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Key Points:

- Dimethyl sulfide (DMS) chemistry in chemistry-climate simulations extended by multiphase methane sulfonic acid (MSA) formation provides more realistic MSA gas-phase concentrations
- Formation of MSA is very sensitive toward reactive uptake on deliquesced aerosol particles
- In the Arctic, the extended DMS chemistry leads to a significantly less negative effective radiative forcing of sulfate aerosol

Supporting Information:

Supporting Information may be found in the online version of this article.

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The Importance of the Representation of DMS Oxidation in Global Chemistry-Climate Simulations

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Abstract The oxidation of dimethyl sulfide (DMS) is key for the natural sulfate aerosol formation and its climate impact. Multiphase chemistry is an important oxidation pathway but neglected in current chemistry-climate models. Here, the DMS chemistry in the aerosol-chemistry-climate model ECHAM-HAMMOZ is extended to include multiphase methane sulfonic acid (MSA) formation in deliquesced aerosol particles, parameterized by reactive uptake. First simulations agree well with observed gas-phase MSA concentrations. The implemented formation pathways are quantified to contribute up to 60% to the sulfate aerosol burden over the Southern Ocean and Arctic/Antarctic regions. While globally the impact on the aerosol radiative forcing almost levels off, a significantly more positive solar radiative forcing of up to +0.1 W m^{-2} is computed in the Arctic (>60°N). The findings imply the need of both further laboratory and model studies on the atmospheric multiphase oxidation of DMS.

Plain Language Summary The emission of dimethyl sulfide (DMS) represents the largest natural reduced sulfur source into the atmosphere. There, DMS can be oxidized to sulfur dioxide, sulfuric acid, or methane sulfonic acid modifying the radiative properties of aerosol particles and clouds. DMS oxidation is represented in chemistry-climate models by a limited number of very simplified reactions. Small changes in the parameter settings can have large effects, that's why these should be as accurate as possible. In this study, the DMS chemistry in ECHAM-HAMMOZ was upgraded. Sensitivity simulations show variations in the natural aerosol radiative forcing due to the different schemes tested in this study. Further laboratory and process studies with models are therefore essential.

1. Introduction

Oceans cover 70% of Earth's surface and are the primary source of atmospheric water vapor and various marine aerosols. Therefore, mass fluxes from the ocean surface into the atmosphere have considerable impact on cloud formation and climate. While emissions of sea spray aerosol are the strongest source of primary marine aerosol, secondary marine aerosol is mainly formed by the oxidation of volatile organic compounds (VOCs), in particular of dimethyl sulfide (DMS) (Carslaw et al., 2010). DMS is a metabolite of marine microorganisms, predominantly emitted from the ocean surface (Carpenter et al., 2012) representing the largest natural atmospheric reduced sulfur source (Andreae, 1990). Main photochemical stable oxidation products of DMS are SO_2, H_2SO_4 and methane sulfonic acid (MSA). These products are known to contribute to new particle formation and growth of existing particles (e.g., Kerminen & Wexler, 1997; O'Dowd & de Leeuw, 2007; Zhang, Khalizov, et al., 2012). Accordingly, DMS oxidation heavily impacts natural aerosol population and thus abundance of cloud condensation nuclei (CCN). Recently, it was found that secondary aerosol formation is very important for CCN above the ocean (Mayer et al., 2020). The importance of DMS oxidation for climate led to the formulation of the highly debated CLAW hypothesis (Carslaw et al., 2010; Charlson et al., 1987; Quinn & Bates, 2011).

Understanding the effect of DMS on atmospheric aerosol and its climate requires the chemical oxidation pathways into SO_2 or H_2SO_4 or MSA to be represented as accurate as possible within chemistry-climate models (CCMs), however without massively expanding the computed reaction mechanism. In contrast to chemical-transport models (CTMs), in which chemical processes can be more explicitly considered, CCMs require a stronger balance between computational efforts and level of detail. Thus, only a small number of

precisely parameterized reactions can be included. DMS reacts via two pathways: (a) H-atom abstraction (Reaction R1) favored at higher temperatures and (b) addition of the oxidant on the sulfur atom (Reaction R2) favored at low temperatures (Atkinson et al., 2004; Barnes et al., 2006). In CCMs, these pathways are often represented following Chin et al. (1996):

$$DMS + OH\ /\ NO_3 \rightarrow SO_2 \quad \text{(R1)}$$

$$DMS + OH \rightarrow 0.75\,SO_2 + 0.25\,MSA \quad \text{(R2)}$$

Various model studies have explored the importance of the DMS oxidation for the global sulfate burden and its climate impact, mostly by applying the above-mentioned reactions (Bopp et al., 2004; Boucher et al., 2003; Gunson et al., 2006; Jones et al., 2001; Kloster et al., 2006; Thomas et al., 2010). These simulations suggest DMS oxidation as very important in the Southern Hemisphere, with a strong negative aerosol-cloud radiative forcing (RF), while in the northern hemisphere, anthropogenic SO_2 emissions are the predominant source of sulfate even above oceans (Gondwe et al., 2003). However, the prospective future phase-out of fossil fuel combustion will promote DMS oxidation to become one of the most important processes to aerosol formation in coastal areas (Perraud et al., 2015). Perraud et al. (2015) simulated that in urbanized coastal areas MSA-induced new particle formation (Bork et al., 2014; Chen et al., 2016; Dawson et al., 2012) will be as important as the one by H_2SO_4. Therefore, the influence of air pollution has to be considered and analyzed by CCM studies to determine the future impact of sulfate/MSA aerosols on Earth's climate, especially with regard to the increasing population in coastal regions.

