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”

Author(s): Jiao Tang et al.

MS No.: acp-2019-584

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 comments 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# 2

This manuscript by Tang et al. describes a detailed chemical analysis on atmospheric brown carbon (BrC) extracted from smoke particles samples. Particle samples were collected from biomass burning, coal combustion, and vehicular emissions. Filter samples were extracted by either water or methanol and were analyzed with emission excitation matrix (EEM) and FTICR-MS with ESI(-) ionization. Six components were extracted from the EEM data using a parallel factor analysis method. A significant amount of effort was present to make correlations between these EEM components with functional groups determined with FTICR-MS. The authors concluded that correlations were observed between EEM components and certain functional groups, indicating that this method can be useful in source apportionment of BrC.

The topic of the manuscript is in-line with the scope of ACP, in particular, the importance of BrC in the atmosphere is emergent, but there is extremely limited chemical information on important individual chromophores. The manuscript is attempting to address this important question. However, I do not recommend publication in ACP in the current form. In addition to a few major scientific questions,

I have significant concerns regarding the literary presentation of the manuscript. It requires a substantial refinement before it can be published in any journal. In particular, I found the manuscript very difficult to read due to ill-structured order of discussion, missing or repeated explanations for abbreviations, frequent references to the SI, as well as numerous grammatical and typological errors.

Response: *Thanks. According to your suggestions. We made a major revision and rewrote the part of FT-ICR mass spectra. We added the analysis of chemical information in different sources and discussed the differences among these sources. We revised the wrong parts, reconstructed the structure of discussion in the revised manuscript.*

Major comments:

EEM and ESI (-) are powerful analytical methods, but I'm afraid that they are not quantitative enough to make meaningful correlation analysis. Light absorptivity should be the primary concern for BrC chromophores, but fluorescence intensity, which is the core of the analysis here, depends on a number of other factors. Meanwhile, ESI(-) is particularly sensitive to compounds with acidic hydrogens, but not to PAHs and other compounds unless they have a carboxylic group. I'm afraid that the positive correlation could be driven by the detection sensitivities of the two methods.

Response: *Previous studies used the correlation analysis to speculate the chemical structures of fluorescent components (Chen et al., 2016a,b; Stubbins et al.,2014). These studies were the basis of my research. It is true because ESI- can only ionize polar compounds and will ignore other strongly absorbing compounds, such as O-PAHs, N-PAHs. According to your suggestions, we thought that using the FT-ICR MS to speculate the possible structures and provide a fundamental confirmation may be very difficult without further chromatographic separation. Thus, we retreated our data and rewrote the part.*

The reconstructed part were mainly presented in Section 3.3-3.4. Also, we updated the results and made some modifications in abstract, introduction, and conclusions.

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 authors use the FTICR-MS to rule out functional groups. Although the authors present a thoughtful interpretation of the FTICR-MS data, caution is required, as what MS provides is the elemental composition, not functional group information. For example, the chemical structures shown in Figure 5 do not contain any acidic functional group, and I double if they can be detected by ESI (-).

Response: *The classified method of function groups was based on the Chen et al. 2016b and the ionized properties of ESI-. In the results of Chen et al., they found fluorescent components had a good correlation with these chemical groups (C-H, C-NH_2, C-OH, C-ONO_2, C=O, COOH), and with ion groups (C_x, CH, CHO_1, CHN, CHO_1N, $CHO_{>1}N$, CS, CO, HO,CO_2, $C_2H_4O_2^+$) of HR-AMS. Thus, we tried to build the relationship between fluorescent components and ion groups of FT-ICR MS. The chemical structures provided in Figure 5 were speculated, not determined.*

In the revised manuscript, we deleted this part, and rewrote it (Section 3.4).

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.

Table 2 is a critical part of the manuscript, presenting the functional group assignment based on FTICR-MS data. However, no explanation is provided for the table at all in the manuscript. Is the left side of the table linked to the right side of the table? The categories shown on the right side of Table 2 (Lipids, proteins, etc.) seem very irrelevant to atmospheric particles, but no explanation is provided in the main text.

Response: *Sorry for making this mistake. The Figure 2 should be Table 2 (Line 375). The left side and right side of the table were the two methods we classified to explore the possible structures of fluorescent components. The right side of the Table 2 is the categories that the compounds located in the domains in Ven krevelen (VK) diagram. In addition, Vk diagram can provide a visual graphic display of compound distribution and identify different composition domains in organic mixtures.*

This part in the revised manuscript has been deleted.

