Correspondence to Review1

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

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 ($W \geqslant 0$ and $H \geqslant 0$).

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).

$Wi \leftarrow \{Wi\ (Hj^{T}Vij)/(\ Hj^{T}HjWi)\}$

$Hj \leftarrow \{Hj\ (Wi^{T}Vij)/(Wi^{T}WiHj)\}$

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:

$5/6 \times$ MDL (method detection limit) (concentration$\leqslant$ MDL)…… …….1)

$[(\text{Error Fraction} \times \text{concentration})^2 + (\text{MDL})^2]^{0.5}$ (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, SO_4^{2-} concentrations varied from the detection limits to 100 μg/m^3.

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 $PM_{2.5}$, 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/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.

Using the NMF model, the five source profiles were extracted, with which we were able to distinguish major emission sources for the winter $PM_{2.5}$ 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.

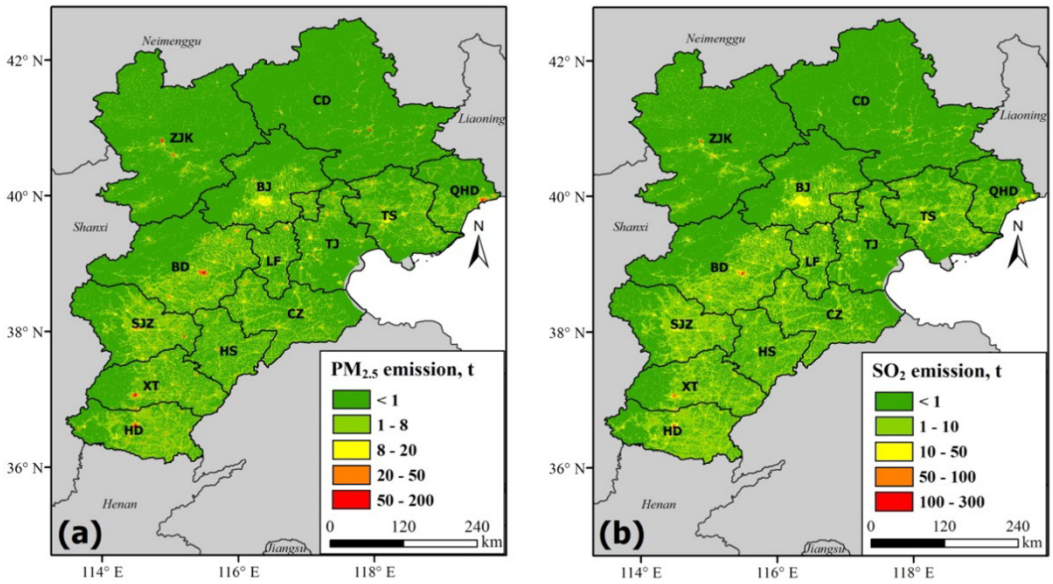
Xie, Y. L., Hopke, P. K., Paatero, P., Barrie, L. A., and Li, S. M.: Identification of source nature and seasonal variations of Arctic aerosol by the multilinear engine, Atmos. Environ., 33, 2549-2562, doi.org/10.1016/S1352-2310(98)00196-4, 1999b.

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 SO_2 and NO_2 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 SO_4^{2-} and NO_3^- against mass and the SO_2/NO_2 ratio increased, whereas fractions of mineral or salt species and trace elements decreased. Between non-haze and haze events, the increase of SO_2 (18.7 to 36.9 ppb) was greater than that that of NO_2 (26.8 to 50.2 ppb). During the three types of haze events, SO_4^{2-} enhancement (4 to 32 %) was also greater than that of NO_3^- (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.

Event	SO_2 (ppbv)	NO_2 (ppbv)	$\frac{SO_2}{NO_2}$	SO_4^{2-} (%)	NO_3^- (%)	$Ca^{2+} + Mg^{2+} + Na^+$ (%)	Trace elements (%)	Dominant wind
Total	21.1	29.4	0.7	19	17	3	4	
Non-haze	18.7	26.8	0.7	18	12	4	6	Northerly
No/Blue alert haze	34.3	50.2	0.7	4	16	3	4	Westerly
Orange alert haze	33.0	41.8	0.8	18	25	2	3	Southerly
Red alert haze	36.9	42.9	0.9	32	31	0	2	Easterly

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) $PM_{2.5}$ and (b) SO_2 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 SO_2 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) $[nSO_4^{2-}/(nSO_4^{2-}+nSO_2)]$ and Nitrogen Oxidation Rate (NOR) $[nNO_3^-/(nNO_3^-+nNO_2)]$ used to be found high during summer (n represents molar concentration), which indicates the efficient conversion of SO_2 and NO_x 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.

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 $\mu g/m^3$. 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” ?

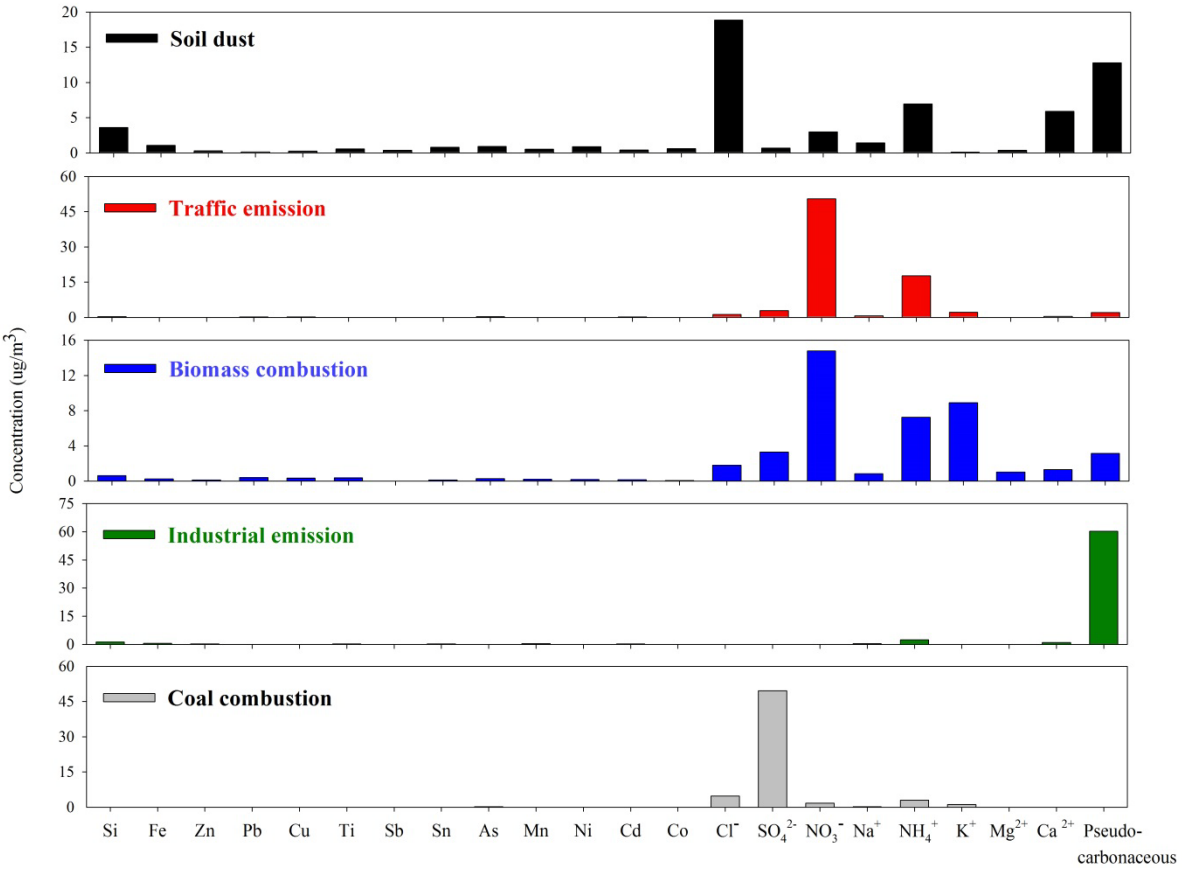
Response 7: GB 3095-2012 is the revision of the GB 3095-1982, which prescribe the “National Ambient Air Quality Standard” of China. In GB 3095-2012, the standard for PM2.5 was added. The word “secondary standard” is removed in the revised manuscript.