Furthermore, the DMS parameterization from Chin et al. (1996) neglects contributions of other important oxidants, in particular BrO radicals (Barnes et al., 2006; Breider et al., 2010) and Cl atoms (Chen et al., 2018; Hoffmann et al., 2016). Additionally, formation of stable compounds such as dimethyl sulfoxide (DMSO) or dimethyl sulfone ($DMSO_2$) (Barnes et al., 2006), whose oxidation affects the predicted yields, is missing. Overall, the Chin et al. (1996) parameterization is not able to reproduce the complexity of DMS oxidation pathways well and potentially leads to biases in climate model predictions.

Recently, the chemistry mechanism MOZ1.0 of the CCM ECHAM-HAMMOZ was extended to treat DMS chemistry in more detail (Schultz et al., 2018). The updated scheme contains ten gas-phase reactions and five organic sulfur compounds:

$$DMS + OH\ /\ NO_3\ /\ Cl\ /\ Br \rightarrow CH_3SO_2 + HCHO + H_2O\ /\ HNO_3\ /\ HCl\ /\ HBr \quad \text{(R3)}$$

$$CH_3SO_2 \rightarrow CH_3O_2 + SO_2 \quad \text{(R4)}$$

$$CH_3SO_2 + O_3 \rightarrow CH_3SO_3 + O_2 \quad \text{(R5)}$$

$$CH_3SO_3 + HO_2 \rightarrow MSA + O_2 \quad \text{(R6)}$$

$$DMS + OH\ /\ BrO \rightarrow DMSO + HO_2\ /\ Br \quad \text{(R7)}$$

$$DMSO + OH \rightarrow 0.6\,SO_2 + HCHO + 0.6\,CH_3O_2 + 0.4\,MSA + 0.4\,HO_2 \quad \text{(R8)}$$

Because of the considered oxidation by the BrO radical and the higher MSA yield, higher gas-phase MSA and lower SO_2 yields can be expected as from Reaction R2. Still, the new scheme misses the new established important pathway of $CH_3SCH_2O_2$, the first radical from H-atom abstraction that undergoes a rapid internal H-atom shift yielding $HOOCH_2SCHO$ and OH recycling (Berndt et al., 2019; Wu et al., 2015). This pathway dominates the chemical fate of $CH_3SCH_2O_2$ and inhibits MSA formation by the H-atom abstraction pathway. Subsequent gas-phase oxidation of $HOOCH_2SCHO$ can finally yield SO_2 or H_2SO_4. Unfortunately, detailed laboratory investigations on the oxidation fate of $HOOCH_2SCHO$ are currently missing. Additionally, the oxidation of DMSO usually yields methanesulfinic acid (MSIA) and oxidation of MSIA yields SO_2 (Barnes et al., 2006). It is suggested that multiphase chemistry of MSIA dominates MSA formation (Barnes

et al., 2006; Hoffmann et al., 2016) and should be included in DMS chemistry schemes of CCMs (Revell et al., 2019).

Significant effects of DMS multiphase chemistry on aerosol particle, CCN concentrations, cloud albedo, and subsequently Earth's radiation budget were suggested by mechanistic model studies, but not proven, because of missing online radiation calculation. Overall, this demonstrates that the DMS chemistry, specifically MSA formation, within CCMs needs further improvements and the inclusion of multiphase chemistry processes. Recently, a condensed DMS multiphase chemistry mechanism was developed for CTMs (Hoffmann et al., 2020), from which a simplified scheme of MSA formation via in-particle chemistry can be derived helping to better describe MSA formation in the atmosphere.

To better represent the DMS multiphase chemistry, however, with respect to the limitations in CCMs, the current implementation in the global CCM ECHAM-HAMMOZ was updated within this study. The model now treats 13 gas-phase reactions (10 more than usually used in CCMs) and, for the first time, accounts for the effects of aerosol particle chemistry on gas-phase MSA formation by implementing a reactive uptake coefficient. Different sensitivity studies were carried out for the year 2017 and compared with measurements, to provide a more realistic DMS oxidation mechanism for use in CCMs.

2. Materials and Methods

2.1. Model Set-Up

The ECHAM-HAMMOZ model (version ECHAM6.3-HAM2.3-MOZ1.0) was run in a configuration similar to experiments by Schultz et al. (2018) with 1.875° × 1.875° horizontal resolution and 47 vertical layers up to 0.01 hPa height. Simulations were performed for year 2017 (plus a three-month spin-up), using prescribed sea surface temperatures and sea ice cover. The model is nudged to ERA-Interim reanalysis from the European Center for Medium-Range Weather Forecasts (ECMWF).

