Response to Referee #2

We would like to thank Atmospheric Chemistry and Physics for giving us the opportunity to revise our manuscript. We thank the referees for their careful reading and thoughtful suggestions on the previous version of our manuscript. We have carefully addressed all of these valuable comments and revised our manuscript accordingly. Below are the point-to-point responses to the general and specific comments as well as our minor corrections.

1. *General comment*

This manuscript concerns with the global impact of aqueous-phase chemistry on the simulation of atmospheric SO_2 *with the CESM2 model. They apply a framework for integrating this chemistry that is similar to the one in use in other models like GEOS-Chem. This approach does not foresee the online calculation of pH. Additionally, not having soluble Fe emissions the authors go on with sensitivity simulations with plausible, at least regionally, of pH and* $[Fe^{3+}]$ *applied globally. Then, an attempt of separating the effects of different parts of the mechanism on* SO_2 *is done but limited by the choice of the reaction categories to exclude at once (more to it below). In general, the manuscript is written well and with a good and clear structure. The topic and the results are interesting. However, I have identified a few points to be addressed/clarified.*

Response: Thank you very much for your valuable comments. As we introduced in lines 210-213 of Section 2.3, the pH values in the Improved case and other cases in Sections 4 and 5.1 are all calculated online by the equilibrium reactions in Tables 1a and 1b. Only the pH values in Section 5.2 are prescribed as a fixed value. See Table S1 for details.

On the other hand, the separation of effects did not directly exclude all the other reaction categories at once. We still retain the basic equilibria and radical reactions in HO_x-chemistry in every case (Please see below and Table S1 for details).

2. *Comments*

In Table 1b most of the references for the reaction kinetics are given to three collections/mechanisms published earlier. Please cite alongside the primary literature for each reaction and not just the modelling *studies that collected sets of reactions. Moreover, it is not explained/justified why the authors blends these (secondary) sources with others (primary) to obtain their own chemical mechanism in CESM.*

Although section 2.2 contains the reaction tables that well done (apart from the secondary references), in the text little is written for describing in words the salient features of the mechanism used here.

I understand the authors wrote a comprehensive introduction on the SO_2*-relevant known chemistry. Howeover, the latest and most reliable data is not necessarily reflected in their mechanism. For instance, the oxidation of S(IV) by* NO_2 *(also mentioned in the text). However, in Table 1b one finds only reaction 199 for* HSO_3^- *and nothing for* SO_4^{--}*. Is the latter neglected because only important at high pH values that are seldom represented in model simulations?*

Furthermore, although Cheng et al., 2016 is cited in the introduction, the low rate constant by Lee and Schwarzt 1982 (by the way the reference is incomplete, please add at least the url https://www.osti.gov/biblio/6567096) is used. This is a 2nd-order reaction rate constant while reaction 199 is obviously 3rd-order. The former is about one order of magnitude larger as reported by a few later studies with the last one being Spindler et al. 2000, DOI: 10.1016/S1352-2310(03)00209-7. These issues I have make me doubt about the statement on line 18 in the abstract about the minor role of N-chemistry for SO_2 *oxidation.*

Response: Thank you for your valuable comments. For the references, in this version of our manuscript we replaced all the secondary sources with primary sources (119 more references in all), as shown in Tables 1a and 1b in the revised manuscript. Meanwhile, the general description of these mechanisms is in lines 155-162 and the illustration of parameters is in lines 180-184 in Section 2.2.

Considering that the main focus of this study is SO_2, we tried our best to summarize the reactions related to SO_2 oxidation, although Table 1 may not include all the aqueous-phase reactions in the atmosphere. As for the oxidation of S(IV) by NO_2, just as you mentioned, this is partially because the pH values of the cloud droplets are mostly in the range of 3-5.5, but the pK_a of H_2SO_3 are 1.76 and 7.21, respectively (Herrmann et al., 2000). Therefore, the main form of S (IV) in cloud droplets is HSO_3^- and we neglected the latter in model simulations.

