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Atmospheric Chemistry and Physics Discussions

Interactive comment on "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" *by* Jiao Tang et al.

Anonymous Referee #2

Received and published: 31 August 2019

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

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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.

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.

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

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group, and I double if they can be detected by ESI(-).

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.

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.

Minor Comments

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

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 . . .”

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)?

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.

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.

Line 292 - What is 'region IV'?

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.

What is AImod?

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?)

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?

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

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

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

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

Line 138 -'difficult' to 'difficulty'

Line 141 - 'Every coal about 1 kg fuels was burned three times'. To 'Coal ($\sim$ 1 kg each) was burned in triplicate."

Line 144 - 'Additional' to 'Additionally,'

Line 151 - 'truck' to ' a truck' or 'trucks'

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

Line 164 - ‘um’

Line 237 - ‘Additional’ to ‘Additionally,’

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.

Line 352 - ‘abundance’ is perhaps a misused word here.

Line 352 - ‘was’ to ‘were’

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

Line 427 - remove ‘be’

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