

Referee # 1

We thank Referee #1 for the helpful comments. Please find our responses below.

General comments

1) The oxidation of DMS by OH happens by two pathways: H-abstraction from the methyl group and OH-addition onto the sulphur atom. The H-abstraction pathway leads predominantly to SO₂. The OH-addition pathway leads predominantly to DMSO (Barnes et al. 2006). The DMSO is then further oxidised into MSIA and subsequently into MSA or SO₂ (see von Glasow and Crutzen, 2004; Zhu et al., 2006; Barnes et al. 2006; Hoffmann et al., 2016). A direct conversion of DMS into SO₂ is unlikely and only convenient if the OH-addition pathway is parameterised. As the present study aims at the investigation on how the formation of DMSO and subsequent multiphase chemistry affects the SO₂ yield, I do not understand why the authors produce DMSO only in a yield of 0.4 and the residual yield is SO₂. The addition pathway has to be revised according to the literature to consider the DMSO formation more adequately including higher yields. $\text{DMS} + \text{OH} \rightarrow \text{DMSO} + \text{HO}_2$ (Schultz et al., 2018)

Response: As shown in Barnes et al. (2006), the (CH₃)₂S-OH adduct is formed via the OH-addition pathway. The (CH₃)₂S-OH adduct reacts with O₂ to produce mainly DMSO under NO_x-free conditions (Arsene et al., 1999; Barnes et al., 2006). However, both Turnipseed et al. (1996) and Hynes et al. (1993) found the yield of DMSO from the (CH₃)₂S-OH + O₂ + NO reaction to be about 0.5 when NO is present in their experiments. It is difficult to extrapolate the yield of DMSO under atmospheric NO_x conditions and DMSO₂ could be formed under low NO_x and low temperature conditions in the remote marine atmosphere (Barnes et al., 2006). The most recent JPL report (Burkholder et al., 2015) also quoted a yield of DMSO from (CH₃)₂S-OH + O₂ + NO reaction to be 0.5 from Turnipseed et al. (1996) and Hynes et al. (1993).

Pham et al. (1995) uses a yield of 0.6 for SO₂ and a yield of 0.4 for DMSO for the addition channel of the DMS+OH reaction in a global three-dimensional chemical transport model, based on laboratory results of Barnes et al. (1988). These yields were also used in other global model studies (Cosme et al., 2002; Spracklen et al., 2005; Breider et al., 2010).

Thus, the OH-addition pathway leads predominantly to DMSO, as argued by the reviewer, only occurs under NO_x-free conditions. The reason why Schultz et al. (2018) used a unity yield of DMSO for the additional channel of DMS+OH reaction was not explained in that paper. It seems more common in the modeling community that the yield of DMSO from the addition channel of DMS+OH reaction is not unity. Since the consequence of the addition channel of DMS+OH reaction is still not well understood, we think it is more reasonable to use the same product yields of SO₂ (0.6) and DMSO (0.4) as previous modeling studies (Pham et al., 1995; Cosme et al., 2002; Spracklen et al., 2005; Breider et al., 2010). To investigate the importance of this assumption, we perform an additional sensitivity run by using a unity yield of DMSO for the addition channel of the DMS+OH reaction. The global DMSO, MSIA and MSA burden increase

by 33%, 50% and 74%, respectively. The global SO₂ and sulfate burden both decrease by 2%.

Changes in the manuscript:

- Add R_{add} to Table 3 as a sensitivity run.
- Add MSA/nssSO₄²⁻ ratio for R_{add} run to Fig. 10.
- At Page 5, Line 11: add “Product yields of 0.6 for SO₂ and 0.4 for DMSO have been commonly used in global models (Pham et al., 1995; Cosme et al., 2002; Spracklen et al., 2005; Breider et al., 2010) based on experiments described in Turnipseed et al. (1996) and Hynes et al. (1993).”.
- At Page 13, Line 19: add “The model run with a unity yield of DMSO from the additional channel of DMS oxidation by OH (R_{add}) largely overestimates MSA/nssSO₄²⁻ observations, with $N_{\text{MB}}=281\%$.”.

2) MSIA and MSA are acids. The dissociation of these acids will increase the effective uptake coefficient. In the present study, no dissociation is implemented. Especially, MSA is a strong acid (pKa = -1.92) and should reside predominantly in its dissociated form in aerosol particles and cloud droplets. Hence, as dissociated MSA will not undergo phase transfer, a much higher amount partitions in the aqueous phase as it is calculated by the modelling approach. However, if the pH of aerosols and cloud droplets would be fixed in the model, the effective Henry’s Law coefficient can easily be calculated. Then, the implementation of the effective Henry’s Law coefficient can be an appropriate way to restrict the numerical costs. Still, in the present model study the pH value is predicted. Thus, the effective Henry’s Law coefficient cannot be used. Therefore, the dissociation has to be treated in the model to enable a realistic partitioning and chemistry of MSIA and MSA.

Response: The acid dissociation of MSIA and MSA was considered in the model, although it was not specifically described. We used the same rate constant for the oxidation of MSA_(aq) and MS⁻ by OH_(aq), for the oxidation of MSIA_(aq) and MSI⁻ by OH_(aq), and for the oxidation of MSIA_(aq) and MSI⁻ by O_{3(aq)}. Now we have used different rate constant for each of these reactions in the updated manuscript (Table 1). The updated MSI⁻+O_{3(aq)} reaction rate constant is about an order of magnitude lower than before, which results in more dissolved MSIA oxidized by OH_(aq) than by O_{3(aq)}. The updated MS⁻+OH_(aq) reaction rate constant is 4.7 times lower than before, which results in a large increase in the global MSA burden (from about 10 to 20 Gg).

Changes to the manuscript:

- In Table 2, add pKa for MSIA and MSA: pKa(MSIA)=2.28 and pKa(MSA)=-1.86 (Hoffmann et al., 2016).
- In Table 1, add “MSI⁻+OH_(aq)→MSA_(aq)”, “MSI⁻+O_{3(aq)}→MSA_(aq)” and “MS⁻+OH_(aq)→SO₄²⁻” and corresponding rate constants.
- At Page 9, Line 21: modified as “Globally, multiphase oxidation in cloud droplets and aerosols by OH_(aq) (53%) and O_{3(aq)} (24%) is the biggest sink of MSIA, followed by gas-phase oxidation by OH (19%).”

- At Page 9, Line30: add “By considering cloud droplets only, Hoffmann (2016) suggested $\text{OH}_{(\text{aq})}$ is more important (1.5 times faster) than $\text{O}_{3(\text{aq})}$ for MSIA oxidation, which is consistent with our results. Since information such as $\text{OH}_{(\text{aq})}$ concentrations in aerosols, aerosol water content and cloud liquid water content were not provided in Hoffmann et al. (2016), we do not further compare our MSIA oxidation by $\text{O}_{3(\text{aq})}$ and $\text{OH}_{(\text{aq})}$ to Hoffmann et al. (2016).”
- At Page 10, Line 12: change “In R_{all} , the global MSA burden is 10 Gg S.” into “In R_{all} , the global MSA burden is 20 Gg S.”
- At Page 10, Line 26: modified as “MSA+ $\text{OH}_{(\text{aq})}$ accounts for 12% of MSA removal in R_{all} , and the rest of MSA is removed via dry (12%) and wet (76%) deposition.”
- At Page 12, Line 29: change “Figures 10 and 11 show that modeled MSA/nss SO_4^{2-} ratios are in good agreement with MSA/nss SO_4^{2-} observations” into “Figures 10 and 11 show that modeled MSA/nss SO_4^{2-} ratios calculated from R_{all} can generally reproduce the spatial variability of MSA/nss SO_4^{2-} observations, especially the latitudinal trend of increasing ratios towards the south where anthropogenic sources of nss SO_4^{2-} are less important. However, modeled MSA/nss SO_4^{2-} ratios overestimate observations by a factor of 2 on average”
- More changes in the MSIA and MSA budgets are shown in Section 3.3, 3.4 and 3.6.2 in the updated manuscript.

3) The implemented kinetic reaction rate constant for MSA with the OH radical is nearly five times higher than the two other ones given in Barnes et al. (2006). Given the comments on the high rate constant in Barnes et al. (2006), I think the lower ones has to be preferred. This will significantly affect also the oxidation of MSA.

Response: In the updated manuscript, the lower rate constant for MSA oxidation has been used (Table 1) ($1.29 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K instead of $6.10 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The global MSA burden increases from 10 Gg to 20 Gg. The modeled MSA/nss SO_4^{2-} ratio for the run with all new reactions added overestimates the observations by a factor of 2 on average, which suggests more MSA oxidation is needed. The high rate constant for MSA oxidation (4.7 times higher) is now used in the sensitivity run $R_{\text{moreMSA+OH}}$.

Changes to the manuscript:

- In Table 1, update rate constant for MSA oxidation.
- At Page 10, Line 12: change “In R_{all} , the global MSA burden is 10 Gg S.” into “In R_{all} , the global MSA burden is 20 Gg S.”
- At Page 10, Line 26: modified as “MSA+ $\text{OH}_{(\text{aq})}$ accounts for 12% of MSA removal in R_{all} , and the rest of MSA is removed via dry (12%) and wet (76%) deposition.”
- At Page 12, Line 29: change “Figures 10 and 11 show that modeled MSA/nss SO_4^{2-} ratios are in good agreement with MSA/nss SO_4^{2-} observations” into “Figures 10 and 11 show that modeled MSA/nss SO_4^{2-} ratios calculated from R_{all} can generally reproduce the spatial variability of MSA/nss SO_4^{2-} observations, especially the latitudinal trend of increasing ratios towards the south where anthropogenic sources of nss SO_4^{2-} are less important. However, modeled MSA/nss SO_4^{2-} ratios overestimate observations by a factor of 2 on average”
- At Page 13, Line 15: add “Due to the small chemical loss of MSA in our model,

MSA/nssSO₄²⁻ in model run without MSA + OH_(aq) ($R_{\text{noMSA+OH(aq)}}$) is similar to that in R_{all} . The model run with a larger reaction rate coefficient of MSA + OH_(aq) ($R_{\text{moreMSA+OH(aq)}}$) results in a decrease in modeled MSA/nssSO₄²⁻ (24% on average) compared to R_{all} .”

4) The oxidation of DMSO in the gas phase yields only 0.95 MSA. The residual 0.05 should be dimethyl sulfoxide (DMSO₂), which will be predominantly being further, but slowly, oxidised into SO₂. Thus, to close the mass balance, a 0.05 yield of SO₂ should be implemented.

Response: In the updated manuscript, we have applied a 0.05 yield of SO₂ to the oxidation of DMSO in the gas phase. This results in negligible changes in the SO₂ budget, as it is a very small source of SO₂ (Fig. 1).

Changes to the manuscript:

- Update “DMSO+OH→0.95MSIA+0.05SO₂^(new)” in Table 1.
- Add a pathway “DMSO→SO₂” with 98 Gg S yr⁻¹ in Fig. 1.

5) The oxidation of DMS can also affect new particle formation. As the authors have stated the formation of MSA by aqueous-phase chemistry will not result in new particle formation. I am missing a discussion how the newly implemented multiphase DMS chemistry scheme affects new particle formation. Have the authors investigated how new particle formation is changed between R_{all} and R_{std} ? Please address this issue in the discussion of the model results.

Response: We did not investigate how new particle formation is changed between R_{all} and R_{std} . This will be an important investigation in the future using an aerosol microphysics model simulation.

Changes to the manuscript:

- At Page 14, Line 16: add “Quantifying the impacts of our updated sulfur oxidation scheme on new particle formation is out of the scope of this study and should be addressed in the future.”.

Minor comments

1) The term ‘multiphase’ means connection of oxidation in gas and aqueous phase. Therefore, the usage of multiphase mechanism or multiphase oxidation addressing oxidation in the aqueous phase is wrong. It has to be stated aqueous-phase mechanism or aqueous-phase oxidation.

Response: In the updated manuscript, we use multiphase oxidation for the process involving gas and aqueous phase, and we use aqueous-phase oxidation for the process happening in the liquid.

Changes to the manuscript:

- In Table 1 and Table 4, change all multiphase reactions into aqueous-phase reactions with corresponding rate coefficients.

2) The conversion yield of DMS into SO₂ and MSA with the new approach is 78% and 13%, respectively. The addition of these numbers does not reach 100%. What are the residual 9%? Are this DMSO and MSIA? These also needs to be stated.

Response: The conversion yield of DMS into SO₂ and MSA in the new approach should not be 100% due to loss of the intermediates DMSO and MSIA via dry and wet deposition.

Changes to the manuscript:

- At Page 14, Line1: modified as “Compared to the standard GEOS-Chem model run, the updated sulfur scheme in this study decreases the conversion yield of DMS to SO₂ ($Y_{DMS \rightarrow SO_2}$) from 91% to 75% and increases the conversion yield of DMS to MSA ($Y_{DMS \rightarrow MSA}$) from 9% to 15%. The remaining 10% of DMS is lost via wet and dry deposition of DMSO and MSIA.”

- In the abstract, add “The remaining 10% of DMS is lost via deposition of intermediates DMSO and MSIA.”

3) Can the authors please provide how much dry and wet deposition contribute to the lifetime of DMSO, MSIA and MSA?

Response: The dry deposition loss contributes 16%, 2% and 12% to the lifetime of DMSO, MSIA and MSA, respectively. The wet deposition loss contributes 11%, 2% and 76% to the lifetime of DMSO, MSIA and MSA, respectively. Chemical oxidation is responsible for the rest of the losses.

Changes to the manuscript:

- At Page 9, Line 1: modified as “DMSO is removed from the atmosphere via gas-phase oxidation by OH (33%), multiphase oxidation by OH in cloud droplets (37%) and aerosols (3%), and dry (16%) and wet deposition (11%). The lifetime of DMSO is about 11 hours.”

- At Page 9, Line 20: modified as “MSIA is mainly removed in the troposphere via both gas-phase and multiphase oxidation by OH, with a lifetime of 4 hours. Dry (2%) and wet (2%) deposition of MSIA accounts for 4% of MSIA removal in the troposphere. Globally, multiphase oxidation in cloud droplets and aerosols by OH_(aq) (53%) and O_{3(aq)} (24%) is the biggest sink of MSIA, followed by gas-phase oxidation by OH (19%).”

- At Page 10, Line 19: modified as “MSA+OH_(aq) accounts for 12% of MSA removal in R_{all} , and the rest of MSA is removed via dry (12%) and wet (76%) deposition. The lifetime of MSA is 2.2 days globally”.

4) Page 2, Line 25: ‘DMS + BrO’ and ‘DMS + OH(g)’ spaces are missing

Response: We have updated the manuscript accordingly.

Changes to the manuscript:

- Add spaces.

5) Page 3, Line 21-22.: Recently, cooking was mentioned as an anthropogenic source for MSA by Dall’Osto et al. (2015)

Response: We have updated the manuscript accordingly.

Changes to the manuscript:

- At Page 3, Line 23: change “MSA has only a natural source” into “MSA is generally considered to have a predominant natural origin”.

6) Page 5, Line 8-11: The authors have mentioned that no Cl is produced from the heterogenous reaction ‘HOBr + Cl⁻ + H⁺’ in the model system. This reaction will lead to BrCl formation. Box model studies show that the photolysis of BrCl is an important source for both Cl and Br radicals in the atmosphere (Bräuer et al., 2013), because it recycles HOBr effectively back to Br. As the authors did not include this production pathway for Cl radicals, I wonder if it is implemented for Br radicals? Please clarify this.

Response: In our model, we used monthly mean Cl mixing ratios from Sherwen et al. (2016). The reason why we used their Cl mixing ratio outputs in our model is that they have a more detailed chlorine chemistry scheme (considering Cl-Br-I coupling) than ours. They considered “HOBr+Cl⁻+H⁺→BrCl” in cloud droplets and sulfate aerosols in their model, but did not include this reaction on sea salt aerosols as this led to unrealistically high bromine abundances over the ocean.

Our model is based on Chen et al. (2017), which includes “HOBr+Cl⁻/Br⁻+H⁺ → BrCl + Br₂” reaction in both cloud droplets, sulfate aerosols and sea salt aerosols. We consider inclusion of sea salt debromination to be a better parameterization of bromine budget in the marine boundary layer. Thus, the BrO mixing ratios in our model are the BrO mixing ratios in Chen et al. (2017) that included “HOBr+Cl⁻+H⁺→BrCl”. In sum, in our model Cl mixing ratios are from Sherwen et al. (2016) and BrO mixing ratios are from Chen et al. (2017).

Changes to the manuscript:

- At Page 5, Line 13: Delete “from the HOBr+Cl⁻+H⁺” reaction” from the sentence “We used monthly mean Cl mixing ratios from Sherwen et al. (2016), which considered Cl-Br-I coupling but did not include chlorine production from the HOBr+Cl⁻+H⁺” reaction on sea salt aerosols that was suggested to be the largest tropospheric chlorine source in Schmidt et al. (2016).”

7) Page 4, Line 13-14: Can you please provide the resolution of the vertical levels?

Response: The matrix below shows the altitude of the upper bound of each layer in km. For example, the first layer is from 0 to 0.123 km; the second layer is from 0.123 km to 0.254 km; the 47th is from 68.392 km to 80.581 km.

[0.123 0.254 0.387 0.521 0.657 0.795 0.934 1.075 1.218 1.363 1.510 1.659
1.860 2.118 2.382 2.654 2.932 3.219 3.665 4.132 4.623 5.142 5.692 6.277
6.905 7.582 8.320 9.409 10.504 11.578 12.633 13.674 14.706 15.731 16.753 17.773
19.855 22.004 24.24 26.596 31.716 37.574 44.286 51.788 59.924 68.392 80.581]

Changes to the manuscript:

- At Page 4, Line 14: Add “The vertical layer thickness ranges from 120-150 m for the first 12 layers to 200-800 m for the 13th-27th layers and >1000 m for the rest (http://acmg.seas.harvard.edu/geos/doc/archive/man.v9-01-02/appendix_3.html#A3.5.2).” .

8) Page 5, Line 15: ‘DMS + O₃(aq)’, ‘DMSO + OH(aq)’, ‘MSIA + OH(aq)’, ‘MSIA + O₃(aq)’, ‘MSA + OH(aq)’ spaces are missing

Response: We have updated the manuscript accordingly.

Changes to the manuscript: Add spaces.

9) Page 5, Line 29-30: Model simulations show that the concentration of OH in the aqueous phase of marine cloud droplets and aerosols can differ up to two orders of magnitude (see Herrmann et al., 2010 or Brüer et al., 2013). This cannot be derived from the approach of Jacob (2005). Have the authors tried to implement these differences in OH concentration between the bulk of aerosol particles and cloud droplets into the modelling framework?

Response: We did not implement different OH concentrations between the bulk aerosol particles and cloud droplets in the model. Instead, we did one sensitivity run by reducing OH concentrations in both cloud droplets and aerosols by two orders of magnitude ($R_{\text{lowOH(aq)}}$). Following the reviewer’s suggestion, we run a sensitivity run by reducing the aerosol OH concentration by a factor of 20, following the maritime condition in Herrmann et al. (2010). As expected, the global DMSO and MSIA burden increase by 1% and MSA burden decreases by 2%. The small changes are due to the fact that the aqueous-phase oxidation by OH_(aq) occurs mainly in clouds instead of aerosols in our model and less oxidation by OH_(aq) in aerosols is compensated by more oxidation in other forms (e.g. oxidation in clouds).

Changes to the manuscript:

- At Page 6, Line 11: add “We conduct another sensitivity simulation by reducing the [OH_(aq)] in aerosols only by a factor of 20 (Herrmann et al., 2010) and found negligible

changes (<2%) in the global sulfur burden.”.

10) Page 6, Line 7: Usually, these rate constants are measured at 298K not 273K.

Response: In the updated manuscript, we do not have this temperature limitation. More aqueous-phase oxidation can occur at low temperature, which affects especially the MSIA burden as aqueous-phase oxidation is the main sink of MSIA (Fig. 1). We agree this is a more reasonable parameterization.

Changes to the manuscript:

- At Page 6, Line 16: delete “Multiphase sulfur reactions added in the model are only activated when the air temperature is above 273 K, to be consistent with the temperature at which their rate constants were obtained (Table 1).”.

11) Page 7, Line 16-17: Measured concentrations of Cl radicals are often in the range of 104 molecules cm⁻³ (Saiz-Lopez and von Glasow, 2012). Have the authors performed a sensitivity study with higher concentrations (e.g. 5x10³ molecules cm⁻³)? How is the contribution then affected?

Response: In the updated manuscript, we have conducted a sensitivity run by increasing the Cl mixing ratio by an order of magnitude. The fraction of DMS oxidized by Cl increases from 4% to 28%. This results in changes in the global DMS (-29%), DMSO (-2%), MSIA (-12%), MSA (10%), SO₂ (-2%) and sulfate (-3%) burden.

Changes to the manuscript:

- At Page 7, Line 17: add “ $f_{[Cl]DMS+Cl}$ increases to 28% in a sensitivity run increasing Cl mixing ratios by an order of magnitude.”.

- At Page 8, Line 2: add “However, a recent study suggests that this is an overestimate of tropospheric Cl abundance (Gromov et al., 2018).”