Tropospheric and stratospheric gas-phase chemistry is calculated with the chemistry model MOZ1.0 (Schultz et al., 2018). Aerosol particle formation and microphysical processes are simulated using the Hamburg Aerosol Model (HAM2.3) (Zhang, Donnell, et al., 2012) describing aerosol particles as an internal mixture of sulfate, black carbon, organic carbon, sea salt, and mineral dust. The aerosol population and microphysical interactions are simulated using seven log-normal size modes. Emission and deposition are treated consistently between particle and gas phase. Particle and trace-gas emissions from anthropogenic sources and biomass burning are taken from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP, Lamarque et al, 2010) inventory. Emissions from terrestrial vegetation are calculated with the Model of Emissions of Gases and Aerosols from Nature (MEGAN2.1, Guenther et al., 2012). The DMS emission is calculated online (Kloster et al., 2006; Lana et al., 2011).

All simulations include full interactions between aerosol particles, gas-phase chemistry, and the climate system. Wet deposition is considered for HNO_3, H_2SO_4, and stable DMS oxidation products.

2.2. DMS Chemistry Mechanisms

The MOZ1.0 DMS chemistry scheme was expanded to incorporate recent findings from mechanistic multiphase modeling studies (Berndt et al., 2019; Hoffmann et al., 2016, 2020). These findings were condensed to fit the computational limitations of ECHAM-HAMMOZ to deal the huge complexity of DMS multiphase chemistry.

First, the H-atom abstraction pathway was updated. The Br-atom oxidation was omitted, whereas Cl-atom oxidation also yields DMSO (Hoffmann et al., 2020). The H-atom abstraction pathway dominantly yields $HOOCH_2SCHO$ (Berndt et al., 2019), whose further chemical fate is not determined, yet. Theoretical investigations of Wu et al. (2015) indicated SO_2 as the main gas-phase product. Furthermore, measurements indicated that $HOOCH_2SCHO$ is rapidly lost during cloud occurrence (Veres et al., 2020; Vermeuel et al., 2020) that is also known for SO_2. It seems likely that in the aqueous phase, $HOOCH_2SCHO$ is oxidized to sulfate. Based on these assumptions and the missing knowledge, the H-atom abstraction pathway was parameterized yielding SO_2, exclusively.

Table 1
List of Model Experiments

Run identifier	Specification
MOZART	Original MOZART mechanism (Schultz et al., 2018)
GAMMA001	Revised abstraction and addition pathway, $\gamma = 0.01$
GAMMA01	Revised abstraction and addition pathway, $\gamma = 0.1$
GAMMA1	Revised abstraction and addition pathway, $\gamma = 1$
HAM	DMS oxidation as in aerosol module HAM (Chin et al., 1996; Feichter et al., 1996)
VARIED	Revised abstraction and addition pathway, $\gamma = 0.1$ for sea salt and $\gamma = 0.01$ for other particles

$$DMS + OH\ /\ NO_3 \rightarrow SO_2 + CH_3O_2 + HCHO + H_2O\ /\ HNO_3 \quad \text{(R9)}$$

$$DMS + Cl \rightarrow 0.82\,SO_2 + 0.82\,HCHO + 0.82\,HCl + 0.82\,CH_3O_2 + 0.18\,ClO + 0.18\,DMSO \quad \text{(R10)}$$

$$CH_3SO_3 \rightarrow CH_3O_2 + SO_3 \quad \text{(R11)}$$

Second, the addition pathway was updated to consider the important multiphase MSIA oxidation.

$$DMSO + OH \rightarrow MSIA + H_2O \quad \text{(R12)}$$

$$DMSO + NO_3 \rightarrow DMSO_2 + NO_2 \quad \text{(R13)}$$

$$DMSO + Cl \rightarrow 0.43\,DMSO_2 + 0.43\,ClO + 0.57\,CH_3SO_2 + 0.57\,HCHO + 0.57\,HCl \quad \text{(R14)}$$

$$MSIA + OH \rightarrow SO_2 + CH_3O_2 + H_2O \quad \text{(R15)}$$

DMSO oxidation by the OH radical produces MSIA, and MSIA gas-phase oxidation yields SO_2. The oxidation of DMSO by the NO_3 radical, leading to dimethyl sulfoxide ($DMSO_2$), is implemented to improve predictions for polluted coastal areas. $DMSO_2$ is very stable against further oxidation (Falbe-Hansen et al., 2000) and removed mainly by deposition.

The formation of MSA is considered by including a reactive uptake for MSIA (Reaction R16) representing a pseudo aqueous-phase formation of MSA.

$$MSIA \xrightarrow{reactive\ uptake} MSA \quad \text{(R16)}$$

As no laboratory data are available, the reactive uptake coefficient was calculated following Hanson et al. (1994). An explanation of the calculation of possible γ values is given in the supplement. The approach is new and able to represent the complexity of multiphase formation pathways of MSA in aerosol particles, see the results Section 3.1.

