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Key Points:

- Provides quantitative comparison of DMS climatology impacts
- Results indicate that the updated climatology shows significant differences
- Simulations suggest that the updated climatology better represents the DMS emissions

Supporting Information:

- Tables S1 and S2 and Figures S1–S7

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Quantifying the impacts of an updated global dimethyl sulfide climatology on cloud microphysics and aerosol radiative forcing

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Abstract One of the critical parameters in assessing the global impacts of dimethyl sulfide (DMS) on cloud properties and the radiation budget is the estimation of phytoplankton-induced ocean emissions, which are derived from prescribed, climatological surface seawater DMS concentrations. The most widely used global ocean DMS climatology was published 15 years ago and has recently been updated using a much larger database of observations. The updated climatology displays significant differences in terms of the global distribution and regional monthly averages of sea surface DMS. In this study, we use the ECHAM5-HAMMOZ aerosol-chemistry-climate general circulation model to quantify the influence of the updated DMS climatology in computed atmospheric properties, namely, the spatial and temporal distributions of atmospheric DMS concentration, sulfuric acid concentration, sulfate aerosols, number of activated aerosols, cloud droplet number concentration, and the aerosol radiative forcing at the top of the atmosphere. Significant differences are observed for all the modeled variables. Comparison with observations of atmospheric DMS and total sulfate also shows that in places with large DMS emissions, the updated climatology shows a better match with the observations. This highlights the importance of using the updated climatology for projecting future impacts of oceanic DMS emissions, especially considering that the relative importance of the natural sulfur fluxes is likely to increase due to legislation to “clean up” anthropogenic emissions. The largest estimated differences are in the Southern Ocean, Indian Ocean, and parts of the Pacific Ocean, where the climatologies differ in seasonal concentrations over large geographical areas. The model results also indicate that the former DMS climatology underestimated the effect of DMS on the globally averaged annual aerosol radiative forcing at the top of the atmosphere by about 20%.

1. Introduction

Estimates suggest that oceanic dimethyl sulfide (DMS) emission is the main natural source of atmospheric sulfur [Bates and Calhoun, 1992; Simó, 2001] and, hence, it is thought to play an important role in the global biogeochemical sulfur cycle. Although large emissions of anthropogenic sulfur are seen over the continents, their magnitude leveled off since the late 1970s in western countries [Smith et al., 2011], and the relative importance of the natural sulfur fluxes is likely to increase in the future due to legislations to “clean up” anthropogenic emissions. The role of marine algae in the induction of atmospheric DMS has been studied in detail over the last two and a half decades fostered by the hypothesized impact of DMS on the climate, commonly known as the CLAW hypothesis [Charlson et al., 1987]. This hypothesis suggested a negative climate feedback loop between phytoplankton, DMS emission rates, cloud condensation nuclei (CCN), and solar radiation reaching the Earth's surface. It is well known that DMS is oxidized to form sulfuric acid (H_2SO_4) and methane-sulfonic acid ($\text{MSA} = \text{CH}_3\text{SO}_3\text{H}$), which contribute to new particle formation, growth and CCN formation, thus affecting the radiation budget [Andreae and Crutzen, 1997; Andreae and Rosenfeld, 2008]. However, the plankton-climate feedback loop has recently been challenged by studies arguing a limited role of DMS in new particle formation in the marine boundary layer (MBL), overcome by the potential of other aerosol sources like sea salt and sea surface organics in supplying CCN numbers [Murphy et al., 1997; Bigg, 2007; Twohy and Anderson, 2008; Carslaw et al., 2010; Quinn and Bates, 2011]. The climate sensitivity of CCN production to future changes in DMS emission rates has also been challenged in a recent modeling study [Woodhouse et al., 2010].

A number of studies have explored the potential links between oceanic DMS emissions and climate using either observations or models that simulate the total impact of DMS on the radiation budget or both. Some in situ and satellite observations have shown a positive correlation between chlorophyll, CCN, and cloud droplet effective radii [Bates and Quinn, 1997; Meskhidze and Nenes, 2006]. Others have shown positive correlations between DMS emission flux and CCN numbers [Andreae *et al.*, 1995; Lana *et al.*, 2012] and negative correlations to cloud droplet radii [Lana *et al.*, 2012]. Computations on satellite data have estimated that DMS emissions could contribute up to 30% of the globally averaged annual CCN column concentration but can be highly variable spatially [Vallina and Simó, 2007]. Several modeling studies with varying degrees of complexity have tried to establish the link between DMS, CCN, and temperature and evaluate the changes in DMS concentration in a warming climate [Gunson *et al.*, 2006; Kloster *et al.*, 2007; Korhonen *et al.*, 2008; Thomas *et al.*, 2010]. It has been suggested that the main pathway of DMS influence on CCN number is nucleation of DMS-derived H_2SO_4 in the free troposphere and subsequent growth by condensation and coagulation [Korhonen *et al.*, 2008]. Global models have yielded large interhemispherical differences in the contribution of DMS to the mean annual column burden of non-sea-salt sulfate [Gondwe *et al.*, 2003; Kloster *et al.*, 2006], with DMS accounting for up to 45% in the Southern Hemisphere compared to only 18% in the Northern Hemisphere. Woodhouse *et al.* [2008] modeled the effects of introducing a perturbed DMS patch in the Southern Ocean and found that it induces high CCN concentrations several thousand kilometers downwind of the patch due to the slow conversion of DMS into CCN. They also showed that the CCN change is not highly sensitive to the sea-to-air flux. However, in a recent modeling study, Woodhouse *et al.* [2013] reported that past and future changes in the spatial distribution of DMS emissions could exert a stronger control on climate than net increases in biological productivity. Significant increases in the number of activated particles (NA) and cloud droplet number concentrations (CDNC) and subsequent decrease in cloud droplet radius were observed over the Southern Ocean in Southern Hemisphere summer months compared to the rest of the year mainly due to the increased phytoplankton blooms resulting in increased DMS production during this season [Thomas *et al.*, 2010]. This study used the aerosol-chemistry-climate general circulation model (GCM) ECHAM5-HAMMOZ and also estimated a large difference in the aerosol radiative forcing at the top of the atmosphere (ARF_TOA) due to oceanic emissions of DMS.