Comments 8: Table 1: Should the number of days with PM2.5/PM10 > 0.5 and < 0.5 add up to the total number of days with comparison to PM10? 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 PM2.5/PM10 < 0.5 = 20 ?

Response 8: Yes, the number of samples for $PM_{2.5}/PM_{10} < 0.5$ 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 $PM_{2.5}$ 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 μg/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 an ammonium, with the ammonia precursor attributed to the same emission source as NOx, 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 5th 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 (δ 15N). 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 $PM_{2.5}$ 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 NOx oxidation rates to NO3- 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 SO2, 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 SO2 in molar units. A similar comparison could be given for NO3- to NOx.

Response 11: You are absolutely right that the oxidation reaction is important because its concentration was high during winter. Since SO_2 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) [$nSO_4^{2-}/(nSO_4^{2-}+nSO_2)$] and Nitrogen Oxidation Rate (NOR) [$nNO_3^-/(nNO_3^-+nNO_2)$] used to be found high during summer (n represents molar concentration), which indicates the efficient conversion of SO_2 and NO_x 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.

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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.

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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.

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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.

Samples	**Pseudo-carbonaceous concentration [μg/m^3]**	
	Average	Standard deviation
No/Blue-alert haze event	102.6	40.0
Entire period	26.2	34.8

Comments 13: Page 10, line 283 – 287: Following from the comment above, how does the sulfate /SO2 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 SO2 emission or the rate of secondary sulfate production from SO2 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 l

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

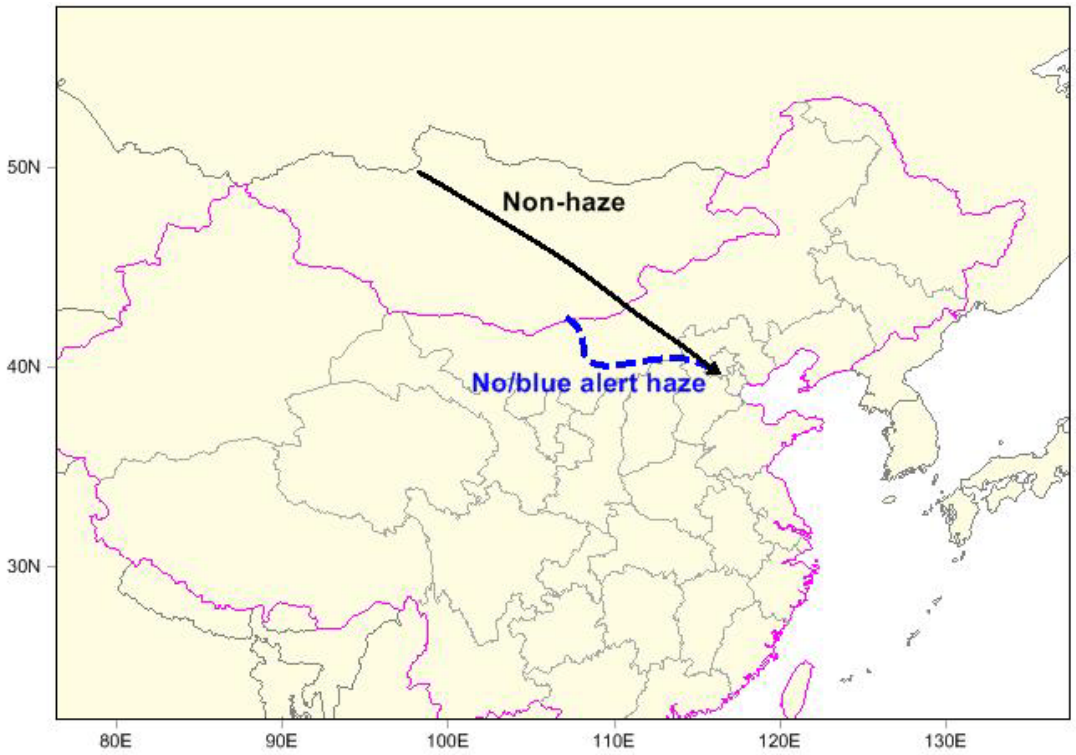
The average SOR and NOR in different levels of haze alerts.

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.: PM2.5 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.

Characteristics and source apportionment of fine haze aerosol in Beijing during the winter of 2013

Xiaona Shang[1], Kai Zhang[2*],Fan Meng[2], Shihao Wang[2], Meehye Lee[1*], Inseon Suh[1], Daegon Kim[3], Kwonho Jeon[3], Xuezhong Wang[2], Yuxi Zhao[2]

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Abstract

For $PM_{2.5}$ filter samples collected daily at the Chinese Research Academy of Environmental Sciences (Beijing, China) from December of 2013 to February of 2014 (the winter period), chemical characteristics and sources were investigated with an emphasis on haze events in different alert levels. During the three months, the average $PM_{2.5}$ concentration was 89 μg m^{-3}, exceeding the Chinese national standard of 75 μg m^{-3} in 24 h. The maximum $PM_{2.5}$ concentration was 307 μg m^{-3}, which characterizes *developed-type* pollution ($PM_{2.5}/PM_{10}$ > 0.5) in the World Health Organization criteria. $PM_{2.5}$ was dominated by SO_4^{2-}, NO_3^-, and pseudo-carbonaceous compounds with obvious differences in concentrations and proportions between non-haze and haze episodes. The non-negative matrix factorization (NMF) analysis provided reasonable $PM_{2.5}$ source profiles, by which five sources were identified: soil dust, traffic emission, biomass combustion, industrial emission, and coal combustion accounting for 13 %, 22 %, 12 %, 28 %, and 25 %, respectively. The dust impact increased with northwesterlies during non-haze periods and decreased under stagnant condition during haze periods. A blue alert of heavy air pollution was characterized by the greatest contribution from industrial emissions (61 %). During the Chinese Lantern Festival, an orange-alert was issued and biomass combustion was found to be the major source owing to firecracker explosions. Red-alert haze was almost equally contributed by local traffic and transported coal combustion emissions from Beijing vicinities (approximately 40 % each) that was distinguished by the highest levels of NO_3^- and SO_4^{2-}, respectively. This study also reveals that the severity and source of haze are largely dependent on meteorological conditions.

