Reply to Referee #1:

This manuscript addresses the chemistry of firework burning particles and its environmental impacts. Based on the chemical analysis of the PM2.5 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 pro-cesses) 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.

Response: 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 bext 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?

Response: 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}. $(NH_4)_2SO_4$ had the largest contribution to b_{ext}, accounting for 36.5±11.7%, followed by NH_4NO_3 (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 $(NH_4)_2SO_4$ (36%), NH_4NO_3 (26%), EC (15%) and OM (15%). During FW particle aging processes, the contribution of $(NH_4)_2SO_4$ increased from 36% (Jan.30) to 67% (Feb.3), while for NH_4NO_3, 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.

Response: 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 SO_4^{2-} from heterogeneous reactions of SO_2 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 $(NH_4)_2SO_4$ reached the highest values at Feb.3 of 36%. From Fig.7 (b), the relative contribution of $(NH_4)_2SO_4$ 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^-, NH_4^+ and NO_3^- (Fig.11a). Though for SO_4^{2-}, 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^+, Ca^{2+}, 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 SO_4^{2-} 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/NO_3^- and NO_3^-/SO_4^{2-} (which showed lowest values at Feb.3) and the variations of SO_4^{2-}/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)"?

Response: 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 2.17×10^8-2.41×10^8 m^3.
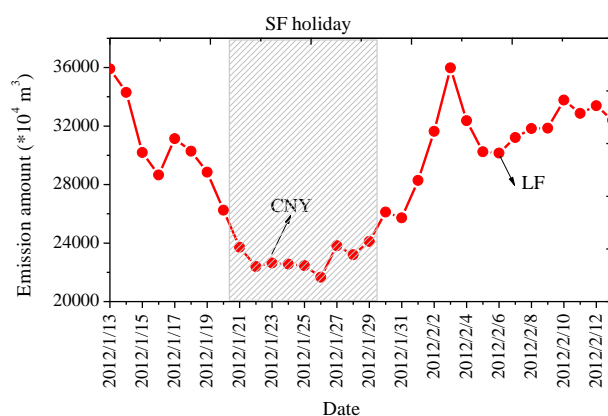

Fig.1 Total emission amounts of flue gases from key stationary sources (including 29 boilers) in Nanjing before, during and after the Spring Festival period of 2012.

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 imput 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.

Response: 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.

Response: 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 PM2.5 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.

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

8. Some typos: Line 20 Page 28626, "holidy" 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, "descreased" should be "decreased". Line 12 Page 28622, "transportation should be "transport".

Response: All have been corrected by "Find and Replace" function of word.

Reply to Referee #2:

This paper addresses the firework contribution to haze PM2.5 during Chinese Spring Festival (SF) in Nanjing, China. It concluded the aging processes of FW particles influence heavily on the human health. Several comments of this paper are summarized as follows,

1)Some mistyping and incorrect words are found throughout the entire MS (e.g. "significnatly", pp. 28611. line 12; " avtivities" pp.28624. line 9). Please be sure using the word "significantly", if using, the significance testing should be done?

Response:　As the data was compared just between CNY and the day before CNY, so statistic analysis could not be done. Then we corrected it into "obviously" (for the abstract and text). We have checked the whole text and deleted "significnatly" when the comparison was just done for few data.

"avtivities" has been corrected into "activities". All have been checked by the "Find and Replace" function of word.

2) The detection limit should be listed in "Chemical analysis" for various chemical species.

Response: The detail analysis methods and quality assurance and control for ICP-MS, ICP-OES, IC, TOR can be found in our former studies and we have pointed it in the text as "the pre-treatment and chemical analysis procedures and quality assurance and control are described detailedly in our previous works (Li et al., 2012; Kong et al., 2014a; 2014b; Li et al., 2014)". As they are both mature methods and widely used, we limited the description of them from the view of length of this paper.

To response to this comment, following information are listed.