One of the critical parameters in estimating the global impacts of DMS on cloud properties and the radiation budget is the emission inventory used in the modeling studies. This is normally derived from a prescribed sea surface concentration climatology and gas exchange parameterization. The emission inventory used can affect the emission rates and, more importantly, the global distribution which has been suggested to impact the total CCN number in addition to the cloud microphysical properties [Woodhouse *et al.*, 2013]. In the past, several methods have been used to obtain realistic global surface seawater DMS distributions using chlorophyll, solar radiation, nutrient distribution, oceanic mixed layer depths, and community structure of phytoplankton [Anderson *et al.*, 2001; Aumont *et al.*, 2002; Simó and Dachs, 2002; Belviso *et al.*, 2004; Vallina and Simó, 2007] or using numerical models that account for production and removal processes of DMS [Kloster *et al.*, 2006; Six and Maier-Reimer, 2006; Bopp *et al.*, 2008; Elliott, 2009; Vogt *et al.*, 2010]. The most widely used global DMS climatology, which provided the emission fields for most of the aforementioned modeling studies on the impact of DMS on the radiation budget, was published more than a decade ago [Kettle *et al.*, 1999; Kettle and Andreae, 2000]. This climatology was constructed using a data set of about 17,000 seawater DMS concentrations [Kettle *et al.*, 1999; Kettle and Andreae, 2000]. Recently, Lana *et al.* [2011] published an updated climatology using a much larger database of observations over the last decade in addition to the data used in the previous climatology (<http://saga.pmel.noaa.gov/dms/>). This climatology made use of about 47,250 data, contributed from all over the world mostly as an integration initiative of the Surface Ocean Lower Atmosphere Study (http://www.bodc.ac.uk/solas_integration/implementation_products/group1/dms/). This updated surface seawater DMS climatology by Lana *et al.* [2011] (henceforth referred to as L10, keeping the nomenclature in line with the original publication) showed considerable differences in concentration and distribution compared to the Kettle *et al.* [1999] and Kettle and Andreae [2000] climatology (henceforth referred to as K00).

In the study by Thomas *et al.* [2010], which used the ECHAM5-HAMMOZ model to study the effect of DMS on cloud properties, the emissions were based on the K00 climatology. With a recent study underlining the importance of spatial distribution over the rate of sea-to-air DMS flux [Woodhouse *et al.*, 2013], we used the same aerosol-chemistry-climate GCM, ECHAM5-HAMMOZ, to quantify the influence of the updated DMS

climatology L10 in comparison to the K00 climatology. Although the paper by *Lana et al.* [2011] discusses in detail the differences between the K00 and L10 climatologies in terms of DMS fluxes, in this study we quantify the impact of different DMS seawater concentrations on sulfate aerosol concentrations, clouds, and radiative balance, using a fully coupled aerosol-chemistry-climate model. Other studies showed the nonlinearity in the impacts of DMS distribution [Woodhouse et al., 2010, 2013; Makkonen et al., 2012] but not necessarily introducing perturbations in the same areas where the large differences in the DMS climatologies are observed. This study quantifies for the first time the global differences in cloud microphysics and aerosol radiative forcing based on these two climatologies based on observations. The changes induced by updating the ocean DMS climatology are discussed in terms of the spatial and temporal distributions of atmospheric DMS, H_2SO_4 , sulfate aerosol (SO_4), NA, CDNC, and ARF_TOA.

2. Methodology

2.1. Model Description

We use the state-of-the-art aerosol-chemistry-climate GCM, ECHAM5-HAMMOZ, to quantify the influence of the updated DMS climatology L10, as compared to the most commonly used climatology, K00. To our knowledge, this study represents the first analysis made using the new seawater DMS climatology with any global model to investigate the impact on cloud microphysics and radiative forcing.

The ECHAM5-HAMMOZ model has been used in the past for studying the impacts of DMS on cloud properties and radiative forcing, and a detailed description of the model, its performance related to sulfur chemistry, and its interaction with aerosols is given in *Thomas et al.* [2010, 2011]. Briefly, the model has three main components: the general circulation model, ECHAM5 [Roeckner et al., 2003]; the tropospheric chemistry module, MOZ, which is based on the chemical mechanism described by *Horowitz et al.* [2003]; and the aerosol module, HAM (Hamburg Aerosol Model) [Stier et al., 2005]. The ECHAM5 model is coupled to a detailed cloud microphysics module [Lohmann et al., 1999, 2007]. A description of the respective modules is given by *Pozzoli et al.* [2008]. The chemistry and aerosol modules interact through photolytic reactions, sulfur chemistry, and heterogeneous chemistry. The HAM module takes into account the major aerosol compounds: sulfate, black carbon, organic carbon, sea salt, and mineral dust. Aerosols are categorized by size into nucleation, Aitken, accumulation, and coarse modes. Mineral dust and sea-salt emissions are calculated interactively following the parameterization schemes of *Tegen et al.* [2002] and *Schulz et al.* [2004], respectively. The sea-salt source function is represented by the combination of the approach of *Monahan et al.* [1986] for small particle range and of *Smith and Harrison* [1998] for the coarse particle range. The MOZ chemical scheme is identical to the one used in the MOZART-2 model and includes 63 tracers and 168 reactions to represent Ox-NOx-hydrocarbon chemistry. We used the RETRO project data set of the year 2000 (<http://www.retro.enes.org/>) for the surface CO, NOx, and hydrocarbon emissions from anthropogenic sources and biomass burning [Schultz et al., 2008]. The anthropogenic and fire emissions of SO_2 , black carbon, and organic carbon are based on the AEROCOM emission inventory [Dentener et al., 2006] representative of the year 2000. The model parameterizations, emissions, and validation are described in *Fadnavis et al.* [2013].

2.2. DMS Emission Parameterization and Sulfur Chemistry

The DMS flux to the atmosphere is computed using either seawater climatology (L10 or K00) and the parameterization of the transfer velocity proposed by *Nightingale et al.* [2000]. The model converts the atmospheric DMS to sulfur dioxide (SO_2) and MSA through reaction with the hydroxyl radical (OH) and nitrate radical (NO_3) [Feichter et al., 1996]. SO_2 is oxidized to H_2SO_4 , whereas MSA is directly converted to H_2SO_4 in the gas phase. The H_2SO_4 concentration in the gas phase can form sulfate aerosols by nucleation of new particles and can grow aerosols by condensation [Vignati et al., 2004]. Heterogeneous reactions involving the condensation of SO_2 on to the surface of sea-salt aerosols and mineral dust particles are also taken into account [Pozzoli et al., 2008]. Sulfate formation from in-cloud oxidation of SO_2 is also considered [Feichter et al., 1996; Stier et al., 2005] using the calculated oxidant fields of O_3 and H_2O_2 . The cloud scheme in the ECHAM5 model is based on a detailed cloud microphysics module following the modified version by *Lohmann et al.* [1999, 2007]. The number of cloud droplets is parameterized as a function of the total aerosol number concentrations, updraft velocity, and a shape parameter that takes into account the aerosol composition and the size distribution.