Reference:

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 have presented a huge amount of work in interpreting the EEM components,

FTICR-MS data, as well as the correlation analysis. The authors deserve a lot of credit for doing such a full-bodied analysis. However, the current conclusions in the manuscript do not appear very helpful for the atmospheric chemistry community, other than demonstrating the heterogeneity and complexity of the system. The authors should reconstruct the discussion and conclusion with more atmospheric implications.

Response: *In fact, EEMs-based method to characterize the atmospheric BrC have been widely used. However, there is no classification system of chromophores in the atmosphere by using fluorescence method, mainly referring to the aquatic environment. Due to the differences in biochemical behavior, transport process, and formation mechanism, there is a big gap between atmospheric and aquatic environment. Therefore, the fluorescence spectra of different sources may provide certain chromophores linked with sources, and combined with FT-ICR MS to speculate the possible structures of fluorescent components, which would provide a reference fluorescence spectrum for the study of brown carbon in the atmosphere.*

In the revised manuscript, we deleted this part and reconstructed the discussions and conclusions.

Minor Comments

The manuscript is titled as "BrC in smoke particles". I personally felt odd that vehicular emissions are also included as smoke particles.

Response: *Thanks. According to your suggestion, we have revised the title.*

The revised title is "Molecular compositions and optical properties of dissolved brown carbon in biomass burning, coal combustion, vehicle emission aerosols illuminated by excitation-emission matrix spectroscopy and FT-ICR MS analysis".

I am not a specialist in PARAFAC and found it difficult to see the concepts and purpose

of PARAFAC until the end of Section 2.5. I recommend the authors added an introductory statement for PARAFRAC either in Introduction of Section 2.5. For example: "The purpose of PARAFRAC is to extract X components from the EEM data based on . .

Response: *Thanks. According to your suggestion, we added the concept of PARAFAC in the introduction.*

Please see lines 88-90 in the revised manuscript.

Regarding water vs methanol extraction. The objectives of investigating WSOC and MSOC is unclear. Is the purpose to investigate BrC with distinct polarities? Is it to investigate "fat-soluble" fraction (Line 271)?

Response: *Previous studies indicated water could not effectively extract the BrC in the aerosols, and found the water-insoluble organic fraction had higher light absorption capacity than water-soluble organic fraction (Chen et al., 2017). So we want to know more about the water-insoluble BrC.*

In the revised manuscript, we added an explanation. Lines 167-170.

Reference:

Chen, Q., Ikemori, F., Nakamura, Y., Vodicka, P., Kawamura, K., and Mochida, M.: Structural and Light-Absorption Characteristics of Complex Water-Insoluble Organic Mixtures in Urban Submicrometer Aerosols, Environ. Sci. Technol., 51, 8293-8303, https://doi.org/10.1021/acs.est.7b01630., 2017.

Related to the previous point, a discussion is needed on why the WSOC and MSOC are so distinct. To my understanding, these two solvents should extract different, but somewhat overlapping classes of organic compounds.

Response: *Water extracts high-polar compounds and methanol extracts medium-polar compounds. If organic matters were extracted individually by water and methanol,*

there were certainly overlapping compounds in the two fractions. However, when we extracted the organic matters using water, and then using methanol, there were fewer overlapping compounds. Meanwhile, we will know more about the variation of optical properties and molecular compositions of water-insoluble organic matter comparing with water-soluble organic matter.

Line 266 - It is a little confusing because Figure 2b is introduced before Figure 1 and the PARAFRAC components. Can the authors consider making Figure 2b an individual figure? Also, to make an argument on MAE is 'higher' or 'lower', more statistics are needed. Instead of presenting Figure 2b as is, I would recommend using a more statistical approach, such as a box and whisker plot.

Response: *Thanks for your suggestions. We have replotted the figure and discussed the light absorption capacity among these different sources, and made a comparison with the other studies.*

Please see line 270-311 in the revised manuscript and the revised Figure 1.

Line 292 - What is 'region IV'?

