Response to Short Comment 1 (SC1) on "Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions" by H. Li et al.

(a) Overview The authors used fine particle data collected in Beijing during the winters of 2014 and 2017 to understand changes in the chemical composition of the PM over a period when particle mass decreased significantly. The results here are consistent with past data, showing a large decrease in PM mass, but also revealing that this is largely because of decreases in sulfate, organics, and unidentified components, as a result of decreasing local and regional emissions. The authors find that meteorology also contributed to lower PM concentrations in 2017 but that this was a smaller factor.

This is an interesting paper with a number of complementary components. On the other hand, there are a number of issues that need to be addressed, as described below. The thermodynamic modeling seems problematic and needs more clarification and information.

We would like to thank Cort Anastasio for giving the constructive and helpful comments and suggestions. In the following, we will answer the comments point by point.

(b) Major Points 1a. Figure 2 and lines 190 – 191: The text states that "All SIA species showed similar diel trends in the two winters: : :". For some species this is true, but for many of the species, the diel variability is much lower in 2017 than in 2014, suggesting that while more local sources dominated in 2014, regional sources are more important in 2017. Take CCOA as an example: in 2014, the concentration varied by a factor of 3, while in 2017 the variation was probably only a factor of 1.5 or less. Can the change in diel variability be used as an indicator of local vs. regional pollution?

SIA species refer to sulfate, nitrate, and ammonium. For the SIA species, they showed similar diel trends in the winters of 2014 and 2017. For many of the other species, especially the primary species, their diel variability was much lower in 2017 than in 2014. However, the changes in the diel variability of these primary species can not be easily used as an indicator of local vs. regional pollution. For example, previous studies reported that coal combustion sources in Beijing were mainly attributed to regional transport from surrounding areas (Wang et al., 2011; Shang et al., 2018). Therefore, we could not rely on the diel variability of CCOA to provide information of local vs. regional pollution.

1b. Of course boundary layer height is a major influence on concentrations as well. I suggest you add a plot of CO as a tracer for BL height. Does plotting the ratio of PM component/CO help disentangle chemistry and BL height? These might be useful supplemental plots.

The ambient variations of PM components are not only controlled by atmospheric chemical reactions but are also influenced by boundary layer developments. According to the comment, we analyzed the CO-scaled concentrations for PM components to eliminate the influence of different dilution/mixing conditions. The corresponding diurnal plots are shown below. By plotting the ratio of PM component/CO, we can more clearly see the photochemical production of sulfate, nitrate, ammonium, and OOA during daytime. These diurnal plots are included in the supplementary information as Fig. S15.
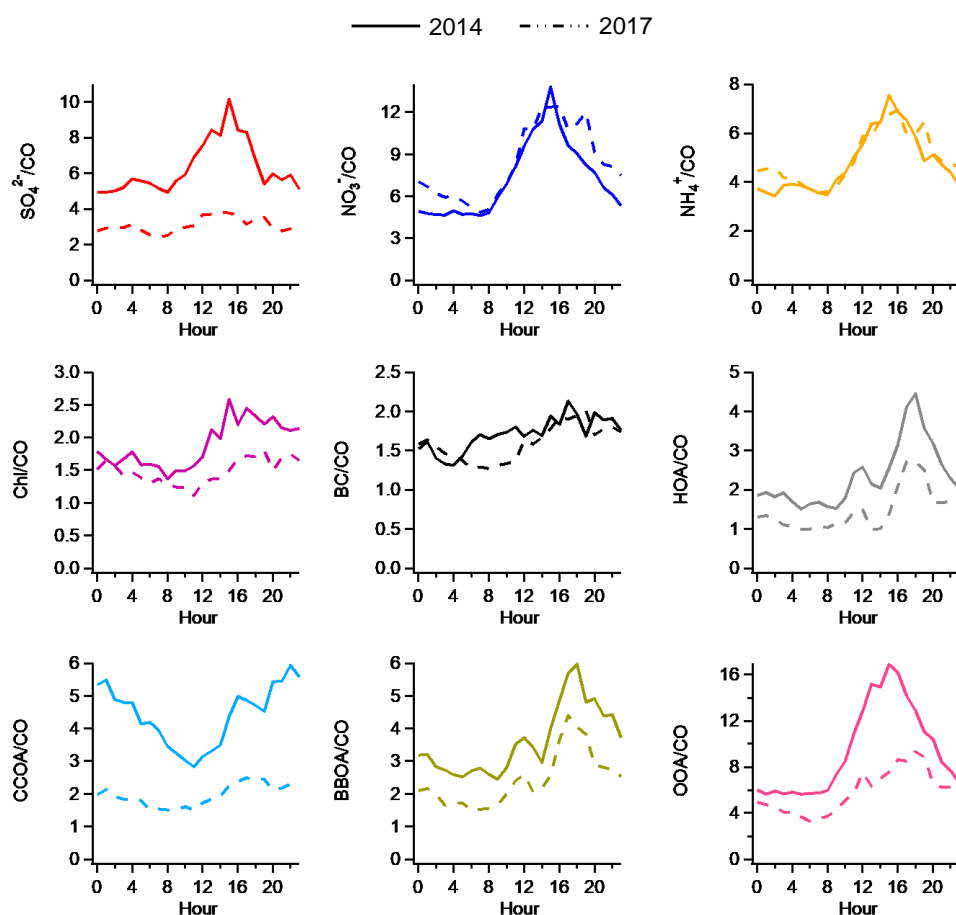
Figure S15. Average diurnal cycles of CO-scaled aerosol species in the winter of 2014 (solid line) and winter of 2017 (dashed line).