2.3. Experimental Setup

For this study, the simulations are performed with a spectral resolution of T42 that corresponds approximately to $2.8^\circ \times 2.8^\circ$ horizontally, with 31 vertical levels from the surface up to 10 hPa and with a 20 min time step. The model is driven by European Centre for Medium-Range Weather Forecasts operational analyses (Integrated Forecast System (IFS) cycle-32r2) meteorological fields (available every 6 h) [Uppala *et al.*, 2005]. In this configuration, the prognostic variables of ECHAM5 (vorticity, divergence, temperature, and surface pressure) are relaxed toward the operational analyses (IFS cycle-32r2) reanalysis data [Machenhauer and Kirchner, 2000]. Model simulations were performed for the year 2003 since there was no significant oceanic/meteorological perturbation event like, e.g., El Niño Southern Oscillation or the Indian Ocean Dipole (http://www.marine.csiro.au/~mcintosh/Research_ENSO_IOD_years.htm). To evaluate the influence of DMS emissions on aerosol number, cloud properties, and radiative forcing, we carry out three 1 year simulations for 2003: the first one is a control run, where DMS emissions from the ocean surface are not considered (CTRL), while the two DMS seawater climatologies, L10 and K00, make up for the other two runs. Other emissions of SO₂, black carbon, organic carbon, sea salt, and dust are held fixed across all simulations. The AMIP2 sea surface temperatures and sea ice cover representative of the year 2003 are specified as a lower boundary condition, and an 18 month spin up is used for these simulations. The sea ice regions are switched off for emissions in the model.

3. Results and Discussion

To quantify the effect of the different climatologies on aerosols, cloud properties, and aerosol radiative forcing, the differences between the two climatologies are expressed by comparing L10-CTRL with K00-CTRL. We also compute the direct differences between the two climatologies (L10-K00). For this study, we focus on atmospheric DMS, H₂SO₄, NA, CDNC, and ARF_TOA as the most indicative variables. In order to highlight seasonal differences, the model results are analyzed as seasonal averages: northern hemispheric winter, spring, summer, and fall as means over December, January, and February (DJF); March, April, and May (MAM); June, July, and August (JJA); and September, October, and November (SON), respectively.

3.1. Differences Between DMS Climatologies

Figures 1a and 1b show seasonal maps of the two surface ocean DMS climatologies (L10 and K00), and Figure 1c depicts the difference (L10-K00). Negative values mean that K00 overestimates the parameter discussed here compared to the L00 climatology. Considerable differences, both regional and seasonal, in the magnitude and geographical distribution can be seen. It can be seen that the surface ocean DMS concentrations are largely overestimated when using the K00 climatology (with DMS sea water concentrations exceeding 15 nmol L^{-1} in some areas) over the Arctic in JJA and coastal Antarctica in DJF and to a lesser extent in other parts of the world mainly close to the continents, e.g., off the east coast in South America during DJF months or in the northeastern Atlantic in spring. Also, the K00 climatology underestimated the seawater DMS concentrations over most of the world's oceans, particularly over the Indian Ocean in DJF, where the large increase in data over the last decade has prompted an upward revision of concentration averages [Lana *et al.*, 2011]. During DJF, areas in the western equatorial Pacific, close to Papa New Guinea, off the African southeast coast, and off the Australian southeast coast also show positive changes. The northeast subarctic Pacific Ocean close to Alaska, which is a high-nutrient, low-chlorophyll (HNLC) region that has been the subject of detailed studies on DMS over the last decade [Wong *et al.*, 2005], also shows increased concentrations in spring and summer in the new climatology. High seawater DMS concentrations in that region have been attributed to the plenitude of small algal cells, mainly the prymnesiophytes *Emiliania huxleyi* and *Phaeocystis* spp. [Levasseur *et al.*, 2006]. These species can cope with the low Fe supply in this HNLC region thanks to their high surface-to-volume ratio. The abundance of these strong dimethyl sulfoniopropionate (DMSP) producers, therefore, explains the high DMSP:chlorophyll *a* ratios and subsequent high DMS concentrations [Royer *et al.*, 2010]. These discrepancies between the climatologies result in differences not only in the absolute emissions of DMS as computed in the model but also in geographical emission fluxes, which have been suggested to play a more important role in controlling the CCN formation and distribution [Woodhouse *et al.*, 2013]. The interannual variability is smaller than the change between the two climatologies at several locations, for example, in the Southern Ocean or the Indian Ocean (where the

Figure 1. Seawater DMS climatologies used in this study: (a) L10, the updated climatology by Lana *et al.* [2011]; (b) K00, the former, widely used climatology by Kettle and Andreae [2000]; and (c) the difference between the two climatologies as split into the four seasons.

K00 climatology did not have any data but was interpolated), and the differences between the two climatologies have been discussed in detail elsewhere [Lana *et al.*, 2011; Lana, 2012]. Here we focus on the differences between the impacts of the two climatologies. It is also important to note that the L10 climatology is not a new climatology but rather an updated climatology and includes all the data from the K00 climatology. The K00 climatology contains seawater DMS observations between 1972 and 1999, while the L10 climatology contains data between 1972 and 2009. For further information about the data included in these climatologies, refer to their original publications [Kettle *et al.*, 1999; Kettle and Andreae, 2000; Lana *et al.*, 2011]. The number of samples in the L10 climatology is a factor of 3 larger and, hence, expected to represent the seawater DMS distribution more accurately compared to K00.

3.2. Comparison With Observations

Climatological observations of atmospheric DMS are rare, and data from only one site (Amsterdam Island: 37.83°S, 77.5°E [Sciare *et al.*, 2000]) were available for a direct comparison with the modeled results. By contrast, discrete observations have been made at several sites around the world, including on research cruises. A compiled data set of discrete atmospheric DMS measurements from all over the world is given in the supporting information (Table S1) and was used to validate the model output. Figure 2 shows the comparison between the observed atmospheric DMS climatology at Amsterdam Island, southern Indian Ocean (1990–1999) and the modeled DMS at the surface using the K00 and L10 climatologies. It should be noted that the Indian Ocean region is one of the regions showing a large change in the L10 climatology as compared to K00 (Figure 1). Using the L10 climatology, the correlation coefficient value shows a strong improvement ($R = 0.83$, $P = 0.001$) as compared to the K00 climatology ($R = 0.45$, $P = 0.15$). This suggests that in the Indian Ocean region, the L10 climatology better represents the seawater DMS distribution as compared to the K00. However, even the L10 climatology does not reproduce the large atmospheric DMS mixing ratios in January and February, suggesting that further work is necessary to better describe the DMS

Figure 2. Comparison between the observed atmospheric DMS climatology at Amsterdam Island, Indian Ocean (1990–1999), and the modeled DMS at the surface using the K00 and L10 climatologies, with associated correlation coefficient (R) and significance value (P) between simulated and observed values. The grey area indicates the standard deviation of the observations.

