

Authors' Responses to Reviewer #1

We appreciate the detailed and constructive comments and suggestions from the reviewer. The point-to-point responses to the comments are listed as below.

The Reviewer comments are *black italic font* and the Author responses are blue font.

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.

Response: We appreciate the valuable comments from the reviewer. We have made changes/modifications to both the main text and the supplemental information. Detailed responses are shown below.

Specific Comments

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.

Response: Thank you. CHONS compounds are obviously subject to nighttime chemical oxidation. In the present study, we investigated the molecular characteristics of CHO, CHON, and CHOS species in a detailed way. Due to the limited length of the paper, the characteristics of CHONS and their volatility estimated by using some molecular corridor method will be discussed in a detailed and thorough way in another manuscript that is under preparation. We have added the following sentence to the manuscript in the end of the introduction in addition to the caption (page 3 lines 8-9):

“In addition, the detailed molecular characteristics of CHNOS species and their volatility using

a molecular corridor method will be present in another study.”

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?*

Response: Because of the limitations of measurement techniques and the lack of authentic standards of OSs that are detected in FT-ICRMS, we have not been able to make the UV-vis measurements of each compound so far. The conclusions resulted from the molecular composition, such as nitro-aromatic compounds, which are potential contributors to light absorption as a component of brown carbon.

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 NO_x, O₃, and OH.” This sentence is a little confusing, what co-variation is being referred to here?*

Response: The co-variation is referred to the previous sentence “...the number concentration of sulfur-containing compounds especially the organosulfates was increased dramatically by the FW event, whereas the number concentration of CHO and CHON doubled after the event.” The number concentration of CHOS compounds was increased dramatically by the FW event at night, and they are mainly subject to nighttime chemical oxidation, e.g., NO₃, N₂O₅. But the number concentration of CHO and CHON doubled after the event during the day with photochemistry. The co-variation of CHO, CHON, and CHOS subgroups in the manuscript is referred to the same variation and different variation after being affected by fireworks emissions, and they are associated with the multiphase redox chemistry driven by NO_x, O₃, and OH. To avoid confusing, we have changed the statement: (page 1 lines 27-28)

“..., which were associated with multiple atmospheric aging processes including the multiphase redox chemistry driven by NO_x, O₃, and •OH.”

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

Response: Phosphorus-containing compounds existed in our samples, but the number and

intensity of them only accounted for less than 0.01% of that in all assigned compounds. We assume that organophosphates should be more abundant in summertime aerosol samples from biogenic origin, not the wintertime ones. Therefore, phosphorus-containing compounds were not included in the discussion of our manuscript that mainly focuses on firework-influenced N- and S-containing aerosols.

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

Response: For the FT-ICR MS analysis, the ion peaks of sodium formate complex ranging from approximately 180 Da to 1200 Da were tuned with an error of less than 1 ppm. And the lower mass cut-off for the ion trap was 100 Da.

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?

Response: We thank the reviewer for this comment. As the data of the work also involves some unpublished articles, our dataset will be available upon request by the readers. There were approximately 67%~71% of the identified peaks were assigned in our samples. And the intensity of them accounted for approximately 70%~75% of the total signal. The information has been added in the manuscript. (page 4 lines 30-31)

“There were approximately 67–71% of the identified peaks were assigned in our samples. The intensity of them accounted for 70–75% of the total signal.”

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?

Response: The assignments of the blank sample with a signal-to-noise ratio three times that of the aerosol sample were removed in our samples. The information has been added in the manuscript. (page 4 line 31- page 5 line 1)

“The molecular formulas in blank filters with a signal-to-noise ratio greater than that of the aerosol samples were subtracted from the real aerosol samples.”

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).

Response: Thank you very much for this suggestion. To clarify, we have changed the presentation in the manuscript (page 6 lines 32 - page 7 line 2):

“the peak intensities of the same ions could be compared among different samples by assuming that matrix effects were relatively constant.”

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.

