Response to Referee 1 (RC1)

Mechanism
I still have some concerns about the mechanism used. As I said in my previous review it has been pulled together from different mechanisms making different assumptions. It is mainly a puling together of mechanisms in pervious models with the inherent assumptions and implications that they have made.

Response: We again appreciate the reviewer's detailed attention to the underlying justifications behind the chemical mechanism we have used for this work. Our newly revised mechanism for this round of review includes multiple improvements, including the addition of new intermediate reactions, updated kinetics for reactions with more recent recommendations, and most importantly original references wherever appropriate. We believe that these changes should satisfy our reviewers' concerns and make the final mechanism a strong replacement for the current simplified DMS oxidation scheme used in the GEOS-Chem model. As with our previous revisions, the overall direction of impacts and final qualitative conclusions remain consistent with our original results. The new set of changes collectively do influence the relative importance of the sinks for DMS, influence the final yield of major products such as HPMTF, MSA and SO_2, and shift the magnitudes of the global mean surface-layer gas-phase sulfur dioxide (SO_2) and sulfate aerosol (SO_4^{2-}) concentrations, as well as aerosol number concentration for all size ranges. Point-by-point responses to other specific comments and concerns are provided below.

It would be useful for the authors to reference their reactions either by the original lab study, from the IUPAC / JPL compilation or when not available indicate that the rate constant has been estimated. For example Novak and Wollesen de Jonge use the DMS+NO3 rate constant but the "original reference" for this comes from the IUPAC recommendation based on rate constant measured in the 1980s. The Saunders et al., 2003 reference doesn't discuss DMS.

Response: We acknowledge the value of original references and have thoroughly revised our reference list. We have also updated several reactions following more recent literature that includes updated reaction kinetics or stoichiometry. We have further simplified our notation, replacing the formula CH_2O with HCHO throughout. These revisions have affected the impact of our expanded mechanism compared to the base case. For example, the global mean surface-layer gas-phase sulfur dioxide (SO_2) mixing ratio now drops by 40% compared to 35% under the previous version, while the sulfate aerosol (SO_4^{2-}) mixing ratio increases on average by 17% compared to 22%. Furthermore, compared to our previous mechanism version, the DMS + OH addition pathway has increased in importance compared with the abstraction pathway, consistent with Cala et. al., 2023. Mechanism and reaction table changes are listed here:

Table 2. Overview of the DMS oxidation mechanism via OH-addition pathway.

Gas-phase reactions	Rate constant (cm³ molecule⁻¹ s⁻¹)	References
DMS + OH → ~~0.60SO₂ +~~ ~~0.4DMSO + CH₃O₂~~ DMSO + HO₂	$9.5\times10^{-39}[O_2]exp(5270/T)/(1+ 7.5\times10^{-29}[O_2]exp(5610/T))$	IUPAC SOx22 (upd. 2006)
DMS + BrO → DMSO + Br	$1.50\times10^{-14}exp(1000/T)$	(Bräuer et al., 2013; Hoffmann et al., 2016)
DMS + O₃ → SO₂	1.50×10^{-19}	(Du et al., 2007; Burkholder et al., 2020)
DMSO + OH → 0.95(MSIA + CH₃O₂)	$6.10\times10^{-12}exp(800/T)$	MCMv3.3.1, (von Glasow and Crutzen, 2004; Burkholder et al., 2020)
MSIA + OH → 0.95(SO₂ + CH₃O₂)	9.00×10^{-11}	MCMv3.3.1
MSIA + OH → 0.05(MSA + HO₂ + H₂O)	9.00×10^{-11}	von Glasow and Crutzen, 2004
~~MSIA + O₃ → MSA~~	~~2.00e-18~~	~~(von Glasow and Crutzen, 2004; Lucas and Prinn, 2002)~~
MSIA + NO₃ → CH₃SO₂ + HNO₃	1.00×10^{-13}	(von Glasow and Crutzen, 2004; Hoffmann et al., 2016)

