Authors' Response Anonymous Referee #2

This manuscript shows a detailed study on $PM_{2.5}$ in urban and suburban site of North China city (Tianjin). The study focused on the concentrations of different chemical components including carbonaceous (EC, OC, SOC, WSOC, WIOC, TC), nitrogenous (WSTN, IN, WSON) and other inorganic ions. Additionally, stable isotopes of total carbon and nitrogen in $PM_{2.5}$ were also shown. This sufficient and comprehensive study can help us further understand the source and atmospheric processes of fine aerosols in regional scale, and the data could help to promote scientific progress within the scope of Atmospheric Chemistry and Physics. However, quite a lot of necessary information that needed to help understanding the whole manuscript is lacking, and the paper is poorly written, the language and expressions need to be further improved. Detailed comments could be found as follows:

Response: We thank the referee for his/her critical reading of the manuscript, appreciation of our work and constructive comments and suggestions, which helped to improve the quality of the MS. The MS is revised according to all the comments from the referee. Our point-by-point responses to all the comments are provided below. Please see the revised MS for details of the revisions.

Specific Comments:

1. Major comments on introduction. The study aimed to explore the origins and atmospheric processes of fine particles through seasonal variations of carbonaceous (EC, OC, SOC, WSOC, WIOC, TC), nitrogenous (WSTN, IN, WSON), other inorganic ions and stable isotopes of TC and TN in urban and suburban site of Tianjin. Therefore, the background in introduction should include: why choose to study $PM_{2.5}$? why EC, OC, SOC, WSOC, WIOC, TC, WSTN, IN, WSON and stable isotopes are important in understanding the source and atmospheric process of aerosols? Why choose to study urban and suburban aerosols in Tianjin? Some of the information is presented in current version of the manuscript, however, more information needs to be added in introduction section. For example, the authors studied EC, OC, SOC, WSOC, WIOC, TC in the $PM_{2.5}$, however, there is only a simple introduction of EC and OC in the second paragraph, then why the authors also explored the seasonal variation of SOC, WSOC, WIOC? Are they important in understanding the source and atmospheric process of fine aerosols? Why? Similar problem also happens in nitrogenous components and other inorganic ions in introduction section. In addition, $\delta^{13}C_{TC}$ and $\delta^{15}N_{TN}$ of aerosols can be used to trace the emission source of aerosols, however, fractionation effects during the formation and transportation might modify the initial value of $\delta^{13}C$ and $\delta^{15}N$ from sources, which might lead to the uncertainties of directly using $\delta^{13}C$ and $\delta^{15}N$ in aerosols to trace source contributions. Therefore, the background about the role of fractionation effects in affecting the $\delta^{13}C$ and $\delta^{15}N$ in aerosols is important to understand the related result and its implications. However, no such information was found in current introduction section.

Response: Following the reviewer's comments/suggestions, we substantially improved the introduction section by adding the required contents on the importance of carbonaceous (EC, OC, WSOC, WIOC and SOC), nitrogenous (IN, ON and WSON) and inorganic ionic components in the revised MS (please see Lines 40-48 and 75-81).

Yes, we agree with the reviewer that the isotope fractionation during the secondary formation and transformation processes of aerosols modify the initial value of $\delta^{13}C$ and $\delta^{15}N$ of the aerosols. However, it would be significant in the case of $\delta^{13}C$ and $\delta^{15}N$ of molecular species, but relatively

lower in the case of the $\delta^{13}C$ and $\delta^{15}N$ of the total carbon (TC) and nitrogen (TN) unless gas-to-particle and/or particle-to-gas transitions are significant, because the TC and TN consist of both the reactants and products. Therefore, it is not possible to assess the influence of the isotope fractionation on the observed $\delta^{13}C$ and $\delta^{15}N$ of TC and TN, respectively, in $PM_{2.5}$. We noted this point in the revised MS (see Lines 88-95).

