Responses to Interactive comment on "Characterization of submicron aerosols during a serious pollution month in Beijing (2013) using an aerodyne high-resolution aerosol mass spectrometer" by Referee #1

This manuscript discusses PM concentrations, chemistry, and sources in Beijing, China during the winter of 2013 when unprecedented concentrations of PM were observed. Measurements were made using a high resolution aerosol mass spectrometer (HRAMS) to probe size-resolved chemical composition of non-refractory material with high time resolution and to determine degrees of chemical aging. This article provides necessary measurements of an extreme PM event and is recommended for publication after major revision is made to the manuscript.

My main concern is that this manuscript has the potential to be a very high impact paper; however, in its current state the manuscript does not provide a clear interpretation of the chemical composition and sources of PM. The abstract for example, focuses on overall trends, which are interesting, but really don't give the reader a clear view of what caused the largest spikes in PM during their sampling period. Buried within the results section, the authors describe high contributions of COA and meteorological conditions where emissions from coal fired power plants contributed to elevated PM concentrations; this should be highlighted in the abstract. A reorganization of the manuscript is strongly suggested with the results clearly shown for different conditions/periods; as it stands, the paper is either divided into periods, diurnal trends, or differences in air masses, which makes it hard to follow. Another issue is that the main periods described (I,II,III) in the manuscript represent a very small portion of the main figures and it is nearly impossible to see the different trends described throughout the manuscript. Either the figures or the periods need to be changed. Lastly, the conclusions section is a reiteration of the abstract and as such needs to be revised. My specific comments can be found below:

We are thankful to the referee #1 for his or her comments and suggestions. We have revised the manuscript accordingly. Listed below are our point-by-point responses in blue to reviewer's comments.

1 Abstract:

Were differences in PMF factors seen between high PM vs lower PM events? How are the sources different based on meteorological conditions and back-trajectories?

Reply: (1) According to the comment, we did a lot of modifications in the revised manuscript. We divided to NR-PM_1 mass concentration into three levels according to the air quality standards which were released in 2012 by the Ministry of Environmental Protection (MEP) of the People's Republic of China, including the daily average mass concentration lower than 25.9 μg m^{-3}, between 25.9 μg m^{-3} and 55.5 μg m^{-3}, and higher than 55.5 μg m^{-3}. Then we added a detailed discussion to compare the composition of NR-PM_1 species and OA components in higher PM and lower PM days. Meanwhile, we also compared the contribution of every cluster in different PM days. The detailed information can be found in Section 3.5 (3.5.1 submicron aerosol composition; 3.5.3 the contribution of clusters)

2 Page 19010, Line 8: State the range to show that PM was variable.
Reply: we added the standard deviation for the related data throughout the manuscript.

3 Page 19010, Line 22-23: What sources likely contributed to PM coming from WNW during this elevated PM event?
Reply: The referees #2 thought that the PBL was expected to be very low (very likely below 500 m for the events) in this pollution month, which was one of the main reasons for the high pollution. We thought this comment is reasonable. Therefore, we reanalyzed the HYSPLIT model and found there were some different results compare the original conclusion. The detailed information can be found in section 3.4.

The PM in every cluster is the combined effect of the all components. The only difference between different clusters is the contribution proportions, and the related information can be found in Fig. 5. The secondary components may be derived from long-distance transmission and the second generation in the local. While the primary components may be derived from the primary sources, such as traffic sources, biomass burning and catering source, etc. Therefore, the high NR-PM_1 pollution in winter is a result of synergistic effects of all pollutants.

4 Introduction:
The introduction is too long. The latter half feels like a review of the AMS, which is not the purpose of this paper. I suggest focusing instead on previous work highlighting known sources of PM in China and seasonal trends in this PM. Most of paragraphs 3 and 4 can be condensed or deleted entirely to improve the flow.
Reply: We reorganized the introduction section. Then, some unnecessary content was deleted and we focused on the discussion about some previous work results. Meanwhile, we added the importance of our study in this section.

5 Experimental:
The authors never really introduce the different periods they talk about. I suggest introducing the different periods mentioned throughout the manuscript and how they are divided (e.g., how high was the PM, what was the air mass back-trajectory from, what were the meteorological conditions?). This could be shown in a table for clarity.
Reply: As the comment about divide the data, the original divide method caused some confusion. Therefore, we divide the data according to the air quality standards. Please refer to the reply for comment 1.

