Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2021-465-RC1, 2021

Comment on acp-2021-465

Anonymous Referee #1

Referee comment on "Measurement report: Particle-size-dependent fluorescence properties of water-soluble organic compounds (WSOCs) and their atmospheric implications for the aging of WSOCs" by Juanjuan Qin et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-465-RC1, 2021

General Comments: This manuscript describes the investigation of the fluorescence properties of water-soluble organic compounds (WSOC) in size-segregated atmospheric particles collected in a rural area of Beijing. To attain these goals, the authors applied different data analysis tools to the excitation-emission matrix (EEM) fluorescence spectra of the WSOC fractions from each particle size-range. The WSOC is well recognized as an important driving factor in climate change due to its light absorption properties. However, our understanding of the chemical and optical properties of the WSOC is still inadequate, particularly when dealing with size-segregated aerosol WSOC fractions. The topic dealt in this manuscript has relevance to the atmospheric research community by providing new insights into the optical properties of size-segregated WSOC, but also by suggesting the impact of photochemical reactions on the fluorescence properties of atmospheric WSOC, which were previously unnoticed in studies focusing only on WSOC from fine atmospheric air particles (PM2.5). Nevertheless, this study has also several shortcomings that need to be adequately addressed by the authors. These are described below, in Specific Comments.

Specific Comments:

Lines 124-127: The text in lines 124-125 is repeating the same information as that provided in lines 115-120. Furthermore, the sentence in lines 126-127 makes more sense in a Introduction section, rather than in a Data analysis section.

Section 2.4.3. Grey relational analysis (GRA): The authors make a strong focus on the novelty of GRA applied to the analysis of EEM fluorescence data. Nevertheless, this is the most obscure section of this study, particularly to those potential readers not familiarized

with this analytical tool. The authors should provide a thorough explanation regarding the meaning of each variable in equations (5) and (6) and their relation to the EEM fluorescence data. Furthermore, it is unclear to which factors are the authors referring to when stating that the "fluorescence intensity is highly affected by WSOC concentrations and many other factors (…)" and that "their relations are not clear". Please, be more clear regarding these issues, and explain why you are considering the particles < 0.26 μm as "the references" (only mentioned in line 256)? Moreover, when referring to the "references", do you mean the EEM fluorescence data of WSOC from particles < 0.26 μm? All these issues need to be adequately addressed and thoroughly explained in the manuscript.

Lines 166-167: The authors state that other researchers also verified a bimodal distribution for the organic matter in other locations within the same region of this study. Firstly, it would be important to clarify whether this bimodal distribution followed the same size distribution as that reported in this study for the summer samples. Secondly, the authors should be aware that the concept of "organic matter" is different from the concept of "WSOC", because in the former you must consider the contribution of atoms (e.g., H, N, S and O) other than carbon to this fraction. This is why it is common to use an aerosol organic mass-to-organic carbon ratio (OM/ OC) to assess the content of organic matter in the air particles in order to achieve a mass closure. Even though it was not possible to estimate the OM/OC ratio in this specific study, it would be interesting to assess whether the organic matter also follows a similar bimodal distribution (see, for example, the work of Li et al. (2020), Science of The Total Environment, 703, 134937, https://doi.org/10.1016/j.scitotenv.2019.134937, for OM/OC ratios for primary and secondary organic aerosols).

Line 168: Is it possible to include some explanations for the fact that the WSOC/OC ratios are higher in winter than in summer. Could this difference be associated to the prevalence of biomass burning emissions in winter?

Lines 175-176: The authors state that "The bulk fluorescence features of WSOC showed evident distinctions among fine particles and coarse mode particles on EEM spectra". In this Reviewer's opinion, these differences between the EEM spectra of fine and coarse mode particles are more evident in terms of the fluorescence intensity rather than in terms of different fluorescence peaks.