12) Page 9 Line 1: Once MSIA is formed, it is quickly, nearly instantaneous, further oxidised in the atmosphere. If 66% of the precursor DMOS stay below 2 km altitude, which processes trigger the 17% smaller contribution of MSIA?

Response: The reason why a larger fraction of DMSO stays below 2 km than MSIA is that MSIA is oxidized faster than DMSO in the marine boundary layer. As shown in Table 1, the reaction rate constant for DMSO_(aq)+OH_(aq) reaction is $6.63 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K while the reaction rate constant for MSI⁻+OH_(aq) reaction is $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in the model. In addition, MSIA can also be oxidized by O_{3(aq)}, which results in even shorter lifetime of MSIA in the marine boundary layer (below 2 km). The MSIA produced via gas-phase oxidation by OH in the upper troposphere has a longer lifetime compared to MSIA in the marine boundary layer due to smaller amount of clouds and aerosols for the MSIA oxidation in the aqueous phase in the upper troposphere. Thus, a larger amount of

MSIA stays in the upper troposphere (above 2 km).

Changes to the manuscript:

- At Page 9, Line 4: add “The smaller fraction of MSIA below 2 km compared to DMSO is due to faster oxidation of MSIA by OH_(aq) and O_{3(aq)} in clouds and aerosols (Table 1).”

13) Page 9, Line 8-10: The addition of all percent leads to 99%, please revise to give 100%.

Response: We have updated this accordingly.

Changes to the manuscript:

- At Page 9, Line 10, modified as “MSIA is mainly removed in the troposphere via both gas-phase and multiphase oxidation by OH, with a lifetime of 4 hours. Dry (2%) and wet (2%) deposition of MSIA accounts for 4% of MSIA removal in the troposphere. Globally, multiphase oxidation in cloud droplets and aerosols by OH_(aq) (53%) and O_{3(aq)} (24%) is the biggest sink of MSIA, followed by gas-phase oxidation by OH (19%).”

14) Page 9 Line 17: ‘Hoffmann’ not ‘Hoffman’

Response: Thank you, this has been fixed.

Changes to the manuscript: Change “Hoffman” into “Hoffmann”.

15) Page 10, Line 13-14: Which OH concentrations are used in these studies? Are these comparable to the present study?

Response: None of those studies (Pham et al, 1995; Chin et al., 1996; 2000; Cosme et al., 2002; Hezel et al., 2011) reported global OH concentrations. In addition, none of those studies included oxidation of MSA by OH_(aq) in clouds and aerosols, as mentioned in the manuscript. The OH concentration in our model has a global annual mean of 1.3×10^6 molecule cm⁻³.

Changes to the manuscript:

- At Page 10, Line 22: add “Information about the global distribution of MSA concentrations and deposition from these previous modelling studies are needed for comparison.”

16) Page 11, Line 9-10: Are there no data of DMS available for 2007? What is with the Cape Verde Observatory at which DMS is permanent measured since 2006 (Carpenter et al., 2010)? Why are these data not used?

Response: We are not able to find reported DMS data for 2007. We would like to

compare our model results with other DMS observations once provided.

Changes to the manuscript: No changes.

17) Page 26, Fig. 4: Over Central Asia, the oxidation of DMS by BrO shows the highest source for DMSO. Why is this reaction so strong in this region? Please provide proper reasons. Furthermore, the authors should consider to discuss the modeled concentration patterns of key oxidants.

Response: The oxidation of DMS by BrO shows the highest source for DMSO over central Asia is because high BrO abundance predicted in the model due to less reactive bromine deposition there (Schmidt et al., 2016). It should be noted that both DMS and DMSO are at very low concentration over central Asia as DMS is emitted from the ocean. This study focus on sulfur oxidation over the ocean. In the updated manuscript, we have added a global distribution of BrO, Cl, OH and O₃ in Figure 12. This study focus on sulfur oxidation and we refer to previous literatures for reasons causing the global distribution of these oxidants.

Changes to the manuscript:

- Add Fig. 12.

- At Page 5, Line 15: add “The global distributions of tropospheric annual-mean concentrations of BrO, Cl, OH and O₃ are shown in Fig. 12. The high BrO abundances over subtropics and polar regions are due to low deposition fluxes of reactive bromine (Schmidt et al., 2016) and the high BrO abundance over Southern Ocean is due to its source from sea salt debromination (Chen et al., 2017). The high Cl abundance over coastal regions in the Northern Hemisphere is due to heterogeneous uptake of N₂O₅ on sea salt aerosols to produce reactive chlorine (Sherwen et al., 2017).”

(18) Comments on the formatting of the references

- 1) Page 15, Line 19: Formatting error of the DOI number.
- 2) Page 15, Line 27: Please provide the DOI number.
- 3) Page 16, Line 3: Formatting error of the DOI number.
- 4) Page 16, Line 6: Formatting error of the DOI number.
- 5) Page 16, Line 8: Please provide the DOI number.
- 6) Page 16, Line 11: Please provide the DOI number.
- 7) Page 16, Line 26: Please provide the DOI number.
- 8) Page 17, Line 11: Formatting error of the DOI number.
- 9) Page 17, Line 30: Formatting error of the DOI number.
- 10) Page 17, Line 32: Please provide the DOI number.
- 11) Page 18, Line 2: Please provide the DOI number.
- 12) Page 18, Line 7: Formatting error of the DOI number.
- 13) Page 18, Line 9: Please provide the DOI number.
- 14) Page 18, Line 18: Please provide the DOI number.
- 15) Page 19, Line 3: Formatting error of the DOI number.

- 16) Page 19, Line 21: Please provide the DOI number.
- 17) Page 19, Line 24: Please provide the DOI number.
- 18) Page 20, Line 29: Formatting error of the DOI number.
- 19) Page 21, Line 8: Formatting error of the DOI number.
- 20) Page 21, Line 10: Please provide the DOI number.
- 21) Page 21, Line 19: Please provide the DOI number.
- 22) Page 21, Line 25: Formatting error of the DOI number.
- 23) Page 21, Line 34: Formatting error of the DOI number.
- 24) Page 22, Line 2: Please provide the DOI number.
- 25) Page 22, Line 5: Formatting error of the DOI number.
- 26) Page 22, Line 8: Formatting error of the DOI number.
- 27) Page 22, Line 12: Formatting error of the DOI number.
- 28) Page 22, Line 14: Formatting error of the DOI number.
- 29) Page 22, Line 19: Please provide the DOI number.
- 30) Page 22, Line 24: Please provide the DOI number.

Response: Thanks for the comments. We have updated the manuscript accordingly.

Changes to the manuscript:

- Format the references accordingly.

Referee # 2

We thank Referee #2 for the helpful comments. Please find our responses below.

One main point comes at the end of the paper. The main subject is the importance of halogen chemistry for the DMS \rightarrow sulphate oxidation pathway. New intermediates and reactions are included in a global chemistry-transport model. This gives better validations of intermediates, like MSA and MSA/nssSO₄ ratios. Also, the main uncertainties in the reaction pathways are clarified. However, for the formation of sulphate aerosol the new pathways have limited impact, simply because this is the end-product. Only the speed of the DMS \rightarrow sulphate conversion may be affected, and maybe some intermediates have efficient dry- or wet deposition pathways. Thus the phrase "...with a simplified DMS oxidation scheme (gas-phase oxidation by OH and NO₃ only) may overestimate sulfate abundances in the pre-industrial environment, potentially leading to underestimates in sulfur aerosol radiative forcing calculations in climate models." seems overstated. I expect no huge impact in sulphate forcing and some reflection on this is recommended. For the rest of my comments, see annotated manuscript. Please also note the supplement to this comment: <https://www.atmos-chem-phys-discuss.net/acp-2018-410/acp-2018-410-RC2-supplement.pdf>

Response: We agree that the new pathways added in model could have limited impact on the sulfate burden if the depositions of DMSO, MSIA and MSA are small so that DMS will be oxidized to form sulfate as an end-product. However, if a large amount of MSA produced from DMS oxidation is removed via deposition instead of being further oxidized to form sulfate, then it could potentially result in a non-negligible change in the sulfate burden. This is the case in this study when using a lower rate coefficient (updated) for the oxidation of MSA by OH_(aq) in cloud droplets and aerosols. We think it is still necessary to mention that the updated sulfur chemistry scheme may be important for sulfur aerosol radiative forcing calculations in climate models.

Changes to the manuscript:

- At Page 14, Line 1: modified as "Compared to the standard GEOS-Chem model run, the updated sulfur scheme in this study decreases the conversion yield of DMS to SO₂ ($Y_{\text{DMS} \rightarrow \text{SO}_2}$) from 91% to 75% and increases the conversion yield of DMS to MSA ($Y_{\text{DMS} \rightarrow \text{MSA}}$) from 9% to 15%. The remaining 10% of DMS is lost via wet and dry deposition of DMSO and MSIA. In order to gain insight into the impacts of our updated sulfur scheme on global SO₂, MSA and sulfate burden, we conducted two sensitivity studies by allowing DMS as the only sulfur source for both the standard model run R_{std} ($R_{\text{std_onlyDMS}}$) and full model run R_{all} ($R_{\text{all_onlyDMS}}$). Compared to $R_{\text{std_onlyDMS}}$, the global DMS, SO₂, MSA and sulfate burden in $R_{\text{all_onlyDMS}}$ decreases by 40%, 17%, 8% and 12%, respectively. The decrease in DMS is mainly due to DMS oxidation by BrO with the updated sulfur scheme. The decrease in SO₂ is due to a lower yield of SO₂ from DMS ($Y_{\text{DMS} \rightarrow \text{SO}_2}$), but is partly compensated by the increase in the DMS oxidation rate. MSA decreases despite an increase in the yield of MSA from DMS ($Y_{\text{DMS} \rightarrow \text{MSA}}$) due to a shorter lifetime in $R_{\text{all_onlyDMS}}$ (2.2 days in $R_{\text{all_onlyDMS}}$ versus 4.1 days in $R_{\text{std_onlyDMS}}$) that is caused by the aqueous-phase sink of MSA via MSA + OH_(aq) and faster deposition of

MSA produced in the MBL. The decrease in sulfate is caused by the decrease in SO_2 but is partly compensated by the inclusion of $\text{MSA} + \text{OH}_{(\text{aq})}$ as a sulfate source, which accounts for 4% of global sulfate production. The decrease in sulfate will be smaller if more MSA is oxidized into sulfate instead of being lost via deposition. In sum, climate models with a simplified DMS oxidation scheme (gas-phase oxidation by OH and NO_3 only) may overestimate SO_2 , MSA and sulfate abundances in the pre-industrial environment, potentially leading to underestimates in sulfur aerosol radiative forcing calculations in climate models. Quantifying the impacts of our updated sulfur oxidation scheme on new particle formation is out of the scope of this study and should be addressed in the future.”

Other comments from the second reviewer shown in the supplement have been accepted in the updated manuscript.

(1) **Comment:** Page 8, Line 7 “The difference between the results from Boucher et al. (2003) and this study is that Boucher et al. (2003) did not include $\text{DMS} + \text{BrO}$ in their model simulation, 5 which could lead to an overestimate of the contribution of $\text{DMS} + \text{O}_{3(\text{aq})}$ as both reactions are most important over the high-latitude oceans during winter.”: since this channel only accounts for 12% of the DMS oxidation, I guess this argument is weak. I would expect that this "missing" oxidation would be divided equally over the remaining DMS oxidation channels.

Response: We agree with the reviewer that the smaller contribution of $\text{O}_{3(\text{aq})}$ to DMS oxidation in our study (2%) compared to Boucher et al. (2003) (6%) is not solely caused by the inclusion of $\text{DMS} + \text{BrO}$ in our study. The fraction of DMS oxidized by $\text{O}_{3(\text{aq})}$ increases from 1.8% in R_{all} to only 2.4% in a sensitivity run without $\text{DMS} + \text{BrO}$ reaction ($R_{\text{noDMS+BrO}}$). We have updated the manuscript accordingly.

Changes to the manuscript:

- Page 8, Line 16, modified as “The difference between the results from Boucher et al. (2003) and this study could be due to the differences in oxidants abundances such as O_3 , OH, BrO and Cl.”

(2) **Comment:** Page 8, Line 27 “Multiphase oxidation is especially important over regions where clouds are frequent and OH concentrations are high, e.g. low- to mid-latitude oceans (Fig. 5).”: somehow counterintuitive, since the gas-phase OH reaction pathway is more important than the multiphase oxidation.

Response: In our model, DMSO is removed from the atmosphere via deposition and oxidation by OH in both the gas phase and the aqueous phase. The aqueous-phase oxidation occurs faster than gas-phase oxidation when a lot of clouds are present (low- to mid-latitude oceans).

Changes to the manuscript:

- Page 9, Line 4: modified as “Multiphase oxidation mainly occurs over regions where clouds are frequent and OH concentrations are high, e.g. low- to mid-latitude oceans (Fig. 5).”

- Page 9, Line 17: modified as “Multiphase production of MSIA mainly occurs over low- to mid-latitude oceans where the OH abundance is high and clouds are frequent (Fig. 6).”

(3) **Comment:** Page 12, Line 16: Add the 23 stations description to a table.

Response: The manuscript is updated accordingly.

Changes to the manuscript:

- Add Table 5: The locations of the 23 stations that provide annual-mean MSA/nssSO₄²⁻ observations.

(4) Other minor changes such adding “the” have been all accepted in the updated manuscript.

DMS oxidation and sulfur aerosol formation in the marine troposphere: a focus on reactive halogen and multiphase chemistry

Qianjie Chen^{1*}, Tomás Sherwen², Mathew Evans^{2,3}, and Becky Alexander¹

¹Department of Atmospheric Sciences, University of Washington, Seattle, WA, USA

²Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, UK

³National Centre for Atmospheric Science (NCAS), University of York, York, UK

^{*}Now at Department of Chemistry, University of Michigan, Ann Arbor, MI, USA

Correspondence to: Becky Alexander (beckya@atmos.washington.edu)

Abstract. The oxidation of dimethyl sulfide (DMS) in the troposphere and subsequent chemical conversion into sulfur dioxide (SO₂) and methane sulfonic acid (MSA) are key processes for the formation and growth of sulfur-containing aerosol and cloud condensation nuclei (CCN), but is highly simplified in large-scale models of the atmosphere. In this study, we implement a series of gas-phase and multiphase sulfur oxidation mechanisms into the GEOS-Chem global chemical transport model, including two important intermediates dimethyl sulfoxide (DMSO) and methane sulphinic acid (MSIA), to investigate the sulfur cycle in the global marine troposphere. We found that DMS is mainly oxidized in the gas phase by OH (66%), NO₃ (16%) and BrO (12%) globally. DMS+BrO is important for the model's ability to reproduce the observed seasonality of surface DMS mixing ratio in the Southern Hemisphere. MSA is mainly produced from multiphase oxidation of MSIA by OH_(aq) (66%) and O_{3(aq)} (30%) in cloud droplets and aerosols. Aqueous-phase reaction with OH accounts for only 12% of MSA removal globally and a higher MSA removal rate is needed to reproduce observations of MSA/nssSO₄²⁻ ratio. The modeled conversion yield of DMS into SO₂ and MSA is 75% and 15%, respectively, compared to 91% and 9% in the standard model run that includes only gas-phase oxidation of DMS by OH and NO₃. The remaining 10% of DMS is lost via deposition of intermediates DMSO and MSIA. The largest uncertainties for modeling sulfur chemistry in the marine boundary layer (MBL) are unknown concentrations of reactive halogens (BrO and Cl) and OH_(aq) concentrations in cloud droplets and aerosols. To reduce uncertainties in MBL sulfur chemistry, we should prioritize observations of reactive halogens and OH_(aq).

1 Introduction

The biogenic emission of dimethyl sulfide (DMS: CH₃SCH₃) from the ocean is the largest natural sulfur source to the atmosphere (Andreae, 1990). After emission, DMS is mainly oxidized in the troposphere, with a lifetime against oxidation of 1-2 days (Chin et al., 1996; Boucher et al., 2003; Breider et al., 2010). The oxidation of DMS and subsequent formation of other sulfur species such as sulfuric acid (H₂SO₄) and methane sulfonic acid (MSA: CH₃SO₃H) are crucial for the formation and evolution of natural aerosols and clouds in the marine boundary layer (MBL) and thus have profound climate

Qianjie Chen 7/21/18 9:56 PM

Deleted: 69

Qianjie Chen 7/21/18 9:56 PM

Deleted: and OH_(aq) (25%)

Qianjie Chen 7/21/18 10:09 PM

Deleted: 38%

Qianjie Chen 7/21/18 10:09 PM

Deleted: is important for the model's ability to

Qianjie Chen 7/21/18 10:10 PM

Deleted: in the Southern Hemisphere

Qianjie Chen 7/20/18 10:59 AM

Deleted: 78

Qianjie Chen 7/20/18 10:59 AM

Deleted: 3

beckya 7/27/18 2:32 PM

Deleted: rest

implications (Charlson et al., 1987; von Glasow and Crutzen, 2004; Thomas et al., 2010). In particular, Carslaw et al. (2013) pointed out that natural aerosols such as those that originate from DMS oxidation account for the largest uncertainty of aerosol radiative forcing in climate models.

5 The atmospheric fate of DMS determines the extent to which DMS affects our climate system. Production of H₂SO₄ and MSA from gas-phase oxidation of DMS-derived products can result in nucleation of new particles under favorable conditions (Kulmala et al., 2000; Chen et al., 2015), with implications for aerosol and CCN number concentrations. Sulfate and MSA formed in the aqueous phase will not result in new particle formation, but will impact the aerosol size distribution with implications for cloud microphysical properties (Kreidenweis and Seinfeld, 1988; Kaufman and Tanre, 1994). The
10 oxidation mechanisms of DMS and subsequent formation of sulfate and MSA are, however, very complicated and still not well understood even after decades of research (Ravishankara et al., 1997; Barnes et al., 2006; Hoffmann et al., 2016). Large-scale models of atmospheric chemistry typically contain very simplified DMS chemistry, and often ignore potentially important reaction intermediates. Most of these models include oxidation of DMS by OH and NO₃ radicals, directly producing SO₂ and MSA, and ignore the formation of dimethyl sulfoxide (DMSO: CH₃SOCH₃) and methane sulphinic acid
15 (MSIA: CH₃SO₂H) intermediates (Chin et al., 1996; 2000; Gondwe et al., 2003; 2004; Berglen et al., 2004; Kloster et al., 2006). Nevertheless, previous large-scale modeling studies suggested that BrO could be an important sink for DMS globally (up to 30%), especially in the remote MBL where BrO mixing ratios can reach ppt levels (Boucher et al., 2003; von Glasow et al., 2004; Breider et al., 2010; Khan et al., 2016). Other oxidants that may be important for DMS oxidation include Cl radicals in the gas phase (von Glasow and Crutzen, 2004; Hoffmann et al., 2016) and O₃ in the gas and aqueous phase
20 (Boucher et al., 2003; Hoffmann et al., 2016).

Some large-scale models have simulated the formation of the DMSO intermediate from DMS oxidation (Pham et al., 1995; Cosme et al., 2002; von Glasow et al., 2004; Castebrunet et al., 2009), which is important as DMSO is highly water soluble (Henry's law constant (H_{DMSO}) on the order of 10^7 M atm⁻¹) and can undergo dry and wet deposition in addition to gas- and
25 aqueous-phase oxidation to MSA or SO₂ (Lee and Zhou, 1994; Campolongo et al., 1999; Barnes et al., 2006; Zhu et al., 2006; Hoffmann et al., 2016). In the cloud-free MBL, DMSO is mainly produced by DMS + BrO and DMS + OH_(g) via the addition channel and is oxidized by OH in the gas phase. In the cloudy MBL, DMSO is mainly produced via DMS + O_{3(aq)} and oxidized via DMSO + OH_(aq) in the aqueous phase (Hoffmann et al., 2016). Knowledge about aqueous-phase concentrations of OH in cloud droplets and aerosols is still very limited. Modeled OH_(aq) concentrations are on the order of 10^{-14} - 10^{-12} M
30 (Jacob, 1986; Matthijssen et al., 1995; Jacob et al., 1989; Herrmann et al., 2000). However, recent observations of OH_(aq), which are derived from the concentrations of dissolved organic compounds, are about two orders of magnitude lower (10^{-16} - 10^{-14} M) (Arakaki et al., 2013; Kaur and Anastasio, 2017). In addition to aqueous-phase oxidation of DMSO by OH_(aq), a box modeling study by Zhu et al. (2006) suggested that SO₄⁻ and Cl₂⁻ could contribute to 34% and 10% of DMSO oxidation in the aqueous phase, respectively, with SO₄⁻ and Cl₂⁻ concentrations of 1×10^{-12} M and 1×10^{-11} M (Herrmann et al., 2000),

respectively. It should be noted that $\text{OH}_{(\text{aq})}$, SO_4^- and Cl_2^- concentrations are poorly known and the contribution of these species to DMSO oxidation will depend on their concentrations.