Aqueous-phase reactions	k_{298} [M⁻¹s⁻¹]	References
DMS (aq) + O₃ (aq) → DMSO (aq) + O₂ (aq)	8.61×10^8	(Gershenzon et al., 2001; Hoffmann et al., 2016)
DMSO (aq) + OH (aq) → MSIA (aq)	6.65×10^9	(Zhu et al., 2003; Hoffmann et al., 2016)
MSIA (aq) + OH (aq) → MSA (aq)	6.00×10^9	(~~Sehested and Holeman, 1996;~~)(Hoffmann et al., 2016; Herrmann et al., 1998)
MSI⁻ (aq) + OH (aq) → MSA (aq)	1.20×10^{10}	(Bardouki et al., 2002; Hoffmann et al., 2016)
MSIA (aq) + O₃ (aq) → MSA (aq)	3.50×10^7	Hoffmann et al., 2016; Herrmann et al., 1998)
MSI⁻ (aq) + O₃ (aq) → MSA (aq)	2.00×10^6	(Flyunt et al., 2001; Hoffmann et al., 2016)
MSA (aq) + OH (aq) → SO₄²⁻	1.50×10^7	(Hoffmann et al., 2016; Herrmann et al., 1998)
MS⁻ (aq) + OH (aq) → SO₄²⁻ (aq)	1.29×10^7	(Zhu et al., 2003; Hoffmann et al., 2016)

Table 3. Overview of the DMS oxidation mechanism involving HPMTF formation.

Gas-phase reactions	Rate constant (cm³ molecule⁻¹ s⁻¹)	References
MSP (CH₃SCH₂OO) → OOCH₂SCH₂OOH	$2.2433\times10^{11}exp(-9801.6/T)\times(1.0348\times10^8/T^3)$	(Berndt et al., 2019; Veres et al., 2020; Wollesen de Jonge et al., 2021)
OOCH₂SCH₂OOH → HPMTF (HOOCH₂SCHO) + OH	$6.0970\times10^{11}exp(-9489/T)\times(1.1028\times10^8/T^3)$	(Berndt et al., 2019; Veres et al., 2020; Wollesen de Jonge et al., 2021)
OOCH₂SCH₂OOH + NO → HOOCH₂S + NO₂ + HCHO	$4.9\times10^{-12}exp(260/T)$	MCMv3.3.1
MSP + HO₂ → CH₃SCH₂OOH + O₂	$1.13\times10^{-13}exp(1300/T)$	MCMv3.3.1, (Wollesen de Jonge et al., 2021)
~~CH₃SCH₂OOH + hv → CH₃SCH₂O + OH~~	~~J(41)~~	~~MCMv3.3.1, (Wollesen de Jonge et al., 2021)~~
CH₃SCH₂OOH + OH → CH₃SCHO	7.03×10^{-11}	MCMv3.3.1
CH₃SCHO + OH → CH₃S + CO	1.11×10^{-11}	MCMv3.3.1

HPMTF + OH→ HOOCH$_2$SCO + H$_2$O	4.00×10^{-12}	(Jernigan et al., 2022a)
HPMTF + OH→ 0.13OCS + 0.87SO$_2$ + CO	1.40×10^{-11}	(Jernigan et al., 2022a)
OCS + OH → SO$_2$	$1.13\times10^{-13}\exp(1200/T)$	(Jernigan et al., 2022a)
HOOCH$_2$SCO → HOOCH$_2$S + CO	$9.2\times10^{9}\exp(-505.4/T)$	(Wu et al., 2015)
HOOCH$_2$SCO → OH + HCHO + OCS	$1.6\times10^{7}\exp(-1468.6/T)$	(Wu et al., 2015)
HOOCH$_2$S + O$_3$ → HOOCH$_2$SO + O$_2$	$1.15\times10^{-12}\exp(430/T)$	(Wu et al., 2015)
HOOCH$_2$S + NO$_2$ → HOOCH$_2$SO + NO	$6.0\times10^{-11}\exp(240/T)$	(Wu et al., 2015)
HOOCH$_2$SO + O$_3$ → SO$_2$ + HCHO + OH + O$_2$	4.0×10^{-13}	(Wu et al., 2015)
HOOCH$_2$SO + NO$_2$ → SO$_2$ + CH$_2$O + OH + NO	1.2×10^{-11}	(Wu et al., 2015)

Table 4. Overview of the MSA-producing branch of the H-abstraction pathway of DMS oxidation.

