Dear reviewer:

Thank you very much for your recommendation of our research “Particle size-dependent fluorescence properties of water-soluble organic compounds (WSOC) and their atmospheric implications on the aging of WSOC”. It is very kind of you to give comprehensive and thoughtful advises on the present research. We have carefully addressed all of the comments and explained them as following paragraphs. We modified the language though out the article as well. Thank you again.

**For Specific Comments:**

**1. 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.

**Thank you for your advice.** We have deleted the repeated description in line 124-125, and moved the sentence in lines 126-127 to lines 65-67of Introduction section, they are now read as:

“Fluorescence indices are important subsidiary approach to statistically analysis EEM data (Qin et al., 2018; Yue et al., 2019), which were determined by the chemical structure of pollutants (Andrade-Eiroa et al., 2013a) thus fluorescent indices and partitioning methods were fairish extending to WSOC analysis.”

**2. 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.

**Thank you for your advice.** We are really sorry for so many confusions in the Grey relational analysis (GRA) section. After seriously consideration, we have reconstructed this section, left detailed information on reference and comparison sequences of GRA in the manuscript and moved the definition of GRA method to supplementary information section 1. They are now read as follows.

In manuscript 2.4.3

“Grey relational analysis (GRA) is a part of the grey system theory proposed by Deng (1982), that can be used to describe the relative changes among factors in a system development process. The detailed calculation of grey relational degree (GRD) was explained in supplementary information. Generally, in GRA, a reference line and one or a series of comparison sequences were selected, the GRD between reference line and comparison line indicated the compactness degree. The fluorescence properties of WSOC were considered as a grey system. Two sets of GRA were performed for WSOC of each season. Firstly, considering the evolution of particle sizes as a changing system, larger particles might come from the accumulation and transformation of smaller particle, especially for ultrafine particles. By setting data of particles smaller than 0.26 µm (WSOC concentrations, AFI or UV) as references and particles larger than 0.26 µm as comparisons, their affinities were analyzed by GRA. Secondly, the fluorescence spectra were generated by part of WSOC, setting the WSOC concentrations as references and AFI (or UV) as comparison, the relations between WSOC and AFI for six stage particles were analyzed.”

In SI section 1

“The fluorescence properties present in an EEM spectrum are multifactor triggered results of concentrations, chemical compositions, and even co-existing ions of carbonate species in WSOC. The principle of GRA is to estimate the similarity and degree of the compactness among factors based on the geometric shape of the different sequences. To perform GRA, references and comparison sequences should be selected and converted to the dimensionless format. The grey relational coefficients ξ of the series and grey relational degree are calculated as follows:

(1)

(2)

In which *y* is the reference sequence and *xi* (*i*=1,2,3...) is the comparison sequences, *ρ* is the distinguishing coefficient always set as 0.5, ξ the grey relational coefficients of individual sample of the series, and *GRDi* is the grey relational degree calculated by the average of *ξi* (Qiu et al. 2012).”

**3. 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).

**Thank you for your advice.** We are sorry for the neglections here. Firstly, we have added the peaks of recorded bimodal distributions in former research. Secondly, after carefully reading the differences between “WSOC” and “organic matter”, we realize that it is inappropriate to using “organic matter” in line 167, and replace it with “WSOC”, besides in the reference articles they are size distributions of WSOC, as well. The sentence is now read as,

“Contemporary researchers observed bimodal distribution of WSOC with their two peaks located at 0.8 µm and 7µm, respectively, in Shenzhen, China, and 0.4-0.5 µm and 2-3 µm in Gwangju, Korea (Yu et al., 2016; Huang et al., 2020).”

**4. 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?

**Thank you for your advice.** We add some comparisons of the WSOC/OC in peer works and find that it is hard to conclude why are the WSOC/OC ratios higher in winter than that in summer. but a research on the seasonal variations of WSOC in Georgia, US report that the in the rural sites non-biomass burning WSOC/OC ratios are higher in winter than that in summer, which is accordant with our present research.

