

Reply to Referee #1:

This manuscript addresses the chemistry of firework burning particles and its environmental impacts. Based on the chemical analysis of the PM_{2.5} sampled during the Spring Festival in Nanjing, the authors studied the mass contribution and the important tracers of fireworks burning particles. The impact on the atmospheric visibility for each important component and the aging processes of firework burning particles were also discussed. The chemical analysis of the composition and aging processes for firework burning particles in this work are systematic and comprehensive. Some of the highlights of this work (e.g. Ba and Sr as the tracers for firework burning, and the increasing contribution of (NH₄)₂SO₄ to visibility degradation during the aging processes) are very important for better understanding the properties of firework burning particles and of interest to the readers. This manuscript could be accepted by ACP before the following issues being addressed.

Thanks for your positive opinions. The authors believe that the data and conclusions in this manuscript will be helpful for the future studies on firework burning particles.

1. The authors include “human health” in the title. However, the health effect is only discussed in section 3.4.2 and only focusing on the heavy metals. The discussion is very brief compared with those about chemical components and visibility. My suggestion is that the authors either add more detailed discussion about the health effect or simply delete “human health” from the title.

We thank for this suggestion. Initially, we focused mainly on the chemical compositions of PM_{2.5} during Spring Festival period. And we obtained the concentrations of heavy metals. Then we thought the risk assessment model could be used here to give some interesting result which may further raise the attention of air pollution problem at this period in China. Detailed health effects raised by heavy metals are out of the scope of this investigation. So we accepted the suggestion and delete “human health” from the title.

2. The increasing contribution of (NH₄)₂SO₄ to visibility degradation is one highlight of this paper, and it is mainly demonstrated by Figure 7(b), which shows the relative percentage contribution of each species. However, the fine particle concentration dramatically decreased during 3rd - 6th Feb because of the weather conditions change. Consequently, the b_{ext} of total fine particles including the (NH₄)₂SO₄ part sharply decreased, as shown in Figure 7(a). In this case, is it more reasonable to compare the relative percentage contributions between the two periods instead of the absolute values?

We thank for this suggestion. Actually in the manuscript, we already discussed the relative percentage contributions (in brackets) to b_{ext} of these chemical species. The relative discussions about Fig.7b are listed below.

“The b_{ext} exhibited higher values at CNY and the following three days, in the range of 301-525 Mm⁻¹. (NH₄)₂SO₄ had the largest contribution to b_{ext}, accounting for 36.5±1.7%, followed by NH₄NO₃ (25.8±8.2%), EC (21.8±9.0%), OM (10.8±4.2%) and soil (5.1±1.8%) (Fig.7b).”

“At CNY, the influence of FW particles on visibility was mainly controlled by (NH₄)₂SO₄ (36%), NH₄NO₃ (26%), EC (15%) and OM (15%). During FW particle aging processes, the contribution of (NH₄)₂SO₄ increased from 36% (Jan.30) to 67% (Feb.3), while for NH₄NO₃, its contribution increased first to 28% at Jan.31 and then decreased to 10% (Feb.3). Similar trend was found for EC, it increased to 22% (Feb.1) and then decreased to 7.6% (Feb.3). For OM, it exhibited decreasing trend, to the lowest value at Feb.2 (5.5%).”

We accepted the comment of item 3 as following and focused the aging of firework burning particles from Jan.30 to Feb.3. Related discussions have been corrected in the “response of item 3” and the manuscript (line 559-571).

3. The period between 31st Jan and 6th Feb was also selected to discuss the aging processes in this manuscript. The authors observed that SO₄²⁻ needs 6 days (2 days more than the other main species) to reduce its concentration to the pre-SF level. However, I don't think that it is a proper time interval to discuss the aging processes. The chemical composition of aerosols could be greatly changed along with the change of weather conditions.