The reactive uptake was implemented for all soluble particles excluding dust. Thresholds for relative humidity of 50% and for temperature of 233 K was included except for sea salt, where only the temperature threshold applies. The new DMS oxidation mechanism is sketched in Figure S2.

In total, six simulations were performed as summarized in Table 1. The first simulation comprises the original DMS oxidation mechanism by Schultz et al. (2018) (designated as MOZART). For the other three simulations, the new DMS oxidation mechanism was used. They differ in the setting of the γ value: (a) $\gamma = 0.01$ as the lower limit representing acidic conditions (GAMMA001), (b) $\gamma = 0.1$ for ambient acidic conditions of pristine sea spray aerosol (GAMMA01) and (c) $\gamma = 1$ as the upper limit in accordance to MSA uptake on water-sulfuric acid solutions (Hanson, 2005) (GAMMA1). In the fifth simulation, the parameterization of Chin et al. (1996) is applied, which corresponds to the representation in the aerosol-climate model version

ECHAM-HAM (HAM). For the sixth simulation, the γ value was set to 0.1 for sea salt and 0.01 for the residual particle classes to account for different particle acidity (VARIED).

3. Results

3.1. Impact on MSA

The evaluation of the new mechanism for both hemispheres cannot be achieved by comparison with measured SO_2 or sulfate aerosol, because anthropogenic emissions dominate at the Northern Hemisphere. Therefore, MSA is used for an evaluation, for that no strong anthropogenic sources are known. However, note, the aerosol module HAM treats MSA as sulfate, because of similar physical properties, e.g., absorption (Myhre et al., 2004), and thus a comparison can only be done for gas-phase MSA.

Figure 1 shows the annual average column total of gas-phase MSA for all simulations (monthly averages are shown in Figures S3 to S8). The global annual average total column MSA concentration is highest for the simulation MOZART (0.74 μg m^{-3}) and lowest for the simulation GAMMA001 (0.082 μg m^{-3}). For the simulations GAMMA01, GAMMA1, HAM and VARIED, average concentrations of 0.26 μg m^{-3}, 0.46 μg m^{-3}, 0.27 μg m^{-3} and 0.19 μg m^{-3} are modeled, respectively. This shows that neglecting MSA formation by the H-atom abstraction leads to a strong reduction of modeled MSA over continents and in polluted marine areas of the Northern Hemisphere, where OH and NO_3-radical related oxidations are important. Expectedly, the MSA concentration increases with increasing γ values. For all simulations, highest MSA concentrations are modeled between 0° and 30°S, which is related to the interplay of high modeled DMS emissions (see Figure S9) together with strong photochemistry. High concentrations over continents for the simulations MOZART and HAM are related to the implemented simplistic gas-phase formation.

The capability of the updated ECHAM-HAMMOZ model to simulate gas-phase MSA formation is evaluated by comparisons with measurements from two field campaigns in 2017. One is a research ship cruise that took place between 40°S and 80°S from November 27 to December 4, 2017 (Yan et al., 2019). The second is a field campaign that took place between March and October 2017 (Stieger et al., 2021) at the Central European TROPOS (ACTRIS) research site Melpitz (51°32 N, 12°54 E). Thus, the evaluation provides accuracy of the applied mechanisms for both the conditions of the polluted Northern and more pristine Southern Hemisphere, respectively.

During the ship cruise, average gas-phase MSA concentrations of 5.9 pptv were observed, with a strong latitude-dependent variability. At southern mid-latitudes, an average of 19.5 pptv was measured, while in the southern polar regions (>60°S), the levels were of single pptv range. The comparison between measurements and model results for the period is provided in Figure 1g and Figure S10. The simulations GAMMA01 and HAM agree best with the measurements followed by the simulation VARIED. As expected, the simulations MOZART and GAMMA1 overpredict the observations, whereas the simulation GAMMA001 underperforms (Figure 1g and Figure S10).

During the Melpitz field campaign, monthly average gas-phase MSA concentrations between 1 and 4 ng m^{-3} were measured. The comparison between measurements and model results for all months is provided in Figure 1h. The comparison shows that the conditions in Melpitz were different to the Southern Hemisphere. For spring and fall, good agreements are found for the simulations GAMMA001, HAM, and VARIED. But for summer, only the simulation GAMMA001 performed well emphasizing the importance of aerosol acidity for MSA formation. The simulations MOZART and GAMMA1 overpredict the observations.

The comparisons show that the implemented reactive uptake of MSIA is key to represent gas-phase formation of MSA in CCMs. However, there is a substantial sensitivity regarding the applied γ values that strongly depends on the aerosol acidity. Nevertheless, the simulations in this study do not include cloud chemistry-related MSA formation that can account for approximately 35% of MSA formation (Hoffmann et al., 2016) nor does ECHAM-HAMMOZ treat particulate MSA. Therefore, further investigations on cloud chemistry have to be performed, but are beyond the scope of this study.