Next, we supplemented the URL of Lee and Schwartz (1982) into the footnote of Table 1b. In Lee and Schwartz (1982), they firstly determined the stoichiometry of the reaction as "2 $NO_2 + SO_2$" according to their experiments. Then they tried to convert the 3rd-order rate constant to 2nd-order (pseudo-second-order rate constant). Finally they set the 2nd-order reaction rate constant as 2.0×10^6 M^{-1} s^{-1}. This rate constant, for reaction rate interpreted according to an overall second-order rate expression (R = k(2)[S(IV)][NO_2]), was 2×10^6 M^{-1} s^{-1} at both pH 6.40 and 5.80. Meanwhile, many other studies also referred to this work and used 2×10^6 M^{-1} s^{-1} as the 2nd-order reaction rate constant, including the references cited in next comment (Seinfeld and Pandis, 2006; Shao et al., 2019; Song et al., 2021).

Compared to Spindler et al. (2003), the reaction used in this study is $NO_2 + SO_2 \rightarrow NO_2^- + SO_3^-$. It is just an incomplete reaction and still need one more NO_2 to oxidize SO_3^- (S(V)) to SO_4^{2-}(S(VI)). While Reaction 199 in our study is an integrated expression of these two steps, so they do not conflict to (Spindler et al., 2003).

3. *It is remarkable that the mechanism the authors put together completely lacks the chemistry of methanol, methyl hydroperoxide and formaldehyde. The latter, in its hydrated form, combines with HSO_3^- to produce HMS which reacts quickly with OH to yield SO_5^-. Recent work on the importance of such chemistry are DOI: 10.1029/2020JD032706 and DOI: 0.5194/acp-21-457-2021. Why only reactions of organic acids with sulfur are considered? Why has this chemistry been neglected? It is well known and acknowledged as a significant source of O_2^- and thus OH. I think this chemistry needs to be considered especially in a study about the importance of SO_2 aqueous-phase sinks.*

Response: Thanks a lot for this important suggestion. We followed the referee's suggestion and incorporated additional 10 aqueous-phase organic species and 60 related reactions, including the reactions relevant to CH_3OH, HCHO, CH_3OOH and HMS^-, as shown in Tables S2a and S2b. We conducted additional two simulations for testing the contribution from this organic chemistry (i.e., (1) "Improved case + Org-chem" and (2) "HO_x-chem case + Org-chem"). The differences between case (1) and the "Improved case" are shown in Fig. R1 and the differences between case (2) and the "HO_x-chem case" are shown in Fig. R2. Both figures indicate the influence from this organic chemistry is typically less than 5%. More specifically, the concentration of SO_2 over China and mixing ratio over the United States only decreased by 1.2% and 0.2%, respectively (as shown in Fig. R3). Consequently, adding these organic species and reactions did not improve the simulation significantly. We added the following discussion in Section 5.3 of the revised manuscript.

