Authors' Responses to Reviewer #3

We appreciate the detailed and constructive comments and suggestions from the reviewers. 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 article studied the characteristic of CHO, CHNO, and CHOS before, during, and after FW event. Many species were detected by FT-ICR MS, and were analyzed through the manuscript. Furthermore, potential sources of these subgroups were also discussed through many calculations. There are many data and analysis methods which help the reader to understand the different pollution characters of aerosols during six periods. The whole article was aimed to discuss the event of firework-related urban aerosols before, during, and after New Year's Eve evening. The author just discussed the redox chemistry driven by NOx, O3, and OH, but the impact of combustion processes during the FW event wasn't discussed. What the relation between combustion processes and the three subgroups? I think the combustion processes is an important factor for the pollution during FW event. For example, there are amount of sulfur in the firework which many contribute the formation of CHOS species. Besides, the meteorology parameters were not contained in the article, which is hardly to analysis the sources of these subgroups studied in the article. for example, the author indicated the "multiphase" redox chemistry is important for the detected species formation, but how about the RH during these periods? The article should be revised according the comments and then can be published.

Response: We really appreciate the valuable comments from the reviewer. The impact of combustion processes during the FW event was discussed as the reviewer comments below (on page 10 lines 24-28; page 11 lines 8-15). Unfortunately, meteorology data were not collected during that period. Thank you very much for giving us such a good suggestion. We will pay attention to collecting meteorological data in the future to discuss the content more comprehensively.

"Nitro-aromatic compounds are produced in the atmosphere via the oxidation of aromatic precursors in the presence of NO_2 (Laskin et al., 2015), and their relative yields increase with NO_2/NO_3 concentrations (Sato et al., 2007;Jang and Kamens, 2001), which can be released in large quantities during FW combustion processes. Moreover, high abundant PAHs from FW emission in the NYE can react more efficiently with NO_2 than their single-ring aromatic counterparts (Nishino et al., 2009)."

"The amount of sulfur in the firework was released into the air with the form of sulfur oxides during the combustion process, and further produced acidified sulfate seed aerosol, which considerably contributed to the formation of a large number of CHOS compounds via acid catalyzed reaction with biogenic and anthropogenic volatile organic compounds (VOCs) (Surratt et al., 2008;Riva et al., 2015). For instance, the CHOS compounds derived from monoterpenes and sesquiterpenes, such as limonene, α/γ-terpinene and β-caryophyllene, were detected only under acidic or strongly acidic sulfate seed aerosol conditions (Surratt et al., 2008;Iinuma et al., 2007a;Iinuma et al., 2007b;Chan et al., 2011). Meanwhile, the high levels of nitrogen oxides emitted by FW burning can promote the formation of some CHOS compounds (Surratt et al., 2008)."

Specific Comments:

Introduction: Why the author studied subgroups of CHO, CHNO, and CHOS during these periods?

Response: Thank you very much for this suggestion. The explanation of the importance in studied subgroups of CHO, CHNO, and CHOS have been presented in the Introduction section. (on page 2 lines 12-26)

"Water-soluble organic carbon (WSOC) is a ubiquitous component of atmospheric aerosols. A large proportion of water-soluble organic matter is composed of HMW organic compounds that contain a substantial fraction of heteroatoms (N, S, O) (Lin et al., 2012;Mazzoleni et al., 2012;Wozniak et al., 2008;Wang et al., 2016). Highly oxygenated molecules contain a wide range of chemical functional groups such as peroxides, hydroperoxides, carbonyls, and per-carboxylic acids (Lee et al., 2019). Organic acids in oxygen-containing species contribute significantly to aerosol acidity. Lots of nitro-aromatic compounds in relatively high molecular weight compounds, often observed in biomass burning aerosols, are potential contributors to light absorption (Laskin et al., 2015;Lin et al., 2015). Moreover, organosulfates substantially contribute to the secondary organic aerosol (SOA) mass (Tolocka and Turpin, 2012), which plays an important role in exploring the formation pathway of SOA (Shang et al., 2016;Riva et al., 2015;Riva et al., 2016;Passananti et al., 2016). Meanwhile, because of their polar and hydrophilic nature, organosulfates can influence the hygroscopic properties of aerosols

(Estillore et al., 2016). Hence, to characterize both the compound class and individual compound level of organic aerosols (OA) is important for exploring the formation mechanisms, physicochemical properties, and environmental effects of firework-related aerosols. Moreover, the large amount of firework emission is an ideal event to understand the contribution of anthropogenic precursors to the formation of organic aerosols."

