

## Correspondence to Review 2

Thank you very much for your thorough and constructive comments on our manuscript acp-2017-515, entitled “Characteristics and source apportionment of fine haze aerosol in Beijing during the winter of 2013”. We made all corrections and revised the manuscript according to your comments. The response is given to each comment. In the revised manuscript, changes are colored in blue.

### Specific comments

**Comments 1:** Page 3, line 53: Does this mean 3 – 16 days per year?

**Response 1:** Yes, it’s for one year and “per year” is added in the manuscript (*Page 3 line 53*).

**Comments 2:** Page 3, line 56: Is there a quantitative estimate for the boundary layer depth?

**Response 2:** Yes, there is. In Zheng et al. (2015), the boundary layer depth was found to be reduced less than 100 m in pollution periods study (*Page 3 line 56*).

**Comments 3:** Page 3, line 62: suggest phrasing: “winter haze episodes are 5 days in duration”

**Comments 4:** Page 3, line 72: replace “Over the past seven years (2000-2006)” with “Over a seven year period (2000-2006)”. Then on line 75, add “: : by 85% over this period”.

**Comments 5:** Page 6, line 157: negative rather than negatice

**Response 3-5:** According to your suggestions, we rephrased and corrected them.

**Comments 6:** Page 6, line 164: The uncertainty description is not clear. What are the units on

“0.3 + the analytical detection limit” ? Is this a relative error, or does it have concentration units ?

**Response 6:** In the present study, we used NMF method with "0.3+DL" for estimating uncertainty according to the method of Xie et al. (1999a; b). In this formula, a constant 0.3 corresponds to the log(Geometric Standard Deviation, GSD) to represent the variation of measurements. In the present study, concentrations of each species were converted into those of standard normal distribution. Then, log(GSD) was calculated from the normalized concentrations for all measured species, which was no greater than 0.3. Therefore, we adopted 0.3 for the uncertainty estimation. The unit of all measurements was set to  $\mu\text{g}/\text{m}^3$ . This method has several advantages. First of all, one set of analytical/method detection limit with an additional additive term enables to avoid zero, which causes instability of factorization analysis (Xie et al., 1999b). In addition, the use of geometric standard deviation is suitable for our measurement set in a wide range of concentrations.