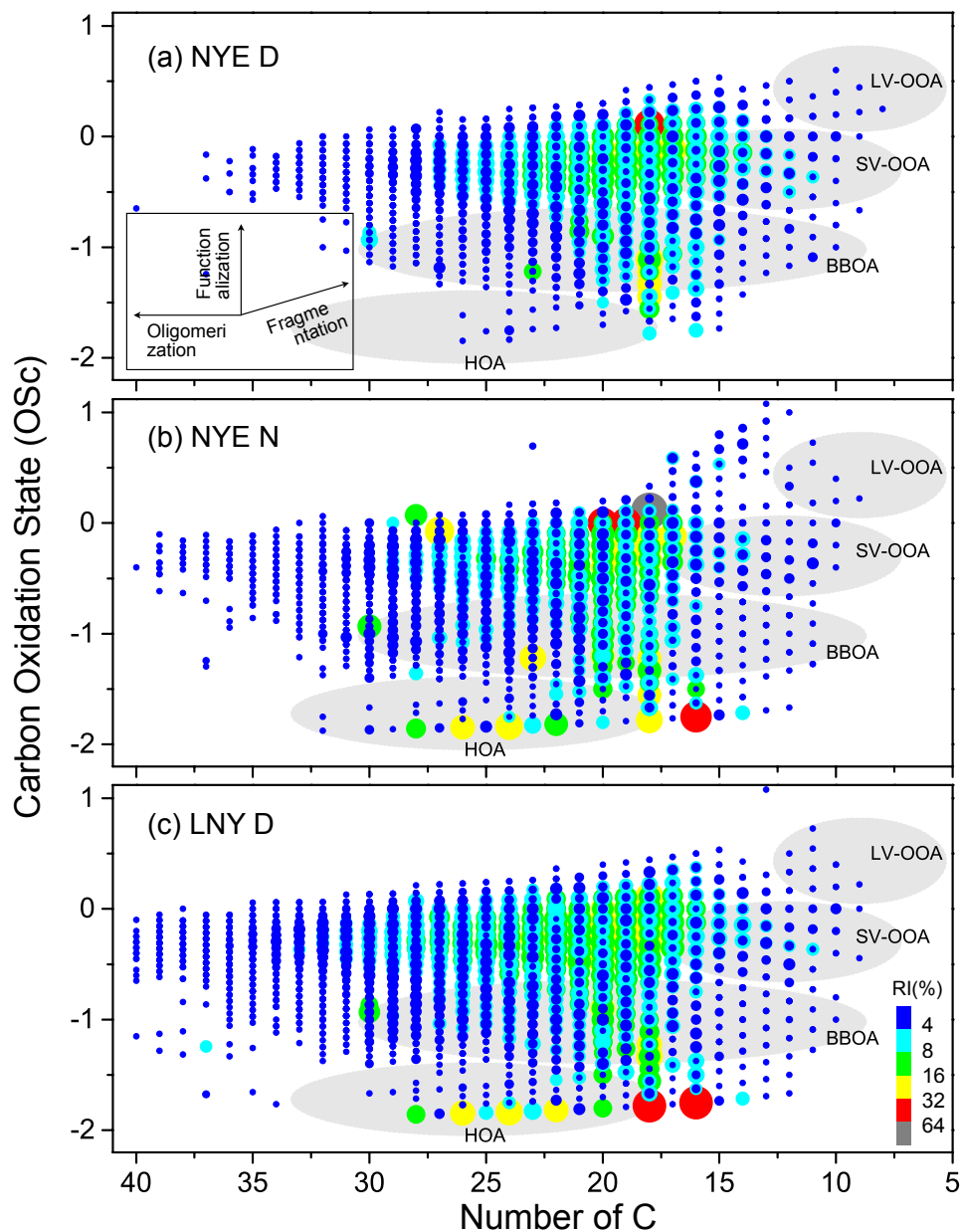
Response: Thank you. The comparison is made for the unique CHO compounds (except for common compounds in two samples) between that only detected in NYE N sample and NYE D sample. To be more accurate and avoid any confusion, we have modified the statements in the manuscript (on page 8 lines 4-6):

“Except for common compounds in two samples, the number and total intensities of the unique compounds in NYE N sample (591 compounds) were slightly increased compared with those only in NYE D sample (376 compounds) (Figure 2).”

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.

Response: We thank the reviewer for this comment. To make it easier to read, we have modified the diagram as presented below. Due to the large amount of data, we presented each sample separately in one chart avoid overlapping. The explanatory graph was added with the lower left corner of the graph (a). The green ovals areas have been replaced by the gray areas.



“**Figure 6.** Overlaid carbon oxidation state (OS_C) symbols for CHO compounds in NYE D (a), NYE N (b), and LNY D (c) samples. The size and color bar of the markers reflects the relative peak intensities of compounds on a logarithmic scale. The gray areas were marked as SV-OOA (semi-volatile oxidized organic aerosol), LV-OOA (low-volatility oxidized organic aerosol), BBOA (biomass burning organic aerosol) and HOA (hydrocarbon-like organic aerosol) (Kourtchev et al., 2016;Kroll et al., 2011).”

