Dear editor Alex Huffman:

Thank you very much for your considerations on our manuscript "Measurement Report: Particle size-dependent fluorescence properties of water-soluble organic compounds (WSOC) and their atmospheric implications on the aging of WSOC", MS No.: acp-2021-465. And thank you for the recognition of our work. We have carefully checked through the manuscript and revised the Figures and vague descriptions as suggested, detailed changes are listed below. A manuscript with tracked changing version and a clean version are uploaded.

Line numbers refer to the submitted "tracked changes" version manuscript.

1) Please adapt title to begin as "Measurement Report: Particle size-dependent …"

Response: Thank you for sorting the manuscript to the best fit form of "Measurement Report". We have added "Measurement Report:" before the original title, they are now read as

"Measurement Report: Particle size-dependent fluorescence properties of water-soluble organic compounds (WSOC) and their atmospheric implications on the aging of WSOC"

2) Abstract, line 12: The mention of fluorescence spectroscopy having been used to "investigate the sources" is a bit of a stretch. It would be more accurate to say something like "…fluorescence spectroscopy was used to investigate optical properties of WSOC as means of inferring information about their atmospheric sources."

Response: Thank you for your advice. The statement of "fluorescence spectroscopy was used to investigate the sources of WSOC" might be over stretched, so we have change them as advised in the Abstract. They are now shown as follows.

Lines 12-13: "3-Dimensional fluorescence spectroscopy was used to investigate the optical properties of WSOC as means of inferring information about their atmospheric sources."

3) I'm not comfortable with the use of the term "EEM" in all cases throughout the manuscript. An EEM is really just a way of plotting fluorescence emission spectra acquired at many separate excitation wavelengths, but doesn't represent a type of spectroscopy fundamentally different from other kinds of fluorescence spectroscopy. For example, in line 48 you state that EEM fluorescence spectroscopy "is an optical instrument." I would change that to say EEMs can be extracted from fluorescence spectra acquired on a fluorescence spectrometer.

Response: Thank you for your advice, and we are sorry for the confusing usage of "EEM" in the manuscript. We have checked through the article and replaced "EEM" with "fluorescence" or deleted them according to the context. Detailed changes with track are listed as follows.

For the inappropriate usage of EEM in line 48, we changed it to "3-Dimensional fluorescence spectroscopy", and added the explanation of EEM in line 51-53.

Line 48-49: “3-Dimensional ~~excitation-emission matrix (EEM)~~ fluorescence spectroscopy is an optical instrument that has been used in analyzing atmospheric WSOC”

Line 51-53: “Excitation-emission matrix (EEM) can be extracted from fluorescence spectra (acquired on a fluorescence spectrometer) and visualized to show fluorescence regions and possible categories of WSOC by the spectral characteristics”

Other changes of “EEM” in the manuscript:

Line 11-12: “~~Excitation-emission matrix (EEM)~~3-Dimensional fluorescence spectroscopy was used to investigate ...”

Line 13: “Sophisticated data analysis on ~~EEM~~fluorescence data was performed to...”

Line 16: “The excitation-emission matrix (EEM) spectra of WSOC varied with particle size...”

Line 56: “... are important subsidiary approaches to statistically analyze ~~EEM data~~fluorescence properties of WSOC.”

Line 104: “the wavelength ranges ~~of EEM~~ were 200-400 nm for excitation and 250-500 nm for emission with 5 nm interval for fluorescence spectroscopy”

Line 172: “The overall fluorescence peaks ~~of EEM~~ were...”

Line 180: “The detailed characteristics of ~~EEM intensity~~fluorescence spectra could be found in SFI spectra.”

Line 201: “Inclusive information was stored in ~~EEM~~fluorescence spectra...”

Line 233: “3.4 ~~EEM fluorophore~~Fluorophores revealed by classification of PARAFAC results”

Line 242: “...to reveal seasonal dependent ~~EEM~~fluorescence spectra. Three components were extracted from winter ~~EEM~~ spectra, including...”

Line 292: “...thereby resulting in a redshift of ~~EEM~~fluorescence spectra...”

