

General Comments: This manuscript titled "Particle size-dependent fluorescence properties of water-soluble organic compounds (WSOC) and their atmospheric implications on the aging of WSOC" describes fluorescence properties of size-segregated WSOC aerosols in a rural area of Beijing. To attain the study objectives, the authors applied different data analysis tools to the excitation-emission matrix (EEM) fluorescence spectra of the size segregated WSOC. The WSOC aerosols represent a significant fraction of organic aerosols and one of the driving factors in climate change due to their light absorption properties. The topic of the study is within the scope of the journal and has relevance to the atmospheric research community. Although the technique used (i.e., EEM fluorescence spectra) in this study might have some limitations (such as difficulties in segregating anthropogenic and bioaerosols WSOC fractions etc) if used alone. However, size-segregated EEM fluorescence spectra (this study) can be helpful in mitigating many of these limitations and understanding anthropogenic and natural sources of WSOC, their atmospheric evolution, and optical properties. Even so, this study has many shortcomings in its current version given below:

Major Comments:

Introduction: Lacks organization and continuity? The reviewer suggests the revision of introduction section to make it more organized and in tandem with the objective of the study.

Line 161: The size distribution of WSOC/OC and WSOC concentration doesn't follow similar trend. Although several studies in the past (Dasari et al., 2019 science advances; Choudhary et al., 2021 environmental pollution) as well as this study (in introduction) have stated that majority of WSOC are secondary (oxidized) in nature. The author can elaborate possible rationales briefly?

Line 174: Figure 1 is not discussed in the manuscript. Either delete it or add some relevant discussion about same?

Line 186-193 and 285-290: The author stated that "The AFI/WSOC ratios ranged from 0.22 to 0.57 in winter and 0.18 to 0.34 in summer, respectively." "Our unpublished research found that the AFI/WSOC ratios were lower than 0.2 for anthropogenic source samples, indicating that this ratio might be higher in oxidized fluorescent WSOC." If that is the case, size distribution of AFI/WSOC should have follow the distribution trend of WSOC/OC (a tracer for photochemical oxidation), but this is not the case in this paper (Figure 3). Explain the rationale/s behind this behaviour?

Line 212: The author stated that Stokes shift (SS) of $1.2 \mu\text{m}^{-1}$ is an important border of hydrophobic and hydrophilic components. And later used Stokes shift of 1.1 to determine ratios of fluorescence intensity in high SS. Elaborate the possible reason/s?

Line 205: HIX (aromaticity) and WSOC/OC (oxidation) ratio following same size distribution trend. How come? This could be an important finding of the manuscript. Add some discussion about same in Discussion and Implication sections.

Line 209, 210, 243: The author categorized Protein-like compounds into biogenic origin. But aerosols partitioned from VOCs (isoprene etc.) emitted from plants also categorized into biogenic aerosols. Does the author also incorporating these aerosols produced from VOCs in Protein-like compounds or it is just bioaerosols? Please clarify?

Line 256: Why did author used particles $<0.26 \mu\text{m}$ as references for Grey relational analysis (GRA)? Why not use size bins where WSOC, UV and AFI are maximum?

Minor Corrections:

In the Reviewer's opinion, the English language needs significant revision throughout the manuscript before acceptance. The some of English-related corrections and other minor

comments are suggested below:

Line 33: Replace "mysterious" with either "Unknown" or "Uncharacterized".

Line 34-35: The sentence lacks continuity. Revise the sentence "incorporating with different highly oxidized functional groups or heteroatoms like" with may be something like "WSOC mixture contains both aromatic nuclei and aliphatic chains (Decesari et al., 2001; Dasari et al., 2019), with functional groups or heteroatoms like hydroxyl, carboxyl, aldehyde, ketone, amino, and other nitrogencontaining groups (Duarte et al., 2007; Cai et al., 2020)".

Line 37: Is the reference "(ParkSeungShik et al., 2017)" is correctly cited and listed in the reference list (also see line 485).

Line 39: Revise "Nuclear magnetic resonance (NMR) and mass spectrometry (MS) are two remarkable analytical methods using to structurally unravel the complex WSOC (Duarte et al., 2020)."

line 46: It is "Accelerator" not "accelerate".

Line 46: Revise the sentence to something like "Isotopic ratio mass spectroscopy (IRMS) and accelerator mass spectroscopy (AMS) are widely used to distinguish organic emissions from fossil combustion sources and biogenic sources using carbon isotopic characteristics (Masalaite et al., 2018; Zhao et al., 2019; Huang et al., 2020)."

Line 50-56: Whole paragraph lacks organization and continuity. The reviewer suggests the revision of the paragraph.

Line 57: Replace "3-Dimensional fluorescence of excitation-emission matrix (EEM)" to "3-Dimensional excitation-emission matrix (EEM) fluorescence spectroscopy"

Line 59: it should be "mainly helpful in investigating"

Line 62: what does author mean by "in early years"? Does author mean "earlier studies", if so, revise the sentence.

Line 65: It should be "analyse" not "analysis"

Line 69: "(great parts of WSOC)"? It should be something like "significant fraction of WSOC"

Line 70: "reversely"?

Line 82: "neighbor particle sizes" should "adjacent particle size bins"

Line 83: The use of "But" is not perfect here. The reviewer suggests to use "and" instead.

Line 94: confusing sentence "All samples were collected by quartz filters (Whatman) were prebaked for 5 hours (500°C) and wrapped by aluminum foil stored at -20°C after sampling." May be revised to "All samples collected on quartz filters (Whatman), prebaked for 5 hours (500°C) before sample collection, were wrapped by aluminum foil after sampling and stored at -20°C."

Line 95: Need clarification? Total 20 groups for 2 seasons or 20 groups each for every season?

Line 106: Should be "The extract was then filtered through a 0.22 μm membrane filter to remove impurities."

Line 113: Confusing? The sentence may be written like "The extraction procedure of samples subjected to fluorescence and ultraviolet-visible (UV-Vis) measurements were same as WSOC detection."

Line 117: Should be "Raman Unit"

Line 124: Revise the sentence "The EEM data were spectrally corrected by blank sample for instrument bias, inner filter effects, Rayleigh scattering, and

most of Raman scatter had been removed" to "The EEM data were spectrally corrected by blank sample to remove interferences from instrument bias, inner filter effects, Rayleigh scattering, and Raman scatter."

Line 133-134: Equations number is not matching? Example: "equation (3)" should be "equation (2)" and "equation (4)" should be "equation (3)"

Line 218: Revise "On a large scale of a π -conjugated system, the...."

Line 222: "Supporting information Figure 3, and Figure 5(c)." should be Figure S3 and Figure S5(c). Do same thing for Figures S1, S2, S4 and Table S1, in Supporting Information.

Line 87 and 228: The full form of PARAFAC is already mentioned on Line 87. No need to repeat it again. Follow same comment for others as well (e.g. GRA on line 249 etc.).