Generally, the comparison shows that the MSA formation induced by H-atom abstraction in the MOZART simulations overestimates MSA in the polluted Northern Hemisphere, where the NO_3-radical related oxidation dominates (Breider et al., 2010). Furthermore, the gas-phase yield of MSA in the Chin et al. (1996)

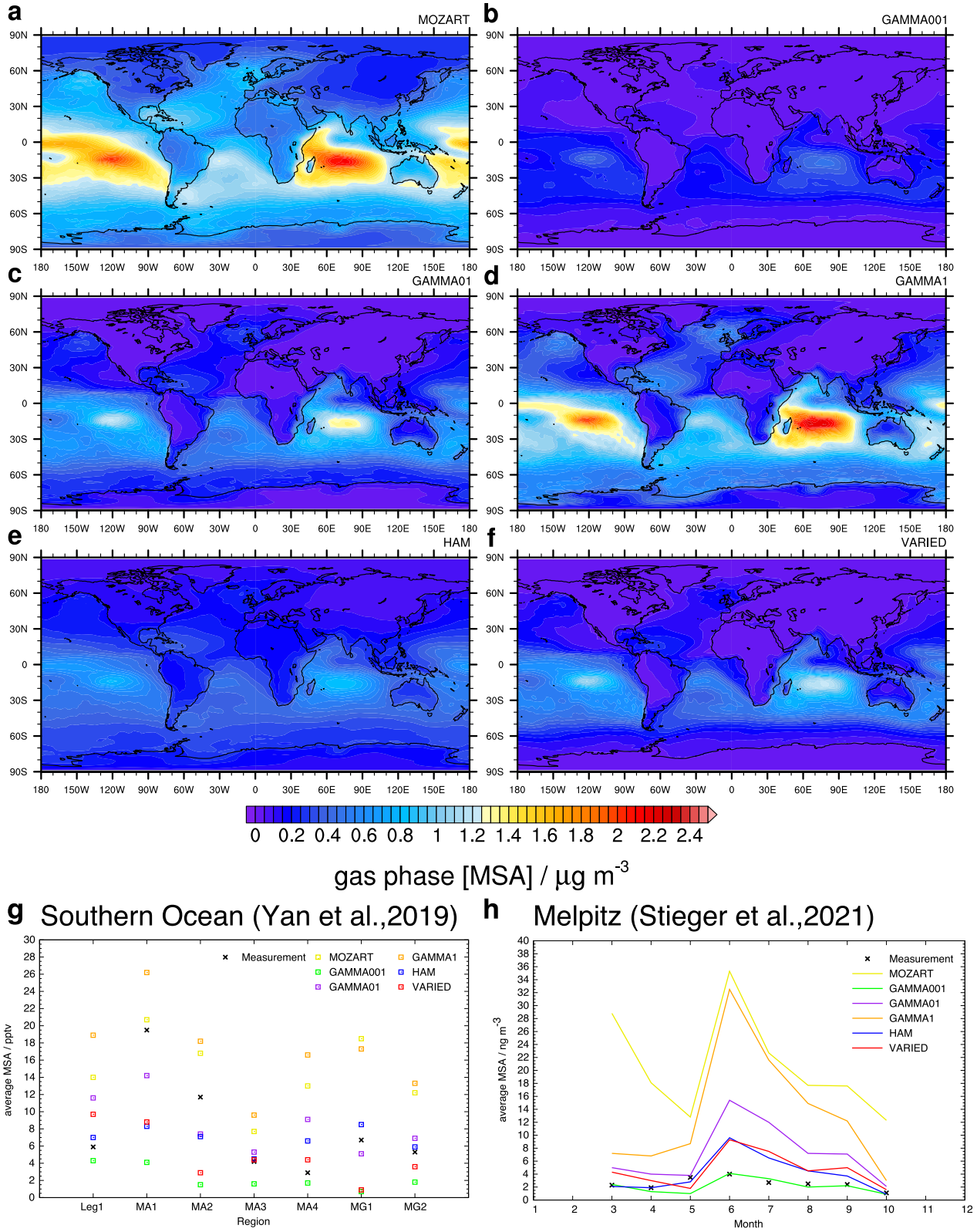

Figure 1. (a–f) Annual average of column total gas-phase MSA concentration in 2017 (g–h) Comparison of measured and modeled gas-phase MSA at ground level.

parameterization is not able to represent the impact of aerosol acidity. Additionally, it is found that decoupled MSA layers in the lower pptv range are modeled near the tropopause in the simulations MOZART and HAM (Figure S10). These result from convective updraft of DMS in the tropics, from where it is distributed poleward. Accordingly, enhanced gas-phase MSA formation occur there. Because of low temperatures (<−20°C) in higher altitudes, the addition pathway is favored there, but aqueous-phase chemistry is probably inhibited. Thus, the parameterization of DMS oxidation within the simulations MOZART and HAM are likely inadequate for representation of MSA formation at high altitudes.

The comparison with field measurements provides indication to recommend the mechanistic scheme of the simulation VARIED for global CCM studies on MSA, as gas-phase MSA is relatively well represented under marine and continental conditions by this setup. The simulations and theoretical considerations also pointed out the importance of aerosol particle acidity. However, this essentially requires further measurements of mass accommodation and reactive uptake coefficients of MSIA for different aerosol types for model input, which have not yet been sufficiently characterized.