6 Also, the paper currently divides the data into periods I-III then later divides the data by air mass back-trajectory; I suggest divvying up the data in one, consistent way and to use this naming scheme either by period or back trajectory consistently throughout the manuscript.
Reply: We divided the data again according to the air quality standards. Then we used this divided data throughout the manuscript.

7 AMS Data Analysis:
This can be considerably shortened by putting details, such as different factor solutions that

are not used in this paper, in the supporting material.

Reply: This section has been shortened now, and related content was showed in supplementary information. In addition, we provided more detailed information about choose the optimal solution, including: (a) Q/Q expected (Q = the sum of squared scaled residuals over the whole dataset) plotted versus the number of factors used in the PMF solution; (b) Q/Q expected plotted versus the rotational forcing parameter (FPEAK) for solutions with 5 factors; (c) Median (the line within the box) and lower/upper quartiles (boxes) of the scaled residuals per m/z; (d,e) time series of the total residual and Q/Q expected contribution for every point in time during the study; (f) 3-factor profiles (mass spectra); and (g) time series the 3-factor solution (with FPEAK = -0.1); (h) 4-factor profiles and (i) time series for the 4-factor solution (with FPEAK=-0.1); (j) 6-factor profiles and (k) time series for the 6-factor solution (with FPEAK=-0.1). In addition a detailed discussion also is added in this part for chose the best solution.

Results:

8 Section 3.1:

Clearly define all the periods before you start to describe pollution events. As written it is hard to follow.

Reply: Please refer to the reply for comment 1.

9 Figure 1: The figures are small and very hard to read. I recommend blowing them up and making the numbers/axes bold. The periods are such a small portion of the figure and it is very hard to see the trends that are being described. Where are the NOx measurements described?

Reply: (1) A new divide data way was used now. Meanwhile, this figure was modified in revised manuscript. Then, it looks better. (2)We added the description about the NO_x measurements, such as the equipment, location, time period and the distance from AMS sample inlet.

10 Page 19019, Line 5: How high was the PM?

Reply: This section has been modified now, and a more detailed discussion has been added in section 3.5.

11 Page 19019, Lines 12-17: Why are the TEOM measurements mentioned if they aren't used?

Reply: The TEOM was used here as the comparative data. Then we can ensure there was not a patently unreasonable data appeared. Therefore, we only described the comparison result of two sets of data simply: "The two measurements are highly correlated, with a linear correlation coefficient (R^2) of 0.88 and a slope of 0.68 (Fig. S5)".

12 Page 19019, Line 18: How did the meteorology change between accumulation and "clean up"?

Reply: We added a detailed analysis about the relationship between the meteorological factors and NR-PM_1 species and OA components mass concentration in section 3.5.

13 Page 19019, Paragraph starting on Line 18: Did the air masses come from different places during the different periods?

Reply: A dedicated compare the air masses in pollution days and non-polluting days has been added in section 3.5.3

14 Page 19019, Line 27: Cite previous work showing that humidity enhances nitrate and sulfate.

Reply: This section has been modified. After reading some literatures (Ge et al., 2012; Shen et al., 2012; Sun et al., 2013), which studied the effect of aqueous-phase processing on NR-PM_1 species. We found that the aqueous-phase processing is a very important factor to affect the concentration of these species when the humidity at a higher level. Therefore, we discussed the effect of humidity on NR-PM_1 species from the new perspective. Then the variation of these species can be explained more reasonable.

(1) Ge, X. L., Zhang, Q., Sun, Y. L., Ruehl, C. R., Setyan, A.: Effect of aqueous-phase processing on aerosol chemistry and size distributions in Fresno, California, during wintertime, Environmental Chemistry, 9, 221-235, dio: 10.1071/EN11168, 2012.

(2) Shen, X., H., Lee, T. Y., Guo, J., Wang, X. F., Li, P. H., Xu, P. J., Wang, Y., Ren, Y., Wang, W., Wang, T., Cam, S. A., Collett, J. L.: Aqueous phase sulfate production in clouds in eastern China, Atmospheric Environment, 62, 502-511, dio: 10.1016/j.atmosenv.2012.07.079, 2012.