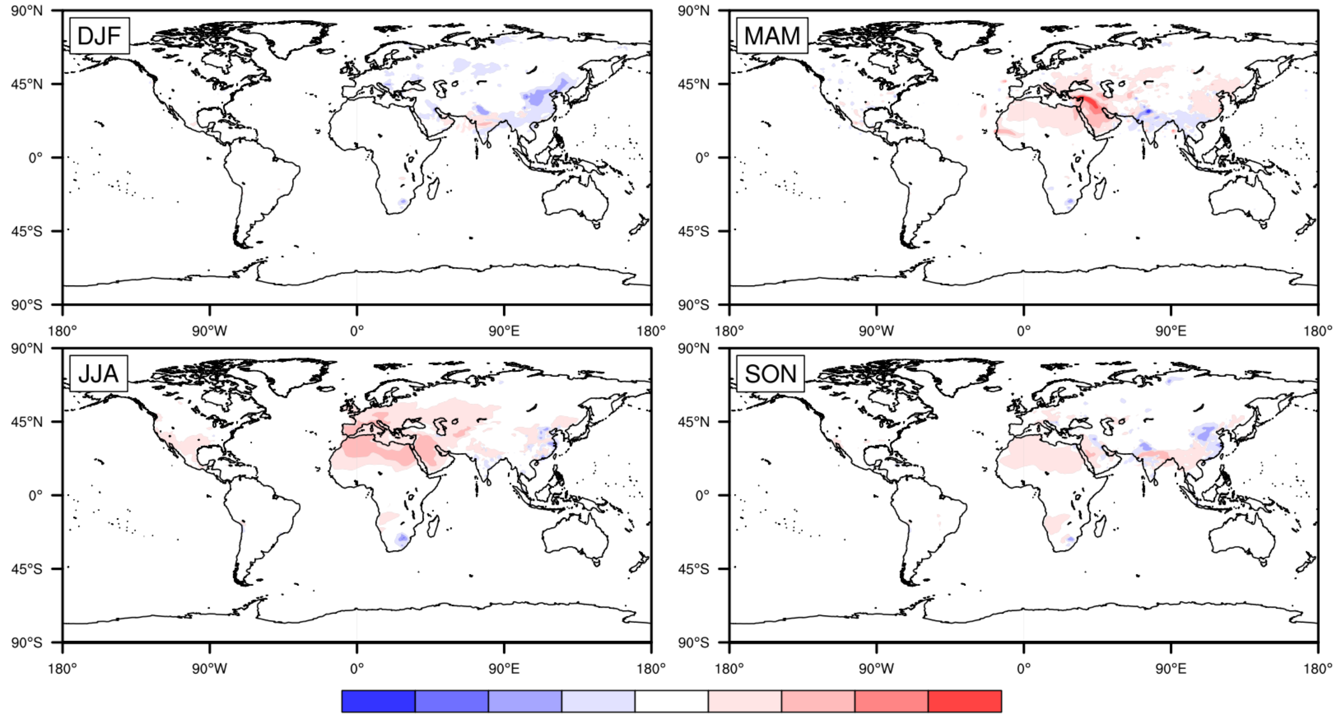

Figure R1: The differences in global seasonally averaged surface SO_2 mixing ratios between the "Improved + Org-chem case" and the Improved case in 2015 (unit: ppbv).

