

### Response to Referee 3 (RC3)

Tashmim et al. report results from the GEOS-Chem global chemical transport model incorporating many recent findings on reactive intermediates in dimethyl sulfide (DMS) oxidation chemistry and quantify impacts on terminal products and aerosol particle size and abundance. This type of integrated analysis is necessary for evaluating the combined impact of the numerous recent revisions to our understanding of DMS chemistry and this work therefore has a high potential value. However, this is dependent on a thoughtful synthesis of reaction mechanisms from various sources which I believe needs some further work in this manuscript. In particular, I have concerns about how details of the reaction of DMS with NO<sub>3</sub> and Cl were implemented (see major comments below). Otherwise I find the work to generally be of a high quality and the results and discussions are well supported. If these apparent issue with the reaction mechanism are resolved along with the other comments below, then I believe this manuscript will likely be suitable for publication in *ACP*.

**Response:** We thank the Reviewer for positive feedbacks and helpful comments. Please find our point-by-point responses provided below.

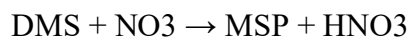
#### Major Comments:

1.) My primary concern with the manuscript is what appears to me to be a mistake in the reaction mechanism resulting in the DMS + NO<sub>3</sub> and DMS + Cl reactions being included twice, which impacts all of the results presented in this analysis. In table 2 the following reaction is listed:



rate:  $1.90\text{e-}13 \cdot \exp(530/T)$  reference: (Burkholder et al., 2015)

And in table 4 the following reaction is listed:



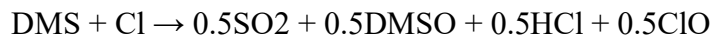
rate:  $1.9\text{e-}13 \cdot \exp(520/T)$  references: (Novak et al., 2021; Wollesen de Jonge et al., 2021)

These are not two distinct chemical reactions. Both reactions are an H-abstraction from DMS by NO<sub>3</sub> with the same rate constant. The only difference is in the assigned products where the reaction in table 2 makes the simplifying assumption that SO<sub>2</sub> is formed at unit yield, while table 4 instead goes through the reactive intermediate species MSP. In reality the reaction in table 2 also proceeds through MSP, this was likely just neglected in the referenced compilation of Burkholder et al., 2015 because the significance of the MSP intermediate for HPMTF chemistry was not known at the time of that data evaluation. Only the Reaction in table 4 should be included in the model. By including both you are double counting this reaction pathway and incorrectly increasing the modelled significance of NO<sub>3</sub> chemistry.

**Response:** We appreciate the catch and have removed the reaction  $\text{DMS} + \text{NO}_3 \rightarrow \text{SO}_2 + \text{HNO}_3 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$  (Table 2), keeping only the reaction  $\text{DMS} + \text{NO}_3 \rightarrow \text{CH}_3\text{SCH}_2\text{OO}$  (MSP) +

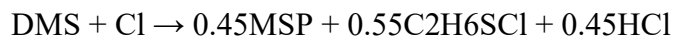
HNO<sub>3</sub> (Table 4) in our revised chemical mechanism, following MCMv3.3.1. and other recent modeling studies (e.g. Novak et al., 2021, Wollesen de Jonge et al., 2021, Novak et al., 2022).

Similarly, for DMS + Cl the following reaction is given in Table 2:



rate: 3.40e-10 reference: (Barnes et al., 2006; Burkholder et al., 2015)

While in Table 4 the following reaction is listed:



Rate: 3.40e-10 reference: (Fung et al., 2022)

Again, these are fundamentally the same reaction resulting in this chemistry being double counted. The only difference is in the simplifying assumptions made about product yields.

**Response:** We removed  $\text{DMS} + \text{Cl} \rightarrow 0.5\text{SO}_2 + 0.5\text{DMSO}$  and kept  $\text{DMS} + \text{Cl} = 0.45 \text{ MSP} + 0.55\text{C}_2\text{H}_6\text{SCl} + \text{HCl}$  to keep the products from addition and abstraction channel. We also updated the rate constant to 3.6e-10 for this reaction according to IUPAC recommendation. In addition to that, we have changed the C<sub>2</sub>H<sub>6</sub>SCl chemistry. Instead of having a null cycle where C<sub>2</sub>H<sub>6</sub>SCl decompose to DMS via the reaction  $\text{C}_2\text{H}_6\text{SCl} \rightarrow \text{DMS} + \text{Cl}$ , it now continues the oxidation as,  $\text{C}_2\text{H}_6\text{SCl} = \text{DMSO} + \text{ClO}$ . With these reactions we find very small change in our results for this loss process shown in Figure 6 and Figure A1 for DMS + Cl channel.

