Response to Referee Comment 1 (RC1) on "Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions" by H. Li et al.

In past publications, the authors have reported on the effects of emission controls on China's air quality. This paper focuses on how those emission changes affect aerosol chemical composition. The authors present a comprehensive analysis involving measurements and models to assess the role of just emissions, apart from transport and meteorological differences. The results are interesting and the topic appropriate for this journal, however some details were missing and in many cases the analysis or description of processes was not of sufficient technical detail, such as the thermodynamic analysis. Also, strong conclusions are made with limited analysis to support them. For example, a major finding seems to be that these changes in emissions altered the aerosol formation mechanisms. It is stated in the Abstract and Conclusions that lower SO2 suppressed rapid sulfate formation through heterogeneous reactions. But it is not clear that this is really shown or tested in a quantitative way, instead it seems to be mostly speculation, based mainly on this hypotheses being consistent with the observations. Line 324 simply states: the results here imply that: : : Could not a chemical transport model, or maybe a simpler 0-D or 1D box model be run to further test this hypothesis? Overall, my recommendation is that the authors check closely if their reported findings are truly supported in the manuscript by quantitative analyses, and if only based on a consistency with expectations, that this clearly be stated. More detailed comments are provided below.

We would like to thank Rodney Weber for giving the constructive and helpful comments and suggestions, especially for the discussions on thermodynamic analysis. In the revised manuscript, more technical details about the thermodynamic analysis have been added according to the comments. One finding that the decrease in SO_2 emissions suppressed the rapid sulfate formation through heterogeneous reactions was speculated based on the ambient observations. We found that compared to the fast SO_2-to-sulfate formation starting from a RH threshold of ~50% in 2014, the promptly increased sulfate formation through heterogeneous reactions was observed to delay to a higher RH of 70% in 2017. Therefore, this is one hypothesis based on the consistency with ambient observations. We have clearly stated it in the Abstract, Sect. 3.2.4, and Conclusions in the manuscript.

In the following, we will answer the comments point by point.

Specific Comments:

Line 59-60; I would think atmospheric chemical reactions (secondary aerosol) and deposition would also be a major contributor to PM2.5 composition.

Agreed. We slightly modified the sentence to "The chemical composition of $PM_{2.5}$ is mainly affected by the following factors: precursor emissions, meteorological conditions, atmospheric chemical reactions, and regional transport and deposition".

Line 136 to 137, in giving the ambient data vs model comparison, state the integration time, ie 24 hr average data?

It has been clearly stated that the data are 24-hour averages.

ISORROPIA calculations: In this paper the model is run without considering nonvolatile cations. Maybe a few words should be added why this is ok, ie, it may be argued that for PM1 this is reasonable. As another example, the nitrate considered in the paper is all semivolatile nitrate (ie, NH4NO3), but it is possible that nonvolatile nitrate also exists in the ambient PM2.5 (eg, Ca(NO3)2). Thus if Ca2+ was considered in the thermodynamic calculations, it could affect predicted pH and NO3- concentrations. Most of this Ca2+ would likely be in the 1 to 2.5 um range, and since the comparison between PM1 and PM2.5 mass is reasonable, the authors could argue that it is not a large contribution. Also, I suggest the authors specifically note what RH range was used in the thermodynamic calculations, many of the assumptions, such as no separate organic/inorganic phases,

etc, may be less likely at lower RH. (say <40 to 50%). Line 231-232 notes that the observed RH was about 33 to 34% in the winter of 2017. This a very low RH to comfortably run ISORROPIA under the metastable assumption without some test on the reliability of the results.

Indeed, including nonvolatile cations in ISORROPIA calculations would influence the model results. But as the reviewer said, nonvolatile cations, i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}, mainly exists in the size range of 1.0 to 2.5 μm in particles and has a minor contribution to PM_1. Therefore, nonvolatile cations are not considered in pH calculation in this study. A previous study by Song et al. (2018) showed that including nonvolatile cations in ISORROPIA calculations did not significantly change the particle pH. Discussions about the effects of nonvolatile cations on pH calculations have been added in the manuscript "The effects of nonvolatile cations (i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}) are not considered in this study because the fraction of nonvolatile cations in PM_1 in Beijing is generally negligible compared to SO_4^{2-}, NO_3^-, and NH_4^+ (Sun et al., 2014). Although nonvolatile nitrate may exist in ambient particles as $Ca(NO_3)_2$ and $Mg(NO_3)_2$, Ca^{2+} and Mg^{2+} are mainly abundant at sizes above 1 μm (Zhao et al., 2017). In addition, the mixing state of PM_1 nonvolatile cations with SO_4^{2-}, NO_3^-, and NH_4^+ remains to be investigated (Guo et al., 2016, 2017). Previous studies showed that including the nonvolatile cations in ISORROPIA-II does not significantly affect the pH calculations unless the cations become important relative to anions (Guo et al., 2016; Song et al., 2018). The sensitivity test for Beijing winter conditions suggested that with nonvolatile cations, the predicted pH values increase by about 0.1 units."