Key words: $PM_{2.5}$, winter haze, Beijing, chemical composition, source apportionment, NMF

1. Introduction

With the increasing $PM_{2.5}$ concentration in northern China, winter haze occurrences increased from 3 to 16 days per year during 2000–2012 (Wang and Chen, 2016). The frequency of haze events during winter is enhanced by meteorological conditions; the minimum daily temperatures typically reach –15 to –20 °C (Wu et al., 2012) and the boundary layer height becomes shallow to less than 100 m (Zheng et al., 2015). Moreover, the combustion of fossil fuel increases at low temperatures (Zhang and Samet, 2015). As the air quality deteriorated, China released its third revision of the "The National Ambient Air Quality Standards" (NAAQS) in 2012 (GB 3095-2012), which stipulated safe $PM_{2.5}$ levels for the first time (Zhang and Cao, 2015). However, the worst haze events in the major cities of China were recorded during the winter of 2012–2013. During January of this period, Beijing experienced almost daily haze and the hourly $PM_{2.5}$ concentration reached 855 μg m^{-3} (Zheng et al., 2015). In Beijing, winter haze episodes were 5 days in duration (Zheng et al., 2015, 2016). The long duration of haze with high $PM_{2.5}$ concentration triggers a red alert for air pollution (Liu et al., 2017), which is the highest level of the heavy air pollution warning system issued in the "Emergency plan for heavy air pollution in Beijing (revised in 2016)" (in Chinese: http://zhengce. beijing.gov.cn/ library/192/33/50/200/806828/96701/index.html).

The concentrations of SO_2, NO_x, and volatile organic compounds (VOCs), which are important precursors of $PM_{2.5}$, vary in different emission and policy implementations. Related particulate compositions (sulfate, nitrate, and organic matter) comprise two thirds of $PM_{2.5}$ (Huang et al., 2014; Hu et al., 2015). Over a seven-year period (2000–2006), SO_2 emission has increased by 53 %, consistent with the increases in power plant emissions from 10.6 Tg to 18.6 Tg (Lu et al., 2010). Particularly in northern China, the emissions from power plants have increased by 85 % over this period. In contrast, SO_2 levels have significantly decreased since 2006, when stricter SO_2 regulations, such as the use of flue-gas desulfurization systems or scrubbers, were imposed (Van der A et al., 2016). The reduction was particularly rapid during 2008–2009. On the other hand, the NO_x concentration increased from 2000 to 2012 (Hong et al., 2016; Cao et al., 2011). This increase is in accord with the increased number of vehicles, which contribute 90 % of the total NO_x emissions in Beijing (Hendrick et al., 2014;

Wu et al., 2012). Meanwhile, the continuous increase in VOC emissions (from 13 Tg/yr in 2000 to 26 Tg/yr in 2012) was mainly driven by industrial processes (~70 %) (Hong et al., 2016). Coal combustion (especially that of raw coal) from households is underestimated in the southern and eastern rural areas of Beijing. Rural coal combustion comprises approximately 75 % of Beijing's total coal combustion (Cheng et al., 2017). After the 2008 Olympic Games, residential coal combustion emitted large amounts of SO_2, NO_x, and VOCs (70, 17, and 43 kt, respectively). In 2013, these amounts had increased twofold to 132, 33, and 81 kt, respectively. At the end of 2013, China issued the Air Pollution Prevention and Control Action Plan (CAAC, 2013), which greatly reduced the precursor emissions in 2014 (Wang et al., 2015).

Under the strict regulations on boiler and industrial emissions, SO_2 concentrations in Beijing significantly decreased during the winter of 2013 and the fuel sulfur was reduced by more than 80 % in 2014 (relative to its 2013 levels) (CAAC, 2013; CAAC, 2015). Over the same period, the NO_x levels were reduced by 6.7 % over the nation, but exceeded the standard by 42 % in Beijing, where local traffic emissions remained high. Meanwhile, the $PM_{2.5}$ pollution is the most severe in the region of southern Beijing, where the annual average concentration reached 150 μg m^{-3} during 2014–2015. The level is comparable to the national standard of PM_{10} (CAAC, 2015; Zhang and Cao, 2015).

Since the 2008 Olympics and 2013 CAACs, heavy industries have been relocated and high-quality fuel has been introduced. Both actions have reduced the concentrations of gaseous precursors (Wang et al., 2009; Van der A et al., 2016), although these reductions are in contrast to the frequent hazes currently observed in Beijing. In recent studies, the $PM_{2.5}$, dust, and SO_2 concentrations in Beijing have been mainly attributed to regional transport (Wang et al., 2014; Yang et al., 2013; Wang et al., 2011). Considering the extreme haze situation in Beijing, researchers have sought the crucial factors of haze formation, usually by identifying the emission sources of $PM_{2.5}$. The source apportionment of $PM_{2.5}$ is commonly analyzed by source receptor models such as positive matrix factorization (PMF) and non-negative matrix factorization (NMF) (Reff et al., 2007; Kfoury et al., 2016). These models have implicated coal and industries as major sources of $PM_{2.5}$ in Beijing (Huang et al., 2014; Zhang and Cao,

2015; Zhang et al., 2013).

Following the severe and frequent haze occurrences in January of 2013, the chemical characteristics and sources of $PM_{2.5}$ in Beijing were extensively investigated (Jiang et al., 2015; Zheng et al., 2015; Zhang et al., 2015; Chen et al., 2017). However, few studies have investigated the winter season of 2013–2014, which immediately followed the enactment of the 2013 CAAC in China. In particular, the source apportionment of Beijing's haze remains unknown (Wu et al., 2016). In the present study, we thoroughly examine the chemical compositions of $PM_{2.5}$ in Beijing during the winter of 2013–2014, and accordingly, diagnose the haze occurrence, probe the local and transported influence on haze, and quantify the critical source contributions.

2. Experiments

Filtered samples of PM_{10} and $PM_{2.5}$ were collected on the roof of a three-story container (~15 m above ground level) at the Chinese Research Academy of Environmental Sciences (CRAES) in Beijing, China (40.04 °N, 116.42 °E), from December of 2013 to February of 2014. The site is located near the four-way intersection of a residential area located between the 5^{th} and 6^{th} ring roads of Beijing.

Aerosols were collected for 24 hours (from 7 pm to 7 pm next day) on a 90-mm polypropylene filter using a medium volume sampler at a flow rate of ~100 L/min (2030, Laoying, China). Seventy $PM_{2.5}$ samples were collected and analyzed. The water-soluble ions (Cl^-, NO_2^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were measured by ion chromatography (IC25, Dionex, USA) with a detection limit between 0.01 and 0.06 μg m^{-3}. The ionic measurement method is detailed in Lim (2009). For trace elemental analysis, the samples were digested by a mixture of acids as described in Zhang et al. (2014). A quarter of each filter was placed into a polytetrafluoroethylene flask and digested with 8 mL of HNO_3/H_2O_2 (6/2 v/v, superpure grade, Merck, Darmstadt) at 180 °C for 8 h. The solution was separated by centrifugation and diluted to 25 mL with ultrapure water. The concentrations of

trace metals (21 species, including Si) were determined by inductively coupled plasma-optical emission spectrometry (Prodigy 7, Teledyne Leeman, USA). The mass concentration of PM_{10} was also determined for comparison with that of $PM_{2,5}$.

The total concentrations of the water-soluble ions and trace elements were subtracted from the $PM_{2.5}$ mass, to provide a measure that likely represents the carbonaceous components that were not directly measured. In this study, therefore, it was referred as the pseudo-carbonaceous components and used for the following discussion. The concentrations of these pseudo-carbonaceous components were comparable to those of $PM_{2.5}$ concentrations observed in Beijing (Ji et al., 2016). A meteorological suite of relative humidity, temperature, and visibility was collected by CRAES from a sharing network of the China Meteorological Data Service Center (CMDC): http://data.cma.cn/en/?r=data/detail&dataCode=A.0012.0001. The gaseous species NO_x, SO_2, CO, and O_3 were measured using commercial analyzers (42i, 43i, 48i, 49i, Thermo Fisher, USA) in CRAES.

The $PM_{2.5}$ source was identified by non-negative matrix factorization (NMF) analysis. Introduced by Lee and Seung (1999, 2001), NMF operates similarly to positive matrix factorization (PMF). Both analysis 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. However, while PMF is a generalized, alternative least-squares method, NMF minimizes the conventional least-squares error and the generalized Kullback–Leibler divergence. The uncertainties in NMF analysis were estimated as 0.3 + the analytical detection limit (Xie et al., 1999a, b).

