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November 6, 2014

Editor, Atmospheric Chemistry and Physics
Dr. Yafang Cheng

Dear Dr. Cheng,

Please find in next pages our point-to-point responses to the comments on our manuscript offered by two reviewers. Most comments by reviewer #4 have been addressed in the ACPD version of the manuscript including a more detailed validation of PMF solution and the uncertainties for K quantification. The reviewer #4 might have missed these changes in our manuscript.

We are confident that we have addressed all comments satisfactorily and that our revised manuscript meets the high quality standards of ACP. We look forward to hearing back from you.

A marked-up manuscript version is also enclosed.

Thank you for your consideration.

Sincerely,

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Response to Reviewer #1

General comments:

The manuscript reports the chemical composition of non-refractory particulate matter with vacuum aerodynamic diameter less than 1 micron (NR-PM_1) measured by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) in Beijing, China during the Chinese Spring Festival. The field study focuses on evaluating the potential impacts of fireworks and a short-term reduction of population in Beijing during the holiday on air quality as well as the significance of secondary aerosol (both inorganics and organics) formation. The manuscript provide important insight in term of air quality control strategies that reducing primary local emissions only have limited influences to improve the air quality in Beijing, thus highlighting the importance of joint efforts over regional scales for air pollution control in northern China. Overall, I recommend this manuscript to be published after addressing the specific comments below:

We thank the reviewer for his/her positive comments.

Specific comments:

1. Section 2.3: There are a few issues on the quantification of K and Cl ions using ACSM data:

1) Page 20623, line 20-21: The meaning of "PMF modelled m/z 74" is unclear. Figure S2 does not provide any explanation. Please provide details.

The "PMF modeled *m/z* 74" was clarified in the revised manuscript as: "The PMF modeled *m/z* 74 refers to the sum of *m/z* 74 in four OA factors, i.e., HOA, COA, CCOA, and OOA."

2)Page 20623, Line 19: Drewnick et al. (2006) did not calibrate their ToF-AMS using chemical standard and thus estimated the RIE of 2.9 for K^+, which is based on the potassium to-sulfate ratio (2.76) determined by PIXE analysis on fireworks aerosol sample from Dutcher et al. (1999). The RIE of K^+ could be instrument dependent. Can the authors perform a similar comparison and comment on the accuracy of using RIE of 2.9 for K^+ quantification in this study?

We agree with the reviewer that quantification of K with AMS might have large uncertainties, and the RIE_K can be instrument dependent. Unfortunately, we were unable to estimate the RIE_K using the approach described in Drewnick et al.(2006) because we didn't have collocated K^+ and sulfur (S) measurements in this study. As a result, RIE_K = 2.9 estimated from fireworks by Drewnick et al.(2006) was used. The AMS quantified K^+ during LFD and LF contributed 4.5% and 4.7% of PM_1, respectively, which is very close to ~5% ($PM_{2.5}$) reported by Cheng et al. (2014). The results suggest that RIE_K = 2.9 is likely reasonable for our study. The large contribution of K during LNY was likely due to the intensified firework emissions (mainly firecrackers), especially between 0:00 – 3:00 am. Because we don't have

The quantification of K^+ might affect the bulk aerosol composition of fireworks, yet it has negligible effects on our discussions on secondary aerosols and the impacts of reduced emissions on aerosol chemistry during the holiday because the three short-term FW events were all excluded.

3) Page 20623, Line 25-26: Organic aerosol contributes to fragment C_3^+ at m/z 36 in ambient environment. Can the authors estimate the uncertainty due to the presence of fragment C_3^+ to the quantification of HCl^+ based on the non-fireworks period?

Based on our winter (2013-2014) measurements by an Aerodyne High-resolution Time-of-Flight Aerosol Mass Spectrometer at the same location, the C_3^+ contributed a negligible fraction to *m/z* 36 (< 0.1%, Figure A1). Therefore, C_3^+ should have minor effects on our quantification of HCl^+ although the measurement was conducted in a different year.

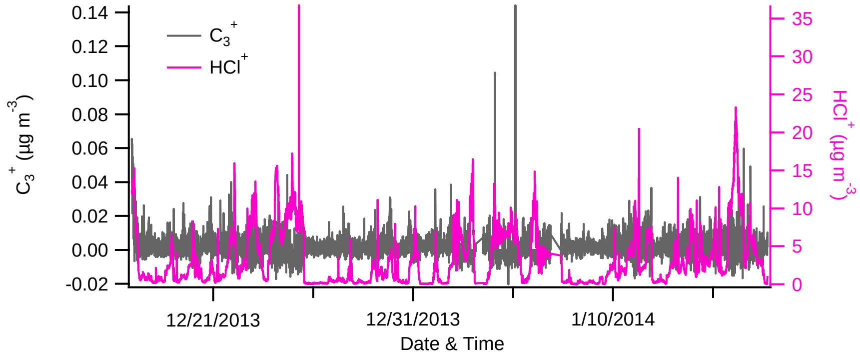

Figure A1. Time series of C_3^+ and HCl^+ at *m/z* 36. The data was from the W-mode measurement by the HR-ToF-AMS

2.Page 20625, line 2-4 and line 20-23: 1) Please confirm whether the meteorological conditions during LF period were stagnant. The wind direction was changing during LF period (It is hard to read in the print out of Figure 1, please see recommendation in technical comments).

Yes, the meteorological conditions during LF period were stagnant. As shown in Figure S9c, the wind speed remained consistently low (~ 1 m s^{-1}) and the wind direction was also consistently from the east.

2) The authors suggest that their estimation represents the upper limits of fireworks aerosol contributed to the total PM due to several reasons. However, it is not clear whether the pollutants in particular PM were carried to or removed from the sampling location due to wind direction changes. Please clarify.

The wind directions during Lunar New Year (LNY) and Lantern Festival (LF) were relatively stable. Thus, minor impacts of transport on our estimation are expected during these two holidays. Different from LNY and LF, there was an evident change of wind direction during Lunar Fifth Day (from north to south and then from south to north). All aerosol species (Figure S1b) including nitrate with minor impacts from fireworks showed synchronous increases between 18:00-21:00, and then decreases between 21:00 - 24:00. We would argue that the transport from outside of the location might have played an important role. However, it is difficult to quantify the contributions of transport based on the measurements in this study.

3. Page 20267, line 12-14: Even though LV-OOA component has been considered as aged secondary organic aerosol (SOA) in ambient, it is likely not straight forward to comment on the nature (primary vs. secondary) of OA generated in FW period based on the mass spectral features alone. First, the FW-OOA mass spectra may depend on the manufacturing materials (such as organic component if any) of firework. Furthermore, the freshly formed SOA (i.e. SV-OOA) are generally less oxygenated (i.e. lower O:C) and has a lower organic signal at m/z 44 than LV-OOA. However, it would be interesting to understand if it is possible to create a highly oxidizing ambient environment during fireworks for LV-OOA production.

We agree with the reviewer that the freshly formed SOA is generally less oxygenated. The mass spectral similarity of FW-OA to LV-OOA might be due to the burning of oxygenated organic materials in fireworks though we don't have further evidence to support it. We thank the reviewer for pointing out such an interesting question that should be addressed in future studies.

4. CAPS measurement: Was there any RH control before the CAPS inlet? Secondary inorganic species are hygroscopic in nature, thus resulting in larger size and higher extinction efficiency under high RH. Please clarify.

A silica gel dryer was put in front of the CAPS monitor during this study. The relative humidity after the dryer is generally below 40%. Therefore, the extinction we measured in this study refers to dry particles. This information is now added in the text.

5. HOA and BC in holiday period: 1) Page 20630, line 24-29: In general, heavy-duty vehicles/diesel trucks emit more black carbon (BC) compared to gasoline vehicle. Reduction of BC and slight increasing of HOA during holiday period suggests that significant fraction of BC was emitted from sources (i.e. coal combustion) other than diesel vehicles in Beijing.

We thank the reviewer's suggestion. Indeed, coal combustion is a large source of BC and CO during heating season (Tian et al., 2008;Zhi et al., 2008). This is also consistent with the relatively similar reductions of BC and CO to CCOA. We added this information into the discussions.

2) Page 20631, line 3-4: The authors argue that HOA showed comparably lower concentration during holiday, but it is contradict to the previous discussion (Page 20630, line 24-25) and Figure 8 (Ratio$_{HD/NHD}$ of HOA _1). Please justify.

Thank the reviewer's carefulness. The HOA showed slightly lower concentration during 11 – 17 February than other periods leading to a slight reduction (~5%) during the long holiday period (7 – 19 February, Figure 8). The results suggest that there was a small holiday effect on HOA reduction, but not as significant as other primary species. If the official holiday (9 – 15 February) was used for the comparison, the HOA showed a slight increase instead, mainly due to the large increase of HOA on 9 February – the first day of the official holiday. For the clarification, we revised the statement and now it reads "HOA showed slightly lower concentration during 11 – 17 February than other periods. In fact, the average HOA showed a slight reduction (~5%) during the long holiday period (7 – 19 February) suggesting a small holiday effect on HOA reduction."

Technical comments:

1. Page 20623, line 17: Please change the equation to "m/z 39 – (m/z 43 x 0.45)"

Changed

2. Figure 1 and Figure S9: 1) K and KCl signals are tracers for the fireworks aerosol particles as shown in Figure S9. Since the focus of Section 3.1 and 3.2 is to investigate the short-term impacts of fireworks on air quality, it is recommended to include time series of K and KCl in Figure 1 and refer the zoom in to Figure S9 in order to clearly illustrate the impacts of fireworks on different aerosol species.

We thank the reviewer's suggestions. The time series of K was included in Figure 1. However it is difficult to read the time series of KCl because its concentration was too low. Given that KCl correlates tightly with K (r^2 = 0.82), it was not included in Figure 1. Following the reviewer's suggestions, we added "A more detailed time series of aerosol species during the three fireworks events are shown in Fig. S9." in the figure caption of Figure 1.

2) Please also include wind direction plots in Figure S9 as it is often discussed in the text but it is hard to compare different time series in Figure 1.

The wind direction and wind speed were included in Figure S9 in the revised manuscript.

3) The gray color for the clean periods is not clearly showed in Figure 1. Please change the color.

The color for the clean periods was changed to light blue for easy reading.

