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 shows 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 199 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 promotes 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 SO_2 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 for 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 nitrate concentrations and underestimates the concentrations of sulfate and ammonia in all seasons, the nitrate partitioning fraction can be biased. 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 makes 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 321-323 as follows: "*The model uses relatively high values of γ_{N2O5}, which may lead to the overestimation of nitrate (McDuffie et al., 2018; Davis et al., 2008; Jaegle et al., 2018). The lack of nitryl chloride formation from the N_2O_5 uptake in the model may contribute to the overestimation of nitrate 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 399-423.

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.

Reviewer #2

The paper presents a comprehensive investigation into the uncertainties in PM2.5 simulated with the GEOS-Chem model for China and potential sources of errors. PM is a complex pollutant and even after the decades of its modelling, most of air quality/chemical transport models are still often struggling with accurate representation of PM, in particular during pollution episodes. Given large uncertainties in descriptions of aerosol chemical and physical processes, the availability of good quality observations is crucial for models' evaluation and constraining. In the presented work, the author compiled and used for the model evaluation an impressive volume of observational data of non-refractive submicron PM components (sulphate, nitrate, ammonium and organic aerosols), as well as aerosol gaseous precursors in China. They also performed a series of sensitivity tests, modifying multiple parameters, to obtain the best model correspondence with the observations.
The paper is in general fairly well written (though the bounty of technicalities sometimes makes reading somewhat heavy); the figures and tables are quite helpful in visualizing and presenting the results. The topic of the paper is highly relevant, the scientific material and findings are quite interesting, and thus after some minor revisions it can be recommended for publication in ACP.

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

My first reaction is that given the impressive amount of testing, the conclusions appear somewhat little constructive and of a rather general character. In other words, it is unclear what would be the first priorities the authors plan to improve the GEOS-Chem's performance with respect to $PM_{2.5}$. Would the authors comment on that?
[R1] We thank the reviewer for the suggestion and have rewritten the conclusion. As stated in the revised version, the heterogeneous formation of sulfate and nitrate as well as the anthropogenic S/IVOC-related SOA are the first priorities to improve the model performance. However, our best model with all the updated factors still biases the nitrate in summer by 210%, which merits further investigations.

The 'best combination' of all tested parameters did not yield a satisfactory model agreement with short term observations in Beijing. Has it been tested against the whole 2006-2016 campaign dataset?
[R2] We did not test the model performance of the "best combination" of all tested parameters against the whole 2006-2016 campaign dataset. The main reason is that we don't have sufficient measurements to constrain the various factors outside Beijing, for example, SO_2 emission and OH levels.

In particular, the GEOS-Chem is shown to have troubles to reproduce observed concentrations of SO_4 and NO_3. Is that for China simulations only? Or was that seen also so for other world's regions? I'd suggest to include in Introduction a small paragraph about that if such evaluations are available.
[R3] The overestimation of nitrate in GOES-Chem was also observed in the US, where the model reproduces sulfate concentrations (Heald et al., 2012). We have added this information in the Introduction in Line 53-54.

Have the authors seen a paper by H. Bian et al.: Investigation of global particulate nitrate from the AeroCom phase III experiment (Atmos. Chem. Phys., 17, 12911–12940, 2017 https://doi.org/10.5194/acp-17-12911-2017)? It does not appear that overestimating NO_3 in Asia is a generic feature among the nine CTM and climate models participating in the paper.
[R4] The EANET measurement sites used in Bian et al. (2017) are mostly located in areas having low NO_x concentrations. By contrast, nearly a half of the measurements in this study are from polluted northern China where the NO_x concentrations are high. The two regions can be different in chemical domains of the sensitivity of aerosol to NH_3 and NO_x emissions and therefore be different in nitrate formation potential (Nenes et al., 2020b). Another multi-model comparisons in Asia also show the overestimation of nitrate in Asia (Chen et al., 2019).

There are other processes, not been investigated in the paper, which could be sources of e.g. NO_3 overestimation, for instance the equilibrium formation of ammonium nitrate. How well does ISORROPIA work for China chemical regime? Has this been studied before? Any reference to the results?
[R5] Previous study in Beijing shows the ISORRPOPIA II model can reproduce the concentrations of sulfate, nitrate, ammonium, and NH_3 with Rs > 0.9 and NMBs within 10% and generally capture the partitioning of NH_3/ammonium (Liu et al., 2017). We except minor bias from ISORRPOPIA compared with the potential biases in the heterogeneous uptake of NO_2 and N_2O_5 as well as other factors related to the precursor oxidation and the removal processes.

Another source of uncertainties is dry deposition velocities of NO_3 and NH_4, which were measured to be higher than typically predicted by the models (E. Nemitz et al.: Concentrations and surface exchange fluxes of particles over heathland; Atmos. Chem. Phys., 4, 1007–1024, 2004 www.atmos-chem-phys.org/acp/4/1007/). Would the authors consider to investigate into this process?
[R6] We agree with the reviewer that the uncertainties in the dry deposition of nitrate and ammonium can contribute to the model biases. However, the relative contributions of the dry deposition of nitrate and ammonium to the total deposition of nitrate+HNO_3 and ammonium+NH_3 is perhaps small (<10%) (Zhao

et al., 2017). We expect a minor influence of such uncertainties on the SIA concentrations.

A minor general comment: winter haze events are mentioned every now and then, without any clear context. Could the authors explain early in the paper why haze occurrence is an issue in the manuscript?

[R7] We thank the reviewer for the suggestion and have added some descriptions about haze in Line 83-87 as follows: "*unusual biases of the meteorological fields and chemical processes may occur during the severe haze periods (daily mean $PM_{2.5}$ > 75 μg m^{-3}) (An et al., 2019). The models often significantly underestimate the $PM_{2.5}$ concentrations during the haze events (Wang et al., 2014; G. J. Zheng et al., 2015). Various model biases from meteorology, emissions, and the physical and chemical processes interact with each other nonlinearly. It is therefore important to evaluate the model for all individual components of $PM_{2.5}$*".

The comments and suggestions to the text:

Line 27. suggesting existing inaccuracies in the processes description (or presentation).

[R8] We have revised this sentence accordingly.

Lines 30-31 and 172-174. It's unclear what heterogeneous SO_2 oxidation reactions are in the model (by H_2O_2, ozone?)

[R9] As stated in the Introduction, the mechanisms for the heterogeneous SO_2 oxidation is still under debate. We used non-mechanism-based parameterizations on RH or ALWC to simulate the heterogeneous sulfate formation.

Lines 34-35. Again, can the author show that ISORROPIA is working properly? Clarify 'related to removal'. Wet or dry, or both.

[R10] As discussed in [R5], the bias from ISORRPOPIA is expected to be minor compared with other potential biases. Because the chemical production, meteorology, and the wet deposition cannot explain the model bias of nitrate, the removal here mainly means dry deposition of HNO_3 and nitrate as well as the photolysis of particulate nitrate. We have revised the text.

Line 42. what is considered to be reasonable?

[R11] We have revised the statement as follows: "*Studies have shown that the CTMs can reproduce the spatial and temporal variations of the surface $PM_{2.5}$ concentrations in China*".

Line 45. 'the model performance on $PM_{2.5}$ is component-dependent' sounds strange. Maybe like:

even though the model represents well observed $PM_{2.5}$, it may happen due to compensation errors in model simulated $PM_{2.5}$ components.

[R12] We have revised the text as follows: "*However, when the simulations of $PM_{2.5}$ components have compensating errors, the model still reproduces the $PM_{2.5}$ mass and biases the evaluation of the effectiveness of the emission control strategies*".

Line 48. I agree to some extend about SOA, but not about sulphate and nitrate (see my Ref. to Bian above). Perhaps the authors mean only specific studies for China.

[R13] We have specified the region as follows: "*Model evaluations in China have reached an agreement that the CTMs generally underestimate the concentrations of organic aerosol (OA) (Fu et al., 2012; Han et al., 2016) and sulfate (Wang et al., 2014; G. J. Zheng et al., 2015) but overestimate the concentrations of nitrate (Wang et al., 2013; Chen et al., 2019)*".

Line 57. Suggestion: The uncertainties in the emissions of primary PM and gaseous precursors of secondary PM are quite large.

[R14] We have revised this sentence accordingly.

Line 82. Suggested: therefore it is important to evaluate the model for all individual components of $PM_{2.5}$

[R15] We have added this to the text in Line 86-87.

Line 83. The measurements' artefacts can also decrease the discrepancies. . . the point is that in such cases, the model evaluation results give a wrong message.

[R16] Yes, we agree. The statement in Line 88 has been revised as follows: "*On the other hand, observations may be biased, which is rarely considered when evaluating the model-observation discrepancies*".

Line 103. Write: Institute of Atmospheric Physics (IAP) – for future use of abbreviation. Could you write here what site type is this (urban/suburban background?)

[R17] Corrections have been made accordingly.

Line 130. Suggestion: For comparison with observations at IAP. Beijing, the model simulations were performed for the ASCM measurements period.

[R18] Corrections have been made accordingly.

Line 132: Do I understand right that model simulations for 2012 meteorological conditions were used for comparison with 2006-2016 observations. Could the authors then say how (un)typical the 2012 weather was. Were year dependent emissions used, or also the same for 2012?

[R19] Yes, the model simulations for 2012 meteorological conditions and emissions are used to comparison with 2006-2016 observations for computation efficiency. The meteorological condition in 2012 is generally typical. Weather parameters like mean wind speed are in the middle range for 2006 to 2016 (Gao et al., 2020). The inter-annual variabilities of emission vary between species (Zheng et al., 2018; Li et al., 2019). For example, the emissions of SO_2 and primary $PM_{2.5}$ decreased by 50% and 40% from 2006 to 2016, respectively. The changes of NO_x emissions are minor. But the NMVOC emissions increased by ~25%. Such changes have been considered in the evaluation of the model-observation discrepancies in Fig. 1. Because the measurements were mostly conducted from 2011 to 2014 (47/77), the bias of using the fixed 2012 emissions on the general model evaluation is not evident.

Line 150. Suggested: 80% which is considered to be a reasonable assumption (instead of 'for simplicity')

[R20] We have deleted "*for simplicity*" in the text.

Line 151. However, Hodzic. . . showed that the results were not very sensitive to. . ...

[R21] We have revised this sentence accordingly.

Line 161-162. What is the relative contribution of non-agricultural NH_3 emissions compared to the agricultural ones? This is important to know when analysing ammonium nitrate formation in cities.

[R22] Nationally, the agriculture emissions contribute to 88.5% of the total emissions of NH_3 (Zhang et al., 2018). Non-agricultural NH_3 emissions are important in urban areas. The contribution of non-agriculture NH_3 may reach 90% during haze periods in some places (Pan et al., 2016; Sun et al., 2017).

Lines 172-180. Move up to Chemistry description, above the emissions.

[R23] We have revised the manuscript accordingly.

Line 182. Suggestion: Model performance for the individual PM components

[R24] We have revised the subtitle as "Compensating errors from simulations of individual $PM_{2.5}$ components".

Line 188: The modelled ammonium concentrations compare with observations better than simulated sulfate.

[R25] We have revised the manuscript accordingly.

Line 191. Further, we find that the model biases. . .
[R26] This sentence has been deleted as suggested in the next comment.

Lines 192 and 208-210 some repetition.
[R27] We thank the reviewer for the suggestion and have reorganized the discussion about seasonality (see R8 in the response to Reviewer #1).

Line 196. Would you expect the model performance to differ over China? Why? How different those regions are (weather, emissions?). Does that mean that the model is insensitive to the differences in meteo and chemical regimes?
[R28] For general model problems like missing heterogeneous production, we expect similar model performance in different regions. If the model bias is related to localized issues like emissions, the model performance might be different among regions. Indeed, the purpose of evaluating the model results spatially is to help diagnosing.

Line 208. Suggestion: On a seasonal basis,..
[R29] We have revised this phrase accordingly in Line 201.

Line 210-11. ..the overestimation of nitrate concentration is largest in spring, summer and autumn.., while the model bias is much smaller in winter. . .
[R30] Corrections are made.

Line 212-213. Are those simulations also with GEOS-Chem and ISORROPIA?
[R31] Yes, simulations in both Wang et al. (2013) and Heald et al. (2012) are based on GEOS-Chem and ISORROPIA II.

Line 214. In all seasons?
[R32] Yes, the overestimation of nitrate occurs in all seasons. We have added "*in all seasons*" in the text.

