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Reply on RC2

Juanjuan Qin et al.

Author 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-AC2>, 2021

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". We have carefully addressed all comments and corrected them in turn. We also have checked through the language. The details are as follows, we also put the replies and supplementary information in the following .zip file. Really thank you again.

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". We have carefully addressed all comments and corrected them in turn. We also have checked through the language. The details are as the following paragraph.

Special comments:

- Line 93: It seems unnecessary to have another repeated "were" at the end of this line.

Thank you for your advice. We checked the article and added "that" before "were" to lead a clause after filters. They are now shown as follows.

"All samples were collected by quartz filters (Whatman) that were prebaked for 5 hours (500°C) and wrapped by aluminum foil stored at -20°C after sampling."

- Line 101: It should be "adapted" rather than "adopted".

Thank you for your advice. We are sorry for the mistake and have corrected it in the sentence.

“the thermal evolution protocol IMPROVE (Interagency Monitoring of Protected Visual Environments) was adapted.”

- Line 115 to 116: Are these parameters for EEM sampling? Please make it clear what are they refer to.

Thank you for your advice. We are sorry for the unclear description in lines 115 to 116. They are now modified as follows.

“To be brief, the wavelength ranges **of EEM** are 200-400 nm for excitation and 250-500 nm for emission with 5 nm intervals (Qin et al., 2018).”

- Line 155: A verb is missing after “ξ”

Thank you for your advice. We are sorry for the carelessness. We have corrected it, and the description of grey relational analysis has moved to supplementary information now.

“ξ is the grey relational coefficients of individual sample of the series”

- Line 181-185: The sentences of this paragraph are hard to read because of lacking the main logic board. Try to describe the seasonality and the size distribution of SFI separately, rather than mixing them.

Thank you for your advice. We are sorry for the confusing descriptions in lines 181 to 185. We have rearranged the logic of this paragraph, by draw primary attention to the fluorophores description, and then describe the seasonal similarities and distinctions of EEM, separately. They are now described as follows.

“The size-segregated EEM spectra of winter and summer WSOC were depicted in Figure 2 (a) and (b), their fluorescence intensities of per unit WSOC (SFI) were plotted in (c) and (d), respectively. The overall fluorescence peaks of EEM were mainly produced among regions □-□ 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 the 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 was different, further quantitative analysis was taken in the later paragraph. The aggregated fluorescence spectra of all size-segregated samples resembled the spectra of TSP and PM_{2.5} in Figure S1 with some differences in details (Chen et al., 2016a; Qin et al., 2018).”

- Line 196-200: Line 196 to line 198 were mainly about the size distributions of FRI $\hat{\alpha}$ \times , however, the description of “FRI $\hat{\alpha}$ ϕ and FRI $\hat{\alpha}$ \times (HULIS) were the most abundant two fluorophores rich in fine particles.” Seems incongruent with the context. Moreover, what is the purpose of adding the reference of Huang et al., (2020) found similar size distribution of protein and HULIS by isotopic method at the end of this paragraph?

Thank you for your advice. We notice that the description of FRI was confusing in lines 196 to 200. The reference of Huang et al., (2020) is unnecessary as well. Thus, the paragraph has been reorganized by separately describing FRI tendencies of winter and summer and the reference is deleted. They are now showed as follows.

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

- Line 243-246: Similar to the former issue, the sentences were uncombined with each other. So the intention of each description is confused. Why do you propose a HULIS1/HULIS2 ratio for winter results? If HULIS1 (or 2) implies a different oxidation state of HULIS, the last sentence should be brought forward.

Thank you for your advice. We checked the phrases in the context and find it is confusing in lines 243-246, because of lacking an explanation on the results of HULIS1/HULIS2 ratio. We add extended the sentence at the end of this paragraph. They are now showed as follows.

“HULIS-1 and HULIS-2 were defined in winter, their ratios HULIS-1 / HULIS-2 were low in ultrafine particles ($<0.26\mu\text{m}$) and coarse mode, and high in fine particles with an aerodynamic diameter ranging between 0.44 to 2.5 μm . HULIS-2 was likely to be freshly emitted fluorescent WSOC and HULIS-1 exhibited fluorescent characteristics of oxidized HULIS (Vione et al. 2019), the low HULIS-1 / HULIS-2 ratios in ultrafine and coarse mode particles might because of more freshly emitted sources in WSOC.”

- Section 3.5: If it is just as my comprehension, the GRD is a factor of reflecting relations between two factors, why does the author use grey relational analysis rather than correlation analysis?

Thank you for your question. The application of GRD in the present research is a result of comparison. We performed both correlation analysis and GRD between WSOC and AFI, but the results were not significant for correlation, on this occasion, the GRD results were applied. As depicted in SI Table S1 the results showed that AFI (or WSOC) between particle sizes had great correlation, it is understandable because the size-segregated samples were collected simultaneously. However the correlations between AFI and WSOC were not significant for most particles, which were out of the expectation, besides, the AFI and WSOC didn't fit with any distribution curves as well. In fact, the AFI was the quantified fluorescence property of WSOC, so we tried GRD analysis and the results suggested good connections between AFI and WSOC. We have put the comparison in the supplementary information Section 4.