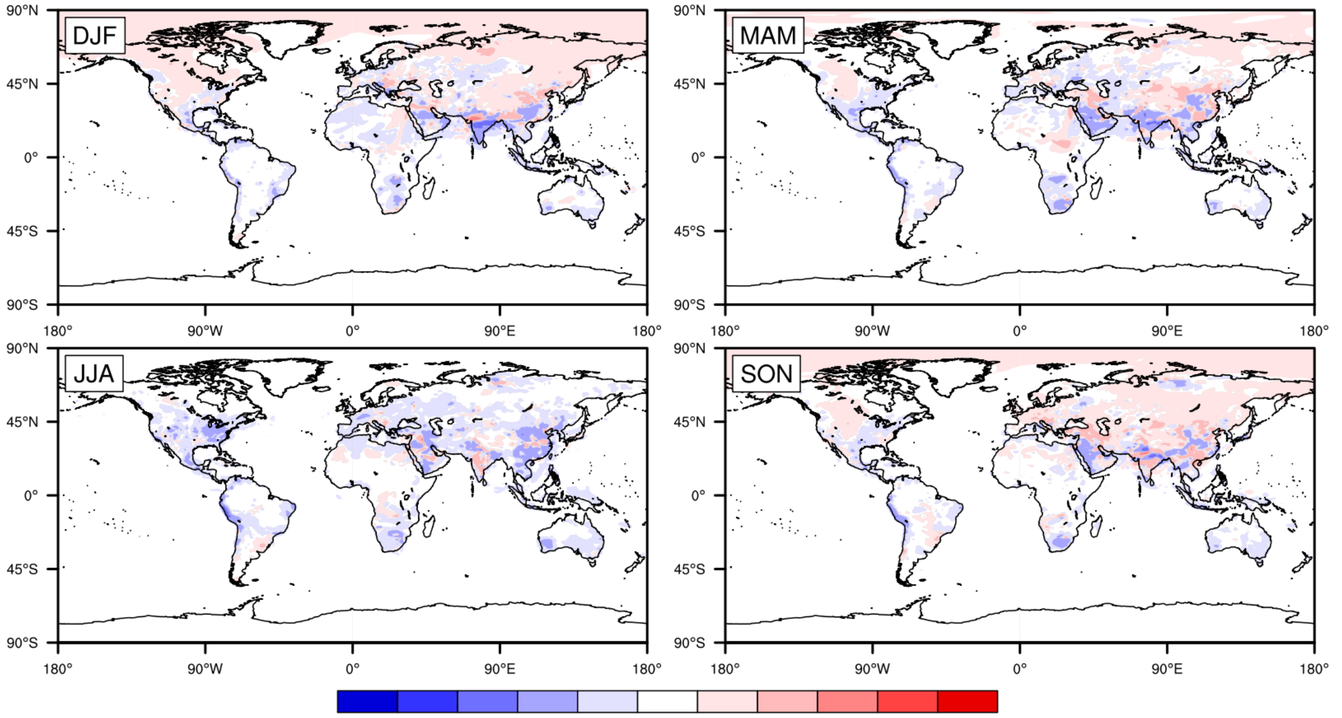

Figure R2: The differences in global seasonally averaged surface SO_2 mixing ratios (ppbv) in 2015 with the incorporation of organic chemistry (case 27 – case 3).

