

Response to Referee 2 (RC2)

This paper explores, within the GEOS-Chem CTM, the impact of a more complex description of the oxidation of DMS on the concentration of sulfur compounds and size resolved aerosol. This is an important area of research with the oxidation of DMS providing a significant, natural background source of sulfur in both the present and past atmospheres. Having a robust understanding of this chemistry is thus vitally important for us to understand both the present day atmospheres and any changes from the preindustrial to the present day. The current representation of the chemistry scheme in this model (the three reactions given in Table 1) is outdated and it is good to see that some development work is taking place.

I however I have two significant concerns about this paper and then a number of smaller ones (described below). Until these major concerns are addressed I don't think the paper is suitable for publication.

Response: We thank the reviewer's constructive feedback and detailed attention to the chemical mechanism we used here. We have revised the mechanism accordingly and addressed all the major and minor issues mentioned here. Our point-by-point responses are provided below.

Major issues:

- **The new chemistry scheme.** The mechanism used for the model is a merging of a number of different mechanisms available in the literature. However, I have some concerns about how this has been done.

The DMS + NO₃ reaction appears to be in twice. It is in the OH addition pathway section and in the H-abstraction pathway section. The rate constant is the same for both pathways but is given different references. I think this essentially means that this reaction is double counted and the DMS+NO₃ channel is twice as fast as it should be. Both the latest IUPAC and NASA data evaluation has a single NO₃ + CH₃SCH₃ → CH₃SCH₂ + HNO₃ reaction for this. Thus any subsequent chemistry needs to come from the further oxidation of CH₃SCH₂. Thus I think that there has been double counting by having this reaction in twice.

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 $\text{DMS} + \text{NO}_3 \rightarrow \text{CH}_3\text{SCH}_2\text{OO} (\text{MSP}) + \text{HNO}_3$ (Table 4) in our revised chemical mechanism, following MCMv3.3.1. and other recent modeling studies (Fung et al., 2022; Novak et al., 2021).

Similarly, I am confused by the DMS+Cl reaction. It has two channels, an abstraction channel ($\text{DMS} + \text{Cl} \rightarrow \text{CH}_3\text{SCH}_2 + \text{HCl}$) and an addition channel ($\text{DMS} + \text{Cl} \rightarrow \text{DMS-Cl}$). The IUPAC recommendation gives the recommendation of 3.6e-10 for both reactions with a 50:50 ratio between the two. This paper seems to follow this recommendation with a reaction of $\text{DMS} + \text{Cl} \rightarrow 0.5\text{SO}_2 + 0.5\text{DMSO} + 0.5\text{HCl} + 0.5\text{ClO}$. However, an additional reaction $\text{DMS} + \text{Cl} \rightarrow 0.45\text{MSP} + 0.55\text{C}_2\text{H}_6\text{SCl} + 0.45\text{HCl}$ is also included in the scheme. This is again is a split between the addition and abstraction reactions (0.55:0.45). But it appears that the overall DMS+Cl reaction is in the mechanism twice. I'm also then a bit confused by the C₂H₆S₂Cl chemistry. I think the only thing that can happen to this in the mechanism is that it falls apart back to DMS+Cl. Thus

the addition channel in this part of the chemistry is effectively a null cycle for DMS oxidation whereas for the other DMS+Cl reaction there is an assumption that it leads to the continued oxidation of the DMS.

Response: We have removed $\text{DMS} + \text{Cl} \rightarrow 0.5\text{SO}_2 + 0.5\text{DMSO}$ and kept $\text{DMS} + \text{Cl} = 0.45\text{MTMP} + 0.55\text{C}_2\text{H}_6\text{SCL} + \text{HCl}$ to keep the products from the addition and abstraction channels. We have also updated the rate constant to $3.6\text{e-}10$ for this reaction according to IUPAC recommendations. Further, we have fixed $\text{C}_2\text{H}_6\text{SCL}$ chemistry as proposed, replacing the previous unintended null cycle with the reaction $\text{C}_2\text{H}_6\text{SCL} = \text{DMSO} + \text{ClO}$. These are important fixes, though we do find only small differences in our overall results after implementing these changes.

The OH-addition reaction between OH and DMS gives SO_2 , MSA and CH_3O_2 as the products. Quoting Pham and Spracklen. Looking at Spracklen they have that channel for the DMS oxidation giving 0.6SO_2 and 0.4DMSO . The DMSO can then react with OH to give MSA. The mechanism included in the model seems to have lumped this together to avoid having to have DMSO as a tracer. However, there is DMSO as a tracer in place for the oxidation of BrO.

