Journal: ACP

Title: "Molecular compositions and optical properties of dissolved brown carbon in smoke particles illuminated by excitation-emission matrix spectroscopy and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis"

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Dear Reviewer:

We were so sorry about the inconvenience because of we provided the revisions which were based on the revised manuscript not the marked. So, we resubmit it. Please see the latest responses.

Thank you so much for your critical suggestion! We appreciate the anonymous reviewers for their helpful comments and detailed language corrections on our manuscript. We considered each comment carefully, and point-by-point responses to each reviewer's comments are listed below. Moreover, the modifications in the revised manuscript are marked in blue. Please see the manuscript for details.

Reviewer#1

This manuscript describes measurements of the fluorescence of atmospheric WSOC, classifying it into separate types using parallel factor analysis, and attempting to correlate these types with high-resolution mass spectrometry data. The measurements of a very good technical quality and will be of interest to those who study aerosol fluorescence, organosulfates, or organonitrates. The work will also support future source apportionment of aerosol by fluorescence measurements. However, some interpretations, conclusions and assertions are not adequately supported by the data presented. For this reason, major revision of the discussion of the mass spectrometry results (and the second half of the abstract) is needed. The work is potentially

publishable after addressing the comments below.

Response: Thanks for your recognition of our work. Due to FT-ICR MS only can provide the molecular composition, not chemical structure. So, the possible structure we gave may be doubtful just dependent on these existing data. According to the comments gave of you, we decided to delete the part of mass spectra and rewrote it.

We added the new parts in sections 3.3 and 3.4 (lines 504-953) in the revised manuscript, which mainly discussed the molecular composition in different solutions of various sources and determined their unique characteristics among these sources. Additionally, some modifications and discussions were added in the abstract, introduction, and conclusion in the revised manuscript.

The citation of previous work in the manuscript has some gaps. For example, it is odd that the manuscript comments on similarities between HULIS and terrestrial humic acids (line 70) without citing the authoritative review on this subject by Graber and Rudich.(1) One A. Laskin paper in the Results section is erroneously cited as "Alexander et al. 2009".

Response: Many thanks for your suggestions. We have added the paper in the text and revised the erroneous cite.

Please see line 108 and line 653.

The authors fundamentally assume that a correlation between a fluorescent component and a set of MS formulas (like "CHON") means that they are determining the molecular compositions of the fluorescent molecules. This may not be true. Molecules with high electrospray ionization efficiencies are not necessarily the same as those with high absorbance or fluorescence. It would therefore be fortuitous if major ESI ions were the

same ones responsible for observed absorbance or fluorescence, without extensive and identical chromatographic separation before each technique.(2, 3) Furthermore, it has been shown that many non-polar brown carbon components in biomass burning aerosol cannot be ionized by ESI.(3) The manuscript should discuss these issues.

Response: Thanks for your suggestions. Previous studies used the correlation analysis to speculate the chemical structures of fluorescent components (Chen et al., 2016a,b; Stubbins et al.,2014). Chen et al., (2016a,b) conducted the correlation analysis of the relative intensities of ion groups (including C_x, CH, CHO_1, CHN, CHO_1N, $CHO_{>1}N$, CS, CO, HO,CO_2, $C_2H_4O_2^+$) in the HR-AMS spectra and relative contents of the fluorescent components. They also found the relationships between relative contents of fluorescent components and relative intensities of chemical groups (C-H, $C-NH_2$, C-OH, $C-ONO_2$, C=O, COOH) in the FT-IR spectra. Stubbins et al., (2014) conducted a Spearman's correlations between relative intensities of FT-ICR MS peaks and the relative intensities of fluorescent components and speculated the possible structure of chromophores. These studies are the basis of our research. However, as you said, this method may be inadequate without chromatographic separation. Thus, we rewrote this part of mass spectra.

The new revised parts were presented in section 3.3-3.4. We discussed the difference in molecular composition in the different sources and determined the factors that affected the light absorption capacity in the source-emission aerosols.

Reference:

Chen, Q., Ikemori, F., and Mochida, M.: Light Absorption and Excitation-Emission Fluorescence of Urban Organic Aerosol Components and Their Relationship to Chemical Structure, Environ. Sci. Technol., 50, 10859-10868, https://doi.org/10.1021/acs.est.6b02541, 2016.