Page 5 Line 28-30: The author ascribed the increase of Mg^{2+} and Ca^{2+} to the dust particles increased were not exactly. Mg would exist in the FW. Did the author get the PM10 data?

Response: We thank the reviewer for the comments. The description about Mg^{2+} has been changed (on page 6 lines 17-19). PM10 were not collected in the study, but the total suspended particles (TSP) were collected and analyzed including aerosols with particle size less than 10 microns.

"In addition, the concentrations of Mg^{2+} and Ca^{2+} were slightly higher in the NYE nighttime than the non-FW periods. They were mainly in the coarse particle mode (Huang et al., 2013;Xu et al., 2015)."

Page 6 Line 20: CHNOS was mentioned here and also in Figure 1. Why the author didn't discuss CHNOS? What the relationship between CHNOS with CHNO and CHOS?

Response: CHONS compounds are obviously subject to nighttime chemical oxidation. Due to the limited length of the paper, their characteristics were discussed in detail with the corresponding nighttime chemistry in detail in another manuscript. To clarify, as suggested by the other reviewers, we have added the following sentence to the manuscript in the end of the introduction (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."

Page 7 Line 8: while the relative abundance of "four" categories compounds: "four" or "three"?

Response: Sorry for the misrepresentation. "four" has been changed to "three" in the revised manuscript. (on page 7 lines 32-33)

"……, while the relative abundance of compounds in three categories was different."

Page 8 Line 18: Xc can help to more precisely identify and characterize aromatic and condensed aromatic compounds in highly complex WSOC mixtures, why AI method was used in the manuscript?

Response: Previous studies have applied the AI method to characterize aromatic compounds for highly complex WSOC mixtures in atmospheric aerosols. For consistency, and for comparison with them, the AI method was used in the manuscript. Meanwhile, Xc was also applied to precisely identify the aromatic species in the manuscript.

Figure 6: I can't understand this picture, the markers can't be seen clearly, the green areas can't be understood.

Response: We thank the reviewer for this comment. To make it clearer, we have modified the diagram as shown below. Due to the large amount of data, we presented each sample separately in one chart. The explanatory graph was added with the lower left corner of the graph (a). The gray areas were the similar molecular composition as characterized by Kroll et al. (2011) and Kourtchev et al. (2016).

