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 # 2

The paper by Zhang et al. reports highly time-resolved PM1 data for Beijing in a polluted winter period. Although the measurement method (HR-ToF-AMS) and data results are timely, the paper in its present form is only an overview of the AMS results, that have been identified in many other regions and in this region in other season. It provides little new science that gives new insights into the chemistry or process in the atmosphere. In comparison with the previous AMS papers, there is also lack of new data analysis methods in this work that can lead to new science. The authors should take full advantage of the highly time- and size-resolved information offered by AMS and give more sophisticated data analysis on pollution events. Some interesting areas of analysis should have been done from the paper as detailed below, and exploring these in a new version of the paper would make it a possible candidate for this journal. Thus, I recommend very major revision of this manuscript in its present form before it can be considered for publication in ACP.

We are thankful to the referee #2 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.

Major comments: 1) A key word of the paper title is "a serious pollution month". After going through this paper, readers may be confused about such title. Almost all of the data analysis is based on the average case of the whole sampling period, which had a mean NR-PM1 mass of 87.4 _g m-3. As reported by Sun et al. (2010) and Huang et al. (2010), the NR-PM1 concentration in summer of Beijing was 61 _gm-3 for 2008 Olympic period and 80 _g m-3 for 2006. It is very reasonable to have some higher NR-PM1 concentrations in winter due to the unfavorable meteorological conditions and more combustion emissions. Therefore, if based on the average case, the observation period cannot be called "a serious pollution month". Actually, the most interesting things for this campaign are the very high pollution events, such as Jan 10-14, Jan 23-24, and Jan 27-31, while the authors failed to discuss the process and chemistry of these events separately, which makes the paper miss the chances to provide new science utilizing this interesting and potentially important dataset. This problem can be clearly seen in the abstract, which gives all the conclusions based on the average case rather than the high pollution events. This is the most important weakness of this paper.

Reply: It is really a very important comment for improve our manuscript. Therefore, we modified a lot of content of the original manuscript. (1) We divided the observational data 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. (2) We deleted the section 3.2 in original manuscript, because it is an average discussion on the diurnal variation, could not provide new result. Then we added section 3.5, which dedicated to compare the difference in pollution days and non-polluting days. This section include four parts, such as compare the submicron aerosol composition, diurnal variations of meteorology factors and NR-PM$_1$ composition, the contribution difference of clusters,

and particle acidity in pollution days and non-polluting days. (3) We added a discussion on the change of mass concentrations and mass fractions of NR-PM$_1$ species and OA components with the increase of NR-PM$_1$ mass loading, and compare with the result in winter in Beijing 2012 (section 3.6). We found the variation will more dramatic when the NR-PM$_1$ mass loading is higher than 210μg m^{-3}, which did not been found in 2012.

2) The PMF results are incomplete in many aspects, and more information about the method should be given in order to a) inform readers not in the AMS community with the technique so that they can better understand the results, b) allow the readers to evaluate whether the PMF solution could be the best choice, since this technique is quite dataset-dependent, and c) provide a record of the details of the analysis as a reference for others. As written, the current paper does not provide enough information to support these points. This is especially important when considering this is the first HR ToF-AMS-PMF paper from this group. i) Mass spectral and time-series variation with seed solution: While there was little change in the Q/Qexp in the seed variability, did the authors look at the actual PMF solutions and compare the time-series and mass spectra? This type of analysis was performed in DeCarlo et al. (2010) and showed significant variability in solutions with similar Q/Qexp. ii) Please report solutions (factor profiles and time-series, as well as their average relative contributions to total OA) for 3 and 5 factors at different fpeak-values and along with the (non-robustified) Q values (i.e., the sum of the scaled residuals) as an important mathematical diagnostic for the PMF solution. In addition, analysis of the residuals of the fit with figures is also necessary. Many other AMS papers in the literature include this information, often in supplemental information (Aiken et al., 2009; Aiken et al., 2010; Allan et al., 2010; De- Carlo et al., 2009; DeCarlo et al., 2010; He et al., 2011; Ulbrich et al., 2009). iii) The abundance of m/z 60 in the HOA mass spectrum indicates that the HOA factor identified here could be a mix of both traffic-related HOA and biomass burning aerosols. Can a biomass burning OA component be separated by rotation for the 5 factor solution? Since biomass burning is usually identified as an important source in this region in winter in the literature, it is strange that no biomass burning OA component was obtained by PMF analysis in this work. In this context, I expect the authors to discuss the potential presence of biomass burning OA in much more detail.