In addition to NMF analysis, the origin of air masses was traced by trajectory analysis. For air masses arriving at 500 m altitude, backward trajectories were computed for 72 hours using HYSPLIT model with GDAS data in SplitR (Stein et al., 2015, https://github.com/rich-iannone/ SplitR).

3. Characteristics of winter $PM_{2.5}$

3.1. $PM_{2.5}$ and PM_{10} mass variations

During the 2013–2014 winter period in Beijing, the mass concentrations of $PM_{2.5}$ and PM_{10} varied in a similar pattern (Fig. 1). Zheng et al. (2015) reported a similar trend between the $PM_{2.5}$ and PM_{10} concentrations. In this study, the average PM_{10} concentration was 142 μg m^{-3}, comparable to the Chinese national standard of 150 μg m^{-3} in 24 h (GB 3095-2012). However, the mean $PM_{2.5}$ concentration was 89 μg m^{-3}, exceeding the standard of 75 μg m^{-3} in 24 h. The $PM_{2.5}$ standard was most severely exceeded in February 2014, when the average concentration (133.5 μg m^{-3}) reached the highest winter concentration in Beijing during the 2005–2015 decade (Lang et al., 2017).

Based on the criteria of the World Health Organization (WHO) (2006), the wintertime air pollution of Beijing was classified as *developed-type*, meaning that the $PM_{2.5}/PM_{10}$ ratio exceeded 0.5 in 70 % of the samples (Table 1). The mean $PM_{2.5}$ concentration of these samples (113 μg m^{-3}) was four times higher than that in *developing-type* pollution (31 μg m^{-3}). In approximately half of the *developed-type* samples, the $PM_{2.5}$ and PM_{10} mass concentrations exceeded the national standards, all of which were collected during haze events. The average $PM_{2.5}$ concentration over 13 haze days reached 198 μg m^{-3} and the visibility was significantly reduced to ~1 km (Fig. 1). In contrast, the $PM_{2.5}$ concentration exceeded the standard without violating the PM_{10} concentration on only a few days. These results well reflect the wintertime characteristics of $PM_{2.5}$ levels in Beijing, which are largely related to haze episodes. The average $PM_{2.5}$ concentration of the *developed-type* was comparable to that of the *developing-type* unless the $PM_{2.5}$ concentration exceeded the standard.

On 12 out of 13 haze days, the pollutant levels met the criteria of heavy air pollution alerts stipulated in the “Emergency plan for heavy air pollution in Beijing (revised in 2016)”. In the lowest level of the four-tier warning system, blue alert, the daily average air quality index (AQI) exceeded 200 on only one day. In Table 1, the one no-alert and three blue-alert haze days are defined as no/blue-alert haze events. The average $PM_{2.5}$ concentration on these days was 168 μg m^{-3} (Table 1). During the red-alert period (February 20–25), the daily $PM_{2.5}$

concentration peaked at 306 μg m^{-3}. A red alert is declared when the air pollution is heavy and severe. During a red alert, AQI exceeds 200 on four consecutive days and exceeds 300 on continuous two of those days. Although the daily average AQI remained higher than 300 during the February 14–16 period, this event was an orange alert because it continued for only three days. The AQI data can be found at http://www.tianqihoubao.com/aqi/beijing-201402.html (in Chinese). Here, we describe episodes in terms of alerts defined in the heavy air pollution system rather than in the haze alert system, because the former definition is based on the daily averaged AQI, whereas the three-tier haze warnings depend on the hourly meteorological parameters (relative humidity and visibility) or $PM_{2.5}$. Because we measured the daily concentrations, the heavy air pollution alert was suitable for our purpose.

3.2. Chemical composition

Throughout the wintertime, the average $PM_{2.5}$ concentration remained close to 90 μg m^{-3}, 20 % above the national standard. The major $PM_{2.5}$ components were SO_4^{2-}, NO_3^-, NH_4^+, and pseudo-carbonaceous compounds, with average concentrations of 18.8, 16.9, 8.5, and 38.6 μg m^{-3}, respectively. Collectively, these four compositions comprised 83 % of the $PM_{2.5}$ mass (Fig. 2). On the 57 non-haze days, the fractional chemical compositions and concentrations of SO_2 and NO_2 were comparable to those of the entire period (70 days). In contrast, the portions of soil minerals such as Ca^{2+} and trace elements (including Si) were 3–4 times higher on non-haze days than on haze days. The Ca^{2+} and Si concentrations were highly correlated (r^2 = 0.8) and were more related to the PM_{10} (r^2 = 0.6) than $PM_{2.5}$ levels. This reflects the significant impact of soil dust on non-haze days (Fu et al., 2012). On haze days, the particle masses, compositions, SO_2, and NO_2 varied widely among the different alert levels.

3.3. Source profiles

The $PM_{2.5}$ sources were identified in an NMF analysis of the measurement data. The data included 8 water-soluble ions, 13 trace elements, and pseudo-carbonaceous compounds. After comparison through a principle component analysis, the principal factors were determined.

Finally, five critical factors were distinguished: soil dust, traffic emission, biomass combustion, industrial emission, and coal combustion (Table 2). The five source profiles are presented in Figure 3. Despite their clear signatures, the contributions of dust and traffic emissions were approximately half those of biomass combustion, industrial emission, and coal combustion (Table 2).

Factor 1 (soil dust) is confirmed by high Ca^{2+}, Si, Fe, Cl^-, and Na^+ contents (Fu et al., 2012). The high concentrations of Cl^- and Na^+ likely originate from dry lake deposits (Abuduwaili et al., 2015), which spread over the northern area of Beijing. Elevated heavy metals suggest the presence of fugitive dust mixed with industry or traffic emissions (Wan et al., 2016). The high loadings of NO_3^- and NH_4^+ in Factor 2 indicate traffic emissions (He et al., 2016). As is well known, NH_3 is emitted from three-way catalytic converters in vehicles (Chang et al., 2016). Factor 3 (biomass combustion) emits large amounts of K^+ and NH_4^+ (Balasubramanian et al., 1999), along with the elements that give exploding fireworks their color (namely Mg, Fe, Al, Ti, Cu, and Si) (Baranyai et al., 2015). The concentrations of these firecracker indicators are most significantly elevated during the Chinese Lantern Festival (14, 15, and 16 of February; Fig. 1). Factor 4 (industrial emissions) is distinguished by high pseudo-carbonaceous materials and heavy metals. Factor 5 (coal combustion) is characterized by high Cl^-, SO_4^{2-}, and NO_3^- contributions, which are absent in Factor 4. Although both Factors 4 and 5 represent the influence of industrial emissions near Beijing, Factor 5 is more clearly sourced from industries requiring high energy, such as iron and steel, cement, and power plants (Tan et al., 2016; Zhang et al., 2013). In contrast, Factor 4 indicates emissions from industrial processes using VOCs as raw materials such as furniture manufacturing, petroleum refining, machinery equipment manufacturing and printing (Wu et al., 2015).

In a previous study, source apportionment by NMF or PMF analysis distinguished 7–8 factors (Zhang et al., 2013), including a secondary formation source. The secondary source was not separated as an individual factor in the present study. As a typical secondary species, SO_4^{2-} dominates in Factor 5. However, a NO_3^- signature appears in all factors except Factor 4. As a megacity, Beijing is surrounded by large satellite cities with industrial complexes. Thus, Beijing is susceptable to emissions from these areas in addition to its own emissions, when

meteorological conditions are met. This will be discussed in detail in the following section. In fact, the atmospheric condition facilitated haze occurrence, leading to the major sources and the degree of aging for aerosols being intimately coupled. Therefore, these five factors primarily represent direct emission sources with secondary sources being implicitly included. In addition, NO_2 is more likely sourced from local emissions, but SO_2 is expected to be transported from nearby regions.