3.2. Impact on Atmospheric Sulfate Aerosol

The different mechanistic schemes impact the sulfate aerosol concentration in pristine and polluted marine and continental environments. Figure 2a shows the annual average column total of sulfate aerosol (total over nucleation, Aitken, accumulation and coarse mode) for the simulation MOZART. Additionally, the quantitative differences between MOZART and the other five simulations are presented (Figures 2b–2f), which were calculated by subtracting the MOZART results from those of the other simulations. The relative alteration calculated by dividing the values in Figures 2b–2f by the results of the simulation MOZART is provided in Figure S11. Monthly values for all simulations are shown in Figures S12 to S17.

Anthropogenic emissions dominate the sulfate over the continents and subtropics. Over the Southern Ocean and in Arctic/Antarctic regions, up to 60% more sulfate are modeled (Figure S11). The annual averaged global vertical totals of sulfate differ between +154 ng m^{-3} and +281 ng m^{-3}, for the simulations GAMMA001, GAMMA01, HAM, and VARIED, respectively. For the simulation GAMMA1, the difference is lower. Generally, omitting the MSA formation by H-atom abstraction leads to a higher total sulfate loading in the simulations compared to MOZART. The sulfate offset is higher when the MSA formation potential due to the reactive uptake is lower, that is, higher DMS to SO_2 oxidation.

Stronger quantitative differences between the five simulations and MOZART occur in coastal regions of East Asia and Papua New Guinea, the Mediterranean Sea, and the Indian Ocean that are characterized by high anthropogenic pollution, that is, high levels of particulate matter and NO_x air pollution. Thus, the NO_3-radical-related DMS oxidation that yields exclusively SO_2 is more important there increasing the sulfate burden. At the Chinese coastline, high particulate matter increases the importance of the reactive uptake of MSIA on aerosol particles resulting in lowered SO_2 formation. This underlines the importance of applying the reactive uptake coefficient for future climate studies. Less significant quantitative differences are modeled for the residual Northern Hemisphere. In the Southern Hemisphere, where the addition pathway is more pronounced, higher column totals of sulfate of up to 1 μg m^{-3} are modeled over the oceans in the simulations GAMMA001 and HAM, because of their lower MSA formation compared to the other simulations (Figure 1).

3.3. Impact on Radiative Forcing

The distinct sulfate loadings between the simulations impact the modeled RF. Figure 3 shows the calculated net solar radiation at the top-of-atmosphere (TOA) for all-sky conditions for the MOZART simulation as well as the differences to the simulations GAMMA001, GAMMA01, GAMMA1, HAM and VARIED, respectively. Additionally, each of the ECHAM-HAMMOZ configurations (GAMMA001 to GAMMA1, VARIED) is related to the difference in TOA solar radiation of the HAM simulation, that is, default DMS-parameterization in ECHAM-HAM.

From Figure 3, it can be seen that on a global scale the different representations of the DMS oxidation have a low impact on the solar radiation at TOA, and the annual average ranges between −0.018 W m^{-2} (VARIED)

