Response to Referee Comment 2 (RC2) on "Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions" by H. Li et al.

This study combines in-situ measurements of PM1 composition in Beijing during the winters of 2014 and 2017 and the simulation results from a regional chemical transport model to investigate the impacts that the clean air actions in China have had on aerosol chemistry. The relative contributions of anthropogenic emissions, meteorological conditions, and regional transport to the changes in aerosol composition in Beijing are also investigated. This is an interesting work and provides a timely and relevant analysis of a current problem – how aerosol pollution in Beijing responded to the implementation of the Air Pollution Prevent and Control Policy. Overall, the manuscript is well written and fits well within ACP's aims and scope. However, the current version may require substantial revision before publication can be considered. A major shortcoming in this manuscript is that the Methods section is very much lacking of important technical details, for example on aerosol source contribution analysis and CMT model performance, thereby raises doubts about the credibility of the results. Moreover, there are some inconsistencies in the results and discussions which could cause concerns about the quality of the data, representativeness of the findings, or validity of the conclusions. Additionally, the figure legends and captions are often too brief to make the figures understandable.

We thank the reviewer for the positive feedback and helpful comments. In the revised manuscript, more technical details in the Method section have been added. In the following, we will answer the comments point by point.

Detailed comments:

Line 44-46, how much did air pollutants reduce between 2013 – 2017 in the Beijing area?

Emission changes of different air pollutants in Beijing with the implementation of the clean air actions was analyzed in details in Section 3.2.2 and Figure 6.

Section 2.2. is cursory and provides very little information on the organic aerosol source apportionment analysis. Details must be provided on how the PMF/ME-2 analysis of the ACSM data was performed, what data treatments were implemented, and how the solution conditions (eg number of factors, a value, fpeak) were selected and evaluated.

For the ME-2 analysis of the ACSM organic data, the mass spectra and error matrices were prepared based on the procedures given by Ulbrich et al. (2009) and Zhang et al. (2011). Detailed evaluations of different solutions were provided in the Supplement, including the factor time series, mass spectra, and diurnal patterns with different *a* values. Corresponding changes can be found in the revised manuscript and Supplement.

In Section 2.3. more information should be provided on the performance of the CMT model at simulating PM2.5 composition and how the modeling results compare to observations for 2014 and 2017 winters separately.

As the reviewer suggested, we added more information about the evaluation of the CMT model performance in Section 2.3 and the Supplement.

Section 2.5 lists three assumptions about aerosol properties in the ISORROPIA modeling. Several references are cited and claimed to support these assumptions for this study. But upon reading the references more closely, they don't seem so as the references either talked about aerosols from different locations or under different meteorological conditions, or simply did not provide direct evidence on aerosol physical states. In fact, given the wintry weather (very low RH and T) and intense local emissions in Beijing, it is hard to believe that internal mixing and single aqueous phase were the prevailing aerosol conditions relevant to this work.

When running the ISORROPIA model, it is assumed that aerosols are internally mixed and composed of a single aqueous phase. Previous study in Beijing during wintertime showed that ISORROPIA predictions with these assumptions were in good agreement with observations (Liu et al., 2017). Up to now, there are no observational data showing whether aerosols are in a metastable (only liquid) or stable (solid plus liquid) state in Beijing in winter (Song et al., 2018). At low RH (RH < 20% or 30%), aerosols are less likely to be in a completely liquid state (Fountoukis and Nenes, 2007; Guo et al., 2016, 2017). Therefore, periods with RH < 30% were excluded in this study and aerosol solutions were assumed to be metastable. Particle liquid-phase separations can occur between the inorganic and organic components. It remains unclear how the phase separations influence pH values. A recent laboratory study suggested that the pH value of the organic-rich fraction under phase separation is about 0.4 units higher than that for a fully mixed aqueous phase (Dallemagne et al., 2016; Song et al., 2018).

Line 168 – 171, there was no mentioning of NH3 and HNO3 measurements in 2.1., but it is mentioned here that the values of NH3+NH4 and NO3+HNO3 were input into the model. Where did the NH3 and HNO3 data come from?

