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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 #1

Received and published: 21 August 2019

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.

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".

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.

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.

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 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 C17H16O4 and C18H16O4 ions from the C2 group to "esters" could use further justification.

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.

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

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.

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

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 H-CHOS, 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.

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

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

Technical corrections

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

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

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

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

Line 241: "componet" should be "component"

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

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

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

Figures 4 and 5 would be improved by labeling the color code as number of oxygen atoms on the graph, not just in the caption.

Lin 516: While no MS structural class was correlated with P2 and P3, the literature designation of these fluorescent peaks is certainly consistent with the prevalence of these peaks in biomass burning samples in this study. This support can be mentioned here.

Figures S2 and S5: “resident” should be “residual”

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”)

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.

References Cited: 1. Graber, E. R.; Rudich, Y., Atmospheric HULIS: How humic-like 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.

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