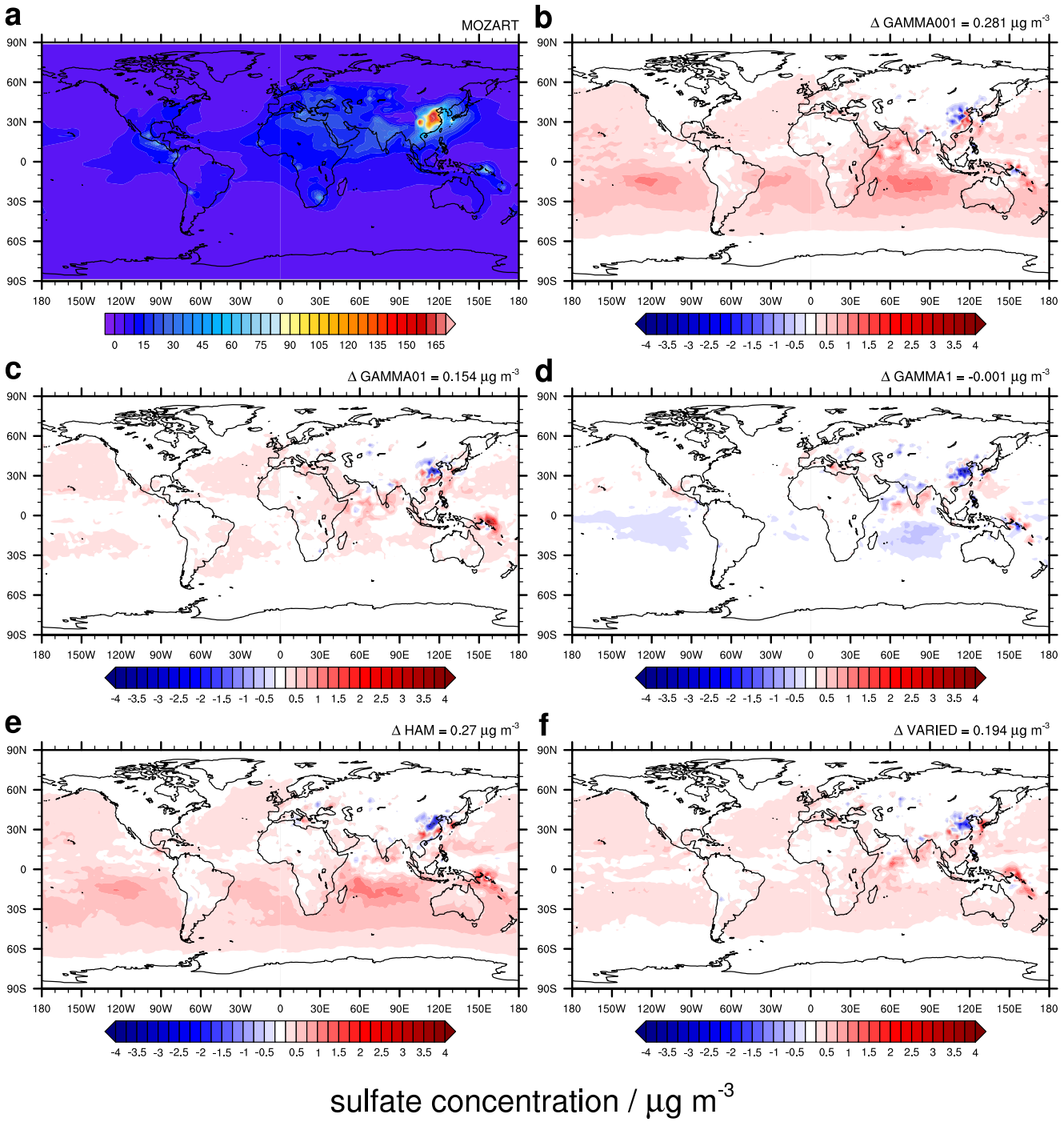

Figure 2. (a) Annual average of column total sulfate aerosol concentration in 2017 for the reference run MOZART and (b)–(f) relative alteration between the run MOZART and the other five sensitivity simulations.

and +0.028 W m^{-2} (GAMMA1). These effects are not statistically significant because of the highly variable nature of the clouds affected; especially true for the tropics. Remarkably, however, all model configurations with extended DMS oxidation simulate a less negative solar RF (positive difference in Figure 3b) of up to +0.1 W m^{-2} in the Arctic (>60°N). The simulation HAM shows a more negative solar RF (negative difference in Figure 3b) of up to −0.1 W m^{-2} there. This is related to lower cloud droplet number concentrations, and thus lower albedo, in the MOZART and GAMMA simulations (Figure S19). These differences result

