

Interactive comment on “Enhanced sulfate formation through SO₂+NO₂ heterogeneous reactions during heavy winter haze in the Yangtze River Delta region, China” by Ling Huang et al.

Anonymous Referee #1

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General Comments

The paper addresses a popular question under active discussion in the literature, i.e., what is driving the rapid sulfate formation during winter PM_{2.5} episodes in China. While many previous papers on the subject drew their conclusions primarily from ambient and/or experimental data (e.g., Wang et al., 2016, Cheng et al., 2016), this is one of the few papers (Wang et al., 2014, Zheng et al., 2015, and Shao et al., 2019) that have used a full chemical transport model as the primary tool. The observed data analyzed came from a site in Shanghai, a megacity outside of the North China Plain (NCP), where the majority of papers on the subject so far have studied. The CAMx model is a chemical

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transport model similar to US EPA's CMAQ model, and has been extensively used and evaluated in research and regulatory modeling in the US and Europe. In this work, the authors demonstrated the adequacy of the model to simulate winter pollution episodes in China, and the improved model performance (sulfate and others) after including heterogeneous oxidation of SO₂ by NO₂ as an additional source of sulfate and doubled amount of emissions of NH₃. The paper is structured and written in a clear, thorough, and objective fashion that gives a reader full details of the model setup, modifications, and performance, allowing one to reproduce the modeling if one wants to. I especially commend the authors for their thorough model evaluation, covering meteorological parameters, sulfate and its precursors, and PM_{2.5}, at the primary observational site and many other sites in the modeling domain. All these merits of the paper make it a solid modeling study and has allowed a closer examination against the standard of whether or not it helps advance the understanding of the subject. The standard inevitably rises higher as the paper appeared after many recent published papers on the same subject, offering various contradicting explanations and opinions. Among these papers, some proposed a single dominating oxidant, such as NO₂ (Wang et al., 2016; Cheng et al., 2016), H₂O₂ (Ye et al., 2018), O₂ catalyzed by transient metals (Guo et al., 2017), or O₂ on acid droplets (Hung and Hoffmann, 2015). Some suggested measurement artifacts to be a major (~1/3) cause (Song et al., 2019). Interestingly, while this paper was under access review for ACPD, another paper was published in ACP presenting a rather comprehensive modeling study using GEOS-Chem, concluding with a detailed sulfate budget for Beijing that is also constrained by oxygen isotope data.

With all these prior studies being the departure point, and to serve the fast evolving discussion on the subject, the paper, if accepted, would be expected to offer a cohesive opinion with convincing arguments supported by results from the new modeling or observations, answering some open questions raised previously, or raising some neglected factors, or confirming some findings with new evidence. In this regard, however, I do feel that despite the aforementioned favorable attributes of the work, such as a unique locality of the site, a reputable model with careful modification, and a thorough

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model evaluation, it evidently falls short of offering unique or novel insights about sulfate production in Shanghai and broader regions of China beyond what have already known from the literature. To be specific, the remarks in the abstract about the uncertainty of NH₃ emissions and potential importance of heterogeneous NO₂ oxidation have not gone far beyond reiterating the rationale of the study design (i.e., doubling NH₃ emissions and adding heterogeneous NO₂ oxidation into CAMx). First, the uncertainty of NH₃ emissions is already a recognized issue, as stated by the authors too, not only in China but also in the US and elsewhere. NH₃ is also just one participant of sulfate chemistry among many others, e.g., SO₂, O₃, H₂O₂, Fe³⁺, Mn²⁺, so the choice of addressing NH₃ only is not a thorough approach. Besides NH₃, SO₂ (NMB = 32%) and O₃ (NMB = -33%) are also too low in the model, while none of H₂O₂, Fe³⁺ and Mn²⁺ is mentioned.