MSIA is generally not included in large-scale models, though it has been considered in some one-dimensional or box models (Lucas and Prinn, 2002; von Glasow and Crutzen, 2004; Zhu et al., 2006; Hoffmann et al., 2016). The Henry's law constant of MSIA has not been measured directly but is thought to be larger than that of DMSO and smaller than that of MSA, on the order of 10^8 M atm^{-1} (Barnes et al., 2006). MSIA is mainly produced from oxidation of DMSO by OH in both the gas and aqueous phase, and removed via further oxidation by OH and O_3 in both the gas and aqueous phase and Cl_2^- in the aqueous phase (von Glasow and Crutzen, 2004; Zhu et al., 2006; Barnes et al., 2006; Hoffmann et al., 2016). Only oxidation of MSIA by OH in the gas phase produces SO_2 , all other pathways lead to MSA formation. The contribution of each pathway towards MSIA oxidation depends on the concentration of each oxidant. Zhu et al. (2006) suggested Cl_2^- is more important than $\text{OH}_{(\text{aq})}$ for MSIA oxidation in the aqueous phase when assuming a Cl_2^- concentration of $1 \times 10^{-11} \text{ M}$ (Herrmann et al., 2000), while Hoffmann et al. (2016) suggested the opposite with a lower Cl_2^- concentration ($1.5 \times 10^{-12} \text{ M}$).

The only source of MSA in the marine troposphere is from oxidation of DMS emitted from the marine biosphere. It thus contains information on both DMS emission flux and chemistry. It has been proposed as an ice-core proxy for sea ice extent in past climates, as a result of melting sea ice releasing nutrients to stimulate phytoplankton growth to produce DMS (Curran et al., 2003; Abram et al., 2010). Other factors such as oxidation mechanisms of DMS and atmospheric circulation can also affect MSA abundance in ice core records (Becagli et al., 2009; Hezel et al., 2011). As DMS is the dominant sulfur source of both MSA and non-sea-salt sulfate (nssSO_4^{2-}) in the remote marine troposphere, the $\text{MSA}/\text{nssSO}_4^{2-}$ molar ratio there reflects sulfur chemistry. In addition, the $\text{MSA}/\text{nssSO}_4^{2-}$ molar ratio has often been used as a measure of marine biogenic contribution to total atmospheric sulfate formation, as nssSO_4^{2-} has both anthropogenic and natural origins while MSA is generally considered to have a predominant natural origin (Andreae et al., 1999; Savoie et al., 2002; Gondwe et al., 2004). MSA is very water soluble, with a Henry's law constant on the order of 10^9 M atm^{-1} (Campolongo et al., 1999), and is mainly removed from the atmosphere via wet and dry deposition with a lifetime of about a week (Pham et al., 1995; Chin et al., 1996; 2000; Cosme et al., 2002; Hezel et al., 2011). One-dimensional modeling studies by Zhu et al. (2006) and von Glasow and Crutzen (2004) suggested that the oxidation of MSA by $\text{OH}_{(\text{aq})}$ in the aqueous phase to form SO_4^{2-} in the MBL could also be a significant loss process of MSA (3-27%) (Zhu et al., 2006; von Glasow and Crutzen, 2004), while a box modeling study by Hoffmann et al. (2016) found it negligible (2%). The different conclusions regarding the role of reaction of MSA with $\text{OH}_{(\text{aq})}$ is due to different assumptions regarding $\text{OH}_{(\text{aq})}$ concentrations, which is highly uncertain.

In this study, we expand upon the current simplified DMS chemistry in a global chemical transport model GEOS-Chem, including the DMSO and MSIA intermediates. We investigate the role of gas-phase and multiphase oxidation of DMS, DMSO, MSIA and MSA for determining their spatial distribution, seasonality, and lifetime and the implications for the

Qianjie Chen 6/17/18 4:49 PM

Deleted: has only a natural source

beckya 7/27/18 2:40 PM

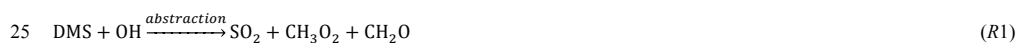
Deleted: are

MBL and global sulfur budget. Observations of DMS mixing ratios from 4 locations and MSA/nssSO₄²⁻ ratios from 23 locations around the globe obtained from previous studies are used to assess the performance of model. We conclude with recommendations for future laboratory experiments and field campaigns, and recommendations for sulfur chemistry that should be included in large-scale models of atmospheric chemistry and climate.

5 2 GEOS-Chem model

In this study, we use a global 3-D chemical transport model GEOS-Chem v9-02 (<http://www.geos-chem.org/>), which is driven by assimilated meteorological data from the NASA Goddard Earth Observing System (GEOS-5, <http://gmao.gsfc.nasa.gov>). It contains detailed HO_x-NO_x-VOC-ozone-BrO_x tropospheric chemistry originally described in Bey et al. (2001), with updated BrO_x and sulfate chemistry described in Parrella et al. (2011), Schmidt et al. (2016) and Chen et al. (2017). The sulfate-nitrate-ammonium aerosol simulation is fully coupled to gas-phase chemistry (Park et al., 2004), with aerosol thermodynamics described in Pye et al. (2009). The sea salt aerosol simulation is described in Jaeglé et al. (2011) and bulk cloud water pH is calculated as described in Alexander et al. (2012). The model contains detailed deposition schemes for both gas species and aerosols (Liu et al., 2001; Amos et al., 2012; Zhang et al., 2001; Wang et al., 1998). All simulations are performed at 4°×5° horizontal resolution and 47 vertical levels up to 0.01 hPa (≈81 km) after a model spin up of one year. The vertical layer thickness ranges from 120-150 m for the first 12 layers to 200-800 m for the 13th-27th layers and >1000 m for the rest (http://acmg.seas.harvard.edu/geos/doc/archive/man.v9-01-02/appendix_3.html#A3.5.2). Year 2007 is chosen as a reference year to be consistent with Schmidt et al. (2016) and Chen et al. (2017). DMS emission flux from the ocean (F) is parameterized following Lana et al. (2011): $F = k_T C_w$, where gas transfer velocity k_T (m s^{-1}) is a function of sea surface temperature and wind speed and C_w (mol m^{-3}) is the DMS concentrations in sea water obtained from Lana et al. (2011). In a sensitivity simulation, we used C_w from Kettle et al. (1999).

The standard model contains only three DMS oxidation pathways in the original version, which produces SO₂ and MSA directly (R1-R3), following Chin et al. (1996) with updated reaction rate coefficients from Burkholder et al. (2015):



The yields of SO₂ and MSA for the addition channel of the DMS+OH reaction are originally from Chatfield and Crutzen (1990), who made simplified assumptions in their 2-D model based on previous laboratory experiments and modeling studies. It should be noted that only gas-phase chemistry was considered when they made the assumptions of the yields of

SO₂ and MSA, which might not represent the real atmosphere as multiphase chemistry has been suggested to be the biggest source of MSA in the atmosphere (Zhu et al., 2006; Hoffmann et al., 2016).

We add the DMSO and MSIA intermediates as two new advected chemical tracers, which undergo chemical production and loss, transport and deposition in the model. We add 12 new chemical reactions in the model, including gas-phase oxidation of DMS by OH (addition channel, modified to produce DMSO instead of MSA), BrO, Cl and O₃, multiphase oxidation of DMS by O₃, both gas-phase and multiphase oxidation of DMSO by OH, both gas-phase and multiphase oxidation of MSIA by OH and O₃, and multiphase oxidation of MSA by OH, as shown in Table 1. The rate coefficients for all gas-phase sulfur reactions are obtained from the most recent JPL report (Burkholder et al., 2015), except for MSIA + O_{3(g)} ($k_{\text{MSIA}+\text{O}_3(\text{g})}$) (Lucas and Prinn, 2002; von Glasow and Crutzen, 2004). The sulfur product yields for gas-phase reactions are obtained from various laboratory and modeling studies as indicated in Table 1. [Product yields of 0.6 for SO₂ and 0.4 for DMSO have been commonly used in global models \(Pham et al., 1995; Cosme et al., 2002; Spracklen et al., 2005; Breider et al., 2010\) based on experiments described in Turnipseed et al. \(1996\) and Hynes et al. \(1993\).](#) All oxidants (OH, O₃, H₂O₂, BrO, HOBr) are simulated in the full chemistry scheme, except for Cl radicals. We used monthly mean Cl mixing ratios from Sherwen et al. (2016), which considered Cl-Br-I coupling but did not include chlorine production on sea salt aerosols that was suggested to be the largest tropospheric chlorine source in Schmidt et al. (2016). We imposed a diurnal variation of Cl abundances based on solar zenith angle, similar to the offline simulation of OH abundances in GEOS-Chem (Fisher et al., 2017). [The global distributions of tropospheric annual-mean concentrations of BrO, Cl, OH and O₃ are shown in Fig. 12. The high BrO abundances over subtropics and polar regions are due to low deposition fluxes of reactive bromine \(Schmidt et al., 2016\) and the high BrO abundance over Southern Ocean is due to its source from sea salt debromination \(Chen et al., 2017\). The high Cl abundance over coastal regions in the Northern Hemisphere is due to heterogeneous uptake of N₂O₅ on sea salt aerosols to produce reactive chlorine \(Sherwen et al., 2017\).](#)

For the multiphase reactions DMS + O_{3(aq)}, DMSO + OH_(aq), MSIA + OH_(aq), MSIA + O_{3(aq)} and MSA + OH_(aq) in cloud droplets and aerosols, we assume a first-order loss of the sulfur species, following the parameterization described in Ammann et al. (2013) and Chen et al. (2017):

$$\frac{d[X]}{dt} = -\frac{c\gamma}{4}A[X], \quad (E4)$$

where X represents DMS, DMSO, MSIA or MSA; c is the average thermal velocity of X (m s^{-1}); A ($\text{m}^2 \text{m}^{-3}$) is the total surface area concentration of aerosols or cloud droplets; γ (unitless) is the reactive uptake coefficient of X that involves gas diffusion (γ_d), mass accommodation (α_b) and chemical reaction (Γ_b) in the aerosols or cloud droplets, as calculated in E5-E7.

$$\frac{1}{\gamma} = \frac{1}{\gamma_d} + \frac{1}{\alpha_b} + \frac{1}{\Gamma_b} \quad (E5)$$

Qianjie Chen 6/17/18 5:33 PM

Deleted: from the HOBr++H⁺ reaction

beckya 7/27/18 2:45 PM

Deleted: small

beckya 7/27/18 2:45 PM

Deleted: s

$$\gamma_d = \frac{4D_g}{cr} \quad (E6)$$

$$F_b = \frac{4H_XRT\sqrt{D_1k_{X+Y}[Y]}f_r}{c} \quad (E7)$$

where r is radius for aerosols or cloud droplets (m); D_g is the gas phase diffusion coefficient of X ($\text{m}^2 \text{s}^{-1}$), calculated as a function of air temperature and air density following Chen et al. (2017). H_X and D_1 are the Henry's law constant (M atm^{-1}) and liquid phase diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) of X, which are summarized in Table 2; R ($=8.31 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1}$) is the universal gas constant. T is air temperature (K); $[Y]$ ($=[\text{OH}_{(\text{aq})}]$ or $[\text{O}_{3(\text{aq})}]$) is the aqueous phase concentration of the oxidant in aerosols or cloud droplets (M), where $[\text{O}_{3(\text{aq})}]$ is calculated assuming gas-liquid equilibrium and $[\text{OH}_{(\text{aq})}]$ is calculated following Jacob (2005) ($[\text{OH}_{(\text{aq})}] = \beta[\text{OH}_{(\text{g})}]$, $\beta = 1 \times 10^{-19} \text{ M cm}^3 \text{ molecule}^{-1}$). This is about two orders of magnitude higher than $[\text{OH}_{(\text{aq})}]$ calculated indirectly from dissolved organic compound observations in Arakaki et al. (2013) and Kaur and Anastasio (2017). Thus, we conduct a sensitivity simulation reducing $[\text{OH}_{(\text{aq})}]$ in cloud droplets and aerosols by two orders of magnitude (Table 3). We conduct another sensitivity simulation by reducing the $[\text{OH}_{(\text{aq})}]$ in aerosols only by a factor of 20 (Herrmann et al., 2010) and found negligible changes ($<2\%$) in the global sulfur burden. k_{X+Y} is the aqueous-phase reaction rate coefficient between X and Y ($\text{M}^{-1} \text{ s}^{-1}$), as summarized in Table 1. f_r ($=\text{coth}(r/l) - l/r$) is the reacto-diffusive correction term, which compares the radius of aerosols or cloud droplets (r) with the reacto-diffusive length scale of the reaction ($l = \sqrt{D_1/(k_{X+Y}[Y])}$) (Ammann et al., 2013). The mass accommodation coefficients (α_b) of DMS, DMSO, MSIA and MSA are given in Table 2.

Twelve model simulations were performed in order to investigate the importance of individual reactions for MBL sulfur chemistry and are described in Table 3. These simulations were designed to explore the role of DMS chemistry versus emissions for the DMS budget, and the importance of gas-phase reactive halogen chemistry and multiphase chemistry for all sulfur-containing compounds.

3 Results and Discussion

3.1 DMS budget

Figure 1 shows the global sulfur budgets for the model run including DMSO and MSIA intermediates and all 12 new reactions (R_{all}). The DMS emission flux from the ocean to the atmosphere (F_{DMS}) is 22 Tg S yr^{-1} , which is similar to that (24 Tg S yr^{-1}) reported in Hezel et al. (2011) and within the range ($11\text{-}28 \text{ Tg S yr}^{-1}$) reported in the literature (Spracklen et al., 2005 and reference therein). F_{DMS} is 18 Tg S yr^{-1} when using sea surface DMS concentrations from Kettle et al. (1999). The tropospheric burden of DMS is 74 Gg S , which is within the range of $20\text{-}150 \text{ Gg S}$ reported in Faloon et al. (2009), and is 40% lower than the standard model run (R_{std}). The lifetime of DMS is 1.2 days in R_{all} , compared to 2.1 days in R_{std} . Surface DMS mixing ratios are highest over Southern Ocean ($\approx 400 \text{ ppt}$) (Fig. 2a) where DMS emissions are highest during summer

Qianjie Chen 6/15/18 4:26 PM

Deleted: μ

beckya 7/27/18 2:51 PM

Deleted: run

beckya 7/27/18 2:51 PM

Deleted: just

Qianjie Chen 7/20/18 5:05 PM

Deleted: Multiphase sulfur reactions added in the model are only activated when air temperature is above 273 K, to be consistent with the temperature at which their rate constants were obtained (Table 1).

Qianjie Chen 7/21/18 10:34 PM

Deleted: Ten

Qianjie Chen 7/14/18 4:17 PM

Deleted: 75

Qianjie Chen 7/14/18 11:28 PM

Deleted: 39

Qianjie Chen 7/14/18 11:28 PM

Deleted: 3

(Lana et al., 2011) and DMS chemical destruction is small due to low OH abundance at high latitudes (DMS lifetime of 2-5 days over Southern Ocean). DMS mainly resides in the lower troposphere, with 86% of the tropospheric burden below 2 km. DMS is mainly oxidized in the gas phase by OH (37% via abstraction channel and 29% via addition channel), followed by NO₃ (16%). The global contribution of OH and NO₃ to DMS oxidation from previous studies is 50%-70% and 20%-30%, respectively, depending mainly on which other oxidants are included (Boucher et al., 2003; Berglen et al., 2004; Breider et al., 2010; Khan et al., 2016). The oxidation of DMS by OH occurs mainly during daytime while oxidation by NO₃ occurs mainly at night due to low nighttime OH production and rapid photolysis of NO₃ during daytime. Fig. 3 shows the global, annual mean distribution of the fractional importance of different DMS oxidation pathways. The relative importance of OH for the oxidation of DMS ($f_{\text{[DMS+OH(g)]}}$) is typically greater than 50% over the oceans. The relative importance of NO₃ for the oxidation of DMS ($f_{\text{[DMS+NO}_3]}$) is typically low over the remote oceans (<10%), but high over the continents and coastal regions (>40%) where NO_x emissions are highest. It should be noted, however, that DMS abundance is low over continents (Fig. 2a).

The relative importance of BrO oxidation of DMS ($f_{\text{[DMS-BrO]}}$) is 12% (global, annual mean), which is within the range suggested by Khan et al. (2016) (8%) and Breider et al. (2010) (16%). $f_{\text{[DMS-BrO]}}$ is highest (>30%) over the Southern Ocean and Antarctica, especially during winter, due to high BrO (up to 0.5 ppt) and low OH and NO₃ abundance. The main uncertainty of the importance of BrO for DMS oxidation resides in the tropospheric BrO abundance, which is rarely measured and is still not well quantified in global models (von Glasow et al., 2004; Simpson et al., 2015). The BrO in our model generally underestimates satellite observations, especially over mid- and high-latitudes (Chen et al., 2017), suggesting that our modeled estimate of the importance of DMS+BrO may be biased low. In order to quantify the contribution of BrO to DMS oxidation, we need to better quantify the BrO abundance through both observation and model development.

The fractional contribution of Cl to DMS oxidation ($f_{\text{[DMS+Cl]}}$) is 4% globally and generally less than 10% everywhere. $f_{\text{[DMS+Cl]}}$ increases to 28% in a sensitivity run increasing Cl mixing ratios by an order of magnitude. In comparison, von Glasow and Crutzen (2004) calculate that about 8% of DMS is oxidized by Cl in the cloud-free MBL during summer in a 1-D model. Hoffmann et al. (2016) estimated that about 18% of DMS is oxidized by Cl under typical MBL conditions in a box model. Both studies used the same $k_{\text{DMS+Cl}}$ as in our study, but Cl concentrations were not reported in either study. The annual-mean tropospheric Cl concentration used in this study is 1.1×10^3 atoms cm⁻³, which is similar to that (1.3×10^3 atoms cm⁻³) in another recent 3-D modeling study (Hossaini et al., 2016). As suggested by Sherwen et al. (2016), Cl concentration could be underestimated in our study, due at least in part to the missing chlorine source from sea salt aerosols and anthropogenic chloride emissions. The largest uncertainty for the importance of Cl for the oxidation of DMS resides in our limited knowledge of Cl concentrations in the troposphere. Due to the difficulty of directly observing Cl, estimates of its abundance are usually derived from non-methane hydrocarbons (NMHC) observations. Using this method, Cl concentration is estimated to be on the order of 10^4 atoms cm⁻³ ($0.2\text{-}80 \times 10^4$ atoms cm⁻³) in the MBL and Antarctic boundary layer (Jobson

et al., 1994; Singh et al., 1996; Wingenter et al., 1996; 2005; Boundries and Bottenheim, 2000; Arsene et al., 2007; Read et al., 2007), with highest concentrations over Tropical Pacific during autumn (Singh et al., 1996). However, a recent study suggests that this is an overestimate of tropospheric Cl abundance (Gromov et al., 2018). Another uncertainty in the atmospheric implications of DMS+Cl originates from its sulfur products, which are most likely CH₃SCH₂ via the abstraction channel and (CH₃)₂S-Cl adduct via the addition channel (Barnes et al., 2006). The CH₃SCH₂ will likely be further oxidized into SO₂, similar to the abstraction channel of DMS+OH, while the (CH₃)₂S-Cl adduct could react with O₂ to produce DMSO. Atkinson et al. (2004) estimated that 50% of DMS+Cl occurs through the abstraction channel and 50% occurs through the addition channel at 298 K and 1 bar pressure, but the abstraction channel could account for more than 95% at low pressure (Butkovskaya et al., 1995). Since DMS+Cl is neither a big sink of DMS nor a big source of DMSO in our study, the yield uncertainties have little influence on the modeled sulfur budgets. However, modeled estimates of DMS+Cl could be too low due to a potential low bias in modeled Cl abundance.

In this study, DMS+O_{3(aq)} is the only multiphase DMS oxidation pathway, which accounts for only 2% of DMS oxidation globally, reaching up to 5% over high-latitude oceans (e.g. Southern Ocean) (Fig. 3). In comparison, in a general circulation model Boucher et al. (2003) calculated that DMS+O_{3(aq)} accounts for about 6% of DMS oxidation globally and 15-30% over oceans north of 60°N and in the 50-75°S latitude band. The difference between the results from Boucher et al. (2003) and this study could be due to the differences in oxidant abundances such as O₃, OH, BrO and Cl. Using a 1-D model, von Glasow and Crutzen (2004) calculated that DMS+O_{3(aq)} accounts for 4-18% of DMS oxidation in the cloudy MBL, which is similar to 5-10% over the Southern Ocean MBL in our model results. The fraction of DMS oxidized by O₃ in the gas phase ($f_{[I]DMS+O_3(g)}=0.5\%$) is smaller than $f_{[I]DMS+O_3(aq)}$, consistent with Boucher et al. (2003). Thus, both the gas-phase and multiphase oxidation of DMS by O₃ represent minor DMS sinks in the global troposphere.

3.2 DMSO budget

The modeled global tropospheric DMSO burden is 8 Gg S, which is 3-4 times larger than in Pham et al. (1995) and Cosme et al. (2002) which did not include production of DMSO from DMS+BrO. Modeled surface DMSO mixing ratio is highest over the Southern Ocean (≈30 ppt) (Fig. 2b) where the DMS mixing ratio is high and BrO is abundant. The high DMSO mixing ratio over Antarctica in our model is due to weak DMSO oxidation by OH in both the gas and aqueous phase. DMSO mainly resides in the lower troposphere, with 67% of the tropospheric burden below 2 km.