2. Major comments on Materials and methods. (1) Locations of the urban and suburban site needs to be indicated in a map to help better understanding of the results; (2) There are results of meteorology and backward air mass trajectories, however, no related information was found in Materials and methods section; (3) Necessary information is lacking. For example, what's the flow rate of the air sampler during sampling period? This is important, cause the authors continuously sampling for 72-h each time, if the flow rate is high, then I'm wondering whether the filter will be saturated or not, especially in winter when $PM_{2.5}$ is high; (3) Further explanation needs to be added to support the feasibility of the method. For example, the authors described "OC and EC were measured using OC/EC analyzer……, based on thermal light transmission ……and assuming the carbonate carbon was negligible." Why the carbonate carbon is negligible, is it really negligible in aerosols of Tianjin? In addition, the authors described that "The N contents of NO_2^-, NO_3^- and NH_4^+ were calculated from their concentrations." but how? the authors need to explain more. Lastly, there are quite large uncertainties in WSTN, WSON etc., however, the authors consider "……such errors do not influence the conclusions drawn from this study.", why? explain more.

Response: Following the reviewer's suggestion, (1) We have added the map of China with the sampling points: urban and suburban areas, (2) noted the data source information of meteorological parameters and backward air mass trajectory in sub-section 2.3, and (3) noted the flow rate of the air sampler in Tianjin in the revised MS.

It has been reported that the C removed by HCl treatment accounted for only 6.3% in total carbon (TC) at Gosan Island, South Korea, where the long-range transported airmasses enriched with dust are the major sources, rather than anthropogenic sources (Kawamura et al., 2004). Whereas in Tianjin, the anthropogenic emissions and subsequent secondary processes are considered as the major sources, and the contribution of soil dust is relatively much lower. That is why, we assumed the carbonate carbon as negligible in this study. We noted this point in the revised MS (see Lines 156-159)

We added the computing method of the N contents of NO_2^-, NO_3^- and NH_4^+ in the revised MS (see Line 201-202). As for the uncertainty of WSTN and WSON, we believe that this study explores the seasonal characteristics and possible sources of $PM_{2.5}$ in Tianjin, rather than the their atmospheric loadings. Since the uncertainty in the measurement of WSTN and WSON is common for samples, we believe that it may not seriously influence the overall conclusions.

3. Major comments on Results and discussion. The prominent problems in results and discussion are that (1) no statistic analysis of the results; (2) no literatures or data are provided to support the some of the explanations of the results. For example, in section 3.2, the authors expressed that "Furthermore, the average concentration of $PM_{2.5}$ found to be higher in spring than in autumn (Table 1), probably due to enhanced eruption of dust from open lands, due to gradual increase in wind speed in spring (Fig. 1).". First of all, the concentration of $PM_{2.5}$ is higher in spring than in autumn, is there any significant difference? Secondly, the authors owe this to "enhanced

eruption of dust from open lands", is there any reference to support this idea? For the other example, from lines 260-265, the authors said "…… the secondary formation of OC might be significant via adsorption and/or NO_3 radical driven oxidation reactions of VOCs." Are there any citations?? "…… the frequent precipitation events might result the enhanced wet deposition of……" Do you have any data about seasonal precipitation amount or reference to support this? These are only some examples chosen from the results and discussion section, in fact, there are quite a lot of sentences that need to be supported by reference. The authors need to carefully double check each sentence and complete with appropriate reference to confirm your conclusions.

Response: Following the reviewer's comments and suggestion, we thoroughly checked our interpretations and provided appropriate citations throughout the Discussion section in the revised MS. In fact, (1) we assessed the possible source of $PM_{2.5}$ based on the correlation between selected carbonaceous and ionic (marker) components and their statistical significance (p value). The p values are noted in the revised MS (see Section 3.3.1).

(2) Yes, the average concentration of $PM_{2.5}$ in spring is significantly higher than that in autumn at both sampling sites, which is twice higher than that in autumn. In fact, the dust storms over Mongolia and China are common in spring that enhance the loading of $PM_{2.5}$ in the East Asian atmosphere (Liu et al., 2011). We noted this point in the revised MS (see Lines 256-259).

