# Authors' Response to Referee #2

**Review of** "Measurement Report: Optical Characterization, Seasonality, and Sources of 2 Brown Carbon in Fine Aerosols from Tianjin, North China: Year-round Observations" by Dong et al.

**Review prepared by**: Dr. Taveen Kapoor and Dr. Rajan Chakrabarty

This study reports the optical properties of water-soluble and methanol-soluble brown carbon (BrC) in fine aerosols ($PM_{2.5}$) sampled over a year in Tianjin, North China. The authors employ a relatively new BrC characterization technique, three-dimensional fluorescence spectroscopy measure the seasonal variations in optical properties of BrC and their chromophore constituents. They evaluated the relationship between BrC and chemical composition in $PM_{2.5}$ and the possible sources of BrC over the sampling region. Overall, the manuscript needs revisions before it can be considered for publication as a measurement report in ACP.

Dear Dr. Taveen Kapoor and Dr. Rajan Chakrabarty,

Thank you very much for your critical reading of the manuscript, appreciation of our work and comments/suggestions, which helped to further improve the quality of the MS. The MS is revised accordingly, and our point-by-point responses to all the comments are provided below. Please see the revised MS for details of the revisions.

**Major comments:**

1) The novelty of this study is in the use of relatively new characterization techniques of BrC. Because of the relative newness, there is a need for justification and more context as to why the authors chose this technique over previously established ones.

The excitation-emission matrix technique is used to understand the fluorescence spectra of organic carbon compounds. The reason for studying the fluorescence of organic compounds is not clear. Also, a range of expected values for the different chromophore groups before indicating the measured values will help the reader to interpret the results better. For example, (L405) a fluorescence index < 1.4 indicates higher aromaticity but later it is said that BrC contain mainly aromatic compounds (L415) despite values of up to 2.23 (L412).

The PARAFAC analysis is used to identify chromophore groups. Three groups have been identified, but information about why there are three groups and not more (or less) has not been mentioned. The selection procedure should be mentioned.

Information on how the humidification index, δ15NTN and δ15CTC are calculated is missing from the manuscript.

***Response:*** Following the referees' comment, we provided the justification/purpose of the use of three-dimensional fluorescence spectroscopy and extraction of the water-soluble and water-insoluble fractions of BrC in the introduction section in the revised MS (see Page 2, Line 14 to Page 3, Line 10).

The reason for the use of EEM technique in this study is to identify the fluorophores and thus the molecular composition of BrC. This point has been clarified in the revised MS introduction section (see Page 2, Lines 27-44). Also provided the reference values of FI, BIX and HIX in Section 3.3.1

of the revised MS.

We clarified the procedure followed to choose 3 fluorophores in PARAFAC analyses in the revised MS (see Section 3.3.2).

We have added the calculation method of the humidification index in the revised MS（see Section 2.3). Since the correlations with isotope data are not significant, we removed this part in the revised MS to avoid any ambiguity.

2) While considerable effort has been put into generating and summarizing the data, the study fails to connect the measurements to provide a coherent picture from the results of the various measured properties (BrC concentrations, absorption, fluorescence, fluorescence, humidification, etc.). Some attempts are made to correlate the two sets of properties using linear correlations, but these do not necessarily lead to consistent results. For example, L302 says that biomass burning is a major source of BrC in the autumn months, but L409 says that terrestrial organic matter is the major source. These apparent contradictions make the manuscript difficult to understand, which may be avoided by providing appropriate context to the measurements being made, as highlighted in the previous comment. A discussion of the interrelationships between the measured properties, with a special emphasis on the new findings from the new measurements will be of great benefit to the scientific community.

***Response:*** Following the reviewer's suggestion in this and previous comment, we revised the MS with substantial improvement in both introduction and results and discussion. Also, we made it clear that the BrC in Tianjin is mainly contributed from mixed (biomass burning and coal combustion) sources based on the fluorescence indices data (see section 3.3.1).

3) L400 and L415 make strong statements about aging of BrC based on the measured humidification index and fluorescence index. The authors are requested to substantiate their claims, as arguments do not seem convincing in their present form, i.e., without any direct measurements of aging.

***Response:*** Following the reviewers' suggestion, we completely revised this section and discussed the possible sources (by tone downing about aging) based on the humidification index (BIX) and fluorescence index (FI) results and their reference values available in the literature.

4) A lot of information provided in the figures and tables may be moved to the supplementary material as the information they provide and the text discussing them is disproportionate. Figures 3, 4, and 11 show scatter plots amongst various measured properties. But most of the discussion on these figures is around just the correlation coefficients and not the actual values (which are summarized in Table 1 already). The authors may consider moving some of the figures to the supplementary material or use a more concise figure to summarize the same information. Similarly, Figures 1, 5, and 7 show time series but the discussion is restricted to seasonal variations.

Table 1 reports the mean and standard deviations of the measured values and the range of values. Providing both sets of information seems redundant, and one set may be moved to supplementary material. Some of the information in these tables is also repeated in Figure 2.