2. Figure 8 and its corresponding text. (i) Why normalize panels (a) and (b) to BC concentrations? Since both the numerator and denominator are changing between 2014 and 2017, the ratio seems less effective as a normalizing factor. What do the plots look like if sulfate and nitrate are not normalized by BC? (ii) The data are very noisy and so the authors have chosen to plot the median values (as the solid circles). But what does it look like if the mean and standard deviation are plotted instead? Are there any significant differences between RH values for a given year? If the authors want to stay with median, they should at least show some interquartile ranges or other measures of variability about the median. (iii) Line 323: ": : :the starting point of SOR growth was clearly delayed in 2017: : :". Given the spread in the data, this is speculative since the median has no associated uncertainty or variability. Can this difference be tested statistically? (iv) Lines 330 – 335. The authors explain that the higher sulfate / (sulfate + SO2) ratio (i.e., SOR) in 2017 at low RH results from less of an oxidant limitation. But isn't an alternative explanation that a higher fraction of the sulfur pollution in Beijing is from regional transport, which would have a higher SOR since it is more aged? (v) The nitrate / (nitrate + NO2) ratio (i.e., NOR) discussion in lines 339 – 344 seems to be missing a few points. First, NOR is a poor measure for the extent of NOx oxidation since it considers only particulate nitrate and not gas-phase HNO3. Under acidic particle conditions (as seems typical in 2014), most N(V) will be gas-phase HNO3, a result of sulfate acidity driving out the particle nitrate. But this is not accounted for if NOR is calculated only with particulate nitrate, as is done here. Running the e-AIM thermodynamic model on the average 2014 data shows that the gas-phase HNO3 concentration is over an order of magnitude higher than particulate nitrate. Thus N(V) / NOx + N(V), with both phases considered for N(V), would be a better measure of NOx oxidation than NOR. ISOROPPIA could be run to examine HNO3(g) in the two years. (vi) As a consideration for future work, it would be enormously helpful to have gas-phase measurements of NH3 and/or HNO3 to constrain the modeled aerosol pH.

