

Response to Referee 1 (RC1)

Tashmim et al report global model simulations of DMS oxidation. The model includes an advanced DMS oxidation scheme that accounts for recent insights into DMS oxidation chemistry. This work builds on the work of Novak et al., where the gas and multiphase chemistry of HPMTF was explored initially in GEOS-Chem. This work significantly advances beyond the study of Novak et al. to investigate the role of DMS+O₃ multiphase chemistry and the impact of the new DMS oxidation mechanisms on particle number and size distributions. The manuscript is well written and should be published following the authors attention to the following points:

Response: We thank the reviewer's positive and constructive feedback. We have addressed and revised the manuscript accordingly. Our point-by-point responses are provided below.

General comments:

The modified version of the model has HPMTF and DMS cloud chemistry. It was not clear to me how DMSO and SO₂ cloud chemistry was treated in the model. This seems to be an important component of sulfur cycling in the MBL that could be addressed here. Was this included, but not discussed or was this chemistry not included in the revised mechanism.

Response: Beyond the HPMTF and DMS cloud chemistry additions we have made, the default version of GEOS-Chem (v12.9.3) does include in-cloud oxidation of SO₂ by H₂O₂, O₃, and O₂ catalyzed by transition metals (Mn, Fe). Since this is not a new addition to the model, we did not highlight that in our manuscript earlier. To clarify the treatment of DMSO, for the reactions of DMS(g) + O₃(aq), DMSO(g) + OH(aq), MSIA(g) + OH(aq), MSIA(g) + O₃(aq) and MSA(g) + OH(aq) in cloud droplets and aerosols, we assume a first-order loss of the gas-phase sulfur species following the parameterization described in Chen et al. 2018 and original references, and we use the same values for physical parameters that were used in that study. To address this comment and better explain these details, we have added the following text in the revised manuscript in lines 255-263:

“For the aqueous-phase reactions listed in Table 2, including the oxidation of intermediates DMSO and MSIA in cloud droplets and aerosols, a first-order loss of the gas-phase sulfur species was assumed following previously used parameterizations and physical parameter values (Chen et al., 2018). Alongside the gas-phase and aqueous-phase reactions relevant to the added DMS oxidation mechanism contributing to the formation of SO₂ and sulfate, the default version of GC-TOMAS used here also includes in-cloud oxidation of SO₂ by H₂O₂, O₃, and O₂ catalyzed by transition metals (Mn, Fe), as well as the loss of dissolved SO₂ 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 percentage of DMS lost to each reaction pathway (e.g., OH, BrO, O₃(aq), NO₃) is cited in the conclusions and features in figure. It is not abundantly clear how these percentages were calculated. Are these the fraction of DMS emitted that is lost to each of these reaction pathways? Or is this the average of the fractional losses (e.g., f(DMS_OH)/total loss) averaged spatially over the entire map? I think it should be (and probably is) the former, but it would be helpful to have confirmation.

Response: This percentage indicates the former case. To avoid confusion, we have updated the captions for Figure 6 and Figure A1 to clarify that the percentage here indicates the fraction of DMS lost to each of this specific reaction pathways.

“Figure 6 Geographic distribution of the annual mean surface layer fraction of total DMS oxidation (percent) attributed to different tropospheric oxidants for simulation MOD (described in Table 5). Percentages in parentheses indicates average contribution to global chemical loss as a fraction of DMS emitted for each reaction pathways presented here.”

“Figure A1 Surface layer geographic distribution of the simulated annual mean fraction of total DMS oxidation (percent) attributed to different tropospheric oxidants for a simulation otherwise the same as simulation MOD except with no sea salt debromination. Percentages in parentheses indicates average contribution to global chemical loss as a fraction of DMS emitted for each reaction pathways presented here. Simulations are described in Table 5.”

Specific Comments

Line 48: Cl and BrO should be in parentheses rather than brackets.

Response: We have replaced the brackets with parentheses in line 49 for Cl and BrO.

Line 81: Are you referring to a multiphase DMS+OH addition pathway or multiphase DMSO chemistry, or a DMS+O₃ pathway. In either case, it would be helpful to be specific.