Figure 8 has two kinds of plots, but the set of line plots is not labelled, and it is unclear what they represent. These likely show the emission and excitation spectra, which are already shown in the

figure set of three-dimensional figures above.

***Response:*** We agree with the reviewers' opinion. Figures 3, 4, 6 and 11 of previous version of the MS are moved into the supplement of the revised MS.

As suggested, only mean and standard deviation data is kept in Table 1 and the ranges and median are provided in the supplement to make the full summary available for the reader in the revised MS. The annual summary and temporal variations are described and discussed, in addition to the seasonal variation in the revised MS. To avoid repetition of the data, Figure 2b-d panels are removed in the revised MS.

Yes, the linear plot in Figure 8 (Fig. 5 in the revised MS) shows the excitation emission wavelengths of the different fluorophore groups. We added annotations and kept in the revised MS to make the volumes more clear to the reader.

5) Differences are reported between the parameters measured during the different seasons, but the statistical significance of the differences are not discussed. These should be added to make the discussion more robust.

Since the authors are checking for associations between the variables, the R value should be reported instead of the R2 value (used as a measure for model predictability). Also, the significance of the correlations reported in L487-489 do not seem correct (R2= 0.01/0.06, having significant correlations, $p < 0.05$). These need to be re-checked.

***Response:*** We improved the discussion about fluorescence indices and other parameters significantly but limited the discussion on correlations between them, because the obtained correlations are not strong (just weak to moderate). We re-checked the *p*-value and found that they are statistically significant ($p < 0.05$), despite weak to moderate correlations, probably due to large dataset.

**Minor comments:**

- Abstract could include context on the need for the measurements.

  ***Response:*** We added the context of need of this study in abstract of the revised MS (see Page 1, Lines 10-12).

- L120: "The blank filters were left in the filter hood for 10 minutes" - not clear what this means and why this was done.

  ***Response:*** We collected the filter blanks to correct the results from the procedural errors / contamination, by placing the filter in hood for 10 mins without turning on the pump. We made it clear to the reader in the revised MS (see Page 3, Lines 42-44).

- L125: OC and EC are not spelled out before first use here.

  ***Response:*** We added the full form of OC and EC in the revised MS (see Page 4, Line 5).

- L120: Should be "thermal-optical carbon analyzer".

  **Response:** We corrected it in the revised MS (see Page 4, Line 8).

- L144: How was the concentration of WSOC determined? In the equation it is implied that all the organic compounds that are water insoluble OC are methanol soluble. While this

may be a fair assumption, the authors may acknowledge that there may be some chromophores that are also methanol insoluble (Shetty et al., 2019).

***Response***: The concentration of WSOC was determined using a total organic carbon analyzer, with the specific experimental method described in our previous paper (Dong et al., 2023;Wang et al., 2019). We noted this in the revised MS (see Page 4, Lines 5-11).

We agree with the reviewers' view that all water-insoluble organic compounds are not soluble in methanol. We noted this point in the revised MS to make our assumption fair (see Page 4, Lines 29-31).

- L159: Please provide a reference for this equation.

  ***Response:*** We cited the references in the revised MS (see Page 5, Line 4).

- L170: Line is unclear and needs to be rephrased.

  ***Response:*** We modified this expression in the MS (see Page 5, Lines 15-17).

- L174: 'C' is a constant and not the concentration of extract"

  ***Response:*** We regret for this mistake and corrected it as "a composition-dependent constant" in the revised MS (see Page 5, Line 19).

- L185: Please provide a reference for the equation.

  ***Response:*** As suggested by the reviewer, we cited references for the equation in the revised MS (see Page 5, Line 30).

- L202: PARAFAC and SOLO are not defined before first use here. Please also provide a link or reference to the code here.

  ***Response:*** We defined them in the introduction in the revised MS (see Page 2, Lines 27 and 33-34). Also, noted the SOLO model in the revised MS (see Page 6, Line 4).

- L214: What is basis of selecting the values of constants in the in the equation to calculate the SFE? Also, a value for backscatter coefficients is provided but is not present in the equation. Why is the mass scattering efficiency being ignored?

  ***Response:*** We chose the values of constants in the equation according to the previous literature (Chen and Bond, 2010;Deng et al., 2022;Tian et al., 2023), and the scattering efficiency is ignored, considering that BrC impacts the radiative effects by light absorption only. We noted this point in the revised MS (see Page 6, Lines 24-26).

- L230: Comparison of measured absorption those reported at sites in the USA, but these are likely to be influenced by very different source. There are several other studies reporting BrC absorption in areas with biomass and coal combustion sources that may offer a fairer comparison.

  ***Response:*** We agree with the reviewers' view. We compared the data from USA as well in order to assess potential influence from fossil fuel combustion emissions, in addition to biomass burning and coal combustion. We have improved the discussion substantially by including the absorption coefficient (Abs) of brown carbon from different sources in the revised MS (see Page 7, Lines 12-46).