3. Page 20267, line 21: Change "overestimate" to "underestimate"?

We revised this sentence to avoid confusion. Now it reads "It should be noted that our approach might overestimate the POA components in FW-OA because of the influences of NFW sources, in particular during the FW period of LF when the local HOA, COA, and CCOA happened to have large increases."

Response to Reviewer #4

The manuscript describes the chemical composition and sources of PM_1 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 journal ACP if these issues are not well resolved.

We thank the reviewer's comments. In the revised manuscript, we significantly expanded the validation of PMF solution and also addressed the uncertainties for the quantification of K.

We disagree with the reviewer that this manuscript is a routine report. Our study not only characterized the short-term fireworks impacts on PM pollution, but also investigated the role of secondary aerosols in PM pollution and the impacts of reduced anthropogenic emissions on aerosol chemistry. In particular, we found that reducing primary local emissions have limited influences to improve the air quality in Beijing, thus highlighting the importance of joint efforts over regional scales for air pollution control in northern China.

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.

We agree with the reviewer that quantification of K with AMS is challenging because of surface ionization issue. Slowik et al. (2010) reported a $RIE_K = 10$ based on the calibration of pure KNO_3 particles, while Drewnick et al. (2006) obtained $RIE_K = 2.9$ based on the comparisons of K/S from fireworks and AMS measurements. Unfortunately we didn't have collocated K measurement, $RIE_K = 2.9$ that was estimated from fireworks was therefore used in this study. The quantified K during LFD and LF contributed 4.5% and 4.7% of PM_1, respectively, which is close to ~5% ($PM_{2.5}$) reported by Cheng et al. (2014). These results suggest that $RIE_K = 2.9$ appear to be reasonable for our study. The large contribution of K during LNY was likely due to the intensified firework emissions (mainly firecrackers), especially between 0:00 – 3:00 am.

Following the reviewer's suggestions, we checked the ratio of m/z 39/23 throughout the study. The average ratio of *m/z* 39/23 during LFD and LF is 8.7 and 11.1, respectively, which is close to 9.0 during the NFW periods. Higher ratio of *m/z* 39/23 (=26.4) was observed during LNY. One explanation is the fireworks burned during LNY were mainly firecrackers which are different from those during LF.

In addition, the K in this study is primarily used to identify the FW events. Although the quantification of K has some uncertainties and might affect the bulk aerosol composition of fireworks to some extent, it has negligible effects on our discussions on secondary aerosol and the impacts of reduced emissions on aerosol chemistry during the holiday because the three short-term FW events were all excluded.

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?

We thank the reviewer's comments. In the revised manuscript, we significantly expanded the supplementary materials on the chosen of PMF solutions.

Fig. A2 shows the mass fraction of OA components as a function of fpeak values. Overall, the contribution of each OA factor was relatively stable across different fpeak values (average ± 1σ; min – max): HOA (14±1.6%; 12 – 16%); COA (14±2.8%; 11 – 17%); CCOA (19±2.7%; 15 – 22%); OOA (51±1.7; 49 – 55%). As shown in Fig. A3a, the time series of four OA factors for 3 different fpeak values (-1, 0, and 1) agree overall well. However, the mass spectra of OA factors have large differences (Fig. A3b). Most mass spectra of OA factors at fpeak > 1 are largely different from the standard mass spectra reported in Ng et al. (2011) and those resolved in winter 2011-2012 (Sun et al., 2013b). Figure A4 showed that the mass spectra of OA factors at fpeak = -1 presented the best correlation with those identified in winter 2011-2012 (Sun et al., 2013b). Therefore, four factor solution with fpeak = -1 was chosen in this study.

The external tracers used to validate the PMF factors include NO_3, SO_4, SO_4+NO_3, Chl, BC, NO_x, CO, *m/z* 60, etc. Similar to previous studies (Sun et al., 2013b), OOA shows the best correlation with NO_3 ($r^2 = 0.90$) and good correlation with SO_4+NO_3 ($r^2 = 0.87$). It's interesting to note that the correlations between HOA+CCOA and BC ($r^2 = 0.88$), NO_x ($r^2 = 0.77$), and CO ($r^2 = 0.63$) are higher than those between HOA and BC/NO_x/CO ($r^2 = 0.36 – 0.47$). These results suggest that coal combustion emissions during wintertime are also important sources of CO, BC and NO_x (Tian et al., 2008;Zhi et al., 2008). CCOA also correlates with *m/z* 60 ($r^2 = 0.77$). Although COA didn't have external tracers to validate, it is very distinct as suggested by its unique diurnal patterns (two peaks corresponding to meal time) and high *m/z* 55/57 ratio.

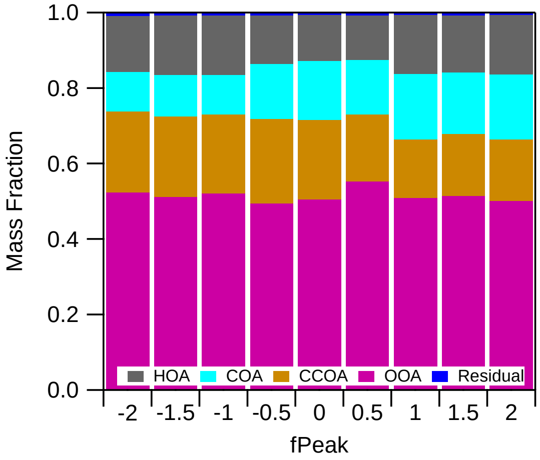

Figure A2. Mass fraction of four OA factors (from 6-factor solution; three OOA factors were combined into one OOA factor) as a function of fpeak values.

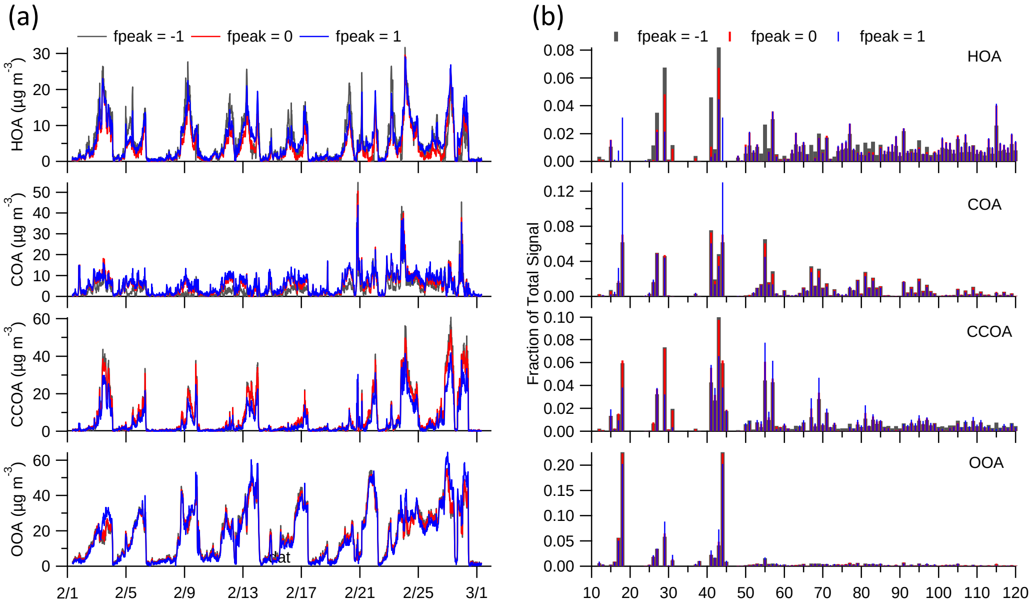

Fig. A3. Time series and mass spectra of four OA factors for three different fpeak values (-1, 0, and 1)

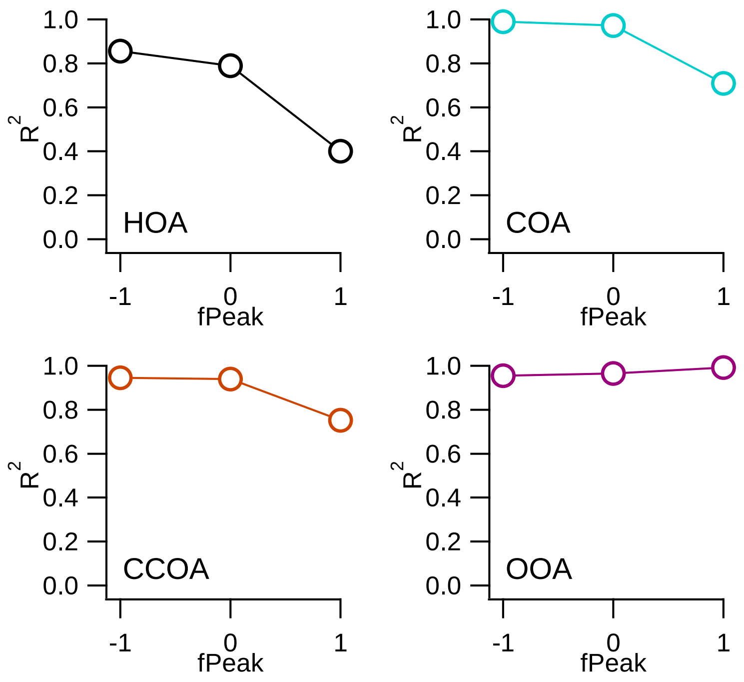

Fig. A4. Mass spectra correlations between this study and those identified in winter 2011-2012 (Sun et al., 2013b).

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.

We tried to extend the number of PMF factors to 10. Unfortunately, the fireworks factor still cannot be resolved. One of the reasons is because fireworks is a small component of OA, while the true components with <5% of the mass are unlikely to be resolved accurately (Ulbrich et al., 2009).

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 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.

