LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-JRNL-471220

Changes in Dimethyl Sulfide Oceanic Distribution due to Climate Change

P. Cameron-Smith, S. Elliott, M. Maltrud, D. Erickson, O. Wingenter

February 18, 2011

Geophysical Research Letters

Final version for publication in GRL (Feb 16, 2011)

Changes in Dimethyl Sulfide Oceanic Distribution due to Climate Change

Philip Cameron-Smith[1], Scott Elliott[2], Mathew Maltrud[2], David Erickson[3], and Oliver Wingenter[4]

[1]Atmospheric, Earth and Energy Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550.

[2]Climate Ocean Sea Ice Modeling (COSIM), Los Alamos National Laboratory, MS B216, Los Alamos National Laboratory, Los Alamos, NM 87545.

[3]Mathematics and Computer Sciences, Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37831.

[4]Geophysical Research Center and Department of Chemistry, New Mexico Institute of Mining and Technology, 801 Leroy Place, Socorro, NM 87801.

Abstract

Dimethyl sulfide (DMS) is one of the major precursors for aerosols and cloud condensation nuclei in the marine boundary layer over much of the remote ocean. Here we report on coupled climate simulations with a state-of-the-art global ocean biogeochemical model for DMS distribution and fluxes using present-day and future atmospheric CO_2 concentrations. We find changes in zonal averaged DMS flux to the atmosphere of over 150% in the Southern Ocean. This is due to concurrent sea ice changes and ocean ecosystem composition shifts caused by changes in temperature, mixing, nutrient, and light regimes. The largest changes occur in a region already sensitive to climate change, so any resultant local CLAW/Gaia feedback of DMS on clouds, and thus radiative forcing, will be particularly important. A comparison of these

results to prior studies shows that increasing model complexity is associated with reduced DMS emissions at the equator and increased emissions at high latitudes.

1. Introduction

The Southern Ocean is a setting for strong teleconnections among the systems of global climate change. Primary production, carbon drawdown and convective return of nutrients are planetary in scale in this region [*Longhurst*, 1998]. Large areas of oceanic surface waters are severely iron limited such that atmospheric dust inputs and human intervention may both be capable of modulating major element geocycling [*Gabric et al.*, 2010; *Wingenter et al.*, 2004]. The mid-latitude westerlies force the Antarctic Circumpolar Current (ACC) and generate Ekman upwelling which may drive Antarctic ice shelf loss [*Alley et al.*, 2008], and perhaps also play into the global meridional overturning [*Toggweiler and Russell*, 2008]. Sulfur cycle climate feedback linkages, such as the CLAW hypothesis [*Charlson et al.*, 1987; *Erickson et al.*, 1990; *Gabric et al.*, 2001] are also largest in the Southern Ocean because sea-air transfer of dimethyl sulfide (DMS) tends to rise with biological productivity, and the source of sulfate aerosols in the atmosphere over the Southern Ocean is dominated by oceanic DMS emissions (as opposed to anthropogenic sulfur emissions).

Models for the distribution of marine DMS have lately been increasing in number and complexity such that a regional portrait of their evolving climate response is constructible. We present here initial results of the consequences of climate change from the most sophisticated ocean sulfur cycle model yet reported, as well as the apparent connection between the sophistication of the model and the predicted response of the sulfur cycle to climate change. The various models, grouped into three generations based on their complexity and formulation, are described in the auxiliary material. The changes in their DMS emissions in response to climate change are somewhat varied, and are summarized in Table 1.

Unfortunately, it is hard to determine the best model using observations because experiments using seawater from different ecosystems with elevated CO_2 and/or temperature show varied responses too [*Lee et al*., 2009; *Kim et al*., 2010; *Hopkins et al*., 2010; *Vogt et al*., 2008; *Wingenter et al*., 2007]. Most of the experiments showed increases in DMS concentration, but a major complicating factor in understanding those results is that the studies each strained out different sizes of the mesozooplankton.

2. Our Modeling & Results

We report here on the first marine sulfur simulations performed in the Community Climate System Model (CCSM; *Collins et al*. [2006]). We used the most recent version of CCSM available at the time, which was an unreleased version between v3.5 and v4.0. CCSM contains the Parallel Ocean Program (POP; *Smith and Gent* [2004]) as its ocean general circulation model and utilizes a carbon/nitrogen/silicon/iron ocean ecosystem model with biological resolution exceeding any of the other models discussed in this paper (diatoms, coccolithophores, diazotrophs and collective picoplankton are all distinguished; *Moore et al*. [2004]). We then attached the DMS mechanism developed and validated by Elliott [2009] for global flux studies, which includes the high sulfur producer *Phaeocystis*, and is described in the auxiliary material. Though still highly parameterized, this DMS model constitutes a steady advance in detail, even relative to the latest studies, and we consider it to be a fourth generation model.