**Comments 7:** Page 7, lines 178-179: What is meant by “secondary standard of GB 3095-2012” ?

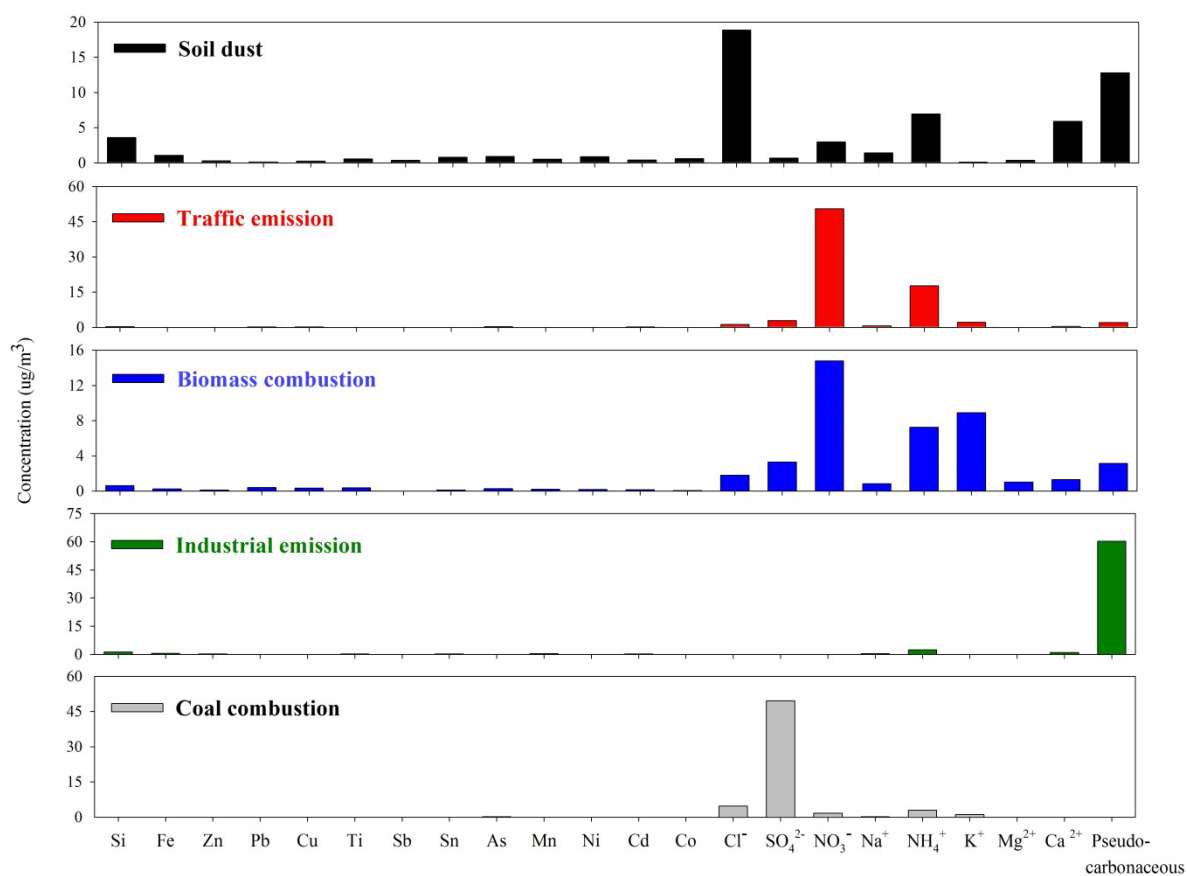
**Response 7:** GB 3095-2012 is the revision of the GB 3095-1982, which prescribe the “National Ambient Air Quality Standard” of China. In GB 3095-2012, the standard for PM<sub>2.5</sub> was added. The word “secondary standard” is removed in the revised manuscript.

**Comments 8:** Table 1: Should the number of days with PM<sub>2.5</sub>/PM<sub>10</sub> > 0.5 and < 0.5 add up to the total number of days with comparison to PM<sub>10</sub>? In other words, 47 + 47 does not equal 67. The text implies that it should (e.g., that 70% of the events were developed type, which would be 47/67). Is the correct number for PM<sub>2.5</sub>/PM<sub>10</sub> < 0.5 = 20 ?

**Response 8:** Yes, the number of samples for PM<sub>2.5</sub>/PM<sub>10</sub> < 0.5 is corrected to be 20 in Table 1 of the manuscript. It was an error.

**Comments 9:** Figure 3: The factors are shown on a log scale to illustrate the contributions from all of the components of chemical composition. However, the log scale hides the large contributions of individual components to each, such as sulfate to coal combustion. Can the figure also be shown on a linear scale for comparison to illustrate which components make large contributions to each factor? A linear scale would increase the contrast.

**Response 9:** The source profile of PM<sub>2.5</sub> is shown in linear-scale below. As you mentioned, the contrast among factors are maximized in linear scale. However, the contributions from low concentrations are hardly seen in this plot. The concentrations of major constituents of atmospheric aerosols vary in wide range. For source apportionment, however, trace elements such as metals play a key role. Thus, it is quite typical to analyze source profiles in log-scale. In the present study, sulfate concentration was raised up to 100  $\mu\text{g}/\text{m}^3$  with metal concentrations remaining low during haze period. Thus, the original plots in log-scale are left in the revised manuscript.



Composition linear-scale profiles of the five factors identified in NMF analysis.

**Comments 10:** Page 9, lines 241-243: Traffic is attributed to a factor with high nitrate and ammonium, with the ammonia precursor attributed to the same emission source as NO<sub>x</sub>, presumably. Should there also be an agricultural factor for the ammonia emissions? Can the authors comment?

**Response 10:** The agricultural or biogenic source for ammonia emission was not distinguished in this study. It is mostly because this study was performed in the megacity of Beijing (the region in the 5<sup>th</sup> ring) during winter. In other study conducted at the same location (CRAES in Beijing) in the winter of 2013 (Wang et al., 2016), the agricultural influence on ammonia was reported to be negligible, based on the measurement of stable nitrogen isotope ( $\delta^{15}\text{N}$ ). They also encountered severe haze events during the experiment period, during which the contribution from agriculture and biogenic source was negligible and the main contribution was from coal combustion and vehicle emissions.