Line 217. The model performs worst in autumn
[R33] We have revised the text accordingly.

Line 218. This is about the only time when the correlation is mentioned. Why it's considered

important here, but not for the other components? Is the relative importance of ASOA greater in summer?

[R34] The correlation of summertime OA is mentioned because the *R* value (0.28) is quite low compared with the values for other seasons (≥0.49). The *R* values are higher for other components and do not vary much by seasons (Table S3). The relative importance of ASOA is greater in winter than summer.

Line 220. –compared to the 2 years of hourly observations. . ..

[R35] We have revised the text accordingly.

Line 223. ..underestimation of sulfate and OA by the overestimation of nitrate. . .

[R36] We have revised the text accordingly.

Line 226-27. Explain exclusion of the observations over 150 ug m^{-3}

[R37] As explained in R3 and R17 of the response to Reviewer #1, the modeled sulfate, nitrate, ammonium, and OA are not specified to any size domain. In polluted environments, the modeled concentrations plausibly represent $PM_{2.5}$ not PM_1. The previous AMS or ACSM measurements are however for PM_1. 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. The submicron-to-fine mass ratios may decrease to 0.5 during the severe haze episodes under high RH. 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 114-116 and Line 236-239.

Line 242. Does that mean: If the evaporation of ammonium nitrate . . .. . .was accounted for in the model, the day time variation.. could be flatter?

[R38] Yes. We have revised the sentences in Line xx. Instead, we would discuss more about the nitrate partitioning fraction.

Line 254. Semivolatile POA scheme previously used? in GEOS-Chem

[R39] Yes, the Simple SOA scheme is a new scheme in GEOS-Chem for SOA simulations.

Line 267. . . .simulations lead

[R40] The correction is made.

Line 271. Suggestion: The uncertainties related with emission data including their temporal profiles)

are considered to be one of the major sources of inaccuracies in modelled concentrations. . ...
[R41] We have revised the text accordingly.

Line 275. It is widely shown that regional models cannot accurately reproduce NO_2 at urban sites. Would the authors really expect the model with a resolution of 50-60 km to be capable of managing that?
[R42] We agree with the reviewer. For a 0.25°×0.3125° horizontal resolution, NO_2 can generally disperse fully in the grid even in summer when the mean wind speed about 1.7 m/s and NO_x lifetime about 5.9 h (Shah et al., 2020). We have clarified the impact of model grid size in Line 291. Good correlations of the simulated NO_2 concentrations at IAP site between 0.5°×0.625° and 0.25°×0.3125° horizontal resolutions (R>0.75) suggest that the model with the resolution of 50-60 km still capture the variations of NO_2 concentrations, perhaps because Beijing is relatively big compared with other urban cities.

Lines 282-285. What is the main sources and relative importance of non-agricultural NH_3? Why is it especially important during haze events?
[R43] Non-agricultural NH_3 emissions are mainly from traffic, biofuel burning, chemical industry, and waste disposal (Kang et al., 2016). The increased contribution from non-agricultural NH_3 emissions in urban areas perhaps results from the limited transport of agricultural NH_3 emission from rural to urban during the haze periods under stagnant weather conditions (Pan et al., 2016). We have made this clear in Line 298-300.

Lines 288-290: Unclear what is said here.
[R44] We have revised this part in Line 304-307 as follows: "*The model also underestimates the aromatic VOC concentrations, similar to previous studies (Liu et al., 2012). Such underestimation would not affect the SOA simulations herein because that the Simple SOA scheme no longer derive aromatic SOA from the aromatic VOC concentrations. Instead, the model treats aromatic SOA as a part of anthropogenic SOA, which is estimated on the basis of the parameterizations on CO*".

Lines 311-12. Should be formulated more clear: The photolysis rate of particle-phase HNO_3 was shown in aged air masses to be higher than for the gaseous HNO_3. . ..., but in Beijing particulate NO_3 may have lower photolysis rates, because. . ...
[R45] We have revised the text accordingly.

Line 315. From the factors
[R46] The correction is made.

Line 319-20. . . .weeks were free of severe haze episodes (with extreme conditions which the model fails to reproduce????)

[47] We have revised the text accordingly.

Line 338. The increased wet deposition of nitrate. . .

[R48] The correction is made.

Line 360. Faster photolysis of particulate nitrate? Sounds contradictory to what is written on lines 311-312

[R49] Photolysis of particulate nitrate would reduce the nitrate concentrations (in turn reduce HNO_3 concentrations by partitioning and increase NOx concentrations), which would lead to better model-observation agreements. We have revised this sentence in Line 382-384 as follows: "*Insufficient dry deposition of HNO_3 and nitrate and the photolysis losses of particulate nitrate to produce HONO and NO_x (Ye et al., 2017) as well as the joint influence of multiple factors (discussed later) are possible explanations for the overestimation of nitrate*".

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Model bias in simulating major chemical components of $PM_{2.5}$ in China

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Abstract. High concentrations of $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) in China have caused severe visibility degradation. Accurate simulations of $PM_{2.5}$ and its chemical components are essential for evaluating the effectiveness of pollution control strategies and the health and climate impacts of air pollution. In this study, we compared the GEOS-Chem model simulations with comprehensive data sets for organic aerosol (OA), sulfate, nitrate, and ammonium in China. Model results are evaluated spatially and temporally against observations. The new OA scheme with a simplified secondary organic aerosol (SOA) parameterization significantly improves the OA simulations in polluted urban areas~~.~~, highlighting the important contributions of anthropogenic SOA from semivolatile and intermediate-volatility organic compounds. The model underestimates sulfate and overestimates nitrate for most of the sites throughout the year. More significant underestimation of sulfate occurs in winter, while the overestimation of nitrate is extremely large in summer. ~~Our~~The model is unable to capture some of the main features in the diurnal pattern of the $PM_{2.5}$ chemical components, suggesting ~~underrepresented~~inaccuracies in the presented processes. Potential model adjustments that may lead to a better representation of the boundary layer height, the precursor emissions, hydroxyl radical~~,~~ concentrations, the heterogeneous formation of sulfate and nitrate, and the wet deposition of nitric acid and nitrate ~~are~~have been tested in the sensitivity analysis. The results ~~suggest~~show that uncertainties in chemistry perhaps dominate the model ~~bias~~biases. The proper implementation of heterogeneous sulfate formation and the good estimates of the concentrations of sulfur dioxide ~~and~~, hydroxyl radical, and aerosol liquid water are essential for the improvement of the sulfate simulation. The update of the heterogeneous uptake coefficient of nitrogen dioxide significantly reduces the modeled concentrations of nitrate~~, and accurate sulfate simulation is important for modeling nitrate.~~. However, the large overestimation of nitrate concentrations remains in summer for all tested

cases. The ~~uncertainty of~~possible bias in the chemical production and the wet deposition of nitrate cannot fully explain the model overestimation of nitrate, suggesting ~~a problem~~issues related to the atmospheric removal~~.~~ of HNO_3 and nitrate. A better understanding of the atmospheric nitrogen budget, in particular, the role of the photolysis of particulate nitrate, is needed for future model ~~studies~~developments. Moreover, the results suggest that the remaining underestimation of OA in the model is associated with the underrepresented production of SOA.

1 Introduction

In developing countries like China and India, the concentrations of $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) often exceed air-quality standards, leading to visibility reduction and negative health effects (Chan and Yao, 2008; Lelieveld et al., 2015). Chemical transport models (CTMs) are valuable tools to evaluate the $PM_{2.5}$ pollution and its health and climate impacts. ~~Many studies~~Studies have shown ~~reasonable simulations~~that the CTMs can reproduce the spatial and temporal variations of the surface $PM_{2.5}$ concentrations in China ~~by the CTMs~~. For example, the Weather Research and Forecasting/Community Multi-scale Air Quality (WRF/CMAQ) model has reproduced the monthly-averaged concentrations of $PM_{2.5}$ at the air-quality sites in 60 Chinese cities (J. Hu et al., 2016). The MICS-Asia Phase III studies further show the normalized mean biases (NMBs) of less than 50% for daily or monthly mean $PM_{2.5}$ concentrations ~~in~~for various CTMs (Gao et al., 2018; Chen et al., 2019). However, when the ~~model performance on~~simulations of $PM_{2.5}$ ~~is component-dependent and may contain compensation~~components have compensating errors, ~~which~~the model still reproduces the $PM_{2.5}$ mass and biases the evaluation of the effectiveness of the emission control strategies. ~~Recent model~~Model evaluations in China have reached an agreement that the CTMs generally underestimate the concentrations of organic aerosol (OA) (Fu et al., 2012; Han et al., 2016) and sulfate (Wang et al., 2014; G. J. Zheng et al., 2015) but overestimate the concentrations of nitrate (Wang et al., 2013; Chen et al., 2019). ~~During~~The underestimation of OA and the ~~severe haze periods,~~overestimation of nitrate also present in the ~~models often significantly underestimate~~studies for the ~~$PM_{2.5}$~~US and Europe, while the sulfate concentrations are reproduced in those regions (~~Wang~~Heald et al., ~~2014; G. J. Zheng~~2012; Drugé et al., ~~2015~~2019; Jiang et al., 2019).

Uncertainties exist in meteorological fields, emission inventories, and the physical and chemical processes, which contribute to the model biases in the $PM_{2.5}$ simulations. For example, models are well recognized to reproduce temperature (T) and relative humidity (RH), but are difficult to capture the near-surface wind fields (Guo et al., 2016a; Gao et al., 2018; J. Hu et al., 2016). Boundary layer structures greatly affect the $PM_{2.5}$ concentrations (Z. Li et al., 2017; Su et al., 2018). Evaluations of the boundary layer (e.g., boundary layer height (BLH)) in the CTMs are ~~however~~ limited (Bei et al., 2017; Chen et al., 2016). For ~~typical~~ primary ~~components~~$PM_{2.5}$ and the secondary precursors of $PM_{2.5}$, the uncertainties of their emissions in Asia ~~range~~are large, ranging from tens to several hundreds of percent (M. Li et al., ~~2017~~2017b). The bottom-up and top-down estimates of the emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3), volatile organic compounds (VOCs) and organic carbon (OC) show significant differences in magnitude and seasonal variability (Koukouli et al., 2018; Qu et al., 2019; L. Zhang et al., 2018; Cao et al., 2018; Fu et al., 2012).

For sulfate, the model underestimation has been attributed largely to the heterogeneous production. The proposed heterogeneous formation mechanisms include the SO_2 oxidation by nitrogen dioxide (NO_2) directly (Cheng et al., 2016; Wang et al., 2016) or indirectly (L. Li et al., 2018), by O_2 via transition-metal-ion (TMI) catalysis (G. Li et al., 2017) or radical chain reactions (Hung and Hoffmann, 2015; Hung et al., 2018), and by hydrogen peroxide (Ye et al., 2018). Among them, TMI-catalyzed oxidation of SO_2 perhaps dominates the sulfate formation during the haze periods, constrained by the observations of sulfate oxygen isotopes (Shao et al., 2019). ~~Although the~~The mechanisms are still under debate~~, the~~. The heterogeneous formation ~~has been~~can however be simplified in models as a reactive uptake process to achieve a better agreement of sulfate concentrations ~~during the haze episodes~~ (Wang et al., 2014; G. J. Zheng et al., 2015; J. Li et al., 2018). ~~For nitrate~~Similar to sulfate, the contribution of heterogeneous chemistry to the nitrate formation remains ~~largely uncertain~~unclear. The uptake coefficients of dinitrogen pentoxide (N_2O_5), NO_2, and nitrate radical ($NO_3\cdot$) are sensitive to experimental conditions and range by orders of magnitude (Bertram and Thornton, 2009; McDuffie et al., 2018; Brown and Stutz, 2012; Spataro and Ianniello, 2014). The parameterizations of nitrate heterogeneous production ~~of nitrate~~ differ significantly among models (Holmes et al., 2019; Alexander et al., 2020; J. Li et al., 2018; Wang et al., 2012). ~~The simulations of sulfate and nitrate affect the simulation of ammonium through thermodynamic equilibrium.~~

For OA, the complexity of its secondary formation and aging processes and the lack of emission inventories of intermediate-volatility (IVOCs) and semivolatile organic compounds (SVOCs) affect the model performance (Chen et al., 2017 and references therein). Substantial model-observation discrepancies present in the comparisons of the mass concentration and the oxidation state of OA as well as the contributions of various formation pathways (Tsigaridis et al., 2014; Heald et al., 2011; Chen et al., 2015). Moreover, the oxidant levels affect the chemical processes (Lu et al., 2018). The model capability in simulating the concentrations of major oxidants like hydroxyl radical ($OH\cdot$) and hydroperoxy radical ($HO_2\cdot$) are rarely evaluated. In addition, unusual biases of the meteorological fields and chemical processes may occur during the severe haze periods (daily mean $PM_{2.5} > 75\ \mu g\ m^{-3}$) (An et al., 2019). The models often significantly underestimate the $PM_{2.5}$ concentrations during the haze events (Wang et al., 2014; G. J. Zheng et al., 2015). Various model biases from meteorology, emissions, and the physical and chemical processes interact with each other nonlinearly. It is therefore important to evaluate the model for all individual components of $PM_{2.5}$.