- L254: "...absorption coefficient of WI-MSBrC was always greater than that of WSBrC across the shorter 256 wavelength..." - this is not true for spring, summer, and autumn months!

  ***Response:*** We corrected it by specifying the particular seasons and wave length range in the revised MS (see Page 8, Lines 10-14).

- L303: Is there a known source of biomass burning during the autumn season that can corroborate this result?

  ***Response:*** No, there is no specific known source of biomass burning in these seasons. However,our other study on $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$, as well as the seasonal variation of $K^+$ and $Cl^-$ concentrations indicated that biomass burning and fossil fuel (coal) combustion are the major sources of carbonaceous aerosols in autumn and winter. We cited this reference in the revised MS (see Page 9, Lines 10-13).

- L308: not clear what is meant by "dust in spring"

  ***Response:*** To make the discussion clear here, we modified it and removed that (dust) phrase in the revised MS (see Page 9, Lines 18-22).

- L330: The finding that AAE_WSOC and AAE_WI-MSOC are similar is a bit surprising since the water insoluble portion is expected to have a stronger absorption and weaker wavelength dependence (please see Saleh, 2020, and references therein).

  ***Response:*** Yes, Saleh et al. (2020) has reported four categories of brown carbon and their extraction efficiency in water and organic solvents and the differences in AAE (Saleh, 2020). It has also been reported that the AAE values of the water extract are greater than those of the acetone and methanol extracts (Shetty et al., 2019), and interpreted that the extraction efficiency of polycyclic aromatic hydrocarbons from methanol or other organic solvents is higher than that from water, leading to a higher absorption at longer wavelengths in the methanol extract and therefore a lower AAE value.

  However, our extraction procedure is different (first with water and then with MeOH) from that of Saleh et al. (2020). We re-calculated and re-checked the data and found that the reported data here is correct. In fact, Li et al. (2020) also reported the mean value of AAE for BrC dissolved in acetonitrile in Xi'an is 6.04, while that for water-soluble brown carbon is 5.11 in winter (Li et al., 2020).

- L358: The results demonstrate the radiative forcing from BrC absorption. Whether or not they contribute significantly to radiative forcing depends on the overall radiative forcing magnitude – please rephrase. The same also needs to be edited in the abstract and summary sections.

  ***Response:*** We modified the expression by changing it to "UV-Vis range" in the revised MS (see Page 13, Lines 22-25).

- L373: It is not clear how a comparison between water soluble and water insoluble would lead to seasonal differences in the remaining part of the sentence.

  ***Response:*** No, it was a language error. In fact, we removed that text, focusing on the discussion of fluorescence indices in this section of the revised MS.

- L376: “more water-soluble chromophores” - relative to what?

  ***Response:*** We removed this text in the revised MS.

- L382: Was SOA calculated or was this a finding from a previous study? Please provide details or a reference.

  ***Response:*** We removed this text in the revised MS.

- L392: Seems to be a typo here – please rephrase.

  ***Response:*** We fully modified this section and took care for any language errors in the revised MS.

- L416: What are terrestrial organics?

  ***Response:*** We used this phrase, terrestrial instead of anthropogenic, based on the terminology given in the literature (Birdwell and Engel, 2010), which refer here is “not biological and microbial” derived organics. We mentioned it including the reference values of indices in the revised MS (see Page 14, Lines 13-21).

- L443-445: What is meant by core consistency and unexplained residues?

  ***Response:*** When SOLO data processing software performs PARAFAC analysis, it needs to evaluate the accuracy of model analysis results through core consistency, which is a parameter configured by the software itself. When we input the number of types of fluorophores, the higher the core consistency, the higher the accuracy of model analysis, and no other residues are not resolved. In other words, it is the percent of variance explained in the data set.

  The unexplained residue refers to the missing fluorescent chromophores. When the core consistency reaches 100%, the resolved chromophores together constitute 100% of the mixture, and no other compounds are left out.

- L455: PLOM not defined before its first use.

  ***Response:*** We defined it in the revised MS (see Page 18, line 16).

- L471, 475: Please provide a reference.

  ***Response:*** We determined the chromophore types according to the excitation and emission wavelengths summarized in Table 2, and the relevant references have been listed in Table 2. We cited the Table 2 here in the revised MS (see Pages 18 & 19, Lines 17 & 2, respectively).

- L278: SOC not defined before its first use.

  **Response:** We defined it in the revised MS (see Page 20, Line 9).

- L554: It is unclear how a similar AAE of WS and WI BrC implies that that the more polar.

  ***Response:*** We removed that phrase in the revised MS.

- L563: What is meant by color clusters?

  ***Response:*** We corrected it to fluorophores in the revised MS (see Page 21, Line 14).

- L567: reference?

***Response:*** Since it is not a concluding point here, we removed it in the revised MS.