Wang, Y. L., Liu, X. Y., Song, W., Yang, W., Han, B., Dou, X. Y., Zhao, X. D., Song, Z. L., Liu, C. Q., and Bai, Z. P.: Isotopic partitioning of nitrogen in PM<sub>2.5</sub> at Beijing and a background site of China, *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2016-187>, 2016.

**Comments 11:** Page 9-10, lines 256-264: The authors suggest that secondary production is a relatively unimportant consideration. However, it is well known that sulfur oxidation rates in winter are typically slow, while NO<sub>x</sub> oxidation rates to NO<sub>3</sub><sup>-</sup> can remain rapid (e.g., Calvert et al., *Nature* 1985). Can the authors comment on the source of sulfate? Does this likely arise from secondary oxidation of SO<sub>2</sub>, or does it rather come from a primary emission of more oxidized sulfur that leads to sulfate? An easy metric here would be the ratio of sulfate to SO<sub>2</sub> in molar units. A similar comparison could be given for NO<sub>3</sub><sup>-</sup> to NO<sub>x</sub>.

**Response 11:** You are absolutely right that the oxidation reaction is important because its concentration was high during winter. Since SO<sub>2</sub> and NO<sub>x</sub> emission are the greatest in winter and the least in summer, the source strength is the greatest in winter. The above statement is to explain the seasonal difference in the study region, comparing the amount of emissions and well-established photochemical reactions.

Indeed, the secondary formation encompasses various processes including photochemical oxidation in gas and aqueous phase and, homogeneous and heterogeneous reactions, which are still poorly understood.

In previous studies, Sulfur Oxidation Rate (SOR) [ $n\text{SO}_4^{2-}/(n\text{SO}_4^{2-}+n\text{SO}_2)$ ] and Nitrogen Oxidation Rate (NOR) [ $n\text{NO}_3^-/(n\text{NO}_3^-+n\text{NO}_2)$ ] used to be found high during summer (n represents molar concentration), which indicates the efficient conversion of SO<sub>2</sub> and NO<sub>x</sub> to sulfate and nitrate, respectively. In this study, the average SOR and NOR were 0.14 and 0.12, respectively. While the average values were relatively low, these ratios were raised in haze events, particularly in red-alert haze (0.32 and 0.35, respectively), indicating enhanced contribution from secondary species.

In addition, high aerosol loading could impose reduction in radiation during winter haze event. Zheng et al., (2015) has reported that in Beijing, solar radiation dramatically decreased to 2.77 MJ m<sup>-2</sup> d<sup>-1</sup> during winter haze episode, compared to clean days (9.36 MJ m<sup>-2</sup> d<sup>-1</sup> on average). In addition, Wang et al. (2014) observed the background level of ozone concentration (< 10 ppb) in Beijing during winter heavy pollution days. The model showed a regional-scale reduction of ozone from 12~44 to less than 12 ppb and OH from 0.004~0.020 to less than 0.004 ppt. These results confirm that photochemical activity was weakened during haze events.

Recently, there has been increasing number of studies conducted in China, reporting the fast conversion of sulfate even in cold season and suggesting possible mechanisms for it (e.g., Wang et al., 2016). Liu et al. (2015) showed that homogeneous and heterogeneous reactions were important to secondary production during haze days.

To avoid the confusion, therefore, this part in *Page 9-10 line 260-267 and the relevant discussion* was reworded with more detailed explanation as follows.

“This study was performed in Beijing during winter when primary emissions are the greatest. As Beijing is a megacity with its own emissions but also surrounded by big satellite cities with industrial complexes, it is apt to be affected by their emissions if meteorological conditions meet. In addition, the study period was characterized by frequent occurrence of severe haze, during which the major sources and the degree of aging were intimately coupled owing to distinct meteorological states. Therefore, these five factors primarily indicate direct emission sources with secondary production implicitly included.”