~~The net model bias caused by the above factors can be non-linear. Various factors may interact with each other and thus alter the model bias, which needs to be evaluated systematically.~~ On the other hand, observations may be biased ~~and contribute to~~, which is rarely considered when evaluating the model-observation discrepancies. For example, filter-based analysis of the $PM_{2.5}$ components can contain positive or negative artifacts for semivolatile species, resulting from improper use of denuder and back-up filters (Liu et al., 2014). Such artifacts are often large (>50%) (Chow, 1995) and have been ignored in most model-observation comparisons (Wang et al., 2013; Qin et al., 2015). Online measurements by aerosol mass spectrometers have less uncertainty (~30%) compared to filter-based analysis (Canagaratna et al., 2007). Most of the measurements are however

conducted for submicron particles (DeCarlo et al., 2006; Ng et al., 2011). The particulate mass in the supermicron domain needs to be considered in the model-observation comparisons (Elser et al., 2016).

In this study, we synthesized a comprehensive dataset of the concentrations of major $PM_{2.5}$ components (i.e., sulfate, nitrate, ammonium, and OA) from 55 online measurements at urban sites and 22 at non-urban sites in China. ~~We evaluate the~~The latest version of GEOS-Chem nested-grid model simulations were evaluated with this dataset as well as a long-term online dataset that consists of hourly measurements of the major $PM_{2.5}$ components from 2011 to 2013 in Beijing. Potential factors that may contribute to the model-observation gaps ~~are~~were discussed. ~~We also~~Sensitivity analyses were conducted ~~sensitivity analysis~~ for two case periods to ~~show~~evaluate the ~~potential~~ contributions of ~~different~~the individual potential factors to the model-observation gaps and the contributions of various combinations of these factors.

2 Description of Observations

The campaign-average mass concentrations of sulfate, nitrate, ammonium, and OA as well as the sampling information are listed in Table S1 of the Supporting Information (SI), including 77 surface online measurements from 2006 to 2016 in China. The dataset covers the regions of North China Plain (NCP), Yangtze River Delta (YRD), Pearl River Delta (PRD), and Northwest China (NW). The measurements ~~are~~were made by Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), quadrupole aerosol mass spectrometer (Q-AMS), and aerosol chemical speciation monitor (ACSM~~) and~~), which are mostly for submicron particles (Y. J. Li et al., 2017). ~~We also compared our model simulations to~~The long-term ACSM measurements of submicron particle composition at ~~the~~an urban site ~~of~~in the Institute of Atmospheric Physics, Beijing (IAP, 39°58′28″ N, 116°22′16″ E) from July 2011 to May 2013 are also used herein (Sun et al., 2015). The long-term data have a time resolution of 15 minutes and were averaged to an hour when comparing with the model results. All data were corrected by collection efficiency as stated in the original publications. ~~Our recent measurements show that the submicron-to-fine ratios for sulfate, nitrate, ammonium, and OA are quite similar (i.e., 0.8) for the summertime and wintertime measurement periods in Beijing except for the severe winter haze episodes under high RH (i.e., about 0.5) (Fig. S1 in SI) (Zheng et al., 2020). For simplicity, we divided the observation data herein~~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 haze episodes under high RH (Fig. S1 in SI) (Zheng et al., 2020; Sun et al., 2020). We therefore divided the submicron observation data by 0.8 for the four species when comparing to the model results.

The meteorological parameters (e.g., T, RH, wind speed, and wind direction) and the concentrations of gaseous pollutants including ozone (O_3), carbon monoxide (CO), SO_2, and NO_2 were measured at the Peking University Urban-Atmosphere Environment Monitoring Station (PKUERS, 39°59’21” N, 116°18’25” E) from July 2011 to May 2013. Both the IAP and PKUERS sites are in the same GEOS-Chem model grid. The monthly mean NH_3 concentrations are taken from the 2007-2010

observations at the IAP site (Pan et al., 2012). The BLH in Beijing (39°48'00" N, 116°28'12" E) was derived from the radiosonde observations at 8 AM, 2 PM (only in the summer), and 8 PM during July 2011 to May 2013 by using bulk Richardson algorithms (Guo et al., 2016b; Guo et al., 2019). All the hours refer to Beijing time (UTC+8). The radiosonde-derived BLH is greater in spring and summer and lower in autumn and winter, which is consistent with the findings from the satellite observations and the ground-based ceilometer measurements (W. Zhang et al., 2016; Tang et al., 2016).

Moreover, the observed concentrations of OH· and HO_2·, gaseous nitrous acid (HONO) and nitric acid (HNO_3), and isoprene in Beijing are taken from literature, including the studies in south Beijing (Wangdu, 38°39'36" N, 115°12'00" E) from 7 June to 8 July 2014 and in north Beijing (Huairou, 40°24'36" N, 116°40'48" E) from 6 January to 5 March 2016 (Tan et al., 2017; Tan et al., 2018; Liu et al., 2019), and additional isoprene measurements at the PKUERS site during the summer of 2011 (Zhang et al., 2014). The observed concentrations of NO_3· and aromatic compounds are taken from the measurements at the PKUERS site in September 2016 (Wang et al., 2017a) and in summer and winter of 2011-2012 (Wang et al., 2015), respectively.

3 Model Description

The atmospheric chemical transport model GEOS-Chem 12.0.0 (~~http://geos-chem.org~~DOI: 10.5281/zenodo.1343547) was run at nested grids with 0.5°×0.625° horizontal resolution over Asia and adjacent area (11°S-55°N, 60°-150°E) and 47 vertical levels between the surface and ~0.01 hPa. Boundary conditions were provided by the global simulations at 2°×2.5° horizontal resolution. Both global and nested simulations were spun up for one month. MERRA2 reanalysis meteorological data from the NASA Global Modeling and Assimilation Office (GMAO) were used to drive the model. ~~Model~~For comparisons with long-term observations at IAP, the model simulations were ~~run~~performed for the ASCM measurement ~~period of July 2011 to May 2013 to compare with long term data sets~~periods. When comparing with the campaign-average data, the model simulations for the year of 2012 were used. For other comparisons, the model simulations were run for the measurement periods.

The GEOS-Chem model simulates the ozone-NOx-hydrocarbon-aerosol chemistry (Park et al., 2003; Park et al., 2004; Liao et al., 2007). Aerosol thermodynamic equilibrium is performed by ISORROPIA-II (Fountoukis and Nenes, 2007; Pye et al., 2009). The simulation of OA includes primary organic aerosol (POA) and secondary organic aerosol (SOA). The model assumes that 50% of POA emitted from combustion sources are hydrophobic and hydrophobic POA converts to hydrophilic POA with an e-folding time of 1.15 days. A ratio of 1.6 is applied to account for the non-carbon mass in POA (Turpin et al., 2000). SOA is simulated by the Simple SOA scheme (Hodzic and Jimenez, 2011; Kim et al., 2015). SOA precursor surrogates are estimated from the emissions of biogenic volatile organic compounds (i.e., isoprene and terpenes) and CO from the combustion of biomass, biofuel, and fossil fuel. The Simple SOA scheme assumes that the irreversible conversion from precursors to particle-phase SOA takes a fixed timescale of 1 day and that 50% of biogenic SOA precursors are emitted as particle-phase SOA. The SOA yields of isoprene and terpenes are set to be 3% and 10%, respectively. The SOA yield of biomass burning emissions is set to be 1.3% of CO, and the yield for fossil-fuel combustion is set to be 6.9%. These yields are

derived from the observed ratios between SOA and CO in aged air masses from the studies in the United States (US) (Hayes et al., 2015) and are able to reproduce the OA mass without detailed SOA chemistry in the southeast US (Kim et al., 2015). Because of the lack of related measurements in China, we did not change these yields herein.

Wet depositions of soluble aerosols and gases include convective updraft, rainout, and washout as described by Liu et al. (2001). SOA is treated as highly soluble with a fixed Henry's law coefficient of 10^5 M atm^{-1} and a scavenging efficiency of 80% ~~for simplicity~~ (Chung and Seinfeld, 2002). The Henry's law coefficients may vary in magnitudes depending on the SOA types (Hodzic et al., 2014). However, Hodzic et al. (2016) ~~shows similar vertical profiles of~~ show that the modeled SOA ~~mass for using the fixed 10^5 M atm^{-1} and~~masses are not sensitive to the ~~volatility dependent~~changes of Henry's law coefficients. Dry deposition is calculated by a standard resistance-in-series model for the aerodynamic, boundary-layer, and canopy-surface resistance (Wesely, 1989).

Heterogeneous uptake of SO_2 into aerosol liquid water is not included in the standard simulations but in the sensitivity runs in Sect. 4.3. The parameterizations of the SO_2 uptake coefficient (γ_{SO2}) include γ_{SO2} depending on RH or on aerosol liquid water content (ALWC) (B. Zheng et al., 2015; J. Li et al., 2018). The heterogeneous uptake of N_2O_5 and NO_2 is an important contributor to nitrate in northern China (Wang et al., 2017b; Wen et al., 2018). The uptake coefficients of γ_{N2O5} and γ_{NO2} on the aerosol surface vary by several orders of magnitude, depending on temperature, particle particle-phase state, composition, ALWC, pH and so on (Bertram and Thornton, 2009; Abbatt et al., 2012; McDuffie et al., 2018 and references therein). The standard model uses relatively high values of γ_{N2O5} and γ_{NO2} (McDuffie et al., 2018; Davis et al., 2008). Lower values are tested in the sensitivity runs. For SOA, the heterogeneous formation varies by sources and aging processes (Donahue et al., 2012). Heterogeneous production of SOA is not tested in the model because of the lack of good parameterizations (Chen et al., 2017).

Global anthropogenic emissions in GEOS-Chem are provided by the Community Emissions Data System (CEDS) (Hoesly et al., 2018), including the monthly emissions of gaseous pollutants (SO_2, NO_x, NH_3, CH_4, CO, and VOCs) and carbonaceous aerosols (black carbon (BC) and OC). Anthropogenic emissions of CO, NO_x, SO_2, BC, OC, and VOCs in China are provided by the Multi-resolution Emission Inventory for China (MEIC v1.3; http://meicmodel.org) for the years of 2010, 2012, and 2014. The emissions in 2011 and 2013 are interpolated from the emissions of the two adjacent years. We use an improved inventory for agriculture emissions of NH_3 in China (L. Zhang et al., 2018). This inventory shows stronger peak emissions in the summer than other inventories such as the Regional Emission in Asia (REAS2), PKU-NH_3, and the Emission Database for Global Atmospheric Research (EDGAR~~) show;~~), which agrees better with the top-down estimates~~. The non-agricultural NH_3 emissions in China are taken from the study done by Huang~~(L. Zhang et al~~. ~~(2012~~., 2018). The non-agricultural NH_3 emissions in China are taken from the study done by Huang et al. (2012), which is based on the year of 2006 and represents the low-end estimates as the emissions increased rapidly after 2006 (Kang et al., 2016; Meng et al., 2017). Tables S2 in SI lists the total anthropogenic emissions of primary $PM_{2.5}$ and the gaseous precursors of $PM_{2.5}$ in China for 2012. The MIX Asian emission inventories are used for the anthropogenic emissions in the rest part of Asia (M. Li et al., ~~2017~~2017b), which has combined the South Korea inventory (CAPSS) (Lee et al., 2011), the Indian inventory (ANL-India) (Lu et al., 2011; Lu and Streets, 2012)

and the REAS2 inventory (Kurokawa et al., 2013). Our simulations used sector-specific MEIC diurnal patterns for the anthropogenic emissions of CO, NO_x, SO_2, BC, OC, and VOCs from power, industry, residential, transportation, and agriculture sectors (Fig. S2 in SI) and the MEIC agriculture diurnal patterns for all anthropogenic emissions of NH_3 in China. NO_x emission from soils and lightning are included in the model (Hudman et al., 2012; Murray et al., 2012). The biogenic emissions are calculated from the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.1) (Guenther et al., 2012). The emissions from biomass burning are provided by the Global Fire Emission Database (GFED4) (Giglio et al., 2013).