Chen, Q., Miyazaki, Y., Kawamura, K., Matsumoto, K., Coburn, S., Volkamer, R., Iwamoto, Y., Kagami, S., Deng, Y., Ogawa, S., Ramasamy, S., Kato, S., Ida, A., Kajii,

Y., and Mochida, M.: Characterization of Chromophoric Water-Soluble Organic Matter in Urban, Forest, and Marine Aerosols by HR-ToF-AMS Analysis and Excitation-Emission Matrix Spectroscopy, Environ. Sci. Technol., 50, 10351-10360, https://doi.org/10.1021/acs.est.6b01643, 2016.

Stubbins, A., Lapierre, J. F., Berggren, M., Prairie, Y. T., Dittmar, T., and del Giorgio, P. A.: What's in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada, Environ. Sci. Technol., 48, 10598-10606, 10.1021/es502086e, 2014.

The interpretation of functional groups from the ESI-MS data should be explained more clearly (line 376). The authors try four different methods (Tables S9 – S16), but it is difficult to understand the differences between them.

Response: *It is very sorry for making a mistake for explaining Table 2 as Figure 2. The classification method as follows: The introduction of functional groups was referred to the study of Chen et al., (2016b) and the ionized properties of ESI-. Left of Table 2 showed the classified method by the functional groups (such as CHO_1, $CHO_{>1}$, $CHO_{\leqslant 2}N$, and $CHO_{>2}N$ and so on), and the right showed the method according to the Ven Krevelen diagram (Patriarca et al., 2019) that made a partition based on their molecular distribution, such as lignin-like, protein-like, lipid-like, and carbohydrates and so on. They were the two classified methods we used. In addition, the potential BrC components could be identified based on the research of Lin et al., (2018) which excepted these compounds that had a low unsaturation degree. Thus, before classification, according to whether determine the potential BrC or not, we obtained four classified methods to build the relationship between fluorescence and molecular composition for further speculating the possible structure of chromophores. Table S9-S16 presented all the results of correlation analysis between the relative intensities of ion groups of FT-ICR MS and the relative abundances of fluorescent components. Finally, we chose the best method of which these functional groups exhibited a significant correlation with these fluorescent components.*

In the new revised part of this manuscript, we attempted to build the relationship between the light absorption capacity of dissolved BrC with the corresponding structures (such as DBE, O/C, MW and so on). The results were presented in Section 3.4 (line 892-953).

Reference:

Chen, Q., Ikemori, F., and Mochida, M.: Light Absorption and Excitation-Emission Fluorescence of Urban Organic Aerosol Components and Their Relationship to Chemical Structure, Environ. Sci. Technol., 50, 10859-10868, https://doi.org/10.1021/acs.est.6b02541, 2016.

Patriarca, C., Bergquist, J., Sjoberg, P. J. R., Tranvik, L., and Hawkes, J. A.: Online HPLC-ESI-HRMS Method for the Analysis and Comparison of Different Dissolved Organic Matter Samples, Environ. Sci. Technol., 52, 2091-2099, https://doi.org/10.1021/acs.est.7b04508, 2018.

The authors should explicitly describe and justify their assumptions in assigning functional groups to formulas. For example, it appears that all compounds with S:O ratios of 1:4 have been assigned as organosulfates, while higher ratios are assigned as organosulfates with additional oxygen functional groups, and lower ratios are assigned to sulfonates. The following chemical arguments suggest that these assignments are C2 not only arbitrary, but incorrect. Sulfonates form from S(IV) + carbonyl reactions, and these reactions also generate products with S:O ratios of 1:4, but with a C-S bond. Thus, this reviewer would argue that the authors' use of S:O ratios to distinguish between sulfonates and organosulfates is invalid. Furthermore, organosulfate production is thought to require acid catalysis at very low pH. The measured near-neutral pH of the WSOC extracts in this work suggests that acids have been mostly neutralized, and therefore organosulfate formation (via acid catalysis) appears to be unlikely. As another example, the assignment of $C_{17}H_{16}O_4$ and $C_{18}H_{16}O_4$ ions from the C2 group to "esters" could use further justification.

