

Interactive comment on “Aerosol composition and sources during the Chinese Spring Festival: fireworks, secondary aerosol, and holiday effects” by Q. Jiang et al.

This paper described the submicron aerosol composition and sources during Chinese Spring Festival in Beijing, with a focus on firework and holiday effect. On-line ACSM was applied. OA source apportionment were done by PMF. The topic of focusing on influences of anthropogenic activity (i.e., firework and population reduction) on changes of aerosol and its sources is interesting. The author find short term effect of firework on PM₁ for being a source of potassium, chloride, sulfate and oxygenated OA. By comparing the compositions of aerosol between Spring Festival and Non Spring Festival periods, the author find a larger reduction of primary species than secondary species due to the less anthropogenic activity in Beijing area, then conclude the controlling primary emission have a limited effect on air quality.

These are interesting results, however, some of the ideas in this paper are not so well organized and written. I firstly read the revised paper without reading comments. I found I have lots of the same questions as the other two reviewers do, e.g., the quantification of potassium with ACSM and the uncertainty of PMF source apportionment results. Although the authors answered all the comments in the responses, their responses to the other two reviewers are not well reflected in the revised manuscript. And also, some conclusions in this paper are needed more precise and careful deductions (see comments below). Thus, I recommend a mayor revision of this paper. The authors should address the questions below and add related necessary contents including the responses to the other reviewers into the paper.

Mayor comments:

- 1) The points of this paper should be addressed more carefully. The logic and English writing in the responses to the comments are much better than the main text of this paper itself.
- 2) About the quantification of potassium. Reviewer #4 already has a good comment on this issue. The authors should clearly address the large uncertainty of potassium measured in this study and let readers be aware of this issue, as well as KCl.

If it is possible, it will also be good that the authors can try KNO₃/KCl calibration and validate the RIE for their own ACSM instrument. Even the tuning will not be exactly the same as it was in field campaign period. Based on the big differences of RIE of K⁺ reported in the literature, 2.9 (Drewnick et al., 2006) or 10 (Slowik et al., 2010), the calibration results on their own instruments should be at least more accurate than the literature values from different instruments with different fireworks.

- 3) I think review #4 is right, HOA and CCOA factors on current solution are either mixed with each other or at least should be switched. It looks like that the current spectrum of HOA in Fig. S5 shows significantly higher m/z 91, m/z 77, m/z 105 and m/z 105 (Please check), which is very similar to the CCOA spectrum in Hu et al. (2013) cited by the authors in the responses. Those ions are supposed to be contributed by PAH species in

the coal combustion plumes (Hu et al., 2013). The diurnal variation of the current CCOA in paper shows similar trend to HOA in the morning but peaks during night. Huang et al. (2010) also shows a high peak in HOA factor in the summer of Beijing. Assuming the main sources of HOA that are vehicle emissions do not change very much among different seasons and years in Beijing, the current CCOA in this paper is more like HOA. About the BBOA influences, the authors should not only consider average f₆₀. Because when OA is more aged, f₆₀ will decrease. And also the influences of biomass burning may not exist for the whole campaign. Thus, please check the scatter plot of f₄₄ vs f₆₀ in this study, then compare it to biomass burning area in the scatter plot reported by Cubison et al. (2011). It should be clear to see if there is biomass burning influences during the campaign.

