

Atmos. Chem. Phys. Discuss., author comment AC1  
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## Reply on RC1

Jiao Tang et al.

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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-AC1>, 2021

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### Response to Anonymous Referee #1

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

**RC1:** This manuscript by Tang et al. represents a in-depth analysis of chromophores and fluorophores present in filter samples collected for an entire year in Bangkok. The authors use Excitation Emission Matrix, parafactor analysis (PARAFAC) and multiple linear regression (MLR) to provide insights into the contribution of potential sources to light absorbing organic compounds (BrC) in the samples collected. The chemical and data analyses were conducted with cautions. A year-round data from Bangkok serves as a precious case study for the community to understand light-absorbing organic compounds and their climate impact. I recommend publication in ACP after addressing the following minor comments.

**AC1:** Thanks for your recognition of our work and for providing valuable suggestions. We have made revisions following the comments (corrections are marked in the revised manuscript), and the responses are shown below.

**RC2:** Figure 1 - the color scale is not explained. Is it normalized to 1 for the highest intensity among all the factors?

**AC2:** We normalized to 0.1 for the highest intensity among all factors. We have added it as following: The color represents that the intensity was normalized to set the maximum as 0.1. Please see line 205-206 in the revised manuscript.

**RC3:** Figure 3 and related discussion. Although I agree with the authors in that the ratio of Abs<sub>365</sub> and WSOC/MSOC is consistent, I also see that Abs<sub>365</sub> is enhanced relative to WSOC/MSOC during the non-monsoon seasons. I wonder if the authors can investigate the ratios and discuss whether WSOC is more absorbing during BB-affected seasons?

**AC3:** We did see that the Abs<sub>365</sub> is enhanced relative to WSOC/MSOC during the non-monsoon seasons. According to Table 1, the concentrations of levoglucosan that are

generally regarded as biomass burning tracers were higher in the non-monsoon seasons than in monsoon season, and the ratios of levoglucosan/TSP also exhibited a similar trend (we have added the ratios in the revised manuscript, Table 1). Thus, we infer that the non-monsoon season was more affected by biomass burning. Correspondingly, both the WSOC and MSOC are more absorbing during the biomass burning-affected seasons (Table 1). Please see line 322-326 in the revised manuscript.

**RC4:** Line 387~ I think a little more discussions regarding the MLR results can be helpful for the community. Can the authors conclude that Abs<sub>365</sub> in both WSOC and MSOC is dominated by a single factor (P4 for WSOC, C4 for MSOC). Is this result consistent with previous EEM and PARAFAC studies?

**AC4:** We have re-detailed the content of this part and please see line 411-419 in the revised manuscript. In this study, we attempted to build an MLR model to explore the relationship between the BrC absorption and fluorescent chromophores, and we thought that the coefficient (not a constant) in the equation represented the strength of the relationships. Thus, we can conclude that Abs<sub>365</sub> is dominated by the single factor (P4 for WSOC, C4 for MSOC).

A similar study was conducted. Chen et al. (2019) thought that organic substances may represent the important causes of DTT (dithiothreitol) consumption and may be mainly contributed by light-absorbing materials. They found only two fluorescent components contribute to the DTT activity, almost all of which is attributed to the C7 chromophores with an emission wavelength of 462 nm (99%).

#### Reference:

Chen, Q., Wang, M., Wang, Y., Zhang, L., Li, Y., and Han, Y.: Oxidative Potential of Water-Soluble Matter Associated with Chromophoric Substances in PM<sub>2.5</sub> over Xi'an, China, *Environ. Sci. Technol.*, 53, 8574-8584, <https://doi.org/10.1021/acs.est.9b01976>, 2019.

**RC5:** Related to my previous comment, for WSOC, both P3 and P4 have an excitation maximum at around 365 nm. However, only P4 has a significant coefficient after MLR analysis. Meanwhile, P3 had a negative coefficient. Why is this?

**AC5:** In our MLR analysis, we set the constraints and manually selected regression model 3 for our optimal model. Regression model 4 is a calculation process and was also abandoned. However, the negative coefficient of P3 with Abs<sub>365</sub> in regression model 4 could be due to the following reasons. First, from the mathematical meaning, in MLR analysis, simple correlation coefficients may not truly reflect the correlation between variables X and Y, because the relationship between variables is complex and they may be affected by more than one variable. Thus, the partial correlation coefficient is a better choice. In this study, to obtain the real correlation, we control the variables P4, P2, and P7 and make a correlation analysis between Abs<sub>365</sub> and P3. The partial correlation analysis shows that Abs<sub>365</sub> and P3 have a negative correlation ( $r = -0.227$ ), which is consistent with the negative coefficient in regression model 4. However, P3 does have an excitation at around 365 nm. According to the study of Phillips and Smith (2014), they explained that light absorption by organic aerosols is governed by a combination of independent as well as interacting chromophores. They introduce the charge transfer (CT) complexes as a significant source of BrC absorption, formed through the interaction between carbonyl and alcohol moieties in organic molecules, are energetically coupled to one another and form a near-continuum of states that absorb light from 250 to 600 nm, which may contribute up to 50% of light absorption (300–600nm) of the water-soluble fraction. In their experiment, they used NaBH<sub>4</sub> to individually reduce carbonyl functional groups in ketones and aldehydes, likely electron acceptors in CT complexes, to the corresponding alcohols. They observed that absorption spectra decrease and fluorescence increase of aqueous

solutions after reduction by NaBH<sub>4</sub> (Phillips and Smith. 2015). This correlation between fluorescence gain and absorption loss demonstrates that the increased fluorescence is unlikely to result from newly created absorbing species and thus likely results from previously existing species that are more strongly fluorescing after reduction. Therefore, we infer that P3 likely a donor to interact with the other components to form CT complexes, resulting in increased absorption, but decreasing fluorescence due to the loss of functional groups. We hope the above points explain the reason that P3 has a negative coefficient with Abs<sub>365</sub>.

### **References:**

Phillips, S. M., and Smith, G. D.: Light Absorption by Charge Transfer Complexes in Brown Carbon Aerosols, *Environ. Sci. Technol.*, 1, 382-386, <https://doi.org/10.1021/ez500263j>, 2014.

Phillips, S. M., and Smith, G. D.: Further evidence for charge transfer complexes in brown carbon aerosols from excitation-emission matrix fluorescence spectroscopy, *J. Phys. Chem. A*, 119, 4545-4551, <https://doi.org/10.1021/jp510709e>, 2015.