Globally, we simulate DMS+BrO is the biggest source of DMSO (44%), followed by the addition channel of DMS+OH (41%), DMS+Cl (9%) and DMS+O_{3(aq)} (6%). The fraction of DMSO produced from DMS+BrO is highest over the high-latitude ocean where OH abundance is low and subtropical oceans where BrO abundance is high, while DMS+Cl and DMS+O_{3(aq)} can account for up to 20% of the DMSO production in coastal regions and mid-latitude MBL, respectively (Fig. 4).

Qianjie Chen 7/14/18 6:33 PM

Deleted: 1

Qianjie Chen 7/21/18 7:16 PM

Deleted: is that Boucher et al. (2003) did not include DMS+BrO in their model simulation, which could lead to an overestimate of the contribution of DMS+O_{3(aq)} as both reactions are most important over the high-latitude oceans during winter

Qianjie Chen 7/14/18 6:35 PM

Deleted: only half of

Qianjie Chen 7/14/18 11:55 PM

Deleted: 66

Qianjie Chen 7/14/18 11:59 PM

Deleted: 45

Qianjie Chen 7/14/18 11:59 PM

Deleted: 42

Qianjie Chen 7/14/18 11:59 PM

Deleted: 4

DMSO is removed from the atmosphere via gas-phase oxidation by OH (33%), multiphase oxidation by OH in cloud droplets (37%) and aerosols (3%), and dry (16%) and wet deposition (11%). The lifetime of DMSO is about 11 hours. Multiphase oxidation mainly occurs over regions where clouds are frequent and OH concentrations are high, e.g. low- to mid-latitude oceans (Fig. 5). Cosme et al. (2002) calculated 85% of DMSO is lost via gas-phase oxidation by OH and the rest 15% via deposition in a global 3-D model, but they did not include heterogeneous loss of DMSO. It has been suggested that heterogeneous loss is the predominant loss process of DMSO in the cloudy MBL in box or 1-D models (Zhu et al., 2006; Hoffmann et al., 2016).

3.3 MSIA budget

MSIA is an important intermediate during the oxidation of DMSO to produce MSA, and has a simulated tropospheric burden of 2 Gg S. The surface MSIA mixing ratio is higher over Antarctica than over the Southern Ocean (Fig. 2c) due to larger removal of MSIA by $O_{3(aq)}$ and $OH_{(aq)}$ in clouds over Southern Ocean. 31% of MSIA resides below 2 km altitude. The smaller fraction of MSIA below 2 km compared to DMSO is due to faster oxidation of MSIA by $OH_{(aq)}$ and $O_{3(aq)}$ in clouds and aerosols (Table 1).

In R_{all} , MSIA is produced from both gas-phase (44%) and multiphase (56%) oxidation of DMSO by OH in cloud droplets and aerosols (Fig. 1). Multiphase production of MSIA mainly occurs over low- to mid-latitude oceans where the OH abundance is high and clouds are frequent (Fig. 6).

MSIA is mainly removed in the troposphere via both gas-phase and multiphase oxidation by OH, with a lifetime of 4 hours. Dry (2%) and wet (2%) deposition of MSIA accounts for 4% of MSIA removal in the troposphere. Globally, multiphase oxidation in cloud droplets and aerosols by $OH_{(aq)}$ (53%) and $O_{3(aq)}$ (24%) is the biggest sink of MSIA, followed by gas-phase oxidation by OH (19%). Multiphase oxidation by $OH_{(aq)}$ is more important over low-latitude oceans where OH abundance is high, reaching up to 70% (Fig. 7). Multiphase oxidation by $O_{3(aq)}$ is more important over high-latitude ocean where OH abundance is low (Fig. 7). Over continents and Antarctica, MSIA is mostly oxidized by OH in the gas phase.

In comparison, Hoffmann et al. (2016) also found that multiphase oxidation is the main sink of MSIA in the MBL in their box model, with $O_{3(aq)}$, $OH_{(aq)}$ and Cl_2^- accounting for 42%, 19% and 10% of MSIA removal, respectively. The rest of MSIA (29%) was removed by $CH_3SO_2(O_2\cdot)$ that was produced as an intermediate during the electron transfer reaction of MSIA with $OH_{(aq)}$ and Cl_2^- in cloud droplets and aerosols. By considering cloud droplets only, Hoffmann (2016) suggested $OH_{(aq)}$ is more important (1.5 times faster) than $O_{3(aq)}$ for MSIA oxidation, which is consistent with our results. Since information such as $OH_{(aq)}$ concentrations in aerosols, aerosol water content and cloud liquid water content were not provided in Hoffmann et al. (2016), we do not further compare our MSIA oxidation by $O_{3(aq)}$ and $OH_{(aq)}$ to Hoffmann et al. (2016). Hoffmann et al.

- Qianjie Chen 7/15/18 12:05 AM
Deleted: 7
- Qianjie Chen 7/15/18 12:05 AM
Deleted: 31
- Qianjie Chen 7/20/18 2:13 PM
Deleted: and
- Qianjie Chen 7/20/18 2:13 PM
Deleted: 29
- Qianjie Chen 7/21/18 7:29 PM
Deleted: 2
- Qianjie Chen 7/21/18 7:45 PM
Deleted: is especially important
- Qianjie Chen 7/15/18 12:11 AM
Deleted: 4
- Qianjie Chen 7/15/18 12:12 AM
Deleted: 41
- Qianjie Chen 7/15/18 12:12 AM
Deleted: MISA
- Qianjie Chen 7/15/18 12:13 AM
Deleted: 53
- Qianjie Chen 7/15/18 12:14 AM
Deleted: 47
- Qianjie Chen 7/21/18 7:48 PM
Deleted: is more important
- Qianjie Chen 7/15/18 12:17 AM
Deleted: 9
- beckya 7/27/18 3:11 PM
Deleted: The d
- Qianjie Chen 7/15/18 12:19 AM
Deleted: 8
- Qianjie Chen 7/15/18 10:23 AM
Deleted: $O_{3(aq)}$ (45%) and
- Qianjie Chen 7/15/18 12:26 AM
Deleted: 16
- Qianjie Chen 7/15/18 12:26 AM
Deleted: 30
- Qianjie Chen 7/15/18 10:39 AM
Formatted: Not Highlight
- Qianjie Chen 7/15/18 10:31 AM
Deleted: but is generally within
- Qianjie Chen 7/15/18 10:31 AM
Deleted: 3
- Qianjie Chen 7/15/18 10:30 AM
Deleted: polar regions

(2016) is the only modeling study that considered multiphase reaction of MSIA with both $O_{3(aq)}$ and $CH_3SO_2(O_2\cdot)$. Zhu et al. (2006) found Cl_2^- to be more important than $OH_{(aq)}$ for MSIA oxidation when assuming Cl_2^- concentration 6 times higher than that used in Hoffmann et al. (2016). Due to our limited knowledge about $CH_3SO_2(O_2\cdot)$ and Cl_2^- production and concentrations in cloud droplets and aerosols, we do not include the multiphase reactions of MSIA with $CH_3SO_2(O_2\cdot)$ and Cl_2^- in this study.

Gas-phase oxidation of MSIA by OH (18%) has important implications for the MSA budget as $MSIA+OH_{(g)}$ has a low yield for MSA formation (SO_2 yield of 0.9) (Kukui et al., 2003). Gas-phase oxidation of MSIA by O_3 is negligible globally (1%). In contrast, Lucas and Prinn (2002) suggest $MSIA+O_{3(g)}$ could compete with $MSIA+OH_{(g)}$ for MSA removal, but the rate coefficient of $MSIA+OH_{(g)}$ is very small in their 1-D model (about two orders of magnitude smaller than ours).

3.4 MSA budget

In R_{all} , the global MSA burden is 20 Gg S, which is within the range of 13-40 Gg S reported in previous modeling studies (Pham et al, 1995; Chin et al., 1996; 2000; Cosme et al., 2002; Hezel et al., 2011). The largest MSA burden is from Hezel et al. (2011), in which DMSO was not included, while the smallest MSA burden is from Cosme et al. (2002), in which DMSO was included. Neglecting the DMSO intermediate in the model could result in an overestimate of MSA production as DMSO is also removed via dry and wet deposition. Note that none of these previous studies consider $DMS+BrO$ and $MSA+OH_{(aq)}$ in their models. Surface MSA mixing ratio is highest over the Southern Ocean, but the peak shifts north compared to DMS, DMSO and MSIA (Fig. 2d). This is due to larger production of MSA by $O_{3(aq)}$ and $OH_{(aq)}$ in clouds (due to higher $O_{3(aq)}$ and $OH_{(aq)}$ concentrations at lower latitudes) over northern part of Southern Ocean compared to the southern part of Southern Ocean. 57% of MSA resides below 2 km altitude, suggesting that MSA is mainly produced in the MBL.

As shown in Fig. 1, MSA is mainly produced from multiphase oxidation of MSIA by OH (66%) and O_3 (30%). $MSIA+OH_{(aq)}$ dominates over low-latitude oceans while $MSIA+O_{3(aq)}$ dominates over high-latitude oceans (Fig. 8). MSA formation occurs mainly in clouds (74%), where the liquid water content is high. Our result is consistent with the general concept that gas-phase MSA formation is small compared to multiphase formation (Barnes et al., 2006; von Glasow and Crutzen, 2004; Zhu et al., 2006; Hoffmann et al., 2016). $MSA+OH_{(aq)}$ accounts for 12% of MSA removal in R_{all} , and the rest of MSA is removed via dry (12%) and wet (76%) deposition. The lifetime of MSA is 2.2 days globally, which is relatively short compared to 5-7 days in previous studies (Pham et al, 1995; Chin et al., 1996; 2000; Cosme et al., 2002; Hezel et al., 2011) without $MSA+OH_{(aq)}$. Information about the global distribution of MSA concentrations and deposition from these previous modelling studies are needed for comparison. The MSA lifetime is lowest (about 1 day) over tropical oceans where clouds are frequent and OH abundance is high. It increases to 2-6 days over Southern Ocean and subtropical oceans. To the best of our knowledge, this is the first study to report global MSA lifetime from a global 3-D model that considers

Qianjie Chen 7/15/18 11:03 AM

Deleted: 30

Qianjie Chen 7/15/18 11:04 AM

Deleted: 10

Qianjie Chen 7/15/18 11:04 AM

Deleted: lower than

Qianjie Chen 6/15/18 4:49 PM

Deleted: leading to no MSA production

Qianjie Chen 7/21/18 11:32 PM

Deleted: The global MSA burden drops to 8 Gg S in our sensitivity simulation without DMS+BrO and increases to 15 Gg S in our sensitivity simulation without $MSA+OH_{(aq)}$, which demonstrates the important role of DMS+BrO for MSA formation and $MSA+OH_{(aq)}$ for MSA removal.

Qianjie Chen 7/15/18 11:20 AM

Deleted: 60

Qianjie Chen 7/15/18 11:25 AM

Deleted: 69

Qianjie Chen 7/15/18 11:24 AM

Deleted: and

Qianjie Chen 7/15/18 11:24 AM

Deleted: OH (25%).

Qianjie Chen 7/15/18 11:49 AM

Deleted: 58

Qianjie Chen 7/15/18 1:09 PM

Deleted: is an important sink of MSA in our model,

Qianjie Chen 7/15/18 1:09 PM

Deleted: ing

Qianjie Chen 7/15/18 11:50 AM

Deleted: 38

Qianjie Chen 7/15/18 1:36 PM

Formatted: Font:Italic

Qianjie Chen 7/15/18 1:36 PM

Formatted: Subscript

Qianjie Chen 7/15/18 1:38 PM

Deleted: . As a result,

Qianjie Chen 7/20/18 4:38 PM

Deleted: t

Qianjie Chen 7/15/18 2:58 PM

Deleted: only 1.4

Qianjie Chen 7/30/18 11:03 PM

Deleted: observations/

Qianjie Chen 7/15/18 3:12 PM

Deleted: 20 hours

MSA+OH_(aq). In the sensitivity run without MSA+OH_(aq) ($R_{\text{noMSA+OH(aq)}}$), the lifetime of MSA increases to 2.5 days. In the sensitivity run with a higher rate constant of MSA+OH_(aq) ($R_{\text{moreMSA+OH(aq)}}$), the lifetime of MSA decreases to 1.7 days.

3.5 Uncertainties in rate constants

The uncertainties in the rate constants for the reactions added in the model are shown in Table 4. The uncertainty factor (f_{298}) used for gas-phase reaction rate constants at 298 K indicates that the reaction rate constant could be greater than or less than the recommended value by a factor of f_{298} . For all gas-phase reactions added in this study, f_{298} varies from 1.2 to 1.5. f_{298} is 1.3 for the DMS+BrO reaction, which adds to the uncertainty in oxidation of DMS by BrO. The global annual mean tropospheric BrO burden varies from 3.6 to 5.7 Gg Br in three recent global modeling studies (Parrella et al., 2012; Schmidt et al., 2016; Chen et al., 2017), but all three of these modeling studies underestimate satellite observations of the tropospheric BrO column from Theys et al. (2010) (e.g. by 44% over Southern Ocean in Chen et al. (2017)). Thus, further investigations are needed in both laboratory determination of the reaction rate constant for DMS+BrO and field observations of the BrO abundance in the troposphere. In addition, we need to better constrain the rate constants for the other two gas-phase reactions DMS+OH (addition pathway) and DMSO+OH ($f_{298}=1.2$). Very few studies have determined the rate constants for the multiphase reactions added in the model (Table 4). The biggest uncertainty resides in the oxidation of MSA by OH_(aq) and the oxidation of MSIA by O_{3(aq)}. The rate constant for the MS⁻+OH_(aq) reactions differs by a factor of 4.7 in Milne et al. (1989) and Zhu et al. (2003), which results in about 30% difference in global annual mean tropospheric MSA burden. Only one box modeling study (Hoffmann et al., 2016) considered the oxidation of MSIA by O_{3(aq)} in clouds and aerosols, using the rate constant measured in Herrmann and Zellner (1997) for the MSIA_(aq)+O_{3(aq)} reaction and Flyunt et al. (2001) for the MS⁻+O_{3(aq)} reaction. As MSIA+O_{3(aq)} and MSA+OH_(aq) are important for MSA production and removal, more laboratory studies are needed to constrain the rate constants for these two reactions.

3.6 Model-observation comparison

3.6.1 Surface DMS mixing ratio

Monthly mean DMS mixing ratios measured at 4 stations around the globe are used to assess modeled DMS: Crete Island (CI; 35°24'N, 25°60'E) (Kouvarakis and Mihalopoulos, 2002), Amsterdam Island (AI; 37°50'S, 77°30'E) (Castebrunet et al., 2009), Cape Grim (CG; 40°41'S, 144°41'E) (Ayer et al., 1995), and Dumont D'Urville (DU; 66°40'S, 140°1'E) (Castebrunet et al., 2009). The DMS data covers the 1997-1999 period for CI, the 1987-2006 period for AI, the 1989-1992 period for CG, and the 1998-2006 period for DU.

Figure 9 shows the comparison between modeled and observed monthly-mean DMS mixing ratio at CI, AI, CG and DU stations. Comparing R_{all} with R_{std} , we can see that in general the modeled DMS mixing ratios match better with observations for the three stations in the Southern Hemisphere with the updated DMS chemistry, especially during Southern Hemisphere

Qianjie Chen 7/21/18 11:36 PM

Deleted: As shown in Sect. 3.6.2, MSA+OH_(aq) has a significant impact on modeled MSA/nss ratio.

Qianjie Chen 7/15/18 6:15 PM

Deleted: +

Qianjie Chen 7/15/18 6:15 PM

Deleted: +

Qianjie Chen 7/15/18 6:15 PM

Deleted: reactions

Qianjie Chen 7/15/18 4:12 PM

Deleted: MSA

Qianjie Chen 7/21/18 11:39 PM

Formatted: Subscript

Qianjie Chen 7/21/18 11:41 PM

Deleted: MSIA+O_{3(aq)} reaction

Qianjie Chen 7/21/18 11:41 PM

Deleted: ,

Qianjie Chen 7/21/18 11:41 PM

Formatted: Not Superscript/ Subscript

Qianjie Chen 7/15/18 6:20 PM

Deleted: account for 69% of MSA production and 38% of MSA removal, respectively

Qianjie Chen 6/15/18 4:57 PM

Deleted: Observations of m

Qianjie Chen 6/15/18 4:57 PM

Deleted: from

winter. Between June and August, the modeled DMS mixing ratios calculated from R_{std} overestimate observations by a factor of 6, 4 and 27 for AI, CG and DU, respectively. In comparison, during the same period, the modeled DMS mixing ratios calculated from R_{all} overestimate observations by a factor of 3 for AI, 50% for CG and a factor of 4 for DU, respectively. The smaller discrepancy between modeled and observed DMS mixing ratio in R_{all} is largely due to DMS+BrO, as indicated by comparing R_{all} with a model run that includes all reactions except DMS+BrO ($R_{\text{noDMS+BrO}}$). It should be noted that BrO is underestimated in our model compared to satellite observations (underestimated by 44% in terms of annual mean tropospheric BrO column between 30°S and 60°S) (Chen et al., 2017), which might partly explain the remaining overestimate of DMS mixing ratios from R_{all} compared to observations.

In addition to DMS chemistry shown above, surface seawater DMS concentrations also affect the modeled DMS mixing ratio. The surface seawater DMS concentration was obtained from Kettle et al. (1999) in R_{Kettle} , instead of from Lana et al. (2011) in R_{all} . The global DMS emission flux from R_{Kettle} is 15% lower than that from R_{all} . Overall, at CI, CG and DU, the modeled DMS mixing ratios from R_{Kettle} are similar to those from R_{all} during most of the year. Much lower DMS mixing ratios were calculated from R_{Kettle} at CI in June, at CG in January and at DU in December and January. At AI, however, the modeled DMS mixing ratios from R_{Kettle} are lower than those from R_{all} in general, which agree better with observations except in December and January. In this study, we focus on the chemistry aspects of the sulfur cycle and thus will not present further discussion on the impact of the DMS sea water climatology on atmospheric DMS abundance.

3.6.2 Surface MSA/nssSO₄²⁻ ratio

Figure 10 shows the comparison between modeled and observed annual-mean MSA/nssSO₄²⁻ ratio at 23 stations around the globe (Table 5). Data for all stations was obtained from Gondwe et al. (2004), except for CI from Kouvarakis and Mihalopoulos (2002) and AI, PA, KO and DC from Casterbrunet et al. (2009). The global distribution of annual-mean MSA/nssSO₄²⁻ obtained from R_{all} , overplotted with observations for these 23 stations are shown in Fig. 11. In addition to the 4 model runs described in Sect. 3.6.1 (R_{all} , R_{std} , R_{Kettle} and $R_{\text{noDMS+BrO}}$), 5 additional model runs were performed by removing ($R_{\text{noMSA+OH(aq)}}$) or increasing ($R_{\text{moreMSA+OH(aq)}}$) aqueous-phase oxidation of MSA by OH, removing all multiphase chemistry involving DMS, DMSO, MSIA and MSA oxidation (R_{noMUL}), decreasing OH_(aq) concentrations in cloud droplets and aerosols by two orders of magnitude ($R_{\text{lowOH(aq)}}$), and using a unity yield of DMSO for the addition channel of DMS oxidation by OH (R_{add}) (see Table 3).