The version of CCSM we used had not been fully tuned and exhibited a large Arctic cold bias that resulted in unrealistically extensive and persistent sea ice. However, comparisons of the climate in the Southern Hemisphere with results from standard CCSM3 simulations (including sea ice extent, SST, zonal wind stress, Drake Passage transport, and a number of other quantities) were sufficiently good that we feel justified in presenting our results for the Southern Hemisphere in this paper. Furthermore, even though we expect the high northern sulfur chemistry to be just as compelling scientifically as that of the Southern Ocean, the DMS effect on cloud brightness is often overshadowed in the northern hemisphere by anthropogenic sulfate [*Schlesinger*, 1997].

We spun up the ocean model without biogeochemistry for one hundred years from rest using climatological states for the atmosphere, sea ice, and land components. The final ocean state was then adopted as the initial condition for a 30 year fully coupled simulation where atmospheric carbon dioxide was set at the late twentieth century value 355 ppm. Major element geocycling in the ocean was also initiated at this point, with initial conditions derived from a variety of data sources and idealized distributions [*Moore et al*., 2004]. The end state of this three decade coupled spinup was then taken as the initial state for two time-slice simulations. In one simulation, atmospheric carbon dioxide remained at 355 ppm. In the second simulation the CO_2 concentration was set at 970 ppm in order to simulate a possible climate for the end of the 21st century (based on the IPCC SRES scenario A1FI given by *IPCC* [2001]). This is at the high end of IPCC SRES estimates, but is entirely plausible given recent estimates of actual emissions [Raupach, et al., 2007; Friedlingstein, et al., 2010]. If CO_2 concentration growth is different than this scenario, then our simulations represent the date at which 970 ppm occurs. Both calculations were carried forward sixty years with constant CO_2 forcing such that the physics and geochemistry of the upper ocean attained an approximate steady state. Using steady-state rather than trend simulations was computationally expedient, avoided ocean spin-up issues for trend runs, and makes the comparison between the two runs much cleaner. This does mean we ignored any lag in system response to the CO_2 forcing, but the primary effect should be just a delay in timing and shouldn't affect our main conclusions about DMS sensitivity to CO_2 forcing. To compare the changes between the two runs we averaged all quantities over the final ten years of the two runs, and we verified that the differences we note in this work exceeded local standard deviations.

We validated the results of our contemporary simulation using the climatology of *Kettle and Andreae* [2000] and the strategies outlined by *Elliott* [2009] and *Le Clainche, et al*., [2010] for uncoupled simulations. Our agreement with the data was comparable to those two works. The surface ocean DMS concentration fields are shown in Figure S1 (auxiliary material) for the two carbon dioxide levels. There are a couple of features worth commenting on here. We see rings of high DMS near Antarctica due to the inclusion of a *Phaeocystis* parameterization. This class of organism generates several times the typical DMSP level (dimethyl sulfoniopropionate, a major DMS precursor) and favors cold water habitat [*Matrai and Vernet*, 1997]. We see a DMS minimum zone between 40ºS and 60ºS that is due in part to the dominance of diatoms, which have very low sulfur content. This circumpolar minimum is less prominent in the DMS climatology of *Kettle & Andreae* [2000], but is present in the work of *Kloster et al*. [2007].

Figure 1 (top) shows the difference in DMS flux between the two simulations at the ocean-atmosphere interface. The annular pattern is due almost entirely to poleward shifts in the phytoplankton community structure, which are important in many marine ecological contexts (e.g. *Hallegraeff* [2010]). As the ocean warms, the diatoms (which dominate south of 40ºS) migrate toward the south, allowing smaller phytoplankton with greater sulfur content to contribute more to the biomass, resulting in elevated DMS flux in the band between 30ºS and 50ºS. The alternating bands between 55ºS and Antarctica are due the southward shift of

Phaeocystis, which becomes dominant under ice retreat due to its cold water preference, but loses habitat toward the north as the ocean warms. Integrated over the entire Southern Hemisphere, the total amount of DMS transferred to the atmosphere in the 970 ppm run dropped by 3.5% compared to the 355 ppm case.