- 4) Line 23: The authors said the contributions estimated in this work would represent the upper limits of firework. However, dilution effects may also impact the aerosols during the firework period, which will reduce the firework contributions to total aerosols. Fig.S9(a) shows clearly that when wind direction changed from NW to NE, all mass concentrations of main components in aerosols dropped substantially. It seems that particles were diluted or scavenged after 21:00 including firework period. This assumption is supported by the continuous decrease of the background OA concentrations from 21:00 on 2/9/13 to 12:00 2/10/13 in Fig. 9(a).
- 5) Line 251-253: “Metals that were largely enhanced during FW period generally contribute a small fraction of PM (Wang et al., 2007; Vecchi et al., 2008). Please define “a small fraction”. And also this statement is conflict to what author saw in this paper. Figure 3 shows that 21% of total PM₁ in firework is contributed by K⁺, let alone the other metal species emitted by the firework.
- 6) Line 252: “Therefore, our results suggest that burning of fireworks has the most impact on aerosol particles in the size range of 1 – 2.5 μm”. Very vague statement. What does “impact” mean? Is firework the source of particle with size range of 1 – 2.5 μm, or through other effect?
- 7) Line 272: The authors stated that it is not impossible for aqueous-phase formation of sulfate during firework, and regarded “sulfate in FW-PM₁ was mainly from the direction emissions of FW”. Is there any other observation that support sulfate can be emitted directly in firework? One reference in this paper: Wang et al. (2007) suggested sulfate may come from heterogeneous catalytic transformations of SO₂. Fe could be the catalyst. Have the authors considered this probability?
- 8) Line 275-277: “most of it (nitrate) was likely from local sources and/or regional transport as supported by the large contributions of local”. If nitrate can be contributed by regional transport during firework period, sulfate and other species also have the probability to be influenced by regional transport. This is conflict with what authors said that sulfate was mainly come from direct emission of firework. One literature reported that “Nitrate was

mainly formed through homogeneous gas-phase reactions of NO₂ during firework. “Fe could catalyze the formation of nitrate through the reaction of α -Fe₂O₃ with HNO₃”. (Wang et al., 2007). Vecchi et al. (2007) and Cheng et al. (2014) also found a rapid increase of NO₃ with a factor of ~5 during firework period. In this paper, the authors saw various fraction of NO₃ in different firework period. High fraction of nitrate (12%) in LFD in this paper was also reported. Why do authors still think the nitrate mainly come from local sources/or regional transport during firework? Have the authors considered other probability like Wang et al. (2007) suggested?

- 9) Changes of absolute mass concentrations of different species in PM₁ between firework period and non-firework period should be considered as well.

Minor comments:

- 1) Experimental part: some important information of instrumentation should be more specifically addressed:
 - What's the RH in the sampling line before ACSM, which will influence CE of ACSM quite a lot (Middlebrook et al., 2011).
 - Did author use a cyclone before ACSM and Aethalometer?
 - What are the detection limits of different species in ACSM? They may be important for clean period in Beijing.
- 2) Figure S9 should be added into the main text. Most of the descriptions in 3.1 section are based on Figure S9. It is hard to figure out what the authors said based on Fig.1, e.g., line 223-225: the authors described the wind changed at 15:00-21:00 based on Fig.1. Whereas, it is not impossible to see that on Fig.1. Fig. S9 looks better.
- 3) Line 315-325: It is confusing that the authors talked about diurnal variations of several species based on their absolute mass concentrations but did not show them in graphs. These graphs should be at least added into supplementary information.
- 4) Line 327: “These results suggest that POA played more important roles than SOA in PM pollution during periods with high organic mass loadings..”. Please define “high mass loading”.
- 5) Line 59: It is not proper to use “despite this” here. It is not a contrast transition between two sentences. Similar to the usage of “despite this” in line 99.
- 6) Line 61-63: “Fine particles from various source emissions can be either primary from direct emissions...or secondary from atmospheric oxidation of gas-phase species.” “Secondary” is not “source emissions”, author cannot category secondary aerosol to be emissions.
- 7) Line 64: “one of the most important primary source”, should be “sources”
- 8) Line 75-76. “However, previous studies on chemical characterization of fireworks in China were mostly based on filter measurements with a time resolution of 12 h or 24

h... which may have large uncertainties in accurate quantification of chemical composition of FW particles”.

Why do filter on firework studies have large uncertainties? The ACSM cannot detect metal and semi-refractory species as the other filter-based techniques. It seems that the ACSM have larger uncertainties than filter method.