“The WSOC/OC ratios were 0.24 to 0.56 in winter and 0.16 to 0.31 in summer, which was lower than the previous records of the polluted period in Beijing, and they were also lower than those of other cities in China (Tian et al., 2014; Wu et al., 2020). Whereas former studied proved that the WSOC/OC ratios tended to be higher in summer than that in winter (Xiang et al., 2017; Qin et al., 2018). Zhang et al., (2012) found similar seasonality of the non-biomass burning WSOC/OC ratios in the urban sites of Georgia, US, but in the rural sites reversed results were detected, which might explain the low WSOC/OC ratios of summer samples in this research. The WSOC/OC ratios were high in fine particles with aerodynamic diameters lower than 1.4 µm and were low in coarse mode (PM2.5-10), which was accordant with former research on clear days in Beijing (characteristic of organic pollution in the size-segregated aerosol Tian et al. (2016)’s results).”

**5. 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.

**Thank you for your advice.** We agree with the reviewer’s opinion that the fluorescence intensities exhibit more distinctions among fine particles and coarse mode particles than the fluorescence peaks, when firstly looking at the spectra. We tended to express that coarse mode particles had their characteristic EEM spectra, and it seems to cause confusion. So we discussed them in the later paragraph by FRI and modified the statements in line 175-176, they are now reading as follows,

“The overall fluorescence peaks of EEM were mainly produced among regions Ⅱ-Ⅴ and the peaks were peak A, peak T, and peak M, which could be categorized as humic-like, tyrosine-like, and oxygenated organic substances, respectively (Qin et al., 2018). The bulk fluorescence properties of WSOC showed both seasonal similarities and distinctions. The fluorophores exhibited increase first and decrease then tendency by having highest intensities in particle sizes between 0.26 to 0.44 µm among two seasons. Although the fluorescence peaks of WSOC were mainly produced at similar regions in winter and summer, their relative abundance were different, further quantitative analysis were taken in the later paragraph.”

**6. 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.

**Thank you for your advice.** We are sorry for the inconsistencies in lines 197-199. We have checked the FRI results in Figure 4 and rephrased the description, they are now showed as following sentences.

“To be brief, in winter, FRI Ⅰ and FRI II (protein-like species) increase with particle size and peaked at coarse mode. FRI Ⅲ and FRI Ⅴ (HULIS) were mainly abundant in fine particles. FRI Ⅳ (microbial related species) showed little variations between particle size 0.26 to 2.5 µm and decreased among 2.5 to 10 µm. In summer, the sum of FRI Ⅰ to FRI Ⅲ showed increase and decreased tendency with peaks value between 0.77 to 1.4 µm, FRI Ⅳ showed reversing variations as FRI Ⅰ-Ⅲ with lowest value among 1.4 to 2.5 µm. FRI Ⅴ didn’t have clear tendency but they showed high portions among 0.26 to 0.44 µm and 0.77 to 1.4 µm.”

**7. 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.

**Thank you for your advice.** The PARAFAC results of summer samples showed an obvious signal of no physical significance. As a fact, we tried 2-7 components PARAFAC analysis, and all results contained this abnormal signal. The spectra were very weak for summer samples, especially for the spectra of large particles at excitation wavelength between 200-230 nm. We tried to avoid the noise by shrinking the start excitation wavelength to 220 nm, however, the results were barely satisfactory. Thus, an unexpected fraction of 17% to 46% of “noise” was depicted in the results. The 3 components result was selected for its TCC values (Tucker congruence coefficient) of all samples were larger than threshold of 0.95 and the half-split validation results determined the model was robust. We added some explanations in the method section of PARAFAC in lines 147-149, they were shown as follows.

“Tucker congruence coefficient (TCC) was determined for each excitation spectrum and emission spectrum results, and a threshold of 0.95 was applied to confirm the spectral congruence. The model was determined by half-split validation.”

