Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text labeled with [R]. Line numbers in the responses correspond to those in the revised manuscript (the version with all changes accepted). Modifications to the manuscript are in *italics*.

Reviewer #1

This paper addresses the important issue of the difficulty models have in correctly simulating $PM_{2.5}$ composition. This is to my knowledge the most comprehensive evaluation of a CTM's performance in China and provides a valuable starting place for the future investigation of many issues, such as the overestimation of nitrate and the underestimation of NH_3, CO, OH, and HO_2. This paper provides an analysis of the performance of the model in all four seasons, which is rare. This paper is well-written and within the scope of ACP and should be published after the minor revisions listed below.

[R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

Major Comments.

My main major comment is that the authors should be more careful in stating potential reasons for model biases, and either perform "back-of-the-envelope" calculations, or quick sensitivity tests to support their conclusions. They have already gone to huge effort to perform a large set of sensitivities, but a little more context on the environment in China could be extremely helpful in interpreting the results. It would be particularly good for example to understand when SIA is sensitivity to NH_3, or HNO_3, or base.

[R1] We thank the reviewer for the suggestion and agree that the sensitivity of SIA to NH_3 or HNO_3 is an important issue for the simulation of $PM_{2.5}$. Nenes et al. (2020a; 2020b) indicate that aerosol pH and ALWC determine the sensitivity of $PM_{2.5}$ to NH_3 or HNO_3 and the reactive nitrogen deposition. Their analysis show that in China, especially in northern China, $PM_{2.5}$ is more likely sensitive to HNO_3 and in some cases to HNO_3+NH_3. The model overestimates the HNO_3 and nitrate concentrations largely in Beijing, suggesting that the model over-predicts the nitrate availability. Analysis of the potential factors to the model bias shows this overprediction cannot be explained by the chemical production and meteorology. We therefore state that the possible explanations include inaccurate dry deposition of HNO_3 and nitrate and the photolysis of particulate nitrate in the model. In particular, the latter remains largely unknown under ambient conditions. However, it is difficult to diagnose more within the scope of this manuscript. We have added related discussions and clarified some details in the revised manuscript (e.g., in Line 249-252, 375-384, and 435-444).

Finally, the conclusions could more clearly state the main findings from this work,

with the key numbers that highlight their findings, such as improvement from reduced NO_2 uptake and the remaining summertime nitrate bias.
[R2] We have revised the conclusion paragraph with key numbers to highlight our findings.

The minor comments below state additional specific suggestions for this.
Minor Comments.
1. Page 4, line 108. I don't quite understand why you need to divide the observation data by 0.8 to compare to the model. Should the model represent both PM_1 and $PM_{2.5}$, and could you not compare to both?
[R3] The modeled sulfate, nitrate, ammonium, and OA are not specified to any size domain. In polluted environments, substantial mass of these species present in the super-micron domain. The modeled concentrations represent $PM_{2.5}$ not PM_1. The previous AMS or ACSM measurements are however for PM_1. Recent measurements in North China Plain suggest that 0.8 is a good coefficient to use for converting PM_1 to the $PM_{2.5}$ mass for these species. We therefore applied 0.8 when comparing the observations to the model results. This coefficient doesn't affect the model evaluation much given the measurement uncertainty of 30% is considered. For clarification, we have revised Line 114-116 as follows "*Model results plausibly represent fine particles not submicron portion in polluted environments. The submicron-to-fine mass ratios are about 0.8 for sulfate, nitrate, ammonium, and OA in summer and winter in NCP and may decrease to 0.5 during the severe winter-haze episodes under high RH (Fig. S1 in SI) (Zheng et al., 2020). We therefore divided the submicron observation data by 0.8 for the four species when comparing to the model results*".

2. Page 4, line 126 – provide the model doi.
[R4] The model doi is added in Line 133.

3. Page 5, line 161 – Is there a citation for "the top-down estimates."?
[R5] We added the citation for the top-down estimates in Line 175.

4. Page 5, line 171 – It would be very useful to have a table of relevant emissions totals for comparison by future studies.
[R6] We have added Table S2 in SI to show the total emissions of primary $PM_{2.5}$ and the gaseous precursors.

