Author Responses to Comments

Notification to the authors:

1. Please ensure that the colour schemes used in your maps and charts allow readers with colour vision deficiencies to correctly interpret your findings. Please check your figures using the Coblis – Color Blindness Simulator (https://www.color-blindness.com/coblis-color-blindness-simulator/) and revise the colour schemes accordingly.

Response: According to the advice, we checked Figures using the Coblis – Color Blindness Simulator and revised the color schemes.

2. Please note that the Figure #12 is unreadable. Take care of a clear image before publishing.

Response: We changed the Figure 12 in the revised MS in order to make its image clear.

Referee#2 Comments

We thank the reviewer for his/her appreciation of our work and comments/suggestions. The MS is revised according to all the comments from the referee, and the point-by-point responses are provided below.

Specific Comments:

Generally, I'm confused by two points that proposed by the authors.

The first one is still, about the application of isotopes to trace the source contributions. In introduction section, the authors stated that the isotopic fractionation is more significant in the case of the isotopic composition of molecular species, but insignificant in the case of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$. However, the authors then added a sentence "unless gas-to-particle and/or particle-to-gas transitions are significant". So, to my understanding, the authors actually indicated that the fractionation effects could be significant on the values of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in aerosols. If so, then the authors can not directly use the values of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in aerosols to explore the source contributions in Sections 3.5 and 3.8, unless the fractionation effect on $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in Tianjin aerosols was clearly discussed.

Response: We thank the referee for raising this point. In fact, "the isotopic fractionation is more significant in the case of the isotopic composition of molecular species, but insignificant in the case of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$, because the TC and TN contents contain both the reactants and products in the particle phase and the gas-to-particle and/or particle-to-gas transitions are not intensive, except under extreme temperatures, even in the case of $NH_4^+ \leftrightarrow NH_3$". In order to avoid such confusion to the reader, we modified our statement in the introduction section, as stated above, in the revised MS (please see Lines 97-101). Therefore, the use of $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in aerosols to explore the source contributions in Sections 3.5 and 3.8, remain logical and valid and do not require any further discussion about the fractionation effect on $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ in Tianjin aerosols.

The second one is the use of WSOC/OC in Section 3.4. I'm quite confused with the explanation of the authors. The authors explained that "…WSOC is mainly generated by oxidation reactions of VOCs in the atmosphere, rather than primary emissions", and stated that "…the mass fraction of WSOC in OC can be regarded as an indicator of aging of aerosols in the atmosphere". Then, the authors also added a sentence that "…when the contribution of the WSOC is insignificant from biomass burning". However, according to the former paragraph and whole manuscript, the biomass burning is a key contributor to the aerosol components in Tianjin aerosols. So the WSOC/OC can still be used to explore the aging of aerosols? Why? The authors need to clarify this.

Response: Both secondary formation from VOCs and emission from biomass burning are the two major sources of WSOC. However, the WSOC/OC has been considered as an indicator for aging of aerosols in the atmosphere when the contribution of the WSOC is relatively low or insignificant from biomass burning emission. Therefore, based on the differences in the WSOC/OC between season and season(s), and their comparability with the literature and the linear relationship between WSOC and OC, we found that the secondary formation of WSOC is more intensive in spring/summer, but its contribution from biomass burning emissions is also significant, particularly in winter and autumn. In order to make it more clear to the reader, we modified and/or added some phrases in 4th paragraph: "WSOC --- Tianjin region", clarifying these points in the revised MS (see Lines 356-376).

Technical corrections:

Line 22: I don't think you have direct evidence to support the idea "…they were mainly driven by NO3 radicals in the former period"

Response: We agree with the referee. In order to avoid any potential misleading, we tone downed it by modifying the phrase: "were mostly" to "might be", in the revised MS (see Line 22).

Line 26: Add SO_4^{2-}, NO_3^- and NH_4^+ following sulfate, nitrate and ammonium, respectively. And double check the whole manuscript to define such abbreviations when they are first referred.

Response: Following the reviewer's suggestions, we added the SO_4^{2-}, NO_3^- and NH_4^+ following sulfate, nitrate and ammonium, respectively, in the revised MS (see Line 26). Also, checked the whole manuscript and given the text for abbreviations, when they referred for first time.

Line 35: Probably better to add a sentence to make it more meaningful, such as "Therefore, it is important to explore the source and formation process of the $PM_{2.5}$".

Response: We added "Therefore, it is important to explore the source and formation process of the $PM_{2.5}$." in the revised MS (see Line 35).

Line 36: change ":" to ",". And, double check whether the "-" (through the whole manuscript) is in English style.

Response: We changed the ":" to "," in the revised MS (see Line 37).

Line 40: Replace "(secondary OC, SOC)" with "to form secondary OC (SOC)"?

Response: We changed the "(secondary OC, SOC)" to "to form secondary OC (SOC)", in the revised MS (see Line 41).

Line 41: Add "," following "37%".

Response: We added the "," following "37%", in the revised MS (see Line 42).

Lines 71-74: I think better move these sentences to lines 127.

Response: Following the reviewer's suggestions, we moved these sentences to Lines 122 -128 in the revised MS.

Lines 123-125: I think the authors should focus on why trace the source and formation process in Tianjin aerosol is important, but not what they are stating in current version.