(3) Secondary organic carbon (SOC) is generated from volatile organic compounds through physicochemical adsorption and photochemical reactions including multiphase reactions (Robinson et al., 2007; Wang et al., 2016). We cited these references in the revised MS (see Lines 293-295).

(4) Unfortunately, we do not have the rain data during the campaign. However, the temperate continental climate with high temperature prevails over the Tianjin region and the East Asian monsoon brings the humid oceanic air masses during summer that result in frequent precipitation events. Previous studies pointed out that more precipitation and stronger atmospheric vertical mixing in the summer was one of the reasons for the decrease of $PM_{2.5}$ concentration in summer (Wang et al., 2016;Luo et al., 2018;Tao et al., 2014). These points and citations are included in the revised MS (see Lines 295-297).

Technical corrections:

1. Line 42: Move "(2127 and 1356 Gg, respectively)" after "2000"; I addition, there are so many "respectively" through the whole manuscript, quite annoying and makes the sentences hard to understand. Generally, "respectively" is always used when to distinguish three or more different items, please double check and change the expressions through the manuscript.

Response: Following the reviewer's suggestion, we took care to avoid using the word "respectively" throughout the text in the revised MS.

2. Line 59, Please delete the "," after "thus".

Response: We deleted the "," mark in the revised MS (see Line 66).

3. Line 73, Change "theier" to "their".

Response: We corrected this typo in the revised MS (see Line 84).

4. Lines 90-91, Better give the area percentage of “agricultural fields and forests” around Tianjin.

Response: Following the reviewer’s suggestion, we added the area information of agricultural fields and forests in order to express the effect of biogenic emissions on aerosols in Tianjin. (see Lines 105-109).

5. Lines 93-94, Still have no idea why Tianjin is the “ideal location”.

Response: As detailed in Lines 103-112 in the revised MS, Tianjin receives the long-range transported air mass from different source regions (land and ocean), depending on season, in addition to the local anthropogenic emissions. That is why, Tianjin is considered as an ideal location for studying the aerosol characteristics of different origins and atmospheric processing (aging) in northern China.

6. Line 104, Change “measurement of its mass” to “mass measurement”.

Response: Following the reviewer’s suggestion, we modified it in the revised MS.

7. Line 131, Please explain “TIC, acidizing” and “wet oxidation”.

Response: Following the reviewer’s suggestion, we briefly described the methods of acidizing and wet oxidation of the sample in the revised MS (see Lines 165-167).

8. Line 173, There is a “, was 0.83”? What’s that mean?

Response: The 0.83 is the propagation error of WSON with the repetitive errors of NO_3^-, NH_4^+ and WSTN, and doesn’t possess any unit.

9. Lines 177-179, Such a long sentence, better break it into two or three sentences.

Response: Following the reviewer’s suggestion, we divided this sentence into two in the revised MS (see Lines 212-214).

10. Lines 180-185, The final $\delta^{13}C$ and $\delta^{15}N$ is relative to VPDB and atmospheric N_2? Better make it clear.

Response: Following the reviewer’s suggestion, we have added the reference standards in the revised MS (see Line 217)

11. Line 202, “…… a small portion of….”? How much?

Response: We noted the value of the portion (8%) in the revised MS (see Line 239).

12. Lines 289-290, So the wood combustion is not belonging to biomass burning?

Response: Yes, the wood combustion also includes under biomass burning. We modified it in the revised MS (see Lines 321-322).

13. Lines 291, 322 “……several times……” “……several times abundant…” How much?

Response: We replaced the word “several” with the value in the revised MS (see Lines 323 and 355)

14. Line 408, “……the NO_3^- is more susceptible for decomposition at higher temperatures……” so the NO_3^- decomposed to what? Which process?

Response: At high temperatures, NH_4NO_3 decomposed into gaseous HNO_3 and NH_3 (Russell et al., 1983). We noted this point in the revised MS (see Lines 442-443).

References:

Please see the citations in the List of References in the revised MS.