Wang, Y., Yao, L., Wang, L., Liu, Z., Ji, D., Tang, G., Zhang, J., Sun, Y., Hu, B., and Xin, J.: Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China, *Sci. China Earth Sci.*, 57, 14–25, 2014.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Zamora, M. L., Hu, M., and Li, J.: Persistent sulfate formation from London Fog to Chinese haze, *Proc. Natl. Acad. Sci.*, 113, 13630–13635, 2016.

Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, *Atmos. Chem. Phys.*, 15, 2969–2983, doi:10.5194/acp-15-2969-2015, 2015.

Liu, X., Sun, K., Qu, Y., Hu, M., Sun, Y., Zhang, F., and Zhang, Y.: Secondary formation of sulfate and nitrate during a haze episode in megacity Beijing, China, *Aerosol Air Qual. Res.*, 15, 2246–2257, 2015.

**Comments 12:** Page 10, line 271: A large carbonaceous component is shown for blue / no alert days. However, there are only 4 days and 4 samples in this category. Is it possible that the deviation of the carbonaceous aerosol from the trend of decreasing contribution as the haze level increases is simply a result of the small number of samples in the blue / no alert category, leading to a statistically anomalous result? Can the authors comment on this?

**Response 12:** Since the experiment was carried out for 3 months in winter, the number of sample are not large enough to draw statistically significant results for each haze event. The haze event is very sensitive to meteorological condition, which shows large variability from year to year. Therefore, the purpose of this study is to better characterize haze events and to understand their causes. In this context, the large contribution from carbonaceous component is clearly a characteristic of blue alert haze for the study period but should be cautious about generalizing the result.

For better understanding, however, we provide a table comparing the average and standard deviation of pseudo-carbonaceous concentration for the entire and no/blue alert haze period. While the deviations are comparable, the average concentrations are different by four times. Therefore, it is likely that there is little chance in our result to be severely biased by the small number of samples.

Comparison of carbonaceous concentration between no/blue alert haze and entire period.

<b>Samples</b>	<b>Pseudo-carbonaceous concentration [<math>\mu\text{g}/\text{m}^3</math>]</b>	
	<b>Average</b>	<b>Standard deviation</b>
<b>No/Blue-alert haze event</b>	102.6	40.0
<b>Entire period</b>	26.2	34.8

**Comments 13:** Page 10, line 283 – 287: Following from the comment above, how does the sulfate /SO<sub>2</sub> ratio vary as the haze alert level increases? Does this ratio increase, decrease, or stay the same? If there is a trend, it may have information about the primary source of sulfate from SO<sub>2</sub> emission or the rate of secondary sulfate production from SO<sub>2</sub> oxidation.

**Response 13:** As stated in Response 11, we examined Sulfur Oxidation Ratio (SOR) and Nitrogen Oxidation Ratio (NOR) for each episode, which is summarized in the table below. They are increased as haze alert-level increases. However, the SORs of the haze events are 1

lower even in red-alert event, compared to those of warm season (0.5~0.7) (Wen et al., 2016).

The average SOR and NOR in different levels of haze alerts.

Haze alert level	SOR	NOR
Non-haze	0.13	0.08
No/blue	0.05	0.16
Orange	0.19	0.31
Red	0.32	0.35

Wen, W., Cheng, S., Liu, L., Chen, X., Wang, X., Wang, G., and Li, S.: PM<sub>2.5</sub> chemical composition analysis in different functional subdivisions in Tangshan, China, *Aerosol Air Qual. Res.*, 16, 1651-1664, 2016.

**Comments 14:** Page 11, lines 325-326: There is not a clear difference in Figure 4 between the blue / no alert trajectories and the non-haze trajectories. Are the authors sure that the 4 days are meaningful in this category to attribute the large contribution of industrial emissions? In Figure 5, this category remains different from the trend in most other categories as the haze severity increases.

**Response 14:** It is just 4 days for no/blue haze event but 57 days for non-haze days, of which trajectories are pretty much scattered. Most of all, the duration of no/blue haze is shorter than a day, for which one sample was taken for a day. Thus, it is highly likely that all 4 trajectories for 24 hours don't correspond to haze occurrence. The difference is better shown when averaging the 6-hour trajectories during the 4 no/blue haze days and 57 no-haze days. These trajectories are compared in the figure below.





Averaged backward trajectories of air masses for 3 days at 6-hour interval during no/blue alert- and non- haze days.