5. Page 5, line 189 – What season was evaluated in Fu et al., 2012 and Zhao et al., 2016? Does the conclusion still hold about the improved model performance with the simple scheme if compared by season?
[R7] Fu et al. (2012) and Zhao et al. (2016) evaluated four seasons. The improved model performance with the Simple SOA scheme holds for all the four seasons. We have revised Line xxx as follows "*The Simple SOA scheme shows improved performance on OA for all seasons (NMB = -0.26, R = 0.70)*".

6. Page 5, line 191 – It might be helpful to readers to start a new paragraph discussing the seasonality of the model bias.

[R8] We have started a new paragraph and moved the original paragraph (two paragraphs later) about seasonality here.

7. Page 7, line 200 – Are you saying that there is too much NH_4 in YRD because there is too much NOx making too much NH_4NO_3?

[R9] We think that the NH_3-rich environment in YRD promote the formation of ammonium nitrate and ammonium sulfate. We have revised the sentence in Line 221-223 for clarification.

8. Page 7, line 204 – The lack of model gradient in SO_4 between urban and rural sites is striking. Do you have an explanation for this? Is there an urban/rural gradient in SO_2 in the model?

[R10] The non-urban sites herein contain rural and suburban sites. The modeled SO_2 concentrations do not show significant urban/non-urban gradients (9.84/10.13 ppbv), possibly because many SO_2 sources like power plants and industry are located outside of urban areas. We think the greater sulfate concentrations observed in urban sites than in non-urban sites are perhaps a result of chemistry that occurs during the transport process but has not been well presented in the model (e.g., the heterogeneous formation of sulfate).

9. Page 7, line 207 – Do you expect model resolution to have an effect on the ability to simulate urban aerosol?

[R11] We expect that the model resolution affects sites nearby sources. The urban sites herein are generally urban background sites, meaning that urban air are well mixed at the sites. The model-observation comparisons are also based on campaign-average values for which pollution plumes should be smoothed out. Moreover, the model grid of 0.5°×0.625° isn't too big compared to the size of the cities in China. The sites are well covered by the model grid boxes. In addition, the differences between the simulated concentrations of sulfate, nitrate, ammonium, and OA by 0.5°×0.625° and 0.25°×0.3125° horizontal resolutions for the sites in Beijing are within 35% with high R value (> 0.9). We therefore do not expect a significant influence of the model resolution on the analysis herein.

10. Page 7, line 208 – Are you saying that winter = haze? It does not appear that you have classified winter data as 'haze'/'not haze', please clarify.

[R12] Severe haze occurred more often in winter than in other seasons. We have clarified in the text that *"the underestimation of sulfate occurs all year round, and the greatest underestimation occurs in winter (NMB = -0.54) (Fig. 1a and Table S3). The seasonality of the model bias is partially explained by the underestimation of SO2 emissions in winter (Wang et al., 2014; Koukouli et al., 2018). Similar to other models, our model failed to reproduce the high sulfate concentrations during the haze periods because of the underrepresented heterogeneous production (Wang et al., 2014; G. J.*

Zheng et al., 2015). Severe haze events occurred more often in winter in China, contributing to the seasonality of the model bias".

11. Page 7, line 218 – Can you be more specific about the possible causes of the seasonality in the OA bias? Could the seasonality imply an issue with biogenic vs. anthropogenic SOA?

[R13] The seasonality in the OA bias is perhaps more contributed by anthropogenic SOA as it dominates the OA mass in most part of China. We have revised in Line 211-214 as follows: "*the underestimation of OA occurs all year round, but the worst bias happens in autumn. Biases in the precursor emissions as well as the assumed nonseasonal conversion rate from precursors to particle-phase SOA are the possible reasons of the seasonality of the OA bias*".

12. Page 7, line 220 – Is it really necessary to show the model biases on a log scale?

[R14] We thank the reviewer for the suggestion and have modified the Fig. S3 and S4 with a linear scale.

13. Figure S3 – what are the red dashed lines?

[R15] The red dashed lines denote the ratios of simulation and observation of 1.3, 1, and 0.7. We have added the description in the figure caption.