Response: *The "region IV' (Ex=225-250nm, Em=356-400nm) is defined as protein-like or tryptophan-like fluorophore according to the previous study (Qin et al., 2018).*

Reference:

Qin, J., Zhang, L., Zhou, X., Duan, J., Mu, S., Xiao, K., Hu, J., and Tan, J.: Fluorescence fingerprinting properties for exploring water-soluble organic compounds in PM 2.5 in an industrial city of northwest China, Atmos. Environ., 184, 203-211, https://doi.org/10.1016/j.atmosenv.2018.04.049, 2018.

Paragraph starting Line 369. It is very confusing that the paragraph started with an introduction to DBE, but the topic rapidly changed to O/C and H/C. The authors should

consider reordering the discussion here.

Response: *In this sentence, the introduction of DBE is to determine the potential BrC using the method and then classified the ion groups.*

In the revised manuscript, we had rewritten it.

What is AImod?

Response: *AI_{mod} is a modified AI value, which can be calculated by considering only half of the oxygen being present in carbonyl functional groups (Koch et al., 2006). AI is the most conservation case and result in underestimation of the structures. Although AImod may improve the aromatic index, it may introduce uncertainties.*

Figure 1 - no color scale explanation. Is each graph normalized to its highest intensity? The readers cannot see the relative importance of the 6 components (i.e., are one or two components much more intense than others?)

Response: *The fluorescence did not normalize by its highest intensity, but the Raman peak of water. In the revised manuscript, we added the score of the 6 components.*

Figures 4 and 5- the authors introduced a region between slope 0.5 and 0.9 on the DBC vs C plot (Line 370). Why not show these lines in Figure 4 and 5?

Response: *According to your suggestion, we added the two linear in the relative graphs in the revised manuscript. (Figure 6; Figure S15, S17, S18).*

Technical Comments - there are more grammatical errors than listed here, please check.

Line 39 - the abbreviation of EEM is already introduced in Line 23.

Response: *Thanks. We have checked these errors carefully in the revised manuscript.*

Line 82 and Line 85 - Chen et al / Lee et al are repeated

Response: *Thanks, We have revised it in the revised manuscript.*

Please see line 90, Chen et al., (2016b) observed…

Line 93, Lee et al., (2013) illustrated…

Line 110 - the abbreviation of EEM is already introduced in Line 64.

Response: *Thanks for reminder, we have revised it and use the abbreviation..*

Line 138 -‘difficult’ to ‘difficulty’

Response: *Thanks for the reminder. We have revised it.*

Line 141 - ‘Every coal about 1 kg fuels was burned three times’. To ‘Coal (~ 1 kg each) was burned in triplicate.”

Response: *The correct expression is that “every coal was burning three times, about 1kg fuels per burn”. And we have revised it.*

Line 144 - ‘Additional’ to ‘Additionally,’

Response: *Thanks. We have revised it.*

Line 151 - ‘truck’ to ‘ a truck’ or ‘trucks

Response: *Thanks. We have revised it.*

Line 162 - ‘MSOC fraction from the methanol extract’ is redundant.

Response: *Thanks. We have deleted it.*

We revised the ‘MSOC fraction from the methanol extract’ to ‘MSOC’ in line 170 in the revised manuscript.

Line 164 - ‘um’

Response: *Thanks. We have revised it.*

We have changed 'um' to 'μm' in line 172 in the revised manuscript.

Line 237 - 'Additional' to 'Additionally,'

Response: *Thanks. We have revised it.*

We have changed the 'Additional' to 'Additionally,' in line 246 in the revised manuscript.

Line 274 to 277 - MAE was higher in methanol extract for biomass burning and coal samples. I could not follow why that indicates a greater variation in chemical composition in MSOC.

Response: *Thanks. It may be some wrong express. According to your suggestion, we have deleted it.*

Line 352 - 'abundance' is perhaps a misused word here

Response: *Thanks for your reminder. We have revised it.*

We changed 'anundance' to 'abundant' in line 390 in the revised manuscript.

Line 352 - 'was' to 'were'

Response: *Thanks. We have revised it.*

Line 356 - Suggestion: 'One possible reason for this concerns the viable coal types' to 'One possible reason for this is the various coal types'

Response: *Thanks for your suggestion. When we rewrote this part, some relative errors may have been deleted in the revised manuscript.*

Line 427 - remove 'be'

Response: *Thanks for your suggestion. Because we rewrote this part, some relative errors may have been deleted in the revised manuscript.*