Response to acp-2022-676-RC2

Comment on acp-2022-676

Anonymous Referee #1

The excitation-emission matrix (EEM) fluorescence spectroscopy is a highly sensitive analytical technique for the identification of the chemical characteristics and sources of atmospheric chromophores. However, some explanation may be inaccurate because the identification of fluorescent components is mainly based on aquatic DOM. This study investigated the EEM spectra of different types of strong light-absorbing organic compounds and water-soluble organic matter in different aerosol samples, soil dust, and purified fulvic and humic acids and some novelty findings were obtained. For example, aromatic compounds containing nitro groups, which show strong absorption and are the major component of atmospheric brown carbon, exhibited no significant fluorescence. In addition, the fluorescent component 1 (235, 270/330 nm) is generally considered as protein-like groups, however the results of this study suggested that it is mainly composed of aromatic acids, phenolic compounds, and their derivatives, with only traces of amino acids in ambient WSOM. In all, this manuscript is well-written and the major data and their interpretation are scientifically sound. I have some suggestions for changes that should be made before the manuscript is published, to wit:

Re: We appreciated the reviewer for the valuable comments and suggestions, 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 comments and suggestions that need to be addressed: (L=Line)

Abstract: the abstract should include quantitative information on the point that are made.

Re: Thanks. We have added some quantitative information in the abstract. Please refer to Lines 40-45.

Line 28. “by .. ” should be changed to “supplemented by an parallel factor (PARAFAC) modeling”.

Re: Thanks. We have changed that to “supplemented by a parallel factor (PARAFAC) modeling”. Please refer to Lines 28-29.

Line 35. The “fluorescent component 1” is confused. I suggest to add “PARAFAC derived” to define it.

Re: Thanks. We have added “PARAFAC derived” to define it in the present manuscript. Please refer to Line 37.

Line 41: The “fluorescent component 3” refer to C3?

Re: Yes. The “fluorescent component 3” refer to C3 in this study. Based on the comments of reviewer #2, this sentence has been removed in the present manuscript.

Line 98. What are “various properties”? The reference here is not appropriate, because it only focused on fluorescence properties of aerosol chromophores. I suggest the authors provide more relevant references.

Re: Thanks. The "various properties" here specifically refer to its light absorption properties. We are sorry for this inappropriate reference. Base on your suggests, we have added more relevant references in the present manuscript. Please refer to Lines 101-102.

References:

Lin, H., and Guo, L.: Variations in Colloidal DOM Composition with Molecular Weight within Individual Water Samples as Characterized by Flow Field-Flow Fractionation and EEM-PARAFAC Analysis, Environ. Sci. Tech., 54, 1657-1667, http://doi.org/10.1021/acs.est.9b07123, 2020.

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.

Jiang, H., Tang, J., Li, J., Zhao, S., Mo, Y., Tian, C., Zhang, X., Jiang, B., Liao, Y., Chen, Y., and Zhang, G.: Molecular Signatures and Sources of Fluorescent Components in Atmospheric Organic Matter in South China, Environ. Sci. Tech. Let., 9, 913-920, https://doi.org/10.1021/acs.estlett.2c00629, 2022.

Line 110. Please add “peaks” after “fluorescence”.

Re: Thanks. We have added ‘peaks’ after ‘fluorescence’ in the present manuscript. Please refer to Line 115.

Section 2.3: Please provide how Raman and Rayleigh scattering was removed from EEM.

Re: Thanks. In this study, the Raman and Rayleigh scattering was removed following a method suggested by Stedmon and Bro (2008) and Murphy et al. (2013), i.e., the Raman and Rayleigh scattering was removed by subtracting Milli-Q water spectra and then insert zero value to the Raman and Rayleigh scattering region. We have added this information in text S4 in the supporting information.

References:

Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R.: Fluorescence spectroscopy and multi-way techniques. PARAFAC, Anal. Meth., 5, 6557, https://doi.org/10.1039/c3ay41160e, 2013.

Stedmon, C. A., and Bro, R.: Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial, Limn. Ocean. Meth., 6, 572-579, https://doi.org/10.4319/lom.2008.6.572, 2008.

EEM. Line 155. Please give a detailed definition of “IFEs”.

Re: In this study, IFEs is the acronym of “inner filter effect”. We have added a detailed definition in the present manuscript. Please refer to Line 165.

Line 163-165. I want to know if all the samples were investigated with the PARAFAC modeling?

Re: In this study, only 77 atmospheric WSOM samples were investigated with the PARAFAC modeling. We have clarified that in the present manuscript. Please refer to Line 173.

Line 190-194. I suggest the authors provide some references to support this point.

Re: Thanks. We have added some references (Chen et al., 2002; Andrade-Eiroa et al., 2013) to support this point in the present manuscript. Please refer to Line 203.

References:

Andrade-Eiroa, Á., Canle, M., and Cerdá, V.: Environmental Applications of Excitation-Emission Spectrofluorimetry: An In-Depth Review I, Appl. Spec. Rev., 48, 1-49, https://doi.org/10.1080/05704928.2012.692104, 2013.