Reply: (1) According to the comment, we reanalyzed the PMF results. We found that the 5 factor may be more reasonable for our measurement despite there was not an obvious decrease of Q/Q expected value. Then the OA can be divided into five components, i.e., two oxygenated (LV-OOA and SV-OOA) organic aerosols, a coal combustion OA (CCOA), a cooking-related (COA), and a hydrocarbon-like (HOA). The MS of CCOA contain a lot of m/z 60 and this is close to the BBOA in other studies. But we thought the main source of this OA component is coal combustion, because: (1) Coal has been widely used in various industries, such as power plants, steel mills and cement production etc. Moreover, coal is the primary energy for heating in northern of China in winter. According to statistics, the total amount of coal in Beijing, Tianjin and Hebei province were 25 million, 50 million and 0.3 billion ton, respectively; (2) The similar OA component also observed in winter in Beijing 2012 by Sun et al., (2013). They made a detailed discussion and found it is more reasonable to define this OA component as CCOA. The detailed information can be found in Sun et al., (2013); (3) Wang et al. (2013)

found that for atmospheric aerosol studies, due to the similarity of organic signals between coal combustion and biomass burning measured by both AMS and ATOFMS, some "biomass burning aerosol tracers" may not be reliable.

The reason for we did not use the 5 factors in original manuscript is because: (1) We found that there was not an obvious decrease of Q/Q expected value; (2) We pay excessive attention on the N/C but ignored the actual situation in Beijing.

(2) After reference the literature of referee suggested. We added some important PMF diagnostic plots in supplementary information, 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 was added in this part for chose the best solution.

3) As one of the most important findings in this campaign, a lot of N-containing fragments and thus NOA was identified. Actually, due to the low concentrations of N-containing fragments in aerosol mass spectra, it is not easy to fit and thus quantify the N-containing ion peaks in the PIKA software. To make the detection of these N-containing fragments convincing and solid, the authors need to present example figures in supplemental information to demonstrate how the HR-MS ion peaks were fitted for the N-containing ions identified by this work, such as C2H7N, C3H8N, CHN, CH3N, CH4N, C2H3N, C2H4N, C6H7N, CH2NO, CH3NO2, etc.
Reply: The PMF results section has be reorganized now.

Other issues: i) Page 19027, Lines 8-10: Please provide appropriate citations to support that amines are from vehicle exhaust.
Reply: The PMF results section has be reorganized now.

ii) Page 19027, Lines 16-20: Since PAN is in the gas phase, how can its decomposition products be detected in the particle phase by AMS? This should be clarified.
Reply: The PMF results section has be reorganized now.

iii) Page 19028 Line 1: This statement may be wrong. From Figure 6a, it is clearly seen that both OOA and NOA had higher concentrations in the evening than in the daytime.
Reply: The PMF results section has be reorganized now. Meanwhile, the diurnal variation was discussed in section 3.5.2.

iv) Page 19028 Lines 5-6: This sentence is very confused, whether NOA was local or regional? Please clarify.
Reply: The PMF results section has be reorganized now.

v) As discussed in the paper, NOA showed many similar characteristics to those of OOA, such as temporal variation, diurnal variation, high O/C and m/z 44. This makes me think whether NOA is a type of OOA, i.e., SV-OOA, which has been identified in many regions but not in this campaign. Thus, the existing OOA could be LV-OOA. This may be a more reasonable explanation of the PMF results. The high nitrogen content of this component may just indicate many N-containing precursors were involved in the formation of SV-OOA.

Reply: This is a very useful for our analysis the PMF result again. In the revised manuscript, the NOA disappeared and the LV-OOA and CCOA were indentified. This result is more reasonable for the actual situation of Beijing.

vi) Page 19032, Lines 7-8 "NOA was identified as a dangerous signal because it included some harmful species": This work only detected some N-containing ions in the mass spectrum, at most, therefore it is not appropriate to evaluate the relevant toxicology of the original compounds in particles and give such conclusion. This sentence should be removed.

Reply: The new PMF results have been used now. This section was deleted.

4) The diurnal patterns of many species (e.g., organics, sulfate, nitrate, OOA and NOA) found in the present study are unusual (strong increase from the daytime until the evening, compared to Sun et al. (2010) and Huang et al. (2010) in Beijing in summer) and can hardly be attributed to the photochemical production as explained by the authors. If the photochemical process dominated, the high concentration levels cannot last to the late evening. This may indicate that other mechanisms like heterogeneous and/or aqueous reactions may be the responsible mechanism. Actually, the high pollution month at the beginning of this year in Beijing was reported to be very foggy and hazy. Under such conditions, as well as the low ambient temperature, photochemical reactions were not expected to be active. In foggy days, liquid water content (more than air temperature) is very likely to be a driving parameter for the temporal variations of these chemical species. As well known, the aqueous production of sulfate from SO2 is much faster than the photochemical production. I strongly encourage the authors to study the recent paper by Ge et al. (Ge, X., Q. Zhang, Y. Sun, C.R. Ruehl, and A. Setyan. Effect of Aqueous-Phase Processing on Aerosol Chemistry and Size Distributions in Fresno, California, During Wintertime. Environmental Chemistry, 9(3), 221-235, 2012), which has a similar dataset to this campaign and concluded that aqueous-phase processes significantly affect submicron aerosol chemistry and microphysics in the Central Valley of California during winter, responsible for the production of secondary species (sulfate, nitrate, ammonium and oxygenated organic aerosol). The authors need fully consider this issue since this will lead to very different conclusions of this paper. In addition, to explore the diurnal variations of species, it is highly recommended that the authors divide the dataset into two groups, i.e., the high pollution period and the relative low concentration period, to discuss in more detail.

