

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

Anonymous Referee #4

Received and published: 28 September 2014

The manuscript describes the chemical composition and sources of PM₁ in Beijing during February 2013, with a focus on the impact of fireworks on PM pollution in the Festival days. The authors measured the aerosol composition with an ACSM and used PMF for source apportionment. Characterization of chemical composition and sources of Chinese particulate matter are certainly of great interest. However, this manuscript is more like a routine study/report. There are quite some weak points (see below), especially the quantification of potassium with ACSM is not convincingly presented and the stability, uncertainty and validation of their PMF solution are lack and/or need substantial improvement. I therefore do not recommend publication in the high profile

C7473

journal ACP if these issues are not well resolved.

Major comments:

1. Quantification of potassium (K⁺) with AMS (ACSM) is very difficult. Potassium RIEs are very sensitive to instrument tuning and can change by orders of magnitude (personal experience: range 5-50). Slowik et al. (2010) for example reported RIE_K = 10 and stated that quantification is very difficult. The reason for that is the tendency of potassium for surface ionization. Depending on the tuning of the spectrometer and exact temperature of the vaporizer the ratio between potassium ions from surface ionization (SI) and electron impact (EI) ionization can vary a lot. Large differences between different instruments (especially different types like ToF-AMS and Q-ACSM) are expected. Even within a measurement campaign RIE_K could change significantly due to changes at the vaporizer surface. The stability of SI/EI during a campaign can be checked by correlating K⁺ to Na⁺ that is affected similarly.
2. The second major issue is related to the stability of their PMF solution and the uncertainty. The authors did not provide any error or uncertainty of their PMF results, while they should at least present the average of a few seed runs and the standard deviations (for both factor profiles and factor time series). In the present manuscript, only profiles and time series are shown. What external tracers were used for the validation of the PMF factors?
3. The OM fireworks contribution is apportioned to all the primary factors, this most probably means that they need one more factor at least to explain the firework episodes.
4. Some factors seem to be mixed, e.g. high m/z 44 in COA, m/z 60 in HOA and COA. This shows the possible mixing between HOA and CCOA. I would have suspected m/z 91 or m/z 95 to be higher in CCOA than in HOA. Diurnal variations also indicate mixing of HOA and CCOA. HOA does not show any rush hour peaks while CCOA shows an evening peak. A short view at the BC diurnal of Fig S8 suggests a higher correlation

C7474

of CCOA with BC than HOA. A BC source partitioning in BC from traffic and BC from wood/coal burning along the lines of Sandradewi et al. (2008) may improve the picture.

5. No BBOA? Why? There seems to be m/z 60 in the HOA and COA. Is f60 above the threshold of 0.3% (Cubison et al. 2011)?

Specific comments:

1. L139: "same aerosol sampling, vaporisation and ionisation" is not correct. ACSM switches between ambient and filter while in the AMS the beam is periodically blocked by a chopper wheel. In addition, the vaporizer chamber is smaller in the ACSM and the filaments are made of different material.

2. L141: not only lower sensitivity but also lower mass resolution.

3. L163: default RIE for SO₄ may significantly differ from the real SO₄_RIE (values between ~0.5 and 1.4 were measured). How does the ion balance look like? Is the aerosol neutralized? Budisulistiorini et al (doi:10.5194/amt-7-1929-2014) presented a way to estimate RIE_SO₄ from the dataset.

4. L170: Is this assumption valid? Under winter conditions, one of the most important sources of K⁺ is biomass burning. As mentioned below, K⁺ contributes to 7% of the total PM₁ during normal days.

5. L178: "inappropriate fragmentation ratio at m/z35". What was the issue? What is the reason for negative m/z 35 values? Any speculation? Could this be an indication of (slowly evaporating) sea salt?

6. L189: what external tracers were used for the validation of the PMF? Why are these correlations not shown? The validation of the PMF results is very weak! Only profiles and time series are shown.

7. FigS1b: Is this behavior also seen in m/z 41 (potassium isotope).

8. FigS2: Do residuals of m/z76 (KCl isotope) have the same pattern? And
C7475

how does the residual of a purely organic fragment look like? Assumptions are only valid if peaks do not show up at organic fragments. Otherwise it is a PMF artifact. PMF does have issues with outliers. Extra caution is necessary for large singular short term plumes. They are routinely excluded from the PMF. See http://www.epa.gov/heasd/documents/PMF_5.0_User_Guide.pdf: "Impacts such as fireworks represent a challenge for PMF and multivariate models because they are infrequent short duration events with high concentrations." and "The user should also examine time series for extreme events that should be excluded from modeling (for example, elevated potassium concentrations on the Fourth of July from fireworks)."

9. Fig4b: Correlation between MS_FW and LV-OOA and the following conclusion that most FW-OA is secondary is invalid!! m/z 44 and m/z 18 dominate the regression and make it almost a two point fit (18 & 44 vs rest) with misleading high R². Correlation of MS_NFW or MS_BG with LV-OOA is probably also close to R²=0.94. Correlation should be shown excluding 44 and 18. Spectra in Fig 4b do show significant differences, e.g. ratios 41/42, 55/57.

10. Fig3: Potassium quantification with extremely high uncertainties in pie charts.

11. FigS9: same as Fig8.

Reference:

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., Leaitch, 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, doi:10.5194/acp-10-2825-2010, 2010.

Sandradewi, J., Prévôt, A. S. H., Alfarra, M. R., Szidat, S., Wehrli, M. N., Ruff, M., Weimer, S., Lanz, V. A., Weingartner, E., Perron, N., Caseiro, A., Kasper-Giebl, A.,

Puxbaum, H., Wacker, L., and Baltensperger, U.: Comparison of several wood smoke markers and source apportionment methods for wood burning particulate mass, *Atmos. Chem. Phys. Discuss.*, 8, 8091-8118, doi:10.5194/acpd-8-8091-2008, 2008.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys.*, 11, 12049-12064, doi:10.5194/acp-11-12049-2011, 2011.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 20617, 2014.

C7477