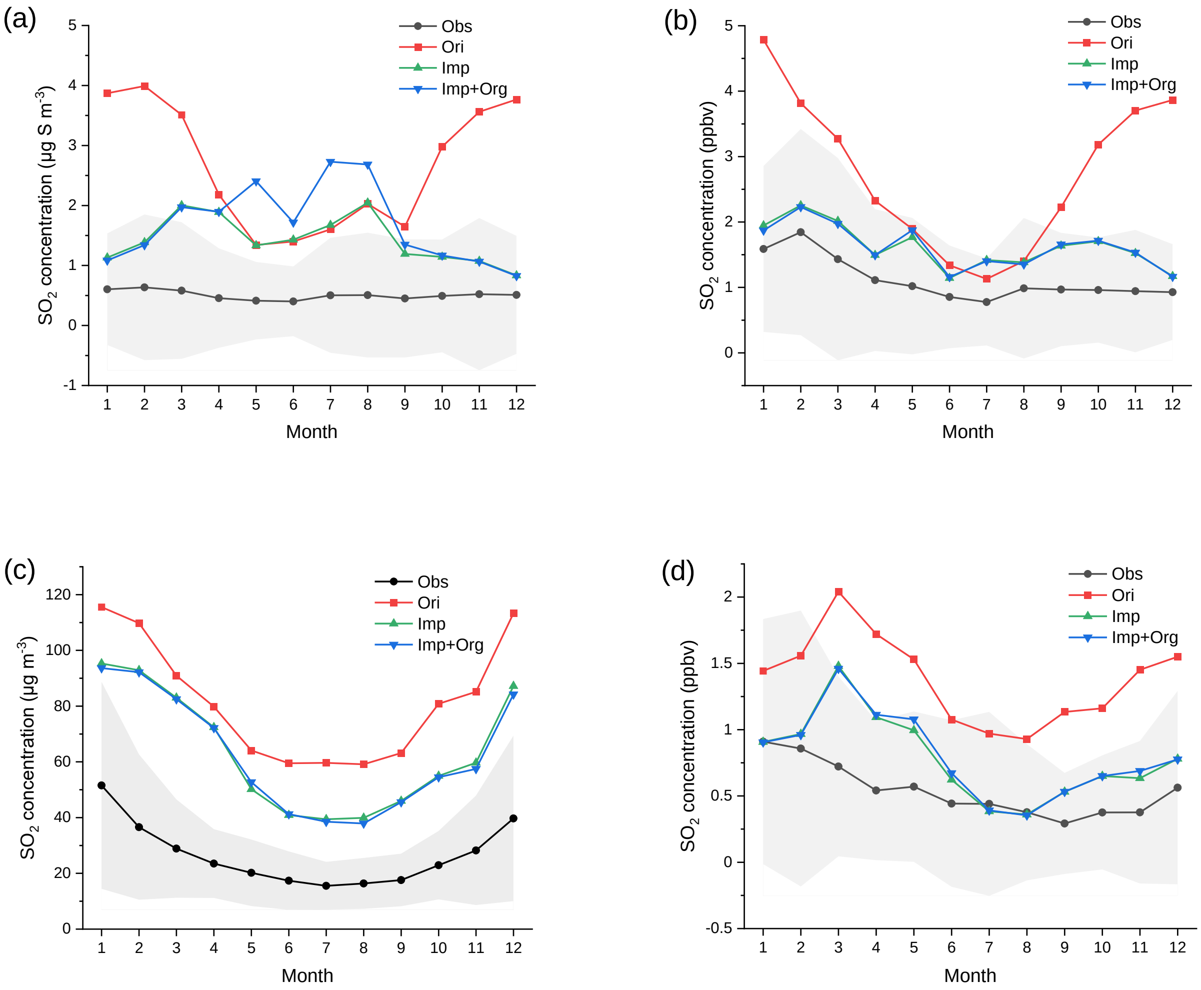

Figure R3: Regional monthly average concentrations (mixing ratios) of SO_2 in EU, US, CN and JK in 2015. The black, red, green and blue lines represent the Observed, Original-simulated, Improved-simulated and "Improved + Org-chem"-simulated concentrations (mixing ratios), respectively. The gray areas represent the standard deviation of Observed concentrations (mixing ratios). The corresponding monitoring networks are (a) EMEP (unit: μg S m^{-3}), (b) EPA (unit: ppbv), (c) CNEMC (unit: μg m^{-3}) and (d) EANET (unit: ppbv).

Revisions:

Section 5.3, lines 476-483:

"Recent studies show that hydroxymethanesulfonate (HMS), formed by aqueous-phase reactions of dissolved HCHO and SO_2, is an abundant organosulfur compound in aerosols during winter haze episodes, and suggest that aqueous clouds act as the major medium for HMS chemistry (Moch et al., 2020; Song et al., 2021). Therefore, it's necessary to further investigate the influence of this organic chemistry on the in-cloud aqueous-phase chemistry system in CESM2. We tried to incorporate 10 aqueous-phase organic species and 60 related reactions, including the reactions

related to CH_3OH, HCHO, CH_3OOH and HMS, as shown in Tables S2a and S2b. We conducted additional simulations for testing the contribution from this organic chemistry. As shown in Fig. S11, incorporating this organic chemistry has a minor effect on SO_2 concentrations, similar to that of carbonate chemistry.”

4. *Table 1a, line 163: here again the kinetic data seems to come from the modelling study by Liang and Jacobson (1999). However, the primary references for the kinetic paramaters are missing. Please cite the primary sources for the data.*

Response: Thank you again for this comment. We have replaced all the secondary sources with primary sources as shown in Tables 1a and 1b in the revised manuscript.

5. *Line 164, footnote b: why using "C" for a rate constant and "k1" and "k2" for the pre-exponential factors and T-dependency? This is confusing. Why then "k2" is multiplied by 500? "k1" is obviously k(298K) but "k2" is not a rate constant. By the way in Table 1a the units of "k1" and "k2" are not given.*

Response: The letters “C”, “k_1”, “k_2” are just referred to Liang and Jacobson (1999). Using “C” for inverse reactions can be distinguished from the rate constant k of the forward reactions. The reason why we use “k_1” and “k_2” in Table 1a unlike the parameters in Table 1b is that their meanings in gas-to-aqueous reactions are different with those in aqueous-to-gas reactions. As we described in lines 180-184, for gas-aqueous reactions, k_1 and k_2 are the molar mass (g mol^{-1}) and mass accommodation coefficients of this species, respectively. And for aqueous-gas reactions, k_1 and k_2 are Henry’s law constants (M atm^{-1}) at 298 K and the enthalpy of dissolution ΔH (kcal mol^{-1}), respectively. The number “500” is the unit conversion factor (Liang and Jacobson, 1999):

$$\frac{\Delta H\ (\mathrm{J\ mol^{-1}})}{\mathrm{R}} = \frac{1000\ \Delta H\ (\mathrm{kJ\ mol^{-1}})}{\mathrm{R}} = \frac{4187\ \Delta H\ (\mathrm{kcal\ mol^{-1}})}{\mathrm{R}} = \frac{4187\ \Delta H\ (\mathrm{kJ\ mol^{-1}})}{8.314\ (\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}})} = 503.6\ \mathrm{k_2} \approx 500\ \mathrm{k_2}$$