“Section 4 Comparison of Pearson correlation analysis and grey relational analysis (GRA) results

In the manuscript file, we performed grey relational analysis to uncover the underlying connections between WSOC and AFI. Since the fluorescence was generated by part of WSOC, it was conjectured that the AFI and WSOC could be present by mathematical method. We tried the correlation analysis firstly in Table S 1. The WSOC (and AFI) of particles <0.26 μm significantly correlated with that of larger particles both in winter and summer. However, the relations between WSOC and AFI were not significant, especially in winter, which was out of the expectation. A possible explanation was that the miscellaneous WSOC in different particles sizes might lead to fortuitous fluorescence intensities.

GRA could reflect the fellowship of factors to the reference line. The relations between WSOC and AFI (Table S 1 (c) on the right) were strong in both seasons. Besides, the GRD variation patterns of decrease first and then increase for six particle size stages were just in contrast to that of humification factors, $\eta_{\text{WH}>320}$, and other fluorescence indices. GRD was negatively correlated with SOC ($p < 0.01$).

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

		Pearson correlation	Grey relational analysis
	μm	a	b
Winter	0.26	1	1
	0.44	0.947**	0.429
	0.77	0.787**	0.724**

	1.4	0.591*	0.399
	2.5	0.637*	-0.141
	10	0.461	0.567*
Summer	0.26	1	1
	0.44	0.990**	0.943**
	0.77	0.956**	0.920**
	1.4	0.946**	0.825*

2.5 0.647 0.827*

10 0.793* 0.635

** Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

- GRA was performed by setting WSOC of 0.26 μm as references and the rest of particle sizes as a comparison.
 - GRA was performed by setting AFI of 0.26 μm as references and the rest of particle sizes as a comparison.
 - GRA was performed by setting WSOC of each particle size as references and corresponding AFI as a comparison."
-
- Line 191: The author state that "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." This "indicating" may not be easily deduced here, and I noticed that these inductions are discussed in lines 282 to line 292, so the description in line 191 can be saving for the later paragraph.

Thank you for your advice. We agree with your perspective that the deduction is inconsequence, and we have deleted it in line 191, they are now shown as follows.

"Our unpublished research found that the AFI/WSOC ratios were lower than 0.2 for anthropogenic source samples."

- Line 293: The first sentence shows weak leadership for this paragraph, it also shows little connections with later context

Thank you for your advice. We add a leading sentence to start the paragraph and reconstruct the sentence order. They are now shown as follows.

"The EEM spectra of WSOC showed size-dependent variation. The size distributions of AFI kept in step with WSOC concentrations and showed monomodal distribution in winter and bimodal distribution in summer peaked in particle sizes between 0.26 to 0.44 μm (Figure 2 (a) and (b)). Accordant with former research, the fluorescence intensities were positively related to WSOC concentrations both in winter and summer (Spearman's $r > 0.8$,

$p < 0.001$) (Qin et al., 2018; Chen et al., 2019). The EEM spectra of size-segregated WSOC mainly exhibit among regions □-□ and they blue-shifted with particle size increase (0.44 to 10 μm), which could be obviously observed from the EEM spectra and the increase of FRI1 and FRI2 and decrease of FRI3 and FRI5. These phenomena are explained below.”

- Line 315 to 318: The conjectured sources of HULIS are not closely related to the former context.

Thank you for your advice. We realized the abrupt deduction on sources of WSOC is reasonable, thus the sentence is deleted now. The context is shown as follows.

“In winter, the wavelength of HULIS-1 was slightly higher than HULIS-2 and their EEM spectra were similar to the PARAFAC results of highly oxygenated species and less oxygenated species in Chen et al (2016b)’s study on the chromophoric WSOC. Only HULIS-1 was distinguished in summer and it could be allocated to highly oxygenated species.”

Minor issues:

1. The tense form should be unified

Thank you for your advice. We have corrected the tense in lines 108, 282, and 306.

“The extracts **were** then sifted by a 0.22 μm membrane filter to remove impurities (Xiang et al., 2017).”

“GRD **was** strongly negatively correlated with estimated secondary organic carbon (SOC)”

“The specific fluorescence area was widened in the ambient sample and thus having a higher AFI/WSOC ratio when WSOC concentrations **were** at a comparable level.”

2. Check the abbreviations and capitalized letters throughout the article, some of them are in the wrong format.

Thank you for your advice. We have corrected abbreviations and capitalized letters in the article.

3. Some of the definite or indefinite articles are missing.

Thank you for your advice. We have corrected the definite or indefinite articles in lines 107, 118, 249, 340, and 351.

“A quarter of **the** filter sample was ultrasonically extracted twice with 5 ml ultrapure water each time and mixed up after extraction.”

“To be brief, **the** wavelength ranges of EEM were 200-400 nm for excitation and 250-500 nm for emission with 5 nm intervals (Qin et al., 2018).”

“C2 was **a** protein-like component”

“which confirmed the application of GRD value as an indicator of **the** aging state of WSOC.”

“the application of **the** EEM method still faces many uncertainties.”

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-465/acp-2021-465-AC2-supplement.zip>