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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular Characterization of Firework-Related Urban Aerosols using FT-ICR Mass Spectrometry" *by* Qiaorong Xie et al.

Anonymous Referee #1

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General comments.

The manuscript presents an analysis of 6 samples collected on the days before, during, and after a major fireworks emission source in Beijing. The authors used FT-ICR MS to characterize the CHO, CHON, and CHOS compounds identified in the samples. The data analysis is thorough and the data sets and results are presented in a clear format. However, there are multiple places where additional information should be included and clarifications given. I recommend this for publication in ACP after the following specific comments are addressed.

Specific Comments

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Discussion paper

1. The CHO, CHON, and CHOS compounds are the only ones discussed here. There are clearly CHONS compounds present in the sample and the caption on Figure 1 says that these compounds “were discussed in other study”. If this study is published, please provide the citation. Also, please include this information somewhere in the text in addition to the caption. The end of the introduction would be a good location.

2. In the abstract and in the conclusions a reference is made to brown carbon molecules. Were any UV-vis measurements made that would support the idea that some of these molecules can absorb visible radiation? If not, was there any observation (by eye) that some of these extracts were more brown?

3. In the abstract, the statement “the co-variation of CHO, CHON, and CHOS subgroups was suggested to be associated with multiple atmospheric aging process of aerosols including the multiphase redox chemistry driven by NOx, O3, and OH.” This sentence is a little confusing, what co-variation is being referred to here?

4. For the experimental, was the possible presence of phosphorous included in the assignment? If not, why?

5. For the FT-ICR, what mass was the instrument tuned too and what is the lower mass cut-off for the ion trap?

6. A file of peak lists and assignments for all the samples would be very helpful for scientists wishing to build on this work. Can this be included as additional supplemental files? What percentage of the identified peaks were assigned? What fraction of the total signal does this correspond to?

7. How was the signal from the field blank handled? Were peaks that were found in the blank excluded? Or was the S/N relative to the blank used?

8. On page 6 lines 13-14 you state “the peak intensities of the ions could be compared by assuming that matrix effects were relatively constant”. Please clarify that this is a sample to sample comparison and not that ion intensities for different compounds

within a sample were compared. Those will be affected by ionization efficiency (as you state).

9. On page 7 lines 16-17 you state: " Moreover, the number and total intensities. . .(Figure 2)." I am confused what comparison is being made here since this paragraph is about CHO compounds, please clarify.

10. The carbon oxidation state discussion and figure have multiple areas of modification:

a. Figure 6 is very hard to read, even with color. I cannot see the blue markers (NYE D) under all the others and especially when they are on top of the green ovals.

b. In the text, it sounds like the authors are saying that compounds with molecular formula that overlap with different green ovals (BBOA, SV-OOA, etc.) correspond to those compound types. Specifically I recommend adjusting the text that starts on line 31 page 8 to clarify that these groupings are for previous measurements of ambient aerosol samples. The phrasing "molecules with OSc between xx and xx with carbon atoms more than 7 are associated with xxx" sounds like the molecules in this study are being assigned to these groups. If this is the intended interpretation, please see my caution in comment 16.

11. On page 9 lines 12-14, the authors state that the molecular weight increased during the FW events for the CHON compounds. However, all these numbers are within the reported error of each other.

12. The paragraph on page 9 starting on line 18 is confusing. Which type of oxidized nitrogen group is being assigned for which sample? Both organonitrates and nitroaromatics are discussed but it is unclear if these are for different samples.

13. The trends shown in Figure 9 are interesting and the caption is appropriately clear on how tentative these assignments are. The text that corresponds to this figure (page 9, lines 28-34) should also be adjusted to indicate that these are not structural

assignments.

14. For the CHOS compounds, is there any reason that some of these could not be primary emissions? Have any FT-ICR studies been carried out with samples collected closer to the FW source?

15. I recommend changing the label for the sulfur section from OSs to CHOS. This will match the rest of the paper, it will decrease confusion with OSc, and will be better given that no MS/MS studies were done to positively identify them as organosulfates (as stated on page 11).

16. On page 12 line 12-13, the authors state: “Moreover, a great part of the FW affected ions with high intensity were potentially the BBOA”. What data is this conclusion being drawn from? Is this coming from the oxidation state figure/analysis? If it is coming from the oxidation state figure, I urge caution with this type of conclusion. The carbon oxidation state is a great metric for analyzing atmospheric aging, but molecules from different sources can have similar carbon oxidation state and carbon number ranges. Please also remember that the analysis here is only looking at material that was bound and then eluted on the SPE column, is water soluble, and is easily ionized in negative ion mode. Caution should be used when making aerosol source identifications from the molecular formulas found here to ones found for different sample types with different preparation steps.

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