14. Page 7, line 222 - Is the summer value for $PM_{2.5}$ really within 30%?

[R16] The median value of the simulation-to-observation ratios for summertime $PM_{2.5}$ is within 30%. In Fig. S3, the upper and lower red dashed lines show the 30%.

15. Page 8, line 227 – Can you please explain the reasoning for excluding data over 150 ug m^{-3}?

[R17] As described in [R3], the model results plausibly represent fine particles not submicron portion in polluted environments in China. The submicron-to-fine mass ratios are about 0.8 for sulfate, nitrate, ammonium, and OA in summer and winter in NCP and may decrease to 0.5 during the severe haze episodes under high RH. We divided the submicron observation data by 0.8 for the four species when comparing to the model results. The test here by excluding data over 150 μg m^{-3} is to exclude the severe haze periods, and thus to prove that the discussion won't be affected by the submicron-to-fine ratio. For clarification, we have revised the text in Line 236-239 as follows: "*Figure S4 in SI shows the simulation-to-observation ratios when excluding the periods of NR-$PM_{2.5}$ mass concentrations over 150 μg m^{-3}. During these periods, the submicron-to-fine ratios may decrease from 0.8 (used herein) to 0.5. The model biases and their seasonal variations in Fig. S4 are similar to the previous results, suggesting insignificant impacts of haze periods on the statistic evaluations*".

16. Page 8, line 231 - Instead of "insignificant", could you state the model bias?
and 17. Page 8, line 233 – Could you give us more statistics on the diurnal cycle, it is hard to see in these plots that nitrate and ammonium are "flatter" than sulfate.

[R18-19] We have added values and revised the statements in Line 241-249 as follows: "*the observed sulfate shows a daytime concentration build-up (2-4 μg m^{-3}) in spring and summer, suggesting a photochemical production (Sun et al., 2015). The wintertime diurnal pattern shows a steady but later enhancement (~5 μg m^{-3}) in the afternoon. The simulated profiles show less daytime concentration elevations (0-2 μg m^{-3}), suggesting insufficient production, overestimated boundary-layer dilution, or removal during the day in the model (Fig. 2a). By contrast, the observed diurnal variations of hourly-mean nitrate and ammonium concentrations are less than sulfate (Fig. 2b-c). The 2-5 times greater concentrations of simulated nitrate at night suggest over-predicted nighttime production, underestimated boundary-layer dilution, or underestimated removal of nitrate. Nighttime production of nitrate by the heterogeneous uptake of N_2O_5 and NO_2 is an important pathway of nitrate production in northern China (Wang et al., 2018; Alexander et al., 2020).* ".

18. Page 8, line 243 – could the ratio of nitrate / nitrate + HNO_3 tell you whether there is an issue with model partitioning at this site?

[R20] The nitrate partitioning fraction is determined by the thermodynamic equilibrium, which depends on aerosol acidity and ALWC. Because the model overestimates sulfate concentrations in summer, underestimates sulfate in winter, and underestimates ammonia concentrations in all seasons. The nitrate partitioning fraction can be biased by various reasons. We therefore did not use it to indicate the partitioning problem. We have revised the text to clarify the overestimation of total nitrate in the model in Line 251-252.

19. Figure 2 – Why is there a morning peak in wintertime OA?

[R21] The morning peak of wintertime OA is mainly caused by the POA emissions from the residential sector (e.g., from residential coal burning). The diurnal profile of the emissions from the residential sector is shown in Fig. S2. We have added this discussion in Line 266-267.

20. Figure S8 – What are the red numbers? Can you explain the large difference in the median vs. mean difference particularly in winter and fall?

[R22] The red numbers are the median values of MERRA2- and radiosonde-derived BLH. We have added the description in the figure caption. MERRA2-derived BLH are sometimes extremely large, leading to high MERRA2-to-observation ratios and subsequently large differences in the median vs. mean.

21. Table 1 – The NMB values for wind direction don't make sense, it seems like they should be much larger.

[R23] We have added the MB values to Table 1. Using the MB values for wind direction make more sense than using NMB.