Reply: Thanks for the useful suggestion. According to the suggestion, we divided the dataset into two groups and compared the difference of meteorological factors, NR-PM$_1$ species and OA components. Meanwhile, we re-analyzed the diurnal variation of NR-PM$_1$ species and OA components after reading some useful references (Ge et al., 2012;

Shen et al., 2012; Sun et al., 2013). The detailed information can be found in section 3.5.2.

(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.

Minor comments:

1) Why there are no BC data reported, which are much helpful to the data interpretation.

Reply: Unfortunately, there was not the BC date in the study period. The new instrument to measure the BC was started used in 6 February 2013. The BC data can be used in future research.

2) Page 19016, Lines 3-5: Support that demonstrates that the selected CE (0.5) is appropriate is quite necessary since CE is dataset-dependent. Especially in this work, the PM concentration ranged very largely. Is a constant CE appropriate for the whole period? In Figure S1, it is clearly seen that the NR-PM1 concentration cannot catch some high concentrations given by TEOM. Proper estimate of CE based on the measured composition can be used and the mass concentrations should be adjusted accordingly.

Reply: Middlebrook et al. (2013) discussed how to choose the appropriate CE value during process the AMS data under different conditions, such as high aerosol acidity, high ammonium nitrate fraction and high RH etc. In our study, the aerosol was acidic (we added a section to analysis the aerosol acidity), while the ammonium nitrate mass fraction (ANMF) almost always lower than 0.2. Therefore, the formula $CE_{dry}=max(0.45, 1.0-0.73 \times (NH_4/NH_{4,predict}))$ can be used in our measurement.

A group $PM_{2.5}$ data which measured by TEOM was used to compare with our results. Because we found that the PM_1 data after 28 January was missed and the instrument also experienced some leakage incidents after consult the administrator of TEOM instruments.

3) Page 19016, Lines 6-7: Have the transmission efficiency and field blank of the silica gel diffusion dryer been tested? For high PM events, the transmission efficiency could be an issue.

Reply: In our group, there are other measurements results can used to compare with the results measured by AMS. In the revised manuscript, we used the $PM_{2.5}$ data measured by TEOM as a reference (Fig. S4), because the PM_1 data after 28 January was missed. We can found that the trends of NR-PM_1 and $PM_{2.5}$ were very close and the difference of mass concentration between was always stable. In addition, the silica gel diffusion dryer has also been used in other studies in Beijing, such as Sun et al, (2012, and 2013). During their studies, this city also experienced many serious pollution events. Therefore, the silica gel diffusion dryer can be used this kind measurement.

4) Page 19016, Lines 18-21: It is important to list the ions that were downweighted or omitted for poor S/R.

Reply: We added the list, i.e. "There were 66 mass fragments (m/z 159-164, 190-191, 198-199, 202-203, 219-220, 263-268, 276-278, 295-301, 346-352, 367-369, 390-391, 418-441) were "weak" and their error estimates are increased by a factor of 2, and 30 mass fragments (m/z 204-205, 221, 257, 262, 319, 365, 444-466) were "bad" and they were removed."

5) Page 19020: A calculation of the particle acidity or ammonium balance for the dataset could be an interesting addition, especially during the high humidity periods.

Reply: A study on the particle acidity was added now. Meanwhile, we compared the difference between pollution days and non-polluting days. The detailed discussion can be found in section 3.5.4

6) Page 19021, Lines 4-8: If one carefully examines the size distributions, it can be found that that of nitrate is more like that of organics rather than sulfate, with a small peak at around 200 nm. This may indicate more production mechanisms of nitrate. The authors need to carefully analyze this feature.

Reply: This section has been modified now. The reasons for the broader size distribution of organics and nitrate also were listed.

7) Page 19024, Lines 10-15: What's the significance of the observed slope of 0.43 in the Van-Krevelan diagram? What is the different mechanism by this slope? Please discuss in more detail.

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.

8) Page 19025, Lines 29-30: What's the correlation of OOA with nitrate? Better or worse than with sulfate? This will give helpful information about the nature of OOA.

Reply: The OOA was divided into LV-OOA and SV-OOA in revised manuscript. But we found that the correlation coefficient R^2 between SV-OOA and nitrate was 0.25. The lower correlation coefficient also was observed before, such as in Barcelona ($R^2=0.22$) and New York ($R^2=0.05$). The lower correlation can be explained by the more complex generation mechanism in winter. This was detailed discussed in section 3.5.2.

9) Page 19029, Lines 17-20: In this pollution month, PBL was expected to be very low (very likely below 500 m for the events), which was one of the main reasons for the high pollution. Are data of the PBL height available for this campaign? It is thus not reasonable to use a starting height of 500 m to calculate back trajectories in this work, and various lower starting heights should be tried and the results should be summarized.

Reply: We thought this comment is reasonable. Therefore, we reanalysis the HYSPLIT model starting at 200 m above ground level in Beijing (39.97 °, 116.37 °) were calculated every 6 h (at 0, 6, 12 and 18:00 LT (local time)) during the entire campaign. Then found there was some different compare the original conclusion. The detailed discussion can be found in section 3.4.