Second, the importance of NO₂ heterogeneous oxidation appears disconnected from, if not in contradiction with, the reported model results. In the best-performing scenario (Het_2NH₃), heterogeneous NO₂ oxidation only explained 16% of the observed sulfate, while standard CAMx sulfate chemistry account for as much as 64%, with another 20% unexplained. Such a diminished role of heterogeneous NO₂ oxidation due largely to low pH among other factors (e.g., strengths of other oxidants and sources) is nevertheless a much more useful and interesting finding from CAMx modeling, thanks to the authors' effort of accounting for pH effect, than the arguably marginal improvement of model performance (from NMB = -36% to NMB = -20%) per se. For instance, given this result, the authors could, as done by Shao et al. (2019), calculate and report a sulfate budget breaking down all sources considered, followed by thorough discussions on the robustness of each source and its relative importance, considering model assumptions and uncertainties, which should include not only NH₃, but also SO₂, O₃, H₂O₂, Fe³⁺, Mn²⁺, etc.. From such a "local" story developed from CAMx modeling and data in Shanghai, a reader would learn how similar or unique the sulfate chemistry is in Shanghai, in comparison to elsewhere in China, or how difficult it is to model it because of various uncertainties and/or assumptions in those poorly understood aspects

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underlying the model. Along these lines, it did occur to me that the authors actually already have all the data needed from their Shanghai site to develop a "local" parameterization, to their aspiration, instead of adopting the gamma value from Wang et al. (2016) (this will be addressed in more detail in my specific comments).

These considerations led me to the recommendation of a major revision, with three general suggestions followed by some specific suggestions.

First, I suggest adding a full description of the standard sulfate mechanism in CAMx, with perhaps a table listing the reactions, equations, parameters, and assumptions (please refer to Table 2 in Shao et al. (2019) as an example), as done for the new source. Currently the readers only are shown how the new source is parameterized, but not what sources are included in the standard CAMx model. The User's manual of CAMx does not provide a dedicated description of sulfate chemistry in the model, but this information is crucial for a paper that dedicated for sulfate chemistry. Also include description of primary emission of sulfate.

Second, I suggest calculating and reporting a budget of sulfate at the SEAS site, breaking down sources to a level of detail similar to Figure 3 in Shao et al. (2019). I also suggest reporting concentrations of key relevant species for sulfate production (e.g., SO₂, O₃, H₂O₂, Fe³⁺, Mn²⁺, in addition to NH₃, which is already addressed), and discuss their roles toward closing the sulfate budget.

Third, the spatial pattern of CAMx-simulated sulfate enhancement by the new pathway and its drivers sounds like an interesting piece (although two figures associated are currently missing) worth highlighting in the main text and abstract. Many of the descriptive statements associated with PM_{2.5}, nitrate, if not so relevant to sulfate, should be removed.

I look forward to seeing an improved manuscript that would evidently help advance the ongoing discussion on the rapid winter sulfate production in China.

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Specific Comments

Abstract:

- I suggest the authors to rewrite the abstract after the revision. - I would not stress “for the first time” among those substantive achievements by this study.

1. Introduction

- I suggest two additional papers be added into the discussion:

Shao et al.: Heterogeneous sulfate aerosol formation mechanisms during wintertime Chinese haze events: air quality model assessment using observations of sulfate oxygen isotopes in Beijing, *Atmos. Chem. Phys.*, 19, 6107-6123, <https://doi.org/10.5194/acp-19-6107-2019>, 2019.

Ye et al.: High H₂O₂ Concentrations Observed during Haze Periods during the Winter in Beijing: Importance of H₂O₂ Oxidation in Sulfate Formation, *Environ. Sci. Technol. Lett.* 2018512757-763.

- “Although the RH dependency of the SO₂ uptake rate has already been implemented in previous 20 studies (e.g. Zheng et al., 2015; Wang et al., 2014), the effect of aerosol pH has not been explicitly included in any modelling studies yet to our knowledge.”

This is not true as Shao et al. (2019) provided a detailed analysis of pH effect with GEOS-Chem.

2. Methodology

2.1 SO₂ + NO₂ mechanism in CAMx

- Please add a section preceding the current Sect. 2.1 to describe standard sulfate chemistry in CAMx in detail, showing what sources are considered, how they are formulated, values of parameters and constants adopted, and references. Refer to Shao et al. (2019) as an example from GEOS-Chem to see the level of detail to be expected.