**8. 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.

**Thank you for your advice.** Sorry again for the unclear descriptions on the GRA results. As mentioned in question 2, we add the detailed information on the reference and comparison lines of GRA in section 2.4.3 and explains the definition of GRD in SI Section1. Besides, we modified the sentences in section 3.5 and deleted the statements in lines 257-258. Moreover, the data acquirement of secondary organic carbon (SOC) was explained in supplementary information in section 2. We noticed that the GRD of WSOC&AFI shows reversing tendency of decrease first and increase afterwards with minimum values between 0.26 to 0.44 μm, and considering the active accumulation properties of ultrafine particles, we conjectured that secondary processes might affect the fluorescence properties of WSOC, by implementing correlation analysis between GRD and SOC concentrations, strong negative correlation results were found both in winter and summer. We add this thought processes in the manuscript. They are now read as follows.

In 2.4.3

“Grey relational analysis (GRA) is a part of the grey system theory proposed by Deng (1982), that can be used to describe the relative changes among factors in a system development process. The detailed calculation of grey relational degree (GRD) was explained in supplementary information. Generally, in GRA, a reference line and one or a series of comparison sequences were selected, the GRD between reference line and comparison line indicated the compactness degree. The fluorescence properties of WSOC were considered as a grey system. Two sets of GRA were performed for WSOC of each season. Firstly, considering the evolution of particle sizes as a changing system, larger particles might come from the accumulation and transformation of smaller particle, especially for ultrafine particles. By setting data of particles smaller than 0.26 µm (WSOC concentrations, AFI or UV) as references and particles larger than 0.26 µm as comparisons, their affinities were analyzed by GRA. Secondly, the fluorescence spectra were generated by part of WSOC, setting the WSOC concentrations as references and AFI (or UV) as comparison, the relations between WSOC and AFI for six stage particles were analyzed.”

In SI section 1

“The fluorescence properties present in an EEM spectrum are multifactor triggered results of concentrations, chemical compositions, and even co-existing ions of carbonate species in WSOC. The principle of GRA is to estimate the similarity and degree of the compactness among factors based on the geometric shape of the different sequences. To perform GRA, references and comparison sequences should be selected and converted to the dimensionless format. The grey relational coefficients ξ of the series and grey relational degree are calculated as follows:

(1)

(2)

In which *y* is the reference sequence and *xi* (*i*=1,2,3...) is the comparison sequences, *ρ* is the distinguishing coefficient always set as 0.5, ξ the grey relational coefficients of individual sample of the series, and *GRDi* is the grey relational degree calculated by the average of *ξi* (Qiu et al. 2012).”

In SI section 2

“The SOC concentrations were calculated by the method proposed by Castro et al. (1999), as follows:

(3)

The results were used to examine the connections between grey relational degree and secondary processes.”

In section 3.5

Lines 266-268: “By setting WSOC (AFI and UV) of particles <0.26 µm as references, and those of larger particles sizes as comparisons, (a) and (b) in Figure 7 depicted the relations among particle sizes in winter and summer, respectively.”

Lines 273-274: “The relations between WSOC and AFI and average UV (described as UV below) of different particles were showed in Figure 7 (c) and (d), respectively for winter and summer.”

Lines 276-279: “However, clear variations of GRD were observed with particle size increasing. It and the pattern was contrast to those of fluorescence indices. Thus, it was speculated that these variations were resulting from secondary transformations of WSOC, because the fluorescence indices implied chemical transformation might happen during particle size increase.”

**For Technical Corrections:**

1. 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.

**Thank you for your advice.** We notice that the language needs to improve at present and have polished the English of this manuscript by professional help.

1. Line 117: where it reads “Roman unit” it should read “Raman unit”..

**Thank you for your advice and very sorry for the mistakes.** We have corrected the wrong character of “Raman” throughout the article. They are now read as follows,

Line 20: “All EEM data in the present research were in Raman unit (R.U.)”