Figures 10 and 11 show that modeled MSA/nssSO₄²⁻ ratios calculated from R_{all} can generally reproduce the spatial variability of MSA/nssSO₄²⁻ observations, especially the latitudinal trend of increasing ratios towards the south where anthropogenic sources of nssSO₄²⁻ are less important. However, modeled MSA/nssSO₄²⁻ ratios overestimate observations by a factor of 2 on average. The normalized mean bias $N_{\text{MB}} (= \frac{\sum_{i=1}^{23} (M_i - O_i)}{\sum_{i=1}^{23} O_i} \times 100\%)$, where M_i and O_i are modeled value and observed value, are in good agreement with observations, with a

Qianjie Chen 6/15/18 4:59 PM

Deleted: at least

Qianjie Chen 6/15/18 4:59 PM

Deleted: s

Qianjie Chen 7/21/18 2:44 PM

Deleted: : Dye (DY; 66°N, 53°E), Heimaey (HE; 63°N, 20°W), United Kingdom (UK; 58°N, 6°W), Mace Head (MH; 53°N, 10°W), Crete Island (CI; 35°N, 25°E), Bermuda (BE; 32°N, 65°W), Tenerife (TE; 28°N, 17°W), Midway Island (MI; 28°N, 177°W), Miami (MI; 26°N, 80°W), Barbados (BA; 13°N, 60°W), Fanning Island (FI; 4°N, 159°W), American Samoa (AS; 14°S, 170°W), New Caledonia (NC; 21°S, 166°E), Norfolk Island (NI; 29°S, 168°E), Amsterdam Island (AI; 38°S, 77°E), Cape Grim (CG; 40°S, 144°E), Palmer (PA; 65°S, 64°W), Dumont D'Urville (DU; 66°S, 140°E), Mawson (MA; 67°S, 63°E), Neumayer (NE; 70°S, 8°W), Halley Bay (HB; 75°S, 26°W), Kohnen (KO; 75°S, 0°E) and Dome C (DC; 75°S, 123°E)

Qianjie Chen 7/22/18 12:08 AM

Deleted: 4

Qianjie Chen 7/22/18 12:08 AM

Deleted: decreasing

Qianjie Chen 7/22/18 12:08 AM

Deleted: less

Qianjie Chen 7/22/18 12:09 AM

Deleted: and

Qianjie Chen 7/16/18 10:46 PM

Deleted: are in good agreement with observations, with a

respectively) for the comparison between modeled and observed MSA/nssSO₄²⁻ ratios in R_{all} is 128%. The large modeled MSA/nssSO₄²⁻ over low-latitude oceans (13°N-37°S) is due to lower anthropogenic sources of nssSO₄²⁻ and to large multiphase MSA production as a result of high cloud liquid water content and oxidant abundance (OH and O₃). Over Antarctica (Stations PA, DU, MA, NE, HB, KO and DC) where aqueous-phase oxidation of MSA is small, modeled MSA/nssSO₄²⁻ ratios are about twice observations on average. In R_{noDMS+BrO}, the modeled MSA/nssSO₄²⁻ ratios decrease compared to R_{all}, which is most evident over stations where DMS+BrO is a large source of DMSO and MSA (e.g. Southern Hemisphere ocean and Antarctica) (Fig. 4). Compared to R_{all}, the modeled MSA/nssSO₄²⁻ ratios from R_{noDMS+BrO} match better with observations, with N_{MB}=40%. However, as shown in Sect. 3.6.1, DMS observations were largely overestimated in R_{noDMS+BrO} (Fig. 9). If multiphase chemistry is switched off (R_{noMUL}), modeled MSA/nssSO₄²⁻ ratios underestimate the observations by 49% on average for all 23 stations. Thus, multiphase sulfur chemistry is important for the model simulation of MSA/nssSO₄²⁻ observations. However, the OH_(aq) concentrations in cloud droplets and aerosols, which range from 10⁻¹⁴ M to 10⁻¹² M in modeling studies (Jacob, 1986; Matthijsen et al., 1995; Jacob et al., 1989; Herrmann et al., 2000) and 10⁻¹⁶ M to 10⁻¹⁴ M in observations (Arakaki et al., 2013; Kaur and Anastasio, 2017), is a large uncertainty in modeling multiphase sulfur chemistry. The model run reducing OH_(aq) concentrations by two orders of magnitude (R_{lowOH(aq)}) results in 25% decrease in MSA/nssSO₄²⁻, with N_{MB}=84%. Due to the small chemical loss of MSA in our model, MSA/nssSO₄²⁻ in model run without MSA + OH_(aq) (R_{noMSA+OH(aq)}) is similar to that in R_{all}. The model run with a larger reaction rate coefficient of MSA + OH_(aq) (R_{highMSA+OH(aq)}) results in a decrease in modeled MSA/nssSO₄²⁻ (24% on average) compared to R_{all}. This reveals the importance of MSA + OH_(aq) for MSA/nssSO₄²⁻ observations, as suggested by von Glasow and Crutzen (2004), Zhu et al. (2006) and Mungall et al. (2018). The model run with a unity yield of DMSO from the addition channel of DMS oxidation by OH (R_{add}) largely overestimates MSA/nssSO₄²⁻ observations, with N_{MB}=281%.

Modeled MSA/nssSO₄²⁻ from R_{std} without multiphase chemistry and DMS+BrO can generally reproduce the meridional trend of observations, with N_{MB}=51%. However, R_{std} overestimates DMS observations (Fig. 9), suggesting that R_{std} produces comparable MSA/nssSO₄²⁻ values for the wrong reasons.

25 4 Implications

Once emitted into the atmosphere through air-sea exchange, biogenic DMS undergoes complicated chemical processes to form SO₂ and MSA in the troposphere. SO₂ can then be oxidized to form sulfate aerosol. Sulfate and MSA produced in the gas phase can nucleate new particles under favorable conditions (Kulmala et al., 2000; Chen et al., 2015), while MSA and sulfate produced in the aqueous phase leads to the growth of existing particles (Kreidenweis and Seinfeld, 1988; Kaufman and Tanre, 1994). Global models such as General Circulation Models (GCMs) and Chemical Transport Models (CTMs) generally consider very simplified gas-phase DMS chemistry, which could result in large biases in SO₂ and MSA prediction. Quantifying the yields of SO₂ and MSA from DMS oxidation is necessary to evaluate the climate impacts of DMS from the

- Qianjie Chen 7/16/18 10:47 PM
Deleted: of
- Qianjie Chen 7/16/18 6:47 PM
Deleted: 9
- Qianjie Chen 7/16/18 11:26 PM
Deleted: The model reproduces the spatial variability of MSA/nss observations very well for Northern Hemisphere stations where anthropogenic sources of SO₂ dominate nss abundance. Over low-latitude oceans (13°N-37°S), modeled ratios overestimate observations, but still capture the latitudinal trend of increasing ratios towards the south where anthropogenic sources of nss are less important.
- Qianjie Chen 7/16/18 11:48 PM
Deleted: though R_{std} is not able to reproduce the spatial variability of observations, it shows good agreement with observations on average (MSA/nss is 0.24 for observations and 0.22 for R_{std}).
- Qianjie Chen 7/17/18 10:25 PM
Deleted: an increase
- Qianjie Chen 7/17/18 10:29 PM
Deleted: which overestimates MSA/nss observations by 92% on average
- Qianjie Chen 7/17/18 11:19 PM
Deleted: Model runs
- Qianjie Chen 7/17/18 11:22 PM
Deleted: or
- Qianjie Chen 7/17/18 11:22 PM
Deleted: smaller
- Qianjie Chen 7/22/18 12:30 AM
Deleted: less
- Qianjie Chen 7/17/18 11:23 PM
Deleted: an increase
- Qianjie Chen 7/22/18 12:33 AM
Deleted: , which largely overestimates MSA/nss observations at low- to mid-latitudes MBL between 28°N and 37°S
- beckya 7/30/18 1:59 PM
Deleted: the interpretation of

ocean ecosystem. Compared to the standard GEOS-Chem model run, the updated sulfur scheme in this study decreases the conversion yield of DMS to SO₂ ($Y_{\text{DMS} \rightarrow \text{SO}_2}$) from 91% to 75% and increases the conversion yield of DMS to MSA ($Y_{\text{DMS} \rightarrow \text{MSA}}$) from 9% to 15%. The remaining 10% of DMS is lost via wet and dry deposition of DMSO and MSIA. In order to gain insight into the impacts of our updated sulfur scheme on global SO₂, MSA and sulfate burden, we conducted two sensitivity studies by allowing DMS as the only sulfur source for both the standard model run R_{std} ($R_{\text{std_onlyDMS}}$) and full model run R_{all} ($R_{\text{all_onlyDMS}}$). Compared to $R_{\text{std_onlyDMS}}$, the global DMS, SO₂, MSA and sulfate burden in $R_{\text{all_onlyDMS}}$ decreases by 40%, 17%, 8% and 12%, respectively. The decrease in DMS is mainly due to DMS oxidation by BrO with the updated sulfur scheme. The decrease in SO₂ is due to a lower yield of SO₂ from DMS ($Y_{\text{DMS} \rightarrow \text{SO}_2}$), but is partly compensated by the increase in the DMS oxidation rate. MSA decreases despite an increase in the yield of MSA from DMS ($Y_{\text{DMS} \rightarrow \text{MSA}}$) due to a shorter lifetime in $R_{\text{all_onlyDMS}}$ (2.2 days in $R_{\text{all_onlyDMS}}$ versus 4.1 days in $R_{\text{std_onlyDMS}}$) that is caused by the aqueous-phase sink of MSA via $\text{MSA} + \text{OH}_{(\text{aq})}$ and faster deposition of MSA produced in the MBL. The decrease in sulfate is caused by the decrease in SO₂ but is partly compensated by the inclusion of $\text{MSA} + \text{OH}_{(\text{aq})}$ as a sulfate source, which accounts for 4% of global sulfate production. The decrease in sulfate will be smaller if more MSA is oxidized into sulfate instead of being lost via deposition. In sum, climate models with a simplified DMS oxidation scheme (gas-phase oxidation by OH and NO₃ only) may overestimate SO₂, MSA and sulfate abundances in the pre-industrial environment, potentially leading to underestimates in sulfur aerosol radiative forcing calculations in climate models. Quantifying the impacts of our updated sulfur oxidation scheme on new particle formation is out of the scope of this study and should be addressed in the future.

MSA in Antarctic ice cores has been related to spring sea ice extent (Curran et al., 2003; Abram et al., 2010) as DMS is emitted in regions of sea ice melt. Our results show that, in addition to DMS emission, tropospheric sulfur chemistry is critical for MSA abundance in the troposphere, as also suggested by observations in inland East Antarctica (Legrand et al., 2017). Compared to the full model run R_{all} , sensitivity studies without DMS+BrO reaction ($R_{\text{noDMS+BrO}}$) and without multiphase oxidation of DMS, DMSO, MSIA and MSA (R_{noMUL}) reduce the global MSA burden by 15% and 75%, respectively. This indicates that reactive halogen and multiphase chemistry are important for the MSA budget in the troposphere, which should be considered when interpreting MSA abundance in ice cores, especially over time periods where the abundance of atmospheric oxidants may have changed.

5 Conclusions

In this study, we investigate the impacts of reactive halogen and multiphase chemistry on tropospheric DMS chemistry by adding 2 new chemical tracers (DMSO and MSIA) and 12 new reactions for both the gas-phase and multiphase oxidation of DMS, DMSO, MSIA and MSA into a global chemical transport model, GEOS-Chem. With the updated DMS chemistry, the DMS burden decreases by 40% globally, mostly due to oxidation of DMS by BrO. BrO oxidation accounts for 12% of DMS oxidation globally, which could be underestimated due to underestimates in BrO abundance in the model, but is within the

Qianjie Chen 7/17/18 11:41 PM

Deleted: 78

Qianjie Chen 7/17/18 11:41 PM

Deleted: 3

Qianjie Chen 7/18/18 12:04 AM

Deleted: 39

Qianjie Chen 7/18/18 12:04 AM

Deleted: 5

Qianjie Chen 7/18/18 12:04 AM

Deleted: 55

Qianjie Chen 7/18/18 12:04 AM

Deleted: 2

Qianjie Chen 7/18/18 12:17 AM

Deleted: relatively small, mostly due to the

Qianjie Chen 7/18/18 12:17 AM

Deleted: 9

Qianjie Chen 7/18/18 12:36 AM

Deleted: 20

Qianjie Chen 7/18/18 12:37 AM

Deleted: 51

range of 8-16% reported in previous studies. Cl is not important for DMS oxidation due to small Cl abundance, but this reaction should be revisited if modeled Cl budgets are substantially revised in the future. Both gas-phase and multiphase oxidation of DMS by O₃ are not important for the global DMS budget and can be neglected in global models.

5 | Dry and wet deposition accounts for 28% of DMSO removal and 4% of MSIA removal globally. The significant role of deposition as a sink for DMSO suggests that DMSO should be included in sulfur chemistry mechanisms, as exclusion of DMSO as an intermediate may result in an overestimate of MSA production from the oxidation of DMS. MSIA is an important intermediate between DMSO and MSA. MSA is mostly (97% globally) produced through aqueous phase oxidation of MSIA by O_{3(aq)} and OH_(aq) in cloud droplets and aerosols. Dry and wet deposition accounts for 88% of MSA removal globally, multiphase oxidation by OH in cloud droplets and aerosols accounts for the rest. We note that the relative importance of deposition versus oxidation as a sink for MSA will depend on the OH_(aq) concentration in cloud droplets and aerosols, which is highly uncertain.

Qianjie Chen 7/22/18 12:45 AM

Deleted: 29

Qianjie Chen 7/22/18 12:45 AM

Deleted: 8

Qianjie Chen 7/22/18 12:46 AM

Deleted: 94

Qianjie Chen 7/22/18 12:47 AM

Deleted: 62

Qianjie Chen 7/22/18 12:50 AM

Deleted: is sensitive to

15 | Modeled DMS mixing ratios agree better (mean square error between model and observation is 44% smaller) with observations with the inclusion of DMS+BrO. The overestimate of MSA/nssSO₄²⁻ observations using our updated sulfur oxidation scheme suggests MSA oxidation is underestimated in the model. The uncertainties of reactive halogen abundances such as BrO and Cl and the aqueous phase oxidant concentrations such as OH_(aq) have limited our ability to model DMS oxidation and MSA formation in the troposphere. Future studies should prioritize the measurements of reactive halogen abundances and OH_(aq) concentrations in cloud droplets, especially in the marine boundary layer.

Qianjie Chen 7/22/18 12:53 AM

Deleted: , and

Qianjie Chen 7/22/18 12:54 AM

Deleted: modeled

Qianjie Chen 7/22/18 12:55 AM

Deleted: ratios

Qianjie Chen 7/22/18 12:55 AM

Deleted: agree better (mean square error between model and observation is 21% smaller) with observations with the inclusion of DMS+BrO and multiphase chemistry associated with DMS, DMSO, MSIA and MSA oxidation

Qianjie Chen 7/30/18 11:47 PM

Deleted: , as also suggested by observations in inland East Antarctica [Legrand et al., 2017].

Qianjie Chen 7/30/18 11:47 PM

Deleted:

20

Acknowledgements

We acknowledge Dr. Johan A. Schmidt for the discussions on tropospheric sulfur and halogen cycles, and providing support for the GEOS-Chem halogen chemistry scheme. We acknowledge Dr. Tom Breider for offering help on DMSO simulation scheme. We acknowledge Dr. Paul Hezel for the help on searching for sulfur species observations, and Dr. Giorgos Kouvarakis for providing DMS data on Crete Island. We acknowledge NSF AGS award 1343077 to B.A. for support of this research.

25

References

Abram, N. J., Thomas, E. R., McConnell, J. R., Mulvaney, R., Bracegirdle, T. J., Sime, L. C., and Aristarain, A. J.: Ice core evidence for a 20th century decline of sea ice in the Bellingshausen Sea, Antarctica, *J. Geophys. Res.*, 115, D23101, doi:10.1029/2010JD014644, 2010.

30

- Alexander, B., Allman, D. J., Amos, H. M., Fairlie, T. D., Dachs, J., Hegg, D. A., and Sletten, R. S.: Isotopic constraints on the formation pathways of sulfate aerosol in the marine boundary layer of the subtropical northeast Atlantic Ocean, *J. Geophys. Res.*, 117, D06304, doi:10.1029/2011JD016773, 2012.
- Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.:
5 Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, *Atmos. Chem. Phys.*, 13, 8045-8228, doi:10.5194/acp-13-8045-2013, 2013.
- Amos, H. M., Jacob, D. J., Holmes, C. D., Fisher, J. A., Wang, Q., Yantosca, R. M., Corbitt, E. S., Galarneau, E., Rutter, A. P., Gustin, M. S., Steffen, A., Schauer, J. J., Graydon, J. A., Louis, V. L. St., Talbot, R. W., Edgerton, E. S., Zhang, Y., and Sunderland, E. M.: Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury
10 deposition, *Atmos. Chem. Phys.*, 12, 591–603, doi:10.5194/acp-12-591-2012, 2012.
- Andreae, M. O.: Ocean-atmosphere interactions in the global biogeochemical sulfur cycle, *Mar. Chem.*, 30, 1–29, doi: 10.1016/0304-4203(90)90059-L, 1990.
- Andreae, M. O., Elbert, W., Cai, Y., Andreae, T. W., and Gras, J.: Non-sea-salt sulfate, methanesulfonate, and nitrate
15 aerosol concentrations and size distributions at Cape Grim, Tasmania, *J. Geophys. Res.*, 104, 21 695–21 706, doi: 10.1029/1999JD900283, 1999.
- Arakaki, T., Anastasio, C., Kuroki, Y., Nakajima, H., Okada, K., Kotani, Y., Handa, D., Azechi, S., Kimura, T., Tshako, A., and Miyagi, Y.: A general scavenging rate constant for reaction of hydroxyl radical with organic carbon in atmospheric waters, *Environ. Sci. Technol.*, 47(15), 8196–8203, doi: 10.1021/es401927b, 2013.
- Arsene, C., Bougiatioti, A., Kanakidou, M., Bonsang, B., and Mihalopoulos, N.: Tropospheric OH and Cl levels deduced
20 from non-methane hydrocarbon measurements in a marine site, *Atmos. Chem. Phys.*, 7, 4661-4673, doi:10.5194/acp-7-4661-2007, 2007.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species, *Atmos. Chem. Phys.*, 4, 1461-1738, doi:10.5194/acp-4-1461-2004, 2004.
- 25 Ayers, G. P., Bartley, S. T., Ivey, J. P., and Forgan, B. W.: Dimethylsulfide in marine air at Cape Grim, 41°S, *J. Geophys. Res.*, 100, 21 013–21 021, doi:10.1029/95JD02144, 1995.
- Bardouki, H., Barcellos da Rosa, M., Mihalopoulos, N., Palm, W.-U., and Zetzsch, C.: Kinetics and mechanism of the oxidation of dimethylsulfoxide (DMSO) and methanesulfinate (MSI-) by OH radicals in aqueous medium, *Atmos. Environ.*, 36, 4627–4634, doi: 10.1016/S1352-2310(02)00460-0, 2002.
- 30 Barnes, I., Hjorth, J., and Mihalopoulos, N.: Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere, *Chem. Rev.*, 106 (3), 940-975, doi: 10.1021/cr020529+, 2006.
- Becagli, S., Castellano, E., Cerri, O., Curran, M., Frezzotti, M., Marino, F., Morganti, A., Proposito, M., Severi, M., and Traversi, R.: Methanesulphonic acid (MSA) stratigraphy from a Talos Dome ice core as a tool in depicting sea ice

Qianjie Chen 6/15/18 3:14 PM

Deleted: <https://doi.org/>

Qianjie Chen 6/15/18 3:15 PM

Deleted: <https://doi.org/>

Qianjie Chen 6/15/18 3:15 PM

Deleted: <https://doi.org/>

- changes and southern atmospheric circulation over the previous 140 years, *Atmos. Environ.*, 43, 1051–1058, doi:10.1016/j.atmosenv.2008.11.015, 2009.
- Berglen, T. F., Berntsen, T. K., Isaksen, I. S. A., and Sundet, J. K.: A global model of the coupled sulfur/oxidant chemistry in the troposphere: The sulfur cycle, *J. Geophys. Res.*, 109, D19310, doi:10.1029/2003JD003948, 2004.
- 5 Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., Li, Q., Liu, H. Y., Mickley, L. J., and Schultz, M. G.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, 106, 23 073–23 095, doi: 10.1029/2001JD000807, 2001.
- Boucher, O., Moulin, C., Belviso, S., Aumont, O., Bopp, L., Cosme, E., von Kuhlmann, R., Lawrence, M. G., Pham, M., Reddy, M. S., Sciare, J., and Venkataraman, C.: DMS atmospheric concentrations and sulphate aerosol indirect radiative forcing: a sensitivity study to the DMS source representation and oxidation, *Atmos. Chem. Phys.*, 3, 49–65, doi: 10.5194/acp-3-49-2003, 2003.
- 10 Boudries, H., and Bottenheim, J. W.: Cl and Br atom concentrations during a surface boundary layer ozone depletion event in the Canadian High Arctic, *Geophys. Res. Lett.*, 27, 517–520, doi: 10.1029/1999GL011025, 2000.
- Bräuer, P., Tilgner, A., Wolke, R., and Herrmann, H.: Mechanism development and modelling of tropospheric multiphase halogen chemistry: The CAPRAM Halogen Module 2.0 (HM2), *J. Atmos. Chem.*, 70, 19–52, doi: 10.1007/s10874-013-9249-6.
- 15 Breider, T. J., Chipperfield, M. P., Richards, N. A. D., Carslaw, K. S., Mann, G. W., and Spracklen, D. V.: Impact of BrO on dimethylsulfide in the remote marine boundary layer, *Geophys. Res. Lett.*, 37, L02807, doi:10.1029/2009GL040868, 2010.
- 20 Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18, JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, <http://jpldataeval.jpl.nasa.gov>, 2015.
- Butkovskaya, N. I., and Le Bras, G.: Mechanism of the NO₃+DMS reaction by discharge flow mass spectrometry, *J. Phys. Chem.*, 98(10), 2582–2591, doi: 10.1021/j100061a014, 1994.
- 25 Campolongo, F., Saltelli, A., Jensen, N. R., Wilson, J., and Hjorth, J.: The role of multiphase chemistry in the oxidation of dimethylsulfide (DMS) - A latitude dependent analysis, *J. Atmos. Chem.*, 32(3), 327–356, doi: 10.1023/A:1006154618511, 1999.
- Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A., Forster, P. M., Mann, G. W., Spracklen, D. V., Woodhouse, M. T., Regayre, L. A., and Pierce, J. R.: Large contribution of natural aerosols to uncertainty in indirect forcing, *Nature*, 503, 67–71, doi:10.1038/nature12674, 2013.
- 30 Castebrunet, H., Martinerie, P., Genthon, C., and Cosme, E.: A three-dimensional model study of methanesulphonic acid to non sea salt sulphate ratio at mid and high-southern latitudes, *Atmos. Chem. Phys.*, 9, 9449–9469, doi:10.5194/acp-9-9449-2009, 2009.

