

## Comment on acp-2021-406

Anonymous Referee #2

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Referee comment on "Influence of atmospheric in-cloud aqueous-phase chemistry on the global simulation of SO<sub>2</sub> in CESM2" by Wendong Ge et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-406-RC2>, 2021

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### General comment

This manuscript concerns with the global impact of aqueous-phase chemistry on the simulation of atmospheric SO<sub>2</sub> 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<sup>3+</sup>] applied globally. Then, an attempt of separating the effects of different parts of the mechanism on SO<sub>2</sub> 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.

### 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<sub>2</sub>-relevant known chemistry. However, the latest and most reliable data is not necessarily reflected in their mechanism. For instance, the oxidation of S(IV) by NO<sub>2</sub> (also mentioned in the text). However, in Table 1b one finds only reaction 199 for HSO<sub>3</sub><sup>-</sup> and nothing for SO<sub>4</sub><sup>--</sup>. 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 made me doubt about the statement on line 18 in the abstract about the minor role of N-chemistry for SO<sub>2</sub> oxidation.

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<sub>3</sub><sup>-</sup> to produce HMS which reacts quickly with OH to yield SO<sub>5</sub><sup>-</sup>. 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<sub>2</sub>-and thus OH. I think this chemistry needs to be considered especially in a study about the importance of SO<sub>2</sub> aqueous-phase sinks.

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 parameters are missing. Please cite the primary sources for the data.

Line 164, footnote b: why using "C" for a rate constant and "k<sub>1</sub>" and "k<sub>2</sub>" for the pre-exponential factors and T-dependency? This is confusing. Why then "k<sub>2</sub>" is multiplied by 500? "k<sub>1</sub>" is obviously k(298K) but "k<sub>2</sub>" is not a rate constant. By the way in Table 1a the units of "k<sub>1</sub>" and "k<sub>2</sub>" are not given.

line 343: this separation of the effects by HO<sub>x</sub>-chemistry and Fe-chemistry is artificial as much of the fuel (HO<sub>2</sub> and O<sub>2</sub><sup>-</sup>) for the Fe-chemistry is produced by the HO<sub>x</sub>-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<sub>x</sub>-chemistry (which also has sulfur-sulfur reactions!) and switching off the other parts of the mechanism. Otherwise the sulfur-sulfur chemistry without involving HO<sub>x</sub> should be separated from the "HO<sub>x</sub>-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.

lines 405-406: the little change is likely affected by the authors using a low rate constant for the S(IV) oxidation by NO<sub>2</sub> (see my previous comment)

### **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.

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.

line 53: Poschl -> Pöschl