High *m/z* 44 in COA has been observed many times in previous studies, e.g., Allan et al. (2010), Crippa et al. (2013), Sun et al. (2011), Sun et al. (2013b), Mohr et al. (2012), etc. The high *m/z* 60 in COA is also consistent with the results from characterization of mass spectra of fresh cooking emissions (Allan et al., 2010;He et al., 2010). The *m/z* 60 in HOA is small. It's possible that HOA and CCOA were not well separated as the reviewer mentioned. The diurnal profile of HOA in Beijing didn't present a morning rush peak as those observed at other urban sites. One of the major reasons is that HOA in Beijing is primarily from the emissions of diesel trucks and heavy duty vehicles that are not allowed inside the city between 6:00 am – 10:00 pm. Similarly, the BC didn't show the morning rush peak as well (Han et al., 2009). More detailed discussions on diurnal profile of HOA in Beijing can be found in Sun et al. (2013a). HOA and CCOA might be mixed. Unfortunately, we don't have more external tracers to further separate them like what has been done in Sandradewi et al. (2008). The reviewer is right that CCOA correlates better with BC than HOA. Indeed, HOA+CCOA correlates better than each individual HOA or CCOA, suggesting that coal combustion and traffic emissions are both important sources of BC in Beijing during wintertime (Tian et al., 2008;Zhi et al., 2008).

A recent study in central eastern China by a high resolution aerosol mass spectrometer (Hu et al., 2013) showed obvious *m/z* 91 and 95 peaks in HOA, but only a pronounced *m/z* 91 in CCOA, which is overall consistent with our results. Similarly, Zhang et al. (2014a) also observed higher *m/z* 91 in HOA than CCOA from the high resolution aerosol mass spectrometer measurements in Beijing during wintertime.

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)?

BBOA was not resolved in this study. The BBOA is generally a small component of OA during heating season (Huang et al., 2014) although it is important during the harvest seasons in China (Zhang et al., 2014b). The small fraction of BBOA , the low sensitivity of unit mass resolution spectra of OA from ACSM measurements plus the relatively similar spectra between BBOA and CCOA (Zhang et al., 2014b) all limit the identification of BBOA factor in this study.

High *m/z* 60 in COA is consistent with previous results that are described above. The *m/z* 60 in HOA is small, but there's possibility that HOA is partially mixed with CCOA. The average f60 for the entire study is ~0.42%, which is slightly higher than 0.3% reported by Cubison et al. (2011). Other factors contributing to the high *m/z* 60 include: 1) the influence of coal combustion emissions, 2) the ACSM f60 was calculated as the fraction of m/z 60 in total OA signal (m/z 12 – 120). The contributions of *m/z*'s > 120 were not included because of the limitation of ACSM commercial-grade mass spectrometer.

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.

The reviewer is right. We revised this sentence as "The ACSM was built upon previous versions of AMS"

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

The lower mass resolution was added in the text.

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.

We agree with the reviewer that the real SO_4^{2-} RIE might significantly differ from the default value. In this study, the aerosol particles appear to be fully neutralized based on the ion balance in Figure A5. Therefore, the ACSM SO_4^{2-} concentration might be reasonably determined. It should be noted that the approach proposed by Budisulistiorini et al. (2014) is based on a full balance of aerosol particles. Such an approach might introduce large uncertainties when aerosol particles are highly acidic.

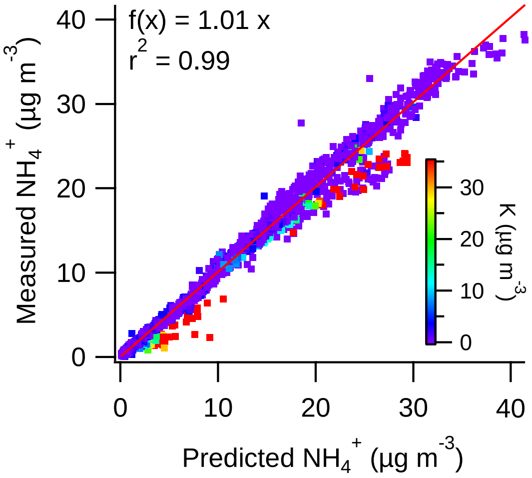

Figure A5. Correlation plot of measured NH_4^+ versus predicted NH_4^+ that needs to fully neutralize the aerosol particles. predicted $NH_4^+ = 18 \times (SO_4^{2-}/96\times2+NO_3^-/62+Chl/35.5)$ (Zhang et al., 2007).

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.

The assumption is rationale because biomass burning is a small fraction of organics (<6%) during wintertime (Zheng et al., 2005;Huang et al., 2014) although it is significant during harvest seasons (Zhang et al., 2014b). We didn't estimate the K^+ during normal days because our assumption is only used to calculate the contribution of K^+ during fireworks events. The 7% below refers to the fraction of chloride not potassium. We clarified this point in the revised manuscript.

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?

The exact reason is still not clear yet. But very likely, it is due to the interferences of sodium chloride from fireworks which has a slow evaporation process in the oven of ACSM. Indeed, we also observed a similar increase of *m/z* 23 as *m/z* 39 during the fireworks events. Figure 4b further shows two evident peaks at *m/z* 58 and 60, which is likely $NaCl^+$ and $Na^{37}Cl^+$, respectively.

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.

The external tracers used to validate the PMF factors include NO_3, SO_4, SO_4+NO_3, Chl, BC, NO_x, CO, *m/z* 60, etc. The profiles and time series of OA factors for different fpeak values were also compared and presented in Figure S6 – Figure S8. Also see our detailed response to major comment 2.

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

The behavior is much weaker for *m/z* 41 because the potassium isotope at *m/z* 41 is only ~7.2% of K (*m/z* 39).

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

Yes, *m/z* 76 has the same residual pattern as *m/z* 74, yet the pure organic fragment *m/z*'s, e.g., *m/z* 42 and *m/z* 43 don't have such residual patterns (Figure A6). The results suggest that our assumption is rationale, and it's not a PMF artifact. We did check the PMF results without fireworks data. The time series and mass spectral profiles are almost identical to those by including fireworks data into PMF analysis. Since we can approximately estimate KCl^+ and $K^{37}Cl^+/^{41}KCl^+$ based on the differences between measured and PMF modeled values, the PMF results by including fireworks data were used in this study.

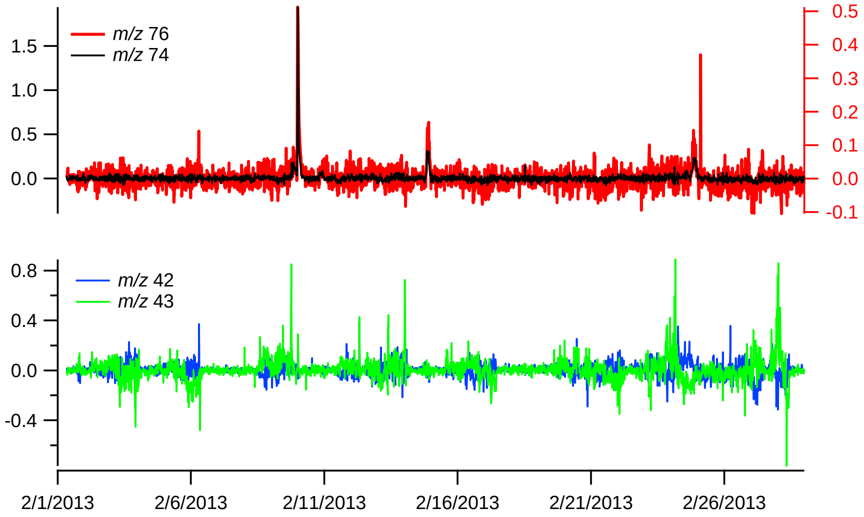

Figure A6. Time series of the PMF residuals of *m/z* 74, *m/z* 76, *m/z* 42, and *m/z* 43.

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.

The R^2 recalculated by excluding m/z 18 and 44 is 0.89 indicating that there are still many similarities between FW-OA and LV-OOA. We would not expect the exact same spectra between FW-OA and LV-OOA. In fact, the mass spectrum of LV-OOA varied significantly at different sites as indicated by the error bar of the standard LV-OOA (see Figure 1 in Ng et al., 2011). The *m/z* ratios also varied largely depending on the sources and aging processes. The main feature of secondary LV-OOA is the high *m/z* 44 (mainly CO_2^+) in the spectrum. Higher fraction of *m/z* 44 (f44) associated with higher oxygen-to-carbon ratio (Aiken et al., 2008) generally indicates more oxidized organic aerosol. Compared to secondary OA, the primary OA, e.g., hydrocarbon-like OA, cooking OA, biomass burning OA etc. generally show much lower f44. Considering above, the high f44 in FW-OA does suggest oxidized OA in this work. Although the exact sources and formation mechanisms are not very clear yet, they are likely from the burning or oxygenated organic compounds in fireworks. Our results are also consistent with those reported by Drewnick et al. (2006) that the OOA-related *m/z*'s (e.g., *m/z* 44) showed large enhancements during New Year's fireworks, yet the HOA-related *m/z*'s (e.g., *m/z* 57) didn't.

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

We agree that the potassium quantification has uncertainties. However, based on the comparisons with previous studies (see our response to major comment 1), the RIE_K = 2.9 and quantified K^+ appear to be reasonable for this work.

11. FigS9: same as Fig8.

Fig. 8 shows the average ratios of HD/NHD by excluding both clean periods (Figure 1) and three fireworks events. Fig. S9 presents the average ratios of HD/NHD by excluding only three fireworks events. They look similar, but different.

References:

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Aerosol Composition and Sources during the Chinese Spring Festival: Fireworks, Secondary Aerosol, and Holiday Effects

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Abstract

Aerosol particles were characterized by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) along with various collocated instruments in Beijing, China to investigate the aerosol composition and sources during the Chinese Spring Festival, 2013. Three fireworks (FW) events exerting significant and short-term impacts on fine particles ($PM_{2.5}$) were observed on the days of Lunar New Year, Lunar Fifth Day, and Lantern Festival. The FW showed major impacts on non-refractory potassium, chloride, sulfate, and organics in PM_1, of which the FW organics appeared to be mainly secondary with its mass spectrum resembling to that of secondary organic aerosol (SOA). Pollution events (PEs) and clean periods (CPs) alternated routinely throughout the study. Secondary particulate matter (SPM = SOA + sulfate + nitrate + ammonium) dominated PM_1 accounting for 63-82% during the nine PEs observed. The elevated contributions of secondary species during PEs resulted in a higher mass extinction efficiency of PM_1 (6.4 $m^2\ g^{-1}$) than that during CPs (4.4 $m^2\ g^{-1}$). The Chinese Spring Festival also provides a unique opportunity to study the impacts of reduced anthropogenic emissions on aerosol chemistry in the city. The primary species showed ubiquitous reductions during the holiday period with the largest reduction for cooking OA (69%), nitrogen monoxide (54%), and coal combustion OA (28%). The secondary sulfate, however, remained minor change, and the SOA and the total $PM_{2.5}$ even slightly increased. These results have significant implications that controlling local primary source emissions, e.g., cooking and traffic activities, might have limited effects on improving air quality during PEs when SPM that is formed over regional scales dominates aerosol particle composition.

