

***Interactive comment on***  
**“Sulfate-nitrate-ammonium aerosols over China:  
response to 2000–2015 emission changes of  
sulfur dioxide, nitrogen oxides, and ammonia” by  
Y. Wang et al.**

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We thank the reviewer for his/her careful reading and thoughtful and constructive comments to improve the analysis and writing of the manuscript. The page and line numbers refer to those in the tracking-change version of the revised manuscript.

General comments: 1. The model evaluation is based on very limited data, and it is hard to determine the validity of the conclusion that model performance is good. The model evaluation is generally presented by comparing observed and modeled

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data averaged over long time periods which can obscure model performance issues. I understand that limited data exist to evaluate the model, but the evaluation is based on seasonal or monthly average comparisons even in situations where weekly average observations are available.

Response: We changed the model-observation comparison at Miyun and Beibei sites from monthly averages to weekly averages. Please refer to the new Figure 6 and the revised discussion in the revised manuscript (pg 14, line 296-312). The conclusion of the model's performance still holds after using the weekly average for comparison.

2. The conclusion that ammonia emissions are over-estimated seems to draw heavily on the finding that model performance for nitrate can be improved by adjusting NH<sub>3</sub> emissions. While ammonia emissions may be over-estimated as the authors indicate, I do not see how a clear understanding of model performance issues for nitrate can be developed based on the limited ambient data and to what degree these issues might be attributed to errors in ammonia emissions.

Response: The reason why we stated ammonia emissions were over-estimated in China is because (1) that's the most possible explanation to correct for the overestimation of nitrate in the model; and (2) a most recent bottom-up inventory of NH<sub>3</sub> in China (Huang et al., GBC, 2012) reported about 30% lower emissions than what we used in the model. Much of our efforts in the manuscript were to elaborate the first reason, including the design of the 2006A case in which NH<sub>3</sub> emissions were reduced by 30%, leading to a large correction of the standard model's overestimation of nitrate. As the reviewer correctly pointed out, this is not direct evidence to support that NH<sub>3</sub> emissions are over-estimated in China, given that we relied on limited observations for model evaluation and that the over-estimate of nitrate is a common modeling issue not only for China but also for the US (Park et al., 2004 and 2006; Heald et al, 2012; Zhang, L. et al., 2012; Kim et al., 2006; Fairlie et al., 2010). We have revised the affirmative statement in the abstract on the overestimation of NH<sub>3</sub> emissions to "the lack of sufficient knowledge on the past and present emissions levels of NH<sub>3</sub> in China" and

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added a brief discussion on the NH<sub>3</sub> emission uncertainties in Section 3 (pg 16, line 363-374).

3. The discussion of inorganic aerosol thermodynamics is highly simplified in this study. The authors almost exclusively refer to solid phase ammonium salts and do not mention the temperature or relative humidity conditions in the study areas. For many atmospheric conditions, the inorganic particle components will exist as separate ions in an aqueous solution rather than as crystalline salts. I understand that a detailed discussion of the actual processes at play could complicate and potentially distract from the discussion. However, improvements could be made in certain areas (e.g., where the authors indicate that decreases in sulfate can “make additional nitrate”).

Response: The reviewer’s point is well taken. We have expanded the discussion of the inorganic aerosol thermodynamics in the introduction (pg 3, line 47-57), the model description section (pg 7, line 147-157), and the result section (Section 5.2, pg 24, line 555 to 566). Please refer to the revised manuscript.

Specific comments: 1.p. 24245, lines 10-12: Transition-metal catalyzed oxidation of sulfur oxides in clouds should also be mentioned

Response: We have mentioned this pathway in the introduction, and provided a more detailed description on the SNA formation mechanism (pg 3, line 47-57). Please refer to the revised manuscript.

2.p. 24245, line 13: “NO<sub>x</sub>” should be “NO<sub>2</sub>”

Response: Corrected.

3.p. 24247, line 19: The aerosol thermodynamics module used is quite old and does not consider the impact of crustal elements that could be important when dust storms impact aerosol concentrations. Why not use a more recent version of GEOS-Chem with ISORROPIA II?