22. Page 9, line 274 – Do you have an explanation for the seasonality in SO_2 that the model is missing? Could this be for example from heating sources that the

inventory doesn't capture?
[R24] The seasonality of SO_2 emission mainly results from the seasonality of emission from the residential sector. Therefore, we agree that the failure of inventory to capture some residential and commercial heating sources can contribute to the weak seasonality in MEIC.

23. Figure 4b – Why compare against NO_2 and not NO_x? The modeling partitioning could also have issues.
[R25] The relative coarse model resolution (about 50 km) limits the model performance of NO in the source region due to its quick conversion to NO_2 before transport through the gird. Compared to NO, NO_2 has a longer lifetime about several hours to nearly one day (Shah et al., 2020), which let it more even with the grid and be better presented by model. Therefore, we used NO_2 rather than NO_x in the model evaluation. Actually, using NO_x will not affect the conclusion.

24. Page 9, line 279 – Could you run a quick sensitivity test to determine whether say turning off NO_2 uptake brings NO_2 into better agreement?
[R26] We have run a sensitivity test for turning off NO_2 uptake. The result shows that the concentration of NO_2 increases by 70.3% and 58.1% in winter and summer, respectively, which agrees better with the observations.

25. Page 9, line 285 – Can you calculate whether aerosol is generally sensitivity to NH_3 or HNO_3 in each season?
[R27] Previous studies show that nitrate is generally sensitive to HNO_3 in summer (Wen et al., 2018) and sensitive to NH_3 during winter haze periods (Xu et al., 2019). Nenes et al. (2020b) also show that the nitrate formation is sensitive to HNO_3 and in some cases to HNO_3+NH_3.

26. Page 9, line 287 – You mean in the simple scheme, right? CO wouldn't affect the semivolatile scheme if I understand correctly?
[R28] Yes, we discuss the SOA precursors here based on the Simple SOA scheme. CO may have little impact on the semivolatile scheme by its effect on OH radicals.

27. Figure 5 – The uncertainties on these observations, particularly the radicals, are large. Could you put error bars, or shading etc., on the observations?
[R29] We thank the reviewer for the suggestion and have added the shading to present the standard deviation of these observations and simulations in Fig. 5.

28. Page 10, line 305 – Not necessarily, depending on conditions, inclusion of $ClNO_2$ can increase nitrate due to $ClNO_2$ photolysis – See Sarwar et al., 2014 (GRL).
[R30] We agree with the reviewer that the effect of inclusion of $ClNO_2$ on nitrate concentration is depending on conditions. Figure 2 in Sarwar et al. (2014) suggests that the heterogeneous $ClNO_2$ production can decrease both summertime and wintertime nitrate concentration in northern China. We have revised the statement in Line xxx as

follows: "*The model uses relatively high values of γ_{N2O5}, which can lead to the overestimation of nitrate (McDuffie et al., 2018; Davis et al., 2008; Jaegle et al., 2018). Besides, the missing formation of nitryl chloride from the N_2O_5 uptake trends to contribute to the nitrate overestimation in northern China (Sarwar et al., 2014)*".

29. Page 10, line 308 – Jaegle et al., 2018 discusses the Eastern United states in winter, I am confused by this reference here. I also can't find the seasonality you reference in these citations, please clarify.

[R31] Jaegle et al., 2018 is the citation for supporting the previous sentence "Biases may also relate to the atmospheric removal of the SIA species". We have corrected it in Line 204-205.

30. Page 10, line 313 – However the lack of daytime HONO is a model issue – does this provide support for photolysis of nitrate?

[R32] Ye et al. 2017 showed low photolysis rates of particle-phase nitrate when there is thick organic coating on $PM_{2.5}$. The lack of daytime HONO is perhaps a result of underrepresented sources (e.g., the heterogeneous formation on the surface of land, buildings and so on).

31. Page 10, line 318 – Just to clarify, you are aiming to address general model biases, not biases specific to haze?

[R33] Yes, we choose the periods during which the mean $PM_{2.5}$ concentrations were lower than 75 ug m^{-3}. We have revised this sentence to clarify.

