

Interactive comment on “Characterization of submicron aerosols during a serious pollution month in Beijing (2013) using an aerodyne high-resolution aerosol mass spectrometer” by J. K. Zhang et al.

Anonymous Referee #2

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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

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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.

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 $\mu\text{g m}^{-3}$. As reported by Sun et al. (2010) and Huang et al. (2010), the NR-PM₁ concentration in summer of Beijing was 61 $\mu\text{g m}^{-3}$ for 2008 Olympic period and 80 $\mu\text{g m}^{-3}$ 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.

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-

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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/Q_{exp} 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/Q_{exp}. 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 f_{peak}-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; DeCarlo 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.

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. Other issues: i) Page 19027, Lines 8-10: Please provide appropriate citations to support that amines are from vehicle exhaust. ii) Page 19027, Lines 16-20: Since PAN is in the gas phase, how can

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its decomposition products be detected in the particle phase by AMS? This should be clarified. 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. iv) Page 19028 Lines 5-6: This sentence is very confused, whether NOA was local or regional? Please clarify. 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. 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

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.

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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.

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

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.

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.

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

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.

6) Page 19021, Lines 4-8: If one carefully examines the size distributions, it can be

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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.

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.

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.

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.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 19009, 2013.

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