1 Introduction

Air pollution caused by fine particles ($PM_{2.5}$) is of great concern in densely populated megacities because of its adverse effects on human health and regional air quality (Molina and Molina, 2004;Chan and Yao, 2008). The health risk of air pollution is greater than expected leading to around 7 million people's death in 2012 according to the latest report by World Health Organization (http://www.who.int/mediacentre/news/releases/2014/air-pollution/en/). The Beijing metropolitan area is one of the most populous megacities in the world with the population reaching 20.69 million by the end of 2012 (Beijing Municipal Bureau of Statistics). According to Beijing Municipal Environmental Protection Bureau, the annual average concentration of $PM_{2.5}$ was 89.5 μg m^{-3} in 2013, about 2.5 times the National Ambient Air Quality Standards of China (35 μg m^{-3} for annual average), which indicates severe fine particle pollution in Beijing. As a result, extensive studies have been made recently to investigate the sources of $PM_{2.5}$. The results showed that secondary inorganic aerosol (SIA = sulfate + nitrate + ammonium), coal combustion, traffic emissions (gasoline and diesel), biomass burning, cooking emissions and dust are the major sources of $PM_{2.5}$ (Zheng et al., 2005;Song et al., 2006;Zhang et al., 2013), and the source contributions varied significantly among different seasons. Despite this, improving air quality in Beijing remains a great challenge due to the very complex sources and dynamic evolution processes of aerosol particles.

Fine particles from various source emissions can be either primary from direct emissions, e.g., fossil fuel combustion and biomass burning, or secondary from atmospheric oxidation of gas-phase species. The fireworks (FW) is one of the most important primary source that can exert significant and short-time impacts on air quality. The fireworks burning emits a large amount of gaseous pollutants, e.g., sulfur dioxide (SO_2) and nitrogen oxide (NO_x) (Vecchi et al., 2008;Huang et al., 2012), and also fine particles comprising organic/elemental carbon, sulfate, potassium, chloride and various metals, e.g., copper (Cu), barium (Ba), strontium (Sr) and magnesium (Mg) (Moreno et al., 2007;Wang et al., 2007;Li et al., 2013). The enhanced short-term air pollution by fireworks can substantially increase health risk levels (Godri et al., 2010;Yang et al., 2014) and reduce visibility for hours (Vecchi et al., 2008). 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 (Wang et al., 2007;Zhang et al., 2010;Feng et al., 2012;Huang et al., 2012;Cheng et al., 2014;Zhao et al., 2014), which may have large uncertainties in accurate quantification of chemical composition of FW particles. Drewnick et al. (2006) first conducted real-time size-resolved chemical composition measurements during the New Year's period in Mainz, Germany using an Aerodyne Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS). To our knowledge, there are no such real-time measurements of chemical composition of aerosol particles during fireworks events in China yet, which limits our understanding on the rapid formation and evolution of fireworks events, and also their impacts on air pollution.

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. Therefore, extensive studies have been conducted in recent years to characterize the sources and formation mechanisms of secondary aerosol (Yao et al., 2002;Duan et al., 2006;Sun et al., 2006;Wang et al., 2006;Guo et al., 2010;Yang et al., 2011;Sun et al., 2013b;Zhang et al., 2013;Zhao et al., 2013). 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. While SIA was relatively well characterized, secondary organic aerosol (SOA) is poorly understood. The recent deployments of Aerodyne Aerosol Mass Spectrometers (AMS) greatly improved our understanding on sources and evolution processes of organic aerosol (OA) in China, and also primary organic aerosol (POA) and SOA by positive matrix factorization (PMF) of organic mass spectra (Huang et al., 2010;Sun et al., 2010;He et al., 2011;Sun et al., 2012;Sun et al., 2013b;Zhang et al., 2014). SOA was found to play different roles among different seasons. While SOA is more significant in summer (Huang et al., 2010;Sun et al., 2010;Sun et al., 2012), POA generally plays a more important role during wintertime (Sun et al., 2013b). Despite this, the role of SOA in fine particle pollution in Beijing is not well known, in particular during wintertime, a season with frequent occurrences of pollution episodes (Sun et al., 2013b;Zhang et al., 2014). Of particular interest, this study took place in the month with the most important holiday in China, i.e., the Spring Festival. The source emissions (e.g., traffic and cooking) had significant changes due to a large reduction of population and anthropogenic activities in the city. This provides a unique opportunity to investigate how source changes affect aerosol chemistry including primary emissions and secondary formation in Beijing. Although Huang et al. (2012) investigated such a holiday effect on aerosol composition and optical properties in Shanghai, the data analyses were limited by daily average composition measurements and also the significantly different meteorological conditions between holiday and non-holiday periods.

In this study, an Aerosol Chemical Speciation Monitor (ACSM) along with various collocated instruments was deployed in Beijing during February 2013. The chemical composition of PM_1 from fireworks is first quantified in Beijing based on the high time resolution measurements of non-refractory submicron aerosol species (organics, sulfate, nitrate, ammonium, chloride, and potassium) and black carbon. The impact of fireworks on PM pollution during Chinese Lunar New Year (LNY), Lunar Fifth Day (LFD), and Lantern Festival (LF) are investigated, and the roles of secondary formation in PM pollution are elucidated. Further, the impacts of reduced anthropogenic emissions during the holiday on primary and secondary aerosols in the city are illustrated, which has significant implications for making air pollution control strategies in Beijing.

2 Experimental

2.1 Sampling site

The measurements in this study were conducted at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58’28’’N, 116°22’16”E), an urban site located between the north third and fourth ring road in Beijing (Sun et al., 2012). Aerosol characterization was performed from 1 February to 1 March 2013, during which three episodes with significant influences of fireworks, i.e., Lunar New Year (LNY), Lunar Fifth Day (LFD), and Lantern Festival (LF), were observed (Fig. 1). The meteorological conditions during the measurement period are reported in Fig. 1. Winds at the ground surface were generally below 2 m s^{-1} and temperature averaged 0.6 °C. Relative humidity (RH) varied periodically with higher values generally associated with higher particulate matter (PM) pollution.

2.2 Aerosol sampling

The chemical composition of non-refractory submicron aerosol particles (NR-PM_1) including organics, sulfate, nitrate, ammonium, and chloride were measured on-line by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) at an approximate 15-min time intervals (Ng et al., 2011b). ~~The ACSM shares the same aerosol sampling, vaporization and ionization modules as~~The ACSM was built upon previous versions of AMS (Jayne et al., 2000;DeCarlo et al., 2006). However, the ACSM has no size information and also a lower sensitivity and lower mass resolution due to the use of a commercial-grade quadrupole mass analyzer (Ng et al., 2011b). The advantage of the ACSM is its robustness for long-term and routine aerosol particle composition measurements. A two-wavelength Aethalometer (Model AE22, Magee Scientific Corp.) was used to measure refractory black carbon (BC) that the ACSM cannot detect.

The light extinction of dry fine particles (b_{ext}, M m^{-1}, 630 nm) was measured by a Cavity Attenuated Phase Shift Spectrometer particle extinction monitor, CAPS PM$_{ex}$ (Massoli et al., 2010). The CAPS PM$_{ex}$ was measured at 1 s time resolution with a precision (3 σ) of 1 M m^{-1}. The mass concentration of PM$_{2.5}$ was determined by a heated Tapered Element Oscillating Microbalance, TEOM, and the collocated gaseous species (including CO, SO_2, NO, NO_x and O_3) were measured by various gas analyzers (Thermo Scientific) at 1 min time resolution. The detailed descriptions of aerosol and gas measurements were given in Sun et al. (2013b).

2.3 ACSM data analysis

The ACSM data were analyzed for the mass concentrations and chemical composition of NR-PM$_1$ using standard ACSM software (v 1.5.3.2) written within Igor Pro (WaveMetrics, Inc., Oregon USA). A composition-dependent collection efficiency (CE) recommended by Middlebrook et al.(2012), CE = max (0.45, 0.0833 + 0.9167 × ANMF), was used to account for the incomplete detection due to the particle bouncing effects (Matthew et al., 2008) and the influences caused by high mass fraction of ammonium nitrate (ANMF). The default relative ionization efficiencies (RIEs) were used in this study, except ammonium (RIE = 6.5) that was determined from IE calibration.

Quantification of K^+ is challenging for ACSM because of a large interference of organic $C_3H_3^+$ at m/z 39 and also uncertainties caused by surface ionization (Slowik et al., 2010). In this work, we found that m/z 39 was tightly correlated with m/z 43 that is completely organics during non-fireworks (NFW) periods (r^2 = 0.87, slope = 0.45, Fig. S1). However, higher ratios of *m/z* 39/43 during FW periods were observed due to the elevated K^+ signal from burning of fireworks. Assuming that *m/z* 39 was primarily contributed by organics during NFW periods, the excess *m/z* 39 signal, i.e., K^+, can then be estimated as *m/z* 39 – *m/z* 43 × 0.45. The $^{41}K^+$ (*m/z* 41) was calculated using its isotopic ratio of 0.0722, i.e., $^{41}K^+ = 0.0722 \times K^+$. The K^+ signal was converted to mass concentration with a RIE of 2.9 that was reported by Drewnick et al. (2006). The KCl^+ (*m/z* 74) and $^{41}KCl^+/K^{37}Cl^+$ (*m/z* 76) were estimated by the differences between the measured and PMF modeled *m/z* 74 (see Fig. S2 for details). Not surprisingly, the quantified KCl^+ highly correlates with K^+ (r^2 = 0.82). The chloride concentration was also biased at *m/z* 35 during some periods (e.g., LNY, Fig. S3~~) mainly~~), which is likely due to the ~~inappropriate default fragment ratio at *m/z* 35~~interferences of NaCl from fireworks. Therefore, Cl^+ (*m/z* 35) was recalculated based on its correlation with *m/z* 36 (mainly HCl^+ with negligible C_3^+ and ^{36}Ar), i.e., *m/z* 35 = 0.15 × *m/z* 36, and $^{37}Cl^+$ was calculated using an isotopic ratio of 0.323, i.e., $^{37}Cl^+ = 0.323 \times {}^{35}Cl^+$. A comparison of the time series of default and recalculated chloride is shown in Fig. S3b.