4. Characteristics of winter haze

4.1. Chemical and meteorological characteristics

The chemical compositions of $PM_{2.5}$ clearly differed on haze in contrast to non-haze days in terms of secondary ions and pseudo-carbonaceous compounds (Fig. 2). The largest fraction of pseudo-carbonaceous compounds (61 %) was accompanied with the smallest proportion of SO_4^{2-} (4%) on no/blue-alert days, suggesting low coal consumption by high-VOC-emitting industries. On orange-alert haze events, the NO_3^- fraction was twice that on non-haze days, and the K^+ and Mg^{2+} proportions were maximized (at 6 % and 1 %, respectively), implying biomass-combustion emission during the Lantern festival in China. The concentrations of SO_4^{2-} and NO_3^- were comparable with the greatest contribution in red-alert haze events. In addition, these species were closely related to the Cl^- (r^2 = 0.8) and NH_4^+ (r^2 = 0.9) concentrations, respectively, suggesting large contributions by coal combustion and vehicle emission. It is also noteworthy that the SO_4^{2-} fraction varied more widely than the NO_3^- fraction (Table S1). Among the three levels of haze events, SO_4^{2-} varied from 4 % to 32 %, whereas NO_3^- varied from 16 % to 31 % and NH_4^+ from 9 % to 11 %. Similarly, although both SO_2 and NO_2 concentrations were the highest in red-alert haze, SO_2 enhancement (relative to non-haze days) was 20 % larger than NO_2 enhancement. Because the sulfur compounds were much more elevated than the nitrogen compounds on haze days (particularly in red-alert haze events), the winter haze in Beijing was concluded to be largely contributed by coal combustion, which emits sulfur compounds. Furthermore, coal emissions are mostly transported from nearby Beijing (Hendrick et al., 2014).

To examine the meteorological conditions favorable for haze occurrence and clarify the

emission source regions, surface weather maps combined with daily average backward trajectories at 500 m were compared during non-haze and haze events. Previous studies also reported that weather conditions were critical for haze formation. In East China, migratory anticyclones and weak pressure gradients were the prerequisites of winter haze from 1980 to 2012 (Peng et al., 2016). High $PM_{2.5}$ episodes in Beijing usually began with weak southerly winds and ended with strong northerly winds (Guo et al., 2014). In this study, the air mass was usually transported from the northwest. As the high pressure system expanded, however, it was trasnported from the west, southwest, and southeast. Throughout this process, the weather condition became increasingly stagnant (Fig. 4) and the haze-alert level increased gradually. The recent study also emphasized the effect of meteorological condition on the severity of haze in Beijing (Cai et al., 2017). When air masses were rapidly transported from the northern desert area (Fig. 4a), mineral species such as Ca^{2+} and Si were enriched on non-haze days and the PM_{10} mass was high. In the western regions of Beijing (Fig. 4b), where various industries manufacture food, drink, furniture, pharmaceuticals, and other products from VOCs (http://www.berkeleysg.com/2016/06/china-manufacturing-distribution-map/), the fraction of pseudo-carbonaceous compounds rose to its maximum as the air mass slightly lingered over the region. During February 14–16, firecracker explosions caused a spike in K^+, Mg^{2+}, and NH_4^+ concentration under the stagnant weather condition, in which the air mass moved very slowly from the southwestern areas, where population density is the highest (Cheng et al., 2017). As the air mass moved eastward toward the high energy-requiring regions (http://berc.berkeley.edu/energy-access-developing-parts-china/) (Fig. 4d), such as Tianjin and Tangshan, where coal consumption is high for industrial use and residential heating (Cheng et al., 2017), the $PM_{2.5}$ and SO_4^{2-} (SO_2) concentrations reached their maxima.

4.2. Source profiles

To quantify each source contribution during the winter haze in Beijing, daily samples were analyzed by NMF and the source profiles during haze and non-haze episodes were compared (Fig. 5). In all samples, the main contributions were industrial, traffic, and coal combustion emissions (22–28 %), followed by soil dust and biomass combustion (13 % and 12 %, respectively). However, soil dust loading, which is associated with elevated fractions of Ca,

Si, and pseudo-carbonaceous matters (Fig. 2), was enhanced to 20 % during non-haze events. Meanwhile, the local traffic contribution decreased as the air mass was rapidly transported from the northwestern desert areas, as mentioned in subsection 4.1.

The three types of haze episodes exhibited strong contrasts not only in their chemical species and source regions, as mentioned above, but also in their source profiles (Fig. 5). No/blue-alert haze was dominated by industrial emissions (61 %) as the airflow passed over the industrial regions manufacturing products from raw VOCs. Consequently, the pseudo-carbonaceous concentration increased. During orange- and red-alert haze events, the dust contribution was negligible and the anthropogenic fraction increased sharply. During the Chinese Lantern Festival (which triggered an orange alert), a biomass signature with the highest K^+ concentration was observed in the air mass transported from the southwestern populated areas of Beijing. The K^+ contribution (35 %) was three times higher than that on non-haze days. During February 20–25, the outflow of the high coal-consuming eastern region enhanced the proportion of coal combustion products to 37 %. Simultaneously, the traffic contribution was the highest at 43 %. The coal and traffic effects were accompanied by two-fold elevations of SO_4^{2-} and NO_3^- in $PM_{2.5}$.

5. Policy implications

During the 2013–2014 winter period in Beijing, the average $PM_{2.5}$ concentration exceeded the standard by 20 %, and in February, reached its highest level in the 2005–2015 decade (Lang et al., 2017). The $PM_{2.5}$ mass closure and concentration of gaseous precursors during the 57 non-haze days were comparable to those of the entire winter period. Mineral dust is an important source of $PM_{2.5}$ and elevates the PM_{10} concentration on non-haze days. The average $PM_{2.5}$ concentrations increased significantly from 65 μg m^{-3} on non-haze days to 168 μg m^{-3} on no/blue-alert days and to 218 μg m^{-3} on red-alert days.

When weather conditions stagnate under weak pressure gradients, the alert levels of heavy air pollution upgrade on haze days. The migratory anticyclones also shift the air masses, causing

wide variations in chemical species and emission sources. During haze days, the NO_2 and NO_3^- concentrations exceed those of SO_2 and SO_4^{2-}, respectively, but the sulfur-containing species vary more widely than the nitrogen species. The sulfur compounds are particularly enhanced in stagnant air masses transported from the Beijing vicinities, including the southern and eastern regions, leading to the large sulfur variation with little change in nitrogen. These results highlights the significant influence of the emissions from industries requiring high energy and using coal in Beijing vicinities and from local vehicles on winter haze formation in Beijing, which is in accordance with findings from previous studies (Hendrick et al., 2014; Wang et al., 2016). To abate the severe haze in Beijing, therefore, it is necessary to reduce vehicle emissions in Beijing and further sulfur emissions from industrial complexes and uncontrolled coal combustion in surrounding cities. For cost-effectiveness, the weather forecast needs to be incorporated into the policy implementation.

6. Conclusion

This study investigated the chemical characteristics of $PM_{2.5}$ during the 2013–2014 winter period in Beijing and identified its sources with an emphasis on haze events by measuring the particle masses, water-soluble ions, and trace elements in filtered samples. Finally, policy implications for controlling haze occurrences in Beijing were deduced from the analysis.