Response: We were referring to OH-addition pathway of DMS forming DMSO and MSIA as the intermediates. We rephrased the lines 83-87 as:

“For example, the OH-addition pathway of DMS forms DMSO and MSIA as the intermediates, which has been identified as a dominant source of MSA via their aqueous-phase oxidation, and a fraction of that MSA subsequently undergoes aqueous-phase oxidation to form sulfate aerosol (Chen et al., 2018; Ishino et al., 2021; Zhu et al., 2006; von Glasow and Crutzen, 2004).”

Line 87: I appreciate that MSP is used in the literature, but I don't know why. What is that an acronym for? I would suggest MTMP.

Response: We have followed the nomenclature of Fung et al. 2022, which used MSP in reference to the methylthiomethyl peroxy radical ($\text{CH}_3\text{SCH}_2\text{OO}\cdot$). We do note that Jernigan et al., 2022a did use the abbreviation MTMP for the same species. Considering that this is a relatively recently identified species, and to maximize clarity in the absence of a fixed standard, we mention both of these alternatives initially and then continue with the more commonly used (so far) abbreviation of MSP throughout the rest of the manuscript. This is written in lines 89-94:

“More recent experimental and laboratory studies have confirmed the formation of methylthiomethyl peroxy radicals ($\text{CH}_3\text{CH}_2\text{OO}\cdot$; abbreviated MSP or MTMP) from the H-abstraction channel of OH oxidation, which can subsequently lead to a series of rapid intramolecular H-shift isomerization reactions, ultimately resulting in the formation of the stable intermediate HPMTF (Berndt et al., 2019; Veres et al., 2020; Vermeuel et al., 2020; Wu et al., 2015; Fung et al., 2022; Jernigan et al., 2022a).”

Line 90: I don't think all of these references are for the last statement (30-50% of DMS ends up as HPMTF). Perhaps distribute the references through the sentence so they refer to the correct statements?

Response: We have rephrased this line and broken it down into two sentences to properly indicate associated references. This is now written in lines 89-98:

“More recent experimental and laboratory studies have confirmed the formation of methylthiomethyl peroxy radicals ($\text{CH}_3\text{CH}_2\text{OO}\cdot$; abbreviated as MSP or MTMP) from the H-abstraction channel of OH oxidation, which can subsequently lead to a series of rapid intramolecular H-shift isomerization reactions, ultimately resulting in the formation of the stable intermediate HPMTF (Berndt et al., 2019; Veres et al., 2020; Vermeuel et al., 2020; Wu et al., 2015; Fung et al., 2022; Jernigan et al., 2022a). It has been reported that 30–46% of emitted DMS forms HPMTF according to different modeling studies and this falls within the observational range from NASA Atmospheric Tomography ATom-3 and ATom-4 flight campaigns where about 30–40% DMS was oxidized to HPMTF along their flight tracks (Fung et al., 2022; Veres et al., 2020; Novak et al., 2021).”

Figure 1: In my version there are no green boxes as referenced in the figure caption (they are orange). Are these the only species and reactions used? More specifically, is DMSO chemistry included? It is discussed in the text surrounding Figure 1, but not highlighted in the figure caption. I appreciate that this may complicate the figure (and I am not suggesting it needs to be added), but if DMSO features in the model, it would be good to state it in the figure caption.

Response: Thank you for spotting this mismatch between the figure and its caption. We have updated the figure and caption using only blue boxes for the three major oxidation products MSA, HPMTF and SO₂, all of which eventually oxidize to sulfate. We do have DMSO and MSIA in the model, which eventually contribute to SO₂ and MSA, but in the figure our intent was to highlight only the major oxidation products for simplicity of the scheme. However, to address this concern we have updated the Figure 1 caption to read:

“**Figure 1** Modified DMS oxidation mechanism used in this work (simulation MOD) showing the formation of major stable oxidation products (blue-outline boxes) including newly identified intermediate HPMTF, and their contribution to new particle formation or growth of existing particles. Note that we include gas-phase and aqueous-phase chemistry of DMSO, MSIA and OCS in the mechanism, which counts towards their contribution to the formation of major oxidation products of DMS, but that these pathways are not explicitly shown here to maintain visual clarity.”

Line 125: The numbers cited here are from the global model simulation across all cloud fields, not just for the cloudy case. Perhaps this was the intent of the sentence, but maybe breaking this into two sentences would help get this point across that the 24% reduction in MBL SO₂ is a global, annual average not from the case study.