(3) Sun, Y. L., Wang, Z. F., Fu, P. Q., Jiang, Q., Yang, T., Li, J., Ge, X. L.: The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China, Atmospheric Environment, 77, 927-934, dio: 10.1016/j.atmosenv.2013.06.019, 2013.

15 Page 19020, Section starting on Line 15: I don't follow any of this discussion of black carbon. Black carbon was not measured and as such speculation of its contribution should not be included.

Reply: We are very sorry for our unclear expression. The purpose of these sentences is: In the study Beijing in 2008 and in New York in 2009, they calculate the contribution proportion of every species included NR-PM_1 and BC. While, we did not measured BC in this study. Thus we cannot compare the contribution proportion of every species directly. Then we excluded the BC and recalculated the contribution proportion of every NR-PM_1 species based on the data which can be found in these two papers. We revised the expression of this section. Then our purpose can be understood easily.

16 Page 19021, Lines 9-16: What did you find and where do you think this mode is coming from? I don't see how the Alfarra study applies to different conditions in a different city.

Reply: We added the related reference which discussed the source of the smaller mode, such as Huang et al., (2010, 2011) and Zhang et al., (2005). Meanwhile, the inappropriate reference was deleted now.

(1) Zhang, Q., Canagaratna, M. R. J., J. T., Worsnop, D. R., and Jimenez, J. L.: Time- and size resolved chemical composition of submicron particles in Pittsburgh: implications for aerosol sources and processes, J. Geophys. Res., 110, D07S09, doi:10.1029/2004jd004649, 2005.

(2) Huang, X.-F., He, L.-Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L.-W., Liu,

X.-G., Zhang, Y.-H., Jayne, J. T., Ng, N. L., and Worsnop, D. R.: Highly time resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos. Chem. Phys., 10, 8933–8945, doi:10.5194/acp-10-8933-2010, 2010.

(3) Huang, X. F., He, L. Y., Hu, M., Canagaratna, M. R., Kroll, J. H., Ng, N. L., Zhang, Y. H., Lin, Y., Xue, L., Sun, T. L., Liu, X. G., Shao, M., Jayne, J. T., and Worsnop, D. R.: Characterization of submicron aerosols at a rural site in Pearl River Delta of China using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos. Chem. Phys., 11, 1865–1877, doi:10.5194/acp-11-1865-2011, 2011.

Section 3.2:

17 Page 19022, Line 14: I don't understand how nitrate was determined to be all from traffic.

Reply: We are sorry for our arbitrarily statement and this sentence was revised now. Our mean is that the traffic emission is the important source of NO_x in urban, which is an important precursor of nitrate. The motor vehicles number is more than 5 million amounts in Beijing. It is really an important source of nitrate precursor in daytime. Moreover, the characteristics of meteorological condition were stable and high humidity, it is not only not conducive the spread and dilution of pollutants but also would cause the formation of secondary pollutants, such as nitrate.

Section 3.3:

18 Page 19024, Lines 10-14: What does this slope/anti-correlation mean?

Reply: The H/C and O/C ratios are good reference for oxidation state and photochemical age of OA. When the H/C ratio is high and O/C ratio is low, the OA is fresher. Contrary, when the H/C ratio is low and O/C ratio is high, the OA is more aged. Generally, the relationship between them is anti-correlation. However, the slope may be different in different studies. This different slope of OA can reflect different aging mechanisms in corresponding observation sites, such as oxidation, volatilization, mixing of air masses or condensation of further products. The popular slope of about -1.0 means that the chemical evolution of OA in the atmosphere may be simply represented by the movement along this line in models. While, when the slope deviation from -1, the evolution of OA in the atmosphere may be more complex. Ng et al. (2011) point out that a slope of -1 suggests addition of a carboxylic group without fragmentation or simultaneous alcohol and carbonyl addition on different carbons as the dominant aging mechanism. A slope of -0.5 would imply carboxylic group addition combined with fragmentation.

Ng, N. L., M. R. Canagaratna, J. L. Jimenez, P. S. Chhabra, J. H. Seinfeld, and D. R. Worsnop (2011), Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11(13), 6,465-6,474.