Line307: “All evidence on ~~EEM~~fluorescence spectra and ~~fluorescence~~ indices discussed above suggested...”

4) Thank you for your edits to Section 2.4.3, however I still find the section somewhat confusing. The definitions of the term GRA and GRD are somewhat confusing, in part because of typos. Section 2.4.3 lists these two definitions: “grey relational analysis (GRA)” and “grey relational degree (GRD)”. But then Section 3.5 and again in Section 1 (line 106) re-defines GRD as “Gary Relational Degree.” Please make these consistent and only define each acronym a total of one time.

Please focus one more time to clarify the development of this topic. The explanation of this section should be understandable without need to reference the supplemental section discussing GRD. As examples:

- In context of this manuscript, it isn’t clear what a ‘system development process’ is (line 179).
- The first sentence introduces GRA, and then the second sentence says that GRD can be calculated using information in the supplement.

- Line 185: “A reference line” – Does this mean a row or column of the EEM spectral matrix? What sequences do you mean? Other spectra?
- What defines a “grey system?” (line 178, 189). Please clarify in context of this manuscript.

Response: Thank you for your advice, and we have reconstructed section 2.4.3 into two parts. In the first paragraph, we explained grey relational analysis, grey system and the applicability of grey relational analysis in environmental research; and then the relations of grey relational analysis and grey relational degree (GRD), the calculation criterion of GRD was explained in brief. While, in the second paragraph, the GRD calculated in the present research was explained.

We also have corrected the confusion statement accordingly. Firstly, the abbreviation of GRA is replaced with “grey relational analysis” and only GRD left to avoid confusion. Secondly, “a system development process” was trying to refer to “grey system” which were not defined in the manuscript. Thus, we have deleted the words “development process” and added some descriptions of grey system. Lastly, the reference line and comparing line are explained in the second paragraph of section 2.4.3.

The revised section 2.4.3 are shown as follows:

“Grey relational analysis is part of the grey system theory proposed by Deng (1982), which can be used to describe the relative changes among factors in a system whose information is partly known (this system is defined as a grey system). Grey relational analysis is suitable for solving complicated problems with interrelationships between multiple factors and variables (Morán et al., 2006). It also has been used for solving environmental issues (Kuo et al., 2008; Xu et al., 2011; You et al., 2017). In the present study, atmospheric particles can be treated as a grey system and proceed grey relational analysis for their high complexity and indeterminacy. Grey relational degree (GRD) is the result of grey relational analysis, the detailed calculation was explained in the supplementary information. Generally, a reference line and one or a series of comparison sequences were selected to calculate GRD, the results is evaluated by threshold 0 to 1, high values indicate closer compactness degree of the reference line and comparison line.

Here, two sets of GRD were obtained from WSOC concentrations and formerly calculated fluorescence indices for each season. Firstly, considering the evolution of particle size as a changing system, larger particles might come from the accumulation and transformation of smaller particles, especially for ultrafine particles. By setting data of all particles <0.26 μm (factors like WSOC concentrations, AFI or UV) as references sequence and corresponding factors for particles larger than 0.26 μm as comparison sequences for each season, their affinities were analysed. Secondly, because only part of WSOC are fluorescent, by setting the WSOC concentrations of all samples as a reference sequence and their AFI (or UV) as a comparison sequence. The GRD between WSOC and AFI were calculated.”

5) Table 1: micrograms, not milligrams, right?

Response: We are sorry for the mistake, it should be micrograms and we have changed it into “$\mu g \cdot m^{-3}$”.

Table 1 Size segregated average WSOC, WSIN concentrations, and their standard deviations.