Formal intercomparisons between DMS models are only beginning to appear for even contemporary DMS distributions [*Le Clainche. et al*., 2010], and there have been no attempts to extend them into the future. Hence, we opt for a qualitative approach in Table 1, focusing on significant climate change over time scales spanning many decades. Comparison of our results to the third generation models shows that our runs amplify their dynamic ecology results. However, distinctions may be drawn with respect to the first and second generation statistical approaches, which tended to be regional and uni- or else bivariate. Their flux changes were consistently positive and in some cases very low in magnitude. Given increasing model domain, resolution, and ecosystem complexity moving downward through the table, it appears that sourcing may be reduced in the central gyre by order ten percent while increases of tens to hundreds of percent are possible at higher latitudes.

3. Analysis and Discussion

Indirect aerosol effects are thought to be critical to climate evolution, and DMS is one of the major precursors for aerosols and cloud condensation nuclei in the marine boundary layer over much of the remote ocean. In this regard, it is clear from our model that a meridional redistribution of DMS flux in the warming world may occur across the entire Southern Hemisphere, with potentially significant effects on high latitude clouds. In global estimates involving constant upward or downward DMS flux changes, average planetary surface temperatures separate by three or more degrees Celsius [*Charlson et al*., 1987; *Gunson et al*., 2006]. Since the Southern Ocean is more cloudy than the global average, and an absorptive surface (the ocean) lies below the clouds, the regional importance of DMS emissions is likely to be even greater.

DMS-albedo coupling has been investigated in models ranging from the conceptual to full atmospheric chemistry-climate simulations [*Charlson et al*., 1987; *Gunson et al*., 2006]. Typically, emissions have been raised or lowered by the same proportion at all locations. However, there are several ways in which regional contrasts may be of greater importance, and seasonal swings in brightness will be superimposed [*Gabric et al*., 2001; *Bopp et al*. 2003; *Vallina et al*. 2007; the present work]. Since our emissions of DMS follow shifts in the distribution of the cold-loving *Phaeocystis*, if the resulting sulfate is able to cool the local ocean, then it is possible that the production of DMSP is an ecosystem adaptation for habitat maintenance. This has echoes of the CLAW/Gaia hypothesis [*Charlson et al*., 1987].

The Southern Ocean is a place where the hydrosphere, cryosphere, atmosphere and marine biosphere interact in a myriad of complex ways. A partial list of coincident features includes: our DMS changes; annular ecosystems and massive circumpolar currents [*Longhurst*, 1998]; the atmospheric Southern Annular Mode (SAM) which is in turn constrained/guided by the Drake passage (60^o south; *Toggweiler and Russell* [2008]); the implied geostrophic westerly winds; ocean acidification; seasonal migration of the ice edge; whale/krill fisheries driven foodweb structure; and Ekman pumping along the Antarctic coast - which may well be implicated in ice sheet destabilization [*Alley et al*., 2008]. Because of the interconnections of all these features, the conclusion of a shift in DMS production causing south polar cooling may be premature. The only real way to evaluate the full effects will be in Earth systems models (ESMs) that couple in atmospheric chemistry and the aerosol indirect effects on clouds.

We must also consider whether any results will be robust to upcoming improvements in the ecodynamics models, which currently constitute the weakest link in such ESM simulations. In a preview of other exercises we have conducted, the DMS shift is usually reinforced with even more sophisticated models. For example, in this paper the low DMSP cyanobacteria are only significant in warmer areas, with their maximum contribution fixed at one half of local biomass based on measurements [*Elliott*, 2009]. But, parameter settings in complete and non-sulfurous ecology schemes [*Gregg et al*., 2003] suggest that future stratification will favor the prokaryotes more dramatically. Thus, gyre concentrations may be overpredicted.

Several authors have noted that flagellates can broaden their influence in a warmer world along with *Phaeocystis* [*Gabric et al*., 2003]. Both classes of organism are notably sulfur rich. The ice algae are also intense producers [*Levasseur et al*., 1994], and it might be expected that as their habitat retreats some degree of compensation should ensue. We are now configuring ice biogeochemical dynamics codes to simulate this prospect. In early runs the effects appear to be locally critical but two dimensional in nature – they are most important along a thin band of surface water tracking the ice margin in the springtime. The latter arguments deal exclusively with the phytoplankton and their cellular make up.