Therefore, it is difficult to use the unified units. To avoid confusion, we described the units to these parameters in the text and footnotes (see lines 180-184). Meanwhile, for more concise expression, we replaced k_2 by “ΔH (J mol^{-1}) / R”, eliminated the factor “500” and updated the corresponding data and formula (see line 171)

6. *Line 343: this separation of the effects by HO_x-chemistry and Fe-chemistry is artificious as much of the fuel (HO_2 and O_2^-) for the Fe-chemistry is produced by the HO_x-chemistry. By shutting down the latter, the former is also strongly depressed. Thus, one can not really see separate effects. It makes sense to always keep the HO_x-chemistry (which also has sulfur-sulfur reactions!) and switching off the other parts of the mechanism. Otherwise the sulfur-sulfur chemistry without involving HO_x should be separated from the "HO_x-chemistry". Anyway, the mentioned "parts" of the mechanism do not interact linearly and their respective effects are not additive. More appropriate for the goal of the section would be a budget for the loss of S(IV) in the aqueous-phase. This would be a good addition to the manuscript.*

Response: We totally agree with the referee's suggestion! We did take that into account and perform the simulations as you suggested. All the simulations (except the Original case with no detailed cloud chemistry) include HO_x-chemistry because the HO_x-chemistry involves most of the critical radicals in aqueous-phase chemistry. Therefore, the cases of Fe, N or carbonate chemistry also include the HO_x-chemistry. More detailed description is shown in Table S1. Then the contributions of Fe, N and carbonate chemistry are calculated by the differences between the results of their corresponding cases and that of the "HO_x-chem only" case. As for the budget for the loss of S(IV) in the aqueous-phase, or the formation of sulfate including its influence on cloud formation and radiative forcing, we highly agree that they are all crucial issues. We will present these results in our follow-up paper. To better describe the simulations, we made some revisions in Section 4 (see below).

Revisions:

Section 4, lines 357-362:

"On the basis of above analysis of the overall detailed aqueous-phase chemistry, it is necessary to discuss the contributions of different aqueous-phase chemical mechanisms in detail. **Cases for four different mechanisms are performed with the corresponding reactions in Table 1. See Table S1 for details about the configuration of individual cases. Given the fact that the HO_x chemistry involves most of the critical radicals in aqueous-phase chemistry, the cases of Fe, N and carbonate chemistry also include the HO_x chemistry. The individual contribution of Fe, N or carbonate chemistry is compared with the HO_x-chem alone case.**"

7. *Lines 405-406: the little change is likely affected by the authors using a low rate constant for the S(IV) oxidation by* NO_2 *(see my previous comment).*

Response: Thanks again for this comment. Please see our responses to *Comment 2*.

8. *Minor comments*

   Line 215: citing Xu et al. 2019 and Yi et al. 2017 for justifying the one-year model spinup is not necessary and very suspicious of authors self-citation. Please remove these citations that anyway have thematically very little to do with the topic of the manuscript.

Response: Thanks, we have removed these two citations in the revised manuscript.

9. *line 236: in Figure 2 mixing ratios are shown and not concentrations. Obviously they are not same. This mistake is done in many other places. It needs to be corrected.*

Response: We replaced all the expression “concentration(s)” to “mixing ratio(s)” where the unit “ppbv” is used. See the revised manuscript for details.

10. *Line 53: Poschl -> Pöschl*

Response: Thanks again for pointing out this mistake. We corrected the spelling of this name in the revised manuscript.

References

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