- 9) Line 83-84: Reference missing: “Secondary aerosol is of more concern compared to primary aerosol because it is formed over regional scales and exerts impacts on air quality over wider areas (Reference).”
- 10) Line 89-92: Reference missing: “SIA was observed to contribute a large fraction of PM_{2.5} and played an enhanced role during haze episodes due to the faster heterogeneous reactions associated with higher humidity. --(Reference) While SIA was relatively well characterized, secondary organic aerosol (SOA) is poorly understood.-- (Reference)”
- 11) Line 99: “Despite this, the role of SOA in fine particle pollution in Beijing is not well known, in particular during wintertime” What’s kind of role of SOA unknown? If the author talked about the SOA mass contribution to total aerosol or OA. Several papers already talked about the fraction of SOA in Beijing winter (Huang et al., 2014; Sun et al., 2014; Zhang et al., 2014).

Comments related to Figures:

Fig.1: Fig.1 shows two blue lines on the top 2 panels without labeling. It is hard to tell the time series of K⁺ from other traces based on the bottom panel.

Fig.3: The label of “chloride” should be consistent with other ions. “Chl” should be “Cl⁻”

Fig.4: It is not proper to say this is the spectrum of OA in FW, since the pronounced m/z 74 also contains KCl and m/z 37 is enhanced by HCl. It will cause confuses.

Fig.8: Why is PM_{2.5} enhanced during non-holiday periods but PM₁ decrease.

Fig.12: Uncertainties of ratios for different species between HD/NHD should be added.

Fig. S2: Please show the scatter plot of K⁺ and KCl.

Fig.S7 The time series of external tracers corresponding to each factor should be shown as well, since author already described them in the comments. It is more direct to see the graph.

Fig. S11 There is no shaded areas on the graph as caption described.

References:

- Drewnick, F., Hings, S. S., Curtius, J., Eerdekens, G., and Williams, J.: Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany, *Atmos Environ*, 40, 4316-4327, DOI 10.1016/j.atmosenv.2006.03.040, 2006.
- Hu, W. W., Hu, M., Yuan, B., Jimenez, J. L., Tang, Q., Peng, J. F., Hu, W., Shao, M., Wang, M., Zeng, L. M., Wu, Y. S., Gong, Z. H., Huang, X. F., and He, L. Y.: Insights on organic aerosol aging and the influence of coal combustion at a regional receptor site of central eastern China, *Atmos. Chem. Phys.*, 13, 10095-10112, 10.5194/acp-13-10095-2013, 2013.
- Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E., and Prevot, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, *Nature*, 514, 218-222, 10.1038/nature13774
<http://www.nature.com/nature/journal/v514/n7521/abs/nature13774.html#supplementary-information>, 2014.
- 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.
- Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, *Aerosol Sci Tech*, 46, 258-271, 10.1080/02786826.2011.620041, 2011.
- Slowik, J. G., Stroud, C., Bottenheim, J. W., Brickell, P. C., Chang, R. Y. W., Liggio, J., Makar, P. A., Martin, R. V., Moran, M. D., Shantz, N. C., Sjostedt, S. J., van Donkelaar, A., Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leitch, W. R., and Abbatt, J. P. D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, *Atmos. Chem. Phys.*, 10, 2825-2845, 10.5194/acp-10-2825-2010, 2010.
- Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., and Yin, Y.: Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013, *Journal of Geophysical Research: Atmospheres*, 119, 2014JD021641, 10.1002/2014jd021641, 2014.
- Zhang, J. K., Sun, Y., Liu, Z. R., Ji, D. S., Hu, B., Liu, Q., and Wang, Y. S.: Characterization of submicron aerosols during a month of serious pollution in Beijing, 2013, *Atmos. Chem. Phys.*, 14, 2887-2903, 10.5194/acp-14-2887-2014, 2014.