emissions. Considering this large disagreement, a factor of 5 for K00 and 2.5 for L10, it is most likely the source strength rather than other contributing factors such as boundary layer ventilation and/or chemical kinetics that leads to the degradation of atmospheric DMS. In the past, Huebert *et al.* [2004] measured sea-air DMS flux transfer velocities in the equatorial Pacific and reported standard deviations of up to 40% at a given wind speed. Bell *et al.* [2013] recently reported that the gas transfer coefficient shows a linear dependence on mean horizontal wind speed at wind speeds up to 11 m s^{-1} , but at higher wind speeds the relationship with wind speed weakens. Lucas and Prinn [2005]

studied parametric sensitivity of the DMS oxidation mechanism in a box model and found that the concentration of DMS is highly sensitive to the vertical mixing coefficient and emissions of DMS. However, it is important to note that the uncertainties in the gas transfer and vertical mixing are still smaller than the 250% difference between the model and the observations for the L10 scenario in January but could be a contributing factor. Even the L10 climatology also contains no data in the Indian Ocean region for the month of January, which could explain the mismatch [Lana, 2012]. The K00 climatology contained very few data in the Indian Ocean and was estimated through interpolations, which could explain the bad representation as compared to L10. For compiled discrete observations from all over the world, the L10 climatology shows a modest improvement in describing the atmospheric DMS as compared to the K00 climatology (Figure S1 in the supporting information); $R = 0.48$ for L10 as compared to 0.44 for K00. A strong correlation with these data is not expected as the model is run with emissions of DMS calculated using the climatologies, as compared to in situ observations that depend on the local environmental conditions. Most of the observations used in this comparison are from the tropical and subtropical regions, and it can be seen in Figure S1 that the model overestimates the atmospheric DMS in several cases. This further makes the case that more observations are needed to update the DMS climatology to get better match with the observations.

We also use the monthly mean total sulfate observations from the University of Miami Aerosol Group-Aerosol Oceanic Chemistry Experiment-Department of Energy-SEA/air EXchange program (UMAG AEROCE-DOE-SEAREX) network (J. M. Prospero, University of Miami, personal communication, 2014, <http://aerocom.met.no/download/AEROCE-SEAREX/>) for validating the model output. Monthly total SO_4 climatologies from 31 stations were available for comparison. Most of these stations are either close to continents or low DMS regions, with just a few stations in regions with high DMS concentrations (Figure 3, top). Sixteen sites out of the 31 sites show a positive correlation between the model outputs and the monthly mean observations. At a further 12 out of these 16 sites, the L10 estimates better the total SO_4 than the K00 climatology (Figure 3, middle, and 3, bottom). Most of the stations where a positive correlation is observed and an improvement is seen are located in the Indian Ocean, Western Pacific, Southern Ocean, or Antarctica. These are the regions where the updated L10 climatology shows a difference as compared to the K00 climatology. No improvement is noticed in the central Pacific region or at any of the sites close to the continents. It should be noted that the continental sites would also be heavily affected by anthropogenic emissions of SO_2 , and hence, the updated climatology is not expected to have a large impact. An improvement in the correlation coefficient (R values) and a decrease in the P values (improvement in significance) in locations where large DMS emissions are observed suggest that L10 climatology shows a significant improvement over the K00 climatologies in these areas.

Figure 3. Correlation coefficients and significance values for the 31 sites from the UMAG AEROCE-DOE-SEAREX network (J. M. Prospero, University of Miami, personal communication, <http://aerocom.met.no/download/AEROCE-SEAREX/>) used to compare the monthly observed total SO_4 and the modeled outputs for the L10 and K00 climatologies. The asterisk values indicate that the R value is significant at 99%. (top) Location of the measurement sites, (middle) correlation coefficients, and (bottom) significance values.

The modeled atmospheric estimates of DMS and SO_4 depend on several factors such as the sea-air transfer parameterization scheme, the reaction kinetics of DMS, winds, etc., in addition to the seawater DMS concentrations. Hence, it is possible that some of the mismatch between the model and observations is due to factors other than the climatology used. A detailed study on the sensitivity of the model to the other contributing mechanisms that would affect the atmospheric response of DMS due to the different DMS climatologies is beyond the scope of this paper. A previous study by Pozzoli *et al.* [2011] performed a hindcast simulation for the period 1980–2005, using K00 for DMS emissions. In their simulations, they did not change the climatology of seawater DMS, but variation in meteorology was included. The authors saw that global DMS emission variability, due to meteorology, is on the order of 1.3%, as the multiyear average of DMS annual emissions was 23.4 Tg(S)/year with standard deviation of 0.3 Tg(S)/year. This suggests that the interannual variations in the global DMS emissions are not on the same order as the differences between the model and observations.

3.3. Differences in Atmospheric DMS and Gaseous H_2SO_4

The differences in the seawater climatologies are reflected in the atmospheric DMS mixing ratios close to the surface at 1000 hPa, as shown in Figure 4 (top). The atmospheric DMS levels in the Arctic and part of the Southern Ocean MBL are significantly reduced in L10 compared to when the K00 climatology is used. Negative differences are also seen in other parts of the world's MBL, especially during MAM, where large areas in the extratropics in the Northern Hemisphere show lower DMS mixing ratios (by ~ 150 pptv). Higher values in the L10 simulation are seen in the Indian Ocean MBL in all seasons but MAM, as well as off the southeast coast of Australia and eastern Pacific in DJF and over the Southern Ocean in JJA. In the latter, a large area below 50°S shows increases of up to 250 pptv. A large positive change in atmospheric DMS of about 850 pptv is seen in the northeast subarctic Pacific Ocean as a result of the addition of new seawater DMS observations in the updated climatology. A figure showing the modeled values of atmospheric DMS for each climatology is given in the supporting information (Figure S2).

Figure 4. The difference between the model output using two climatologies (L10-K00) for (top) atmospheric DMS mixing ratios at 1000 hPa, (middle) atmospheric H_2SO_4 mixing ratios at 850 hPa, and (bottom) sulfate (SO_4) mixing ratios at 850 hPa.

It is known that the largest gaseous H_2SO_4 mixing ratios due to DMS chemistry occur over the Southern Ocean during the southern hemispheric summer (DJF) (refer to Figure S3). Figure 4 (middle) shows the difference in the H_2SO_4 mixing ratios, resulting from DMS oxidation chemistry, at 850 hPa. Large differences between DMS climatologies are evident both spatially and seasonally (Figure 4, middle). Higher concentrations when using the L10 climatology is mostly simulated in the Southern Hemisphere. The geographical changes in H_2SO_4 mixing ratios, however, do not correlate directly with changes in the DMS emissions or atmospheric DMS concentrations at the surface. This is not surprising considering the complex nature of the conversion of DMS into H_2SO_4 (involving multistep oxidation by OH and NO_3 and depending on the meteorological conditions near the source point); the effect of DMS oxidation is expected to be seen at considerable distances away from the emission region [Woodhouse *et al.*, 2008].

Decrease in H_2SO_4 mixing ratios with the updated climatology is observed in large areas of the Southern Ocean during DJF and MAM. In JJA and SON, the decrease is more limited to the northern latitudes, with the largest decrease seen in the Arctic, where it extends to MAM. Higher DMS emissions in the Indian Ocean and the western equatorial Pacific are reflected in H_2SO_4 mixing ratios. The Southern Ocean also shows increases during JJA and SON (>0.1 pptv—more than 50% of the H_2SO_4 load). The increase in SON in particular is an example of the complex nature of conversion of DMS into H_2SO_4 , where even a small change in DMS causes a noticeable change in the H_2SO_4 mixing ratio. A similar effect, although with more regional heterogeneity, is observed in summer DJF months, where areas with a small increase in DMS in the Southern Hemisphere show a strong increase in H_2SO_4 , even if it is regionally limited due to the large areas of decreased DMS. Increases in the subarctic northeast Pacific Ocean occur all year round and are distinctly higher in SON. A regionally limited increase is observed during DJF in the Australian sector of the Southern Ocean, not far away from the increase in atmospheric DMS further north; this illustrates the importance of transport and lifetime of the DMS to H_2SO_4 conversion.