Figure 3: “Size distributions of WSOC and AFI in winter and summer. AFI was in Raman unit.”

1. Line 211: where it reads “p-conjected” it should read “p-conjugated”.

**Thank you for your advice and very sorry for the mistake.** We have corrected the word “conjected” to “conjugated” in line 211.

“Stokes shift is the energy loss of fluorophore relaxation which might associate with the π-conjugated system and electron cloud density (Lakowicz, 2006).”

1. Line 219: The reference “(Valeur and Berberan-Santos, 2012)” is not accurately listed in the reference list (see line 373).

**Thank you for your advice and very sorry for the mistake.** We have checked the reference list and found that the author order is inversed, it is now corrected.

“the electron in the ground state needs lower excitation energy jumping to the excited state (Berberan-Santos and Valeur, 2012).”

1. 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.

**Thank you for your advice and very sorry for the neglection.** The captions in supplementary information file have all corrected as Figure S# and Table S#, they are quoted as Figure S# and Table S# in the manuscript as well.

1. Line 271: where it reads “indicter” it should read “indicator”.

**Thank you for your advice and very sorry for the mistake.** We have corrected the word in line 271.

“GRD between WSOC and AFI could serve as an indicator of secondary formation in present research.”

1. Figure 1 is not mentioned nor discussed in the manuscript, although it is presented at the end as being part of the manuscript.

**Thank you for your advice and very sorry for the mistake.** We are tending to show the sampling site information in Figure 1 and neglected to refer to it, we add “The air quality index weighted 72h backward trajectories during sampling period were exhibited in Figure 1.” in method section 2.1

1. 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.

**Thank you for your advice.** We add “Em” in horizontal axis and “Ex” in vertical axis, representing emission and excitation, respectively, in Figure 2

**一群不同颜色的盒子

中度可信度描述已自动生成**

1. Figure 3 caption: where it reads “Roman unit” it should read “Raman unit”.

**Thank you again for your advice.** We have corrected the wrong character of “Raman” in the Figure 3 caption. They are now read as follows,

Figure 3: “Size distributions of WSOC and AFI in winter and summer. AFI was in Raman unit.”

1. 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”.

**Thank you for your advice and we are sorry for missing units in Table 1.** The chemical concentrations are all in units of mg∙m-3. We corrected the wrong word of deviations in the caption as well.

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

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Species (mg∙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 |
| NO3- | 2.08±1.43 | 9.42±8.46 | 5.64±5.61 | 7.37±8.9 | 6.72±9.44 | 1.92±3.28 |
| SO42- | 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 |
| NH4+ | 1.05±0.57 | 2.9±2.15 | 2.05±1.82 | 2.4±2.77 | 1.67±2.18 | 0.44±0.67 |
| Mg2+ | 0.01 | 0.01 | 0.02±0.01 | 0.05±0.04 | 0.18±0.21 | 0.08±0.09 |
| Ca2+ | 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 |
| NO3- | 0.48±0.44 | 3.5±3.32 | 1.37±1.35 | 1.04±0.86 | 4.76±4.22 | 1.49±1.37 |
| SO42- | 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 |
| NH4+ | 0.79±0.53 | 2.56±1.99 | 1.18±1.02 | 0.63±0.55 | 0.5±0.46 | 0.1±0.08 |
| Mg2+ | 0.01 | 0.01 | 0.01 | 0.02±0.01 | 0.12±0.08 | 0.05±0.03 |
| Ca2+ | 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 |

1. Please, update the year of the reference Almeida et al. (Environ. Sci. Technol. 54, 1082-1091), since it was published in 2020.

**Thank you for your advice.** We have modified the publish year of reference Almeida et al. (2020) both in the manuscript and reference list. They are now read as follows.

Line 30: “WSOC is the active fraction of organic particles, comprises 10% to 80% of organic compounds (Qin et al., 2018; Almeida et al., 2020; Cai et al., 2020).”