Qianjie Chen 6/15/18 3:17 PM

Deleted: <https://doi.org/>

- Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, 326 (6114), 655-661, doi: 10.1038/326655a0, 1987.
- Chatfield, R. B. and Crutzen, P. J.: Are there interactions of iodine and sulfur species in marine air photochemistry?, *J. Geophys. Res.*, 95(D13), 22319–22341, doi:10.1029/JD095iD13p22319, 1990.
- 5 Chen, H., Ezell, M. J., Arquero, K. D., Varner, M. E., Dawson, M. L., Gerber, R. B., and Finlayson-Pitts, B. J.: New particle formation and growth from methanesulfonic acid, trimethylamine and water, *Phys. Chem. Chem. Phys.*, 17, 13699-13709, doi:10.1039/c5cp00838g, 2015.
- [Chen, Q., Geng, L., Schmidt, J. A., Xie, Z., Kang, H., Dachs, J., Cole-Dai, J., Schauer, A. J., Camp, M. G., and Alexander, B.: Isotopic constraints on the role of hypohalous acids in sulfate aerosol formation in the remote marine boundary layer, *Atmos. Chem. Phys.*, 16, 11433-11450, doi: 10.5194/acp-16-11433-2016, 2016.](#)
- 10 Chen, Q., Schmidt, J. A., Shah, V., Jaeglé, L., Sherwen, T., and Alexander, B.: Sulfate production by reactive bromine: Implications for the global sulfur and reactive bromine budgets, *Geophys. Res. Lett.*, 44, 7069–7078, doi:10.1002/2017GL073812, 2017.
- Chin, M., Jacob, D. J., Gardner, G. M., Foreman-Fowler, M. S., Spiro, P. A., and Savoie, D. L.: A global three-dimensional model of tropospheric sulfate, *J. Geophys. Res.*, 101(D13), 18667–18690, doi:10.1029/96JD01221, 1996.
- 15 Chin, M., Jacob, D. J., Gardner, G. M., Foreman-Fowler, M. S., Spiro, P. A., and Savoie, D. L.: A global three-dimensional model of tropospheric sulfate, *J. Geophys. Res.*, 101(D13), 18667–18690, doi:10.1029/96JD01221, 1996.
- 20 Cosme, E., Genthon, C., Martinerie, P., Boucher, O., and Pham, M.: The sulfur cycle at high-southern latitudes in the LMDZT General Circulation Model, *J. Geophys. Res.*, 107(D23), 4690, doi:10.1029/2002JD002149, 2002.
- Curran, M. A. J., van Ommen, T. D., Morgan, V. I., Phillips, K. L., and Palmer, A. S.: Ice core evidence for Antarctic sea ice decline since the 1950s, *Science*, 302(5648), 1203–1206, doi:10.1126/science.1087888, 2003.
- 25 Du, L., Xu, Y., Ge, M., Jia, L., Yao, L. and Wang, W.: Rate constant of the gas phase reaction of dimethyl sulfide (CH₃SCH₃) with ozone, *Chem. Phys. Lett.*, 436(1), 36-40, doi:10.1016/j.cplett.2007.01.025, 2007.
- Faloona, I.: Sulfur processing in the marine atmospheric boundary layer: A review and critical assessment of modeling uncertainties, *Atmos. Environ.*, 43, 2841–2854, doi:10.1016/j.atmosenv.2009.02.043, 2009.
- Fisher, J. A., Murray, L. T., Jones, D. B. A., and Deutscher, N. M.: Improved method for linear carbon monoxide simulation and source attribution in atmospheric chemistry models illustrated using GEOS-Chem v9, *Geosci. Model Dev.*, 10, 4129-4144, doi:10.5194/gmd-10-4129-2017, 2017.
- 30 [Flyunt, R., Makogon, O., Schuchmann, M. N., Asmus, K. D., and von Sonntag, C.: OH-Radical-induced oxidation of methanesulfinic acid. The reactions of the methanesulfonyl radical in the absence and presence of dioxygen, *J. Chem. Soc. Perkin Trans. 2*, 5, 787-792, doi: 10.1039/B009631H, 2001.](#)

Qianjie Chen 6/15/18 3:18 PM

Deleted: Castebrunet, H., Martinerie, P., Genthon, C., and Cosme, E.: A three-dimensional model study of methanesulphonic acid to non sea salt sulphate ratio at mid and high-southern latitudes, *Atmos. Chem. Phys.*, 9, 9449-9469, <https://doi.org/10.5194/acp-9-9449-2009>.

Qianjie Chen 6/15/18 3:19 PM

Deleted: <https://doi.org/>

- Gershenson, M., Davidovits, P., Jayne, J. T., Kolb, C. E., and Worsnop, D. R.: Simultaneous uptake of DMS and ozone on water, *J. Phys. Chem. A*, 105, 7031–7036, [doi:10.1021/jp010696y](https://doi.org/10.1021/jp010696y), 2001.
- Gondwe, M., Krol, M., Gieskes, W., Klaassen, W., and de Baar, H.: The contribution of ocean-leaving DMS to the global atmospheric burdens of DMS, MSA, SO₂, and NSS SO₄⁼, *Global Biogeochem. Cycles*, 17, 1056, [doi:10.1029/2002GB001937](https://doi.org/10.1029/2002GB001937), 2003.
- Gondwe, M., Krol, M., Klassen, W., Gieskes, W., and De Baar, H.: Comparison of modeled versus measured MSA:nss SO₄²⁻ ratios: A global analysis, *Global Biogeochem. Cy.*, 18, GB2006, [doi:10.1029/2003GB002144](https://doi.org/10.1029/2003GB002144), 2004.
- Gromov, S., Brenninkmeijer, C. A. M., and Jöckel, P.: A very limited role of tropospheric chlorine as a sink of the greenhouse gas methane, *Atmos. Chem. Phys.*, 18, 9831–9843, [doi:10.5194/acp-18-9831-2018](https://doi.org/10.5194/acp-18-9831-2018), 2018.
- Herrmann, H. and Zellner, R.: Removal and interconversions of oxidants in the atmospheric aqueous phase, Part 2 (RINOXA 2), Universität Essen, 1997.
- Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P., and Zellner, R.: CAPRAM2.3: A Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry, *J. Atmos. Chem.*, 36, 231–284, [doi:10.1023/A:1006318622743](https://doi.org/10.1023/A:1006318622743), 2000.
- Hezel, P. J., Alexander, B., Bitz, C. M., Steig, E. J., Holmes, C. D., Yang, X., and Sciare, J.: Modeled methanesulfonic acid (MSA) deposition in Antarctica and its relationship to sea ice, *J. Geophys. Res.*, 116, D23214, [doi:10.1029/2011JD016383](https://doi.org/10.1029/2011JD016383), 2011.
- Hoffmann, E. H., Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., and Herrmann, H.: An advanced modeling study on the impacts and atmospheric implications of multiphase dimethyl sulfide chemistry, *P. Natl. Acad. Sci. USA*, 113, 11776–11781, [doi:10.1073/pnas.1606320113](https://doi.org/10.1073/pnas.1606320113), 2016.
- Hossaini, R., Chipperfield, M. P., Saiz-Lopez, A., Fernandez, R., Monks, S., Feng, W., Brauer, P., and von Glasow, R.: A global model of tropospheric chlorine chemistry: Organic versus inorganic sources and impact on methane oxidation, *J. Geophys. Res. Atmos.*, 121, 14,271–14,297, [doi:10.1002/2016JD025756](https://doi.org/10.1002/2016JD025756), 2016.
- Jacob, D. J.: Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, *J. Geophys. Res.*, 91(D9), 9807–9826, [doi:10.1029/JD091iD09p09807](https://doi.org/10.1029/JD091iD09p09807), 1986.
- Jacob, D. J., Gottlieb, E. W., and Prather, M. J.: Chemistry of a polluted cloudy boundary layer, *J. Geophys. Res. Atmos.*, 94(D10), 12975–13002, [doi:10.1029/JD094iD10p12975](https://doi.org/10.1029/JD094iD10p12975), 1989.
- Jacob, D. J., Field, B. D., Li, Q., Blake, D. R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H. B., and Guenther, A.: Global budget of methanol: Constraints from atmospheric observations, *J. Geophys. Res.*, 110, D08303, [doi:10.1029/2004JD005172](https://doi.org/10.1029/2004JD005172), 2005.
- Jaeglé, L., Quinn, P. K., Bates, T. S., Alexander, B., and Lin, J.-T.: Global distribution of sea salt aerosols: new constraints from in situ and remote sensing observations, *Atmos. Chem. Phys.*, 11, 3137–3157, [doi:10.5194/acp-11-3137-2011](https://doi.org/10.5194/acp-11-3137-2011), 2011.

Qianjie Chen 6/15/18 3:20 PM

Deleted: <https://doi.org/>

- Jobson, B. T., Niki, H., Yokouchi, Y., Bottenheim, J., Hopper, F., and Leaitch, R.: Measurements of C2-C6 hydrocarbons during the Polar Sunrise 1992 Experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res.*, 99, 25 355–25 368, doi: 10.1029/94JD01243, 1994.
- 5 Kaufman, Y. and Tanre, D.: Effect of variations in super-saturation on the formation of cloud condensation nuclei, *Nature*, 369, 45–48, doi:10.1038/369045a0, 1994.
- Kaur, R. and Anastasio, C.: Light absorption and the photoformation of hydroxyl radical and singlet oxygen in fog waters, *Atmos. Environ.*, 164, 387-397, doi: 10.1016/j.atmosenv.2017.06.006, 2017.
- Kettle, A., Andreae, M., Amouroux, D., Andreae, T., Bates, T., Berresheim, H., Bingemer, H., Boniforti, R., Curran, M., DiTullio, G., Helas, G., Jones, G., Keller, M., Kiene, R., Leck, C., Levasseur, M., Malin, G., Maspero, M., Matrai, P., 10 McTaggart, A., Mihalopoulos, N., Nguyen, B., Novo, A., Putaud, J., Rapsomanikis, S., Roberts, G., Schebeske, G., Sharma, S., Simo, R., Staubes, R., Turner, S., and Uher, G.: A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month, *Global Biogeochem. Cy.*, 13, 399–444, doi: 10.1029/1999GB900004, 1999.
- Khan, M. A. H., Gillespie, S. M. P., Razis, B., Xiao, P., DaviesColeman, M. T., Percival, C. J., Derwent, R. G., Dyke, J. 15 M., Ghosh, M. V., Lee, E. P. F., and Shallcross, D. E.: A modelling study of the atmospheric chemistry of DMS using the global model, STOCHEM-CRI, *Atmos. Environ.*, 127, 69–79, doi: 10.1016/j.atmosenv.2015.12.028, 2016.
- Kloster, S., Feichter, J., Maier-Reimer, E., Six, K. D., Stier, P., and Wetzell, P.: DMS cycle in the marine ocean-atmosphere system – a global model study, *Biogeosciences*, 3, 29–51, doi:10.5194/bg-3-29-2006, 2006.
- Kouvarakis, G. and Mihalopoulos, N.: Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate 20 and non-sea-salt sulfate in the aerosols phase in the eastern Mediterranean atmosphere, *Atmos. Environ.*, 36, 929–938, doi:10.1016/S1352-2310(01)00511-8, 2002.
- Kreidenweis, S. M. and Seinfeld, J. H.: Nucleation of sulfuric acid-water and methanesulfonic acid-water solution particles: implications for the atmospheric chemistry of organosulfur species, *Atmos. Environ.*, 22(2), 283-296, doi: 10.1016/0004-6981(88)90034-0, 1988.
- 25 Kukui, A., Borissenko, D., Laverdet, G., and Bras, G. L.: Gas phase reactions of OH radicals with dimethyl sulfoxide and methane sulfonic acid using turbulent flow reactor and chemical ionization mass spectrometry, *J. Phys. Chem. A*, 107, 5732–5742, doi:10.1021/jp0276911, 2003.
- Kulmala, M., Pirjola, L., and Mäkelä, J. M.: Stable sulphate clusters as a source of new atmospheric particles, *Nature*, 404, 66–69, doi:10.1038/35003550, 2000.
- 30 Lana, A., Bell, T. G., Simó, R., Vallina, S. M., Ballabrera-Poy, J., Kettle, A. J., Dachs, J., Bopp, L., Saltzman, E. S., Stefels, J., Johnson, J. E., and Liss, P. S.: An updated climatology of surface dimethylsulfide concentrations and emission fluxes in the global ocean, *Global Biogeochem. Cy.*, 25, GB1004, doi:10.1029/2010GB003850, 2011.
- Lee, Y.-N. and Zhou, X.: Aqueous reaction kinetics of ozone and dimethylsulfide and its atmospheric implications, *J. Geophys. Res.*, 99(D2), 3597–3605, doi:10.1029/93JD02919, 1994.

[Legrand, M., Preunkert, S., Weller, R., Zipf, L., Elsässer, C., Merchel, S., Rugel, G., and Wagenbach, D.: Year-round record of bulk and size-segregated aerosol composition in central Antarctica \(Concordia site\) – Part 2: Biogenic sulfur \(sulfate and methanesulfonate\) aerosol, *Atmos. Chem. Phys.*, 17, 14055-14073, doi:10.5194/acp-17-14055-2017, 2017.](#)

- 5 Liu, Q.: Kinetics of aqueous phase reactions related to ozone depletion in the arctic troposphere: bromine chloride hydrolysis, bromide ion with ozone, and sulfur(IV) with bromine and hypobromous acid, Ph.D. thesis, Department of Chemistry, Purdue University, USA, 253 pp., 2000.
- Liu, Q. and Margerum, D. W.: Equilibrium and kinetics of bromine chloride hydrolysis, *Environ. Sci. Tech.*, 35, 1127–1133, doi: 10.1021/es001380r, 2001.
- 10 Lucas, D. D. and Prinn, R. G.: Mechanistic studies of dimethylsulfide oxidation products using an observationally constrained model, *J. Geophys. Res.*, 107, doi: 10.1029/2001JD000 843, 2002.
- Martin, L. R. and Good, T. W.: Catalyzed oxidation of sulfur dioxide in solution: The iron-manganese synergism, *Atmos. Environ.*, 25A, 2395–2399, doi:10.1016/096016869190113L, 1991.
- Matthijsen, J., Bultjes, P. J. H., and Sedlak, D. L.: Cloud model experiments of the effect of iron and copper on tropospheric ozone under marine and continental conditions, *Met. Atmos. Phys.*, 57(1–4), 43–60, doi: 10.1007/BF01044153, 1995.
- 15 Milne, P. J., Zika, R. G., and Saltzman, E. S.: Rate of reaction of dimethyl sulfoxide, and dimethyl sulfone with hydroxyl radical in aqueous solution, American Chemical Society, ACS Symposium Series, American Chemical Society, Washington, DC, pp. 518–528 (Chapter 33), 1989.
- 20 Mungall, E., Wong, J. P. S., and Abbatt, J. P. D.: Heterogeneous oxidation of particulate methane sulfonic acid by the hydroxyl radical: kinetics and atmospheric implications, *ACS Earth Space Chem.*, 2(1), 48-55, doi: 10.1021/acsearthspacechem.7b00114, 2018.
- Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate- ammonium aerosols in the United States: Implications for policy, *J. Geophys. Res.*, 109, D15204, doi:10.1029/2003JD004473, 2004.
- 25 Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickley, L. J., Miller, B., Evans, M. J., Yang, X., Pyle, J. A., Theys, N., and Van Roozendael, M.: Tropospheric bromine chemistry: implications for present and pre-industrial ozone and mercury, *Atmos. Chem. Phys.*, 12, 6723-6740, doi:10.5194/acp-12-6723-2012, 2012.
- Pham, M., Müller, J., Brasseur, G. P., Granier, C., and Mégie, G.: A three-dimensional study of the tropospheric sulfur cycle, *J. Geophys. Res.*, 100, 26,061– 26,092, doi: 10.1029/95JD02095, 1995.
- 30 Pye, H. O. T., Liao, H., Wu, S., Mickley, L. J., Jacob, D. J., Henze, D. K., and Seinfeld, J. H.: Effect of changes in climate and emissions on future sulfate-nitrate-ammonium aerosol levels in the United States, *J. Geophys. Res.*, 114, D01205, doi:10.1029/2008JD010701, 2009.

- Ravishankara, A. R., Rudich, Y., Talukdar, R., and Barone, S. B.: Oxidation of atmospheric reduced sulphur compounds: perspective from laboratory studies, *Phil. Trans. R. Soc. Lond. B.*, 352, 171–182, doi:10.1098/rstb.1997.0012, 1997.
- Read, K. A., Lewis, A. C., Salmon, R. A., Jones, A. E., and Bauguutte, S.: OH and halogen influence on the variability of nonmethane hydrocarbons in the Antarctic Boundary Layer, *Tellus B.*, 59, 22–38, doi:10.1111/j.1600-0889.2006.00227.x, 2007.
- Read, K. A., Lewis, A. C., Bauguutte, S., Rankin, A. M., Salmon, R. A., Wolff, E. W., Saiz-Lopez, A., Bloss, W. J., Heard, D. E., Lee, J. D., and Plane, J. M. C.: DMS and MSA measurements in the Antarctic Boundary Layer: impact of BrO on MSA production, *Atmos. Chem. Phys.*, 8, 2985–2997, doi:10.5194/acp-8-2985-2008, 2008.
- Saltzman, E. S., King, D. B., Holmen, K., and Leck, C.: Experimental determination of the diffusion coefficient of dimethylsulfide in water, *J. Geophys. Res.-Oceans*, 98, 16481–16486, doi:10.1029/93JC01858, 1993.
- Savoie, D. L., Arimoto, R., Keene, W. C., Prospero, J. M., Duce, R. A., and Galloway, J. N.: Marine biogenic and anthropogenic contributions to non-sea-salt sulfate in the marine boundary layer over the North Atlantic Ocean, *J. Geophys. Res.*, 107, AAC3-1-AAC3-21, doi:10.1029/2001JD000970, 2002.
- Schmidt, J. A., Jacob, D. J., Horowitz, H. M., Hu, L., Sherwen, T., Evans, M. J., Liang, Q., Suleiman, R. M., Oram, D. E., Le Breton, M., Percival, C. J., Wang, S., Dix, B., and Volkamer, R.: Modeling the observed tropospheric BrO background: Importance of multiphase chemistry and implications for ozone, OH, and mercury, *J. Geophys. Res.-Atmos.*, 121(11), 155–157, doi:10.1002/2015JD024229, 2016.
- Schweitzer, F., Magi, L., Mirabel, P., and George, C.: Uptake rate measurements of methanesulfonic acid and glyoxal by aqueous droplets, *J. Phys. Chem. A*, 102, 593–600, doi: 10.1021/jp972451k, 1998.
- Sehested, K. and Holeman, J.: A pulse radiolysis study of the OH radical induced autoxidation of methanesulfinic acid, *Radiat. Phys. Chem.*, 47(3), 357–360, doi:10.1016/0969-806X(95)00115-E, 1996.
- Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., Jacob, D. J., Dix, B., Koenig, T. K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A. S., and Ordóñez, C.: Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem, *Atmos. Chem. Phys.*, 16, 12239–12271, doi:10.5194/acp-16-12239-2016, 2016.
- Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, *Chem. Rev.*, 115, 4035–4062, doi:10.1021/cr5006638, 2015.
- Singh, H. B., Gregory, G. L., Anderson, B., Browell, E., Sachse, G. W., Davis, D. D., Crawford, J., Bradshaw, J. D., Talbot, R., Blake, D. R., Thornton, D., Newell, R., and Merrill, J.: Low ozone in the marine boundary layer of the tropical Pacific ocean: Photochemical loss, chlorine atoms, and entrainment, *J. Geophys. Res.*, 101, 1907–1917, doi: 10.1029/95JD01028, 1996.
- Spracklen, D. V., Pringle, K. J., Carslaw, K. S., Chipperfield, M. P., and Mann, G. W.: A global off-line model of size-resolved aerosol microphysics: I. Model development and prediction of aerosol properties, *Atmos. Chem. Phys.*, 5, 2227–2252, doi:10.5194/acp-5-2227-2005, 2005.

Qianjie Chen 6/15/18 3:22 PM

Deleted: <https://doi.org/>

Qianjie Chen 6/15/18 3:23 PM

Deleted: .