Figure 5. The difference between the model output using two climatologies (L10-K00) for (top) number of activated aerosols (NA) at 850 hPa, (middle) column-integrated cloud droplet number concentration (CDNC), and (bottom) aerosol radiative forcing at the top of the atmosphere (ARF_TOA). Negative ARF_TOA means that there is a net cooling at the TOA.

3.4. Differences in Sulfate Aerosol, NA, and CDNC

The difference in the SO_4 aerosol mixing ratios at 850 hPa is shown in Figure 4 (bottom). The largest effects of DMS are observed in the tropical and extratropical regions during all seasons with the peak globally averaged effect of DMS occurring in DJF (refer to Figure S4). Small negative differences are observed in the Southern Ocean, close to the Antarctic continent, reflecting the decrease in seawater DMS between the two climatologies. Regionally decreased SO_4 is also observed in the north equatorial Atlantic and Pacific during MAM. The largest increases ($>100\%$) are simulated over the Indian Ocean during DJF, JJA, and SON, over the Pacific in JJA and SON, and over southern equatorial Atlantic in JJA. This increase is relatively larger than those of DMS or H_2SO_4 , illustrating the nonlinear nature of the conversion of DMS to sulfate aerosols. Positive differences are also observed in the eastern Pacific during JJA and SON and in the southern equatorial Atlantic during JJA.

The number of activated aerosols at 850 hPa is shown in Figure 5 (top). As expected, the largest effect of DMS on NA is observed in the Southern Hemisphere during DJF in both the K00 and L10 model runs, reflecting the large production of DMS during the southern hemispheric summer (refer to Figure S5). The L10 climatology induces lower NA concentrations by almost 50% close to Antarctica in DJF and to a lesser extent in MAM over the Southern Ocean as a result of reduced DMS seawater concentration. During these two seasons, high values are observed over Southeast Asia when using the updated climatology which is in agreement with the increases in the DMS and H_2SO_4 mixing ratios. Large-scale increases are simulated during JJA and SON, especially in the Southern Hemisphere. Increases of up to 1×10^8 particles m^{-3} are obtained in the Indian Ocean and eastern Pacific regions, which represents an almost 100% rise from K00 to L10. Compared to the DMS "off" CTRL simulation, this amounts to an anomaly of about 25% in the number of activated aerosols. The relative increase in the NA concentrations is much larger than the relative increase in DMS or H_2SO_4 and reflects the complex nature of the conversion, which depends not only on the emission strength but also on the rates of oxidation and coagulation/condensation, for which the OH concentrations and the water vapor content

play critical roles. A similar feature was also observed in the SO_4 mixing ratios (Figure 4) with maxima over tropical and extratropical regions owing to the high concentrations of OH and water vapor. The increase in the NA concentrations during JJA and SON suggests that DMS concentrations could play an even more important role in determining the magnitude of the marine NA concentrations during these seasons than previously considered [Thomas *et al.*, 2010].

The effects of the differences in NA numbers are reflected in column-integrated CDNC (Figure 5, middle); regions of high CDNC are consistent with regions of high NA, and vice versa (Figures S5 and S6). Thus, decreases in CDNC are obtained close to Antarctica during DJF (Figure 5, middle). A reduction of about -1.8×10^9 droplets m^{-2} amounts to a decrease of almost 60%, suggesting that the use of the K00 climatology results in an overestimation of the DMS impact on clouds in this region. Smaller decreases of about -0.5×10^9 droplets m^{-2} are also simulated during MAM over large areas in the Southern Ocean. Similar to the NA, large positive differences are also observed in JJA in the 10°S – 40°S latitude belt, with an increase of almost 150% over the Indian Ocean due to the L10 climatology. This can be of extra significance because this season coincides with the Asian summer monsoon. Increased CDNC could have an effect on the precipitation patterns over Asia, since the winds that feed the monsoon circulation over India originate in the Indian Ocean. Assessing the effects of DMS on precipitation would require further in-depth analyses that are beyond the scope of this paper.

3.5. Difference in the ARF_TOA

The aerosol radiative forcing is evaluated as the difference between perturbed and unperturbed radiative fluxes caused by aerosol while keeping the same meteorology. This includes both the short-wave and long-wave radiative fluxes. The perturbed radiative fluxes correspond to the fluxes obtained using the L10 and K00 DMS climatologies, whereas the unperturbed radiative fluxes correspond to those without any ocean DMS emissions (CTRL simulation) owing to both aerosol direct and indirect effects (the aerosol-cloud feedback mechanisms are enabled). Previous studies have attempted to quantify the effect of DMS on ARF_TOA and have suggested it to be significant. Gabric *et al.* [2001] predicted that an increase in DMS flux of 1–6% in the midlatitude Southern Ocean would result in a cooling effect of -0.3 W m^{-2} , while Bopp *et al.* [2004] calculated that a 3% increase in global mean DMS flux would lead to a global cooling of -0.05 W m^{-2} . Local changes up to -1.5 W m^{-2} were simulated in the midlatitude Southern Ocean. Gunson *et al.* [2006] estimated a radiative effect of -1.8 W m^{-2} due to a doubling of the DMS emission flux. Thomas *et al.* [2010] found that the contribution of DMS to the radiative budget was -2.0 W m^{-2} . Similar to Thomas *et al.*, in this study, the difference in the annually averaged net radiative fluxes at the TOA in the simulation with K00 from the CTRL simulation (under the same meteorological conditions) gives a radiative forcing due to a DMS of -1.49 W m^{-2} . While computed with the L10 DMS climatology, the annual radiative forcing adds further -0.30 W m^{-2} to that with K00, increasing the DMS-derived cooling to -1.79 W m^{-2} . This represents an additional cooling of 20% just by updating the DMS climatology. However, large seasonal and geographical heterogeneity in the regional differences is seen (of up to $\pm 10 \text{ W m}^{-2}$). Figure 5 (bottom) shows the mapped effect of a change in the DMS climatology on the aerosol radiative forcing at the top of the atmosphere (ARF_TOA) (refer to Figure S7). In the Southern Ocean during DJF, the L10 climatology has a lower negative forcing by almost 50% with respect to the K00 in the 0 – 180°W sector, owing to reduced DMS emissions. In the 0 – 180°E sector, conversely, the effect is the opposite. Similar longitudinal dissimilarity was obtained for NA and CDNC (Figure 5). In other parts of the world during the same season (DJF), the updated climatology mostly induces further cooling. The global effect is the addition of -0.22 W m^{-2} to yield a global seasonal cooling of -2.73 W m^{-2} , which represents a 9% increase with respect to the K00 climatology. During MAM, no clear regional pattern is noticeable, and the DMS-derived ARF_TOA amounts to -1.37 W m^{-2} with L10, which represents a 9% decrease of the global cooling computed with K00 (-1.51 W m^{-2}). In JJA and SON, clear increases in the negative ARF_TOA are observed in the Southern Hemisphere with L10, in agreement with the increases in NA and CDNC. The cooling is almost 100% more in the L10 climatology as compared to the K00 climatology in certain regions over the Indian, Pacific, and Atlantic Oceans. The globally averaged radiative cooling change during JJA is -0.49 W m^{-2} (63% extra cooling), which yields an updated seasonal DMS-derived ARF_TOA of -1.26 W m^{-2} , and -0.61 W m^{-2} (51% extra cooling) during SON, yielding a seasonal DMS-derived ARF_TOA of -1.79 W m^{-2} .

