

## Authors' Responses to Reviewer #2

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.

*Xi et al. propose a study on the characterization of ambient aerosols using an FT-ICR. 6 samples were analyzed and compared to evaluate the impact of firework on air quality. Overall the data reported in this study are coherent and the structure of the paper is clear. However, additional information should be added as well as some explanation to make this paper more comprehensive.*

**Response:** We thank the reviewer for his/her comments. We have tried our best to modify and improve the quality of our manuscript.

*Page 2, lines 8-9: please reformulate.*

**Response:** The sentence has been reformulated: (page 2 lines 8-9)

“Moreover, real-time chemical composition measurements illustrated that FW-related organics were mainly secondary organic material (Jiang et al., 2015).”

*Page 2, line 31: Please provide more information regarding the sampling of the aerosol: the size of the particles; i.e., PM1, 2.5, 10? high-volume samplers?*

**Response:** Total suspended particles were collected by a high-volume sampler with pre-combusted quartz filters. To clarify, we adjust the statement in the manuscript (page 3 lines 12-14):

“Total suspended particle (TSP) sampling was conducted on the roof of a building (8 m above ground level) in the campus of the Institute of Atmospheric Physics, Chinese Academy of Sciences (39°58'28" N, 116°22'13" E), a representative urban site in the central north part of Beijing. TSP samples...”

*Page 3, line 2-3: I recommend the authors to use a simpler naming system. e.g., before-FW-1, after-FW-2, during-FW-1,... it would be much easier to follow the discussion.*

**Response:** Thank you very much for this suggestion. We once used your suggested method as the sample name before. Both daytime and nighttime samples were discussed in the present

study. Thus, we want to keep our expression in the current manuscript as it is.

*Page 4, line 1: The authors should explain why these samples were analyzed only in negative mode.*

**Response:** We thank the reviewer for this comment. It was because that we mainly analyzed the water-soluble fraction in aerosols, which is easily ionized in negative ion mode. The explanation has been added in the revised manuscript. (on page 4 lines 14-15)

“Because the target species were water-soluble polar compounds, all the samples were analyzed in the negative ionization mode...”

*Page 4, section 2.4: - why did the authors choose an  $S/N > 6$ , which is more restricting? Why not using an  $S/N$  ratio  $> 3$ , which is commonly defined as  $LoD$ ?*

**Response:** The main purpose of increasing  $S/N$  ratio is to reduce the interference of noise peak and improve the reliability of molecular formula identification.

*- Is the peak assignment perform before or after blank subtraction? While the authors mentioned that blank filters were collected and analyzed, no information is providing regarding how the blank samples were used for the data analyzing.*

**Response:** We thank the reviewer for this comment. The peak assignment for real samples performed after the blank subtraction. As the reviewer suggested, the information has been added in the manuscript. (page 4 line 32-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.”

*- Why did the authors start at  $m/z$  185 rather than  $m/z$  100 as mentioned earlier in the manuscript? A significant amount of potential OA compounds can be missing.*

**Response:** For the FT-ICR MS analysis, the lower mass cut-off for the ion trap was 100 Da. To get more precise and as much information as possible about the compounds, some previous studies mainly aimed at the compounds of  $m/z$  100 ~ 400, but relatively high molecular weight compounds of  $m/z$  200 ~ 700 were analyzed in this study.

*- The authors should not claim any semi-quantitative results as the sensitivity of the ESI is*

*extremely dependent on the functional groups of individual compounds as reported in many studies.*

**Response:** The peak intensities of the ions was a sample to sample comparison among different samples and not a compound to compound comparison within a sample. The intensity of same compounds with similar functional groups were compared among various samples. To clarify, we have changed our state in the manuscript as reviewer #1 suggested (page 6 line 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.”

*Page 5, lines 26-28: The authors should provide either some references or some supporting information to support their statement.*

**Response:** Thank you. Some related references have been provided with the statement in the manuscript (page 6 lines 15-18).

“Fossil fuel combustion and vehicle emissions have been reported as important sources of NO<sub>3</sub><sup>-</sup> in Beijing (Ianniello et al., 2010; Wang et al., 2014), while these sources minimized due to a sharp decline in the population and vehicle; most of the people leave Beijing for their hometowns during the Spring Festival (Yang et al., 2014; Zhang et al., 2017b).”