(i) BC is an aerosol species coming from only primary emissions and its variations well reflect the influence of atmospheric mixing conditions. The ratio of sulfate and nitrate to BC can better represent the contributions from chemical reactions. Plots not normalized by BC are shown below.
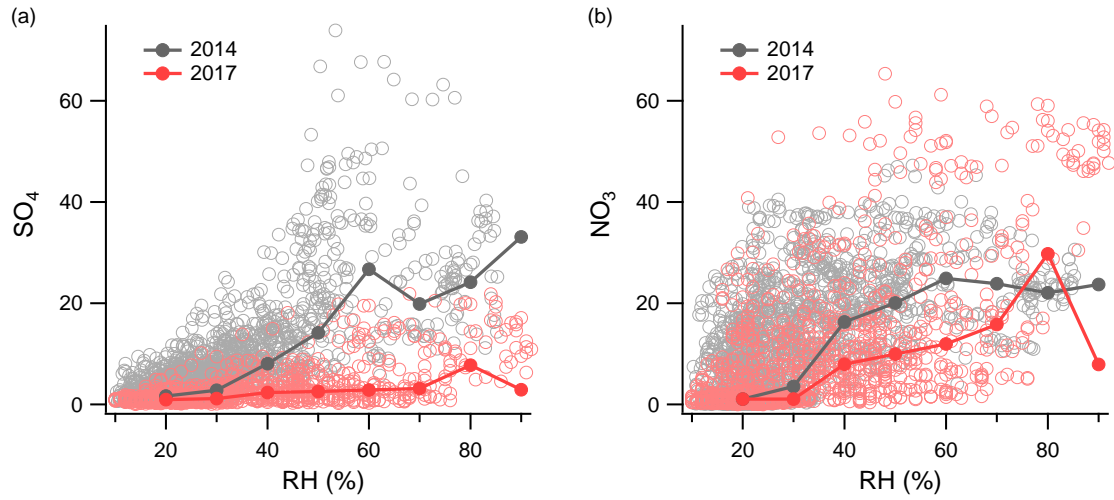
(ii) Figures with the mean and standard deviations are displayed below. They show no significant differences from the results with median values. The use of median values can to some extent avoid the bias by the odd values.
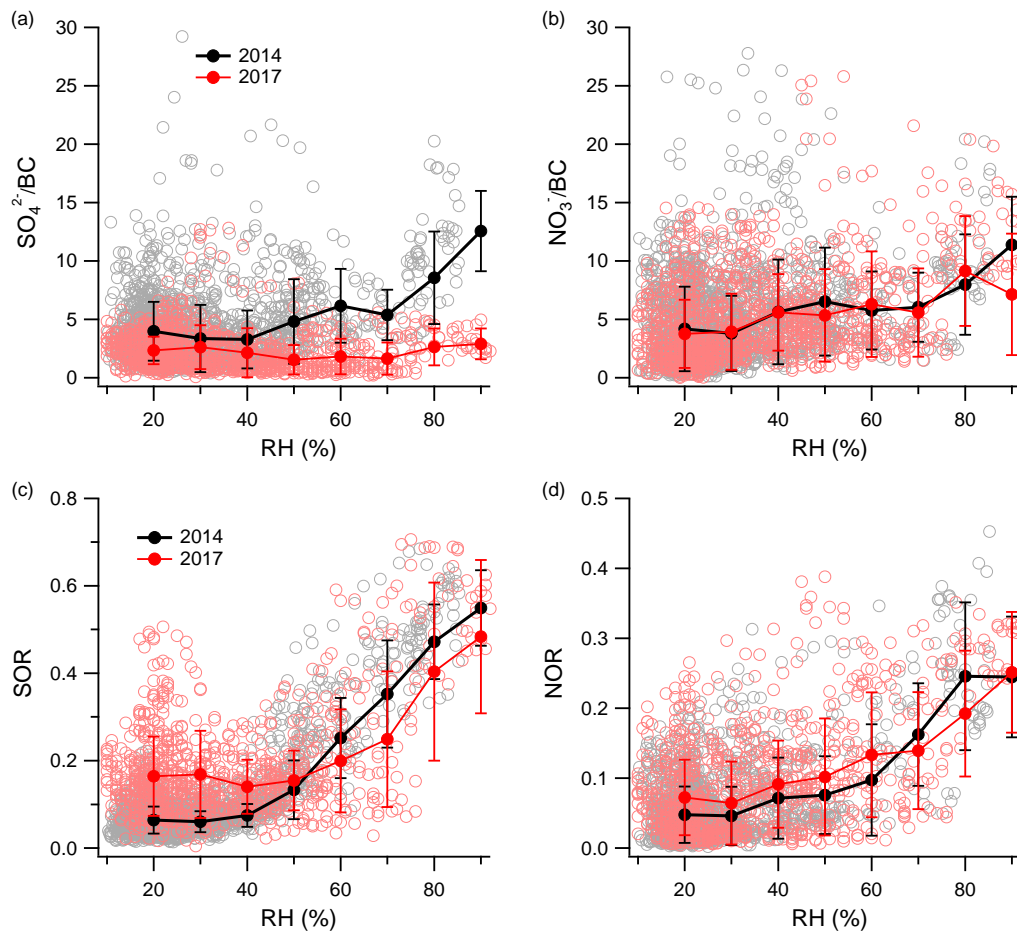
(iii) In this study, there were around 3-month and 2-month hourly data points for the winters of 2014 and 2017, respectively. To make the comparison between 2014 and 2017 more visible, we checked the mean and median