4. Conclusions

In this study, we use the ECHAM5-HAMMOZ aerosol-chemistry-climate general circulation model to quantify the influence of the updated DMS climatology on the spatial and temporal distributions of atmospheric DMS concentration, sulfuric acid concentration, sulfate aerosols, number of activated aerosols, cloud droplet number concentration, and the aerosol radiative forcing at the top of the atmosphere. Comparison with observations of atmospheric DMS and total SO_4 shows that the L10 climatology better simulates these parameters, especially in areas where large DMS emissions occur, such as the Southern Ocean, or where large differences with the K00 climatology are observed, viz., the Indian Ocean and western Pacific. The simulations indicate that regionally, reduced effects of DMS are seen in the 0–180°W sector of the Southern Ocean during the southern hemispheric summer due to the L10 climatology displaying lower concentrations, while increased effects are observed in large areas in the Indian Ocean and the Pacific Ocean during most seasons. Globally, the updated climatology leads to greater production of H_2SO_4 , NA, and CDNC and leads to an annually averaged DMS-derived aerosol radiative forcing at the top of the atmosphere of -1.79 W m^{-2} , which is larger than the cooling computed with the former DMS climatology by -0.30 W m^{-2} (20%), with much larger seasonal and regional differences. This work shows that the use of the updated DMS climatology should be incorporated into models built to investigate the role of sulfur emissions and chemistry on climate. Finally, it should be remembered that although we are using a state-of-the-art aerosol-chemistry-climate coupled model, some emerging issues, such as ternary nucleation of H_2SO_4 and MSA with organics [Dawson *et al.*, 2012; Riccobono *et al.*, 2014], are not considered, and further work is necessary to quantify the impact of the new emerging processes.

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References

- Anderson, T. R., S. A. Spall, A. Yool, P. Cipollini, P. G. Challenor, and M. J. R. Fasham (2001), Global fields of sea surface dimethylsulphide predicted from chlorophyll, nutrients and light, *J. Mar. Syst.*, *30*(1–2), 1–20, doi:10.1016/S0924-7963(01)00028-8.
- Andreae, M. O., and P. J. Crutzen (1997), Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, *Science*, *276*(80), 1052–1058.
- Andreae, M. O., and D. Rosenfeld (2008), Aerosol–cloud–precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, *Earth Sci. Rev.*, *89*(1–2), 13–41, doi:10.1016/j.earscirev.2008.03.001.
- Andreae, M. O., S. J. de Mora, and W. Elbert (1995), Biogenic sulfur emissions and aerosols over the tropical South Atlantic: 3. Atmospheric dimethylsulphide, aerosols and cloud condensation nuclei, *J. Geophys. Res.*, *100*(D6), 11,335–11,356, doi:10.1029/94JD02828.
- Aumont, O., S. Belviso, and P. Monfray (2002), Dimethylsulfoniopropionate (DMSP) and dimethylsulphide (DMS) sea surface distributions simulated from a global three-dimensional ocean carbon cycle model, *J. Geophys. Res.*, *107*(C4), 3029, doi:10.1029/1999JC000111.
- Bates, T. S., and J. A. Calhoun (1992), Variations in the methanesulfonate to sulfate molar ratio in marine aerosol particles over the South Pacific Ocean, *J. Geophys. Res.*, *97*(D9), 9859–9865, doi:10.1029/92JD00411.
- Bates, T. S., and P. K. Quinn (1997), Dimethylsulphide (DMS) in the equatorial Pacific Ocean (1982–1996): Evidence of a climate feedback?, *Geophys. Res. Lett.*, *24*(8), 861–864, doi:10.1029/97GL00784.
- Bell, T. G., W. De Bruyn, S. D. Miller, B. Ward, K. Christensen, and E. S. Saltzman (2013), Air–sea dimethylsulphide (DMS) gas transfer in the North Atlantic: Evidence for limited interfacial gas exchange at high wind speed, *Atmos. Chem. Phys.*, *13*(21), 11,073–11,087, doi:10.5194/acp-13-11073-2013.
- Belviso, S., C. Moulin, L. Bopp, and J. Stefels (2004), Assessment of a global climatology of oceanic dimethylsulphide (DMS) concentrations based on SeaWiFS imagery (1998–2001), *Can. J. Fish. Aquat. Sci.*, *61*, 804–816, doi:10.1139/F04-001.
- Bigg, E. K. (2007), Sources, nature and influence on climate of marine airborne particles, *Environ. Chem.*, *4*(3), 155, doi:10.1071/EN07001.
- Bopp, L., O. Boucher, O. Aumont, S. Belviso, P. Monfray, and M. Pham (2004), Will marine dimethylsulphide emissions amplify or alleviate global warming? A model study, *Can. J. Fish. Aquat. Sci.*, *61*, 826–835.
- Bopp, L., O. Aumont, S. Belviso, and S. Blain (2008), Modelling the effect of iron fertilization on dimethylsulphide emissions in the Southern Ocean, *Deep Sea Res., Part II*, *55*, 901–912, doi:10.1016/j.dsr2.2007.12.002.
- Carslaw, K. S., O. Boucher, D. V. Spracklen, G. W. Mann, J. G. L. Rae, S. Woodward, and M. Kulmala (2010), A review of natural aerosol interactions and feedbacks within the Earth system, *Atmos. Chem. Phys.*, *10*, 1701–1737, doi:10.5194/acp-10-1701-2010.
- Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren (1987), Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, *326*(16), 655–661.
- Dawson, M. L., M. E. Varner, V. Perraud, M. J. Ezell, R. B. Gerber, and B. J. Finlayson-Pitts (2012), Simplified mechanism for new particle formation from methanesulfonic acid, amines, and water via experiments and ab initio calculations, *Proc. Natl. Acad. Sci. U.S.A.*, *109*(46), 18,719–18,724, doi:10.1073/pnas.1211878109.
- Dentener, F., et al. (2006), Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed data-sets for AeroCom, *Atmos. Chem. Phys.*, *6*, 4321–4344.
- Elliott, S. (2009), Dependence of DMS global sea-air flux distribution on transfer velocity and concentration field type, *J. Geophys. Res.*, *114*, G02001, doi:10.1029/2008JG000710.
- Fadnavis, S., K. Semeniuk, L. Pozzoli, M. G. Schultz, S. D. Ghude, S. Das, and R. Kakatkar (2013), Transport of aerosols into the UTLS and their impact on the Asian monsoon region as seen in a global model simulation, *Atmos. Chem. Phys.*, *13*, 8771–8786, doi:10.5194/acp-13-8771-2013.
- Feichter, J., E. Kjellström, H. Rodhe, F. Dentener, J. Lelieveld, and G. Roelofs (1996), Simulation of the tropospheric sulphur cycle in a global climate model, *Atmos. Environ.*, *30*(10/11), 1693–1707.
- Gabric, A. J., P. H. Whetton, and R. Cropp (2001), Dimethylsulphide production in the subantarctic Southern Ocean under enhanced greenhouse conditions, *Tellus B*, *53B*(3), 273–287, doi:10.1034/j.1600-0889.2001.01244.x.