	Species (μg·m^{-3})	<0.26 μm	0.26-0.44μm	0.44-0.77μm	0.77-1.4μm	1.4-2.5μm	2.5-10 μm
Winter	Cl^-	0.42±0.25	1.36±1.21	0.83±0.72	1.03±0.98	1.19±1.27	0.43±0.45
	NO_3^-	2.08±1.43	9.42±8.46	5.64±5.61	7.37±8.9	6.72±9.44	1.92±3.28
	SO_4^{2-}	1.05±0.6	4.36±3.87	3.21±3.68	5.44±9.43	4.68±7.03	1.18±1.52
	Na^+	0.12±0.05	0.21±0.1	0.16±0.08	0.2±0.1	0.52±0.6	0.24±0.25
	NH_4^+	1.05±0.57	2.9±2.15	2.05±1.82	2.4±2.77	1.67±2.18	0.44±0.67
	Mg^{2+}	0.01	0.01	0.02±0.01	0.05±0.04	0.18±0.21	0.08±0.09
	Ca^{2+}	0.06±0.01	0.11±0.03	0.15±0.08	0.4±0.25	1.67±1.35	0.93±0.9
	K^+	0.08±0.04	0.37±0.3	0.24±0.24	0.25±0.25	0.18±0.18	0.05±0.06
	OC	4.49±1.93	11.04±7.2	5.67±4.49	5.45±6.26	5.07±3.88	3.4±5.17
	EC	0.38±0.18	0.93±0.47	0.67±0.43	0.72±0.69	0.62±0.78	1.65±4.37
	WSOC	1.66±0.7	4.73±2.96	2.96±2.41	3.21±4.33	2.31±2.55	0.64±0.5
	WSOC/OC	0.38±0.07	0.43±0.07	0.56±0.27	0.51±0.15	0.37±0.14	0.24±0.25
Summer	Cl^-	0.05±0.02	0.1±0.04	0.07±0.03	0.07±0.02	0.16±0.1	0.11±0.06
	NO_3^-	0.48±0.44	3.5±3.32	1.37±1.35	1.04±0.86	4.76±4.22	1.49±1.37
	SO_4^{2-}	1.63±1.18	7.14±6.64	2.59±2.42	1.28±1.13	0.72±0.51	0.2±0.12
	Na^+	0.29±0.08	0.37±0.17	0.25±0.06	0.23±0.06	0.27±0.09	0.19±0.03
	NH_4^+	0.79±0.53	2.56±1.99	1.18±1.02	0.63±0.55	0.5±0.46	0.1±0.08
	Mg^{2+}	0.01	0.01	0.01	0.02±0.01	0.12±0.08	0.05±0.03
	Ca^{2+}	0.05±0.01	0.08±0.02	0.08±0.03	0.16±0.09	1.21±0.87	0.62±0.49
	K^+	0.03±0.02	0.14±0.11	0.05±0.04	0.04±0.02	0.06±0.02	0.02±0.01
	OC	2.67±0.98	3.93±2.22	1.39±0.67	1.14±0.41	3.5±1.21	2.22±1.76
	EC	0.38±0.12	0.44±0.16	0.2±0.09	0.22±0.06	0.34±0.22	0.5±0.52
	WSOC	0.67±0.25	1.27±0.86	0.46±0.31	0.33±0.21	0.57±0.18	0.27±0.18
	WSOC/OC	0.26±0.08	0.3±0.07	0.31±0.1	0.27±0.1	0.17±0.04	0.16±0.12

6) Figures:

a. Figure 2: Clarify what “Ex” and “Em” are in the caption, making clear these are wavelengths of excitation or emission, and including the units in the caption. Please also clarify why the x-axis legend only covers one of the six columns.

Response: We are sorry for missing annotative information in the graph, we have modified them now.