We agree with the reviewer that RH ranges influence the liquid or solid phases of atmospheric aerosols. So far, there are no observational data showing whether aerosols are in a metastable or stable state in Beijing wintertime (Song et al., 2018). According to previous studies, at low RH, especially when 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, we exclude periods when RH < 30% in this study. After that, an average RH value of 50% is now used in the thermodynamic calculations assuming that aerosols were in metastable states. We also did a sensitivity study assuming that solid phases are present. For that case, over 88% of the data resulted in pH values approximating 7.6 with few variations, which is unrealistic. After the correction, the average pH values for year 2013, 2014, and 2017 are 4.5, 4.8, and 5.3, respectively. The results indicate a moderately acidic condition for aerosols in Beijing in winter, consistent with previous studies (Guo et al., 2017; Liu et al., 2017; Song et al., 2018). The correction did not change the trend of pH variation from 2013 to 2017 because the reduced sulfate concentration played a dominant role in pH variation. The corresponding explanations and corrections have been added and updated in the manuscript. "Up to now, there are no observational data showing whether aerosols are in a metastable or stable state in Beijing in winter (Song et al., 2018). According to previous studies, 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." "During 2013-2017, the average particle pH varied from 4.5 to 5.3, with a significant decrease in sulfate concentration, resulting in a more neutral atmospheric environment. The pH values here agree reasonably with previous ISORROPIA-II calculations, showing that fine particles are moderately acidic in northern China during wintertime (Guo et al., 2017; Liu et al., 2017; Song et al., 2018)."

Figures in the manuscript showing the results of thermodynamic analysis have also been updated:
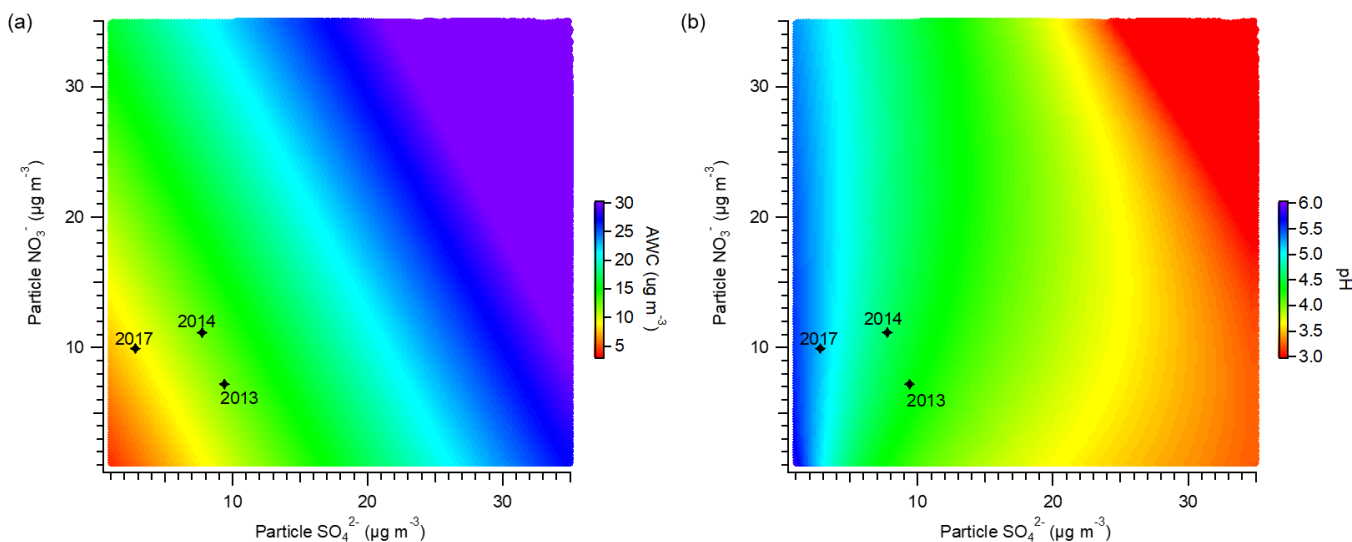
Figure 9. Sensitivity of (a) AWC and (b) particle pH to the mass concentrations of particulate sulfate and nitrate. The stars indicate the average winter conditions for the years 2013, 2014, and 2017.
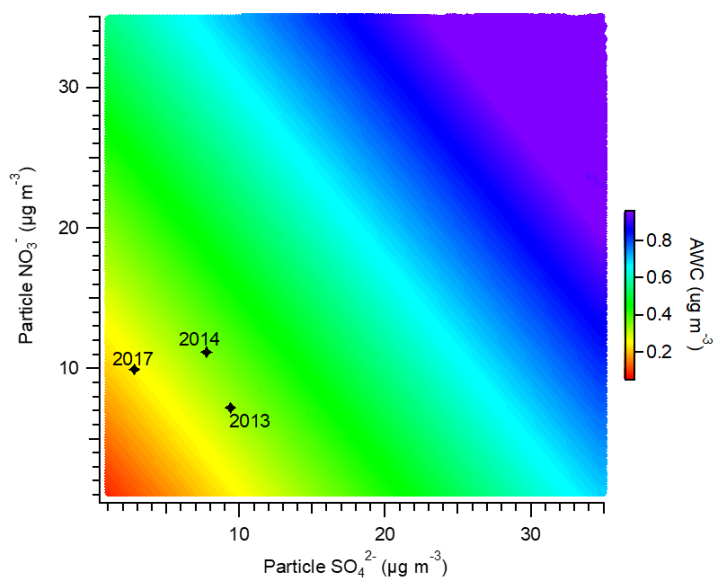