Gas-phase reactions	Rate constant (cm^3 molecule^{-1} s^{-1})	References
DMS + OH → MSP (CH$_3$SCH$_2$OO) + H$_2$O	$1.12\times10^{-11}\exp(-250/T)$	IUPAC SOx22 (upd. 2006)
DMS + Cl → 0.45MSP + 0.55C$_2$H$_6$SCl + 0.45HCl	3.60×10^{-10}	(Fung et al., 2022; Enami et al., 2004)
C$_2$H$_6$SCl → DMSO + ClO	4.00×10^{-18}	(Hoffmann et al., 2016; Urbanski and Wine, 1999)
DMS + NO$_3$ → MSP + HNO$_3$	$1.9\times10^{-13}\exp(520/T)$	MCMv3.3.1, (Novak et al., 2021; Wollesen de Jonge et al., 2021; Atkinson et al. 2004)
MSP + NO → CH$_3$SCH$_2$(O) + NO$_2$	$4.9\times10^{-12}\exp(260/T)$	MCMv3.3.1
~~MSP + CH$_3$O$_2$ → CH$_3$SCH$_2$(O) + O$_2$~~	~~3.74e-12~~	~~(Saunders et al., 2003)~~
MSP + MSP → 2HCHO + 2CH$_3$S	1.00×10^{-11}	(von Glasow and Crutzen, 2004)
CH$_3$SCH$_2$(O) → CH$_3$S + HCHO	1.0×10^{6}	MCMv3.3.1
CH$_3$S + O$_3$ → CH$_3$S(O) + O$_2$	$1.15\times10^{-12}\exp(430/T)$	MCMv3.3.1; (Atkinson et al., 2004)
CH$_3$S + O$_2$ → CH$_3$S(OO)	$1.20\times10^{-16}\exp(1580/T)$	MCMv3.3.1; (Atkinson et al., 2004)
CH$_3$S + NO$_2$ → CH$_3$SO + NO	$3.00\times10^{-12}\exp(210/T)$	IUPAC SOx60 (upd. 2006); (Atkinson et al., 2004)
CH$_3$SO + O$_3$ → CH$_3$O$_2$ + SO$_2$	4.00×10^{-13}	IUPAC SOx61 (upd. 2006); (Borissenko et al., 2003)
CH$_3$SO + NO$_2$ → 0.75(CH$_3$SO$_2$ + NO) + 0.25(SO$_2$ + CH$_3$O$_2$ + NO)	1.20×10^{-11}	(Borissenko et al., 2003; Atkinson et al., 2004)
CH$_3$S(OO) → CH$_3$(O$_2$) + SO$_2$	$5.60\times10^{16}\exp(-10870/T)$	(Atkinson et al., 2004)
CH$_3$S(OO) → CH$_3$SO$_2$	1.00	(Campolongo et al., 1999; Hoffmann et al., 2016)
CH$_3$S(OO) → CH$_3$S + O$_2$	$3.50\times10^{10}\exp(-3560/T)$	MCMv3.3.1
CH$_3$SO$_2$ + O$_3$ → CH$_3$SO$_3$ + O$_2$	3.00×10^{-13}	MCMv3.3.1; (von Glasow and Crutzen, 2004)
CH$_3$SO$_2$ → CH$_3$(O$_2$) + SO$_2$	$5.00\times10^{13}\exp(-9673/T)$	MCMv3.3.1; (Barone et al., 1995)
CH$_3$SO$_2$ + NO$_2$ → CH$_3$SO$_3$ + NO	2.20×10^{-11}	(Atkinson et al., 2004)
CH$_3$SO$_3$ + HO$_2$ → MSA + ~~O$_2$~~	5.00×10^{-11}	MCMv3.3.1; (von Glasow and Crutzen, 2004)
CH$_3$SO$_3$ → CH$_3$(O$_2$) + H$_2$SO$_4$	$5.00\times10^{13}\exp(-9946/T)$	MCMv3.3.1
MSA + OH → CH$_3$SO$_3$	2.24×10^{-14}	MCMv3.3.1

The H abstraction path chemistry I'm a bit confused about. We get to CH3S and then this can primary react with O2 to form CH3S(OO) with a rate constant of 1.2e-16*exp(1580). However, the back reaction for this CH3S(OO)-->CH3S is missing from the reaction scheme but is in the MCM and is substantially faster. This wouldn't matter so much if the only fate of CH3S was reaction with O2 but it can also react with O3. Why is this reaction missing?