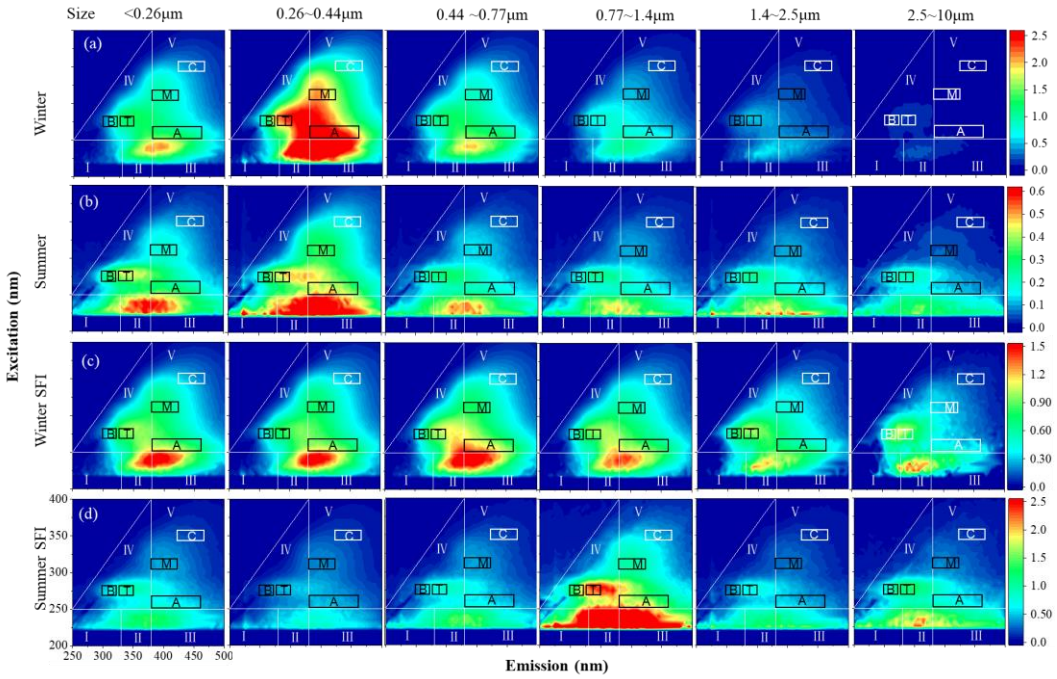

Figure 2 EEM spectra of size segregated samples in winter and summer, their excitation and emission wavelength range were the same and only showed in first EEM of (d). All spectra were partitioned into five regions and assigned as protein-like pollutants (I and II), fulvic acid (III), soluble microbial byproduct-like substances (IV), and humic-like acid (V), respectively (Birdwell and Engel 2010). Peak A, B, C, M, and T were generally considered as humic-like fluorophores, tyrosine-like fluorophores, humic-like carbon with larger molecular weight, marine humic-like fluorophore, and tryptophan-like fluorophores (Coble 1996). (a) and (b) were the size segregated EEM spectra of winter and summer samples, respectively (Unit: R.U.), (c) and (d) were the corresponding EEM spectra of fluorescence emitted per unit of WSOC carbon (Unit: R.U.·L·mg^{-1}).

b. Figure 4: Please place Fluorescence regional integration (FRI) somewhere in the figure caption. Additionally, the values on the x-axis run into one another. Don't make the font size any smaller, but otherwise consider how to revise the x-axis. No y-axis label.

Response: **Thank you for your advice,** we have added "Fluorescence regional integration (FRI)", rotated the x-axis label and added y-axis label in Figure 4.