For the accuracy of ICP-MS, geochemistry reference matter (GSS-2) made by the Center of National Standard Matter was analyzed; for ICP-OES, reference matters GBW0741, GBW07404 and GBW07406 were adopted. The analysis results are listed as the supplementary file of Kong et al. (2014a) and shown below.

For ICP-MS and ICP-OES analysis, as the limitation of equipments, we analyzed the samples in the Central Lab for Geology and Mineral in Hebei Province which belongs to the Ministry of Land and Resources of China. It is a professional analysis lab which has been assessed by General Administration of Quality Supervision, Inspection and Quarantine of China. They are familar with analysis for trace species. The QA and QC are well established and the author believed that the data are reasonable.

Twelve blank solutions were analyzed, the detection limits were calculated as three times of standard deviation as following Table 1 shown.

Table 1 Detection limits for ICP-MS　　units：μg

Elements	Mean（n=12）	Detection limits (3s)
Li	0.0004	0.0002
Be	0.0002	0.0001
Na	2.5300	0.7639
P	0.0422	0.0229
K	0.9920	1.0271
Sc	0.0002	0.0001
V	0.0008	0.0017
Cr	0.0964	0.0168
Mn	0.0155	0.0094

Co	0.0004	0.0004
Ni	0.0083	0.0091
Cu	0.0437	0.0260
Zn	0.1159	0.1144
As	0.1018	0.0143
Rb	0.0027	0.0054
Y	0.0004	0.0003
Mo	0.0013	0.0012
Cd	0.0002	0.0003
Sn	0.0046	0.0011
Sb	0.0009	0.0007
Cs	0.0001	0.0001
La	0.0007	0.0040
Ce	0.0007	0.0006
Sm	0.0001	0.0001
W	0.0022	0.0069
Tl	0.0001	0.0001
Pb	0.0118	0.0054
Bi	0.0001	0.0001
Th	0.0002	0.0001
U	0.0001	0.0001

For ICP-OES analysis, twelve blank solutions were analyzed, the detection limits were calculated as three times of standard deviation as following Table 2 shown.

Table 2 Detection limits for ICP-OES　　　units：µg

Elements	Si	Al	Ca	Mg	Fe	Ti	Ba	Sr	Zr
DL	1.39	0.95	1.07	0.16	1.21	0.18	0.011	0.004	0.085

DL: detection limits

For the accuracy of ICP-OES analysis, GBW07401, GBW07404 and GBW07406 samples were analyzed, the relative standard deviations (RSD) were listed in Table 3.

Table 3 Analysis accuracy for ICP-OES（µg/g）

Elements	GBW07401			GBW07404			GBW07406		
	Reference value	Analysis value	RSD (%)	Reference value	Analysis value	RSD (%)	Reference value	Analysis value	RSD (%)
Si	292600	291100	0.4	238100	234027	1.2	266100	263416	0.7
Al	75100	74296	0.8	124100	125240	0.6	112400	114190	1.1
Ca	12290	12329	0.2	1858	1904	1.7	1572	1560	0.5
Mg	10900	10547	2.3	2950	2868	2.0	2050	2060	0.3
Fe	36300	36910	1.2	72000	71740	0.3	56600	55824	1.0
Ti	4830	4865	0.5	10800	10574	1.5	4390	4313	1.3
Ba	590	592	0.2	213	213	0.0	118	120	1.2

Sr	155	156	0.5	77	76.5	0.5	39	39	0.0
Zr	245	234	3.2	500	511	1.5	220	211	3.0

Table 4 listed the accuracy for ICP-MS analysis.