Response: To address this concern, we have added the reaction $CH_3S(OO) \rightarrow CH_3S + O_2$ with a rate constant of $3.50\times10^{10}exp(-3560/T)$, following MCMv3.3.1. In addition, CH_3S in our revised version reacts with NO_2 via $CH_3S + NO_2 \rightarrow CH_3SO + NO$ with a rate constant of $3.00\times10^{-12}exp(210/T)$, following IUPAC SOx60 (upd. 2006) and Atkinson et al., 2004.

Why isn't the reaction between CH3SH2OOH and OH included as it is the the MCM? Is this not competative against the photolysis? What is J(41)

Response: We have added the reaction of CH_3SH_2OOH and OH as follows from Table 3. along with oxidation of the product CH_3SCHO to generate CH_3S based on MCMv3.3.1. In the previous version, the photolysis reaction appears to be a typo in the reaction table, and was not present in the model mechanism itself. Even though there is a photolysis reaction for CH_3SH_2OOH according to MCMv3.3.1, we have decided to not include any photolysis reaction for our current mechanism for simplicity and consistency with comparable works. We do agree that the following two reactions are impactful enough to include, again following the example of similar work (Wollesen de Jonge et al., 2021, Cala et al., 2023):

Gas-phase reactions	Rate constant (cm³ molecule⁻¹ s⁻¹)	References
$CH_3SCH_2OOH + OH \rightarrow CH_3SCHO$	7.03×10^{-11}	MCMv3.3.1
$CH_3SCHO + OH \rightarrow CH_3S + CO$	1.11×10^{-11}	MCMv3.3.1

The mechanism then produces CH3S(OO) which in this mechanism has 2 fates. Decomposition to give CH3(O2) or decomposition to give CH3SO2. So I think CH3(O2) is meant to be CH3O2 as used previously here? The CH3S(OO) in this mechanism can also decompose to give CH3SO2. I don't see this reaction in the MCM (https://mcm.york.ac.uk/MCM/species/CH3SOO). There is a CH3SO2 in the MCM but its formed from CH3SOO2 rather than from CH3SOO. Where does the rate constant of 1s-1 for the rearrangement of CH3S(OO) Into CH3SO2 come from? Can the authors clarify what is going on here?

Response: We thank for pointing out the issue with the reference. We did add the original reference for this rearrangement reaction in Table 4 as follows. It is originally from Campolongo et al., 1999 and is further usd by Fung et al., 2022, Hoffmann et al., 2016 and Wollesen de Jonge et al., 2021. We have also added an additional reaction for $CH_3S(OO)$ based on MCMv3.3.1 in the revised version as mentioned below from Table 4:

Gas-phase reactions	Rate constant (cm^3 molecule^{-1} s^{-1})	References
$CH_3S(OO) \rightarrow CH_3SO_2$	1.00	(Campolongo et al., 1999; Hoffmann et al., 2016)
$CH_3S(OO) \rightarrow CH_3S + O_2$	$3.50 \times 10^{10} exp(-3560/T)$	MCMv3.3.1

What happens to the CH3SCH2O which is formed from the CH3SCH2OOH photolysis?

Response: We do not have the photolysis reaction in the revised manuscript. In our revised mechanism CH_3SH_2OOH oxidizes by OH to CH_3SCHO, which further oxidizes by OH to CH_3S according to MCMv3.3.1 as shown in Table 3 along with further oxidation of CH_3S listed in Table 4.

Where the authors have ignored reactions in the MCM chemistry they should indicate why and give new references. It would be useful if the text of the paper described the choices use but the authors in constructing the scheme. What is the basis of the reactions?

Response: We have gone back through our mechanism description to add further clarification on original studies for key reactions. Relevant lines are listed below:

Line 194 – 199 in the revised manuscript:
"We further implement and evaluate a custom chemical mechanism for DMS oxidation, referred to as "MOD" (Table 2-4), representing an integration of three individual DMS oxidation mechanism updates explored previously using GEOS-Chem and CAM6-Chem. This mechanism also includes HPMTF loss to clouds and aerosols via heterogenous chemistry, dry and wet deposition of HPMTF, along with further improvement based on recent literature updates to chemical kinetics (Chen et al., 2018; Fung et al., 2022; Veres et al., 2020; Novak et al., 2021; Cala et al., 2023)."