2.) The results of Jernigan et al. (2022) show that HPMTF is the primary precursor to OCS formation from DMS oxidation with  $\text{HPMTF} + \text{OH} \rightarrow 0.13 \text{ OCS} + 0.87 \text{ SO}_2$ . At a minimum, this should be considered as it will reduce the overall SO<sub>2</sub> production from DMS oxidation which will impact the results presented in this manuscript. The overall yield of OCS is also therefore highly dependent on HPMTF multiphase loss processes. With minimal additional analysis, this work could also provide a valuable update on to the GEOS-Chem modeling results from Jernigan et al. (2022). I do not feel strongly that extended analysis of OCS production should be included, but do feel that some comment on the impacts on SO<sub>2</sub> production are necessary beyond what is included at lines 91-95.

**Response:** Previously we had an indirect OCS formation pathway in the model as follows:



Followed by Jernigan et al., 2022a, in our revised mechanism, beside this reaction mentioned earlier, we added the following reactions as OCS formation and loss pathway as part of the DMS oxidation mechanism.

- a)  $\text{HPMTF} + \text{OH} \rightarrow 0.13 \text{ OCS} + 0.87 \text{ SO}_2 + \text{CO}$
- b)  $\text{OCS} + \text{OH} \rightarrow \text{SO}_2$

With these two additional reactions, we find that rather than 38% reduction in SO<sub>2</sub> formation now we have 35% reduction in SO<sub>2</sub> due to stepwise conversion of HPMTF to SO<sub>2</sub> via OCS, although yield of SO<sub>2</sub> from non-HPMTF pathway decreases to 45.3% from 52.4%. Note that we have made changes to few other reactions in the revised mechanism which does not involve OCS, so these changes in percentage of SO<sub>2</sub> might not be entirely attributed to the reactions involving OCS. We have added a description of this near lines 102-106:

“With the latest experimental findings on heterogeneous loss process of HPMTF and experimentally validated oxidation reactions for OCS formation directly from HPMTF it is necessary to include these reactions as part of the DMS oxidation mechanism as these will have impact on overall yield of SO<sub>2</sub>, thus affecting the formation probability of CCN (Jernigan et al., 2022a, b).”

Lines 471-475:

“One of the reactions that possibly contributes to delayed formation and reduction of SO<sub>2</sub> concentration is the first-generation OCS formation from OH oxidation of HPMTF. We find that addition of cloud and aerosol loss significantly decreases the OCS production, especially at the high cloud cover region as previously reported (Jernigan et al., 2022a)”

3.) SO<sub>2</sub> mixing ratios were measured during the ATom-4 campaign at suitable precision to be informative in background marine air masses ([https://daac.ornl.gov/ATOM/guides/ATom\\_SO2\\_LIF\\_Instrument\\_Data.html](https://daac.ornl.gov/ATOM/guides/ATom_SO2_LIF_Instrument_Data.html)). A comparison of measured and modelled SO<sub>2</sub> could be a very useful addition.

**Response:** We have added this comparison with explanation in Figure 2c. Line 340-355:

“We also compared the SO<sub>2</sub> concentrations measured during ATom-4 by Laser Induced Fluorescence (LIF) and simulation MOD values for nearest neighbor grid cells are shown in Figure 3c across different altitude. Modeled surface SO<sub>2</sub> concentrations are lower than those observed during ATom-4 missions across the vertical scale shown here for simulation MOD. The greater SO<sub>2</sub> losses results in a shorter SO<sub>2</sub> lifetime (from 1.4 d to 1.3 d) for simulation MOD relative to simulation BASE. The reduction in modeled SO<sub>2</sub> is largest over the Southern Ocean (shown later in Fig. 7a) where heterogeneous oxidation of HPMTF is most efficient and irreversible. Removing the heterogeneous loss of HPMTF increases the modeled SO<sub>2</sub> compared to simulation MOD with underprediction remaining for altitudes > 1km. Remaining model biases could be at least partially attributed to uncertainty in DMS oxidation processes along with other non-DMS sources contributing high concentration of SO<sub>2</sub>. Aside from uncertainty in DMS emissions and oxidation, recent understanding of marine sulfur chemistry such as methanethiol (CH<sub>3</sub>SH) oxidation has been reported as an significant source of SO<sub>2</sub> in the marine atmosphere and could help reduce the bias, a possibility deserving further investigation (Berndt et al., 2023; Novak et al., 2022). Overall the DMS oxidation chemistry implemented in this work reduces the model observation bias close to the surface (up to 1km) compared to BASE GEOS-Chem chemistry.”