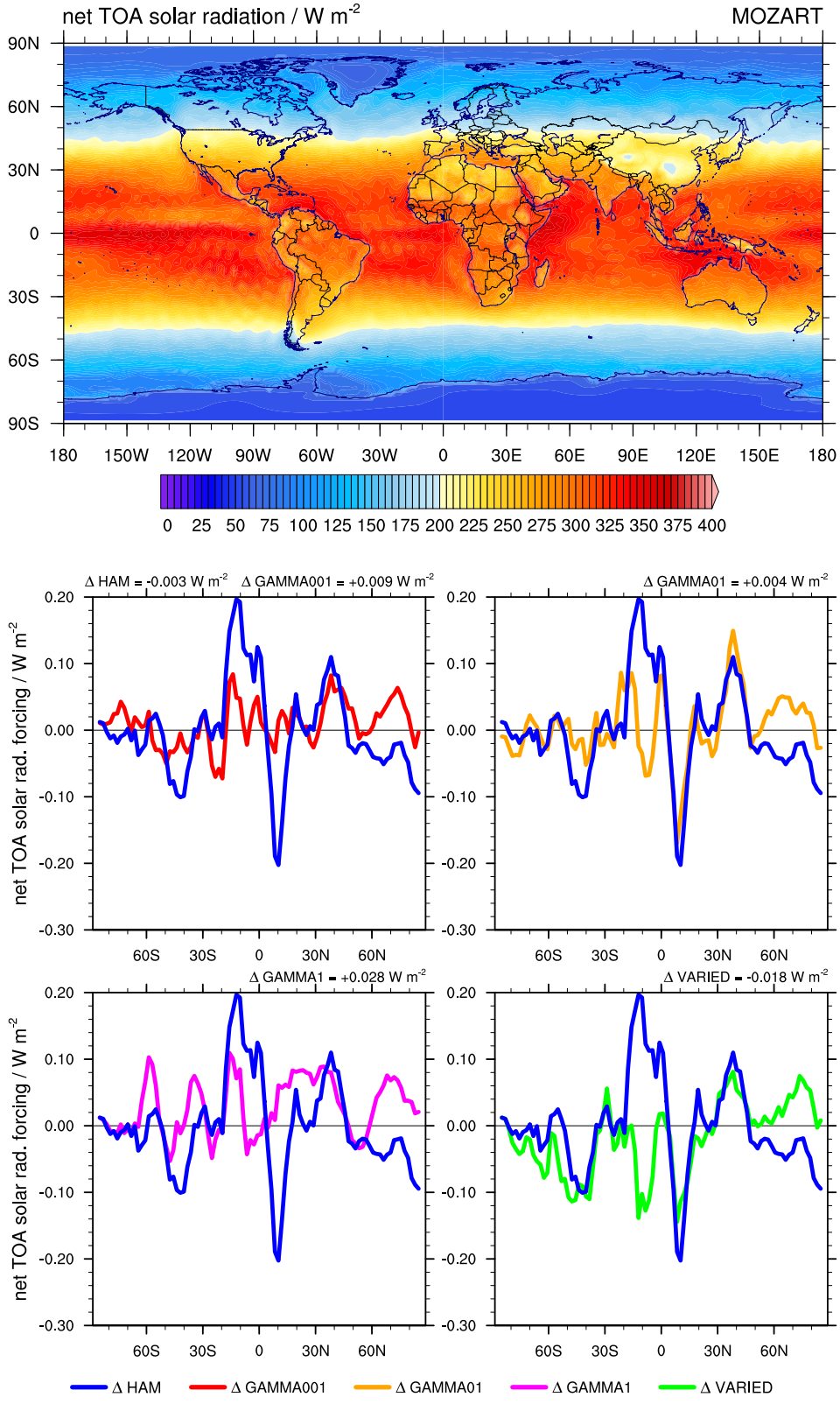

Figure 3. (a) Annual mean net solar radiation at TOA for all-sky conditions for year 2017 of the reference run MOZART and (b) zonally averaged differences between the MOZART run and the other five sensitivity simulations.

from the different SO_2 lifetimes toward gas-phase oxidation. The probability of gas-phase SO_2 oxidation into H_2SO_4 is HAM > MOZART > GAMMA, because of the increasing number of oxidation steps and oxidant molecules needed to oxidize DMS into SO_2. Thus, the probability of aerosol particles to grow to CCN size by condensation of H_2SO_4 is highest in the simulation HAM. Note that in the pristine atmosphere of the Arctic, such small changes have a big impact. Equally, such phenomena would be modeled when the formation of stable products other than SO_2 from the H-atom abstraction pathway are implemented.

The findings have important implications for model projections of the Arctic climate change, as state-of-the-art CCMs use a standard DMS description as in the HAM model setup. The results suggest that the negative RF of natural aerosol in the Arctic may be overestimated unless a more sophisticated representation of DMS oxidation is considered. As the observed sea ice retreat continues, this is of even greater importance because of the expected increase in biological activity in this region (Abbatt et al., 2019).

4. Conclusions

In this study, the multiphase DMS-oxidation scheme of the chemistry mechanism in the CCM ECHAM-HAMMOZ was improved. The reactive uptake of MSIA on aerosol particles to yield MSA was integrated, which can also be implemented into any other CCM. The model system was tested by sensitivity simulations, where the γ value was modulated between 0.01 and 1, to evaluate the effects of the applied multiphase chemistry approaches compared to a DMS-oxidation scheme, widely used in state-of-the-art CCMs, and to the ECHAM-HAMMOZ chemistry scheme.

The simulations were compared to measurements of gas-phase MSA and showed good agreement, when the reactive MSIA uptake was considered. However, total gas- and aqueous-phase formation of MSA is still not well represented because of lacking in-cloud MSA formation in the model version. It is concluded that for a realistic representation of DMS oxidation into MSA in CCMs, it is mandatory to consider the effect of both reactive uptake and cloud chemistry. Large uncertainties still exist for the reactive uptake requiring further laboratory investigations. The simulations demonstrated that a γ value of 0.1 for sea salt and 0.01 for other particle classes is well suited to predict measured gas-phase MSA concentrations over the mid- and high-latitude southern oceans and continents. Additionally, detailed investigations of the H-atom abstraction channel are required to understand $HOOCH_2SCHO$ oxidation.

The study shows that the inclusion of MSA formation via reactive uptake of MSIA into a CCM lead to a significantly lower negative aerosol RF in the Arctic (>60°N) of up to +0.1 W m^{-2} in comparison to the widely used representation by Chin et al. (1996).

Overall, the present study reveals that current implementations of DMS oxidation within CCMs are not detailed enough for realistic representation of associated aerosol-climate effects. Biases still exist in the formation of SO_2 as current parameterizations might overestimate CDNC formation. Based on this study and considering current limitations, a DMS oxidation scheme in CCMs is recommended that includes the formation of $DMSO_2$ and reactive uptake of MSIA ($\gamma = 0.1$ or $\gamma = 0.01$ depending on aerosol acidity) and an exclusive formation of SO_2 from the H-atom abstraction pathway, until more is known about the atmospheric fate of $HOOCH_2SCHO$.

Data Availability Statement

The ECHAM-HAMMOZ model source code and all required input data are available to the scientific community according to the HAMMOZ Software License Agreement through the project website: https://redmine.hammoz.ethz.ch/projects/hammoz. The data that support the findings of this study are openly available in zenodo at http://doi.org/10.5281/zenodo.4646768.

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