Qianjie Chen 6/15/18 3:23 PM

Deleted: <https://doi.org/>

Qianjie Chen 6/15/18 3:23 PM

Deleted: <https://doi.org/>

- Stefels, J., Steinke, M., Turner, S., [Mailin, G., and Belviso, S.](#): Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling, *Biogeochemistry*, 83, 245–275, [doi: 10.1007/s10533-007-9091-5](#), 2007.
- 5 Theys, N., Van Roozendaal, M., Hendrick, F., Yang, X., De Smedt, I., Richter, A., Begoin, M., Errera, Q., Johnston, P. V., Kreher, K., and De Mazière, M.: Global observations of tropospheric BrO columns using GOME-2 satellite data, *Atmos. Chem. Phys.*, 11, 1791-1811, [doi:10.5194/acp-11-1791-2011](#), 2011.
- Thomas, M. A., Suntharalingam, P., Pozzoli, L., Rast, S., Devasthale, A., Kloster, S., Feichter, J., and Lenton, T. M.: Quantification of DMS aerosol-cloud-climate interactions using the ECHAM5-HAMMOZ model in a current climate scenario, *Atmos. Chem. Phys.*, 10, 7425-7438, [doi:10.5194/acp-10-7425-2010](#), 2010.
- 10 Troy, R. C. and Margerum, D. W.: Non-metal redox kinetics: Hypobromite and hypobromous acid reactions with iodide and with sulfite and the hydrolysis of bromosulfate, *Inorg. Chem.*, 30, 3538–3543, [doi:10.1021/ic00018a028](#), 1991.
- von Glasow, R. and Crutzen, P. J.: Model study of multiphase DMS oxidation with a focus on halogens, *Atmos. Chem. Phys.*, 4, 589-608, [doi:10.5194/acp-4-589-2004](#), 2004.
- von Glasow, R., von Kuhlmann, R., Lawrence, M. G., Platt, U., and Crutzen, P. J.: Impact of reactive bromine chemistry in the troposphere, *Atmos. Chem. Phys.*, 4, 2481-2497, [doi:10.5194/acp-4-2481-2004](#), 2004.
- 15 Wang, Y., Jacob, D. J., and Logan, J. A.: Global simulation of tropospheric O₃-NO_x-hydrocarbon chemistry: 1. Model formulation, *J. Geophys. Res.*, 103(D9), 10713–10725, [doi:10.1029/98JD00158](#), 1998.
- Wingenter, O. W., Kubo, M. K., Blake, N. J., Smith, T. W., Blake, D. R., and Rowland, F. S.: Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights, *J. Geophys. Res.*, 101, 4331–4340, [doi:10.1029/95JD02457](#), 1996.
- 20 Wingenter, O. W., Sive, B. C., Blake, N. J., Blake, D. R., and Rowland, F. S.: Atomic chlorine concentrations derived from ethane and hydroxyl measurements over the equatorial Pacific Ocean: Implication for dimethyl sulphide and bromine monoxide, *J. Geophys. Res.*, 110, D20308, [doi:10.1029/2005JD005875](#), 2005.
- 25 Zhang, L., Gong, S.-L., Padro, J., and Barrie, L.: A Size-segregated Particle Dry Deposition Scheme for an Atmospheric Aerosol Module, *Atmos. Environ.*, 35(3), 549–560, [doi:10.1016/S1352-2310\(00\)00326-5](#), 2001.
- Zhu, L., Nicovich, J. M., and Wine, P. H.: Temperature-dependent kinetics studies of aqueous phase reactions of hydroxyl radicals with dimethylsulfoxide, dimethylsulfone, and methanesulfonate, *Aquat. Sci.*, 65, 425– 435, [doi:10.1007/s00027-003-0673-6](#), 2003.
- 30 Zhu, L., Nicovich, J. M., and Wine, P. H.: Kinetics studies of aqueous phase reactions of Cl atoms and Cl₂- radicals with organic sulfur compounds of atmospheric interest, *J. Phys. Chem. A*, 109, 3903– 3911, [doi: 10.1021/jp044306u](#), 2005.

Qianjie Chen 6/15/18 3:24 PM

Deleted: ,

Qianjie Chen 6/15/18 3:24 PM

Deleted: et al.

Qianjie Chen 6/15/18 3:26 PM

Deleted: <https://doi.org/>

Qianjie Chen 6/15/18 3:26 PM

Deleted: <https://doi.org/>

Qianjie Chen 6/15/18 3:28 PM

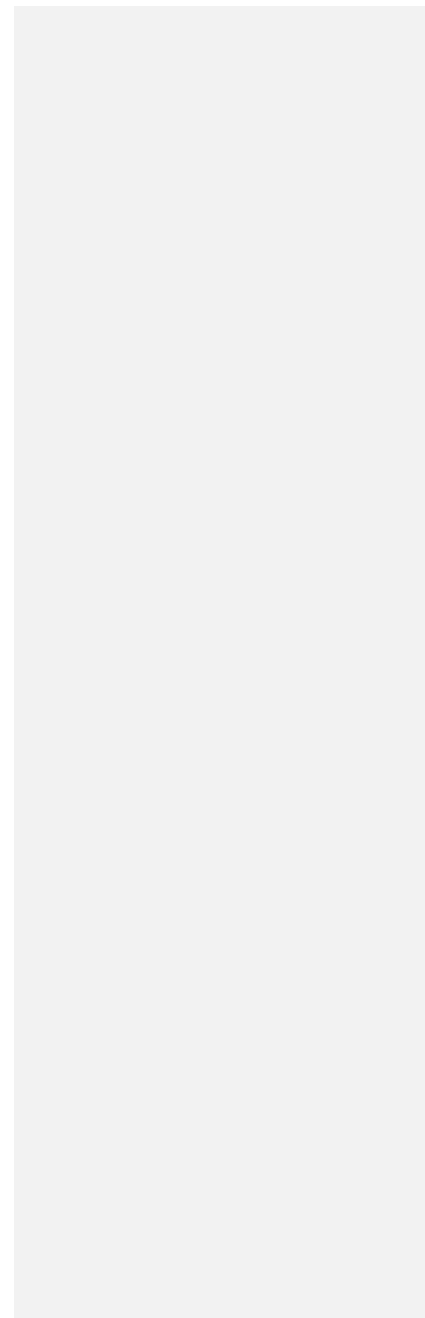
Deleted: <https://doi.org/>

Qianjie Chen 6/15/18 3:28 PM

Deleted: <https://doi.org/>

Zhu, L., Nenes, A., Wine, P. H., and Nicovich, J. M.: Effects of aqueous organosulfur chemistry on particulate methanesulfonate to non-sea salt sulfate ratios in the marine atmosphere, *J. Geophys. Res.*, 111, D05316, doi:10.1029/2005JD006326, 2006.

5
10
15
20
25
30



Figures

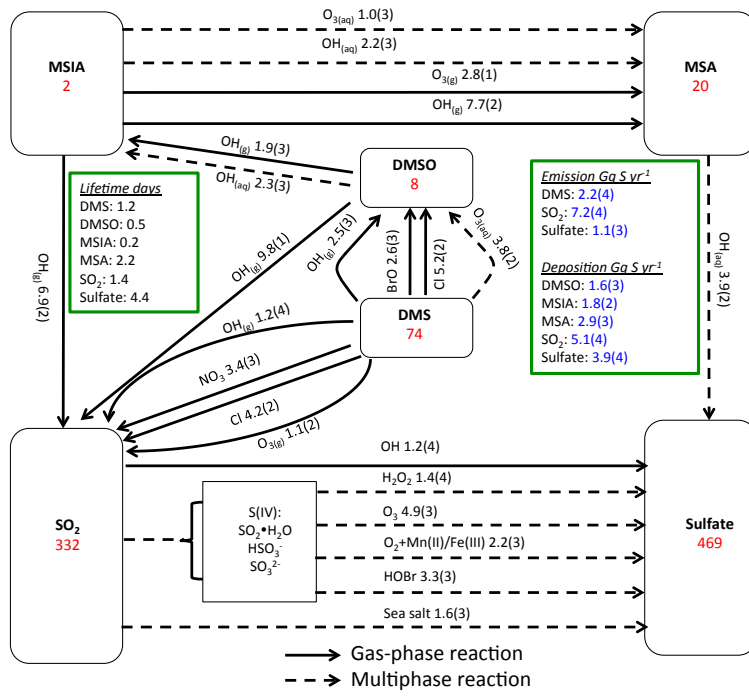
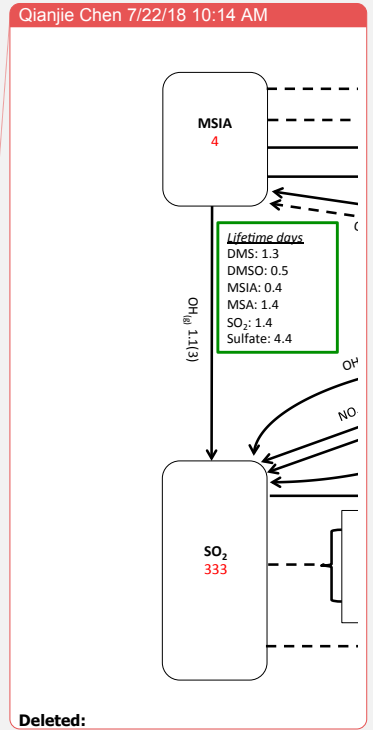


Figure 1: Global sulfur budgets for R_{all} . Inventories (inside the boxes) are in units of Gg S. Solid arrows represent gas-phase reactions while dashed arrows represent aqueous-phase reactions. Production and loss rates above arrows are in the unit Gg S yr⁻¹. Read 1.9(3) as 1.9×10^3 Gg S yr⁻¹.



Deleted: Deleted: of

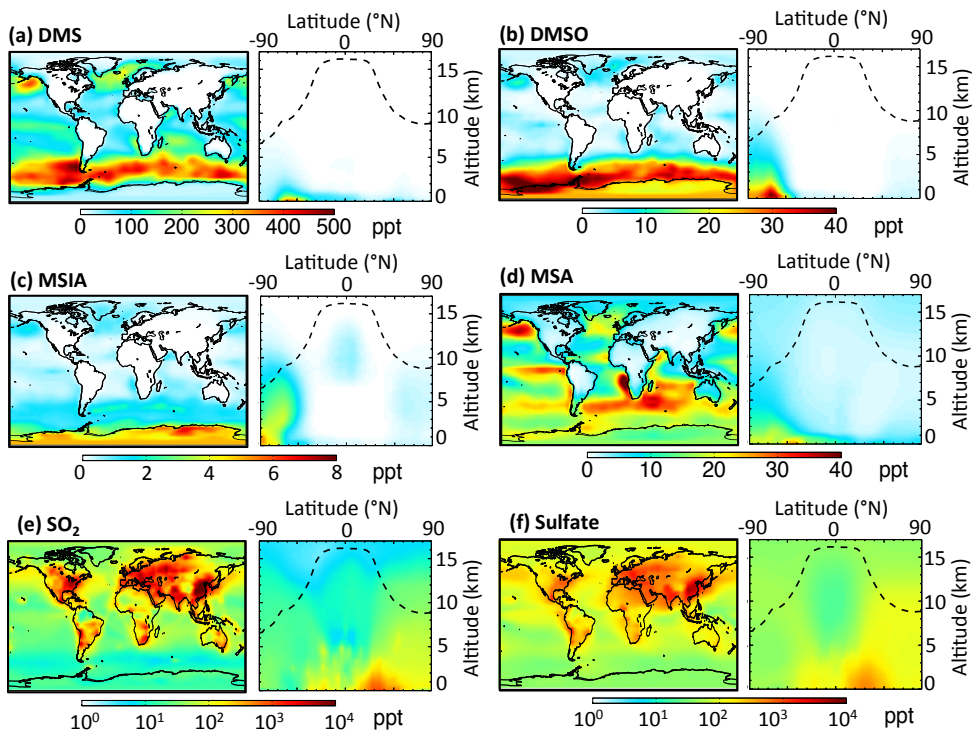
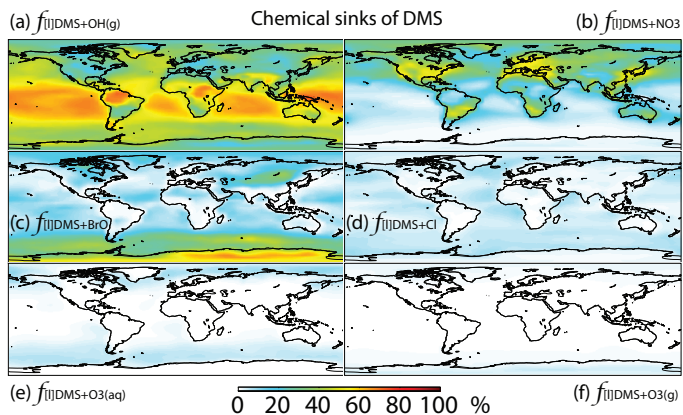


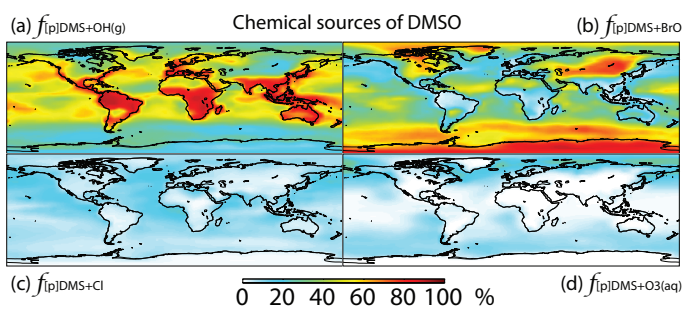
Figure 2: Horizontal distribution of annual-mean surface mixing ratios (ppt) and vertical distribution of mixing ratios for (a) DMS, (b) DMSO, (c) MSIA, (d) MSA, (e) SO₂ and (f) sulfate. The dashed line indicates the climatological tropopause height.

5

10



5 **Figure 3:** Global tropospheric distribution of annual-mean percentage of DMS oxidized in the troposphere via (a) $\text{DMS}+\text{OH}_{(g)}$ ($f_{[\text{I}]\text{DMS}+\text{OH}(g)}$), (b) $\text{DMS}+\text{NO}_3$ ($f_{[\text{I}]\text{DMS}+\text{NO}_3}$), (c) $\text{DMS}+\text{BrO}$ ($f_{[\text{I}]\text{DMS}+\text{BrO}}$), (d) $\text{DMS}+\text{Cl}$ ($f_{[\text{I}]\text{DMS}+\text{Cl}}$), (e) $\text{DMS}+\text{O}_3(\text{aq})$ ($f_{[\text{I}]\text{DMS}+\text{O}_3(\text{aq})}$) and (f) $\text{DMS}+\text{O}_3(g)$ ($f_{[\text{I}]\text{DMS}+\text{O}_3(g)}$).



10 **Figure 4:** Global tropospheric distribution of annual-mean percentage of DMSO produced via (a) $\text{DMS}+\text{OH}_{(g)}$ ($f_{[\text{P}]\text{DMS}+\text{OH}(g)}$), (b) $\text{DMS}+\text{BrO}$ ($f_{[\text{P}]\text{DMS}+\text{BrO}}$), (c) $\text{DMS}+\text{Cl}$ ($f_{[\text{P}]\text{DMS}+\text{Cl}}$) and (d) $\text{DMS}+\text{O}_3(\text{aq})$ ($f_{[\text{P}]\text{DMS}+\text{O}_3(\text{aq})}$).

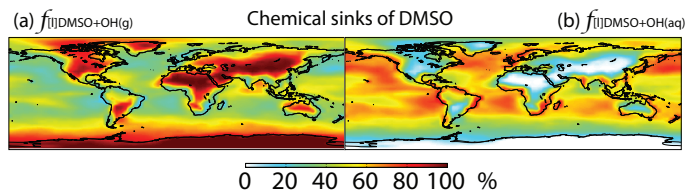
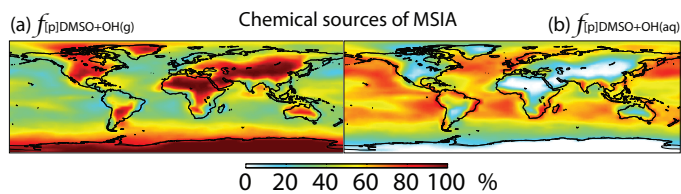
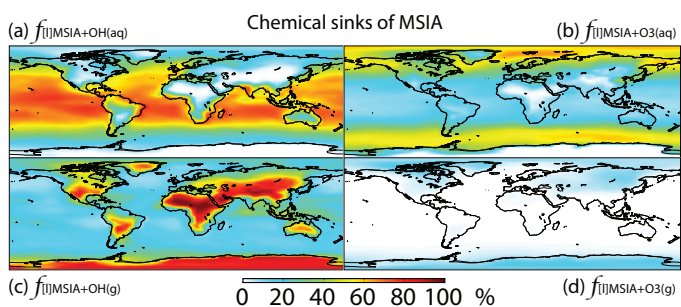


Figure 5: Global tropospheric distribution of annual-mean percentage of DMSO oxidized via (a) $DMSO+OH_{(g)}$ ($f_{[DMSO+OH(g)]}$) and (b) $DMSO+OH_{(aq)}$ ($f_{[DMSO+OH(aq)]}$).



5 Figure 6: Global tropospheric distribution of annual-mean percentage of MSIA produced in the troposphere via (a) $DMSO+OH_{(g)}$ ($f_{[p]DMSO+OH(g)}$) and (b) $DMSO+OH_{(aq)}$ ($f_{[p]DMSO+OH(aq)}$).



10 Figure 7: Global tropospheric distribution of annual-mean percentage of MSIA oxidized in the troposphere via (a) $MSIA+OH_{(aq)}$ ($f_{[MSIA+OH(aq)]}$), (b) $MSIA+O_{3(aq)}$ ($f_{[MSIA+O3(aq)]}$), (c) $MSIA+OH_{(g)}$ ($f_{[MSIA+OH(g)]}$) and (d) $MSIA+O_{3(g)}$ ($f_{[MSIA+O3(g)]}$).

Unknown
Formatted: Font:Times

Unknown
Formatted: Font:Times

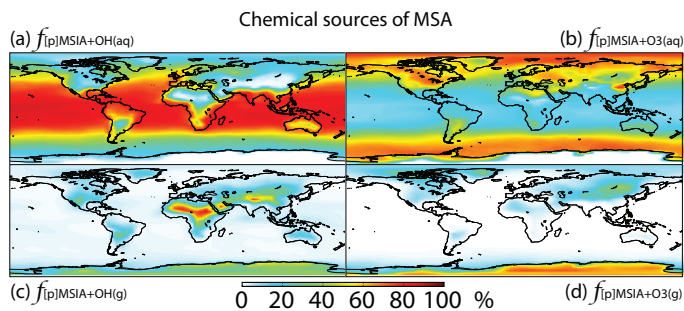


Figure 8: Global tropospheric distribution of annual-mean percentage of MSA produced in the troposphere (a) $f_{[p]MSIA+OH(aq)}$, (b) $f_{[p]MSIA+O_3(aq)}$, (c) $f_{[p]MSIA+OH(g)}$ and (d) $f_{[p]MSIA+O_3(g)}$.

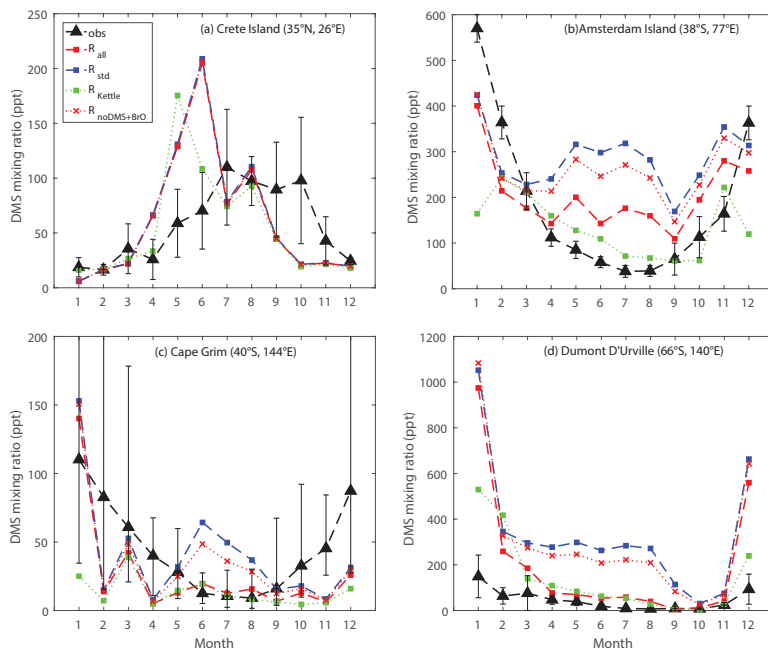


Figure 9: Comparison between modeled and observed monthly mean surface DMS mixing ratios at (a) Crete Island (CI), (b) Amsterdam Island (AI), (c) Cape Grim (CG), and (d) Dumont D'Urville (DU) stations.