19 Page 19024, Lines 14-16: How are we to interpret these contributions of different elements?

Reply: The elemental composition is one of most important physicochemical properties of OA. It can influence the density, moisture absorption ability, and vapor pressure of OA. The contribution of different elements is different with the change of the study sites, and this information is basic information of element analysis. We can analysis the atomic ratios and

OM/OC ratio based on these information. Then we can determine the degree of oxidation of OA in the study site.

Section 3.4:

20 Paragraph starting on Page 19024, Line 26: This much detail about divvying up the OOA is unnecessary, just state that this wasn't done.

Reply: The unnecessary content was deleted now.

21 Page 19026, Line 20: Cooking is also a large contributor to other regions as well.

Reply: We added a comparison about the COA contribution with the results in other foreign cities. After the modify, the sentences is "Due to the uniqueness of Chinese cooking habits and culture, cooking emissions have been regarded as one of the major organic aerosol sources in urban Chinese environments and the contribution to OA (20%) is slightly higher than in some foreign cities, such as in Barcelona (17.0%) and New York city (16.0%) (Sun et al., 2011; Mohr et al., 2012)."

22 Page 19027, Sentence ending on line 5: I'm not sure how to interpret the O/C and OM/OC of NOA for the dataset.

Reply: According to the suggestion of referees #2, we found five factors may be more reasonable for our study, and then a CCOA (coal combustion OA) was indentified. Because we all known that the coal combustion a very important PM source in winter in Beijing. Then the results are more in line with the actual situation of Beijing. This was discussed in section 3.3.

23 Page 19027, Line 8: Please specify the ions used so we can also see them in the mass spectra.

Reply: The original section has been modified. Please refer to the reply for comment 22.

24 Page 19027, Line 16: How were these concentrations arrived at?

Reply: The original section has been modified. Please refer to the reply for comment 22.

25 Page 19028, Sentence ending on Line 6: In addition to citing other papers, it is also important to state where you think the observed NOA is coming from. It is also surprising that given the different source contributions (e.g. amines, urea, PAN) that they all show the same pattern.

Reply: The original section has been modified. Please refer to the reply for comment 22.

26 Page 19028, Lines 7-9: I thought OOA was higher than HOA from Figure 5.

Reply: We are sorry for our unclear statement. The purpose of this sentence is that the HOA has been identified in previous studies. Now, it is modified to "HOA has been extensively identified in previous factor analyses of AMS ambient aerosol datasets (Huang et al., 2010; Mohr et al., 2012; He et al., 2011)"

Section 3.5:

27 This whole section needs some polish with the observed differences in source and composition clearly laid out for the different trajectories. In general, I feel like the periods described throughout the manuscript should perhaps be arranged by air mass trajectory otherwise describing periods I-III particularly in Section 3.1 and then these new clusters in Section 3.5 are quite confusing to follow. I also suggest moving this section up in the manuscript to link chemistry with sources and meteorology.

Reply: We reorganized this section now. This section (section 3.4 in revised manuscript) was used to discuss the effect of air mass on the NR-PM_1 species and OA components mass concentration in whole period. In addition, a comparison about the difference in pollution days and non-polluting days was added in section 3.5.3.

28 Page 19029, Lines 12-16: HYSPLIT has been used MUCH more extensively than this. Also, these two studies seem to be used for a lot of interpretation throughout the manuscript.

Reply: Of course, the HYSPLIT model is a very useful air trajectory model and can used more extensively than this. But our study is focus on the NR-PM_1, thus the purpose here is want to show it has been used to explore the influence of regional transport on PM_1 loading and composition at many sampling sites. We thought it is not necessary to show it has been used in other areas, because many scholars are very familiar with this model. Of course, if the referee still thinks it is necessary to add the introduction about this model has been used in other areas, we will add the related information and references.

There is limited study on the NR-PM_1 based on the HR-ToF-AMS until now in Beijing. Therefore, these previous studies are very important for us. Moreover, it is more valuable compare the results which were measured in the same city, because the geographical environment are same. However, when we compare the results in different cities, the reasons which caused the difference of results will more complex.

29 Page 19030, Lines 8-12: A coal-fired power plant source of PM would also explain your elevated sulfate during the major PM events.

Reply: We reanalysis the HYSPLIT model and found there was some different compare the original conclusion (detailed reason please refer to reply for comment 3). The detailed information can be found in section 3.4.