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- After looking at the reported data and Wang et al. (2016), I think it is actually possible to develop a “local” parameterization, and I strongly encourage the authors to make an attempt to do so, rather than start with the value of γ from Wang et al. (2016) and back calculate k_0 . The γ in Wang et al. (2016) was derived from ambient observational data in their Table S5. Most of those were available from this paper as well. The steps taken can be as follows. First, one can use observed minus modeled sulfate concentration from standard model during selected episodes to obtain the amount of sulfate that is not accounted for by the model, i.e., ΔSO_4 ; calculate $d[\Delta\text{SO}_4]/dt$ using observed length of time for sulfate buildup during selected episodes (EP1 – EP4 for instance); calculate γ using Eq.(2), by plugging in measured SO₂ concentration and aerosol surface area, which can be the value assumed in CAMx, if not measured. In the next step, one can use measured NO₂, RH and calculated LWC and pH in Table S1 to get the RH dependence function (Eq.(4)). Such a parameterization is supposed to yield better modeling results. This new parametrization can also be compared to those from Beijing and discuss why they agree/disagree.

- In Eq. 4., what is the basis for assuming k_0 to be constant when RH increases from 56% to even higher values? This assumption would be expected to suppress sulfate production under very high RH, a very favorable condition for heterogeneous sulfate production.

- Elaborate on what df is in Eq. 5 and how it is calculated in the model.

2.2 Model configuration

- Page 5, line 30: “we removed the original heterogeneous sulfate formation reaction which only included a simple parameterization based on RH (Zheng et al. 2015) in the distributed version”. Please elaborate on what the reaction is and what oxidant it includes.

- Page 6, line 30: “we used ammonia observations from a similar urban site nearby”. When model performance is examined, is the modeled ammonia from the grid cell

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covering SAES site or from FDU site?

3. Results and Discussion

3.2 Simulated PM concentrations at SAES site

“Impact of both (noHet vs. Het_2NH3)”

Page 9, line 33 – Page 10, line 3: “This could be related to still biased ammonia emissions, less direct emissions of sulfate and/or SO₂, and/or missing of other sulfate formation pathways that needs further investigation. Another explanation is that the SO₂ + NO₂ heterogeneous reactions implemented in this study were parameterized based on observations in Beijing but the simulation is performed over the YRD region. It would be ideal to use local observations for model parameterization in future studies.”

These discussions are too general and speculative, and should be further developed into one of the major sections of the paper, based on additional model diagnostics, calculations, and comparisons against other studies. Below are excerpts of questions to be addressed.

- Ammonia emission was already doubled resulting in ~30% overestimate of the observed. How would it further help enhance sulfate production? Direct emission of sulfate in the model needs to be reported. Primary sulfate contributes more than 20% in Beijing according to Shao et al. (2019). What is the contribution to sulfate in Shanghai and YRD? Regarding the parameterization, how much larger gamma needs to be to reach the observed amount of sulfate? Can the RH dependence function be improved to yield better performance? These questions can be answered by devising a “local” parameterization as outlined above. Standard sulfate chemistry is not mentioned in this discussion, but should definitely be a focus of discussion, because numerous factors can affect its contribution, such as levels of H₂O₂, Fe³⁺, Mn²⁺, assumed aerosol particle properties in the scheme, etc. A most straightforward way of presenting and discussing these results is to have a sulfate budget, and then go over the source one by

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one, noting their dependencies and robustness of representation by the model. Figure 3 from Shao et al. (2019) gives an example.

- Once a sulfate budget is available, it would be constructive to compare and discuss it in the context of previous studies, observational and modeling. For instance, Ye et al. (2018) suggested that H₂O₂ oxidation should be the dominating sulfate formation pathway in Beijing based on their observed amount of H₂O₂. How much H₂O₂ does CAMx predict? Without observed values from Shanghai, perhaps one could compare modeled values in Beijing to those observed by Ye et al. (2018). The 10-ppb O₃ level at the SEAS site is much higher than the Beijing haze case (1 ppb) assumed by Cheng et al. (2016) and Wang et al. (2016), but similar to what Shao et al. (2019) has in Beijing (9 ppb). O₃ is underestimated by 33% by CAMx. Does that partly explain the 19% unaccounted? Guo et al. (2017) speculated catalyzed oxidation with metals (Fe³⁺, Mn²⁺) to be important. Does CAMx result agree with their speculation? How much Fe³⁺ and Mn²⁺ does CAMx simulate? How do they compare to those in GEOS-Chem by Shao et al. (2019)?