Response: We break this line into two sentences to better explain the meaning of these percentages. This is now rephrased in lines 133-138:

“Other work has used direct airborne eddy covariance flux measurements to explain the chemical fate of HPMTF in the MBL, finding that in cloudy conditions chemical loss due to aqueous phase reactions in clouds is the major HPMTF removal process (Novak et al., 2021). In the same study, global model simulations showed a 35% reduction in global annual average SO₂ production from DMS and a 24% reduction in the near-surface (0 to 3 km) global annual average SO₂ concentrations over the ocean as a result of this process (Novak et al., 2021).”

Table 4: What is MSP + MO₂?

Response: In the earlier version MSP + MO₂ means CH₃SCH₂OO· + CH₃O₂. Here, CH₃O₂. (Methylperoxy radical) is abbreviated as MO₂ following the GEOS-Chem chemical mechanism. In the revised version we have replaced MSP + MO₂ with MSP + CH₃O₂ in Table 4 for clarity.

Table 5 caption: It would be helpful to fully explain what $\text{HPMTF} \rightarrow \text{SO}_4^{2-}$ means. I think you mean there is a 100% S-yield of SO_4^{2-} . Also, is gamma here really the activity coefficient? I think you mean uptake coefficient.

Response: By $\text{HPMTF} \rightarrow \text{SO}_4^{2-}$ we mean loss of HPMTF via cloud and aerosol results in instant formation of SO_4^{2-} . However, losses in clouds follow entrainment-limited uptake which controls the rates of mixing between cloudy and clear air in the chemical rate expression (Novak et al., 2021; Holmes et al., 2019). Here, gamma (γ) is the reactive uptake coefficient for these loss processes. In the revised version we have used an experimental value of γ for the aerosol loss of HPMTF and modified and corrected Table 5 footnote at lines 223-224 as:

“* Instantaneous formation of sulfate via HPMTF cloud and aerosol loss reactive uptake coefficient (γ) of 0.0016.”

Line 224: $\text{OH} + \text{HPMTF}$ was measured in Jernigan et al. it would be best to cite that.

Response: In the revised manuscript we used the experimentally determined rate constant of $1.40 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for this reaction and corrected this near line 250-252 along with proper reference suggested here. The new line is line 237-240:

“We use a rate constant of $1.40 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for $\text{HPMTF} + \text{OH}$, which is determined based on concentration of other known sulfur species (DMS, DMSO, SO_2 and methyl thioformate; MTF; CH_3SCHO ; a structurally similar proxy to HPMTF) and evaluated using a box model (Jernigan et al., 2022a).”

Line 236: I don't think it matters at all (since loss is diffusion limited in the cloud) but the HPMTF uptake coefficient to dilute cloud droplets should not be faster than that to the aerosol. I would use the experimentally determined value from Jernigan for both. Again, I don't think it matters for the simulation.

Response: We have used reactive uptake coefficients (γ) of 0.0016 for both cloud and aerosol loss of HPMTF, which represents the experimentally determined value of $\gamma(\text{HPMTF})$ to deliquesced NaCl (Jernigan et al., 2022b). As predicted by the reviewer, we find little difference in percent of HPMTF lost to cloud since the loss is diffusion limited. However, on a fractional basis the percentage of HPMTF lost to aerosol does increase from 2.3% to 3.4%.

Line 280: How are these fractions of DMS loss calculated? Is this taking the map (in Figure 3) and calculating and average % or is this weighted by the amount of DMS that is lost. Given the strong spatial gradients in DMS I think this makes a difference.

Response: For line 407, the numbers mentioned as “full conversion yield of DMS into SO₂ (82.5%) and MSA (17.5%)” is presented in Fig. A3a. We have added the reference of this figure at the end of this line (lines 406-408 in the revised manuscript). This is for the case of BASE simulation and calculated by the fraction of DMS emitted that is lost as MSA and SO₂. On the other hand, Fig. 6 represents fraction of DMS emitted lost to each of the specific reaction pathways mentioned as the header of individual maps.

Line 286: What are the “two possible pathways” Shouldn’t DMS+NO₃ make MTMP with 100% yield? I am really surprised that DMS+NO₃ accounts for 15% of the total DMS loss? That seems big to me as I’d expect [NO₃] to be almost zero at the surface over the ocean. Perhaps some more discussion on this point is needed.