Thanks for this query. We re-analyzed the data and re-considered the conclusions. From Fig.2 (a), there was an obvious decreasing of relative humidity from 77.3% to 43.6% between Feb.3 and Feb.4. The low relative humidity is not favourable for the formation SO₄²⁻ from heterogeneous reactions of SO₂ on crustal materials directly from FW which has been verified as one of the aging mechanisms of firework particles. From Fig.6 (a), the mass percentages of (NH₄)₂SO₄ reached the highest values at Feb.3 of 36%. From Fig.7 (b), the relative contribution of (NH₄)₂SO₄ to b_{ext} reached the highest values of 67%. From Fig.10, the tracers of fireworks burning-Sr and Ba decreased to the lowest levels at Feb.3. Same situations could be found for K⁺, Cl⁻, NH₄⁺ and NO₃⁻ (Fig.11a). Though for SO₄²⁻, it did not decrease to the levels of Jan. 29, the authors believed that new emissions were introduced at Feb.4. It can be verified by the concentrations of Ba, Sr, K⁺, Ca²⁺, Ca and Na⁺ which all slightly increased at Feb.4. Therefore, the new emissions could be regarded as scattered fireworks burning at surroundings. Then at Feb.5, a rainfall (9 mm) decreased the concentrations of them. So the variations of SO₄²⁻ at Feb.5 and Feb.6 could not be simply distinguished as the aging of intensive fireworks burning particles at CNY's Eve.

Meanwhile, from the variations of soot-EC/NO₃⁻ and NO₃⁻/SO₄²⁻ (which showed lowest values at Feb.3) and the variations of SO₄²⁻/K⁺ and Cl⁻/K⁺ (which showed the highest values at Feb.3), the aging of firework burning particles at CNY's Eve can influence the air quality for about four days. The author believed this conclusion is more reasonable. This time scale is also in accordance with former studies (Drewnick et al., 2006; Feng et al., 2012). Also from Jan.30 to Feb.3, there were no sharp changes of the weather conditions, with the temperature, relative humidity and wind speed varying in 6.8-13.9°C, 74.3%-88.2% and 1.4-2.6 m s⁻¹, respectively.

The author accepted this suggestion, and the conclusions and relative discussions were corrected (Line 23-24, Line 569-571 and Line 676-677).

The data and conclusions here are the first time considering the aging of fireworks burning particles and are indicative for future studies. We thought that more works are needed to study the aging of fireworks burning particles especially in smog chamber. It is now being considered in our future research plan.

4. According to Figure1, an iron smelt plant located to the east of the sampling site. I wonder what was the operation condition of this iron smelt plant during 3rd - 6th Feb with strong east wind. It seems that the plant must be shut down (which is unusual), since there was no source concentration from iron smelt during SF as shown in Figure 9. The iron smelt source concentration was nearly none for Pre-SF, SF and After-SF but is 7.2% for Whole period. The authors didn't give the exact dates for the Whole period. Does the Whole period equal “Pre-SF + SF + After-SF”, or equal “Pre-SF + SF + After-SF + 7th-11th Feb (the weekdays not discussed in the manuscript)”?

In China, it is difficult to get the monitoring data for stationary sources from local environmental protection agency. We failed to get the emission data for this iron smelt plant. Luckily, we have a joint program with the Jiangsu Environmental Monitoring Center and obtained the daily emission data for key stationary sources (including industrial plants and power plants) of Nanjing for the year of 2012. All these stationary sources are fueled with coal. In 2012, the Chinese New Year (CNY) day is January 23 and the Lantern Festival (LF) day is Feb.6. Then we select the date period from Jan.13 to Feb.13 to see the variation of flue gases during Chinese Spring Festival (SF) period as following figure shown. It can be seen that the emission of flue gases at SF period was low and steady, varying in 2.17×10^8 - $2.41 \times 10^8 \text{ m}^3$.

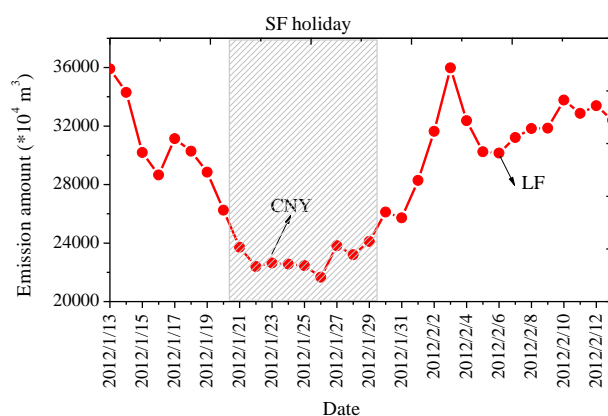


Fig.1 Total emission amounts of flue gases from key stationary sources (including 29 boilers) in Nanjing before, during and after the Spring Festival period of 2012.