~~Heterogeneous uptake of SO_2 into aerosol liquid water is not included in the standard simulations but in the sensitivity runs in Sect. 4.3. The parameterizations of the SO_2 uptake coefficient (γ_{SO2}) include γ_{SO2} depending on RH or on aerosol liquid water content (ALWC) (B. Zheng et al., 2015; J. Li et al., 2018). The heterogeneous uptake of N_2O_5 and NO_2 is an important contributor to nitrate in northern China (Wang et al., 2017; Wen et al., 2018). The uptake coefficients of γ_{N2O5} and γ_{NO2} on the aerosol surface vary by several orders of magnitude, depending on temperature, particle-particle phase state, composition, ALWC, pH and so on (Bertram and Thornton, 2009; Abbatt et al., 2012; McDuffie et al., 2018 and references therein). The standard model uses relatively high values of γ_{N2O5} and γ_{NO2}. Lower values are tested in the sensitivity runs. For SOA, the heterogeneous formation varies by sources and aging processes (Donahue et al., 2012). We did not include any heterogeneous production of SOA because of the lack of good parameterizations (Chen et al., 2017).~~

4 Results and Discussion

4.1 Compensating errors ~~in simulating~~from simulations of individual $PM_{2.5}$ components

Figure 1 shows the scatter plots of the simulated and the observed campaign-average concentrations of secondary inorganic aerosol (SIA) and OA over China as well as the statistical values such as NMB, root mean square error (RMSE), and Pearson's correlation coefficient (R) for the model-observation comparisons. For most of the sites, the sulfate concentrations are underestimated (NMB = −0.39, R = 0.45), while the nitrate concentrations are overestimated (NMB = 0.82, R = 0.57) by the model. Such underestimation for sulfate and the overestimation for nitrate in CTMs is a known problem for China (Gao et al., 2018; Chen et al., 2019). The ~~simulations of~~model performance for ammonium ~~concentrations~~ (NMB = 0.06, R = 0.58) ~~are~~is better than the ~~simulations~~performances for sulfate and nitrate. For OA, previous model studies typically underestimate the OA mass concentrations by over 40% (Fu et al., 2012; Zhao et al., 2016). ~~The model herein shows improved performance by using the Simple SOA scheme (NMB = −0.26, R = 0.70). Moreover, the model biases vary by season. For example, the sulfate concentrations are mostly underestimated in winter (Fig. 1*a*) when the SO_2 emissions are plausibly underestimated (Wang et al., 2014; Koukouli et al., 2018). The model-observation agreement for nitrate is the best in winter (Fig. 1*b*~~The Simple SOA scheme shows improved performance on OA for all seasons (NMB = −0.26, R = 0.70).

On a seasonal basis, the underestimation of sulfate occurs all year round, and the greatest underestimation occurs in winter (NMB = −0.54) (Fig. 1*a* and Table S3). The seasonality of the model bias is partially explained by the underestimation of SO_2

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. By contrast, the nitrate concentrations are largely overestimated in all seasons, especially in spring, summer, and autumn (NMB = 0.79-1.28). Wang et al. (2013) showed the summertime overestimation for East Asia. Heald et al. (2012) showed the summer-, autumn-, and winter-time overestimation for the eastern US. The model bias is smaller in winter (NMB = 0.41) when higher concentrations of nitrate present (Fig. 1*b*). For ammonium, the model underestimates its concentrations in winter and spring but overestimates its concentrations in summer and autumn. Both the uncertainties of HNO_3 and NH_3 simulations may affect the modeled ammonium concentrations (Wen et al., 2018; Xu et al., 2019). Similar to sulfate, the underestimation of OA occurs all year round, and the model performs worst 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 for the seasonality of the OA bias. The *R* value is much lower in summer (i.e., 0.28 compared with ≥ 0.49 in other seasons), showing more complexity of the biases in the OA simulations.

Tables ~~S2, S3,~~S4 and ~~S4~~S5 in SI list the statistical values for the model-observation comparisons in different regions~~,~~ and urban ~~or~~versus non-urban sites~~, and various seasons~~, respectively. The model biases for sulfate, nitrate, and OA are consistently positive or negative among regions (Table ~~S2~~S4), suggesting that the model biases are general problems in China. The underestimation of sulfate is over 40% (NMB) in most regions except YRD, and the overestimation of nitrate is over 80% (NMB) in most regions except NW. The OA simulations show much lower NMB (−10%) and RMSE values in YRD and PRD than in NCP and NW. For ammonium, the model significantly overestimates its concentrations in YRD and underestimates its concentrations in NW. The former may be explained by the excessive formation of ammonium nitrate and ammonium sulfate through thermodynamic equilibrium under conditions of abundant NH_3 ~~emissions (L. Zhang et al., 2018) and overestimated nitrate concentrations (Wang et al., 2013)~~ in YRD in the model~~.~~ (L. Zhang et al., 2018). The latter is likely a result of combined factors including emissions, meteorology, and thermodynamic equilibrium. Moreover, the mean observed concentrations of sulfate, nitrate, ammonium, and OA at urban sites are 20-90% greater than those at non-urban sites (Fig. 1 and Table ~~S3~~S5). The model ~~also~~ shows greater simulated concentrations of nitrate, ammonium, and OA at urban sites, ~~similar to~~which is consistent with the observations. The model-observation gaps for nitrate (NMB = 1.22) and ammonium (NMB = 0.33) are greater in non-urban areas, whereas the gaps for sulfate (NMB = −0.44) and OA (NMB = −0.31) are greater in urban areas. This result suggests perhaps different driving forces of the model biases for the SIA species.

~~For seasonal variations, the underestimation of sulfate occurs all year round, and the greatest underestimation occurs in winter (NMB = −0.54) (Table S4). Similar to other models, our model failed to reproduce the high sulfate concentrations during the winter haze periods (Wang et al., 2014; G. J. Zheng et al., 2015). By contrast, the nitrate concentrations are largely overestimated in spring, summer, and autumn (NMB = 0.79-1.28). The model bias is much smaller in winter (NMB = 0.41) when higher concentrations of nitrate present. Wang et al. (2013) also showed the summertime overestimation for East Asia.~~

~~Heald et al. (2012) showed the summer-, autumn-, and winter-time overestimation for the eastern US.~~ ~~To sum up, the large overestimation of nitrate happens in most seasons and regions, and is more severe in non-urban sites.~~ ~~For ammonium, the model underestimates its concentrations in winter and spring but overestimates its concentrations in summer and autumn. Both the uncertainties of HNO_3 and NH_3 simulations may affect the modeled ammonium concentrations (Wen et al., 2018; Xu et al., 2019).~~ ~~The underestimation of OA is another year-round problem, and the worst case happens in autumn. The *R* value however is much lower in summer (i.e., 0.28 compared with ≥ 0.5 in other seasons), showing the complexity of the OA simulations.~~

The model simulations are further compared ~~to~~with the ~~long-term~~2-year hourly observations in Beijing. Figure S3 in SI shows the simulation-to-observation ratios for the SIA species and OA. The mean and median values of the simulation-to-observation ratios of the mass concentrations of non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$) are generally within the measurement uncertainty of 30%. Compensation of the underestimation of sulfate and OA ~~and~~by the overestimation of nitrate leads to the good performance on NR-$PM_{2.5}$. The seasonal variations of the model biases for the SIA species and OA in Beijing are consistent with the findings in the nation-wide comparisons (Table ~~S4~~S3), except that the greatest underestimation of OA occurs in spring instead of autumn. 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 ~~those in Fig. S3~~the previous results, suggesting insignificant impacts of haze periods on the statistic evaluations.

Figure 2 shows the diurnal patterns of the observed and the simulated concentrations of sulfate, nitrate, ammonium, and OA for four seasons in Beijing. Considerable differences exist. For instance, 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 ~~however~~ show ~~insignificant~~less daytime ~~concentrations~~concentration elevations ~~in the model,~~(0-2 μg m^{-3}), suggesting insufficient production, overestimated boundary-layer dilution, or removal during the day in the model (Fig. 2*a*). By contrast, the observed diurnal variations of hourly-mean nitrate and ammonium concentrations ~~show flatter diurnal patterns~~are less than sulfate (Fig. ~~2*b-c*).~~2*b-c*). The 2-5 times greater concentrations of simulated nitrate at night suggest over-predicted nighttime production, underestimated boundary-layer dilution, or underestimated atmospheric removal of nitrate. Nighttime production of nitrate by the heterogeneous uptake of N_2O_5 and NO_2 is ~~a major~~an important pathway of nitrate production in northern China (Wang et al., 2018; Alexander et al., 2020)~~. The 2-5 times greater concentrations of simulated nitrate at night suggest overpredicted nighttime production, underestimated boundary-layer dilution, or underestimated removal of nitrate.~~. On the other hand, the simulated profiles for nitrate and ammonium show large reductions of daytime concentrations especially in summer, which are not shown in the observed profiles. ~~This may suggest insufficient daytime production of nitrate, overestimated daytime boundary-layer dilution or removal, or overestimated evaporation of ammonium nitrate in the model. It is unclear whether the model treats the thermodynamics of evaporation properly when particles are coated with OA (Li et al., 2016). The model~~

~~largely overestimates gaseous HNO_3 concentrations in Beijing (Fig. S5 in SI). If the evaporation of ammonium nitrate is limited because of the coating, the daytime variations of ammonium nitrate can be flatter and the daytime HNO_3 concentrations may be lower.~~The model largely overestimates daytime gaseous HNO_3 concentrations in Beijing (Fig. S5 in SI). The total nitrate (particulate nitrate + gaseous HNO_3) accumulated excessively in the model simulations, which needs further investigations.

For OA, the model is unable to reproduce the midday and evening peaks for all seasons (Fig. 2*d*). Previous positive matrix factorization (PMF) analysis of the OA mass spectra suggests that cooking emissions contribute to the midday peaks of the OA concentrations and the evening peaks are driven by mixed primary emissions including cooking, traffic, and coal combustion (W. Hu et al., 2016; Sun et al., 2015). Cooking emissions are not included explicitly in the model, and the emissions of POA and SOA precursors from traffic and coal combustion are uncertain (Tao et al., 2018; Peng et al., 2019). We compared the modeled POA and SOA with PMF-derived POA and oxygenated OA (OOA) (Sun et al., 2018). The model reproduces the monthly mean concentrations of PMF-derived POA (Fig. 3*a*), suggesting that the MEIC POA inventory generally represents the particle-phase SVOCs emissions under ambient conditions. The model underestimation of OA is mainly from SOA as indicated by the underestimation of the monthly mean concentrations of PMF-derived OOA (i.e., 50-70% of the observed OA mass) (Fig. 3*b*). Figures S6 and S7 in SI show the model performance of the Simple SOA scheme and the traditional scheme (so-called Semivolatile POA scheme in GEOS-Chem) in simulating OA. The Semivolatile POA scheme significantly underestimates both POA and SOA. ~~This scheme treats 1.27 times of the POA inventory as the SVOC emissions, among which only 1.5% of the carbon remains as POA (Pye and Seinfeld, 2010)~~This scheme treats 1.27 times of the POA inventory as the SVOC emissions, among which only 1.5% of the carbon remains as POA (Pye and Seinfeld, 2010). There is also a lack of constraints on the SOA production from IVOCs and SVOCs. In addition, the modeled profiles show earlier morning peaks of OA especially in winter, which is mainly caused by the POA emissions of the residential sector. The lack of this feature in the observed OA mass suggests perhaps an overestimation of this source.