The samples were collected daily at CRAES, Beijing, China, from December of 2013 to February of 2014. During the winter period, the overall average $PM_{2.5}$ concentration in Beijing was 89 μg/m^3, exceeding the Chinese national standard of 75 μg/m^3 in 24 h. The excess was linked to high occurrence of haze events in February of 2014. The high $PM_{2.5}$ episodes were concurrent with PM_{10} exceedance. Seventy percent of the samples were identified as *developed-type* in the WHO criteria; that is, their $PM_{2.5}/PM_{10}$ ratios exceeded 0.5. All 13 recognized haze events in this study were included in the *developed-type*.

The chemical compositions showed that secondary ions were doubled on haze days relative to non-haze days, but mineral species were halved during haze events. For the 70 daily $PM_{2.5}$

samples, NMF analysis was performed and the source profiles were compared between haze and non-haze days. The analysis identified five principle sources, of which industrial emission, coal combustion, and traffic emission comprised similar fractions of 28 %, 25 %, and 22 %, respectively. The soil-dust and biomass-combustion sources were well distinguished and contributed 13 % and 12 %, respectively. Comparing the source profiles between non-haze and haze events, the impact of soil dust was most noticeable on non-haze days, when the air masses rapidly transported from northwestern desert areas and brought high concentrations of Ca^{2+} and Si into Beijing. However, nearby transport of industrial, biomass combustion, and coal combustion emissions, along with local traffic emission, contributed to haze events under stagnant weather conditions. The contributions of these four sources increased by up to 61 %, 35 %, 37 %, and 43 % in no/blue-alert, orange-alert, and red-alert days, respectively. The industries that are mainly located to the west of Beijing use VOCs as raw materials, elevating the pseudo-carbonaceous components in $PM_{2.5}$. Biomass combustion increases during the firework displays of the Lantern Festival (February 14–16). At that time, the K^+ and Mg^{2+} concentrations are maximized. When a red-alert was issued for six days in 2014, the contribution of SO_4^{2-} and NO_3^- increased by factors of 3 and 2, respectively, from their non-haze levels. Overall, the sulfur compounds (SO_2 and SO_4^{2-}) varied much more widely than the nitrogen compounds (NO_2 and NO_3^-) through haze events, implying the substantial contribution of industrial emissions from coal combustion in surrounding cities. The high level of nitrogen compounds suggests local vehicle emissions as a main source of winter haze in Beijing. This study also emphasizes the role of weather condition in haze formation by building up stagnant condition that facilitates the transport of industrial emissions from Beijing vicinities. These findings will be applicable to policy making.

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593 **Table 1.** Statistics of $PM_{2.5}$ mass concentrations.

$PM_{2.5}$ mass classification	Number	$PM_{2.5}$* [μg m^{-3}]
Chemical and NMF analysis	70	
Comparison with PM_{10} mass	67	89
$PM_{2.5}/PM_{10} > 0.5$	47	113
$PM_{2.5} > 75$ μg m^{-3} and $PM_{10} > 150$ μg m^{-3}	23	168
$PM_{2.5} > 75$ μg m^{-3} and $PM_{10} < 150$ μg m^{-3}	5	113
$PM_{2.5} < 75$ μg m^{-3} and $PM_{10} < 150$ μg m^{-3}	19	39
$PM_{2.5}/PM_{10} \leq 0.5$	20	31
Haze days#	13	198
Red alert	6	218
Orange alert	3	216
No/blue alert	4	168

594 * Average concentration

595 # Heavy air pollution alert

596 **Table 2.** Sources identified by NMF analysis.

Factor	Contribution	Sources
Factor 1	13 %	Soil dust
Factor 2	22 %	Traffic emission
Factor 3	12 %	Biomass combustion
Factor 4	28 %	Industrial emission
Factor 5	25 %	Coal combustion

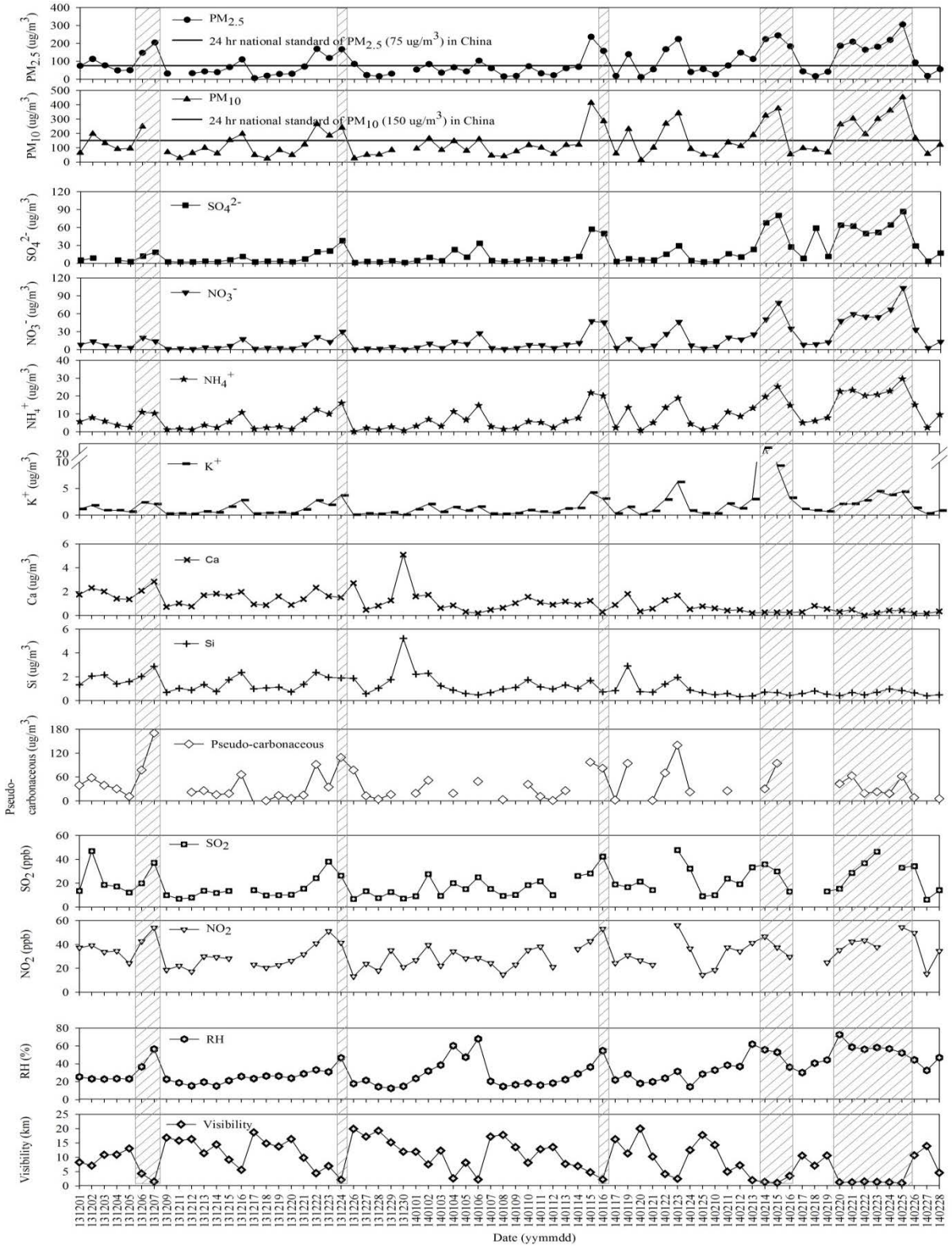


Figure 1. Variations in mass and chemical compostions of $PM_{2.5}$, PM_{10} mass, gaseous precursors, and meteorological parameters measured from Dec. 1, 2013 to Feb. 28, 2014. Horizontal lines indicate the Chinese national standards of PM concentrations in 24 h and the vertically shaded regions denote the 13 haze days.

