Response to acp-2022-676-RC3

Comment on acp-2022-676

Anonymous Referee #2

In this study, EEM data of different types of strongly light-absorbing organic compounds, water-soluble organic matter (WSOM), soil dust, and purified xanthic and humic acids from different aerosol samples (combustion source samples and ambient aerosols) were investigated in a comprehensive manner using the EEM-parallel factor method. This work can be recommended for publication in Atmospheric Chemical and Physics after the authors address some issues as follows.

Re: Thanks for your important suggestions. These criticism and suggestions will greatly improve the quality of this manuscript. And we have revised the manuscript based on the comments and suggestion 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.

Lines 129-130: What is the purpose of setting up soil samples? Please explain it in detail.

Re: Thanks for your comments. In this study, the soil samples were also selected and tested because it is also an important source of atmospheric WSOM (Chen et al., 2020). On the one hand, soil and/or dustfall, have been reported to be an important source of atmospheric BrC, such as in Xi'an, Northern China (Chen et al, 2020; 2021) and a suburban site in Athens, Greece (Vasilatou et al., 2017). On the other hand, the terrestrial humic-like fluorescent components were commonly attributed to the contribution from soil in many studies (Liu et al., 2019; Ge et al., 2021). Therefore, soil samples were also selected to test the EEM method in this study. We have added a brief description in the revised manuscript. Please refer to Lines 138-140.

References:

Chen, Q., Li, J., Hua, X., Jiang, X., Mu, Z., Wang, M., Wang, J., Shan, M., Yang, X., Fan, X., Song, J., Wang, Y., Guan, D., and Du, L.: Identification of species and sources of atmospheric chromophores by fluorescence excitation-emission matrix with parallel factor analysis, Sci. Total Environ., 718, 137322, https://doi.org/10.1016/j.scitotenv.2020.137322, 2020.

Chen, Q., Hua, X., Wang, Y., Zhang, L., and Chang, T.: Semi-continuous measurement of chromophoric organic aerosols using the PILS-EEM-TOC system, Atmos. Environ., 244, 117941, https://doi.org/10.1016/j.atmosenv.2020.117941, 2021.

Ge, Z., Gao, L., Ma, N., Hu, E., and Li, M.: Variation in the content and fluorescent composition of dissolved organic matter in soil water during rainfall-induced wetting and extract of dried soil, Sci. Total Environ., 791, 148296, https://doi.org/10.1016/j.scitotenv.2021.148296, 2021.

Liu, C., Li, Z. W., Berhe, A. A., Xiao, H. B., Liu, L., Wang, D. Y., Peng, H., and Zeng, G. M.: Characterizing dissolved organic matter in eroded sediments from a loess hilly catchment using fluorescence EEM-PARAFAC and UV-Visible absorption: Insights from source identification and carbon cycling, Geoderma, 334, 37-48, https://doi.org/10.1016/j.geoderma.2018.07.029, 2019.

Vasilatou, V., Diapouli, E., Abatzoglou, D., Bakeas, E. B., Scoullos, M., and Eleftheriadis, K.: Characterization of PM2.5 chemical composition at the Demokritos suburban station, in Athens Greece. The influence of Saharan dust, Environ. Sci. Pollut. Res., 24, 11836-11846, https://doi.org/10.1007/s11356-017-8684-3, 2017.

Lines 134: Additional details whether the blank $PM_{2.5}$ sample was collected, please add this information.

Re: Thanks. In this study, field blank samples were also collected during each sampling period. We have added this information in Section 2.1 in the revised manuscript. Please refer to Lines 146-147.

Lines 411-412: "The relatively higher C3 content in CZ could be attributed to the comparatively high contribution of soil dust in the suburban region". Please provide more evidence for the higher contribution of suburban soil dust to atmospheric $PM_{2.5}$.

Re: Thanks. In this study, the CZ sampling site is located at a typical suburban area (see S1.4 in SI file). In general, ambient aerosol in suburban region may have more contribution from soil dust, as shown in some previous studies (Vasilatou et a;l., 2017; Wu et al., 2019). Moreover, in this study, the relative contribution of Ca^{2+} in CZ $PM_{2.5}$ (1.8±1.2%) are higher than that in GZ $PM_{2.5}$ (1.5%±0.8). Therefore, we can concluded that the higher contribution of soil dust in the suburban region. We have added these information in the present manuscript. Please refer Line 432-433.