*Page 5, lines 29: How do the authors know the distribution of the ions/compounds as a function of the size provide either reference or supporting information.*

**Response:** Some related references have been provided with the statement in the manuscript (on page 6 lines 17-19).

“In addition, the concentrations of Mg<sup>2+</sup> and Ca<sup>2+</sup> 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, lines 2-4: While the concentrations of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and K<sup>+</sup> are significantly different, this is not really the case for WSOC: there is an increase ~ a factor of 2, but what's the daily variability? It is hard to conclude that FW produces a sharp increase. In other words, is the increase statistically different?*

**Response:** The original expression was overstated. We have adjusted the presentation of the

content (on page 6 lines 21-23).

“Simultaneously, the WSOC concentration peaked sharply in the NYE nighttime. Moreover, the WSOC/OC ratio was higher during the FW period than non-FW periods, indicating more water-soluble OC was formed during the FW event.”

*Page 6, line 12: How do the authors know the ionization efficiency of the observed compounds? i.e., the concentrations of some ions can be very high but with very poor ionization efficiency. This statement is purely speculative*

**Response:** The statement was not very appropriate as the reviewer mentioned. The water-soluble fraction eluted from the SPE column is easily ionized in negative ion mode. To be more careful, we have adjusted the presentation of the content (on page 6 lines 30-31).

“ESI is sensitive to polar compounds, and the compounds reported in this study is easily ionized in the negative ion mode (Qi et al., 2020).”

*Page 6, lines 13-14: That’s an incorrect assumption/statement. The matrix effect is one aspect. I strongly encourage the authors to check basic studies on ESI and revise their manuscript. Indeed the peak intensity can be impacted by the matrix but also depends on the ionization efficiency of individual compounds which is based on the functional groups present in each compound.*

**Response:** The peak intensity can be impacted by the ionization efficiency of individual compounds, which is based on the functional groups present in each compound. This is a sample to sample comparison for the same compounds and not that ion intensities for different compounds within a sample were compared. To clarify, we have made our statement more carefully in the manuscript (page 6 line 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 (Kourtchev et al., 2016; Lin et al., 2012a).”

*Page 6, line 19: This is actually surprising and not consistent with "normal" product distribution. Indeed in most of the previous studies, most of the identified ions are between 150-250 (i.e., monomers type) and a second mode is present between 300- 400 (dimers or high molecular weight compounds), see the previous characterization using ESI-MS (QTOF, Orbitrap, and FT-ICR). The authors should comment on such a curious product distribution.*

*The authors should clearly mention that probably the vast majority of the compounds were lost during the sampling preparation.*

**Response:** Thank you very much for this suggestion. There were some reasons for the differences between some previous studies and the present manuscript. Firstly, the distribution of monomers with  $m/z$  150-250 and dimers with  $m/z$  300-400 mainly aimed at compounds derived from low molecular weight precursors, such as  $\alpha/\beta$ -pinene. The distribution was observed in Zhang et al. (2017a) for highly oxygenated multifunctional compounds in  $\alpha$ -Pinene secondary organic aerosol, and Romonosky et al. (2017) for aqueous photochemistry of secondary organic aerosol of  $\alpha$ -pinene and  $\alpha$ -humulene. But our study looked at the complex mixture of the organic compounds in ambient aerosols. There is no such a single mass spectrogram distribution for them, as the same to the previous researches (Jiang et al., 2016; Tao et al., 2014; Lin et al., 2012b). Secondly, the Ultra High Resolution mass spectrometry such as QTOF, Orbitrap, and FT-ICR MS analysis has a different mass range and center of mass due to the differences of resolution and quality accuracy. Most of the identified ions in previous researches mentioned above were between 150-500 Da, and the high intensity peaks were between 200-300 Da or there was no obvious high intensity peak range. The majority ranges of compounds in our study analyzed by 15.0 T FT-ICR MS were from 150 to 700 Da, with the high intensity peaks between 250 and 450 Da. Finally, as the reviewer mentioned, it worth noting that some fractions of compounds might be lost during the sampling preparation, particularly for the low molecular weight ones. This note has been added in the revised manuscript. (on page 7 lines 5-9)

“Thousands of formulae (~6000–9500) were obtained in each spectrum with the majority ranged from 150 to 700 Da. The molecular weights of formulae with high intensity primarily distributed between 300 and 400 Da, which were higher than previous studies with 200 - 300 Da. On the one hand, the compounds being explored in present study have a larger mass range; on the other hand, it was worth noting that some fractions of compounds might be lost during our sampling preparation, particularly for the low molecular weight ones.”

