmos., 124, 10546-10563, https://doi.org/10.1029/2019jd031149, 2019.

Lin, P., Aiona, P. K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S. A., and Laskin, A.: Molecular Characterization of Brown Carbon in Biomass Burning Aerosol Particles, Environ. Sci. Technol., 50, 11815-11824, https://doi.org/10.1021/acs.est.6b03024, 2016.

Lin, P., Bluvshtein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass Burning Event, Environ. Sci. Technol., 51, 11561-11570, https://doi.org/10.1021/acs.est.7b02276, 2017.

Lin, P., Fleming, L. T., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Comprehensive Molecular Characterization of Atmospheric Brown Carbon by High Resolution Mass Spectrometry with Electrospray and Atmospheric Pressure Photoionization, Anal. Chem., 90, 12493-12502, https://doi.org/10.1021/acs.analchem.8b02177, 2018.

RC4: Line 112 - Include units of electrical resistivity.

AC4: We have added the units of electrical resistivity (resistivity of > 18.2 MΩ) in the revised manuscript. Please see line 114 in the revised manuscript.

RC5: Line 113 - Replace "GFFs" with "QFFs".

AC5: Thanks for your revision, we have revised it.

RC6: Line 213 - Please consider rephrasing the sentence beginning with "Although one

exceptional component was detected..." The meaning is not clear to me.

AC6: In this part, we wanted to express that one additional fluorescent component was identified in the new 145-model (the model contains the total EEMs of 60-sources samples and 85-Thailand TSP samples) for WSOC and MSOC fraction comparing with the 85-model (the model only contains the EEMs of 85-Thailand TSP samples), respectively. Now, we have revised the sentence as follows: It should be noted that one additional fluorescent component was identified each for the WSOC and MSOC fractions in the new 145-model, respectively, but these components were only highly characterized by source emission samples. Please see line 219-224 in the revised manuscript.

RC7: Line 335 - Mention the range of measured pH values.

AC7: The pH values of WSOC fraction for all the samples were within the range of 5–7, generally thinking it didn't affect the absorbance according to a prior study (Chen et al., 2016). We have added it, please see line 350-351 in the revised manuscript.

Reference:

Chen, Q., Ikemori, F., and Mochida, M.: Light Absorption and Excitation-Emission Fluorescence of Urban Organic Aerosol Components and Their Relationship to Chemical Structure, Environ. Sci. Technol., 50, 10859-10868, https://doi.org/10.1021/acs.est.6b02541, 2016.

RC8: Line 341 - I am surprised by how much more absorptive the WSOC is than the MSOC. Can comparisons also be made for specific periods dominated by biomass burning emissions, identified using the PMF analysis or even simply the MODIS active fire spots? I would expect MSOC to be significantly more absorptive than WSOC during these periods.

AC8: We observed that WSOC were more absorption than the MSOC in our study. We also check the biomass burning-impacted periods by the biomass burning tracer level (i.e., levoglucosan concentration and the ratio of levoglucosan/TSP, see Table 1), whereas WSOC is still more absorption than MSOC. Similarly, Bikkina et al. (2020) observed that the marine-impacted aerosols of the Bay of Bengal showed higher MAE_{365} values in the WSOC fraction than MSOC fraction (only extract using methanol), and they explained it due to two plausible reasons. First, the BrC aerosols over Bay of Bengal have a contribution from a different source (i.e., maritime influence) and contain BrC-chromophores that are more soluble in water than methanol. Secondary, there could be significant photobleaching effects of different chromophores. However, Kim et al. (2016) reported that the light absorption contributed by water-insoluble organic carbon (WISOC) exhibited a clear seasonal variation in Seoul, with the strong light absorption contributed by WISOC in summer, while WSOC was the main contributor in the other seasons. They attributed it to that photochemically generated secondary organic aerosols from anthropogenic emissions seem to be the main source in summer, whereas aged/oxidized compounds were the main source in the other seasons. Thus, we infer that the different sources and atmospheric processes would impact the distribution of WSOC and WISOC fractions.

Also, laboratory experiment shows that intermediate relative humidity (55–65%) promoted secondary BrC formation (Kasthuriarachchi et al., 2020). Considering the high temperature and humidity (Table S1), high WSOC/OC ratios (50%±9.9%), and tropical monsoon climate in Thailand, it would promote more water-soluble chromophores over

Thailand. The modified part is in the line 363-373 in the revised manuscript.

References:

Bikkina, P., Bikkina, S., Kawamura, K., Sudheer, A. K., Mahesh, G., and Kumar, S. K.: Evidence for brown carbon absorption over the Bay of Bengal during the southwest monsoon season: a possible oceanic source, Environ Sci Process Impacts, 22, 1743-1758, https://doi.org/10.1039/d0em00111b, 2020.

Kasthuriarachchi, N. Y., Rivellini, L.-H., Chen, X., Li, Y. J., and Lee, A. K. Y.: Effect of relative humidity on secondary brown carbon formation in aqueous droplets, Environ. Sci. Technol., 54, 13207-13216, https://doi.org/10.1021/acs.est.0c01239, 2020.