- Gondwe, M., M. Krol, W. Gieskes, W. Klaassen, and H. de Baar (2003), The contribution of ocean-leaving DMS to the global atmospheric burdens of DMS, MSA, SO_2 , and NSS SO_4^{2-} , *Global Biogeochem. Cycles*, 17(2), 1056, doi:10.1029/2002GB001937.
- Gunson, J. R., S. A. Spall, T. R. Anderson, A. Jones, I. J. Totterdell, and M. J. Woodage (2006), Climate sensitivity to ocean dimethylsulphide emissions, *Geophys. Res. Lett.*, 33, L07701, doi:10.1029/2005GL024982.
- Horowitz, L. W., et al. (2003), A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res.*, 108(D24), 4784, doi:10.1029/2002JD002853.
- Huebert, B. J., B. W. Blomquist, J. E. Hare, C. W. Fairall, J. E. Johnson, and T. S. Bates (2004), Measurement of the sea-air DMS flux and transfer velocity using eddy correlation, *Geophys. Res. Lett.*, 31, L23113, doi:10.1029/2004GL021567.
- Kettle, A. J., and M. O. Andreae (2000), Flux of dimethylsulfide from the oceans: A comparison of updated datasets and flux models, *J. Geophys. Res.*, 105(D22), 26,793–26,808, doi:10.1029/2000JD900252.
- Kettle, A. J., et al. (1999), 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. Cycles*, 13(2), 399–444, doi:10.1029/1999GB900004.
- Kloster, S., J. Feichter, K. D. Six, P. Stier, and P. Wetzel (2006), Biogeosciences DMS cycle in the marine ocean–atmosphere system—A global model study, *Biogeosciences*, 3, 29–51, doi:10.5194/bg-3-29-2006.
- Kloster, S., K. D. Six, J. Feichter, E. Maier-Reimer, E. Roeckner, P. Wetzel, P. Stier, and M. Esch (2007), Response of dimethylsulfide (DMS) in the ocean and atmosphere to global warming, *J. Geophys. Res.*, 112, G03005, doi:10.1029/2006JG000224.
- Korhonen, H., K. S. Carslaw, D. V. Spracklen, G. W. Mann, and M. T. Woodhouse (2008), Influence of oceanic dimethyl sulfide emissions on cloud condensation nuclei concentrations and seasonality over the remote Southern Hemisphere oceans: A global model study, *J. Geophys. Res.*, 113, D15204, doi:10.1029/2007JD009718.
- Lana, A. M. C. (2012), Marine aerosols, their precursors and their influence on clouds over the global ocean, Universitat Politècnica de Catalunya, Institut de Ciències del Mar (ICM-CSIC).
- Lana, A., et al. (2011), An updated climatology of surface dimethylsulfide concentrations and emission fluxes in the global ocean, *Global Biogeochem. Cycles*, 25, GB1004, doi:10.1029/2010GB003850.
- Lana, A., R. Simó, S. M. Vallina, and J. Dachs (2012), Potential for a biogenic influence on cloud microphysics over the ocean: A correlation study with satellite-derived data, *Atmos. Chem. Phys.*, 12, 7977–7993, doi:10.5194/acp-12-7977-2012.
- Levasseur, M., et al. (2006), DMSP and DMS dynamics during a mesoscale iron fertilization experiment in the Northeast Pacific—Part I Temporal and vertical distributions, *Deep Sea Res., Part II*, 53, 2353–2369, doi:10.1016/j.dsr2.2006.05.023.
- Lohmann, U., J. Feichter, C. C. Chuang, and J. E. Penner (1999), Prediction of the number of cloud droplets in the ECHAM GCM, *J. Geophys. Res.*, 104(D8), 9169–9198, doi:10.1029/1999JD900046.
- Lohmann, U., P. Stier, C. Hoose, S. Ferrachat, S. Kloster, E. Roeckner, and J. Zhang (2007), Cloud microphysics and aerosol indirect effects in the global climate model ECHAM5-HAM, *Atmos. Chem. Phys.*, 7(13), 3425–3446, doi:10.5194/acp-7-3425-2007.
- Lucas, D. D., and R. G. Prinn (2005), Parametric sensitivity and uncertainty analysis of dimethylsulfide oxidation in the clear-sky remote marine boundary layer, *Atmos. Chem. Phys.*, 5(6), 1505–1525, doi:10.5194/acp-5-1505-2005.
- Machenhauer, B., and I. Kirchner (2000), Diagnosis of systematic initial tendency errors in the ECHAM AGCM using slow normal mode data-assimilation of ECMWF reanalysis data, *Clivar Exch.*, 5, 9–10.
- Makkonen, R., A. Asmi, V.-M. Kerminen, M. Boy, A. Arneth, P. Hari, and M. Kulmala (2012), Air pollution control and decreasing new particle formation lead to strong climate warming, *Atmos. Chem. Phys.*, 12(3), 1515–1524, doi:10.5194/acp-12-1515-2012.
- Meskhidze, N., and A. Nenes (2006), Phytoplankton and cloudiness in the Southern Ocean, *Science*, 314(5804), 1419–1423, doi:10.1126/science.1131779.
- Monahan, E., D. Spiel, and K. Davidson (1986), A model of marine aerosols generation via whitecaps and wave disruption, in *Oceanic Whitecaps and Their Role in Air-Sea Exchange*, pp. 167–174, D. Reidel, Norwell, Mass.
- Murphy, D. M., D. S. Thomson, and A. M. Middlebrook (1997), Bromine, iodine, and chlorine in single aerosol particles at Cape Grim, *Geophys. Res. Lett.*, 24(24), 3197–3200, doi:10.1029/97GL03195.
- Nightingale, D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, 14(1), 373–387, doi:10.1029/1999GB900091.
- Pozzoli, L., I. Bey, S. Rast, M. G. Schultz, P. Stier, and J. Feichter (2008), Trace gas and aerosol interactions in the fully coupled model of aerosol-chemistry-climate ECHAM5-HAMMOZ: 1. Model description and insights from the spring 2001 TRACE-P experiment, *J. Geophys. Res.*, 113, D07308, doi:10.1029/2007JD009007.
- Pozzoli, L., G. Janssens-Maenhout, T. Diehl, I. Bey, M. G. Schultz, J. Feichter, E. Vignati, and F. Dentener (2011), Re-analysis of tropospheric sulfate aerosol and ozone for the period 1980–2005 using the aerosol-chemistry-climate model ECHAM5-HAMMOZ, *Atmos. Chem. Phys.*, 11(18), 9563–9594, doi:10.5194/acp-11-9563-2011.
- Quinn, P. K., and T. S. Bates (2011), The case against climate regulation via oceanic phytoplankton sulphur emissions, *Nature*, 480, 51–6, doi:10.1038/nature10580.
- Riccobono, F., et al. (2014), Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles, *Science*, 344(6185), 717–721, doi:10.1126/science.1243527.
- Roeckner, E., et al. (2003), *The Atmospheric General Circulation Model ECHAM5: Part 1*, Max Planck Institute for Meteorology, Hamburg, Germany.
- Royer, S.-J., et al. (2010), Microbial dimethylsulfoniopropionate (DMSP) dynamics along a natural iron gradient in the northeast subarctic Pacific, *Am. Soc. Limnol. Oceanogr.*, 55(4), 1614–1626, doi:10.4319/lo.2010.55.4.1614.
- Schultz, M. G., A. Heil, J. J. Hoelzemann, A. Spessa, K. Thonicke, J. G. Goldammer, A. C. Held, J. M. C. Pereira, and M. van het Bolscher (2008), Global wildland fire emissions from 1960 to 2000, *Global Biogeochem. Cycles*, 22, GB2002, doi:10.1029/2007GB003031.
- Schulz, M., G. de Leeuw, and Y. Balkanski (2004), Sea-salt aerosol source functions and emissions, in *Emissions of Atmospheric Trace Compounds*, pp. 333–359, Springer, New York.
- Sciare, J., N. Mihalopoulos, F. J. Dentener, and L. Sciare (2000), Interannual variability of atmospheric dimethylsulfide in the southern Indian Ocean, *J. Geophys. Res.*, 105(D21), 26,369–26,377, doi:10.1029/2000JD900236.
- Simo, R. (2001), Production of atmospheric sulfur by oceanic plankton: Biogeochemical, ecological and evolutionary links, *Trends Ecol. Evol.*, 16(6), 287–294.
- Simó, R., and J. Dachs (2002), Global ocean emission of dimethylsulfide predicted from biogeophysical data, *Global Biogeochem. Cycles*, 16(4), 1078, doi:10.1029/2001GB001829.
- Six, K. D., and E. Maier-Reimer (2006), What controls the oceanic dimethylsulfide (DMS) cycle? A modeling approach, *Global Biogeochem. Cycles*, 20, GB4011, doi:10.1029/2005GB002674.
- Smith, M., and N. Harrison (1998), The sea spray generation function, *J. Aerosol Sci.*, 29, 189–190.