*What is the reason to remove a major fraction of the organic compounds during the sampling preparation (i.e., page 3, lines 26-27)?*

**Response:** In ambient aerosols the organic components are mixed with inorganic constituents (e.g., ammonium, sulfate, nitrate, and sodium ions), which are abundant and greatly exceed the

concentrations of individual organics. Because of the special ionization mode of ESI FT-ICR MS, the presence of inorganic ions will interfere with the ion source and affect the detection results. Therefore, the inorganic salt ions should be removed from the extracts before they enter the instrumental analysis. To do that, the extracts were loaded on a solid phase extraction cartridge (Oasis HLB, Waters, USA) for desalting, which have been applied in most previous studies about ESI FT-ICR MS (Lin et al., 2012b; Bao et al., 2017; Gurganus et al., 2015; Yassine et al., 2014; Jiang et al., 2016; Mazzoleni et al., 2010). Simultaneously, some fraction of low molecular weight organic molecules, and sugars were also not retained by the cartridge. But, it had little effect on the results, as the study primarily focuses on organic compounds with relatively large molecular weights by ESI FT-ICR MS (For the FT-ICR MS analysis, lower mass cut-off for the ion trap was 100 Da and the mass limit was from 185 Da to 1000 Da). The reason has been briefly added in the revised manuscript. (on page 4 lines 8-9)

“The extract was combined and loaded onto a SPE cartridge (Oasis HLB, Waters, U.S.) for desalting...”.

*Page 6, line 33 and page 7, lines 1-2: This is overstated, the authors should provide deeper statistical analysis before making such a statement. Are the numbers really statistically different?*

**Response:** Thank you. The statements seem a bit decisive. To be more carefully, the conclusion has been made more rigorous. (on page 7 lines 23-25)

“These results suggested that FW emission contributes the formation of relatively high molecular weight compounds in urban aerosols. In addition, the average DBE values, an indicative of degree of unsaturation, increased from  $9.35 \pm 4.01$  in the NYE daytime to  $10.1 \pm 4.82$  in the NYE nighttime and  $11.2 \pm 4.98$  in the LNY daytime.”

*Page 7, line 8: Please provide numbers to support such a statement.*

**Response:** Thank you very much for this suggestion. The detailed numbers of high molecular weight compounds have been provided. (on page 7 lines 32-33, page 8 lines 1-2)

“..., FW emission dramatically increased the amounts of HMW (>400 Da) organic compounds from 3022 compounds in the NYE daytime to 4264 compounds in the NYE nighttime and 5206 compounds in the LNY daytime, while the relative abundance of three categories compounds were different.”

*Page 7, lines 12-14: I am confused by this sentence. Why did the authors refer to Ms2 studies while they didn't perform such an analysis.*

**Response:** We thank the reviewer for this comment. We agree that this sentence is redundant here and may cause some confusion. It was deleted in the revised manuscript. The original sentence was only to explain that there were different types of CHO compounds according to previous studies. And the main content of this article was not to discuss some individual compound structures. So, MS/MS studies have not been included in the study.

*Page 7, line 30: This statement is incorrect. It is not in urban aerosol but in the filter extract, i.e., after removing a major fraction of organic aerosol components.*

**Response:** We thank the reviewer for this comment. The filter extract was the fraction of water-soluble organic matter in urban aerosol. To clarify, the statement has been adjusted more carefully (on page 8 lines 19-21):

“As shown in Figure 4, the high intensity CHO compounds in the fraction of water-soluble organic matter in urban aerosols are primarily with C numbers of 15–27 and DBE values of 6–15, indicating that they potentially have one or more benzene rings in their molecules.”

*Page 9, lines 20-27: This section is confusing. please clarify, i.e., within the same paragraph the authors claim that CHON with O>3 are likely organonitrates and a few lines below nitroaromatics. In addition, the authors should keep in mind the difference in terms of ionization efficiency of such compounds: i.e., compounds containing nitro-functional groups have a very high ionization efficiency (e.g., nitroaromatics), unlike organonitrate compounds.*

**Response:** We thank the reviewer's comments. The nitro-aromatics were mainly discussed among different samples in our study. To clarify, the confusing parts were removed in the revised manuscript.

*Why is the CHONS group not discussed in the paper?*

**Response:** CHONS compounds are obviously subject to nighttime chemical oxidation. Due to the limited length of the paper, their characteristics were discussed in detail in another manuscript, especially for the investigation of the volatility of CHONS estimated by a molecular corridor method. To clarify, we have added the following sentence to the manuscript

in the end of the introduction as Reviewer #1 suggested (on 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.”

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