Chen, J., Gu, B. H., LeBoeuf, E. J., Pan, H. J., and Dai, S.: Spectroscopic characterization of the structural and functional properties of natural organic matter fractions, Chemosphere, 48, 59-68, https://doi.org/10.1016/s0045-6535(02)00041-3, 2002.

Line 220: Please remove the "and aquatic DOM" from sentence.

Re: Thanks. We have removed that from this sentence. Please refer to Line 230.

Line 277. Please add some references to support the similarities to EEM of BB and CC WSOM.

Re: Thanks. We have added some references to support that in the present manuscript. Please refer to Line 288.

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, http://doi.org/10.1016/j.scitotenv.2020.137322, 2020.

Fan, X., Cao, T., Yu, X., Wang, Y., Xiao, X., Li, F., Xie, Y., Ji, W., Song, J., Peng, P., amp, apos, and an: The evolutionary behavior of chromophoric brown carbon during ozone aging of fine particles from biomass burning, Atmos. Chem. Phys., 20, 4593-4605, http://doi.org/10.5194/acp-20-4593-2020, 2020.

Cao, T., Li, M. J., Zou, C. L., Fan, X. J., Song, J. Z., Jia, W. L., Yu, C. L., Yu, Z. Q., and Ping, P. A.: Chemical composition, optical properties, and oxidative potential of water- and methanol-soluble organic compounds emitted from the combustion of biomass materials and coal, Atmos. Chem. Phys., 21, 13187-13205, http://doi.org/10.5194/acp-21-13187-2021, 2021.

Yang, Y., Qin, Y., Qin, J., Zhou, X., Xv, P., Tan, J., and Xiao, K.: Facile Differentiation of Four Sources of Water-Soluble Organic Carbon in

Atmospheric Particulates Using Multiple Fluorescence Spectral Fingerprints, Environ. Sci. Tech. Let., 9, 359-365, http://doi.org/10.1021/acs.estlett.2c00128, 2022.

Line 310. To support the opinion in L311-312 “Although the fluorescence intensities varied with different sites and seasons, the EEM spectra of WSOM were very similar”, I suggested the authors to add more examples for the EEM fluorescence spectra of aerosols from different sites and seasons.

Re: Thanks for your important suggestion. We added more examples to support the opinion in the present manuscript. Please refer to Lines 321-326.

“Similar fluorescence bands have been previously identified in the EEM fluorescence spectra of WSOM from $PM_{2.5}$ in the cold and warm seasons in Aveiro, Portugal (Matos et al., 2015), the High Arctic atmosphere (Fu et al., 2015), Godavari, Nepal (Wu et al., 2019), Lanzhou and Xi’an, northwestern China (Qin et al., 2018; Chen et al., 2020), Chongqing, southwestern China (Wang et al., 2020), and Harbin, northeastern China (Ma et al., 2022).”

Line 304-315: What is the purpose of the EEM spectrum being divided into five regions in Figure 2, and also have a discussion about them. Also in Line 311-312: “Although the fluorescence intensities varied with different sites and seasons, the EEM spectra of WSOM were very similar”. It may be more appropriate to replace “EEM spectra” with “shape of the EEM spectra”.

Re: Thanks for your careful review. The fluorescence region integral (FRI) is a method to indicate the relative intensity of fluorescence in different regions (e.g., the five regions mentioned here) (Chen et al., 2003). Some FRI parameters can be used to indicate the physical/chemical properties of dissolved organic matter, such as the hydrophobicity parameter, humification parameter and Stokes shift parameter (Yang et al., 2022). In our draft, we want to use the FRI method to interpret the EEM spectra of atmospheric WSOM. However, the result is poor and no significant differences were observed, so was not shown in the paper. We are sorry for the careless checking on the lines in Figure 2. In the present manuscript, we have removed that from Figure 1 and 2.

In addition, we have replaced “EEM spectra” with “shapes of the EEM spectra” in the revised manuscript. Please refer to Line 328.

References:

Chen, W., Westerhoff, P., Leenheer, J. A., and Booksh, K.: Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter, Environ. Sci. Tech., 37, 5701-5710, https://doi.org/10.1021/es034354c, 2003.

Yang, Y., Qin, Y., Qin, J., Zhou, X., Xv, P., Tan, J., and Xiao, K.: Facile Differentiation of Four Sources of Water-Soluble Organic Carbon in Atmospheric Particulates Using Multiple Fluorescence Spectral Fingerprints, Environ. Sci. Tech. Let., 9, 359-365, https://doi.org/10.1021/acs.estlett.2c00128, 2022.

Line 319-320: “To better explain the various fluorophores in different atmospheric WSOM samples, the EEM spectra were resolved with the EEM–PARAFAC tool”. This sentence is repeated with the meaning expressed above, suggest deleting this sentence.

Re: Thanks. We have removed this sentence in the present manuscript.

Line 326-328: It is written: “In general, these fluorescent components have been interpreted based on the knowledge of fluorescence characteristics of aquatic DOM.”. However, in Line 329-332, the reference you cited was atmospheric WSOC.