Response: *Thanks for your suggestion. When S:O>4, the -OSO$_3$H structure (sulfate group) is more easily deprotonates by ESI-, and these compounds are more likely organosulfates, which has been demonstrated by many studies (Jiang et al., 2016, Mo et al.,2018; Song et al.,2018). When S:O<4, it is not possible to form the -OSO$_3$H structure due to few O atoms, and It may form C-S bonds or sulfonates. These structures that presented here were speculated and not identified, because FT-ICR mass spectra could not provide structural information. In fact, having studies had detected similar chemical structure in biomass burning and coal combustion experiments which assigned as organosulfates (Song et al., 2018;). Maybe we provided a wrong structure for the assignment of C$_{17}$H$_{16}$O$_4$ and C$_{18}$H$_{16}$O$_4$ ions to "esters", because we think it cannot be ionized by the ESI-.*

Reference:

Mo, Y., Li, J., Jiang, B., Su, T., Geng, X., Liu, J., Jiang, H., Shen, C., Ding, P., Zhong, G., Cheng, Z., Liao, Y., Tian, C., Chen, Y., and Zhang, G.: Sources, compositions, and optical properties of humic-like substances in Beijing during the 2014 APEC summit: Results from dual carbon isotope and Fourier-transform ion cyclotron resonance mass spectrometry analyses, Environ. Pollut., 239, 322-331, https://doi.org/10.1016/j.envpol.2018.04.041, 2018.

Song, J., Li, M., Jiang, B., Wei, S., Fan, X., and Peng, P.: Molecular Characterization of Water-Soluble Humic like Substances in Smoke Particles Emitted from Combustion of Biomass Materials and Coal Using Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Environ. Sci. Technol., 52, 2575-2585, https://doi.org/10.1021/acs.est.7b06126, 2018.

Jiang, B., Kuang, B. Y., Liang, Y., Zhang, J., Huang, X. H. H., Xu, C., Yu, J. Z., and Shi, Q.: Molecular composition of urban organic aerosols on clear and hazy days in Beijing: a comparative study using FT-ICR MS, Environ. Chem., 13, 888-901, https://doi.org/10.1071/en15230, 2016.

Line 63: The phrase "little structural information is available" is misleading. There have been several studies, most involving Alex Laskin, that determined detailed chemical

structures in biomass burning aerosol extracts. Some of these studies are eventually cited in this manuscript, but they should be briefly summarized here.

Response: Thanks for your suggestions. The HPLC-PDA-HRMS has been used to investigate optical properties and chemical composition of BrC compounds. Thus, we have revised it.

Please see lines 88-93 in the revised manuscript. We revised it as the following phrase "Recently, many studies have investigated the optical properties and molecular characteristic of BrC in laboratory simulated combustion (Budisulistiorini et al., 2017;Lin et al., 2018;Lin et al., 2016;Song et al., 2019) and their light absorption in controlled vehicle emissions (Xie et al., 2017)".

Line 103: It is inappropriate to follow the statement "Concerns about the environmental and health effects of vehicle emissions have existed for decades" with only a single citation from 2015, unless the citation is a comprehensive review. This underreferencing happens at several points in the introduction.

Response: Thanks for your suggestions. We have revised and checked it.

The revised parts were in lines 150-153. The revised phrase is "Residential CC and BB emissions, and motor vehicle emissions are significant anthropogenic sources of air pollutants, exceptionally fine particulate matter (PM $_{2.5}$) on urban and regional scales (Gentner et al., 2017;Yan et al., 2015;Zhang et al., 2018;Chen et al., 2015)".

Line 278: It is stated that measured MAEs are higher in this study than in previous lab studies of biomass and coal burning aerosol. Some explanation for this difference should be given. There is no other discussion of MAEs in the manuscript.

Response: Thanks for your suggestions. The topic on our study is the fluorescence characteristic from different sources and dig out the chemical structures of chromophores using FT-ICR MS. Therefore, that is the reason we explained little about the light absorption in this study. According to your suggestions, we added more

discussions about the light absorption in different sources, and conducted a comparison of their light absorption.

Please see lines 339-384 in the revised manuscript.

Line 320: The meaning of this sentence is unclear. What "other" fluorescent components are referred to?

Response: The "other" denoted the remaining fluorescent components except for C3 and C1.

In the revised manuscript, we deleted this sentence because we found it is useless.

Lines 33, 413, 464, 514: The authors appear to treat negative and positive correlations the same way in their interpretations. If P1 and P6 are negatively correlated with HCHOS, this would mean that P1 and P6 fluorophores are formed whenever H-CHOS is not present, but the authors go on to attribute P1 and P6 to H-CHOS here, in the conclusion, and in the abstract.