Yes, the coal-fired power plant source is a very important source of PM, and we added the contribution of coal combustion on NR-PM_1. In addition, the CCOA also been indentified in section 3.3.

30 Page 19030, Line 13: What industrial sources are around Beijing?

Reply: The industrial sources around Beijing are very complex. Because there are a lot of polluting industries were migrated to the area around Beijing for the 29th Olympic Games in 2008. These industries include power plants, chemical plants, steel mills, building industry etc.

31 Page 19030, Lines 17-19: This sentence is very confusing. So the air masses have emissions from cities that are not high in nitrates? I would think traffic emissions would produce a lot of nitrate.

Reply: We are sorry for our unclear statement. The purpose of this sentence is NO_x is mainly emission form traffic sources. Meanwhile, it is the precursors of nitrate. Therefore, the air mass which passed over cities would carry large amounts of nitrate. Please refer to the reply for comment 17.

32 Page 19030, Lines 23-27: What is this rotation and how is it supposed to explain changes in chemistry?

Reply: The counterclockwise rotation is the order of observe the clusters, the order is cluster 1 → cluster 2 → cluster 3 → cluster 4 → cluster 5. This sentence is the analysis about the contribution proportion change of different species in different clusters. Because we found these clusters are passed over different area, including cleaning areas, industrial areas and urban areas etc.

33 Page 19031, Lines 1-13: This paragraph seems unnecessary, especially if the same periods are used to describe the chemistry, PM, and meteorology.

Reply: Before this paragraph, all discussion in this section is a whole discussion about the effect of air mass transport on the serious pollution month in Beijing. It is just an average result. However, we could not obtain the information on the change of the contribution in different pollution periods, such as the lower and higher PM pollution periods. Therefore, this paragraph is a more detailed analysis, a good supplement for the previous analysis. Moreover, this analysis could tell us which cluster is the main contributor in heavy pollution period or in cleaning period. So, we hope keep this paragraph. Meanwhile, this section was added in section 3.5 in revised manuscript.

Conclusions:

34 This is pretty much the abstract verbatim. Briefly summarize your findings then discuss the implications. What were the major sources during those high PM events? What sources should we be thinking about regulating? Are they hazardous to human health based on their composition?

Reply: The conclusions section has been reorganized according to the comment now.

Figures:

35 Figure 1: The temporal mainly shows data that doesn't fall within the main periods (I, II, III) discussed throughout the manuscript. Either enhance those periods or divide up the periods differently. This applies for most of the figures showing a temporal for all the data.

Reply: A new method of divide the data was used in revised manuscript. And we use the new method throughout the manuscript. Please refer to the reply for comment 1.

36 Figure 8: Could the resolution of the map be changed to show different regions a bit clearer? It would also be helpful to mark major cities, sources such as power plants, etc.

Reply: The map was generated by the HYSPLIT model automatically. The similar resolution maps were also used in other studies, such as Fig. 5 in Huang et al., 2010; Fig. 10 in Sun et al., 2010; Fig. 8 in He et al., 2011, etc.. But we provided the satellite images in supplementary information file (Fig. S1 and S7). We can found the sources around Beijing clearly. It is very

useful for readers to understand the source around Beijing.

37 Technical Details:
Throughout the manuscript, change “tow” to “two”
Reply: “tow” was replaced with “two” throughout the manuscript.

Page 19010, Line 10: Change “increasing fraction of the NR-PM1 load as NR-PM1 loading increased” to “increasing fraction of NR-PM1 as the mass conc of PM1 increased”
Reply: This sentence was changed.

Page 19011, Line 11: Delete "Meanwhile”
Reply: "Meanwhile” was deleted.

Page 19011, Line 25: Change “compositions” to “composition”
Reply: It was changed.

Page 19015, Line 23: The word should be “deconvolute”
Reply: It was changed.

Page 19021, Line 9: Delete “the” before “decreasing size”
Reply: It was deleted.

Page 19026, Line 28: After “despite” add “the fact that”
Reply: It was added.
Page 19026, Line 29: Delete “the” after “As”
Reply: It was deleted.

Page 19027, Line 1: Change “more resemble” to “are more similar”
Reply: It was changed.