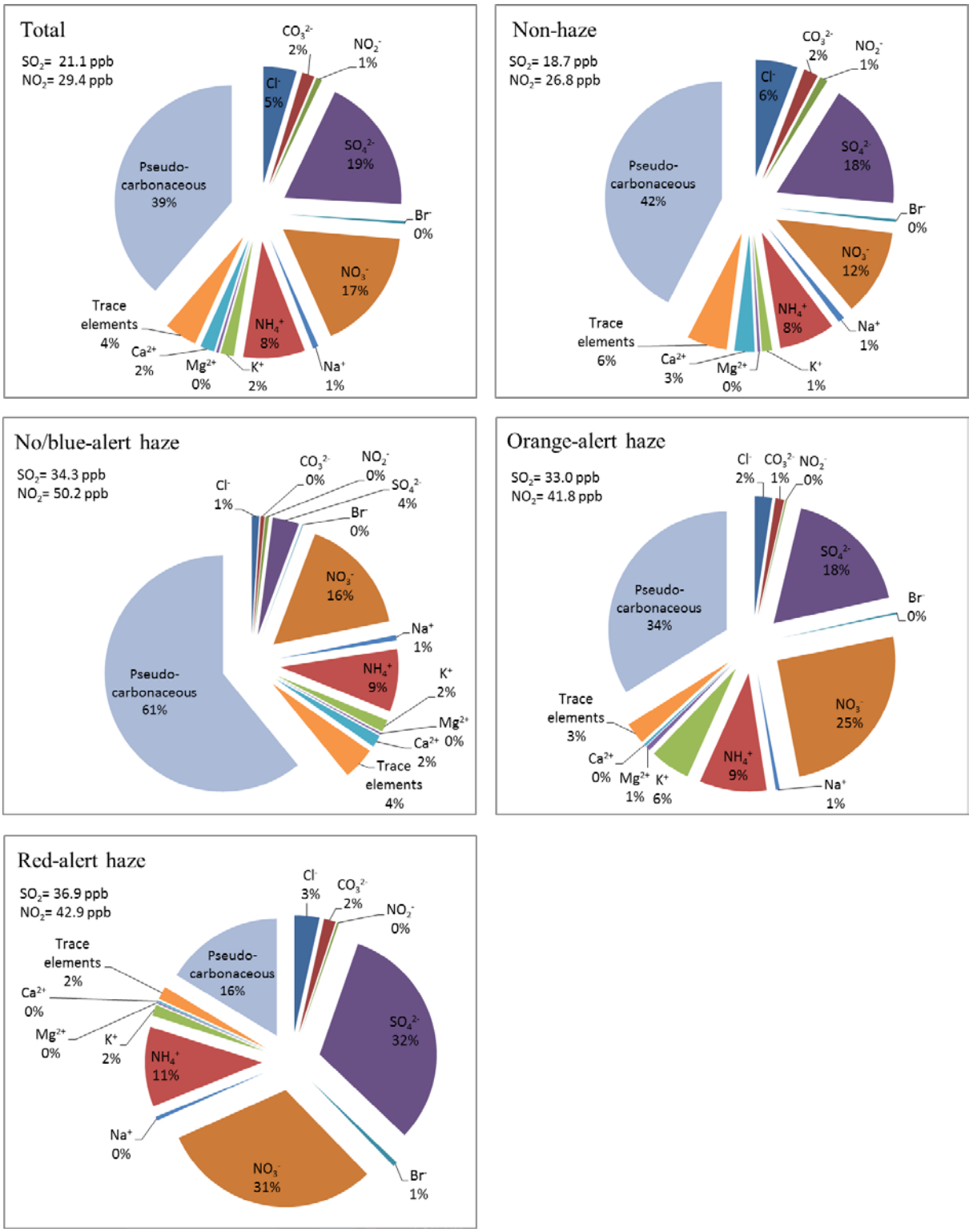
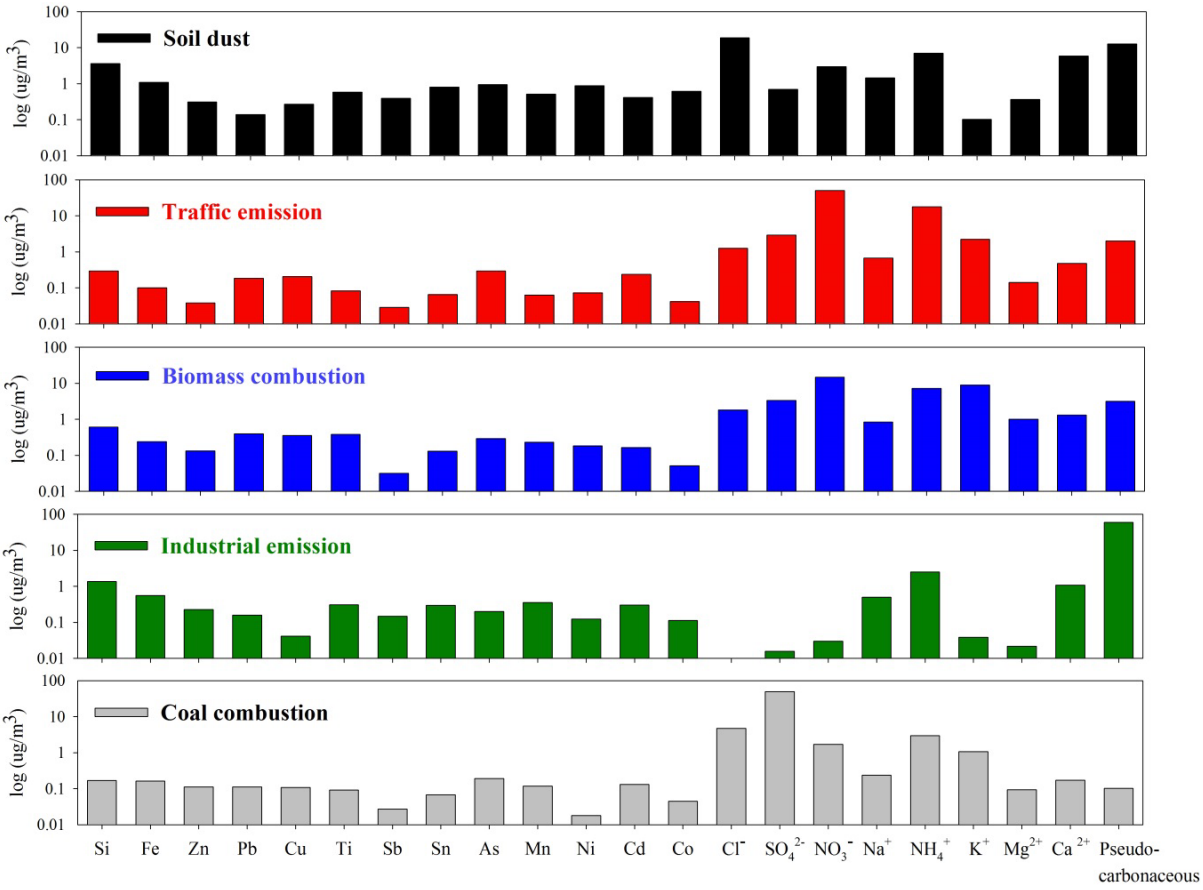


Figure 2. $PM_{2.5}$ mass contributions of water-soluble ions, trace elements, and pseudo-carbonaceous matter during the entire period (top left), non-haze days (top right), and haze days at blue-alert (center left), orange-alert (center right), and red-alert (bottom left) warning levels. The average SO_2 and NO_2 concentrations are also given.