Figure 10. Sensitivity of the ammonium partitioning ratio to the mass concentrations of particulate sulfate and nitrate. The stars indicate the average winter conditions for the years 2013, 2014, and 2017.

In the experimental section, there was no discussion of measurement of HNO3 or NH3 (gas species), yet ISORROPIA was run such that these data are needed, ie, run in forward mode. More information is needed in the paper on how the model was run without these critical gas phase species.

To investigate how the variations in particulate nitrate and sulfate concentrations affect aerosol properties, this study used ISORROPIA-II to generate the contour plots in Fig. 9 and Fig. 10. ISORROPIA-II was run in the forward mode, which calculates the equilibrium partitioning with the total concentration of both gas and particle phase species. Previous study shows that the forward mode is less sensitive to measurement error than the reverse mode (Hennigan et al., 2015). To run the model, a selected sulfate concentration with the average temperature, RH, and total ammonia concentration ($NH_3 + NH_4^+$) during the winters of 2014 and 2017 was input to ISORROPIA-II, where the total nitrate concentration ($HNO_3 + NO_3^-$) was left as the free variable. The gaseous HNO_3 and NH_3 concentrations were not directly measured in this work. To estimate the NH_3 concentration, an empirical equation derived based on long-term measurements in winter in Beijing was applied, NH_3 (ppb) = 0.34 × NO_x (ppb) + 0.63 (Meng et al., 2011). On average, the NH_3 concentration was

estimated to be around 14.0 μg m^{-3} during the winters of 2014 and 2017 in Beijing, consistent with previous observations in the same season (Meng et al., 2011; Zhao et al., 2016; Zhang et al., 2018). For gaseous HNO$_3$, the total NO$_3^-$ concentration (HNO$_3$+aerosol NO$_3^-$) varying from 0.2 to 75 μg m^{-3} was used as the input.

More discussions about the consideration of gaseous HNO$_3$ and NH$_3$ concentrations have been added in the manuscript as follows: "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 175 or in Table 1 title state this is observational data (not model).

It has been clearly stated in the title of Table 1.

Line 258, what does Until 2017 mean? These changes were completed by 2017?

It means that these changes have been completed by the end of 2017. To make it more clearly, we changed "Until 2017" to "By the end of 2017".

Line 311, does not tell the complete story. There are publications, see below, that show the predictions of Cheng et al. 2016 and Wang et al, 2016 are likely not correct due to their incorrect calculation of fine particle pH and that this proposed heterogeneous chemistry is highly sensitive to pH. This counter argument should also be noted here in this paper for completeness.

Liu, M., Y. Song, T. Zhoh, Z. Xu, C. Yan, M. Zheng, Z. Wu, M. Hu, Y. Wu, and T. Zhu (2017), Fine Particle pH during Severe Haze Episodes in Northern China, Geophys. Res. Lett., 10.1002/2017GL073210.

Guo, H., R. J. Weber, and A. Nenes (2017), High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Sci. Reports, 7(12109), DOI:10.1038/s41598-41017-11704-41590.

Song, S., M. Gao, W. Xu, J. Shao, G. Shi, S. Wang, Y. Wang, Y. Sun, and M. B. McElroy (2018), Fine particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atm. Chem. Phys., 18, 7423-7438.