In this study, we thought that the emission from the industrial sources are low and steady during SF period. And this has been reflected by the concentrations of chemical species in Section 3.1.2 and Section 3.2 and the source contributions from coal combustion (Section 3.3.2). Meanwhile this opinion has been listed in former studies, as “most industrial activities shut down in China with low energy consumption during this period (Feng et al., 2012; Huang et al., 2012; Li et al., 2013)” in section 3.3.2. And in this study, it was mainly reflected by the contributions of coal combustion (considering these industrial plants are all fueled with coal).

For the source contributions, as the limited sampling numbers for each period, we try to give reasonable and convincing results and explanation. For each separate period, few factors were extracted. Coal combustion and industrial processes could not be distinguished well. For the whole period, more samples were used as input and more factors were extracted. We try to distinguish the sources from iron smelt, industrial processes and coal combustion as the supplementary file-S8 shown. In S8 (d), factor 5 hold higher load with Mo and Mn and factor 8 exhibited higher load with Mg, Ti and Fe. We then attribute factor 5 to iron smelt and factor 8 to industrial processes. We thought that more samples are needed to give more reasonable source apportionment results in future studies. For example, the filter sampling time interval can be shortened in three or six hours and online-monitoring equipments could be used together. For the source contributions in Fig.9, the author believed that current results could be accepted as the contributions of coal combustion and firework burning are representative of the real situation for the changing of sources before, during and after SF in China.

The whole period included “Pre-SF+SF+After-SF” and it has been added after Figure. 9.

5. In the manuscript, data from 7th to 11th Feb were not shown because they are weekdays with other main pollution sources than fireworks burning. Accordingly, the authors should show the 7th-11th break in Figures 2, 6, 7, 10 and 11. I strongly suggest that these data should be presented (at least in the supplementary material) and be compared with the Pre-SF and After-SF data.

Thanks for this query. Actually, there were no data for these days as my daughter was born and I was at hospital during this period (7th to 11th Feb). In China, the winter vacation of university covering the Spring Festival holiday always lasts to the days after the Lantern Festival day. The birthday of my daughter was two weeks earlier than the day suggested by the doctor and it disturbed the sampling plan. At that moments, the other co-authors (both students and teachers) were at home, all far from the university. And at that period, it was not convenient to buy the railway tickets. So we have to stop the sampling works in these days. While it should be noted that from Feb.7, people for other occupations have to work and the industrial plants are re-started. The typical period for Spring Festival holiday with reduced emission sources is ended at Feb.7. Therefore, we thought that the sources for aerosols at Feb.7-Feb. 11 are similar with those at Feb.12-Feb.20 in this study. I feel very sorry for this.

The breaks in Figures 2, 6,7,10 and 11 were shown.

6. A lot of abbreviations (maybe too many) were used throughout the manuscript. In equation (1) and (2) in section 2.4.3, what are the meanings for BD and PEF? I cannot find the annotation of these two abbreviations in either the manuscript or the Table A1.

We are sorry for this error. BD should be AT and it has been added in the Abbreviations glossary.

PEF: the particle emission factor, which is used for the assessment of soil or dust. It is related with wind speed and the vegetable cover of surface.

We feel sorry for this direct copy from our former paper for the assessment of heavy metals in soil and road dust. In fact, it is not used in this study for heavy metals in atmospheric particles. The equation has been corrected.

7. The PM_{2.5} samples were collected for 24 hours in this work, but the starting point (12:00 am?) was not given in the paper. The detailed time scale for the 24-hours sampling should be given in the Methodology Section.

They were collected from about 08:00 am to 08:00 am the next day (line 193).

8. Some typos: Line 20 Page 28626, “holiday” should be “holiday”. Line 9 Page 28611, Line 1 Page 28615, Line 1 Page 28624, Line 2 Page 28625, Line 18 Page 28626, Line 21-22 Page 28629 and Line 18-20 Page28630, “decreased” should be “decreased”. Line 12 Page 28622, “transportation should be “transport”.

All have been corrected by “Find and Replace” function of word.