Re: We are sorry for these wrong citations. In the revised manuscript, we have changed that with the references related to the fluorescence spectra of aquatic DOM. Please refer to Lines 342-346.

References:

Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy, Marin. Chem., 51, 325-346, http://doi.org/10.1016/0304-4203(95)00062-3, 1996.

Liu, L., Song, C., Yan, Z., and Li, F.: Characterizing the release of different composition of dissolved organic matter in soil under acid rain leaching using three-dimensional excitation-emission matrix spectroscopy, Chemosphere, 77, 15-21, http://doi.org/10.1016/j.chemosphere.2009.06.026, 2009.

Wünsch, U. J., Bro, R., Stedmon, C. A., Wenig, P., and Murphy, K. R.: Emerging patterns in the global distribution of dissolved organic matter fluorescence, Anal. Meth., 11, 888-893, http://doi.org/10.1039/c8ay02422g, 2019.

Zhang, Y. L., Gao, G., Shi, K., Niu, C., Zhou, Y. Q., Qin, B. Q., and Liu, X. H.: Absorption and fluorescence characteristics of rainwater CDOM and contribution to Lake Taihu, China, Atmos. Environ., 98, 483-491, http://doi.org/10.1016/j.atmosenv.2014.09.038, 2014.

Zhou, Y., Yao, X., Zhang, Y., Shi, K., Zhang, Y., Jeppesen, E., Gao, G., Zhu, G., and Qin, B.: Potential rainfall-intensity and pH-driven shifts in the apparent fluorescent composition of dissolved organic matter in rainwater, Environ. Pollut., 224, 638-648, http://doi.org/10.1016/j.envpol.2017.02.048, 2017.

Line 334. Please add the “terrestrial” after “aquatic”.

Re: Added. Please refer to Line 348.

Line 351-354: the reference is missing.

Re: Thanks. We have added some references in the present manuscript. Please refer to Lines 367-368.

References:

Bianco, A., Passananti, M., Deguillaume, L., Mailhot, G., and Brigante, M.: Tryptophan and tryptophan-like substances in cloud water: Occurrence and photochemical fate, Atmos. Environ., 137, 53-61, http://doi.org/10.1016/j.atmosenv.2016.04.034, 2016.

Song, T., Wang, S., Zhang, Y., Song, J., Liu, F., Fu, P., Shiraiwa, M., Xie, Z., Yue, D., Zhong, L., Zheng, J., and Lai, S.: Proteins and Amino Acids in Fine Particulate Matter in Rural Guangzhou, Southern China: Seasonal Cycles, Sources, and Atmospheric Processes, Environ. Sci. Tech., 51, 6773-6781, http://doi.org/10.1021/acs.est.7b00987, 2017.

Vione, D., Albinet, A., Barsotti, F., Mekic, M., Jiang, B., Minero, C., Brigante, M., and Gligorovski, S.: Formation of substances with humic-like fluorescence properties, upon photoinduced oligomerization of typical phenolic compounds emitted by biomass burning, Atmos. Environ., 206, 197-207, http://doi.org/10.1016/j.atmosenv.2019.03.005, 2019.

Mahamuni, G., Rutherford, J., Davis, J., Molnar, E., Posner, J. D., Seto, E., Korshin, G., and Novosselov, I.: Excitation–Emission Matrix Spectroscopy for Analysis of Chemical Composition of Combustion Generated Particulate Matter, Environ. Sci. Tech., 54, 8198-8209, http://doi.org/10.1021/acs.est.0c01110, 2020.

Line 387-390. Similar questions above. Can these two samples be representative? I suggest the authors summarize more samples in detail.

Re: Thanks. According to your suggestion, we have added more examples in the present manuscript. Please refer to Lines 401-406.

“Similar fluorescent substances have also been identified in the study of atmospheric aerosol fluorescent chromophores, such as the highly oxygenated HULIS in Nagoya, Japan (Chen et al., 2016a), Lanzhou, China (Qin et al., 2018), Xi’an, China (Chen et al., 2020), a haze event in Harbin (Ma et al., 2022), and humic-like compounds with more aromatic and unsaturated bond in Godavari, Nepal (Wu et al., 2019) and Tianjin, China(Deng et al., 2022).”

Line 388: Please explain the “HULIS-1” used here. HULIS-1 of what?

Re: In this study, the ‘HULIS-1’ is the highly oxygenated HULIS in atmospheric WSOM (Chen et al., 2016). We have clarified that in the present manuscript. Please refer to Line 402.

Line 389: It may be more appropriate to replace “component 2” with corresponding compound.

Re: Thanks. We agreed with your suggestion and have used “humic-like compounds with more aromatic and unsaturated bonds” to replace “component 2” in the revised manuscript. Please refer to Line 405.

Line 485-487. The conclusion on contributions of fluorophores within CZ WSOM was wrong.

Re: We are sorry for this clerical error. In the present manuscript, we have corrected that in the conclusion. Please refer to Lines 485-489.