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.

Response: Thank you. To clarify, we have adjusted the statement about the interpretation of different compound types (SV-OOA, LV-OOA, BBOA, and HOA) to:

“As shown in Figure 6, different OSC value and C number indicate different types of compounds as previously characterized by Kroll et al. (2011). The semi-volatile and low-volatility oxidized organic aerosol (SV-OOA and LV-OOA) have the values of OSC between -1 and +1 and carbon atoms less than 13, which are associated with that are produced by multistep oxidation reactions. The biomass burning organic aerosol (BBOA) has lower OSC, with OSC between -0.5 and -1.5 and carbon atoms more than 7. The molecules with OSC less than -1 and carbon atoms more than 20 might be associated with hydrocarbon-like organic aerosol (HOA).” (page 9 lines 20-25)

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.

Response: The average molecular weights were 415 ± 93 Da in the NYE daytime and 472 ± 112 Da in the LNY daytime, which increased by about 14%. We changed the expression to be conservative: (page 10 lines 4-5)

“Their average molecular weights were 445 ± 100 Da in the NYE nighttime and 472 ± 112 Da in the LNY daytime, respectively, compared to 415 ± 93 Da in the NYE daytime.”

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 nitro- aromatics are discussed but it is unclear if these are for different samples.

Response: We thank the reviewer for this comment. N_1O_3 – N_1O_{14} and N_2O_3 – N_2O_{13} subgroups were classified for CHNO compounds in all samples. The nitro-aromatics were mainly discussed among different samples in our study. To clarify, we explained the descriptions more carefully: (page 10 lines 10-12)

“CHNO compounds were classified to N_1O_3 – N_1O_{14} and N_2O_3 – N_2O_{13} subgroups in all samples

by the number of N and O atoms in their molecules (Figures 7 and S5). The total abundance of N_1O_n subgroups was twice as much as that of N_2O_n subgroups in each sample.

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.

Response: Thank you very much for this suggestion. To clarify, it has been adjusted (page 10 lines 21-23).

“...Figure 9 displays ion intensity distributions of four nitro-aromatic compounds (i.e. $C_{10}H_7O_3N$, $C_{11}H_9O_3N$, $C_{12}H_{11}O_3N$, and $C_{16}H_{79}O_3N$) detected in biomass burning aerosols by Lin et al. (2015), which were just assigned by their molecular composition but not the chemical structure. ...”

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?

Response: The similar molecular composition of some of CHOS compounds derived from aliphatic, biogenic, and aromatic VOCs were detected in the FW-related aerosols, which might be evidence that they are secondary organic aerosols. We have added them in the revised manuscript as below. There have been no similar FT-ICR studies of the FW-related aerosols. Our group will try to collect these samples to answer such a good question in the future study. (on page 12 lines 22-25)

“Moreover, the aliphatic OSs of $C_{12}H_{24}O_5S$, $C_{18}H_{36}O_6S$, and $C_{10}H_{16}O_9S$, and the biogenic OSs of $C_{10}H_{18}O_5S$ and $C_{10}H_{16}O_7S$, which were separately derived from alkanes and fatty acids (Riva et al., 2016; Passananti et al., 2016; Shang et al., 2016) and α/β -pinene (Surratt et al., 2008), and their corresponding family series ($C_nH_{2n}O_5S$, $C_nH_{2n}O_6S$, $C_nH_{2n-4}O_9S$, $C_{10}H_{2n-2}O_5S$ and $C_nH_{2n-4}O_7S$) were all detected in the aerosols.

...

For instance, $C_9H_{10}O_5S$, $C_{10}H_{10}O_6S$, and $C_{10}H_{10}O_7S$, derived from 2-MeNAP (Riva et al., 2015), and their corresponding family series ($C_nH_{2n-8}O_5S$, $C_nH_{2n-10}O_6S$, and $C_nH_{2n-10}O_7S$) were detected in FW-related aerosols.”

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).

Response: As the reviewer suggested, we change some fraction of OSs to CHOS in the manuscript (on page 12 line 9, page 13 line 23). But, because organosulfates were an important fraction of CHOS species, they were tentatively assigned by the same methods as previous studies and discuss in detail. This is more conducive to its classification and the source explains.

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.

Response: Thank you very much for this suggestion. The conclusion was just from the oxidation state analysis. For lack of sufficient evidence, we have removed this conclusion from the revised manuscript.

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