Lines 197-199: The authors state that "FRI â ¢ and FRI â ¤ (HULIS) were the most abundant two fluorophores rich in fine particles." The authors are considering the total fluorescence intensity of these two regions? Figure 4 suggests that FRII is the most abundant fluorophore in fine particles for both summer and winter samples.

Furthermore, the authors also state that "FRI â £ (microbial related species) peaked between 1.4 to 2.5 μm and showed little variations with particle size increase." However, Figure 4 depicts different results: for the winter samples, FRIV accounts for 23% for particles between 0.26 and 2.5 μm, whereas for the summer samples, the lowest percentage of FRIV (15%) is reported for particles between 1.4 to 2.5 μm. The authors

should correct these inconsistencies in their assessment of the results.

Lines 238-239: If component C3 (assigned to HULIS-2, in line 237) has no physical significance and is considered as a "noise signal", why it is quantified in Figure 6, for the Summer samples? Does it means that 17 to 46% of the fluorescence intensity of PARAFC components for each particle size, in summer samples, is due to "noise signal"? This should be clarified in the manuscript, alongside with a reference to the variance of the model and the core consistency value for each particle size, for the winter and summer samples.

Section 3.5: As above mentioned, the lack of explanations regarding the GRD analysis applied to the EEM fluorescence data is the main issue of this work. For example, in line 256, which are the comparing factors (and why) and why the particles below 0.26 μm were used as references? In lines 257-258, what do you mean with the statement "The GRD of WSOC, AFI, and UV between particle sizes were basically well among both seasons."?

Furthermore, in lines 267-268, the authors state that "GRD were strongly negatively correlated with estimated secondary organic carbon (SOC) concentrations with correlation efficient r at -0.64 ($p<0.000$) in winter and -0.63 in summer." Where is the data regarding the estimate of SOC in the collected air particles samples? What was the method followed by the authors to estimate the amount of SOC in the collected samples? Additional data and explanations are required here for a better understanding of how fluorescent WSOC is highly affected by secondary processes, and that GRD between WSOC and AFI could serve as an indicator of secondary formation.

Technical Corrections:

- In this Reviewer opinion, the English language needs extensive revision throughout the manuscript in order to improve not only its reading, but also to clarify the structure and discussion of the scientific results and conclusions.
- Line 117: where it reads "Roman unit" it should read "Raman unit".
- Line 211: where it reads "p-conjected" it should read "p-conjugated".
- Line 219: The reference "(Valeur and Berberan-Santos, 2012)" is not accurately listed in the reference list (see line 373).
- Line 222: In my opinion, "Figure 3" should appear as "Figure S3" in the text, because the authors are referring to Figure S3 of the Support Information. Please, also see my comment below on Figures S1, S2, S4, S5 and Table S1, in Supporting Information.
- Line 271: where it reads "indicter" it should read "indicator".
- Figure 1 is not mentioned nor discussed in the manuscript, although it is presented at the end as being part of the manuscript.

- Figure 2: please, clarify which axis correspond to the Emission and Excitation wavelengths in order to facilitate the analysis of the EEM spectra by the potential reader.
- Figure 3 caption: where it reads “Roman unit” it should read “Raman unit”.
- Table 1: please, include the units of the WSOC and WSIN concentrations (micrograms per cubic meter?). Moreover, in Table’s caption, where it reads “standard divisions” it should read “standard deviations”.
- Please, update the year of the reference Almeida et al. (Environ. Sci. Technol. 54, 1082-1091), since it was published in 2020.
- Supporting information: the organization and cross-reference, in the main text, of the data presented in the Supporting Information needs to be better addressed. For example, there is no reference in the main text to Figures S1, S2, S4, S5 and Table S1. The authors should also clarify the purpose of these figures and table and how these data were obtained and how it is being used to support the main results and discussion presented in the manuscript. In this regard, as an example, in Figure S2 caption, it is unclear to which particles size correspond the EEM spectra in Figure S2(a), as well as to which stidies are the authors referring to in Figure S2(b) and S2(c).