Response: Thanks for your suggestion. We have rewritten this part, please see Section 3.3-3.4.

Line 35, 519-520: These conclusions are questionable. See earlier comments about esters and sulfonates versus organosulfates

Response: The structures of these fluorescent components were speculated and not identified. Thus, we deleted this part and rewrote it.

Please see Section 3.3-3.4 in the revised manuscript.

Tables S5 and S6: It seems inappropriate to report either averages or total intensities across different types of samples like this, without some justification.

Response: According to your suggestion, we have deleted it.

Technical corrections

There are a fair number of grammatical errors in the manuscript, which are not listed here. Fortunately, the meaning usually remains clear.

Response: Thanks, we have carefully checked it.

Line 49: the authors refer to the "near UV and UV/visible ranges," which are overlapping. Do they mean "near UV and visible ranges"?

Response: Thanks for your reminder, we have corrected it.

We revised "near UV and UV/visible ranges," to "near UV and visible ranges" in the revised manuscript. Please see line 78.

Line 162: this statement would be clearer if the difference was explained. Is it true that MSOC is different in this study because WSOC has already been removed?

Response: As we stated in the text, this fraction was that we used methanol to re-extract the water-extracted filter. So, it is true that MSOC is different from WSOC.

In the revised manuscript, we explained the reason we used the methanol to secondary-extraction. Please see lines 226-229.

Line 213: The authors should briefly discuss what kinds of compounds will be missed by negative mode ESI. Will N-heterocycles be detected?

Response: Thanks for your suggestion. The missing compounds in the ESI- may be some nonpolar or less polar compounds such as PAHs, O-PAHs, N-PAHs, and saturated hydrocarbons, and N-heterocyclic alkaloid compounds.

We added this discussions in the revised manuscript. Please see line 648-653.

Line 241: "componet" should be "component"

Response: Thanks, we have revised it in line 317 in the revised manuscript.

Line 366: What kinds of differences? Differences in fluorescence? The fluorescence of sample 36 is not shown in Figures S9 or S10.

Response: The differences denoted the relative abundance of CHON in anthracite combustion and bituminous coal combustion. The previous study indicated that CHON was mainly detected in the biomass burning particles, but our study found that the CHON was abundant in coal combustion particles. Thus, we introduced the types of coal fuels that may be responsible for these differences. The sample 36 should be 38.

In the revised manuscript, we rediscussed it. Please see lines 685-688.

Line 371: This description of axes appears to be describing Figures 3 and 4, but these figures are not mentioned until later

Response: The axes were not used to describe Figure 3 and 4, but only used to determine the potential BrC compounds where data inside the region were potential BrC.

Line 375: The wrong figure is referenced here, I think

Response: Thanks. This should be Table 2.

Figures S2 and S5: "resident" should be "residual"

Response: Thanks. We have revised it.

Figures S9 and S10: It would save readers a lot of time searching around if these samples where labeled with their sources on this graph (e.g. "bituminous coal")

Response: According to your suggestions. In the revised version, we labeled the sources on the graph.

Please see Figure 4, 6 and Figure S9, S10, S11, S18 in the revised manuscript.

Figure S11 caption: Different regions are identified, but not labeled on the graph. It is not clear what the reader can do with this information without further graphing.

Response: Thanks. According to your suggestions. In the revised manuscript, we marked this information on the graph.

References Cited: 1. Graber, E. R.; Rudich, Y., Atmospheric HULIS: How humiclike are they? A comprehensive and critical review. Atmos. Chem. Phys. 2006, 6, 729-753. 2. Lin, P.; Aiona, P. K.; Li, Y.; Shiraiwa, M.; Laskin, J.; Nizkorodov, S. A.; Laskin, A., Molecular Characterization of Brown Carbon in Biomass Burning Aerosol Particles. Environ Sci Technol 2016, 50, (21), 11815-11824. 3. Lin, P.; Fleming, L. T.; Nizkorodov, S. A.; Laskin, J.; Laskin, A., Comprehensive Molecular Characterization of Atmospheric Brown Carbon by High Resolution Mass Spectrometry with Electrospray and Atmospheric Pressure Photoionization. Anal. Chem. 2018, 90, (21), 12493- 12502.

Response: We had cited the references of 2 and 3 in the previous version. In the revised version, we add the new cite in the line 108.