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Interactive comment on "Characteristics and source apportionment of fine haze aerosol in Beijing during the winter of 2013" *by* Xiaona Shang et al.

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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.

General Comments

Printer-friendly version

Discussion paper

Comment 1: NMF is an approach which is less widely used by the community of PM source appointment than PMF or PMF/ME-2. It would be useful for the readers to judge the quality of the analyzed results if the authors could provide more details about the possible difference between NMF and PMF in the part of methods. It is well known that the use of such kind of statistical analysis tool is quite arbitrary. There are some plausible interpretations about the extracted factors in the paper. But please add uncertainty analysis of the NMF results.

Response 1: We agree with your view toward statistical analysis. PMF is more widely used than NMF for source apportionment for atmospheric particulate matter. Also, the result of statistical analysis is fairly arbitrary and should be interpreted with caution. In this study, we used NMF rather than PMF for the following reasons.

(1) Non-negative matrix factorization (NMF) is similar to positive matrix factorization (PMF) as mentioned in the text (Page 6 Line 158-161). Both methods find two matrices (W and H, termed the contribution matrix and the source profile matrix, respectively) that best reproduce the input data matrix (V) using the same factorization approach ($V = WH$) as a positive constraint ($W \geq 0$ and $H \geq 0$). However, difference between PMF and NMF lie in the method of treating negative factors and the algorithms which guarantee the solution matrices of W and H to be non-negative. When treating negative factors, PMF forces them to be positive, but in NMF only non-negative factors are used. It means that more tweaking is exerted to PMF, whereas less number of factors is extracted in NMF. If all conditions met, therefore, PMF analysis will provide more detailed information on sources, compared to NMF.

In addition, the additive update rule used in algorithms of PMF is applied to a multiplicative update rule for NMF method (shown below), which ensures the square root of the sum of squared differences of the elements to be non-increasing. Due to this improvement, the non-negative W and H matrices are initially guaranteed so that the tweaking of ad hoc non-negativities of PMF is not necessary at all for NMF (Lee and Seung, 2001). Wi ← {Wi (HjTVij)/(HjTHjWi)} Hj ← {Hj (WiTVij)/(WiTWiHj)}

2) The uncertainty level is very important to PMF treatment. To calculate uncertainties, there are two methods employed for the EPA PMF 5.0 (User's manual, https://www.epa.gov/air-research/epa-positive-matrix-factorization-50-fundamentals-and-user-guide): observation- and equation-based uncertainty. The former requires an estimate of the uncertainty for each species in each sample. The observation-based uncertainty of components can be evaluated by repeated observations (cost a lot of time and resources) or by using several different instruments/methods (not available in this study) (see https://www.nist.gov/pml/nist-technical-note-1297). Hence, the equation-based uncertainty is usually used in PMF model, which provides species-specific parameters for each sample. The equation-based uncertainty can be calculated as follows:

5/6 × MDL (method detection limit) (concentration≤ MDL)…….…………..1) [(Error Fraction × concentration)2 + (MDL)2]0.5 (concentration> MDL)……………..2) , where error fraction (EF) is the percentage of uncertainty.

In Equation 2), uncertainty includes three terms, EF, concentration, and MDL, which is suitable for higher concentrations whereas Equation 1) is better for lower concentrations.

This study analyzed samples for winter season (three months), during which concentrations ranged from the level of detection limit for clean continental background to the extremely high level of severe haze event. For instance, SO42- concentrations varied from the detection limits to 100 µg/m3.

For PMF uncertainty calculation (e.g., Reff et al., 2007), the analytical uncertainty is the most critical factor. As stated in the text, carbonaceous concentrations were not directly measured but indirectly estimated in this study and thus, their analytical uncertainty is not available.

For source apportionment of PM2.5, therefore, 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 μg/m3. 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.

Using the NMF model, the five source profiles were extracted, with which we were able to distinguish major emission sources for the winter PM2.5 and haze aerosols of Beijing, even though the specific type of industry or secondary factors were not separated. Particularly, the sources apportioned by NMF analysis are well incorporated into the history of air masses estimated by backward trajectory analysis under gradual change in meteorological conditions (Fig. 5).

Xie, Y. L., Hopke, P. K., Paatero, P., Barrie, L. A., and Li, S. M.: Identification of Source Nature and Seasonal Variations of Arctic Aerosol by positive matrix factorization, J. Atmos. Sci., 56, 249–260, 1999a. Xie, Y. L., Hopke, P. K., Paatero, P., Barrie, L. A., and Li, S. M.: Identification of source nature and seasonal variations of Arctic aerosol by the multilinear engine, Atmos. Environ., 33, 2549-2562, doi.org/10.1016/S1352-2310(98)00196-4, 1999b.

Comment 2: The authors concluded that “To abate the severe haze in Beijing, therefore, it is necessary to reduce vehicle emissions in Beijing and further sulfur emissions from industrial complexes in surrounding cities.” But this is not fully supported by the data presented in this work. Can you prove that local emissions are dominated by vehicles? Can you prove that sulfur emissions are mainly from industrial complexes in surrounding cities? How about the uncontrolled coal burning for sulfur emissions?