4.2 Potential contributors to the model-observation discrepancies

We focus here on measurements in Beijing to discuss about the potential contributors to the model bias. Table 1 lists the statistics including mean bias (MB), NMB, and RMSE of T, RH, wind speed, wind direction, and BLH between the MERRA2 outputs and the observations in Beijing. The MERRA2 reanalysis reproduces T (NMB < 2%) and RH (NMB < 15% except for winter) but is unable to reproduce the wind speed and directions. Large RMSE for surface wind directions is a common problem in meteorological reanalysis products as well as the WRF simulations. The overestimation of wind speed (1-2 times) is slightly greater than the bias reported in other studies and may cause some underestimation of $PM_{2.5}$ (J. Hu et al., 2016; Wang et al., 2014). The MERRA2 slightly overestimates 2 PM BLH compared with the radiosonde measurements in summer (NMB = 0.34). For 8 AM and 8 PM, MERRA2 underestimates the radiosonde-derived BLH in autumn and winter. Bei et al. (2017) indicated that the ~~uncertainty~~uncertainties in temperature and wind field simulations ~~leads~~lead to the frequent

underestimation of the nighttime BLH in January 2014 in Beijing by the ensemble WRF meteorology. Such underestimation of BLH may lead to overestimated nighttime concentrations of $PM_{2.5}$ in autumn and winter. The large RMSE values for the BLH comparisons at 8 AM and 8 PM suggest that the nighttime simulation of $PM_{2.5}$ may have greater meteorological uncertainty than the daytime simulation (Fig. S8 and Table 1).

The uncertainties related with the emission ~~inventories of SIA and SOA precursors~~data including their temporal profiles are considered to be important ~~model inputs~~sources of inaccuracies in modeled concentrations (~~Huang~~M. Li et al., ~~2014~~2017a). The uncertainty of SO_2 emissions affects surface sulfate concentrations. Our model underestimates SO_2 concentrations in winter and overestimates its concentrations in summer in Beijing (Fig. 4*a*). Consistently, top-down estimates suggest lower SO_2 emissions in summer and higher in winter in China compared with the MEIC inventory (Koukouli et al., 2018). Improving SO_2 emissions may reduce the model bias for sulfate. Our model largely underestimates NO_2 concentrations year round (Fig. 4*b*). The bottom-up NO_x inventory has about 50% of uncertainty (M. Li et al., ~~2017~~2017b). Top-down estimates suggest however lower NO_2 emissions in Beijing and its surrounding area than the MEIC inventory (Qu et al., 2017)~~.~~, which conflicts with the underestimation of NO_2. The relatively coarse model grid is probably a reason for the low modeled NO_2 concentrations at the site. Moreover, laboratory and field measurements show that the NO_2 uptake coefficient (γ_{NO2}) on the aerosol surface ranges from 10^{-8} to 10^{-4} (Spataro and Ianniello, 2014 and references therein; M. Li et al., 2019 and references therein). The default GEOS-Chem model uses a relatively high γ_{NO2} of 10^{-4}, which may cause the underestimated NO_2 concentrations as well as the overestimated concentrations of nitrate, daytime HNO_3~~, HONO, (Fig. S5),~~ and ~~nitrate and needs further evaluation~~nighttime HONO (Fig. S9) ~~(Alexander et al., 2020).~~(Alexander et al., 2020). The NO_2 concentration increased over 70% when the model turned off the NO_2 uptake. For NH_3, the model underestimates its monthly mean concentrations in Beijing (Fig. 4*c*). The non-agriculture NH_3 emissions are based on the year of 2006 and can be greater in 2012 because of the rapid economic growth (Kang et al., 2016; Meng et al., 2017). Several studies show that the non-agriculture emissions are the dominant NH_3 sources during haze periods in Beijing when the transport of rural agricultural NH_3 emission to urban is limited under stagnant weather conditions (Pan et al., 2016; Sun et al., 2017). The underestimation of NH_3 affects the ammonium simulations when the thermodynamic equilibrium is ~~limited by gaseous NH_3. For SOA precursors, Fig.~~sensitive to HNO_3+NH_3 (Nenes et al., 2020). For SOA precursors, Figure 4*d* shows that the model underestimates surface CO concentrations in Beijing, which may contribute to the model underestimation of anthropogenic SOA. The modeled summertime isoprene concentrations in Beijing are lower than the observations by 20-~~50~~90%, affecting the simulations of biogenic SOA (Table ~~S5~~S6 in SI). The model also underestimates the aromatic VOC concentrations, similar to previous studies (Liu et al., 2012). ~~However, such~~Such underestimation ~~has little influence on~~ would not affect the SOA simulations herein because that ~~aromatic SOA is modeled by the parameterization on CO in~~ the Simple SOA scheme no longer derive aromatic SOA from the aromatic VOC concentrations. Instead, the model treats aromatic SOA as a part of anthropogenic SOA, which is estimated on the basis of the parameterizations on CO.

Oxidants are essential to chemical ~~conversion~~conversions. Figure 5*a-b* shows the modeled and the observed concentrations of OH· and HO_2· radicals in Beijing. The peak concentrations of OH· and HO_2· radicals are underestimated by a factor of 1.5-2 and 2-4, respectively, explained by the missing source of daytime HONO (Fig. S9) (Liu et al., 2019; L. Zhang et al., 2016; J. Zhang et al., 2018). Such underestimation suggests insufficient atmospheric oxidation capacity in the model, meaning reduced formation of sulfate and nitrate. Figure 5*c* shows that the model overestimates the surface O_3 concentrations in winter. Common problems have been reported in other studies in China and other northern hemisphere places by various CTMs (J. Hu et al., 2016; Travis et al., 2016; Young et al., 2018; J. Li et al., 2019). Nevertheless, the overestimated O_3 has little influence on the SOA simulation by the Simple SOA scheme and has minor impacts on SIA because of the dominant contribution from the photochemical and heterogeneous pathways. Moreover, NO_3· affects the formation of nitrate and SOA (Ng et al., 2017). Measurements of NO_3· in Beijing shows nighttime peak concentrations of less than 6 pptv in summer and below the detection limit of 2.~~7 pptv in winter.~~4 pptv in winter (Wang et al., 2017a). The modeled concentrations are three times greater than the peak concentrations in summer (Fig. 5*d*), suggesting a possible overestimation of nighttime oxidation.

In addition, the heterogeneous production of sulfate and SOA are not included in the standard models, leading to certain underestimations. The model uses relatively high values of γ_{N2O5} ~~and ignores the formation~~ , which may lead to the overestimation of nitrate (McDuffie et al., 2018; Davis et al., 2008; Jaegle et al., 2018). The lack of nitryl chloride formation from the N_2O_5 uptake~~, both leading~~ in the model may contribute to the overestimation of nitrate in northern China (~~McDuffie~~Sarwar et al., ~~2018; Davis et al., 2008; Jaegle et al., 2018~~2014). Another bias is the high default value of γ_{NO2} as described previously. Biases may also relate to the atmospheric removal of the SIA species~~.~~ (Jaegle et al., 2018; Luo et al., 2019). For example, the GEOS-Chem model underestimates the wet deposition of nitrate in China by 15-23%, especially in urban areas ~~in summer~~, which may affect both nitrate and ammonium in summer when the wet-deposition fluxes are large (Zhao et al., 2017; Xu et al., 2018~~; Jaegle et al., 2018; Luo et al., 2019~~). The model possibly overestimates the surface resistance of HNO_3 ~~is overestimated in the model~~ (Shah et al., 2018)~~, although the~~. The test with doubling the deposition velocity of HNO_3 however suggests a minor impact of this factor on the nitrate simulations (Heald et al., 2012). ~~The~~Finally, the photolysis of particle-phase nitrate may be significant and affect the nitrate concentrations (Romer et al., 2018; Kasibhatla et al., 2018). In Beijing, the photolysis rate of particle-phase nitrate ~~affects the loss of nitrate (Romer et al., 2018; Kasibhatla et al., 2018). In Beijing, particulate nitrate may have lower photolysis rates because of the high mass concentrations~~ remains unclear, and the thick coating of $PM_{2.5}$ may reduce the photolysis (Ye et al., 2017).

4.3 Relative importance of various factors to the model bias

~~For~~From the ~~various~~ factors described above, we chose the ones that are expected to significantly affect the $PM_{2.5}$ simulations and can be constrained by ambient or laboratory measurements to conduct the sensitivity analysis. Their potential contributions to the model bias of $PM_{2.5}$ components are evaluated for two case periods, 21-26 August 2012 and 21-27 December 2012 for summer and winter, respectively. The simulations for both weeks show the highest *R* value for the correlations with the

observations during the seasons. ~~Both of the~~The two weeks are ~~absent from~~chosen to address general model biases that are not specific to haze conditions. No severe haze episodes occurred during ~~which unusual biases of the meteorological fields and chemical processes may occur~~the two weeks.

The tested factors for the sensitivity runs are listed in Table 2. Case 0 represents the standard model simulations. The nighttime BLH was multiplied by 3.6 based on the lowest median value of the MERRA2-to-observation ratios at 8 AM and 8 PM (Fig. S8) when the original BLH was lower than 500 m (i.e., the median of the observed BLH) in Case 1. The SO_2 emissions in China were multiplied by 0.8 in summer and 1.5 in winter in Case 2 based on the minimum and maximum values of the ratios between the top-down estimates provided by Koukouli et al. (2018) and the MEIC inventory (Fig. S10), respectively. The non-agriculture NH_3 emissions in China were scaled up by 1.4 as suggested by Kang et al. (2016) in Case 3. In Case 4, the reaction rate coefficients for the reactions that directly involve OH· oxidation and affect the formation and loss of $PM_{2.5}$ such as the gaseous formation of sulfuric acid and HNO_3 and the oxidation of HNO_3 were multiplied by 1.5 in summer and 2 in winter to offset the influence of underestimated OH· concentrations. The multipliers of 1.5 and 2 were derived on the basis of the largest ratio of simulated to observed hourly mean OH· concentrations between 9 AM to 3 PM. In terms of the heterogeneous formation of sulfate, we added two types of parameterizations for γ_{SO2} in Cases 5 and 6. One derives the uptake coefficient of SO_2 from RH ($\gamma_{SO2\text{-}RH}$) (B. Zheng et al., 2015), and the other calculates the coefficient as a function of ALWC ($\gamma_{SO2\text{-}ALWC}$) (J. Li et al., 2018). The former is in the order of 10^{-5}, and the latter is in the range of 10^{-6} to 10^{-4}. For comparisons, the uptake coefficients are 5×10^{-5} in G. Li et al. (2017) and 10^{-9} to 10^{-3} in Shao et al. (2019). In Case 7, we reduced the value of γ_{N2O5} from the parameterization of Evans and Jacob (2005) to 10^{-3} to represent the lower end in the world-wide observations (McDuffie et al., 2018 and references therein). Similarly, the γ_{NO2} was modified from 10^{-4} to 10^{-6} in Case 8 according to the median value of recent laboratory results (Spataro and Ianniello, 2014 and references therein; M. Li et al., 2019 and references therein). The increase of wet deposition of nitrate is tested, for which we applied the seasonal variation to in-cloud condensation water for rainout parameterization and updated the washout parameterization of HNO_3 based on the method introduced by Luo et al. (2019) in Case 9. Cases 10 to 50 are the runs with various combinations of the modifications in Cases 1 to 9 (Table ~~S6~~S7 in SI) for the two case periods. We did not ~~test any parameter related to~~run tests for OA because of the lack of sufficient ambient and laboratory constraints. Scaling up the CO emissions in fall and winter (Fig. 4*d*) would lead to significant overestimation of OA in non-urban areas.

Figure 6 shows the simulation-to-observation ratios of hourly mean mass concentrations of NR-$PM_{2.5}$, sulfate, nitrate, and ammonium for Cases 0 to 9. The nocturnal BLH, the non-agriculture NH_3 emissions, the OH· levels, and the wet deposition of nitrate have minor impacts on the model performance of these components. The updated SO_2 emissions in Case 2 ~~can significantly~~substantially improve the model simulation of sulfate in Beijing, although further improvements are needed in winter. Similar to previous findings, the heterogeneous uptake of SO_2 in Case 5 and 6 increases the simulated sulfate concentrations and leads to better model-observation comparisons in winter (B. Zheng et al., 2015; J. Li et al., 2018). However, both of the cases lead to the overestimation of sulfate concentrations in summer. The nitrate overestimation in summer leads

to the overpredicted ALWC that promotes the excess heterogeneous sulfate formation. The variances of the simulation-to-observation ratios for both cases are ~~also~~ greater than the standard simulation in Case 0, indicating the limitation of ~~those~~the heterogeneous parameterizations. Mechanistic approach other than using indirect indicators like RH and ALWC along with accurate SO_2 emissions as discussed in Sect. 4.2 may be necessary to improve the seasonality of the sulfate simulation.