Response: We have removed the reaction $\text{DMS} + \text{NO}_3 \rightarrow \text{SO}_2 + \text{HNO}_3 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$ and kept only one DMS + NO₃ reaction which gives MSP with 100% yield. With that being the only loss process of DMS via NO₃, we find this reaction accounts for 12.8% of the total DMS loss with major loss happening in the NH coastal regions due to high NO_x emission from nearby land-based sources. However, over the ocean this is mostly less than 10% except for upper to mid-latitude Northern Hemisphere. Note that previous modeling studies have reported even higher values for the global average percent loss of DMS by NO₃ (16% and 22.5% by Chen et al. 2018 and Fung et al. 2022). With the change in chemistry and associated results we have revised the main text to address this question near lines 412-415:

“NO₃ oxidation of DMS accounts for another 12.8% of global DMS chemical losses, comparable to values found in previous studies (Chen et al., 2018; Fung et al., 2022). Over the ocean the NO₃ loss pathway is strongest in the NH coastal regions due to outflow of NO_x sources from over the land, whereas for the SH values are generally less than 10%.”

Figure 5, Line 352: These DMS measurements look very, very low. I think it is appropriate to question whether they are correct. Also, what measurements are used to create Figure 5?

Response: Thank you for noticing this issue. We did find an error in processing the input data for ATom-4 comparison using the planeflight diagnostic of the model and fixed it in the revised manuscript. This error does not impact any results other than Figure 3, and resolving this issue has improved our comparisons with observations and other simulations. We have added two more model simulations output for this vertical profile in the revised manuscript which are BASE and MOD_noHetLossHPMTF. In Figure 3a of the revised manuscript, the DMS measurements shown are now comparable to other literature sources that have used the same measurements for model/observation comparisons (Fung et al., 2022; Novak et al., 2021). For Figure 5 (now Figure 3), we do mention in the main text that the measurements used are from ATom-4 aircraft observations on the NASA DC-8 aircraft. The measurements used here were done by Iodide CIMS, Whole Air Sampler (WAS) and Laser Induced Fluorescence (LIF) for HPMTF, DMS and SO₂ respectively, and the links to those datasets were provided under the ‘Data Availability’ section. We also revised the caption for Figure 3 as:

“**Figure 3** Vertical profiles of (a) DMS, (b) HPMTF and (c) SO₂ mixing ratios from ATom-4 observations (black) and model with simulation MOD sampled along the ATom-4 flight tracks (red) binned every 500 m of flight altitude. Also shown are modeled results without HPMTF heterogeneous loss with simulation MOD_noHetLossHPMTF (yellow), and for BASE GEOS-Chem chemistry (blue). Box plot whiskers show full range of distribution at each altitude bin. DMS observations are from Whole Air Samples (WAS) while HPMTF DC-8 observations are from iodide ion chemical ionization time-of-flight mass spectrometer (CIMS). SO₂ observations from ATom-4 campaign were measured by Laser Induced Fluorescence (LIF).”

Figure 6: Without constraining the DMS flux, I don’t think it is possible to attribute the improvement in model-measurement of [DMS] to inclusion of DMS+BrO. It is very likely that the DMS emissions are driving this.

Response: We agree that DMS emissions play a crucial role in our comparison, as they vary considerably with changes in sea surface DMS climatology, and we acknowledge that improved and validated high-resolution inventories will be necessary to address some of these questions. Here we simply intend to highlight and explain changes between standard and modified chemistry, and to note that the impact of the DMS + BrO reaction is one possible contribution to improved model-measurement agreement. Fig. 5b shows that modeled losses of DMS are especially strong in the upper latitudes of both hemispheres, where DMS + BrO is shown to be an important chemical loss process. Thus, with identical (if imperfect) DMS emissions driving both BASE and MOD cases we can say that within the expanded mechanism DMS + BrO appears to play a meaningful role, reducing DMS concentrations compared to BASE and bringing them closer to observations. To better describe these results, in the revised manuscript we have rephrased and added lines 289-293:

“Similarly, for Amsterdam Island major overpredictions are apparent for the BASE simulation compared to MOD for the months of May-August. One reaction that may play a role in this shift

is $\text{DMS} + \text{BrO}$, which as indicated earlier is responsible for a faster overall chemical loss of DMS, in particular over the southern hemisphere high latitudes.”