values. Both of them indicated that compared to the winter of 2014, the starting point of SOR growth with RH was delayed in the winter of 2017.

(iv) With the implementation of the clean air actions, SO_2 emissions were reduced in both Beijing and the surrounding regions. Compared to 2014, Beijing was less influenced by polluted air masses from regional transport, which has been analyzed in detail in Sect. 3.2.3. Therefore, the increase of SOR in 2017 at lower RH is more likely to be caused by the weakened oxidant limitation on SO_2 oxidations.

(v) 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, the calculation of NOR without the consideration of gas-phase HNO_3 has no significant influence on the discussion of NO_x oxidation.

(vi) We agree that the gas-phase measurements of NH_3 and HNO_3 are important for the calculation of aerosol pH. As we stated in the response to Rodney Weber, gas-phase NH_3 and HNO_3 were considered in the ISORROPIA calculations in this work.

3. Figure 9 and its corresponding text. (i) This figure indicates that the aerosol pH in 2014 was approximately 5, but this is inconsistent with the average composition indicated in Table 1. Using the averages for 2014 in Table 1, assuming protons make up the missing positive charge (which I assume was also done in ISORROPIA) and using a relative humidity of 60% in the e-AIM model results in a pH of -0.04 assuming a proton activity coefficient of 1; the pH is -0.7 if the e-AIM activity coefficient (4.22) is used. These results were done allowing solids to form, but it shouldn't change significantly if solids were not allowed to form. While the pH undoubtedly varies between samples, it is hard to believe the typical pH is near 5 given the ion imbalance in the data. (ii) Is the range of pH values given in line 361 (pH 5.0 to 6.2) from their work? Why is it for 2013 – 2017, rather than just the two winters of this study? It's not clear that the authors did much with the ISORROPIA data: why not report ALW and pH for every sample? This would be very useful information. (ii) The 2017 average data in Table 1 has a net positive charge, requiring a nonsensical negative concentration for protons that is of similar magnitude (though smaller) than the proton concentration from the 2014 data. This prevents use of a thermodynamic model and suggests that there are other charged species, likely organics, which are affecting the ion balance and the pH calculation. This should be discussed. Were the authors able to calculate ALW and pH values for the 2017 data? (iii) Under the acidic conditions I calculated for 2014, the value of NO3- / (HNO3 + NO3-) is very small, in contrast to the values described in the manuscript. (v) Similarly, I calculate a NH4+/NHx ratio near unity in 2014, in contrast to the small values reported in the text.

(i) According to ISORROPIA calculations, the average pH was around 4.8 in the winter of 2014, consistent with the results from previous studies. Many researches have shown that aerosols are moderately acidic in Beijing during wintertime (Guo et al., 2017; Liu et al., 2017; Song et al., 2018). In this study, the ISORROPIA was run in the forward mode. In addition to aerosol chemical compositions, gas-phase NH_3 and HNO_3 were also input into the model. Since only conditions with RH > 30% were considered, aerosols were assumed to be in a metastable state. Details about the ISORROPIA calculations were provided in the revised manuscript. A few studies have demonstrated that ion balance and equivalent ratios can not be used to predict the acidity of particles, especially under ammonia-rich conditions (Hennigan et al., 2015; Guo et al., 2016; Song et al., 2018). Song et al. (2018) showed that pH values calculated using the forward mode of thermodynamic models are not sensitive to the ion balance.