The positive matrix factorization (PMF) with the algorithm of PMF2.exe in robust mode (Paatero and Tapper, 1994) was performed on organic aerosol (OA) mass spectra (*m/z* 12 – 120) to resolve distinct OA components from different sources. The PMF results were evaluated with an Igor Pro-based PMF Evaluation Tool (PET, v 2.04) (Ulbrich et al., 2009) following the procedures detailed in Zhang et al. (2011). After a careful evaluation of the spectral profiles, diurnal variations and correlations with external tracers, a 6-factor solution with rotational forcing parameter fpeak = -1 (Q/Q_{exp} = 4.3) was chosen, yielding a hydrocarbon-like OA (HOA), a cooking OA (COA), a coal combustion OA (CCOA), and three oxygenated OA (OOA) components, which were recombined into one OOA component. The four OA components show very similar mass spectral profiles (r^2 = 0.86 – 0.99) and diurnal variations (Fig. S4) to those observed during winter 2011-2012 (Sun et al., 2013b). A detailed summary of key diagnostic plots of the PMF solution are given in Fig. S5 – Fig. S8.

3 Results and discussion

3.1 Identification and quantification of fireworks events

Burning of fireworks has been found to emit a large amount of K^+, which can be used to identify the FW events (Drewnick et al., 2006;Wang et al., 2007). As shown in Fig. 1 and Fig. S9, three FW events with significantly elevated K^+ were observed on the days of Lunar New Year (LNY, 9-10 February), Lunar Fifth Day (LFD, 14 February), and Lantern Festival (LF, 24 February), respectively. All three FW events started approximately at 18:00 and ended at midnight except LNY with a continuous FW impact until 4:00 on the second day. Fig. 1 shows that the relative humidity was generally below 30% during LNY and LFD. While the wind speed at the ground surface remained consistently below 2 m s^{-1}, it was increased to ~ 4 m s^{-1} at the height of 100 m. Also note that there was a wind direction change in the middle of the two events. The meteorological conditions during LF were stagnant with wind speed generally below 2 m s^{-1} across different heights. The relative humidity was ~50% and the temperature averaged 3.5°C.

To estimate the contributions of fireworks, we first assume that the background concentration of each species has a linear variation during FW period. A linear fit is then performed on the 6 h data before and after FW events. The difference between the measured and the fitted value is then assumed as the contribution from FW. The typical examples for estimating FW contributions are shown in Fig. S10. It should be noted that this approach might significantly overestimate the FW contributions of primary species (e.g., HOA, COA, CCOA, and BC) that were largely enhanced during the typical FW periods (18:00 – 24:00) due to the increased local emissions (see Fig. S11 for diurnal variations). However, it should have a minor impact on secondary species (e.g., SO_4^{2-}, NO_3-, and OOA) because of their relatively stable variations between 18:00-24:00. As shown in Fig. 1, all aerosol species showed substantial increases from 15:00 to 21:00 on the day of LNY which coincidently corresponded to a gradual change of wind direction. Therefore, regional transport might have played dominant roles for the evolution of chemical species during this period. For these reasons, only the FW contributions between 23:30, 9 February and 3:30, 10 February when the meteorological conditions were stable were estimated. The FW contributions during LFD might also be overestimated due to the influences of regional transport as suggested by the wind direction change in the middle. Considering above, the contributions estimated in this work would represent the upper limits of FW.

3.2 Mass concentration and chemical composition of FW aerosols

Figure 1 shows the time series of mass concentrations of PM_1, $PM_{2.5}$, and submicron aerosol species from 1 February to 1 March 2013. Because ACSM cannot measure the metals (e.g., Sr, Ba, Mg, etc.) that were significantly enhanced during FW periods (Wang et al., 2007;Vecchi et al., 2008) , the PM_1 in this study refer to NR-PM_1 (= Org + SO_4^{2-} + NO_3^- + NH_4^+ + Chl+ K^+ + KCl) + BC. The $PM_{2.5}$ showed three prominent FW peaks with the maximum concentration occurring at ~00:30 during LNY and ~21:30 during LFD and LF, respectively. The peak concentration of $PM_{2.5}$ during LNY is more than 10 times higher than the China National Ambient Air Quality Standard (75 μg m^{-3}, 24 h average). The average FW-$PM_{2.5}$ mass concentrations during three FW events all exceeded 100 μg m^{-3}. These results suggest that fireworks have large impacts on fine particle pollution, yet generally less than half day (approximately 10 h for LNY, and 6 h for LFD and LF). The PM_1 also showed increases during the FW periods, yet not as significant as $PM_{2.5}$. In fact the correlation of PM_1 versus $PM_{2.5}$ shows much lower $PM_1/PM_{2.5}$ (0.08 – 0.19) ratios during three FW events than that observed during NFW periods (0.90) (Fig. 2). One of the reasons is likely due to the mineral dust component and metals from fireworks that ACSM did not measure. However, the metals that were largely enhanced during FW periods generally contribute a small fraction of PM (Wang et al., 2007;Vecchi et al., 2008). Therefore, our results suggest that burning of fireworks has the most impact on aerosol particles in the size range of 1 – 2.5 μm. Consistently, Vecchi et al. (2008) found the best correlation between the fireworks tracer, Sr, and the particles between 700-800 nm (mobility diameter, D_m) which is approximately equivalent to 1.9 – 2.2 μm in D_{va} (vacuum aerodynamic diameter, D_{va}) with a density of 2.7 g cm^{-3} (Zhang et al., 2010).

Figure 3 shows the average chemical composition of PM_1 and OA from fireworks and also the background composition during LNY, LFD and LF. The background PM_1 during LNY and LFD showed typical characteristics of clean periods with high fraction of organics (> ~50%), whereas that during LF was dominated by SIA (52%). As a comparison, organics constituted the major fraction of FW-PM_1, contributing 44 – 55% on average. During LNY, FW exerted large impacts on potassium and chloride whose contributions were elevated to 21% and 15% of PM_1, respectively, from less than 7% (Chl) in the background aerosols. The large increases of potassium and chloride were also observed during LFD and LF, and previous studies in Beijing (Wang et al., 2007;Cheng et al., 2014). As shown in Fig. 3, FW also emitted a considerable amount of sulfate, accounting for 7% - 14% of PM_1. Sulfate correlated strongly with SO_2 during all three FW events (r^2 = 0.49 -0.92). Given that the relative humidity was low, < 30% during LNY and LFD, and ~ 50% during LF, aqueous-phase oxidation of SO_2 could not play significant roles for the sulfate formation (Sun et al., 2013a). Therefore, sulfate in FW-PM_1 was mainly from the direction emissions of FW. Compared to sulfate, FW appeared to show minor impacts on nitrate, for example, 4% and 2% during LNY and LF, respectively. Although nitrate contributed 12% of FW-PM_1 during LFD, most of it was likely from local sources and/or regional transport as supported by the large contributions of local HOA and COA in OA (Fig. 3b) and also a wind direction change in the middle.

The OOA contributed dominantly to OA during LNY, which is 79% on average (Fig. 3a). As shown in Fig. 4, the mass spectrum of FW-organics is highly similar to that of low-volatility OOA (LV-OOA, $r^2 = 0.94$; $r^2 = 0.89$ by excluding *m/z* 18 and 44) (Ng et al., 2011a) indicating that the FW-organics is likely emitted in secondary. Consistently, Drewnick et al. (2006) also found large enhancements of OOA-related *m/z*'s (e.g., *m/z* 44) during New Year's fireworks, but HOA-related *m/z*'s (e.g., *m/z* 57) are not significant contributors to FW organics. OOA contributed a much smaller fraction of OA during LF (28%) due to the large contributions of POA components (72%). Although the OOA contributions varied during three FW events, their absolute concentrations were relatively close ranging from 5.8 to 7.9 μg m^{-3}. It should be noted that our approach might overestimate the POA components in FW-OA ~~were likely from~~because of the influences of NFW sources~~ that were overestimated by the approach in this work~~, in particular during the FW period of LF when the local HOA, COA, and CCOA happened to have large increases. By excluding the POA components in FW-OA, FW on average contributed 15 – 19 μg m^{-3} PM_1 during three FW events.

3.3 Secondary aerosol and PM pollution

The PM_1 (NR-PM_1 + BC) varied largely across the entire study with daily average mass concentration ranging from 9.1 to 169 μg m^{-3}. The average PM_1 mass concentration was 80 (±68) μg m^{-3}, which is approximately 20% higher than that observed during winter 2011-2012

(Sun et al., 2013b). Organics composed the major fraction of PM_1, accounting for 43%, followed by nitrate (22%), sulfate (14%), ammonium (13%), BC (5%) and chloride (3%). The OA composition was dominated by OOA (53%) with the rest being POA. Compared to winter 2011-2012 (Sun et al., 2013b), this study showed significantly enhanced OOA (53% vs. 31%) and secondary nitrate (22% vs. 16%), indicating that secondary formation have played important roles in the formation of pollution episodes.

Figure 1d shows that submicron aerosol species alternated routinely between pollution events (PEs) and clean periods (CPs) throughout the entire study. The PEs generally lasted ~1 – 2 days except the one on 23 – 28 February that lasted more than 5 days, whereas the CPs were shorter, generally less than 1 day. In total, 9 PEs and 9 CPs were classified in this study (Fig. 1). A statistics of the mass concentrations and mass fractions of aerosol species during the 9 PEs is presented in Fig. 5. The average PM_1 mass concentration ranged 68 – 179 $\mu g\ m^{-3}$ during PEs with the total secondary particulate matter (SPM = OOA + SO_4^{2-} + NO_3^- +NH_4^+) accounting for 63 – 82%. The average mass concentration of SPM for the 9 PEs was 86 (±32) $\mu g\ m^{-3}$, which is nearly 3 times primary PM (PPM = HOA + COA +CCOA + BC + Chl) (30 ±9.5 $\mu g\ m^{-3}$). SPM consistently dominated PM_1 across different PM levels (69 – 75%), but generally with higher contributions (up to 81%) during daytime (Fig. 6b). The diurnal cycle of SPM presented a gradual increase from 50 to 70 $\mu g\ m^{-3}$ between 10:00 – 20:00, indicating evident photochemical production of secondary species during daytime. It should be also noted that all secondary species showed ubiquitously higher mass concentrations than those of primary species (Fig. 5a).