Response: The aerosol thermodynamic equilibrium module used in new versions of

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GEOS-Chem is ISORROPIA  $\hat{E}$ , which considers a more complex aerosol system including other ions such as  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $Cl^-$  (Fountoukis and Nenes, 2007). But we found that ISORROPIA  $\hat{E}$  produces more nitrate than RPMARES does and this made the model performance for nitrate even worse in China. Recent evaluation of the model's performance on SNA simulation also found large biases of nitrate simulation using ISORROPIA  $\hat{E}$  (Heald et al., 2012, ACP; Pye et al., 2009, JGR). That's why we did not use the more recent version of GEOS-Chem. We've clarified this point in the revised manuscript (Section 2, pg 7, line 147-157)

4. p. 24249, line 14, "poor  $NH_3$  conditions": I know what you are trying to say here, but please rephrase this for clarity.

Response: We have changed the 'poor  $NH_3$  conditions' to ' $NH_3$ -limited conditions'.

5. p. 24250, line 4: Please provide more details on the measurement methods. Later in the manuscript, there is mention of the challenges in measuring nitrate, so it would be helpful to mention the measurement techniques that were used.

Response: We have added one paragraph at the end of section 2.2 to describe the measurement methods. Please to the revised manuscript (pg 11, line 243 – 253).

6. p. 24251, line 6: Based on the limited data and disagreements between observations and predictions in Figure 4, one should not conclude that the model has "excellent ability" in representing the spatial heterogeneity.

Response: We agree. We've changed "excellent ability" to "has some success".

7.p. 24251, line 15: What filter material was used to collect aerosols for the nitrate measurements? The degree of volatilization of nitrate from filters is highly dependent on filter material.

Response: The filter material is Teflon and nylon. As the filter material should not absorb acid and alkali gases, Teflon filters are preferred. However,  $NH_4NO_3$  can dissociate on the Teflon filter, followed by the escape of gaseous  $NH_3$  and  $HNO_3$  which

can cause negative biases in measurement. At the two sites, to reduce the negative bias of NH<sub>4</sub>NO<sub>3</sub> sampling, the post-posed nylon filter is applied which can absorb the volatilized NH<sub>4</sub>NO<sub>3</sub> from the pre-posed Teflon filter. We have clarified the filter material issue in section 2.2 (pg 11, line 243 – 253).

8.p. 24251 and p. 24252, Figure 5 and 6: The observations at MY and BB are based on weekly averages, right? Why not evaluate model predictions at this time resolution rather than averaging to the seasonal and monthly time scales?

Response: Yes, we have weekly averages of SNA observations at MY and BB sites. We have now used the weekly averages at the two sites for model evaluation. Please refer to the new figure 6 and the revised section 3 in the revised manuscript (pg 14, line 296-312).

9. p. 24256, lines 7-9: Why would the presence of dust be expected to lower nitrate? Nitric acid can react with calcium carbonate in dust to form calcium nitrate, and so the presence of dust could increase nitrate. This pathway could be particularly important in an ammonia-limited environment.

Response: We agree with the reviewer that the presence of dust may increase nitrate, as also suggested by Zhang et al. (1999, JAM) and Fairlie et al. (2010, ACP), but we expect most of the nitrate formed by this pathway to exist in the coarse mode. In the manuscript, we focused on nitrate in the fine mode (PM<sub>2.5</sub>) both in the observations and model outputs. Furthermore, nitric acid uptake on coarse mode dust can also react with NO to produce NO<sub>2</sub>:  $\text{HNO}_3 + \text{NO} \rightarrow \text{HONO} + \text{NO}_2$ , which can lead to lower HNO<sub>3</sub> concentrations (Mochida and Finlayson-Pitts, JPC, 2000) and thus lower fine mode nitrate concentration in high dust loading regions. In any case, these pathways involving dust cannot explain the modelled lower SNA concentrations over NC in spring, as the model version used in the manuscript does not include the module of HNO<sub>3</sub> uptake on dust and its reaction with NO, so the discussion on dust's impact on SNA is in fact irrelevant and should be removed. In the revised manuscript, we removed the

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discussion on dust and explained the low SNA concentrations in spring to high wind speed that favors dispersion and export of SNA to other regions (pg 20, line 461-462).

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