Response: This appears to be a typo in the reaction Table 2 of the manuscript. We had this reaction in the model as $\text{DMS} + \text{OH} \rightarrow 0.60\text{SO}_2 + 0.4\text{DMSO} + \text{CH}_3\text{O}_2$, and we have corrected Table 2 to address this.

The basis for some of these rates is some rather old complications of recommended rates (Saunders et al., 2003, Burkholder et al., 2015). There are more upto date recommendations in the the literature by both IUPAC and JPL. It would be very useful to update the mechanism to these recommendations rather than relying on some rather elderly rate constants.

Response: We acknowledge the need for better rate constants and have updated the kinetics of several reactions according to IUPAC and JPL recommendations along with following more recent literature offering updated reaction kinetics or stoichiometry. For some reactions we have also gone to MCMv3.3.1 values. In total, these revisions have impacted our results by decreasing the global mean surface-layer gas-phase sulfur dioxide (SO_2) mixing ratio by 35% compared to 38% and enhancing sulfate aerosol (SO_4^{2-}) mixing ratio by 22% compared to 16%, compared to the previously submitted version of the manuscript. Overall, we can say the revised mechanism shows updates in the magnitude of the changes mentioned previously, while maintaining the general direction of changes, along with associated conclusions and narrative. We greatly appreciate the guidance and opportunity to make these improvements. Changes to the manuscript for the reaction table thus to the mechanism are listed here:

Gas-phase reactions	Rate (s^{-1})	References	Table No.
$\text{DMS} + \text{OH} \rightarrow 0.60\text{SO}_2 + 0.4\text{DMSO} + \text{CH}_3\text{O}_2$	$8.2 \times 10^{-39} [\text{O}_2] e^{5376/T} / (1 + 1.05 \times 10^{-5} ([\text{O}_2]/[\text{M}]) e^{3644/T})$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	(Burkholder et al., 2015; Pham et al., 1995; Spracklen et al., 2005)	2
$\text{DMS} + \text{BrO} \rightarrow \text{DMSO} + \text{Br}$	$1.50\text{e-}14 * \exp(1000/T)$	(Bräuer et al., 2013; Hoffmann et al., 2016)	2
$\text{DMS} + \text{O}_3 \rightarrow \text{SO}_2$	$1.50\text{e-}19$	(Burkholder et al., 2015; Du et al., 2007)	2

