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 #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, 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 bias 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 reproduce 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., 2020). 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 relatively

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 84-87 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 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 are expected to be minor compared with other potential biases. Because the chemical production, meterology, and the wet deposition cannot explain the model bias of nitrate, the removal here mainly mean 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: "*have shown that the CTMs can reproduce the spatial and temporal variations of the surface PM2.5 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".

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 follow: "*Recent model evaluations in China have reached an agreement that CTMs generally underestimate the concentrations of organic aerosol (OA) and sulfate but overestimate the concentrations of nitrate*".

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 conditions 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 NOx 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 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 result 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 298-230.

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 380-384 as follows: "*Insufficient dry deposition of HNO_3 and nitrate and photolysis losses of particulate nitrate (i.e., to produce HONO and NO_x) in the model as well as the joint influence of multiple factors (discussed later) are possible explanations for the overestimation of nitrate*".

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