~~The reduced γ_{N2O5} in Case 7 leads to a minor reduction of simulated nitrate concentrations, suggesting that the uncertainty of heterogeneous uptake of N_2O_5 is not the main cause of the overestimation of nitrate. The simulations with more reasonable γ_{NO2} in Case 8 are able to reproduce the observed nitrate concentrations in winter, indicating that biased NO_2 uptake is an important contributor to the overestimation of nitrate. However, the updated γ_{NO2} alone is insufficient to correct the nitrate concentrations in summer, suggesting additional factors that contribute to the summertime overestimation. Given that the model overestimates both of the summertime concentrations of HNO_3 (Fig. S5) and nitrate, the bias is perhaps related to the insufficient removal of them. The updated wet deposition of nitrate can reduce the summertime monthly mean concentrations by about 20% (Fig. S11) but is still minor in terms of the large overestimation. Greater dry deposition of HNO_3 and faster photolysis of particulate nitrate as well as the joint influence of multiple factors (as discussed later) are possible ways to solve the remaining overestimation.~~

The reduced γ_{N2O5} in Case 7 leads to a minor reduction of simulated nitrate concentrations, suggesting that the uncertainty of heterogeneous uptake of N_2O_5 is not the main cause of the overestimation of nitrate. The simulations with more reasonable γ_{NO2} in Case 8 are able to reproduce the observed nitrate concentrations in winter, indicating that the biased NO_2 uptake is an important contributor to the overestimation of nitrate and nighttime HONO (Fig. S9). However, the reduced γ_{NO2} alone is insufficient to correct the nitrate concentrations in summer. In China, especially in northern China, the nitrate formation is likely more sensitive to HNO_3 than to NH_3 under the control of aerosol acidity and ALWC (Nenes et al., 2020). The model shows the excessive nitrate availability when the photochemical and nighttime production might be underestimated because of the underestimated oxidant concentrations. The insufficient improvements by constraining the heterogeneous chemical production in Case 7-8 suggests that the nitrate bias is perhaps related to the insufficient removal of nitrate or HNO_3 in the model. The updated wet deposition of nitrate in Case 9 can reduce the summertime monthly mean concentrations by about 20% (Fig. S11) but is still minor compared with the large overestimation. Insufficient dry deposition of HNO_3 and nitrate and the photolysis losses of particulate nitrate to produce HONO and NO_x (Ye et al., 2017) as well as the joint influence of multiple factors (discussed later) are possible explanations for the overestimation of nitrate. Nemitz et al. (2004) indicated greater dry deposition velocities of nitrate than the values used typically in models. However, the relative contributions of the dry deposition of nitrate and ammonium to the total deposition of nitrate+HNO_3 and ammonium+NH_3 is small (<10%) (Zhao et al., 2017). We expect a minor influence of such uncertainties on the issue of nitrate overestimation. Heald et al. (2012) showed a minor impact of the uncertainty in the dry deposition of HNO_3 on the nitrate simulations. The photolysis of particulate nitrate is therefore likely substantial, which has been ignored in the model simulations.

Sulfate and nitrate simulations interact with each other through thermodynamic equilibrium~~, especially in winter when NH_3 emissions are lower than in summer~~. As shown in Fig. 6, adding the heterogeneous formation of sulfate reduces the simulation-to-observation ratios of nitrate in winter (i.e., the median ratio from 2.6 to 1.8-2.3 in Cases 5-6) and the simulated weekly mean concentrations of nitrate by 16-36% (Fig. S12*a*). The heterogeneous formation of sulfate may affect aerosol pH and ALWC that determine the sensitivity of nitrate formation to NH_3 or to HNO_3 (Nenes et al., 2020). On the other hand, the reduced γ_{NO2} leads to the reduction of the simulation-to-observation ratios of sulfate (i.e. about 0.1 reduction of the median ratios) and the weekly mean simulated sulfate concentrations by 12-20% (Fig. S12*b*). The reduced γ_{NO2} decreases the HONO concentrations by 98% and hence the OH· levels by 26-74% in Beijing, which leads to lower concentrations of sulfate. Besides, the reduced γ_{NO2} decreases ALWC through reducing nitrate, which also slows down the heterogeneous sulfate formation.

Figure 7 shows the ~~*R* and~~ improvements of absolute NMB (|NMB|) and *R* values ~~of~~for the sulfate and nitrate simulations ~~for Case 0, and~~ in Cases 5, 6, and 8 (~~i.e.,~~with updated heterogeneous formation~~),~~ of sulfate and nitrate) and Cases 10 to 50 relative to Case 0. In winter, the parameterization of heterogeneous sulfate formation on RH in ~~Case 5~~the cases with $\gamma_{SO2\text{-}RH}$ improves *R* but leads to greater |NMB|, while the parameterization on ALWC in ~~Case 6 leads to near-zero~~the cases with $\gamma_{SO2\text{-}ALWC}$ improves |NMB| but ~~little changes of~~slightly decreases *R*~~.~~ (Fig. 7*a*). By contrast, ~~Case 5 leads to~~all the cases with $\gamma_{SO2\text{-}RH}$ or $\gamma_{SO2\text{-}ALWC}$ show worse *R* values ~~of both *R* and |NMB|, and Case 6 only affects *R*~~ in summer~~.~~, and only the cases with $\gamma_{SO2\text{-}ALWC}$ generally improve |NMB|. The results suggest that the parameterization on ALWC ~~seems to be~~is better in terms of the overall model performance than the parameterization on RH. The decreased *R* in summer in ~~Case 6~~the cases with $\gamma_{SO2\text{-}ALWC}$ is perhaps because that the biased inorganic aerosol concentrations and the underrepresented organic contribution in the ALWC calculations lead to large uncertainty in the ~~estimated~~simulated ALWC and sulfate concentrations (Pye et al., 2009). For nitrate, the ~~change of~~cases with updated γ_{NO2} ~~in Case 8 leads to~~ show large improvements of ~~either *R* or~~ |NMB| in both seasons~~.~~ (Fig. 7*b*). The changes of *R* are small.

The combination of the heterogeneous factors with other factors in Cases 10-50 shows various changes in model improvements. For ~~example, the combination of factors related to heterogeneous formation of sulfate,~~cases with $\gamma_{SO2\text{-}ALWC}$, updating SO_2 emissions~~, OH· levels,~~ and reducing γ_{NO2} ~~shows worse *R* or~~ lead to the most significant further improvements in |NMB| ~~compared to Case 6 in winter (Fig. 7*a*) but improved model performance~~especially in summer (Fig. ~~7*b*~~7*a*). Such interaction suggests that the parameterization of heterogeneous sulfate formation is sensitive to the precursor concentrations, the oxidation, and the ~~oxidation conditions. Therefore, accurate SO_2 emissions and well-reproduced oxidant conditions are necessary for improving the sulfate simulation.~~nitrate-induced ALWC in China. For nitrate, the combinations of the γ_{NO2} ~~factor~~case with ~~other factors can worsen *R* and |NMB| in winter. In particular, the combination of the improved γ_{NO2} with the implementation of~~ heterogeneous sulfate formation ~~and the updated SO_2 emission lead to the greatest reduction of *R* and increase of |NMB| among cases~~can worsen *R* in winter (Fig. ~~7*c*~~7*b*), explained by the limitation of NH_3 relative to high sulfate ~~concentrations.~~concentration that affects the nitrate partitioning. This impact is perhaps smaller in summer because of the greater NH_3 emissions. ~~Accurate sulfate simulation therefore is important for the improvement of the simulation of wintertime~~

~~nitrate in Beijing.~~ The combination of ~~various factors~~the reduced γ_{N2O5} with the improved γ_{NO2} leads to the ~~consistent~~most significant further reduction of |NMB| in summer~~ (Fig. 7*d*).~~ , and other factors lead to minor |NMB| improvements.

Case 50 represents the combination of all factors (including $\gamma_{SO2\text{-}ALWC}$ not $\gamma_{SO2\text{-}RH}$). It shows an *R* value of 0.8/0.9 (winter/summer) and an |NMB| value of 0.05/0.3 for sulfate, and an *R* value of 0.8/0.7 and an |NMB| value of 0.3/2.1 for nitrate. By contrast, the standard simulation in Case 0 shows an *R* value of 0.9/0.9 and an |NMB| value of 0.6/0.3 for sulfate, and an *R* value of 0.9/0.7 and an |NMB| value of 2.0/4.7 for nitrate. For sulfate, the |NMB| is largely improved in winter by the combination of all factors. In summer, the influence of all factors seems being canceled out and therefore leads to an insignificant change in |NMB|. For nitrate, the combination of all factors can greatly improve the |NMB| in both seasons, although the overestimation of nitrate is still very large in summer.

5 Conclusions

We evaluated the GEOS-Chem model simulations with a national-wide dataset in China and a long-term hourly dataset in Beijing for sulfate, nitrate, ammonium, and OA. The underestimation of sulfate and the overestimation of nitrate concentrations for most of the sites ~~are consistent with previous findings.~~suggest general problems in the model. The Simple SOA scheme significantly improves the OA simulations in China, suggesting that the SOA formation from anthropogenic precursors is perhaps the main reason for the underestimation of OA in previous studies. The remaining underestimation of OA is plausibly associated with the insufficient SOA production in the model. The model-observation agreement shows significant seasonality. Sulfate is mostly underestimated in winter, and nitrate is significantly overestimated ~~except~~ in ~~winter. Our~~all seasons. The model is unable to reproduce the diurnal patterns of nitrate and ammonium. Sensitivity analysis for factors related to meteorology, emission, chemistry, and ~~atmospheric removal~~wet deposition with laboratory constraints show that uncertainties in chemistry perhaps dominate the model bias. Among the ~~various~~ individual factors, updated heterogeneous parameterizations ~~of~~for SO_2 and NO_2 ~~efficiently~~ significantly reduce the model-observation gaps of sulfate and nitrate~~,~~ (decreasing winter/summer |NMB| by 0.48/0.09 and 1.98/1.51), respectively. ~~The impacts of various factors on model improvements are canceled out in some cases. Overall, the combination of all factors significantly improves the simulation for~~Accurate sulfate ~~and nitrate. Because of the~~ simulations in China may be achieved by joint ~~influence among factors, accurate SO_2 emissions as well as well-reproduced oxidant conditions and~~ factors, for example, heterogeneous sulfate formation ~~are essential for accurate sulfate simulation. Good sulfate simulation improves the nitrate simulation in urban areas~~along with ~~high anthropogenic emissions. Mechanistic approaches other than parameterization on RH~~ accurate SO_2 emissions and well-reproduced oxidant and ALWC ~~are needed to~~ conditions. Good sulfate simulations improve the ~~seasonality of the~~ nitrate simulations by altering the sensitivity of nitrate formation to HNO_3 or to HNO_3+NH_3, especially in winter when NH_3 might be limited. The combination of all factors biases sulfate ~~simulation. The summertime overestimation of~~by 30% in summer and nitrate ~~remains the biggest problem in the model~~by 30% in winter, which ~~requires~~are within the measurement uncertainties. However, the all-factor simulations still overestimate nitrate by 210% in summer (470% in standard simulations), highlighting the model issues

related to atmospheric removal of HNO_3 and nitrate. The insufficient dry and wet deposition of HNO_3 and nitrate likely play minor roles, suggesting that the photolysis of particulate nitrate might be substantial in polluted environments. The nitrate simulations require a better understanding of the atmospheric reactive nitrogen budget, especially the role of the photolysis of particle-phase nitrate. Simultaneous measurements of major reactive nitrogen species including NO_x, N_2O_5, NO_3·, HONO, HNO_3, NH_3, and particle-phase nitrogen in the field campaigns can provide critical data sets for future model investigations. ~~For OA, the remaining underestimation is plausibly associated with the insufficient SOA production in the model, which merits further explicit investigations.~~

Data availability. Data presented in this manuscript are available upon request to the corresponding author.

Author contributions. QC designed the study. RM performed the model simulations and conducted the data analysis. YS, JG, KL, YZ, SC, LZ, YZ, XC, YL, ZT, and XM provided the observation data. QZ provided the MEIC inventories and the diurnal profiles of emissions. QC and RM prepared the manuscript with contributions from PIP, MS, JG, and KL.

Competing interests. The authors declare that they have no conflict of interest.