Line 225-247 in the revised manuscript:
"As shown in Table 2, the modified DMS chemistry simulations examined here include gas- and aqueous-phase oxidation of DMS and its intermediate oxidation products by OH, NO_3, O_3, and halogenated species as previously explored in an older version of GEOS-Chem (Chen et al., 2018). The aqueous-phase reactions in cloud droplets and aerosols were parameterized assuming a first-order loss of the gas-phase sulfur species (Chen et al., 2018). Further building upon this previous mechanism, the scheme used here also includes the formation and loss of HPMTF as previously tested in the global climate model CAM6-Chem as shown in Table 3 (Veres et al., 2020). Table 4 presents the third piece of the mechanism: a gas-phase MSA-producing branch of the H-abstraction pathway in the DMS chemistry bridging the other two sets of the reactions (Fung et al., 2022). To avoid addition of SO_3 oxidation chemistry we have replaced SO_3 with H_2SO_4 followed by previous work for the decomposition reaction of CH_3SO_3 (Table 4). A similarly integrated mechanism (Table 2-4) has been previously explored using the CAM6-Chem model with a focus on radiation budget impacts, which is improved in this work through updated rate constants and the inclusion of additional relevant reactions (Fung et al., 2022; Novak et al., 2021; Wollesen de Jonge et al., 2021; Cala et al., 2023). The newly added reactions

and their respective rate constants are largely based on the MCMv3.3.1, along with the literature cited in the Table 2-4 reference list. We use a rate constant of 1.40×10^{-11} cm^3 molecules^{-1}s^{-1} for HPMTF + OH, which was previously determined based on concentrations of other known sulfur species (DMS, DMSO, SO$_2$ and methyl thioformate; MTF; CH$_3$SCHO; a structurally similar proxy to HPMTF) and evaluated by box model (Jernigan et al., 2022a). An exploration of reaction rate uncertainty for the HPMTF+OH reaction (Table 3), including both high and low end limits of 5.5×10^{-11} cm^3 molecules^{-1}s^{-1} and 1.4×10^{-12} cm^3 molecules^{-1}s^{-1} resulted in only minor impacts on the fate of HPMTF and ultimate sulfate formation in our simulations (Novak et al., 2021; Wu et al., 2015)."

Also can there consistent representation of the numbers in the tables. Sometimes the multiplication is represented by a * sometimes x sometime exponentials are represented as exp sometimes as e. There is a missing subscript on the O2 on the addition pathway. Why is there units on this and not the other reactions? The table labels these as rates but they are rate constants. Is there a need to give 5 significant figures on the HPMTF rate constants and 3 on the others?

Response: We thank the reviewer for such detailed attention to the representation of the reaction tables and revised the tables based on the suggestions. Multiplications are now represented by '×' symbol. The exponential function is now consistently represented by 'exp', and scientific notation 'e's have been replaced with '10^x' wherever needed in Table 1-4. We further addressed the subscript issue for the OH addition pathway of DMS, and have removed the listed unit for this reaction. We have named this column "Rate constant" where many of them have temperature dependent expression. For the HPMTF reaction significant figures, we wanted to maintain the precision of the original reference, and so kept the rate constant values as they originally appeared.

Perhaps the authors could use the model given by the reaction table in https://acp.copernicus.org/preprints/acp-2023-42/acp-2023-42.pdf to give the appropriate sources for the reactions? It would also probably help if they considered this mechanism and thought about whether theirs is consistent?

Response: We thank the reviewer for referring us to the UKCA chemistry-climate model. We agree that the referenced UKCA publication is a useful example that we have used as a reference point for our gas-phase mechanism choices.

A diagram of the reaction mechanism would help to clarify the mechanism.

Response: We thank the reviewer for this suggestion. To help further clarify our mechanism modifications we have redesigned Figure 1 to include additional details, including improved visual representation of key species and reaction pathways.

Other aspects.
There is quite a large change in DMS burden (38%) from the inclusion of the new mechanism. The BrO only constitutes ~20% of the total loss now. It would be useful to assess how the OH,

NO3, O3, BrO concentrations have changed between the model simulations. How much of the change in the burden is the additional routes and how much is a change in the oxidant concentrations? This isn't clear to me and without some sense of how the oxidants have changed it is hard to tell.