Response: Following the reviewer's advice, we completely changed this statement as follows: "Therefore, the investigation of the Tianjin aerosols sources and formation processes provide better insights on the types of aerosol sources at regional level, in addition to the local industrial and domestic pollutant emissions in North China.", in the revised MS (see Lines 120-122), to highlight the importance of this study.

Line 160: The authors better color the area of Tianjin instead of using a red star.

Response: We changed the map of Tianjin in the revised MS (see Figure 1).

Line 218: Explain how the 0.83 was obtained.

Response: 0.83 is the propagating error in WSON estimation.

If Q is some combination of sums and differences, i.e.

$$Q = a+b+c+\cdots+c-(x+y+\cdots+z),$$

then

$$\delta Q = \sqrt{(\delta a)^2+(\delta b)^2+\cdots+(\delta c)^2+(\delta x)^2+(\delta y)^2+\cdots+(\delta z)^2}$$

δQ is the propagating error. (Reference a summary of error propagation.)

WSON = WSTN − IN, IN = (14/42) × NO_3^- + (14/18) × NH_4^+, Thus,

δWSTN is 0.82, δNO_3^- is 0.10, δNH_4^+ is 0.15, are the random error generated during the experimental operation, according to the parallel experiment calculation.

$$\delta IN = \sqrt{(\frac{14}{62})^2\times(\delta NO_3^-)^2+(\frac{14}{18})^2\times(\delta NH_4^+)^2} = \sqrt{(\frac{14}{62})^2\times(0.10)^2+(\frac{14}{18})^2\times(0.15)^2} = 0.12$$

$$\delta WSON = \sqrt{(\delta WSTN)^2-(\delta IN)^2} = \sqrt{(0.82)^2+(0.12)^2} = 0.83$$

Line 223: IRMS

Response: We modified "IrMS" to "IRMS" in the revised MS (see Line 224 and Line 227).

Line 234: why 5 days??

Response: Since Tianjin weather is influenced by East Asian monsoon, the air masses arrived in Tianjin are mostly originate at regional scale. That is why, in order to understand the potential source regions at regional level during the campaign, we selected the backward air mass trajectories for 5-day period. We noted this point in the revised MS (see Lines 236-237).

Line 236: The authors should add some sentences about the descriptions of statistical analysis and remember to adjust the title of the 2.3 Section correspondingly.

Response: Following the reviewer's suggestions, we briefly described the data statistical analysis and added a phrase in the subsection title accordingly in the revised MS (see Lines 233 & 237-240).

Lines 263-264: Add citations.

Response: We added citations in the revised MS (see the Line 269).

Line 289: Replace "fruitful" with "effective".

Response: We changed "fruitful" to "effective" in the revised MS (see Line 294).

Line 312: Delete "and".

Response: We deleted "and" in the revised MS (see Line 317).

Line 339: "40,0"??

Response: We changed "40,0" to "40.0" in the revised MS (see Line 344).

Lines 375-378: Why the high concentrations of NO_3^- in aerosols could accelerate the oxidation reaction of VOCs by NO_3 radicals? Which process? Clarify it.

Response: Recently, based on model simulations and CIMS measurements, it has been found that NO3 radical oxidation of VOCs, particularly monoterpenes, through unimolecular reactions is one of the significant sources of SOA (Draper et al., ACS Earth & Space Chem., 3, 8, 1460-1470, 2019). We added this point with citation in the revised MS (see Line 384).

Figure 5. Add p-value after each regression function.

Response: We added the p-value at the Fig. 5 in the revised MS.

Line 402: Wrong number of -6.5.

Response: We corrected the typo: "−6.5" to "−26.5", in the revised MS (see Line 408).

Line 404: Double check whether the "±" is in English style.

Response: We checked whole text in the revised MS to make sure the "±" is in English style.

Lines 455-458: Why the increased emission in winter is not regarded as the reason for the peaked NO_3^-

concentration in winter?

Response: Yes, we agree with the reviewer's view. The enhanced emissions in winter could have also been made the higher levels of NO_3^- than that in other seasons. In addition, due to the large temperature difference between winter and summer, the atmospheric chemical process caused by temperature should have also been made certain contribution. We added the emission contribution in the revised MS (see Lines 461-462).

Lines 461-462: Why the oceanic source of SO_4^{2-} is not regarded as the reason for higher concentrations of SO_4^{2-} in summer than spring?

Response: Yes, we agree with the reviewer's view. The oceanic source of SO_4^{2-} is one of the reasons for higher concentration of SO_4^{2-} in summer, and we mentioned it in the revised MS (see Lines 469-470).

Lines 493-494: Keep consistent of "p", and double check the style of "≥".

Response: We checked whole text in the revised MS to make sure that the "p" and "≥" are in English style and uniform.

Lines 572-574: I don't think the authors can draw such conclusion based on the discuss above, because there is no discussions on the seasonal change of $\delta^{15}N_{TN}$ at all.

Response: We discussed the seasonal change of $\delta^{15}N_{TN}$ in Lines 540-543 showed in Figure 7 the revised MS. The $\delta^{15}N_{TN}$ showed higher value in summer which might be caused by marine air mass and biogenic emissions, while the low value of $\delta^{15}N_{TN}$ in winter, driven by primary emission. Such seasonal changes in $\delta^{15}N_{TN}$ suggest that the aerosol N might be substantially influenced by season-specific source(s) and/or the chemical aging of N species. Therefore, we believe that the conclusion drawn here is logical. However, we modified/added the phrases to tone down the conclusion in the revised MS (see Lines 579-581).