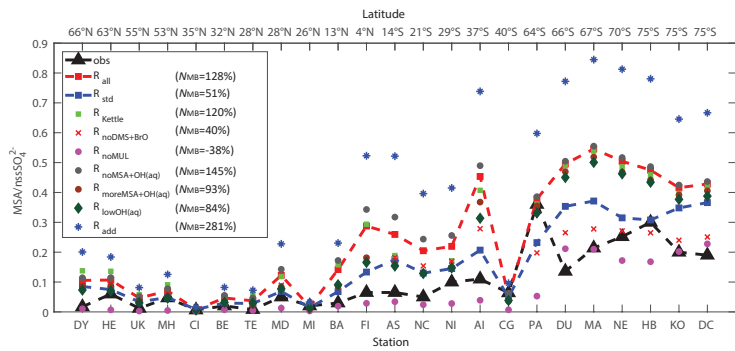


Figure 10: Comparison between modeled (nine model runs described in Table 3) and observed (obs, black triangle) annual mean surface $\text{MSA}/\text{nssSO}_4^{2-}$ ratios at 23 stations around the globe. The normalized mean bias $N_{\text{MB}} = \frac{\sum_{i=1}^{23} (M_i - O_i)}{\sum_{i=1}^{23} O_i} \times 100\%$, where M_i and O_i are modeled value and observed value, respectively, is shown in inset.

Qianjie Chen 7/22/18 1:48 PM
Deleted: eight

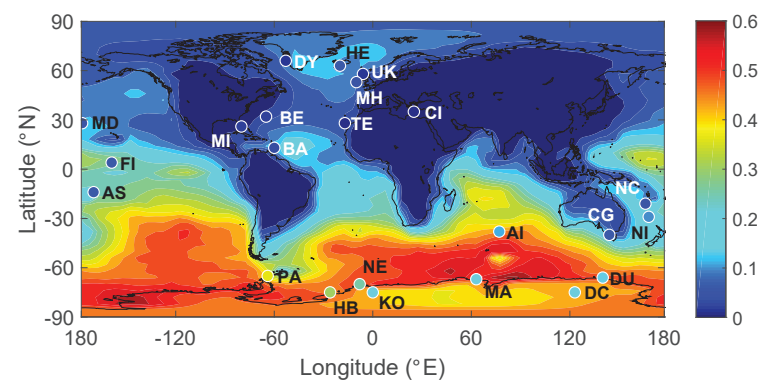


Figure 11: Global distribution of annual mean surface $\text{MSA}/\text{nssSO}_4^{2-}$ molar ratios from the full model run (R_{all}), overlotted with observed annual mean surface $\text{MSA}/\text{nssSO}_4^{2-}$ ratios from 23 stations around the globe.

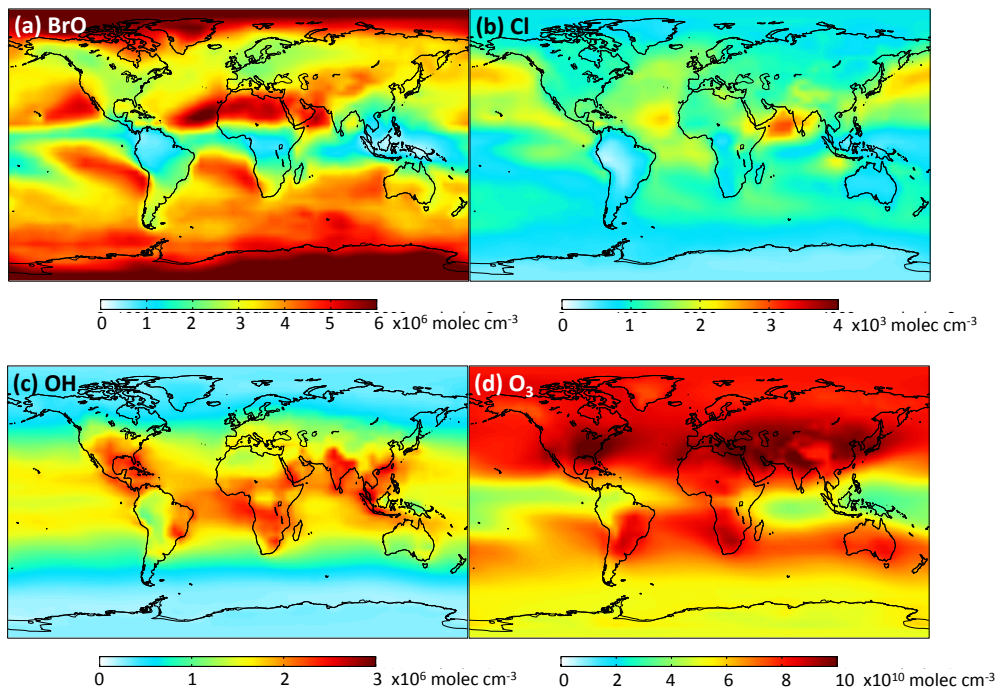


Figure 12: Global tropospheric distribution of annual-mean gas-phase (a) BrO, (b) Cl, (c) OH and (d) O₃ concentration.

5

10

Tables

Table 1. Overview of sulfur chemistry in the full model run (R_{all}) with DMSO and MSIA intermediates and all 12 new reactions.

Gas-phase reactions	k_{298} [$\text{cm}^3 \text{s}^{-1}$]	$-E_a/R$ [K]	Reference
$\text{DMS} + \text{OH} \xrightarrow{\text{abstraction}} \text{SO}_2 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$	4.69×10^{-12}	-280	Burkholder et al. (2015)
$\text{DMS} + \text{OH} \xrightarrow{\text{addition}} 0.6\text{SO}_2 + 0.4\text{DMSO} + \text{CH}_3\text{O}_2^{(\text{new})}$	see note ^(a)		Burkholder et al. (2015); Pham et al. (1995); Spracklen et al. (2005)
$\text{DMS} + \text{NO}_3 \rightarrow \text{SO}_2 + \text{HNO}_3 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$	1.13×10^{-12}	530	Burkholder et al. (2015)
$\text{DMS} + \text{BrO} \rightarrow \text{DMSO} + \text{Br}^{(\text{new})}$	3.39×10^{-13}	950	Burkholder et al. (2015)
$\text{DMS} + \text{O}_3 \rightarrow \text{SO}_2^{(\text{new})}$	1.00×10^{-19}	0	Burkholder et al. (2015); Du et al. (2007)
$\text{DMS} + \text{Cl} \rightarrow 0.5\text{SO}_2 + 0.5\text{DMSO} + 0.5\text{HCl} + 0.5\text{ClO}^{(\text{new})}$	3.40×10^{-10}	0	Burkholder et al. (2015); Barnes et al. (2006); IUPAC ^(e)
$\text{DMSO} + \text{OH} \rightarrow 0.95\text{MSIA} + 0.05\text{SO}_2^{(\text{new})}$	8.94×10^{-11}	800	Burkholder et al. (2015); von Glasow and Crutzen (2004)
$\text{MSIA} + \text{OH} \rightarrow 0.9\text{SO}_2 + 0.1\text{MSA}^{(\text{new})}$	9.0×10^{-11}	0	Burkholder et al. (2015); Kukui et al. (2003); Hoffmann et al. (2016); Zhu et al. (2006)
$\text{MSIA} + \text{O}_3 \rightarrow \text{MSA}^{(\text{new})}$	2.0×10^{-18}	0	Lucas and Prinn (2002); von Glasow and Crutzen (2004)
$\text{SO}_2 + \text{OH} \xrightarrow{\text{O}_2, \text{H}_2\text{O}} \text{H}_2\text{SO}_4 + \text{HO}_2$	see note ^(b)		Burkholder et al. (2015)
Aqueous-phase reactions	k_{298} [$\text{M}^{-1} \text{s}^{-1}$]	$-E_a/R$ [K]	Reference
$\text{DMS}_{(\text{aq})} + \text{O}_{3(\text{aq})} \rightarrow \text{DMSO}_{(\text{aq})} + \text{O}_{2(\text{aq})}^{(\text{new})}$	8.61×10^8	-2600	Gershenson et al. (2001)
$\text{DMSO}_{(\text{aq})} + \text{OH}_{(\text{aq})} \rightarrow \text{MSIA}_{(\text{aq})}^{(\text{new})}$	6.63×10^9	-1270	Zhu et al. (2003)
$\text{MSIA}_{(\text{aq})} + \text{OH}_{(\text{aq})} \rightarrow \text{MSA}_{(\text{aq})}^{(\text{new})}$	6.00×10^9	0	Sehested and Holcman (1996)
$\text{MSI}^- + \text{OH}_{(\text{aq})} \rightarrow \text{MSA}_{(\text{aq})}^{(\text{new})}$	1.20×10^{10}	0	Bardouki et al. (2002)
$\text{MSIA}_{(\text{aq})} + \text{O}_{3(\text{aq})} \rightarrow \text{MSA}_{(\text{aq})}^{(\text{new})}$	3.50×10^7	0	Hoffmann et al. (2016)
$\text{MSI}^- + \text{O}_{3(\text{aq})} \rightarrow \text{MS}^{-(\text{new})}$	2.00×10^6	0	Flyunt et al. (2001)
$\text{MSA}_{(\text{aq})} + \text{OH}_{(\text{aq})} \rightarrow \text{SO}_4^{2-}^{(\text{new})}$	1.50×10^7	0	Hoffmann et al. (2016)
$\text{MS}^- + \text{OH}_{(\text{aq})} \rightarrow \text{SO}_4^{2-}^{(\text{new})}$	1.29×10^7	-2630	Zhu et al. (2003)

Qianjie Chen 7/14/18 4:15 PM

Deleted: ^(new)

Qianjie Chen 7/14/18 10:41 AM

Deleted: multiphase

Qianjie Chen 7/14/18 10:41 AM

Deleted: _g

Qianjie Chen 7/14/18 10:41 AM

Deleted: _g

Qianjie Chen 7/14/18 10:41 AM

Deleted: _g

Qianjie Chen 7/14/18 10:02 AM

Deleted: 1.20

Qianjie Chen 7/14/18 10:02 AM

Deleted: ¹⁰

Qianjie Chen 7/14/18 10:02 AM

Deleted: Bardouki et al. (2002)

Qianjie Chen 7/14/18 10:41 AM

Deleted: _g

Qianjie Chen 7/14/18 10:41 AM

Deleted: _g

Qianjie Chen 7/14/18 10:15 AM

Deleted: 6.1

Qianjie Chen 7/14/18 10:21 AM

Deleted: -2630

Qianjie Chen 7/14/18 10:17 AM

Deleted: Milne et al. (1989); Zhu et al. (2003); Barnes et al. (2006)

$\text{HSO}_3^- + \text{H}_2\text{O}_{2(\text{aq})} + \text{H}^+ \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O}_{(\text{aq})}$	$2.36 \times 10^{3(\text{c})}$	-4760	Jacob (1986)
$\text{HSO}_3^- + \text{O}_{3(\text{aq})} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{O}_{2(\text{aq})}$	3.20×10^5	-4830	Jacob (1986)
$\text{SO}_3^{2-} + \text{O}_{3(\text{aq})} \rightarrow \text{SO}_4^{2-} + \text{O}_{2(\text{aq})}$	1.00×10^9	-4030	Jacob (1986)
$\text{S(IV)} + \text{O}_{2(\text{aq})} \xrightarrow{\text{Mn(II), Fe(III)}} \text{SO}_4^{2-}$	see note ^(d)		Martin and Good (1991)
$\text{HSO}_3^- + \text{HOBr}_{(\text{aq})} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{Br}^-$	3.20×10^9	0	Liu(2000);Chen et al.(2016; 2017)
$\text{SO}_3^{2-} + \text{HOBr}_{(\text{aq})} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{Br}^-$	5.00×10^9	0	Troy and Margerum (1991)

^(new) New reaction added in the model.

(a) $k(T, [\text{O}_2], [\text{M}]) = 8.2 \times 10^{-39} [\text{O}_2] e^{5376/T} / (1 + 1.05 \times 10^{-5} ([\text{O}_2]/[\text{M}]) e^{3644/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(b) low pressure limit: $3.3 \times 10^{-31} (300/T)^{4.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$; high pressure limit: $1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(c) Rate constant between $\text{HSO}_3^- + \text{H}_2\text{O}_{2(\text{aq})}$ at pH=4.5.

5 (d) The metal-catalyzed sulfate production rate is calculated from the following expression:

$$-\frac{d[\text{SO}_4^{2-}]}{dt} = 750[\text{Mn(II)}][\text{S(IV)}] + 2600[\text{Fe(III)}][\text{S(IV)}] + 1.0 \times 10^{10}[\text{Mn(II)}][\text{Fe(III)}][\text{S(IV)}]$$

Detailed description about [Mn(II)] and [Fe(III)] concentrations can be found in Alexander et al. (2009).

(e) IUPAC: http://iupac.pole-ether.fr/htdocs/datasheets/pdf/SOx13_Cl_CH3SCH3.pdf

10 **Table 2.** Henry's law constant at 298 K ($H_{X(298)}$), mass accommodation coefficient (α_b) and aqueous-phase diffusivity at 298

K ($D_{l(298K)}$) for DMS, DMSO, MSIA and MSA, and acid dissociation constant (pK_a) for MSIA and MSA at 298 K.

	$H_{X(298)}$ [M atm ⁻¹]	$-\Delta H/R$ [K]	Reference	pK_a	Reference	α_b	Reference	$D_{l(298K)}$ [m ² s ⁻¹]	Reference
DMS	0.56	-4480	Campolongo et al. (1999)	/	/	0.001	Zhu et al. (2006)	1.5×10^{-5}	Saltzman et al. (1993)
DMSO	1×10^7	-2580	Campolongo et al. (1999)	/	/	0.1	Zhu et al. (2006)	1.0×10^{-5}	Zhu et al. (2003)
MSIA	1×10^8	-1760	Campolongo et al. (1999)	2.28 ^(a)	Wudl et al. (1967)	0.1	Zhu et al. (2006)	1.2×10^{-5}	Same as MSA
MSA	1×10^9	-1760	Campolongo et al. (1999)	-1.86 ^(b)	Clarke and Woodward (1966)	0.1	Zhu et al. (2006)	1.2×10^{-5}	Schweitzer et al. (1998)

^(a) $\text{CH}_3\text{SO}_2\text{H} \leftrightarrow \text{CH}_3\text{SO}_2^- + \text{H}^+$

^(b) $\text{CH}_3\text{SO}_3\text{H} \leftrightarrow \text{CH}_3\text{SO}_3^- + \text{H}^+$

Table 3. Overview of model runs.

Model run	Specification
R_{all}	Full model run including all reactions described in Table 1, including the DMSO and MSIA intermediates; sea surface water DMS concentration obtained from Lana et al. (2011)
R_{std}	Standard run which includes gas-phase oxidation of DMS by OH and NO ₃ only, with no DMSO or MSIA intermediates
R_{Kettle}	R_{all} ; sea surface water DMS concentration obtained from Kettle et al. (1999)
$R_{noDMS+BrO}$	R_{all} ; without DMS+BrO reaction
R_{noMUL}	R_{all} ; without multiphase oxidation of DMS, DMSO, MSIA and MSA
$R_{noMSA+OH(aq)}$	R_{all} ; without MSA+OH _(aq) reaction
$R_{lessMSA+OH(aq)}$	R_{all} ; $k_{MSA+OH(aq)}/4.7$ (Zhu et al., 2003)
$R_{lowOH(aq)}$	R_{all} ; reduce OH _(aq) concentrations in cloud droplets and aerosols by a factor of 100
R_{add}	R_{all} ; a unity yield of DMSO for the addition channel of DMS+OH reaction ^a
R_{10Cl}	R_{10Cl} ; increase Cl mixing ratios by a factor of 10
$R_{all_onlyDMS}$	R_{all} ; DMS emission from the ocean is the only sulfur source
$R_{std_onlyDMS}$	R_{std} ; DMS emission from the ocean is the only sulfur source

^aThe product yield for the addition channel of the DMS+OH reaction is highly uncertain. Product yields of 0.6 for SO₂ and 0.4 for DMSO have been commonly used in global models (Pham et al., 1995; Cosme et al., 2002; Spracklen et al., 2005; Breider et al., 2010) based on experiments described in Turnipseed et al. (1996) and Hynes et al. (1993), and is used in this study (e.g., in R_{all}). Experiments under NO_x-free conditions suggest a DMSO yield near unity (Arsene et al., 1999; Barnes et al., 2006), as used in the sensitivity simulation R_{add} .

10

15

Table 4. The uncertainties of the rate constants for the 12 reactions added in the model. The uncertainty factor f_{298} means the reaction rate constant may be greater than or less than the recommended value by the factor f_{298} . Type “R”, “L” and “M” represents values obtained from “ literature reviews”, “laboratory measurements” and “modeling studies”, respectively.

Gas-phase reactions	f_{298}	Type	Reference
DMS+OH ^{addition} → ...	1.2	R	Burkholder et al. (2015)
DMS+BrO → ...	1.3	R	Burkholder et al. (2015)
DMS+O ₃ → ...	1.2	L	Du et al. (2007)
DMS+Cl → ...	1.2	R	Burkholder et al. (2015)
DMSO+OH → ...	1.2	R	Burkholder et al. (2015)
MSIA+OH → ...	1.4	R	Burkholder et al. (2015)
MSIA+O ₃ → ...	1.5	M	Lucas and Prinn (2002)
Aqueous-phase reactions	$k_{298} [M^{1-n} s^{-1}]$	Type	Reference
DMS _(aq) +O _{3(aq)} → ...	(8.6±8.1)×10 ⁸	L	Gershenson et al. (2001)
	(6.1±2.4)×10 ⁸	L	Lee and Zhou (1994)
DMSO _(g) +OH _(aq) → ...	(6.6±0.7)×10 ⁹	L	Zhu et al. (2003)
	7.5×10 ⁹	M	Hoffmann et al. (2016)
	(4.5±0.4)×10 ⁹	L	Bardouki et al. (2002)
	(5.4±0.3)×10 ⁹	L	Milne et al. (1989)
MSIA _(aq) +OH _(aq) → ...	(6.0±1.0)×10 ⁹	L	Sehested and Holcman (1996)
MSI ⁻ +OH _(aq) → ...	(1.2±0.2)×10 ¹⁰	L	Bardouki et al. (2002)
	7.7×10 ⁹	M	Zhu et al. (2006)
MSIA+O _{3(aq)} → ...	3.5×10 ⁷	M	Hoffmann et al. (2016)
MSI ⁻ +O _{3(aq)} → ...	2.0×10 ⁵	L	Flyunt et al. (2001)
MSA _(aq) +OH _(aq) → ...	1.5×10 ⁷	M	Hoffmann et al. (2016)
MS ⁻ +OH _(aq) → ...	(1.3±0.1)×10 ⁷	L	Zhu et al. (2003)
	(6.1±1.1)×10 ⁷	L	Milne et al. (1989)

- Qianjie Chen 7/15/18 3:36 PM
Deleted: multiphase
- Qianjie Chen 7/15/18 3:44 PM
Deleted: g
- Qianjie Chen 7/15/18 3:41 PM
Deleted: MSIA_(g)
- Qianjie Chen 7/15/18 3:36 PM
Formatted Table
- Qianjie Chen 7/15/18 3:44 PM
Deleted: (6.0±1.0)×10⁹
- Qianjie Chen 7/15/18 3:44 PM
Deleted: L
- Qianjie Chen 7/15/18 3:44 PM
Deleted: Sehested and Holcman (1996)
- Qianjie Chen 7/15/18 3:45 PM
Deleted: MSIA_(g)
- Qianjie Chen 7/15/18 3:47 PM
Deleted: 3.5
- Qianjie Chen 7/15/18 3:47 PM
Deleted: 7
- Qianjie Chen 7/15/18 3:50 PM
Deleted: M
- Qianjie Chen 7/15/18 3:50 PM
Deleted: Hoffmann ...lyunt et al. (200116 ... [2]
- Qianjie Chen 7/15/18 4:07 PM
Deleted: 6.1...0.11.1 ... [3]
- Qianjie Chen 7/15/18 4:04 PM
Deleted: MSA_(g)
- Qianjie Chen 7/15/18 4:07 PM
Deleted: Milne ...hu et al. (20031989...; Zhu... [4]
- Qianjie Chen 7/15/18 4:07 PM
Deleted: 1.3...1.10.1 ... [5]
- Qianjie Chen 7/15/18 4:07 PM
Deleted: Zhu...et al. (19892003 ... [6]

5

Table 5. The locations of the 23 stations that provide annual-mean MSA/nssSO₄²⁻ observations.

Station name	Location	Station name	Location
Dye (DI)	66°N, 53°E	American Samoa (AS)	14°S, 170°W
Heimaey (HE)	63°N, 20°W	New Caledonia (NC)	21°S, 166°E
United Kingdom (UK)	58°N, 6°W	Norfolk Island (NI)	29°S, 168°E
Mace Head (MH)	53°N, 10°W	Amsterdam Island (AI)	38°S, 77°E
Crete Island (CI)	35°N, 25°E	Cape Grim (CG)	40°S, 144°E
Bermuda (BE)	32°N, 65°W	Palmer (PA)	65°S, 64°W
Tenerife (TE)	28°N, 17°W	Dumont D'Urville (DU)	66°S, 140°E
Midway Island (MD)	28°N, 177°W	Mawson (MA)	67°S, 63°E
Miami (MI)	26°N, 80°W	Neumayer (NE)	70°S, 8°W
Barbados (BA)	13°N, 60°W	Halley Bay (HB)	75°S, 26°W
Fanning Island (FI)	4°N, 159°W	Kohnen (KO)	75°S, 0°E
		Dome C (DC)	75°S, 123°E