Response: To address this concern and question, we have added Figure A7 showing concentrations of the major oxidants OH, NO_3, O_3 and BrO for MOD and MOD-BASE. To make the comparison of the oxidant concentrations of figure A7 with the values in Table B1, we have updated and changed the units for the oxidants in Table B1 except for OH to make them consistent with each other. We hope that this can resolve the questions regarding changes in oxidant concentration between major simulation BASE and MOD.
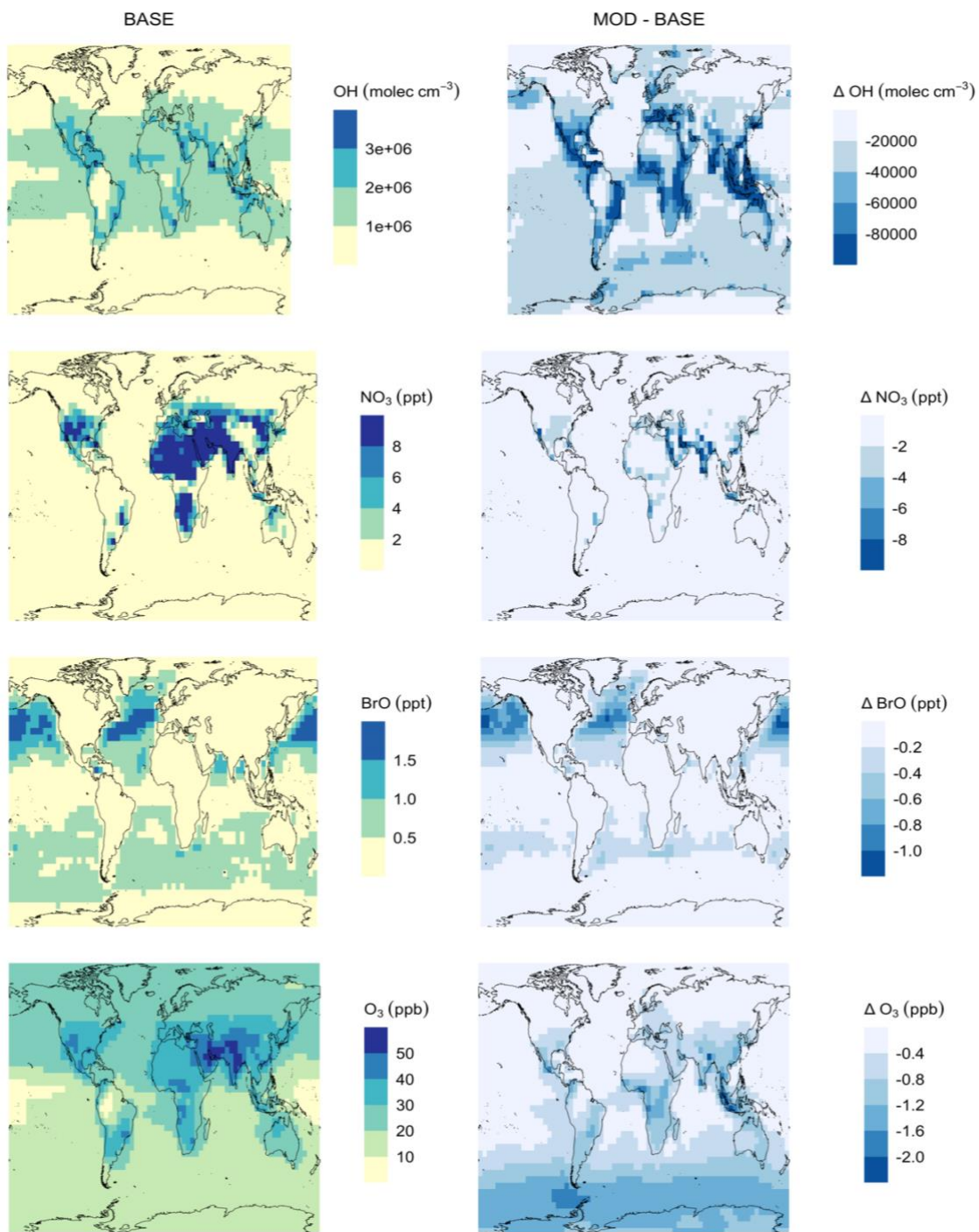
Figure A7 Geographic distribution of mean surface oxidant concentrations for simulation (a) BASE and (b) MOD - BASE. Simulations are described in Table 5.