Kim, H., Kim, J. Y., Jin, H. C., Lee, J. Y., and Lee, S. P.: Seasonal variations in the light-absorbing properties of water-soluble and insoluble organic aerosols in Seoul, Korea, Atmos. Environ., 129, 234-242, https://doi.org/10.1016/j.atmosenv.2016.01.042, 2016.

RC9: Line 343 - On a similar note, here or in Section 2.1, please clarify how MSOC was prepared. Was it extracted from nascent filters or filters already extracted with water? If the latter, "MSOC" is perhaps inaccurate since many methanol-soluble compounds will have already been extracted into water, and it could be more precise to refer to MSOC as water-insoluble BrC throughout.

AC9: Thanks for your suggestions. MSOC in this study is the latter, which was extracted using methanol from filters already extracted with water. According to the previous studies (Liu et al., 2013; Shetty et al., 2019), only water cannot effectively extract the BrC constituent, and the remaining part of the filter is water-insoluble fraction. To understand the optical characteristics of these water-insoluble materials, the remaining filter extracted after purified water was further freeze-dried and extracted with methanol to obtain the MSOC. We have clarified it and please see line 115-117 in the revised manuscript.

The reason that we choose “MSOC” to represent the methanol-extracted organic fraction in this study is that methanol could not completely extract these substances which cannot dissolve in water. Further, we wanted to make a comparison with the result of our previous study with a similar extraction method (Tang et al., 2020). Similarly, Chen et al. (2019) also used “WSM” to represent the water-soluble matter and “MSM” represent the methanol-soluble matter in the same manner as our extraction method.

References:

Chen, Q., Mu, Z., Song, W., Wang, Y., Yang, Z., Zhang, L., and Zhang, Y. L.: Size□Resolved Characterization of the Chromophores in Atmospheric Particulate Matter From a Typical Coal□Burning City in China, J. Geophys. Res.-Atmos., 124, 10546-10563, https://doi.org/10.1029/2019jd031149, 2019.

Liu, J., Bergin, M., Guo, H., King, L., Kotra, N., Edgerton, E., and Weber, R. J.: Size-resolved measurements of brown carbon in water and methanol extracts and estimates of their contribution to ambient fine-particle light absorption, Atmos. Chem. Phys., 13, 12389-12404, https://doi.org/10.5194/acp-13-12389-2013, 2013.

Shetty, N. J., Pandey, A., Baker, S., Hao, W. M., and Chakrabarty, R. K.: Measuring light absorption by freshly emitted organic aerosols: optical artifacts in traditional solvent-extraction-based methods, Atmos. Chem. Phys., 19, 8817-8830,

https://doi.org/10.5194/acp-19-8817-2019, 2019.

Tang, J., Li, J., Su, T., Han, Y., Mo, Y., Jiang, H., Cui, M., Jiang, B., Chen, Y., Tang, J., Song, J., Peng, P., and Zhang, G.: Molecular compositions and optical properties of dissolved brown carbon in biomass burning, coal combustion, and vehicle emission aerosols illuminated by excitation–emission matrix spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry analysis, Atmos. Chem. Phys., 20, 2513-2532, https://doi.org/10.5194/acp-20-2513-2020, 2020.

RC10: Line 383 - I think it is important to mention this point, that not all chromophores in BrC are fluorophores, in the introduction.

AC10: Many thanks for your suggestions, we have added this point in the introduction. Please see line 80-81 in the revised manuscript.

RC11: Line 420 - Perhaps discuss Figures S15-16 here as corroborating evidence for the importance of biomass burning.

AC11: Here we made an error previously. We mistakenly brought the fluorescence intensity of components of the 145-model into the PMF model, and the correct data should be that of the 85-model. Thus, we revised it in the revised manuscript and there were slightly different source-contribution from the previous. Further, to more detailly explain the importance of biomass burning, we added the time-series of light absorption and fluorescence components contributed by different sources resolved by the PMF model (Figure 6 and Figure S15). The biomass burning contribution for BrC absorption at 365 nm, and P4 and C4 components is reduced in the monsoon season. Combining the fire spots and backward trajectory (Figure S16-S17), the time series of source contribution points out that high biomass burning contribution is related to the higher local fire spots (i.e., pre-hot season, hot season, and cool season) and air mass from the continent. Jiang et al. (2021) observed increases in biomass burning contributions to BrC absorption during the winter period that was dominant in continental-origin air masses. We have added more discussion in this part (line 448-458) in the revised manuscript.

Reference:

Jiang, H., Li, J., Sun, R., Liu, G., Tian, C., Tang, J., Cheng, Z., Zhu, S., Zhong, G., Ding, X., and Zhang, G.: Determining the Sources and Transport of Brown Carbon Using Radionuclide Tracers and Modeling, J. Geophys. Res.-Atmos., 126, https://doi.org/10.1029/2021jd034616, 2021.