Agreed. The corresponding argument has been noted in the manuscript as follows: "Recently, studies have found that SO$_2$ oxidation by NO$_2$ in aerosol water with near neutral aerosol acidity, which is usually ignored in current model simulations, plays an important role in the persistent formation of sulfate during haze events in northern China (B. Zheng et al., 2015; Cheng et al., 2016; Wang et al., 2016). Others pointed out that regardless of the high NH$_3$ levels, aerosols are always moderately acidic in northern China, and there are probably other alternative formation pathways contributing to fast sulfate production in haze pollution (Guo et al., 2017b; Liu et al., 2017; Song et al., 2018)."

Line 318-319, define SOR and NOR (ie, what does the acronym stand for?)

The SOR and NOR stand for sulfur oxidation ratio and nitrogen oxidation ratio, respectively. This has been clearly clarified in the manuscript as "The sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) were further estimated as the molar ratio of sulfate to the sum of sulfate and SO$_2$ and the molar ratio of nitrate to the sum of nitrate and NO$_x$, respectively, to quantify the degree of SO$_2$ and NO$_x$ oxidations (Zheng et al., 2015; Li et al., 2016)."

Lines 339 to 344. Although this discussion tends to follow the Seinfeld and Pandis discussion of sulfate/nitrate/ammonium interactions, it is largely based on weak intuitive arguments and not a rigorous thermodynamic discussion. It is suggested that these types of statements be avoided. Below are possible other ways to discuss the interplay between sulfate, nitrate and ammonium and gas species, nitric acid and ammonia:

Change: Particulate nitrate in PM2.5 is mainly formed through the neutralization of HNO3 with NH3 to something like: Semivolatile PM2.5 particulate nitrate is formed through the partitioning of HNO3 to the particle phase, which is more favored at higher aerosol pH. pH is affected by gas phase NH3 concentrations, where higher NH3 generally leads to higher pH and so possibly more particulate nitrate.

Thanks for the suggestions. We have revised the text accordingly.

Change: Nitrate formation was also affected by the competition for available NH3 between sulfate and nitrate. In the atmosphere, NH3 prefers to react first with H2SO4 to form ammonium sulfate due its stability. To: Because sulfate is nonvolatile, when it is a significant fraction of the aerosol mass it has a dominant influence on aerosol pH, making the aerosol acidic (low pH). In contrast ammonium and nitrate are semivolatile and so their particle-phase concentrations depend on the meteorological conditions (T, RH) their corresponding gas phase concentrations, (NH3 and HNO3 respectively) and aerosol pH. For example, at high sulfate and moderate NH3 concentrations the aerosol can be too acidic for partitioning of HNO3, but at higher NH3, or if sulfate concentrations drop sufficiently (or RH increases), particle pH will increase and can reach a point at which HNO3 partitioning can occur and nitrate aerosol formed. Lower T also favors partitioning to the particle phase through Henry's law constants.

Thanks for the suggestions. We have modified the text accordingly.

As for the last line, when RH>60% maybe an additional explanation for the trend in Fig8d is that as RH increases liquid water levels increase resulting in higher pH, which allows more nitrate to partition to the aerosol through a feedback loop, as is discussed later in the paper. That is, the increase in NOR may be due to more than just heterogeneous nitrate production.

Agreed. This additional explanation has been added as "In addition, as RH increases, the AWC increases accordingly, resulting in higher aerosol pH. This allows more semivolatile nitrate to partition to the particle phase through a feedback loop, thus favoring the formation of particulate nitrate."

Line 366-369, In Fig S9a provide a reference for the calculation of epsilon(NO3-). This pH of 3 at which the sensitivity of epsilon(NO3-) changes, as found in this work, was discussed in detail by Guo et al., ACP 2018, which should be cited.

A reference for the calculation of $\in (NO_3^-)$ has been added. The reference of Guo et al., ACP 2018, has been cited.

Finally, there are a number of studies reporting pH in Beijing over different periods. Some of these did analysis to test the thermodynamic model predictions, which was not done here. A summary of these papers and comparison to pH reported in this paper is warranted to support this analysis.

According to the comments above regarding the thermodynamic analysis, summarization of previous studies reporting pH in Beijing and comparison with results in this study have been included in the manuscript. In addition, more information were added: "Previous studies showed that including the nonvolatile cations in ISORROPIA-II does not significantly affect the pH calculations unless the cations become important relative to anions (Guo et al., 2016; Song et al., 2018). The sensitivity test for Beijing winter conditions suggested that with nonvolatile cations, the predicted pH values increase by about 0.1 units."

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