Table 4 Analysis accuracy for ICP-MS

Elements	Mean analysis value/µg	Reference value /µg	SD/µg	RSD/%
Li	20.85	22	1.664	6.54
Be	1.74	1.8	0.062	3.59
Na	12094	12020	500	4.11
Mg	6024	6240	134	2.23
Al	51548	54539	1951	3.78
P	423	446	17.12	4.18
K	22541	21056	1662.8	7.84
Ca	17523	16850	864.1	4.93
Sb	1.18	1.3	0.076	6.56
Sc	9.87	10.7	0.149	1.52
Ti	2584	2710	126.7	4.74
V	59	62	2.33	3.98
Cr	49.5	47	1.80	3.63
Mn	541.2	510	15.98	2.97
Co	9.24	8.7	0.19	2.04
Ni	20.54	19.4	1.52	7.44
Cu	17.0	16.3	1.17	7.00

SD: Standard deviation; RSD: relative standard deviation

Description "the relative standard deviations between real values for standard materials and analyzing results were in the range of 1.5-14.7% and the detection limits were from 0.0001 to 1.39 µg for each element" and "The method detection limits (MDLs) for IC were 0.0258 mmol/L for Na^+, 0.0021 mmol/L for NH_4^+, 0.0066 mmol/L for K^+, 0.0053 mmol/L for Mg^{2+}, 0.0030 mmol/L for Ca^{2+}, 0.0051 mmol/L for F^-, 0.0144 mmol/L for Cl^-, 0.1215 mmol/L for NO_3^- and 0.0696 mmol/L for SO_4^{2-}, respectively" could be found in Kong et al. (2014a). The MDLs for TC and OC was 0.93 µg C cm^{-2} and 0.82 µg C cm^{-2}, respectively (Kong et al., 2012).

Kong, S. F., Ji, Y. Q., Lu, B., Zhao, X. Y., Chen, L., Bai, Z. P., Xu, Y. H., Liu, Y., and Jiang, H.: Characteristic of $PM_{2.5}$, PM_{10} and TSP source profiles for fugitive dust in a coastal oilfield city, China, Aerosol Air Qual. Res., 14, 2017-2028, 2014a.

Kong, S. F., Ji, Y. Q., Lu, B., Bai, Z. P., Chen, L., Han, B., and Li, Z.Y.: Chemical compositions and sources of atmospheric PM_{10} in heating, non-heating and sand periods at a coal-based city in northeastern china. Journal of Environmental Monitoring, 2012, 14: 852-865

3) Please add" (Fig.4)" to the line 15 of PP.28623 when describing the data.

    Response: It has been added in line 361.

4) PP.28623, line 22: Please show the unit of the wind speed.

Response: It has been added in line 365.

5) The inconsistent data are foundin the line 8 of PP.28625 (33.7) with the data in Table 1 (37.7).

Response: We have checked the data and sorry for this pencil error. It has been corrected as 37.7 in the text (line 407).

6) English should be polished by a English native speaker.

Response: We have polished the paper for another three times and ask for help of an expert at this field with more than eight years research experiences in UK.

Reply to Referee J. Williams:

jonathan.williams@mpic.de

Dear Authors, I would like to draw two relevant papers to your attention. They are also focused on firework emissions and could help your results and discussion section. The aforementioned papers describe firework emissions from temperate mid-latitudes and are worthy of comparison in terms of absolute amount of particulate, species, temporal profile and longevity.

Drewnick, F., S. S. Hings, J. Curtius, G. Eerdekens, and J. Williams: Measurement of fine particulate and gas-phase species during the New Year's Fireworks 2005 in Mainz, Germany. Atmos. Environment , 40, 4316-4326, 2006.

Williams, J., F. Drewnick, S. S. Hings, J. Curtius, G. Eerdekens, T. Klüpfel, and T. Wagner: Firework emissions for satellite validation ? Environ. Chem. 2, 1-2, doi:1071/EN05022, 2005.

We really appeciate for the information. The two references have been added. Some data are interesting and favored the obvervation in this study. Following has been added in section 3.4.1 (line 571-line 575).

"Drewnick et al. (2006) found that after about three or four days, though the aerosol mass concentrations droped to about one-third of the concentrations for Near Year's firework burning period, the relative compositions of aerosols were similar. And the mass concentrations of nitrate, sulfate and ammonium increased again after about three days." This information could be found in Fig.2 and related discussions in Drewnick et al. (2006).

The directly emission of KCl from fireworks burning has also been verified by Drewnick et al. (2006).