In the revised manuscript, discussions were added about how the gas-phase NH_3 and HNO_3 were considered in this study. "The gaseous HNO_3 and NH_3 concentrations were not directly measured during our campaign. But long-term measurements in Beijing showed that gaseous NH_3 concentration correlated well with NO_x concentration in winter (Meng et al., 2011). Therefore, the empirical equation derived from Meng et al. (2011), NH_3 (ppb) = 0.34 × NO_x (ppb) + 0.63, was applied to estimate the gaseous NH_3 concentration. On average, the NH_3 concentration was approximated to be 14.0 μg m^{-3} during the winters of 2014 and 2017, consistent with previous observations jn the same season of Beijing (Meng et al., 2011; Zhao et al., 2016; Zhang et al., 2018). The total nitrate concentration, including both gaseous HNO_3 and particulate nitrate, varied from 0.2 to 75 μg m^{-3} for the sensitivity study."

Line 110, missing numbers after "0." What "a" values were used?

For the ME-2 analysis, an optimal solution of four factors with the *a* value of 0 was accepted.

Line 167 -168, what does "the transition in aerosol composition" mean in this sentence?

The transition in aerosol composition refers to the variations in nitrate and sulfate concentrations. During the winters of 2014-2017, the mass concentrations of both sulfate and nitrate decreased due to the implementation of the clean air actions. The reduction in sulfate concentration was higher than that in nitrate concentration. In this study, we investigated how the variations in nitrate and sulfate concentrations influence particle properties.

Line 186 – 188, the Xu et al. study was also conducted in Beijing in the winters of similar years, but the nitrate to sulfate ratios reported there were much lower than in this study. Normal measurement uncertainty could not explain such large discrepancies (more than a factor of two in difference). Was it due to measurement artifacts or does it suggest some issues with the representativeness of the measurement data? What's the implication for the validity of the conclusions presented in this paper?

The study by Xu et al. (2019b) performed aerosol measurements in Beijing from the mid of November to the mid of December in 2014 and 2016. In this work, field measurements were conducted in Beijing from 6 December to 27 February in the year of 2014 and from 11 December to 2 February in the year of 2017. For the same year of 2014, ambient observations were performed in different months in the study by Xu et al. (2019b) and in this work. Different emission intensities and different meteorological conditions influence the formation of particulate nitrate and sulfate in different months. In this work, one of the conclusions is that the ratio of nitrate/sulfate was higher in winter 2017 than in winter 2014 with the implementation of the clean air actions. The decrease in nitrate concentration was larger in the winter of 2017 than in the winter of 2014. This is consistent with the conclusions by Xu et al. (2019b).

Line 205 – 206, organics were higher than sulfate and nitrate and in both 2014 and 2017, so calling Beijing aerosol pollution being "sulfate-driven" or "nitrate-driven" does not seem logical.

The driving factors in this work refers to the species whose mass fractions increased with the increase of aerosol loadings, consistent with the discussions in previous studies (Wang et al., 2014, Li et al., 2017, 2018; Sun et al., 2018; Xu et al., 2019a). The driving factors favored the development of haze pollution and the increase of aerosol mass concentrations. While organics composed a high fraction of aerosols in both 2014 and 2017, the mass fraction of organics in aerosols decreased with the increase of aerosol loadings.

Line 259, for coal usage reduction in addition to quoting the absolute amount, it would be also interesting in knowing the relative amount of reduction.

The total coal usage for coal-fired boilers is around 20.4 million tons in Beijing in 2013. By the end of 2017, the coal use was reduced by more than 17 million tons in Beijing due to emission controls of coal-fired boilers. In other way, the coal usage in Beijing was reduced by ~83% for coal-fired boilers compared to 2013.