## Other Comments:

What SO<sub>2</sub> heterogenous chemistry is included in this work?

**Response:** We do have cloud chemistry of SO<sub>2</sub> in the default version of GEOS-Chem (v12.9.3) which includes in-cloud oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and O<sub>2</sub> catalyzed by transition metals (Mn, Fe) as well as oxidation by HOBr and HOCl. Since this is not a new addition to the model, we did not highlight that in our manuscript. To address this comment, we have added line 258-263 in the revised version as:

“Alongside the gas-phase and aqueous-phase reactions relevant to the added DMS oxidation mechanism contributing to the formation of SO<sub>2</sub> and sulfate, the default version of GC-TOMAS used here also includes in-cloud oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and O<sub>2</sub> catalyzed by transition metals (Mn, Fe), as well as the loss of dissolved SO<sub>2</sub> by HOBr and HOCl, all of which are passed to TOMAS to account for sulfate production (Chen et al., 2017; Wang et al., 2021).”

The sensitivity runs with and without sea-salt aerosol debromination are appreciated given remaining uncertainties in BrO measurements and model implementations. Is it correct that the revised debromination mechanism of Wang et al. 2021 was not used here? If so what is the motivation for this? This comment is based on the references included in the methods section in lines 171-172.

**Response:** We have used the default debromination mechanism available for GEOS-Chem v12.9.3 and that does not include revisions from Wang et al. 2021. We did include sensitivity runs with and without sea-salt aerosol debromination just to evaluate the contribution of this process in resolving some uncertainty associated with BrO.

Can you show a figure of the global distribution of BrO in the MOD and MOD without sea salt debromination model cases? Otherwise it is difficult for the reader to make absolute comparisons for either model case to measurements of BrO.

**Response:** We have added a global distribution of BrO for MOD and MOD without sea salt debromination as Figure A6 and mentioned that in lines 428 – 431:

“As would be expected, these simulations show much lower BrO formation (as shown in Fig. A6) and resulting chemical impacts, with overall oxidation contributions comparable to previous literature (Schmidt et al., 2016; Wang et al., 2021).”

Table 3 and lines 224 - 230: Jernigan et al. (2022) provides an experimental value for k(HPMTF + OH) of 1.4E-11 cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> which is a useful validation of the assumed value of 1.1E-11 cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> used here and in Vermeuel et al. (2020) and Novak et al. (2021). This should be referenced.

**Response:** In the revised manuscript we used the experimentally determined rate constant of 1.40 × 10<sup>-11</sup> cm<sup>3</sup> molecules<sup>-1</sup>s<sup>-1</sup> for this reaction and addressed this in Table 3 and near line 237-240 along with proper reference suggested here. The change to the manuscript involves line 237-240:

“We use a rate constant of  $1.40 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  for HPMTF + OH, which was previously determined based on concentrations of other known sulfur species (DMS, DMSO, SO<sub>2</sub> and methyl thioformate; MTF; CH<sub>3</sub>SCHO; a structurally similar proxy to HPMTF) and evaluated by box model (Jernigan et al., 2022a).”

Line 388 and onward: You should make clear what the altitude range is for the quoted reductions and enhancements are in the simulation. Presumably these are for some near surface range and not total column?

**Response:** Correct, this is not for the total column. We have added the term ‘surface layer’ at line 453 and elsewhere while mentioning such numbers which represents the vertical level 1 of GEOS-Chem.

Figure 9. It appears that much of the particle number increase is for  $D_p > 200 \text{ nm}$ . What is the size range where CCN abundance is most sensitive to particle growth? Some additional context for the reader may be useful in connecting changes in particle size bins to potential changes in CCN abundance.

**Response:** For better understanding we added line 536-538:

“The fraction of newly formed particles that can reach the CCN size is dependent on the particle growth rates, especially for particle sizes below 10 nm, where we see highest coagulation losses to larger particles.”