Reference: “Almeida, A. S., Ferreira, R. M. P., Silva, A. M. S., Duarte, A. C., Neves, B. M. and Duarte, R.: Structural features and pro-inflammatory effects of water-soluble organic matter in inhalable fine urban air particles, Environ Sci Technol, 54, 1082–1091, <https://doi.org/10.1021/acs.est.9b04596>, 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 studies are the authors referring to in Figure S2(b) and S2(c).

**Thank you very much for your advices.** We are sorry for the neglection of not emphasizing the supporting information in manuscript. The supplementary information has all quoted in the manuscript now.

**Lines 210-211:** “Some other fluorescence indices were listed in Table S1.”

Table S 1 The grey relational degree of WSOC and AFI between six particle sizes.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Pearson correlation | | | Grey relational analysis | | |
|  | µm | a | b | c | a | b | c |
| Winter | 0.26 | 1 | 1 | 0.129 | 1.000 | 1.000 | 0.950 |
|  | 0.44 | 0.947\*\* | 0.429 | 0.020 | 0.883 | 0.824 | 0.871 |
|  | 0.77 | 0.787\*\* | 0.724\*\* | 0.335 | 0.833 | 0.879 | 0.933 |
|  | 1.4 | 0.591\* | 0.399 | 0.596\* | 0.766 | 0.830 | 0.928 |
|  | 2.5 | 0.637\* | -0.141 | 0.875\*\* | 0.771 | 0.779 | 0.974 |
|  | 10 | 0.461 | 0.567\* | 0.664\* | 0.808 | 0.840 | 0.982 |
| Summer | 0.26 | 1 | 1 | 0.854\*\* | 1.000 | 1.000 | 0.930 |
|  | 0.44 | 0.990\*\* | 0.943\*\* | 0.975\*\* | 0.656 | 0.700 | 0.853 |
|  | 0.77 | 0.956\*\* | 0.920\*\* | 0.874\*\* | 0.612 | 0.720 | 0.929 |
|  | 1.4 | 0.946\*\* | 0.825\* | 0.687 | 0.672 | 0.720 | 0.921 |
|  | 2.5 | 0.647 | 0.827\* | 0.225 | 0.645 | 0.750 | 0.922 |
|  | 10 | 0.793\* | 0.635 | 0.739\* | 0.577 | 0.641 | 0.948 |

**Lines 184-186:** “The aggregated fluorescence spectra of all size-segregated samples resembled the spectra of TSP and PM2.5 in Figure S1 with some differences in details (Chen et al., 2016a; Qin et al., 2018).”

(a)

 

(b)



(c)

图表, 表面图

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Figure S1 EEM spectra of present research and other studies. (a) The integrate EEM spectra of six-stage particles for winter and summer. (b) and (c) were the fluorophores in Chen et al.(2016) and Qin et al. (2018).

**Lines 189-190:** “the spectra of fine particles saw wide overlaps with that of PM2.5 in Figure S2 (matched with anthropogenic sources and secondary sources of our study)”

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Figure S2 The EEM spectra of coarse mode particles in region Ⅳ were accordant with the fluorescence regions of biogenic sources.

Line 232: “Size-segregated stokes shift, average SS and ηSS>1.1 were plotted in Figure S4 and Figure S5.”

图表, 直方图

描述已自动生成

Figure S4 Stokes shift of fluorescent WSOC in different particle sizes. Hydrophobic fractions tend to have higher intensity in stokes shifts >1.2, possibly as a result of the larger scale of the π conjugated system or higher π-electron density. In contrast, hydrophilic contents (such as polysaccharides) usually have lower aromaticity and, hence, smaller π-conjugated systems.



Figure S5 Some fluorescence indices that were not presented in our article. (a) and (b) were the size distribution of average fluorescence intensity of SS (purple bars) and ηSS>1.1 (orange lines) for winter and summer, respectively.