Literature reviews have recently shown that microbial ecology will also be critical to the comprehension of sulfur during the next century (e.g. *Stefels et al.* [2007]). It is possible that bacterial trace element demand, demethylation yield, ultraviolet or temperature sensitivity, and taxonomy must all be accounted with fidelity. Most of these processes are now lacking for all the models we have described. Unfortunately, the number of metabolic and chemical channels which must be simulated in ocean ecosystem models is already computationally expensive, the requisite parameter sets remain highly uncertain, and both problems grow rapidly with increasing model sophistication. Future models will therefore benefit from experimental data that can constrain the critical parameters for these processes and the behavior of the overall system to climate changes. Examples of valuable, measurable quantities include the reduced sulfur and precursor compounds (particularly concentrations of DMSPp, DMSPd, DMS, and DMS flux to the atmosphere), producing/consuming organism densities, and sulfur processing rates using isotope injection. To test responses to climate change, it would be valuable to sample areas naturally high in ocean acidity such as upwelling regions [*Hauri et al*., 2009] as a proxy for future changes to phytoplankton physiology and ecosystem community structure.

Conclusions

We have reported here on a state-of-the-art global ocean biogeochemical simulation of DMS distribution and fluxes for atmospheric CO_2 concentrations of 355 ppm and 970 ppm, corresponding to present-day and a possible 2100 scenario respectively. We find changes in DMS flux to the atmosphere of 50% or more over large regions of the Southern Ocean due to concurrent sea ice changes and shifts in ocean ecosystem composition. A comparison of these results to prior studies shows that increasing model complexity is associated with reduced DMS emissions at the equator and increased emissions at high latitudes.

Acknowledgements. We thank two anonymous reviewers for their suggestions. National laboratory authors were supported by the U.S. DOE OBER SciDAC project. Wingenter was supported by the NMIMT Geophysical Research Center. We used the Oak Ridge Leadership Facility at the Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. Part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

Alley, R. B., M. Fahnestock, and I. Joughin (2008), Understanding glacier flow in changing times, *Science*, **322**, 1061-1062.

Bopp, L., O. Aumont, S. Belviso, and P. Monfray (2003), Potential impact of climate change on marine dimethyl sulfide emissions, *Tellus*, **55B**, 11-22.

Charlson, R.J., J.E. Lovelock, M.O. Andreae, and S.G. Warren (1987), Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, **326**, 655-661.

Collins, and 14 co-authors (2006), The Community Climate System Model Version 3 (CCSM3), *Journal of Climate*, 19, 2122-2143.

Elliott, S. (2009), Dependence of DMS global sea-air flux distribution on transfer velocity and concentration field type, *J. Geophys. Res. (Biogeosci.*), 114, G02001, doi:10.1029/2008JG000710.

Erickson, D. J. III, S. Ghan, and J. Penner (1990), "Global ocean to atmosphere dimethyl sulfide flux," *J. Geophys. Res*. **95**, 7543-7552.

Friedlingstein P., and 9 co-authors (2010), Update on CO2 emissions, *Nature Geoscience,* **3**, 811-812, doi:10.1038/ngeo1022.

Gabric, A., P.H. Whetton, and R. Cropp (2001), Dimethylsulphide in the Subantarctic Southern Ocean under enhanced greenhouse conditions, *Tellus*, **53B**, 273-287.

Gabric, A., R. Cropp, T. Hirst, and H. Marchant (2003), The sensitivity of dimethyl sulfide production to simulated climate change in the eastern Antarctic Southern Ocean, *Tellus*, **55B**, 966-981.

Gabric, A., R. Simo, R.A. Cropp, A.C. Hirst, and J. Dachs (2004), Modeling estimates of the global emission of dimethylsulfide under enhanced greenhouse conditions, *Global Biogeochem. Cycles*, **18**, GB002183.

Gabric, A. J., R. A. Cropp, G. H. McTainsh, B. M. Johnston, H. Butler, B. Tilbrook, and M. Keywood (2010), Australian dust storms in 2002–2003 and their impact on Southern Ocean Biogeochemistry, *Global Biogeochem. Cycles*, **24**, GB2005, doi:10.1029/2009GB003541.

Gregg, W. W., P. Ginoux, and N. W. Casey (2003), Phytoplankton and iron: a global three dimensional biogeochemical model, *Deep Sea Res. II,* **50** 3143-3169.

Gunson, J. R., S. A. Spall, T. R. Anderson, A. Jones, I. J. Totterdell, and M.J. Woodage (2006), Climate sensitivity to ocean dimethyl sulfide emissions, *Geophys. Res. Lett.*, **33**, GL24928.

Hallegraeff, G.M. (2010), Ocean climate change, phytoplankton community responses and harmful algal blooms: A formidable predictive challenge. *J. Phycol*. **46**, 220-235.