607

608 **Figure 3.** Composition profiles of the five factors identified in NMF analysis.

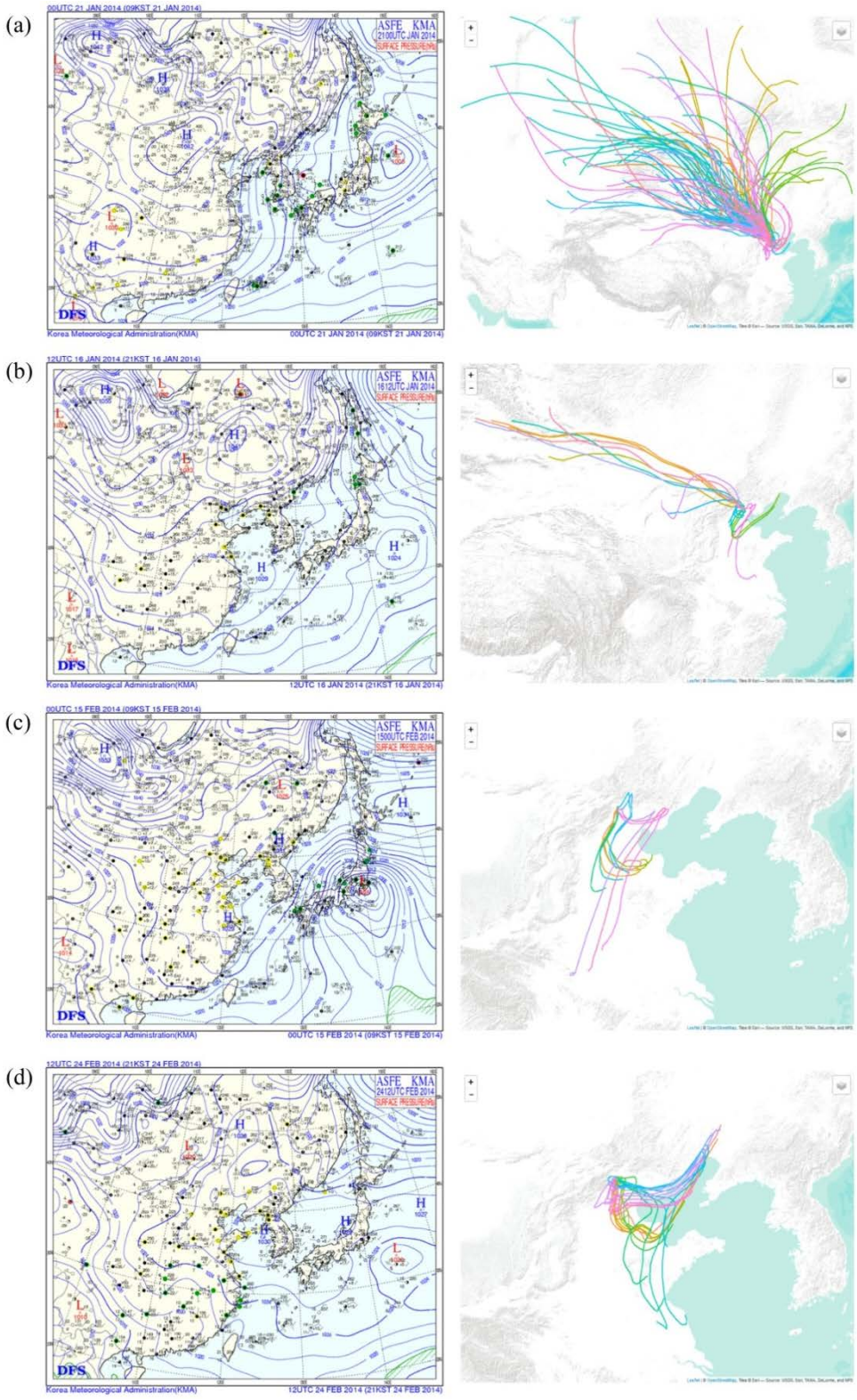
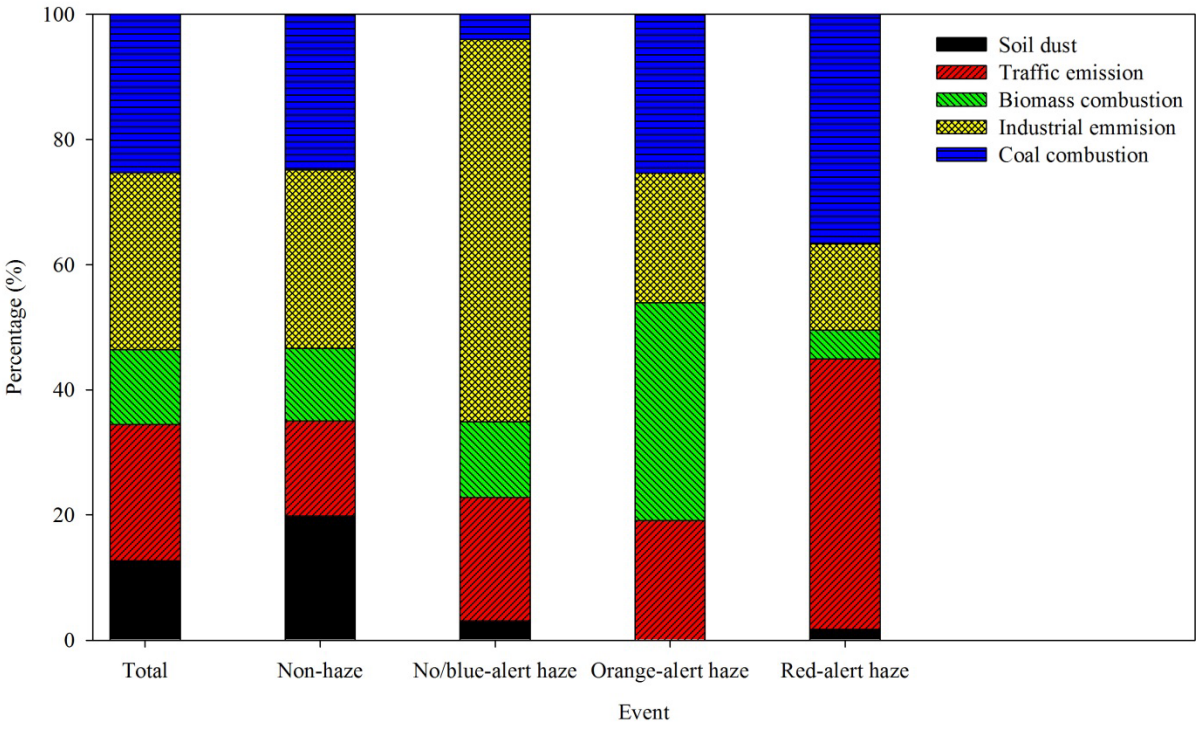


Figure 4. Surface weather maps and 72-h backward trajectories on days of (a) non-haze (57 days), (b) no/blue-alert haze (4 days), (c) orange-alert haze (3 days), and (d) red-alert haze (6 days). Trajectories were calculated twice a day at 18 and 06 UTC for non-haze days in (a) and every 6 hours at 12, 18, 24, and 06 UTC for haze days in (b), (c), and (d).



614

615 **Figure 5.** Comparison of source contributions (left to right) over the entire winter, during
616 non-haze events, and during no/blue-alert, orange-alert, and red-alert haze events.