$\text{OOCH}_2\text{SCH}_2\text{OOH} + \text{NO} \rightarrow \text{CH}_3\text{O}_2\text{S} + \text{NO}_2 + \text{HCHO}$	$4.9\text{e-}12 * \exp(260/T)$	(Saunders et al., 2003)	3
$\text{MSP} + \text{HO}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OOH} + \text{O}_2$	$1.13\text{e-}13 * \exp(1300/T)$	MCMv3.3.1, (Wollesen de Jonge et al., 2021)	3
$\text{CH}_3\text{SCH}_2\text{OOH} + h\nu \rightarrow \text{CH}_3\text{SCH}_2\text{O} + \text{OH}$	J(41)	MCMv3.3.1, (Wollesen de Jonge et al., 2021)	3
$\text{HPMTF} + \text{OH} \rightarrow \text{HOOCH}_2\text{SCO} + \text{H}_2\text{O}$	$4.00\text{e-}12$	(Jernigan et al., 2022)	3
$\text{HPMTF} + \text{OH} \rightarrow 0.13\text{OCS} + 0.87\text{SO}_2 + \text{CO}$	$1.40\text{e-}11$	(Jernigan et al., 2022)	3
$\text{OCS} + \text{OH} \rightarrow \text{SO}_2$	$1.13\text{e-}13 * \exp(1200/T)$	(Jernigan et al., 2022)	3
$\text{DMS} + \text{Cl} \rightarrow 0.45\text{MSP} + 0.55\text{C}_2\text{H}_6\text{SCI} + 0.45\text{HCl}$	$3.60\text{e-}10$	(Fung et al., 2022; Enami et al., 2004)	4
$\text{C}_2\text{H}_6\text{SCI} \rightarrow \text{DMSO} + \text{ClO}$	$4.00\text{e-}18$	(Hoffmann et al., 2016)	4
$\text{MSP} + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2(\text{O}) + \text{O}_2$	$3.74\text{e-}12$	(Saunders et al., 2003)	4
$\text{DMS} + \text{NO}_3 \rightarrow \text{SO}_2 + \text{HNO}_3 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$	$1.90\text{e-}13 * \exp(530/T)$	(Burkholder et al., 2015)	2
$\text{DMS} + \text{Cl} \rightarrow 0.5\text{SO}_2 + 0.5\text{DMSO} + 0.5\text{HCl} + 0.5\text{ClO}$	$3.40\text{e-}10$	(Barnes et al., 2006; Burkholder et al., 2015)	2
$\text{HOOCH}_2\text{SCH}_2\text{O} \rightarrow \text{HOOCH}_2\text{S} + \text{CH}_2\text{O}$	1.0e6	(Saunders et al., 2003)	3
Aqueous-phase reactions	$k_{298} [\text{M}^{-1}\text{s}^{-1}]$	References	Table No.
$\text{DMS}(\text{aq}) + \text{O}_3(\text{aq}) \rightarrow \text{DMSO}(\text{aq}) + \text{O}_2(\text{aq})$	8.61×10^8	(Gershenson et al., 2001; Hoffmann et al., 2016)	2
$\text{DMSO}(\text{aq}) + \text{OH}(\text{aq}) \rightarrow \text{MSIA}(\text{aq})$	6.65×10^9	(Zhu et al., 2003; Hoffmann et al., 2016)	2
$\text{MSIA}(\text{aq}) + \text{OH}(\text{aq}) \rightarrow \text{MSA}(\text{aq})$	6.00×10^9	(Sehested and Holcman, 1996; Hoffmann et al., 2016)	2
$\text{MSI}^-(\text{aq}) + \text{OH}(\text{aq}) \rightarrow \text{MSA}(\text{aq})$	1.20×10^{10}	(Bardouki et al., 2002; Hoffmann et al., 2016)	2
$\text{MSIA}(\text{aq}) + \text{O}_3(\text{aq}) \rightarrow \text{MSA}(\text{aq})$	3.50×10^7	(Hoffmann et al., 2016)	2
$\text{MSI}^-(\text{aq}) + \text{O}_3(\text{aq}) \rightarrow \text{MSA}(\text{aq})$	2.00×10^6	(Flyunt et al., 2001; Hoffmann et al., 2016)	2
$\text{MSA}(\text{aq}) + \text{OH}(\text{aq}) \rightarrow \text{SO}_4^{2-}$	1.50×10^7	(Hoffmann et al., 2016)	2
$\text{MS}^-(\text{aq}) + \text{OH}(\text{aq}) \rightarrow \text{SO}_4^{2-}(\text{aq})$	1.29×10^7	(Zhu et al., 2003; Hoffmann et al., 2016)	2

Overall, I feel that the new chemistry scheme has rather crudely merged previously developed chemistry schemes without much thought to the underlying assumptions in these scheme. These previous schemes have made various approximations, but the new mechanism doesn't seem to have understood these approximations and developed a scheme which is capable of either removing these approximations or by dealing with them appropriately. It has just patched things on top of each other. It would be advantageous to read the primary literature, the IUPAC and NASA recommendations for rate constants and use these as the basis of creating a consistent mechanism which uses the latest current thinking for this oxidation Unless the mechanism can be better updated and it then better explained I don't think the basis of this work is built on weak foundations.

Response: We do appreciate the concern for building a consistent, up-to-date mechanism for DMS oxidation and have taken all these suggestions to heart. Our revised mechanism comprises multiple improvements, including the removal of incorrectly duplicated oxidation reactions, updated kinetics for reactions that have more recent recommendations and, in some cases, better explanations for reaction choices. We hope that these changes make sense and believe that they strengthen the mechanism as recommended. While the overall direction of impacts and final qualitative conclusions remain consistent with previous results, these changes collectively redistribute the relative importance of the sinks for DMS, affect the major products yield such as HPMTF, MSA and SO₂, and shift the magnitudes of the global mean surface-layer gas-phase sulfur dioxide (SO₂) and sulfate aerosol (SO₄²⁻) as well as aerosol number concentration for all size ranges.