References:

Vasilatou, V., Diapouli, E., Abatzoglou, D., Bakeas, E. B., Scoullos, M., and Eleftheriadis, K.: Characterization of $PM_{2.5}$ chemical composition at the Demokritos suburban station, in Athens Greece. The influence of Saharan dust, Environ. Sci. .Pollut. Res., 24, 11836-11846, https://doi.org/10.1007/s11356-017-8684-3, 2017.

Wu, L., Luo, X.-S., Li, H., Cang, L., Yang, J., Yang, J., Zhao, Z., and Tang, M.: Seasonal Levels, Sources, and Health Risks of Heavy Metals in Atmospheric $PM_{2.5}$ from Four Functional Areas of Nanjing City, Eastern China, Atmosphere, https://doi.org/10, 419, 10.3390/atmos10070419, 2019.

Section 3.4. The paper also mentions that some brown carbon fractions have strong absorbance but not fluorescence characteristics, so is it reasonable to analyze the relationship between absorbance and fluorescence using Pearson correlation coefficient?

Re: Thanks. We agreed with your comments. Numerous studies have demonstrated that some brown carbon fractions, such as nitroaromatic compounds (NACs) are the major light-absorbing fraction in the atmospheric BrC, which accounting for more than 60 % of the total light absorption intensity at 300–500 nm (Huang et al., 2021; Lin et al., 2017), however, most of the NACs did not exhibit any fluorescence. It is obvious that the fluorescent index only represent a part of BrC rather than total BrC, therefore, the analysis of the relationship between absorbance and fluorescence using Pearson correlation coefficient should be unreasonable. Based on your suggestion, we have removed this section in the present manuscript.

References:

Huang, R.-J., Yang, L., Shen, J., Yuan, W., Gong, Y., Ni, H., Duan, J., Yan, J., Huang, H., You, Q., and Li, Y. J.: Chromophoric Fingerprinting of Brown Carbon from Residential Biomass Burning, Environ. Sci. Tech. Let., 9, 102-111, http://doi.org/10.1021/acs.estlett.1c00837, 2021.

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. Tech., 51, 11561-11570, http://doi.org/10.1021/acs.est.7b02276, 2017.

In Introduction part, Section 3.1 and 3.3, some new references associated with WOSM molecular and chemical functional group profiles should be added to support the finding of this study, such as:

1). Light absorption properties and molecular profiles of HULIS in $PM_{2.5}$ emitted from biomass burning in traditional "Heated Kang" in Northwest China. Sci. Total Environ. 2021, 776, 146014.;

2). Seasonal and diurnal variation of $PM_{2.5}$ HULIS over Xi'an in Northwest China: Optical properties, chemical functional group, and relationship with reactive oxygen species (ROS). Atmos. Environ. 2022, 268, 118782.;

3). Optical properties, chemical functional group, and oxidative activity of different polarity levels of water-soluble organic matter in $PM_{2.5}$ from biomass and coal combustion in rural areas in Northwest China. Atmos. Environ., 2022, 283.

4) Optical properties, molecular characterizations, and oxidative potentials of different polarity levels of water-soluble organic matters in winter $PM_{2.5}$ in six China's megacities. Science of The Total Environment, 2022, 853: 158600

Re: Thanks, these new references have been added in the revised manuscript. Please refer to Lines 51-54, 60, 424-425.

Line 451: The conclusion of this part is not prominent enough, suggesting a more in depth analysis and better conclusions.

Re: Thanks. According to your critical comments on "the relationship between absorbance and fluorescence" as shown above. We have removed this section.

Figure 3 was lost the legend, please redraw this figure.

Re: Thanks, we redraw the Figure 3 with completed legends. Please refer to the new Figure 3.

Please add the necessary comments for Figure 4, what does each line represent?

Re: Thanks for your comments. We have added a legend in Figure 4, the colored box represents the data range of 25%-75%, the horizontal line within the box represents the median line (50%), the error bar represents the 1.5 times the standard deviation, the circle in the box represents the mean value of the data, the triangles in the bottom and top represent the minimum and maximum values of the data. And dot in the right of the box represents the overall data coupled with Gaussian distribution line. In addition, we also added some comments on it in the revised manuscript. Please refer to the revised Figure 4 and Lines 421-431.

The language overall is acceptable, except for a few places which fail to meet the required level, advice on Grammar from a native writer of English would be helpful.

Re: Thanks. We have asked an English expert to edit English in our manuscript.