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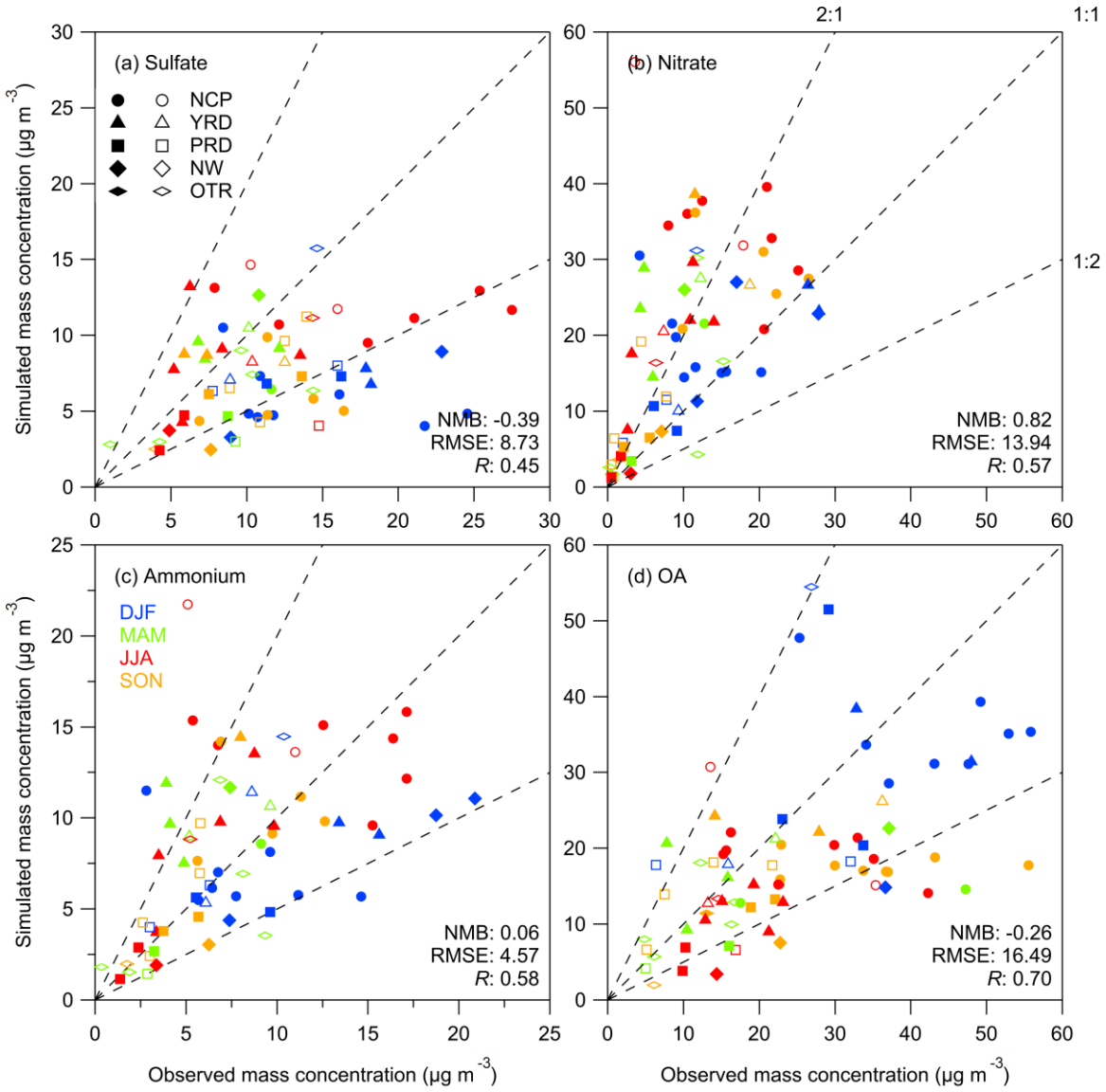

Figure 1. Scatter plots of the simulated and observed campaign-average mass concentrations of (a) sulfate, (b) nitrate, (c) ammonium, and (d) OA in China. The solid and open symbols represent the urban and non-urban sites, respectively. Colors and shapes of the symbols represent seasons and regions, respectively. The observations were conducted during 2006 to 2016 for submicron particles and the data were divided by a submicron-to-fine ratio of 0.8. The model simulations were run for the year of 2012.

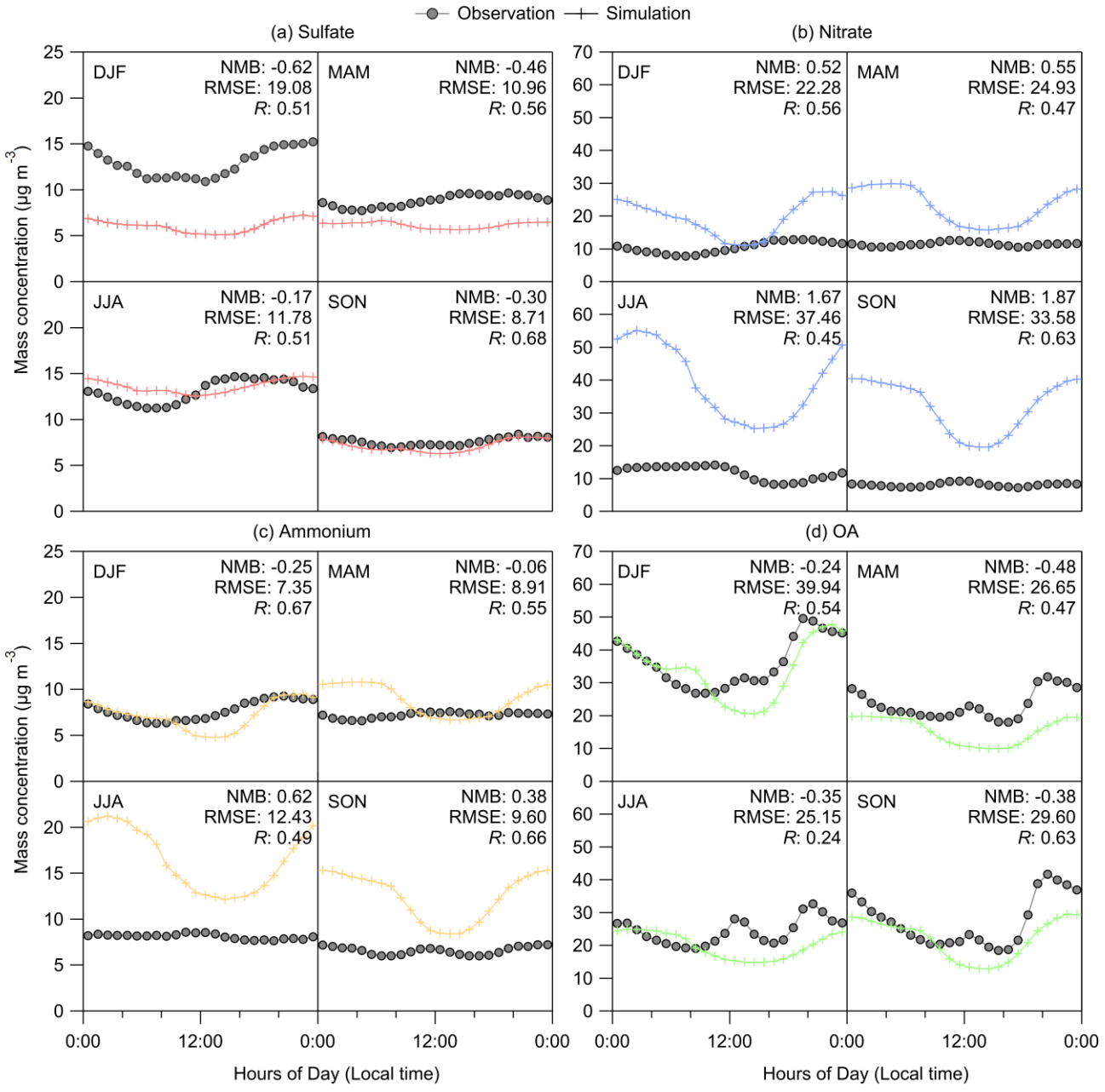

Figure 2. Diurnal profiles of the simulated and observed hourly mean concentrations of (a) sulfate, (b) nitrate, (c) ammonium, and (d) OA at the IAP site in Beijing from July 2011 to May 2013. The observed concentrations were divided by a submicron-to-fine ratio of 0.8.

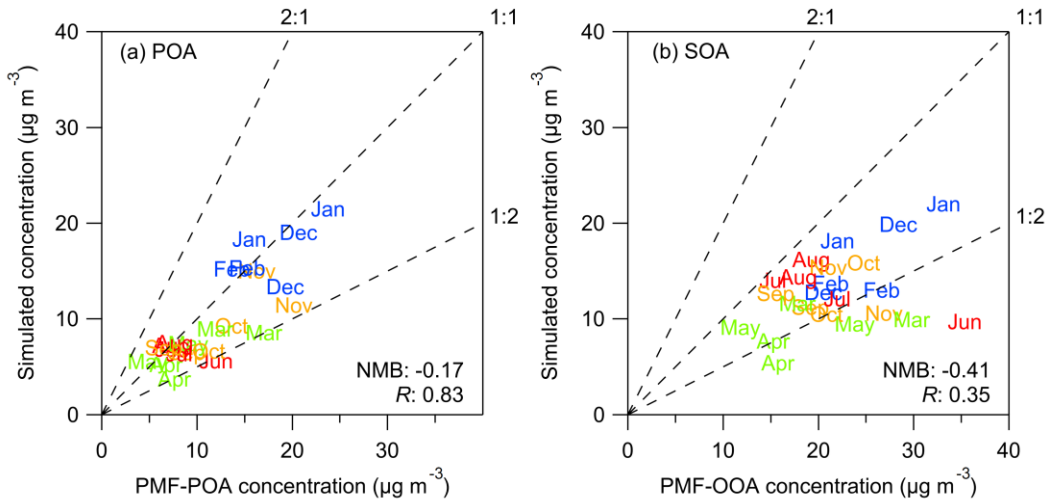

Figure 3. Scatter plots of the monthly mean concentrations of (a) simulated POA and PMF-derived POA and (b) simulated SOA and PMF-derived OOA at the IAP site in Beijing from July 2011 to May 2013. The observed concentrations were divided by a submicron-to-fine ratio of 0.8.

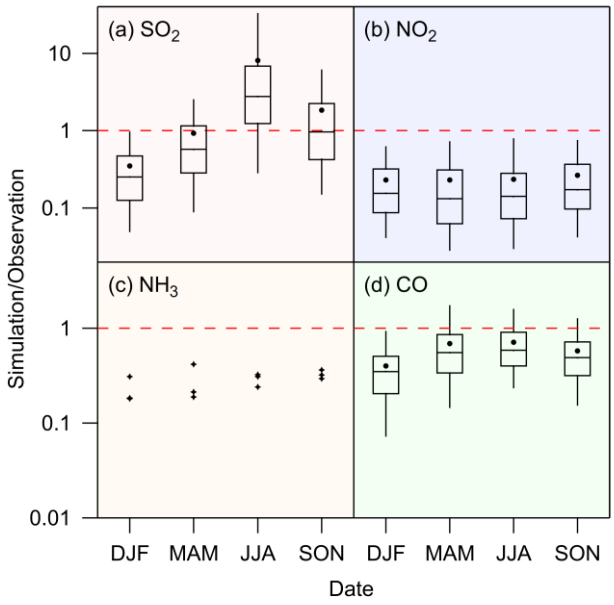

Figure 4. The simulation-to-observation ratios of the concentrations of (a) SO_2, (b) NO_2, (c) NH_3, and (d) CO in Beijing. The upper and lower edges of the boxes, the whiskers, the middle lines, and the solid dots in panels a, b, and d denote the 25th and 75th percentiles, the 5th and 95th percentiles, the median values, and the mean values of the simulation-to-observation ratios of the hourly mean concentrations of the corresponding species at the PKUERS site from July 2011 to May 2013, respectively. The solid dots in panel c represent the simulation-to-observation ratios of the monthly mean concentrations of NH_3 at the IAP site from December 2007 to November 2010. The red dashed lines show the 1:1 simulation-to-observation ratio.