Figure 2, according to the diurnal profiles, HOA concentration in 2014 was 2-3 times lower than 2017. If HOA is representative of emissions from transportation, is this level of decrease consistent with the decrease in emissions according to emission inventory? Moreover, the decrease of BC concentration from 2014 to 2017 was between 30-40% but the reduction of total combustion POA (sum of CCOA, BBOA and HOA) was close to 70%. This would suggest some very large, probably unrealistic, changes in the combustion emission factors.

Compared with 2014, the HOA concentration in 2017 was reduced by around 50%. Consistently, emissions of primary organic carbon from transportation decreased by around 30% in Beijing from 2014 to 2017 according to the emission inventory. Compared to 2014, both BC concentration and POA concentration were reduced largely in 2017. This is not only caused by the changes in the combustion emission factors via the more advanced control technology but also contributed by the reduced usage of traditional fuels, i.e., coal and biomass, through the application of clean energy.

Line 289 – 292, the comparisons of PM1 concentrations between different air trajectory classes do not logically lead to a conclusion about how much Beijing aerosol was influenced by polluted air masses transported from surrounding areas. Beijing has local pollution sources which could cause high PM events as well. In fact, in the paragraph immediately beneath, the authors reported that CMT simulation indicates that regional transport contributes to only 30 -40% of PM2.5 in Beijing.

Back trajectory analysis shows the air masses paths as they move through time and space before they arrive at the receptor site. Different aerosol concentrations for different air masses indicate the influence of regional transport. For example, due to the high emissions of air pollutants and sever aerosol pollutions in the southern surrounding areas of Beijing, air masses transported from the south of Beijing usually showed higher PM_1 concentrations than the air masses from others regions. According to back trajectory analysis, Beijing was less influenced by polluted air masses from surrounding areas in 2017. This is consistent with the results of CMT model simulations, which showed that the lower $PM_{2.5}$ concentration from regional transport contributed around 40% to $PM_{2.5}$ reduction in Beijing in 2017. The results are not contradictory to the main conclusion that emission reductions in Beijing and its surrounding regions played a dominant role in air quality improvement during 2014-2017.

Section 3.2.4, 2nd paragraph, what are the rationales for using SO4/BC and NO3/BC ratios in the analysis? Sulfate is a secondary species with formation time scales usually much longer than the emission time scales of BC. So the physical meaning of SO4/BC ratio is unclear.

The absolute concentration of sulfate and nitrate in the atmosphere is not only controlled by atmospheric chemical reactions but also influenced by boundary layer developments. By using SO_4/BC and NO_3/BC in the analysis, we can see more clearly how the secondary formation of sulfate and nitrate varied compared to primary emissions.

Section 3.2.4, 2nd paragraph, nitate/(nitrate+NOx) is not a proper index for the oxidation ratio of nitrogen. Discussions related to NOR should be either removed or revised.

According to the ISORROPIA calculations in this study, the fraction of particulate nitrate in total nitrate was higher than 0.99 for the average winter conditions in both 2014 and 2017. Therefore, it is meaningful to use nitrate/(nitrate+NO_x) to evaluate the oxidation ratio of nitrogen without the consideration of gas-phase HNO_3.

For the discussions of the relationship between SOR and RH, it is important to point out that RH was measured locally at the sampling site but sulfate was mostly formed on a regional scale, ie, in air masses upwind of Beijing. Is it valid to assume that in-situ RH measurement data are representative of the RH conditions in the air masses where sulfate was formed?

The locally measured RH was largely influenced by the RH of the air masses transported from the upwind direction. For example, the RH in Beijing is usually low when the dry northwesterly/northeasterly air masses arrive. When Beijing is influenced by the humid southerly air masses, the RH in Beijing is high (An et al., 2019). Therefore, in-situ RH measurements are representative of the RH conditions in the air masses where sulfate was formed. Relationship between sulfate and the locally measured RH has been discussed a lot by previous studies (Zheng et al., 2015; Li et al., 2017; Fang et al., 2019).

Line 330 -331, does the higher SOR in 2017 than 2014 necessarily demonstrate "a higher sulfate production rate in 2017"? A relatively larger contribution from background air masses could also lead to higher SOR.