The SOA generally contributed more than 50% to OA with an average of 55% during the PEs except the episode on 3 February (35%). It's interesting to note that the contribution of POA increased as a function of organic loadings which varied from ~35% to 63% when organics was above 80 μg m^{-3} (Fig. 6c). Such behavior is mainly caused by the enhanced CCOA at high organic mass loadings, which was also observed during winter 2011 – 2012 (Sun et al., 2013b). These results suggest that POA played more important roles than SOA in PM pollution during periods with high organic mass loadings. In fact, POA showed even higher concentrations than OOA at nighttime (0:00 – 8:00) due to the intensified local emissions, e.g., coal combustion for heating. Despite this, the role of POA in PM pollution was compensated by the elevated secondary inorganic species as a function of PM loadings (Fig. 6a) leading to the consistently dominant SPM across different pollution levels. Figure 7a shows an evidently lower contribution of organics to PM_1 during PEs than CPs. The elevated secondary inorganic species during PEs were closely related to the increase of RH (Fig. 1). For example, during the pollution episode on 3 February, the sulfate concentration increased rapidly and became the major inorganic species when RH was increased from ~60% to > 90%. The gaseous SO_2 showed a corresponding decrease indicating aqueous-phase processing of SO_2 to form sulfate, consistent with our previous conclusion that aqueous-phase processing could contribute more than 50% of sulfate production during winter 2011-2012 (Sun et al., 2013a).

The compositional differences between PEs and CPs also led to different mass extinction efficiency (MEE, 630 nm) of PM_1 (Fig. 7b). The higher MEE (6.4 m^2 g^{-1}) during PEs than CPs (4.4 m^2 g^{-1}) is primarily due to the enhanced secondary species, and also likely the increases of aerosol particle sizes although we don't have size data to support it. Similar increases of mass scattering efficiency from clean periods to relatively polluted conditions were also observed previously in Beijing and Shanghai (Jung et al., 2009;Huang et al., 2013). It should be noted that the MEE of PM_1 in this study refers to $PM_{2.5}$ b_{ext}/PM_1. If assuming PM_1 on average contributed 70% of $PM_{2.5}$, the real MEE of PM_1 during PEs and CPs would be 4.5 and 3.1 m^2 g^{-1}, respectively.

3.4 Holiday Effects on PM Pollution

Figure 8 shows a comparison of aerosol species, gaseous species, and meteorological parameters between holiday (HD) and non-holiday (NHD) periods. The official holiday for the Spring Festival was 9 – 15 February. However, we noted a large decrease of cooking aerosols from 7 February until 19 February (Fig. S4c), whose emissions were expected to be stable under similar meteorological conditions. The decrease of COA was likely due to the reduction of the number of population in Beijing, which agreed with the fact that most migrants from outside Beijing were leaving for hometown before the official holiday. Therefore, 7 – 19 February was used as a longer holiday for a comparison. It was estimated that approximately half of population (9 million) left Beijing before Spring Festival (http://news.xinhuanet.com/yzyd/local/20130208/c_114658765.htm). Such a great reduction in human activities would exert a large impact on aerosol composition and sources in the city during holidays. To better investigate the HD effects on PM pollution, the data shown in Fig. 8 excluded the CPs marked in Fig. 1. The data with the CPs included are presented in Fig. S12.

The differences between HD and NHD for primary species varied largely among different species. COA showed the largest reduction (69%) among aerosol species with the average concentration decreasing from 5.8 μg m^{-3} during NHD to 1.8 μg m^{-3} during HD. The contribution of COA to OA showed a corresponding decrease from 12% to 4%. Given the similar meteorological conditions between HD and NHD, e.g., RH (46% vs. 52%) and wind speed (1.3 m s^{-1} vs. 1.2 m s^{-1}), the reduction of COA clearly indicated a large decrease of population and the number of restaurants open during HD. The CCOA showed approximately 30% reduction during HD, and its contribution to OA decreased from 23% to 18%. Not surprisingly, chloride showed a similar reduction as CCOA because it was primarily from coal combustion emissions during wintertime (Sun et al., 2013b). Figure 8 also shows a significant reduction (54%) for NO, indicating much less traffic emissions in the city during HD. The HOA, however, even showed a slight increase during HD, which appeared to contradict with the reduction of two combustion-related tracers, BC and CO (~20%). ~~The results~~This can be explained by the fact that coal combustion is a large source of BC and CO during heating season (Tian et al., 2008;Zhi et al., 2008). Consistently, BC and CO showed relatively similar reductions to CCOA. Therefore, the minor variations of HOA might indicate that the number of heavy-duty vehicles and diesel trucks that dominated HOA emissions (Massoli et al., 2012;Hayes et al., 2013) remained little change during HD period although that of gasoline vehicles was largely decreased. It should be noted that HOA showed a large peak on 9 February – the first day of the official holiday (Fig. S4) when more traffic emissions were expected due to many people leaving for hometown. After that, HOA showed ~~comparably~~slightly lower concentration during 11 – 17 February than other periods~~ indicating~~. In fact, the average HOA showed a slight reduction (~5%) during the long holiday ~~effects~~period (7 – 19 February) suggesting a small holiday effect on HOA reduction. Together, the total primary aerosol species (PPM) showed an average reduction of 22% because of holiday effects.

Nitrate showed the largest reduction among secondary species by 22% during HD, primarily due to a reduction of its precursors NO and NO_2. Results here suggest that reducing traffic emissions would help mitigate the nitrate pollution in the city. Compared to nitrate, sulfate showed minor changes (2%) between HD and NHD, and OOA even showed a slight increase (6%) during HD. One of the reasons is that secondary sulfate and OOA were mainly formed over regional scale and less affected by local production, consistent with their relatively flat diurnal cycles (Fig. S11). Ammonium showed a reduction between nitrate and sulfate because ammonium mainly existed in the form of $(NH_4)_2SO_4$ and NH_4NO_3. Overall, secondary species showed generally lower reductions than primary species with the total secondary species (SPM) showing an average reduction of 9% during HD. The joint reductions of PPM and SPM led to an average reduction of 13% for PM_1 during HD. However, these reductions did not help alleviate the fine particle pollution during HD. The $PM_{2.5}$ excluding FW impacts even showed 27% increase from 96 $\mu g\ m^{-3}$ during NHD to 122 $\mu g\ m^{-3}$ during HD. The longer holiday (LHD, 7 – 19 February) showed similar influences on both primary and secondary species as the official holiday (9 – 15 February). COA, CCOA, and NO are the three species with the largest reductions during LHD (> 50%). However, HOA, SO_4^{2-}, OOA, and $PM_{2.5}$ showed rather small changes (< ±7%). Therefore, results in this study suggest that controlling the primary source emissions, e.g., cooking and traffic emissions in the city can reduce the primary particles largely, yet has limited effects on secondary species and the total fine particle mass. One of the reasons is that the severe PM pollution in Beijing is predominantly contributed by secondary species (see discussions above) that are formed over regional scales. Reducing the primary source emissions in local areas would have limited impacts on mitigation of air pollution in the city. Similarly, Guo et al. (2013) reported a large reduction of primary organic carbon (OC) from traffic emissions and coal combustion during the 2008 Olympic Summer Games when traffic restrictions and temporary closure of factories were implemented. However, secondary OC was not statistically different between controlled and non-controlled periods. Our results highlight the importance of implementing joint efforts over regional scales for air pollution control in north China.

4 Conclusions

We have characterized the aerosol particle composition and sources during the Chinese

Spring Festival, 2013. The average PM_1 mass concentration was 80 (±68) μg m^{-3} for the entire study with organics being the major fraction (43%). Nine pollution events and nine clean periods with substantial compositional differences were observed. The secondary particulate matter (= SOA+ sulfate + nitrate + ammonium) played a dominant role for the PM pollution during the nine PEs. The contributions of SPM to PM_1 varied from 63% to 82% with SOA on average accounting for ~55% of OA. As a result, the average mass extinction efficiency of PM_1 during PEs (6.4 m^2 g^{-1}) was higher than that during CPs (4.4 m^2 g^{-1}). Three FW events, i.e., LNY, LFD, and LF, were identified, which showed significant and short-term impacts on fine particles, and non-refractory potassium, chloride, and sulfate in PM_1. The FW also exerted a large impact on organics that presented mainly in secondary as indicated by its similar mass spectrum to that of oxygenated OA. The holiday effects on aerosol composition and sources were also investigated by comparing the differences between holiday and non-holiday periods. The changes of anthropogenic source emissions during the holiday showed large impacts on reduction of cooking OA (69%), nitrogen monoxide (54%), and coal combustion OA (28%) in the city, yet presented minor influences on secondary species. The average SOA and the total $PM_{2.5}$ even increased slightly during the holiday period. Results here have significant implications that controlling the local primary source emissions, e.g., cooking and traffic activities, might have limited effects on improving air quality during polluted days when SPM dominated aerosol composition for most of time. Our results also highlight the importance of implementing joint measures over regional scales for mitigation of air pollution.

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Figure Captions:

Fig. 1. Time series of meteorological parameters (a) relative humidity (RH) and temperature (T); (b) wind direction (WD) and wind speed (WS) at the height of 100 m; mass concentrations of (c) $PM_{2.5}$ and NR-PM_1 + BC and (d) submicron aerosol species. Also shown in (a) and (b) is the temperature and wind speed at the height of 8 m which are in blue. The extinction coefficient (b_{ext}) at 630 nm is shown in (c). Three events, i.e., Lunar New Year (LNY), Lunar Fifth Day (LFD) and Lantern Festival (LF) with significant influences of fireworks are marked in (c). In addition, the classified clean periods (CPs) and polluted events (PEs) are marked as shaded ~~gray~~light blue and pink areas, respectively. – A more detailed time series of aerosol species during the three fireworks events are shown in Fig. S9.

Fig. 2. Correlation of PM_1 vs. $PM_{2.5}$ with the data segregated into three fireworks events (LNY, LFD, and LF) and non-fireworks periods (NFW). The blank circles represent FW data between 18:00 – 23:30 on 9 February which had large influences from NFW sources.