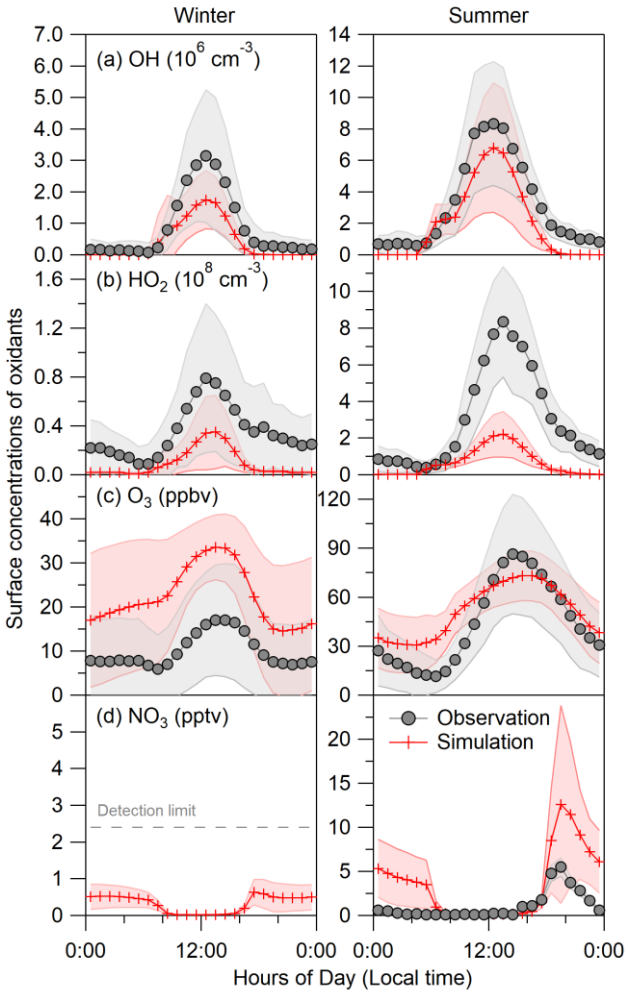

Figure 5. Diurnal profiles of the hourly-mean simulated and observed concentrations of (a) OH and (b) HO_2 radicals at the Wangdu site from June to July 2014 and at the Huairou site from January to March 2016, (c) O_3 at the PKUERS site from July 2011 to May 2013, and (d) NO_3 radicals at the PKUERS site in January and September 2016 in Beijing. The shaded areas indicate mean value ± 1 standard deviation.

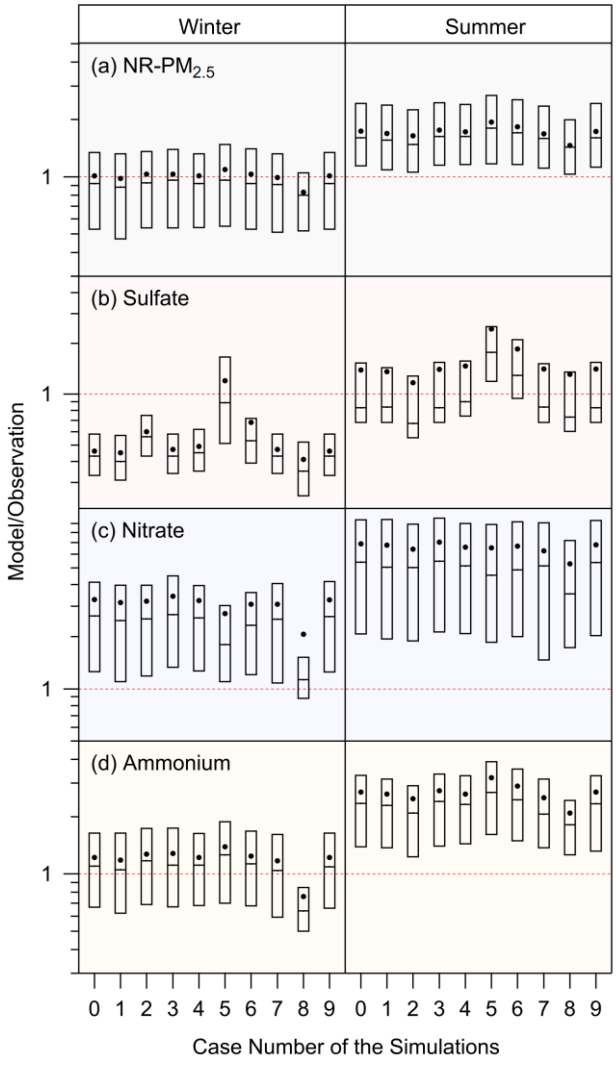

Figure 6. Box and whisker plots of the simulation-to-observation ratios of hourly mean mass concentrations of (a) NR-$PM_{2.5}$, (b) sulfate, (c) nitrate, and (d) ammonium for the standard simulation (i.e., Case 0) and Cases 1 to 9 during the selected wintertime and summertime periods. The upper and lower edges of the boxes, the middle lines, and the solid dots denote the 25th and 75th percentiles, the median values, and the mean values, respectively. The red dashed lines show the 1:1 simulation-to-observation ratio.

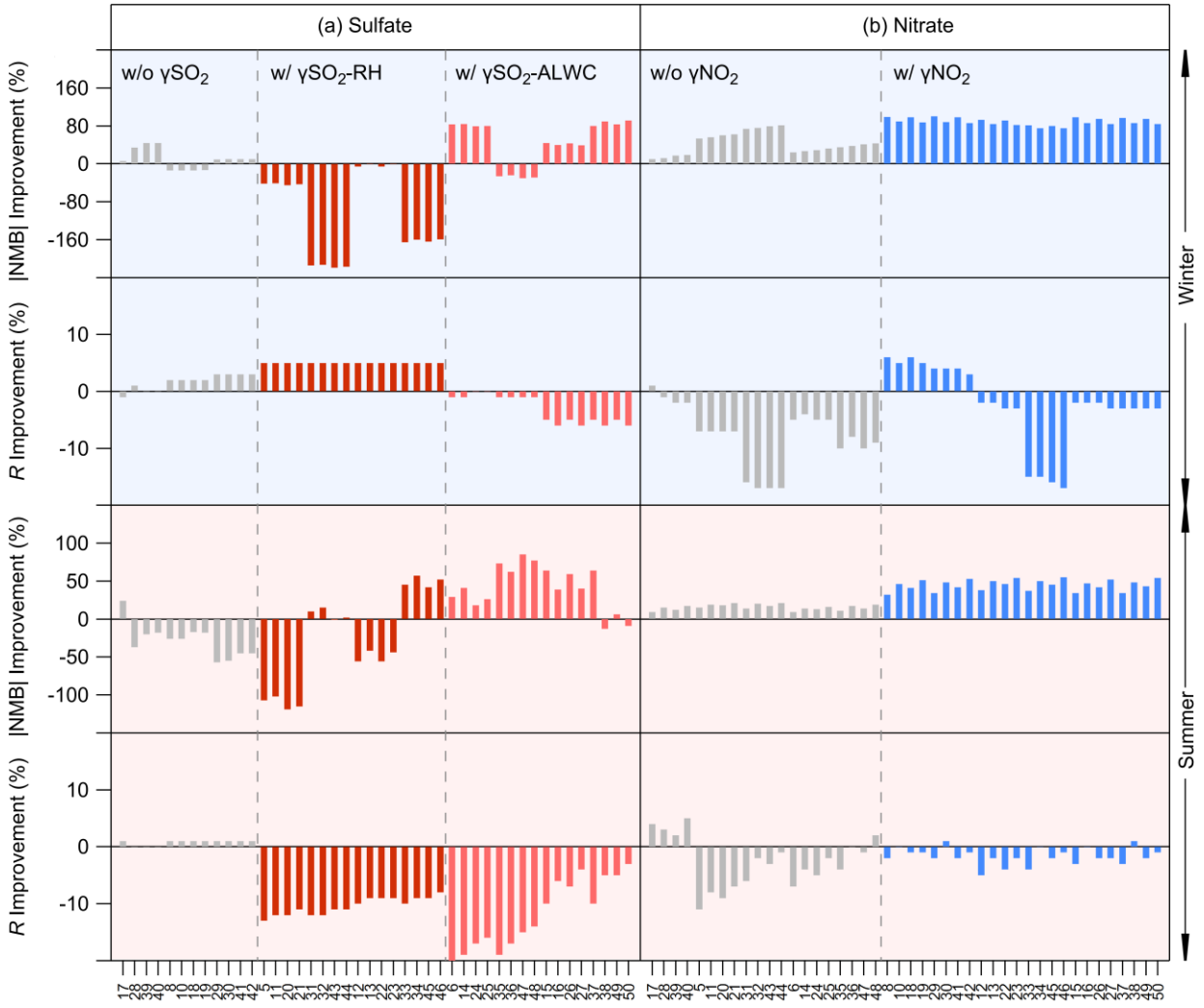

Figure 7. The improvements of the *R* and the |NMB| values for (a) sulfate and (b) nitrate in Cases 10-50 relative to Cases 0 (standard) during the selected wintertime and summertime periods. For comparisons, Cases 5 (w/. $\gamma_{SO2\text{-}RH}$), 6 (w/. $\gamma_{SO2\text{-}ALWC}$), and 8 (reduce γ_{NO2}) are also plotted. Positive values in |NMB| or *R* improvement mean improved simulations.

Table 1. Comparisons of the observed and simulated meteorological parameters, including T, RH, wind speed, wind direction, and BLH, for the four seasons during the period of July 2011 to May 2013 at the PKUERS site. "OBS" and "SIM" represent the mean values of the observations and simulations, respectively.

		DJF	MAM	JJA	SON
T (K)	OBS	270.96	286.42	300.46	289.38
	SIM	266.70	281.74	296.83	285.55
	MB	-4.26	-4.68	-3.63	-3.84
	NMB (%)	-1.57	-1.63	-1.21	-1.33
	RMSE	4.63	5.06	4.04	4.28
RH (%)	OBS	32.57	34.00	61.91	46.15
	SIM	45.32	38.92	63.78	49.44
	MB	12.75	4.92	1.87	3.28
	NMB (%)	39.15	14.47	3.01	7.12
	RMSE	17.33	13.36	10.67	15.64
Wind Speed ($m\ s^{-1}$)	OBS	1.53	2.23	1.71	1.82
	SIM	4.23	4.90	3.47	4.57
	MB	2.71	2.67	1.76	2.75
	NMB (%)	177.27	119.34	102.84	150.82
	RMSE	3.40	3.50	2.34	3.50
Wind Direction (°)	OBS	322.63	291.49	231.82	304.83
	SIM	175.62	147.12	336.22	182.09
	MB	-39.44	-2.76	-4.26	-22.08
	RMSE	126.44	128.69	122.92	125.30
BLH: 2 PM (m)	OBS	n.a.	n.a.	1338.74	n.a.
	SIM	n.a.	n.a.	1788.73	n.a.
	MB	n.a.	n.a.	449.99	n.a.
	NMB (%)	n.a.	n.a.	33.61	n.a.
	RMSE	n.a.	n.a.	647.00	n.a.
BLH: 8 AM (m)	OBS	389.60	468.18	373.28	356.30
	SIM	203.95	518.11	518.79	252.14
	MB	-185.64	49.93	145.51	-104.16
	NMB (%)	-47.65	10.66	38.98	-29.23
	RMSE	497.37	680.43	396.69	487.38
BLH: 8 PM (m)	OBS	436.39	618.33	502.45	417.24
	SIM	482.20	1003.04	501.51	636.58
	MB	45.81	384.71	-0.94	219.34
	NMB (%)	10.50	62.22	-0.19	52.57
	RMSE	703.30	1159.34	840.49	940.83

Table 2. Details of the sensitivity simulations from Cases 1 to 9.

Case No.	Tested Factors	Modifications in the model	Reference
1	BLH	Multiply by 3.6 for nighttime if the BLH is lower than 500 m	This study
2	SO_2	Summer: multiply SO_2 emission by 0.8 Winter: multiply SO_2 emission by 1.5	Koukouli et al. (2018)
3	NH_3	Multiply non-agriculture NH_3 emission by 1.4	Kang et al. (2016)
4	OH level	Summer: multiply $PM_{2.5}$-related reaction rates by 1.5 Winter: multiply $PM_{2.5}$-related reaction rates by 2	This study
5	$\gamma_{SO2\text{-}RH}$	Add-in: between 2×10^{-5} to 5×10^{-5} depending on RH	B. Zheng et al. (2015)
6	$\gamma_{SO2\text{-}ALWC}$	Add-in: between 10^{-6} to 10^{-4} depending on ALWC	J. Li et al., (2018)
7	γ_{N2O5}	Change γ_{N2O5} from 0.02 (global mean) to 10^{-3}	McDuffie et al., (2018)
8	γ_{NO2}	Change γ_{NO2} from 10^{-4} to 10^{-6}	M. Li et al., (2019)
9	Wet deposition	Use the seasonal varied in-cloud condensation water and update the empirical washout rate for HNO_3	Luo et al., (2019)