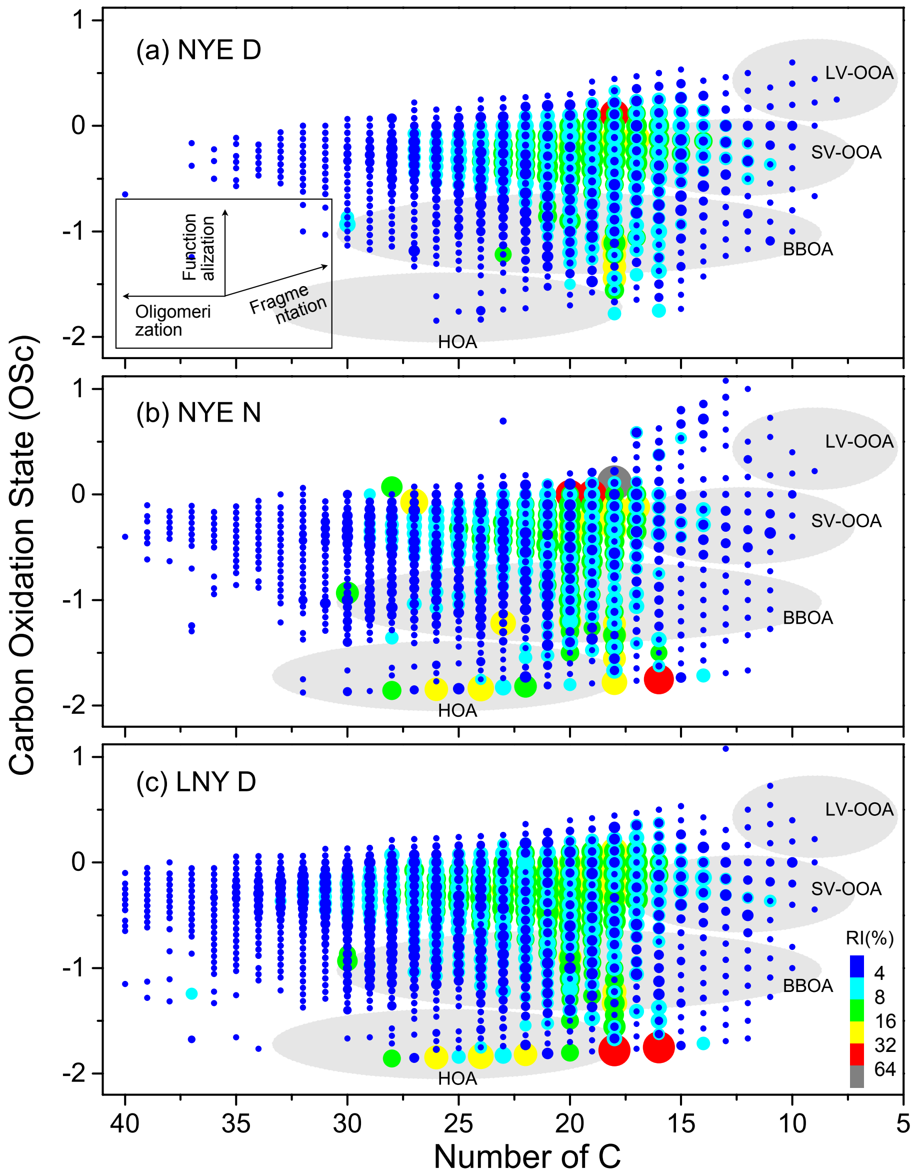

Figure 6. Overlaid carbon oxidation state (OS_C) symbols for CHO compounds in NYE D (a), NYE N (b), and LNY D (c) samples. The size and color bar of the markers reflects the relative peak intensities of compounds on a logarithmic scale. The gray areas were marked as SV-OOA (semi-volatile oxidized organic 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).

Page 10 Line21-24, Page 11 Line 25: The author highlights the importance of nighttime chemical oxidation to the formation of CHOS compounds, what was the evidence? How the combustion process impacted the formation of CHOS during FW event?

Response: Different from the daytime samples, the CHOS compounds considerably increased in NYE nighttime sample with large FW emission. It indicated that there were unknown formation pathways of CHOS compounds with nighttime chemical oxidation. The combustion process of FW has been included in discussion in the manuscript. (page 11 lines 8-15)

"The amount of sulfur in the firework was released into the air with the form of sulfur oxides during the combustion process, and further produced acidified sulfate seed aerosol, which considerably contributed to the formation of a large number of CHOS compounds via acid catalyzed reaction with biogenic and anthropogenic volatile organic compounds (VOCs) (Surratt et al., 2008;Riva et al., 2015). For instance, the CHOS compounds derived from monoterpenes and sesquiterpenes, such as limonene, α/γ-terpinene and β-caryophyllene, were detected only under acidic or strongly acidic sulfate seed aerosol conditions (Surratt et al., 2008;Iinuma et al., 2007a;Iinuma et al., 2007b;Chan et al., 2011). Meanwhile, the high levels of nitrogen oxides emitted by FW burning can promote the formation of some CHOS compounds (Surratt et al., 2008)."

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