Response 2: Our conclusion is based on the measurements of SO2 and NO2 in conjunction with sulfate and nitrate, and comparison of their relative enhancement in several haze events under different meteorological conditions. This information is summarized in the Table below and given as supplementary information. From non-haze to red-alert haze, the portion of SO42- and NO3- against mass and the SO2/NO2 ratio increased, whereas fractions of mineral or salt species and trace elements decreased. Between non-haze and haze events, the increase of SO2 (18.7 to 36.9 ppb) was greater than that that of NO2 (26.8 to 50.2 ppb). During the three types of haze events, SO42- enhancement (4 to 32 %) was also greater than that of NO3- (16 to 31 %). These results demonstrate that the variation in concentration and fraction was greater for nitrogen than sulfur compounds depending on meteorological condition, which suggests the larger contribution of local sources to nitrogen than to sulfur. âĂČ Regarding uncontrolled coal burning, a recent study by Cheng et al. (2017) emphasizes its contribution to sulfur emission in Beijing region. The southern and eastern region of Beijing (Tianjin and Tangshan as stated in Page 11 line 314) were recognized as main source regions, from which haze forming air masses were transported to Beijing during orange- and red- alert haze in this study.

Spatial distribution of (a) PM2.5 and (b) SO2 emissions from household coal combustion in the BTH region in heating season of 2013 (Cheng et al., 2017).

In the wintertime of Beijing, air mass was usually transported from the northwest with high wind speed. What we observed in the present study is that as the high pressure system developed, winds were shifted westward and then gradually to the southwest and southeast. As a result, the stagnated condition was intensified and the haze-alert level was raised (Fig. 4). When air masses were rapidly transported from the northern area, no pollution alert was issued. As the air mass slightly lingered over the western regions, blue-alert haze occurred. With the air mass moved very slowly from the southwestern areas, orange-alert haze event lasted for three days. As the air was severely stagnated, the red-alert haze occurred in Beijing for five consecutive days, when air was coming from the east. It is in accordance with the result of recent study, emphasizing the effect of meteorological condition on the severity of haze in Beijing (Cai et al., 2017) (added in revised manuscript of Page 11 line 316-318).

Cai, W., Li, K., Liao, H., Wang, H., and Wu, L.: Weather conditions conducive to Beijing severe haze more frequent under climate change, Nat. Clim. Change, 7, 257-262, doi:10.1038/nclimate3249, 2017.

Specific Comments:

1. In the part of introduction, the authors may add descriptions on the current alert system implemented in Beijing.

Response 1: More detailed information on the alert system of Beijing is given in INTRODUCTION with a relevant website for air pollution alert regulations (Page 3 line 63-67). The criteria are given in association with individual haze event in Page 7-8 line 197-207.

2. The term “pseudo-carbonaceous” in Figure 2 and other place of corresponding text sounds strange. Maybe the authors can use “Particulate organic matter”.

Response 2: The “pseudo-carbonaceous” include EC as well as OC, even though OC concentrations are usually higher than those of EC. Because carbonaceous compounds were not measured, but estimated from other measurements in this study, it should be clarified. In this context, we employed the terminology “pseudo” in front of carbonaceous compounds.

3. Line 260 – 261 “This study was performed in winter, during which the chemical composition of PM2.5 was likely to be more dependent on source strength rather than photochemical oxidation,” this argument is ambiguous. The secondary species like NO3- and SO42- must come from atmospheric oxidation processes. I think even in winter chemical composition of PM2.5 was also related to both source strength and oxidations. Also as shown in Figure 2, sulfate and nitrate were always dominating

chemical compositions especially for the conditions of pollution episodes.

Response 3: You are absolutely right that the oxidation reaction is important because its concentration was high during winter. Since SO2 and NOx 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) [nSO42–/(nSO42–+nSO2)] and Nitrogen Oxidation Rate (NOR) [nNO3–/(nNO3–+nNO2)] used to be found high during summer (n represents molar concentration), which indicates the efficient conversion of SO2 and NOx 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-2 d-1 during winter haze episode, compared to clean days (9.36 MJ m-2 d-1 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.

4. Line 262 – 264 “In addition, NO2 is more likely sourced from local emissions, but SO2 is expected to be transported from nearby regions.” This is a good argument. But more discussions or evidences are required to support this argument.

Response 4: The response 3 is also relevant to this point. A table is given as supplementary information.

5. Line 273, what could be the high VOCs emitting industries? Please be more specific.

Response 5: The industrial processes using VOCs as raw materials such as furniture manufacturing, petroleum refining, machinery equipment manufacturing and printing (Wu et al., 2015). The description was added in Page 9 line 254-255 of revised manuscript.

Technical Comments: Line 202, 203 et al., I suggest the authors to present the concentrations of PM consistently for the significant figure as Line 177, 180 and 187, e.g. change 168.4 μg/m3 to 168 μg/m3.

Response: The significant figures were corrected in revised manuscript.

Please find figure in pdf file given as supplement.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-515/acp-2017-515-AC1-supplement.pdf

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