With the implementation of the clean air actions, SO_2 emissions were reduced in both Beijing and the surrounding regions. According to back trajectory analysis, Beijing was less influenced by polluted air masses from regional transport in 2017 and sulfate contributed a smaller fraction in the air masses transported from surrounding areas. Therefore, the higher SOR in 2017 than 2014 indicates the higher sulfate production rate in 2017.

Line 544- 545, this citation is incomplete

Updated.

Figures in the supplementary materials are fuzzy, need to use better resolution.

The fuzzy figures in the Supplement have been updated to better resolution.

Figure S6d, explain how to read the figure and the meanings of N-E, W-N, E-S, S-W?

The diurnal pattern in Figure S6d showed the diurnal variations in the contributions of different wind directions. The meanings of N-E, W-N, E-S, and S-W were already explained in the manuscript as "from north to east (N-E; $0^o \leq WD < 90^o$), east to south (E-S; $90^o \leq WD < 180^o$), south to west (S-W; $180^o \leq WD < 270^o$), and west to north (W-N; $270^o \leq WD \leq 360^o$)".

Figure S7, what do the color bars stand for?

The color bars indicate the variations of $PM_{2.5}$ concentration, which was labelled in the figure.

References

Fang, Y., Ye, C., Wang, J., Wu, Y., Hu, M., Lin, W., Xu, F., and Zhu, T.: RH and O3 concentration as two prerequisites for sulfate formation, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-284, in review, 2019.

Li, H., Zhang, Q., Zhang, Q., Chen, C., Wang, L., Wei, Z., Zhou, S., Parworth, C., Zheng, B., Canonaco, F., Prévôt, A. S. H., Chen, P., Zhang, H., Wallington, T. J., and He, K.: Wintertime aerosol chemistry and haze evolution in an extremely polluted city of the North China Plain: significant contribution from coal and biomass combustion, Atmos. Chem. Phys., 17, 4751-4768, https://doi.org/10.5194/acp-17-4751-2017, 2017.

Li, H., Zhang, Q., Zheng, B., Chen, C., Wu, N., Guo, H., Zhang, Y., Zheng, Y., Li, X., and He, K.: Nitrate-driven urban haze pollution during summertime over the North China Plain, Atmos. Chem. Phys., 18, 5293-5306, https://doi.org/10.5194/acp-18-5293-2018, 2018.

Sun, P., Nie, W., Chi, X., Xie, Y., Huang, X., Xu, Z., Qi, X., Xu, Z., Wang, L., Wang, T., Zhang, Q., and Ding, A.: Two years of online measurement of fine particulate nitrate in the western Yangtze River Delta: influences of thermodynamics and N2O5 hydrolysis, Atmos. Chem. Phys., 18, 17177-17190, https://doi.org/10.5194/acp-18-17177-2018, 2018.

Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhang, Q., Philip, S., and Xie, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models, Journal of Geophysical Research: Atmospheres, 119, 10,425-410,440, 10.1002/2013JD021426, 2014.

Xu, Q., Wang, S., Jiang, J., Bhattarai, N., Li, X., Chang, X., Qiu, X., Zheng, M., Hua, Y., and Hao, J.: Nitrate dominates the chemical composition of PM2.5 during haze event in Beijing, China, Sci Total Environ, 689, 1293-1303, https://doi.org/10.1016/j.scitotenv.2019.06.294, 2019a.

Xu, W., Sun, Y., Wang, Q., Zhao, J., Wang, J., Ge, X., Xie, C., Zhou, W., Du, W., Li, J., Fu, P., Wang, Z., Worsnop, D. R., and Coe, H.: Changes in Aerosol Chemistry From 2014 to 2016 in Winter in Beijing: Insights From High-Resolution Aerosol Mass Spectrometry, Journal of Geophysical Research: Atmospheres, 124, 1132-1147, 10.1029/2018JD029245, 2019b.

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, https://doi.org/10.5194/acp-15-2969-2015, 2015.