- Smith, S. J., J. van Aardenne, Z. Klimont, R. J. Andres, A. Volke, and S. Delgado Arias (2011), Anthropogenic sulfur dioxide emissions: 1850–2005, *Atmos. Chem. Phys.*, *11*, 1101–1116, doi:10.5194/acp-11-1101-2011.
- Stier, P., J. Feichter, S. Kinne, S. Kloster, E. Vignati, J. Wilson, L. Ganzeveld, I. Tegen, and M. Werner (2005), The aerosol-climate model ECHAM5-HAM, *Atmos. Chem. Phys.*, *5*, 1125–1156.
- Tegen, I., S. P. Harrison, K. Kohfeld, I. C. Prentice, M. Coe, and M. Heimann (2002), Impact of vegetation and preferential source areas on global dust aerosol: Results from a model study, *J. Geophys. Res.*, *107*(D21), 4576, doi:10.1029/2001JD000963.
- Thomas, M. A., P. Suntharalingam, L. Pozzoli, S. Rast, A. Devasthale, S. Kloster, J. Feichter, and T. M. Lenton (2010), 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.
- Thomas, M. A., P. Suntharalingam, L. Pozzoli, A. Devasthale, S. Kloster, S. Rast, J. Feichter, and T. M. Lenton (2011), Rate of non-linearity in DMS aerosol-cloud-climate interactions, *Atmos. Chem. Phys.*, *11*, 1175–1183, doi:10.5194/acp-11-1175-2011.
- Twohy, C. H., and J. R. Anderson (2008), Droplet nuclei in non-precipitating clouds: Composition and size matter, *Environ. Res. Lett.*, *3*(4), 045002, doi:10.1088/1748-9326/3/4/045002.
- Uppala, S. M., et al. (2005), The ERA-40 re-analysis, *Q. J. R. Meteorol. Soc.*, *131*(612), 2961–3012, doi:10.1256/qj.04.176.
- Vallina, S. M., and R. Simó (2007), Strong relationship between DMS and the solar radiation dose over the global surface ocean, *Science*, *315*(5811), 506–508, doi:10.1126/science.1133680.
- Vignati, E., J. Wilson, and P. Stier (2004), M7: An efficient size-resolved aerosol microphysics module for large-scale aerosol transport models, *J. Geophys. Res.*, *109*, D22202, doi:10.1029/2003JD004485.
- Vogt, M., S. M. Vallina, E. T. Buitenhuis, L. Bopp, and C. Le Quéré (2010), Simulating dimethylsulphide seasonality with the Dynamic Green Ocean Model PlankTOM5, *J. Geophys. Res.*, *115*, C06021, doi:10.1029/2009JC005529.
- Wong, C. S., S. E. Wong, W. A. Richardson, G. E. Smith, and M. Arychuk (2005), Temporal and spatial distribution of dimethylsulfide in the subarctic northeast Pacific Ocean: A high-nutrient–low-chlorophyll region, *Tellus*, *57B*, 317–331.
- Woodhouse, M. T., G. W. Mann, K. S. Carslaw, and O. Boucher (2008), New directions: The impact of oceanic iron fertilisation on cloud condensation nuclei, *Atmos. Environ.*, *42*(22), 5728–5730, doi:10.1016/j.atmosenv.2008.05.005.
- Woodhouse, M. T., K. S. Carslaw, G. W. Mann, S. M. Vallina, M. Vogt, P. R. Halloran, and O. Boucher (2010), Low sensitivity of cloud condensation nuclei to changes in the sea-air flux of dimethyl-sulphide, *Atmos. Chem. Phys.*, *10*(16), 7545–7559.
- Woodhouse, M. T., G. W. Mann, K. S. Carslaw, and O. Boucher (2013), Sensitivity of cloud condensation nuclei to regional changes in dimethyl-sulphide emissions, *Atmos. Chem. Phys.*, *13*, 2723–2733, doi:10.5194/acp-13-2723-2013.