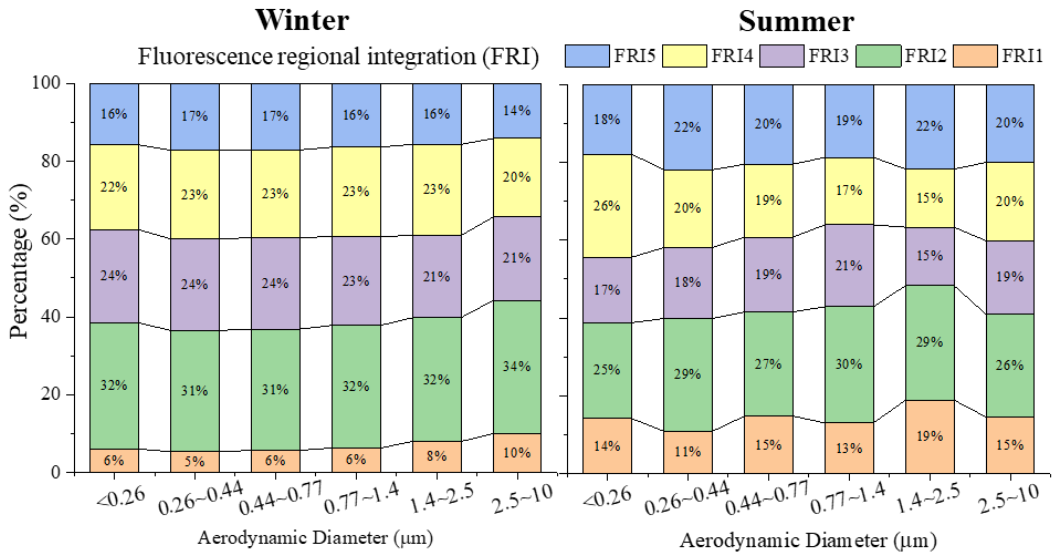

Figure 4 Size distribution of fluorescence regional intensity for winter and summer. FRI1-FRI5 was FRI of fluorescence region I to V.

c. Figure 6: The font size on the axes and legends of this figure is too small to read easily.

Response: Thank you for your advice, we have enlarged the font size of axes and legends of Figure 5 and Figure 6.

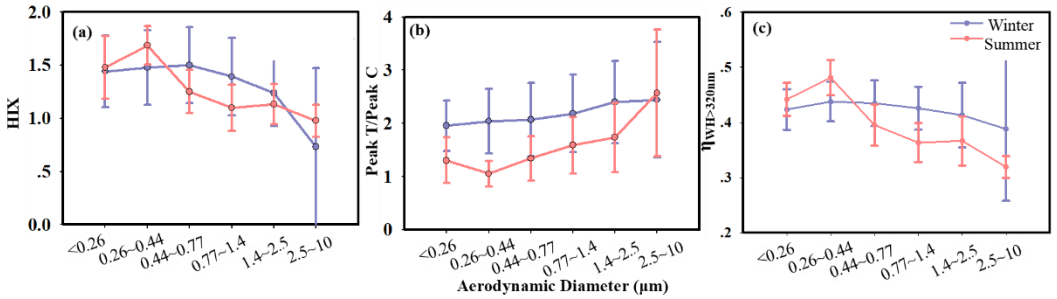

Figure 1 Humic index and Peak T/Peak C ratio served as indictors of humification degree and the biodegradable possibility of WSOC. (a) HIX in different particle sizes, large HIX value indicated high humification degree or high aromaticity of fluorescent organics. (b) Peak T/Peak C ratios of different particle sizes. The large value indicated more microbial metabolites in the fluorescent organics. (c) showed the size distributions of $\eta_{WH>320}$ for winter and summer samples, respectively.