Fig. 3. Average chemical composition of PM_1 and OA from fireworks and background during three FW events.

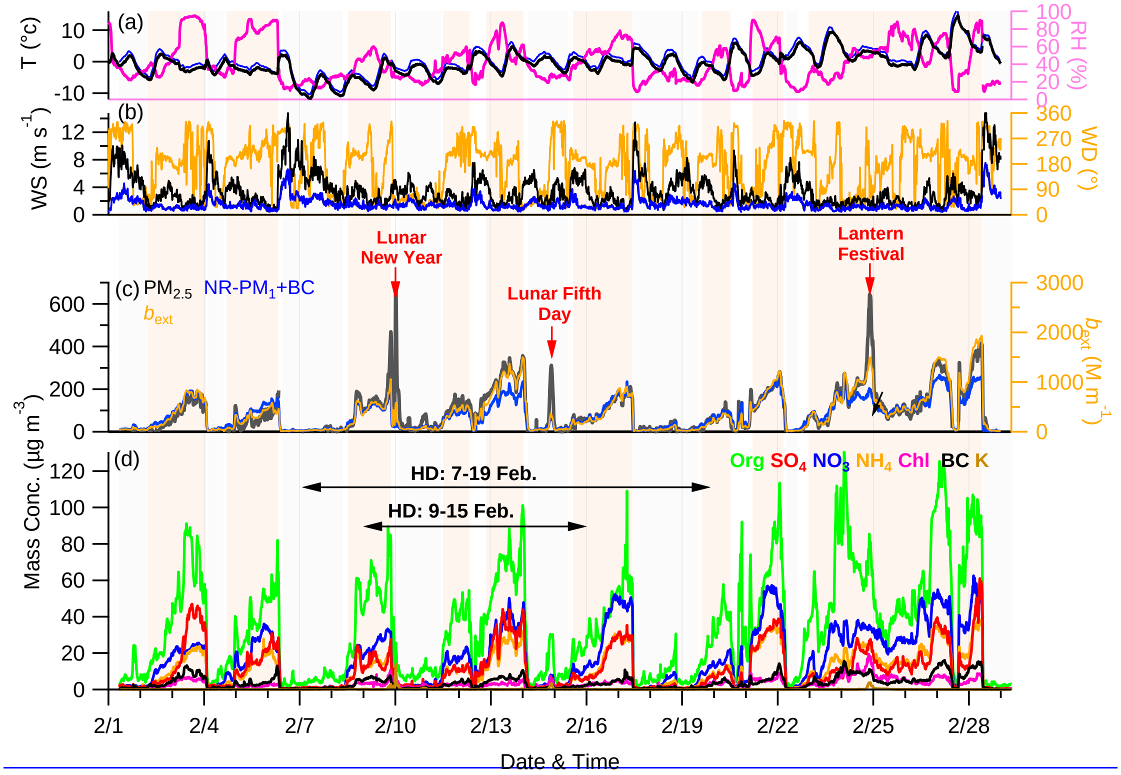
Fig. 4. (a) Average mass spectra (MS) of OA during the firework period of Lunar New Year (23:30, 9 February – 3:30, 10 February) and the period of background (BG, 4:30 – 11:00, 10 February). (b) Comparison of the difference spectrum from (a), i.e., $MS_{FW+BG} - MS_{BG}$, with the average LV-OOA spectrum in Ng et al.(2011a). Five *m/z*'s, 37 ($^{37}Cl^+$), 58 ($NaCl^+$), 60 ($Na^{37}Cl^+$), 74 (KCl^+), and 76 ($K^{37}Cl^+$/ $^{41}KCl^+$) with significant influences of fireworks are marked.

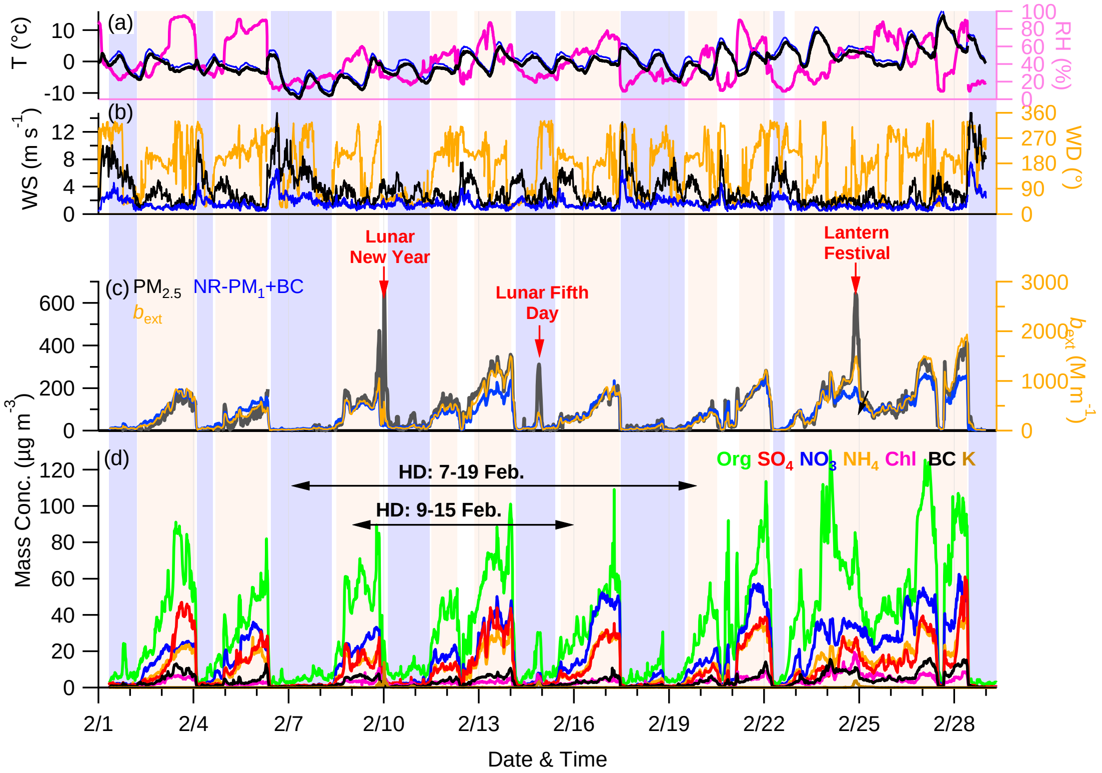
Fig. 5. Box plots of (a) mass concentrations and (b) mass fractions of aerosol species for 9 pollution events marked in Fig. 1. The mean (cross), median (horizontal line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) are shown for each box.

Fig. 6. Left: variations of chemical composition of (a) organics, SNA (=sulfate + nitrate + ammonium), and others (the rest species in PM_1); (b) SPM and PPM; and (c) SOA and POA as a function of PM_1 and organics loadings, respectively. Right panels show their corresponding diurnal compositions.

Fig. 7. (a) Average mass fraction of organics (f_{Org}) as a function of PM_1 mass, and (b) correlations of extinction coefficients ($PM_{2.5}$) vs. PM_1 for 9 pollution events (PEs) and 9 clean periods (CPs) marked in Fig. 1. The error bar represents one standard deviations of the average for each event.

Fig. 8. The average ratios of aerosol species, gaseous species, PM mass concentrations, extinction coefficient, and meteorological parameters between holiday (HD) and non-holiday (NHD) periods. Two different holidays, i.e., the official holiday of 9 – 15 February and the longer holiday of 7 – 20 February were used for averages. Also note that the averages were made by excluding clean periods and firework events during both HD and NHD days.





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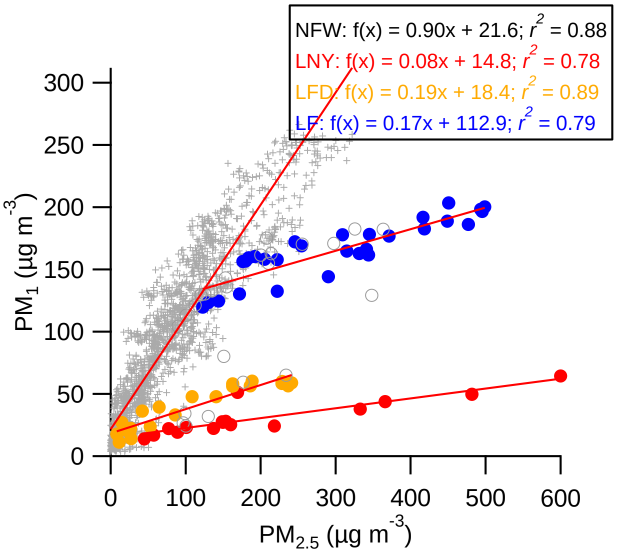

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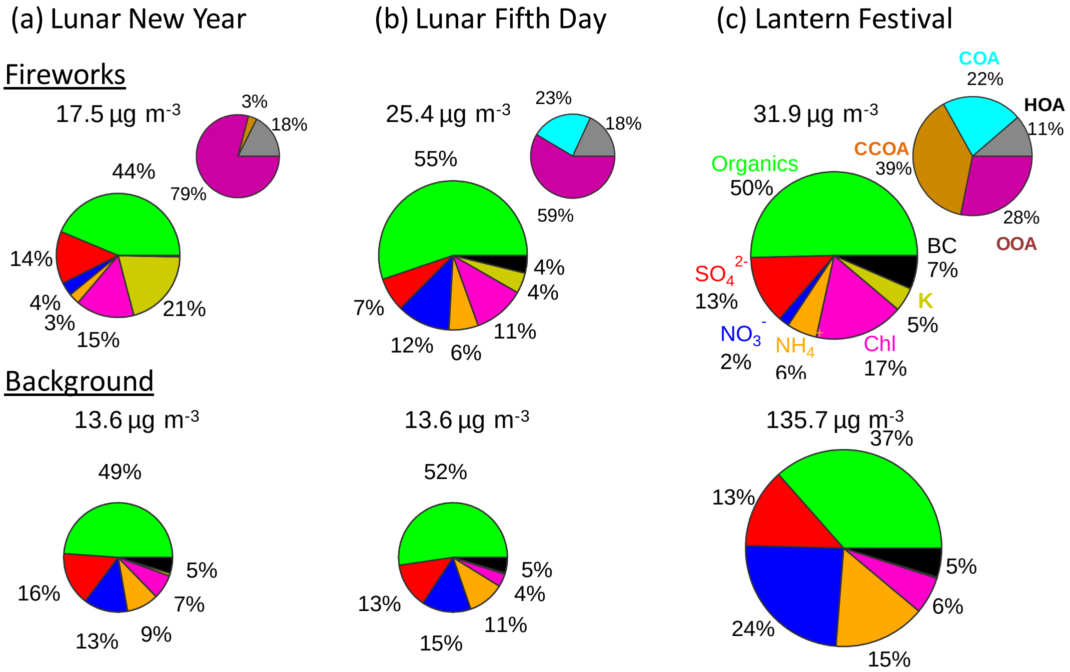