32. Page 11, line 340 – Did you run all 50 sensitivity simulations at nested resolution? Did you also consider the effect of resolution itself? See Zakoura and Pandis, 2018 (Atmospheric Environment)

[R34] Yes, we run all simulations at nested resolution. The differences between the simulated concentrations of sulfate, nitrate, ammonium, and OA by 0.5°×0.625° and 0.25°×0.3125° horizontal resolutions for the sites in Beijing are within 35% with high *R* value (>0.9) for all seasons. We therefore do not expect a significant influence of the model resolution on the analysis herein.

33. Page 11, line 341 – Why not test whether scaling up winter and fall CO improves model SOA in the simple scheme?

[R35] We did tested this. However, scaling up the emissions of CO in the Simple SOA scheme to increase anthropogenic SOA leads to the significant overestimation of SOA in non-urban areas. We have added this point in the text.

34. Figure 6 – It might help to have a horizontal line through the 1-1 line so we can see when the model is over or under estimating.

[R36] We thank the reviewer for the suggestion and have added the 1-1 line in Fig. 6.

35. Page 11, line 350 – Would the model bias in nitrate impact aerosol water and

thus result in overestimated sulfate particularly using the ALWC parameterization?
[R38] Yes, the overestimated ALWC in summer due to the overestimation of nitrate concentration may affect the heterogeneous sulfate formation and lead to the overestimated summertime sulfate concentration in Case 6 (based on ALWC parameterization). We have added this discussion in Line 367-368.

36. Page 11, line 354 – Isn't this conclusion supported by the extreme model overestimate of HONO in Figure S9?
[R39] Yes, the updated γ_{NO2} can significantly reduce the overestimation of nighttime HONO concentration. We have revised this sentence and added this information.

37. Figure 6, case 8, Why is the median so much more impacted than the mean?
[R40] In panel c, case 8 fails to capture low nitrate concentrations of < 0.5 ug m^{-3}, leading to large simulation-to-observation ratios (>5). This significantly affects the mean value of the simulation-to-observation ratios other than the median value.

38. Page 12, line 360 – Why not test these things?
[R41] There are lack of parameter constraints for testing the dry deposition of HNO_3 and the photolysis of particulate nitrate. We therefore did not test them in this study.

39. Page 12, line 362 – Why does increasing sulfate reduce nitrate in the model?
[R42] The heterogeneous formation of sulfate may affect aerosol pH and ALWC that determine the sensitivity of nitrate formation to ammonia and nitrate availability, especially in winter when NH_3 emissions are low (Nenes et al., 2020b). We have revised this discussion in Line 387-388.

40. Figure 7. I understand the authors aim in Figure 7, but it is difficult to follow. Possibly a table would be easier for the reader to understand.
[R43] We have updated Fig. 7 and the corresponding text in Line 394-420.

41. General comment – is there any reason to think that in-cloud oxidation of SO_2 is underestimated? Could model cloud biases be part of the issue?
[R44] The in-cloud oxidation of SO_2 mainly from the oxidation of H_2O_2 and O_3. The observed H_2O_2 concentration (0.51 ppbv) in Beijing (Wang et al., 2016) are consistent with the simulated concentration (0.43 ppbv). Fig. 6 shows that O_3 concentration is overestimated. Both do not indicate the underestimation of in-cloud sulfate formation. Also, because sulfate concentrations can be generally reproduced in the US by Geos-Chem (Heald et al., 2012), we think the model cloud biases less likely affect the simulations herein.

42. Conclusions – it would help the reader to be more specific in the conclusions about the impact of your sensitivities. For example, accurate SO_2 emissions result in XX improvement in the model agreement with SO_4. Generally, if the authors

could put in the conclusions more numbers on their findings, for example, even our most improved model is still biased by XX % in summer, it could help improve citations by future modeling studies.

[R45] We have revised the conclusion with specific information.

43. Page 13, line 410 – Can you provide the explanation for this here? Why is this the case?

[R46] The overestimation of sulfate with worse R in summer suggests that the parameterization of heterogeneous sulfate formation on RH and ALWC are insufficient, and therefore mechanistic approaches might be needed to improve the seasonality of the sulfate simulations.

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