- Since almost everything is underestimated as shown in Figure S4, a common cause such as meteorology misrepresentation is not ruled out. This is mentioned briefly but not explored in detail. Could there be a relationship between sulfate bias and biases of meteorological parameters?

“Sulfate formation under selected episodes”

- I think these episodes should be further analyzed in a quantitative fashion, as done by Wang et al. (2016) and Cheng et al. (2016). By closer examining the variations of sulfate and its depending variables, it might be possible to see similarities or differences in sulfate formation regimes among these episodes, or compared to reported cases from Beijing. For instance, I made an attempt to roughly calculate the ratios of sulfate to SO₂ for clean, transition, and polluted conditions, using data from Figures S5 and S6, and found it interesting that they are actually somewhat similar to those reported

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by Wang et al. (2016) for the three conditions.

- EP3 is evidently an anomaly among the four episodes. Are the modeled wind speeds during this episode too high or direction erroneous? It is hard to tell from Table S3 or Figure S3. Please take a closer look and provide a more satisfactory explanation. SO₂ emission change from 2013 to 2014 would not affect only EP3 but also other episodes, so is not a plausible explanation for the anomaly.

3.2.2 Nitrate and ammonium concentrations

3.2.3 PM_{2.5} concentrations

I think these two sections ought to be moved down after Sections 3.3 and 3.4, as they do not help solve the sulfate problem. The discussions on PM_{2.5} are somewhat distractive and premature, given the large biases in sulfate and OC. I suggest moving this part to supplement, if the title and focus of the paper is on sulfate.

3.3 Predicted aerosol pH at the SAES site

This section is important and should be moved up following section 3.2 in helping explain the sulfate result. Have you looked at temporal variability of pH and see if there is correlation with sulfate production?

3.4 Spatial impact of the SO₂ + NO₂ heterogeneous reactions and ammonia emissions in YRD region

3.5 Simulated sulfate concentrations over China

Too many numbers and descriptive statements appear in these two sections as distractions. It appears to be an intriguing finding that despite all the compounding factors, pH value and ammonia stand out to regulate the spatial pattern of sulfate enhancement from the new pathway, which to me is worth further verifying and discussion, although Figures S7 and S8 are currently missing. I suggest this section be merged into one to as a dedicated section on spatial pattern and its driving factors, with the two fig-

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ures moved to the main text. The result from this analysis should be mentioned in the abstract.

Technical Corrections

Abstract

“In addition, ammonia emissions need to be carefully estimated.” and “Substantial efforts are needed to improve the accuracy of ammonia emissions inventory” are duplicated statements.

Section 2.1

Eq.(6) $k_{net} \rightarrow k_{het}$

I think you meant to say Table S2 and Table S5, when you say “We used the data in Table S2 and S4 of Wang et al. (2016) to back calculate the RH dependency of k_0 . . .”

Section 3.1.1

“Bias of predicted wind speed is within 0.31 degree.” Please report correct wind speed bias with unit of m/s, and verify bias of wind direction. 0.31 degree is very small.

3.2.2

Typo/omission:

“This reduces nitrate underestimation substantially during polluted period from -42 % to -20 % but also leads to even higher nitrate overestimation during clean 25 and transition periods *but*.”

Table S3

What is the unit of wind direction?

Figure S4 and Table S4.

The NMB and IOA appear differently in Table S4 (NMB = -72%, IOA = 0.52) and Figure

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S4 (NMB = -60%, IOA = 0.55). Please check and correct.

References cited in this review

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Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, *Scientific Reports*, 7, 12109, doi:10.1038/s41598-017-11704-0, 2017.

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