- **DMS and HPMTF Concentrations.**

After developing this new chemistry oxidation scheme the modelled DMS and HPMTF concentrations are compared to those from the ATOM-4 mission. The model does pretty poorly for DMS and surprisingly well for HPMTF. This leaves the authors in a difficult position. The DMS emissions could be wrong, but that would imply that the HPMTF is then right for the wrong reason. The DMS emissions could be right but the DMS lifetime was too long but that would imply an error in the chemistry mechanism. Or the DMS observations could be incorrect. They show the seasonal cycle from one surface site which looks pretty good as additional justification, but this doesn't seem sufficient.

Response: We acknowledge that the model seems to compare poorly with DMS observations from the ATOM-4 mission, which makes agreement for other species somewhat surprising at face value. Related to this comment, we did find an error in the scripts used for the ATOM-4 vertical profile plots of DMS and HPMTF, which has been resolved in the current version. This error did not impact any results or figures other than the vertical profiles (now Figure 3). We have also added boxplots to Figure 3 for various mechanism perturbations to help contextualize the comparison with observations, including one in which HPMTF is not lost to cloud and aerosols, and one for the original BASE GEOS-Chem mechanism.

In Figure 3a of the revised manuscript we see that DMS output is still overpredicted, but much less so than with BASE chemistry. These findings are comparable to other literature sources that have used the same measurements for model/observation comparisons (Fung et al., 2022; Novak et al., 2021). Considering the good agreement with long term surface DMS measurements (Figure 2,

including an additional site), it is also possible that the underlying DMS emissions themselves are reasonable in terms of global seasonal budgets, but poorly resolved on finer spatiotemporal scales, especially at our coarse $4^{\circ} \times 5^{\circ}$ horizontal grid, leading to some of the differences in agreement seen here.

After resolving the error in our vertical profile plots, the model with full chemistry (MOD) compares poorly with HPMTF observations from the ATom-4 mission, revealing a strong low bias. Without heterogeneous losses of HPMTF to clouds and aerosols (shown in orange in Figure 3) this bias reverses to show a slight overprediction, indicating high sensitivity of the model to these processes. We acknowledge these issues in the text and note the need for additional work constraining these rates and processes.

Finally, we note that the remaining issues with ATom-4 DMS comparisons are consistent with those found in other similar studies, with which our results compare favorably (Novak et al. 2021 and Fung et al. 2022), and that comparisons against DMS and HPMTF are in any case much improved relative to base GEOS-Chem chemistry. While the development of improved DMS emissions and the resolution of HPMTF cloud and aerosol loss rates are outside the scope of this work, we do agree that these improvements should be a high priority for the modeling community and would in turn greatly benefit chemical mechanism evaluation and development.

It would be useful to discuss the DMS emissions in the model more. What is the emission in the model? How does this compare to previous studies? Are the model emissions higher / lower than other studies etc? How much wiggloroom is there here for improving the model performance?

Response: To address this comment regarding DMS emissions in GEOS-Chem we have added lines 396-405:

“The global DMS emission flux (F_{DMS}) from ocean to the atmosphere is 22 Tg S yr^{-1} and is within the range of $11\text{--}28 \text{ Tg S yr}^{-1}$ simulated by GEOS-Chem and other models in previous studies (Lennartz et al., 2015; Spracklen et al., 2005; Hezel et al., 2011, Fung 2022, Chen 2018). Our F_{DMS} is higher than the 18 Tg S yr^{-1} which uses sea surface DMS concentration from Kettle et al. (1999) as reported (Chen et al 2018) indicating the DMS emission varies with change in sea surface DMS climatology. The analysis and improvement of DMS emissions directly is not a part of this work, but we note that improved and validated inventories for DMS will certainly play a role in subsequent oxidation product comparisons. We recommend ongoing evaluation of DMS emissions inputs to complement the expanded chemical mechanism development we present here.”

If think that more analysis is needed to show that the DMS concentration calculated by the model are 'reasonable' and that the ATOM DMS observations can be reconciled with the model. I would suggest that more comparisons with surface sites would provide the increased confidence here. It seems difficult to go onto the next stage of the analysis (the impact on aerosols), without having confidence in the ability of the model to get the DMS concentrations right. At the moment there is some doubt.