(ii) The pH values reported in the manuscript were calculated by this study. It has already been stated in the manuscript that "Data for the winter of 2013 were acquired from Sun et al. (2016)." While the ALW and pH were calculated for almost every sample, we did not report them in this study. The research focus of section 3.3 is to investigate how the clean air actions influence particle properties in different years.

(ii) As we stated above, the ion balance is not a good criteria to evaluate particle acidity, especially under ammonia-rich conditions. In addition to aerosol chemical compositions, gas-phase NH_3 and HNO_3 were also input into the thermodynamic model to calculate the pH values.

(iii) For the winter conditions of 2014, the fraction of particulate nitrate in total nitrate was higher than 0.99 according to ISORROPIA calculations. This is consistent with the results of Guo et al. (2018), which showed that the fraction of particulate nitrate in total nitrate was approaching 1 under Beijing winter conditions when aerosol pH was above 3.

(v) A NH_4^+/NH_x ratio near unity means that almost all NH_x remains in the particle phase, which is not possible in the winter of Beijing in 2014. Previous observations showed abundant existence of gas-phase NH_3 in urban Beijing during wintertime (Meng et al., 2011; Zhao et al., 2016). The ISORROPIA predictions by Guo et al. (2018) demonstrated that with the gas-phase NH_3 concentration above 5 $\mu g \ m^{-3}$, NH_4^+/NH_x ratio stays lower than 0.4.

(c) Minor Points 1. Throughout the manuscript, it would be much better (and more consistent with the other inorganic nomenclature in the paper) to use "Cl–" as the abbreviation for chloride rather than "Chl".

Changed.

2. lines 183-184: This sentence is unclear. Clearer wording would be "The decreases in particulate nitrate and ammonium during this period were 1.3 and 1.5 g m–3, respectively."

Changed.

3. Figure 1. The second line of the figure caption is unclear. These are not "rates", but rather decreases in concentrations, yes? Also, three significant figures in the decreases seems one too many.

The second sentence in the caption of Figure 1 were changed to "The decreases in the mass concentrations of different components from 2014 to 2017 are as follows".

4. line 188: It is odd that the Xu nitrate/sulfate ratios are approximately half of the values in the current work. Why this discrepancy?

The measurements in winter 2014 in this study were conducted from the start of December to the end of February while those by Xu et al. (2019) were from the mid of November to the mid of December. Different emission intensities and different meteorological conditions influence the formation of particulate nitrate and sulfate in different months.

5. lines 203-204: Sulfate is a minor fraction of haze in 2014 as well as 2017, so this statement isn't very useful. It would be better to indicate the sulfate contributions to each of the pollution classifications in 2017.

In the winter of 2014, the fraction of sulfate in total aerosol was more than 10% for all pollution levels. Therefore, it is not a minor fraction. Compared to 2014, sulfate comprised a smaller fraction of haze development in 2017. This has been stated in the revised manuscript.

6. lines 204–205: This description of nitrate contribution is for 2017?

Yes. This has been clearly stated in the revised manuscript.

7. line 208: State the 2014 and 2017 OA concentrations along with the overall decline.

The OA concentrations in the winters of 2014 and 2017 have been stated in the revised manuscript.

8. line 209: "The contribution from HOA was 2.6 g m–3: : :". This is not as clear as it should be: better to state something like "HOA decreased by 2.6 g m–3: : :".

The sentence has been changed to "The decrease in the mass concentration of HOA was 2.6 $\mu g \ m^{-3}$".

9. lines 240 – 241: It is not clear what cases A, B, C, and D refer to. Are these panels of Fig. S7?

The explanations of cases A, B, C, and D was provided in the experimental method, section 2.3.

10. lines 258-259: This is unclear. Should "Until 2017: : :" be "By 2017: : :"?

Changed.

11. line 298: The 57.9% is not a "rate" and likely has one too many significant figure.

It has been changed to "a decrease of 57.9% in its mass concentration".

(d) Recommendation I recommend that the paper be accepted after major revisions to address the points above.

References

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