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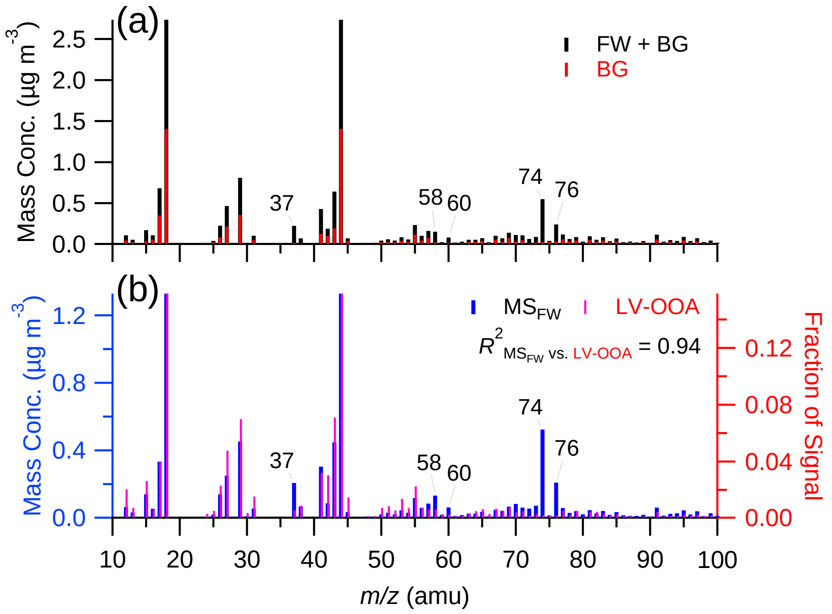

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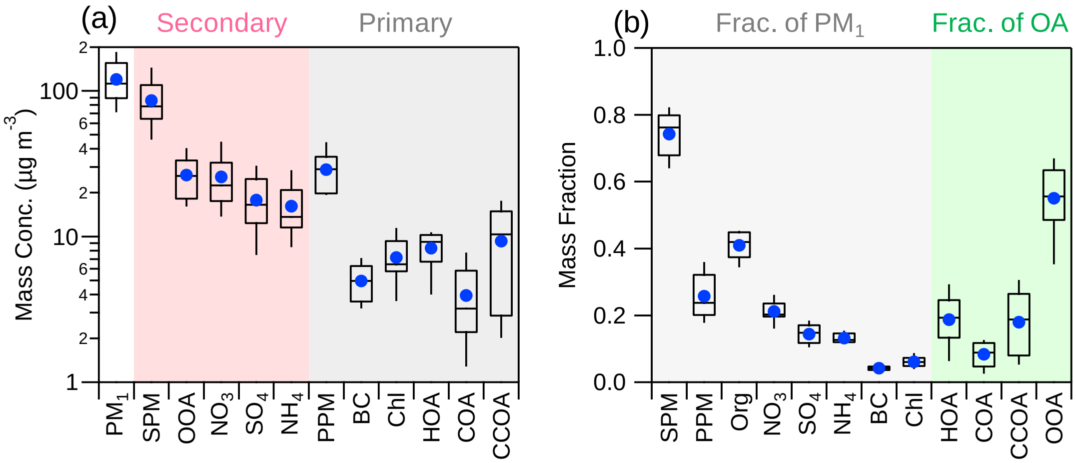

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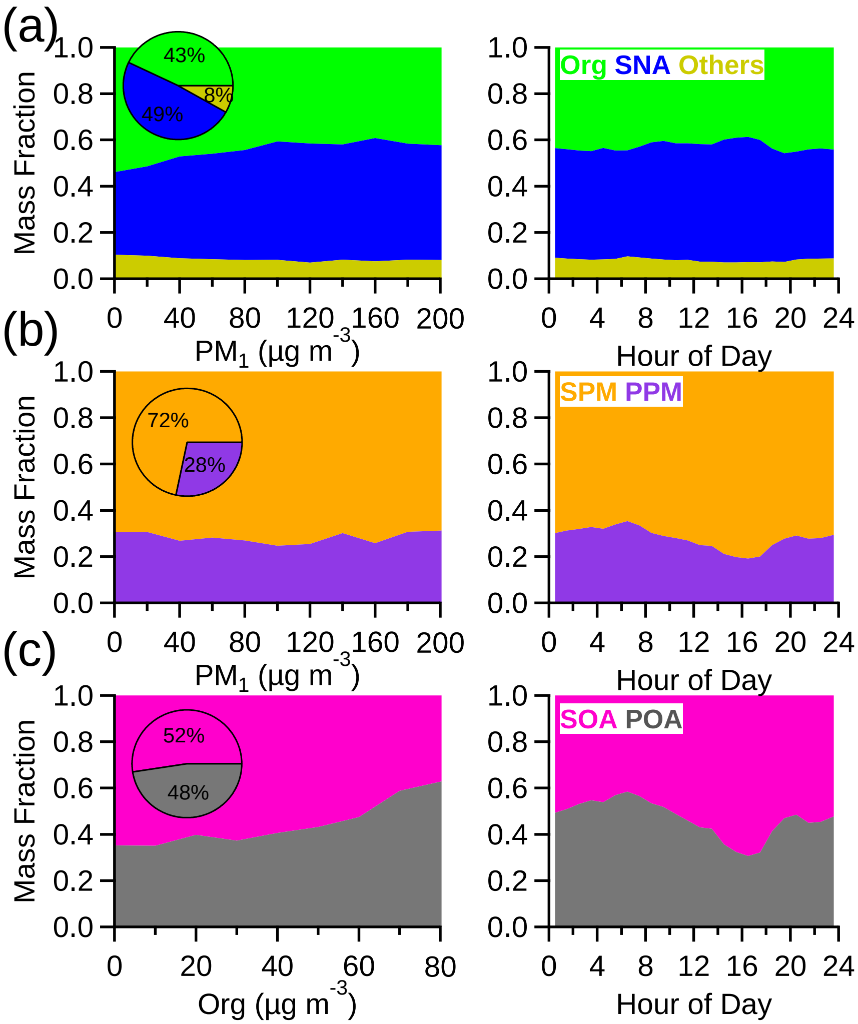

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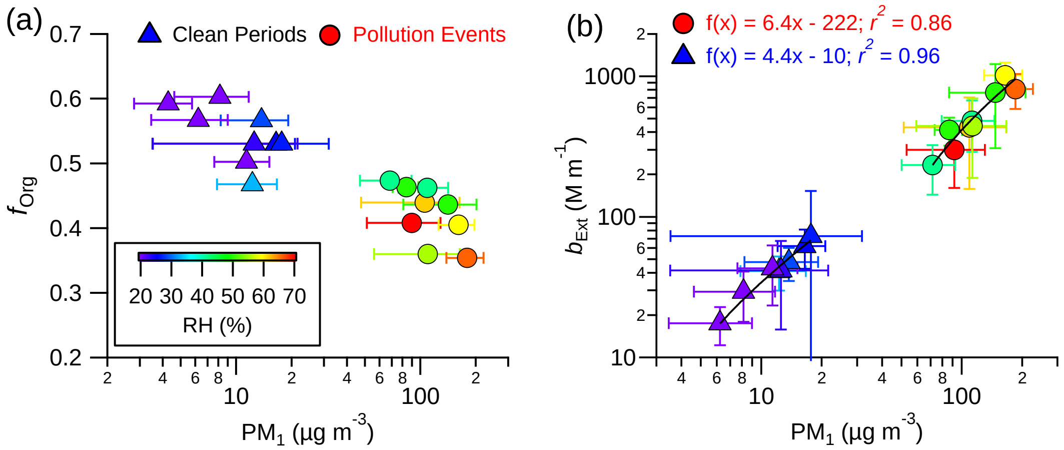

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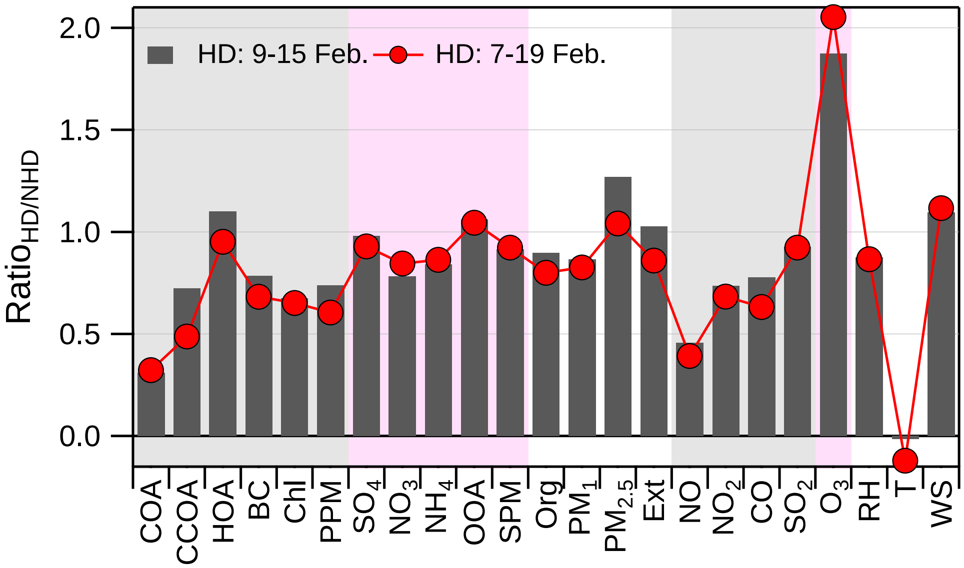

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