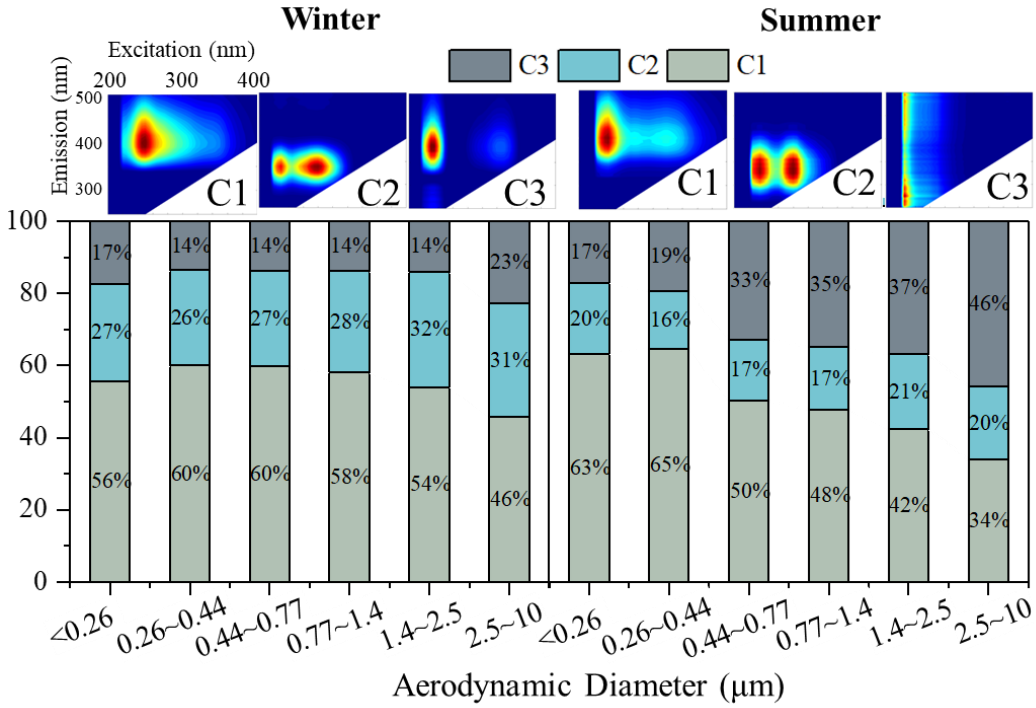

Figure 2 PARAFAC results of EEM in winter and summer respectively. Three components were extracted of both seasons, the portions of each component for different particle sizes were shown as well.

d. Figure 7: No x-axis label or units.

Response: We are sorry for the mistakes. The x-axis label is added, while the GRDs are of no unit, since they are calculated by normalized data.

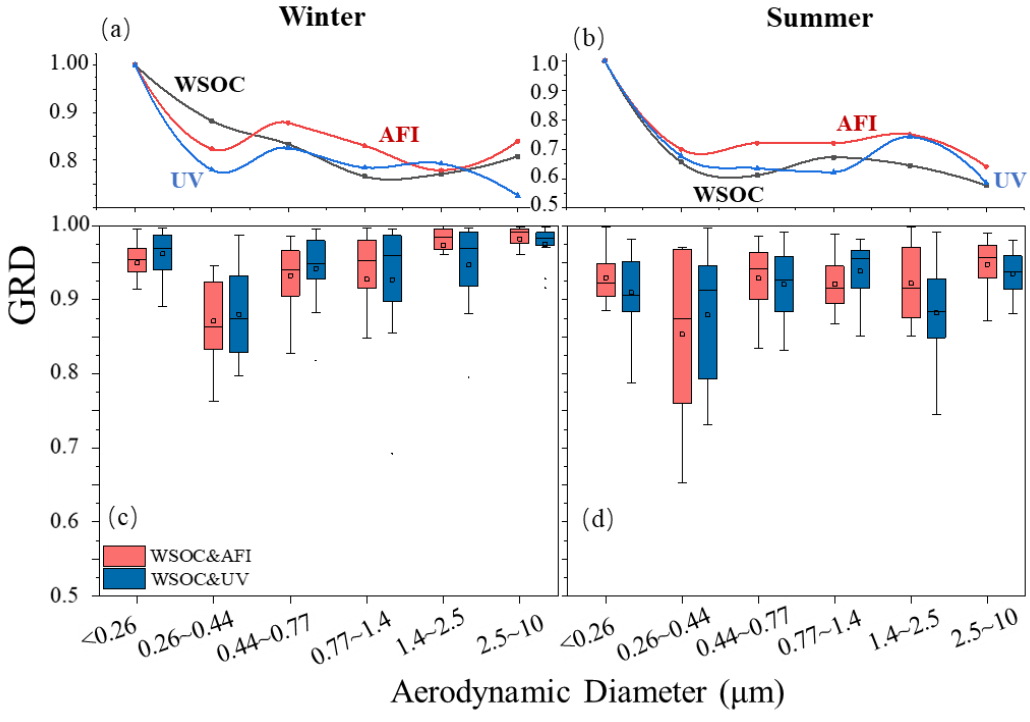

Figure 3 GRD of size segregated WSOC, AFI, and average UV. (a) and (b) GRD calculated

by WSOC, AFI, and average UV of each sample, setting data of <0.26 μm as references, GRD (<0.26) =1; (c) and (d) GRD between WSOC and light absorption indices, setting WSOC as references.