Response: We have added one more surface site (now Figure 2 in the revised version) of long term observations to compare model versus surface observations of DMS, providing further evaluation

of model performance. We find that our DMS oxidation mechanism again does well in comparison with the BASE simulation by narrowing the gap between model and observation for both sites shown in Figure 2. Considering the use of emissions inventories that may poorly represent spatiotemporal distributions of DMS emissions, we believe that our results provide broad support for overall modeled DMS budgets and expanded chemistry, while highlighting biases and uncertainties in the details for exactly where and when that DMS is emitted.

Minor issues:

Table 1. Can the rate constants be put into this table?

Response: We have added the rate constants in the Table 1.

Table 1. The three DMS oxidation reactions in the standard GEOS-Chem chemical mechanism

Reactions	Rate (s ⁻¹)	
DMS+ OH _(abstraction) → SO ₂ + CH ₃ O ₂ + CH ₂ O	1.20e-11*exp(-280/T)	(R1)
DMS+ OH _(addition) → 0.75 SO ₂ + 0.25 MSA + CH ₃ O ₂	8.2×10⁻³⁹[O₂]^{5376/T}/(1+1.05×10⁻⁵([O₂]/[M])^{3644/T})	(R2)
DMS+ NO ₃ → SO ₂ + HNO ₃ + CH ₃ O ₂ + CH ₂ O	1.90e-13*exp(530/T)	(R3)

Figure 1. Where do the numbers come from for this table. It would be useful to point towards the simulation that is being used?

Response: The numbers on the arrows were indicating the production and loss rates in the units of Gg S yr⁻¹. The numbers in the box next to the scheme were emission flux of DMS (in Gg S yr⁻¹), burdens (GgS) and deposition (Gg S yr⁻¹) calculated from different diagnostic outputs of the simulation. However, in the revised version we removed all the numbers from the scheme and put that into a table in the Appendix section, as Table B1 along with flux of DMS, lifetime of major sulfur compounds in the mechanism and global mean concentration of major oxidants. We also rephrased the Figure caption for Figure 1 to include the name of the simulation that is represented by the scheme as:

“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.”

Page 6. It might be beneficial to start with a description of the gas phase aspects of the model before moving to the aerosol scheme?

Response: We have revised the methodology section by starting with an explanation of the gas-phase aspects of the tropospheric chemistry option in the model, and then introduce the aerosol scheme as part of the size distribution analysis.

Page 8. The literature contains other DMS oxidants (IO, Br, etc) Why were these not included in the scheme? They may be considered small but it would be good to explain that.

Response: We have added the reason in lines 448-451:

“Due to slower reaction kinetics and lower fractional contribution reported earlier compared to BrO with DMS and uncertainty in surface concentration and kinetics for photochemically generated halogenated species such as Br, IO we did not include them in our chemical scheme (Chen et al., 2018).”

Page 10. A table of DMS emissions and global (hemispheric sinks) would be useful here. Lifetimes to different oxidants would also provide some useful way of comparing the different oxidation routes in the BASE and the MOD simulations. It would also be useful to provide information on the global (hemispheric) mean concentration of important oxidants (OH, Cl, NO₃, O₃, BrO etc).

Response: We have added all these details in Table B1 of the appendix section.

Line 280. Does the MOD simulation have wet and dry deposition of DMS? Could more information be provided about that?

Response: We have added line 271-274 as:

“In all our simulations including MOD, DMS is advected and undergoes chemical loss and transport but does not undergo dry or wet deposition. However, dry and wet deposition of oxidation products such as DMSO, MSIA, MSA and HPMTF are included.”

Line 323. I would put the model / measurement comparisons section before the budget details. I would start with an analysis of the model’s ability to simulate DMS (both from aircraft and from the group) and then move onto HPMTF.

Response: We have reorganized the result discussion section by first introducing the model-observation comparisons for DMS for two different surface sites and then for the ATom-4 aircraft data versus model output of DMS and HPMTF respectively to establish the model’s ability to capture these species. Later we move on to the analysis of the overall budget and specific sinks for DMS followed by the implications of our chemical mechanism in influencing the size distribution of resulting aerosol in the final part of the results and discussion section.

Line 388. Is there a 37% reduction in the global SO₂ burden with the change of chemistry? Or is that a spatially averaged fractional change?

Response: By this we mean a 37% reduction (this was a typo in the submitted manuscript and was supposed to be 38%, now it is 35% in the revised version) in the global surface production of SO₂ with the change of chemistry (simulation MOD) compared to the simplified DMS chemistry of BASE simulation (now line 457-458 of the revised manuscript). This is not a spatially average fractional change.