Hauri C., N. Gruber, G. K. Plattner, S. Alin, R. A. Feely, B. Hales, and P. A. Wheeler (2009), Ocean Acidification in the California Current System, *oceanography*, **22**, 60-71.

Hopkins, F. E., S. M. Turner, P. D. Nightingale, M. Steinke, D. Bakker, and P. S. Liss (2010), Ocean acidification and marine trace gas emissions. *Proc. Natl. Acad. Sci.*, **107**, 760–765.

IPCC, 2001: Houghton, J.T.,Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson (eds.), *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Kettle, A. J. and M. O. Andreae (2000), Flux of dimethyl sulfide from the oceans: A comparison of updated data sets and flux models, *J. Geophys. Res.*, **105**, 26793-26808.

Kim, J. M., and 14 co-authors (2010), Enhanced Production of Oceanic Dimethylsulfide Resulting from CO_2-Induced Grazing Activity in a High CO_2 World. *Environ. Sci. & Tech.*, **44**, 8140-8143.

Kloster, S. and 7 co-authors (2007), Response of dimethylsulfide (DMS) in the ocean and atmosphere to global warming, *J. Geophys. Res.*, **112**, doi:10.1029/2006JG000224.

Le Clainche, Y. and 18 co-authors (2010), A first appraisal of prognostic ocean DMS models and prospects for their use in climate simulation. *Global Biogeochem. Cycles*, **24**, doi:10.1029/2009GB003721.

Lee, P. A., and 11 co-authors (2009) Effects of increased pCO_2 and temperature on the North Atlantic spring bloom. III. Dimethylsulfoniopropionate. *Mar. Ecol. Prog. Ser.*, **388**, 41–49.

Levasseur, M., M. Gosselin, and S. Michaud (1994), New source of dimethylsulfide (DMS) for the arctic atmosphere: ice diatoms, *Mar. Biol.*, **121**, 381-387.

Longhurst, A. (1998), *Ecological Geography of the Sea*, Academic, San Diego, California.

Matrai, P., and M. Vernet (1997), Dynamics of the vernal bloom in the marginal ice zone of the Barents Sea: Dimethyl sulfide and dimethylsulfoniopropionate budgets, *J. Geophys. Res.*, **102**(C10), 22965-22979.

Moore, J. K., S. Doney, and K. Lindsay (2004), Upper ocean ecosystem dynamics and iron cycling in a global 3D model, *Global Biogeochem. Cycles*, **18**, doi:10.1029 /2004GB002220.

Raupach, M. R., G. Marland, P. Ciais, C. Le Quéré, J. G. Canadell, G. Klepper, and C. B. Field (2007), Global and regional drivers of accelerating CO2 emissions, *Proc. Natl. Acad. Sci.*, **104** (24), 10288-10293, doi:10.1073/pnas.0700609104

Schlesinger, W.H. (1997), *Biogeochemistry: an analysis of global change*, 2nd edition: Academic Press, San Diego, California.

Smith, R. D., and P. R. Gent (2004). Reference manual for the Parallel Ocean Program (POP): ocean component of the Community Climate System Model (CCSM2.0 and 3.0). *Tech. Rep. LA-UR-02-2484*, Los Alamos National Laboratory, Los Alamos, NM, 75 pp. (Available from: http://www.ccsm.ucar.edu/models/ccsm3.0/pop/)

Stefels, J., M. Steinke, S. Turner, G. Malin and S. Belviso (2007), Environmental constraints on the production and removal of the climatically active gas dimethylsulphide, *Biogeochemistry*, **83**, 245-275.

Toggweiler, J. R., and J. Russell (2008), Ocean circulation in a warming climate, *Nature*, **451**, doi:10.1038.

Vallina, S. M., R. Simo, and M. Manizza (2007), Weak response of oceanic dimethylsuflide to upper mixing shoaling induced by global warming, *PNAS*, **104**, 16004-16009.

Vogt M., M. Steinke, S. Turner, A. Paulino, M. Meyerhoefer, U. Riebesell, C. LeQuere and P. Liss (2008), Dynamics of dimethylsulphoniopropionate and dimethylsulphide under different CO_2 concentrations during a mesocosm experiment, *Biogeosciences* **5**, 407–419.

Wingenter, O.W., K.B. Haase, P. Strutton, G. Friederich, S. Meinardi, D.R. Blake, F.S. Rowland (2004), Changing concentrations of CO, CH_4, C_5H_8, CH_3Br, CH_3I, and dimethyl sulfide during the Southern Ocean Iron Enrichment Experiments, *Proc. Natl. Acad. Sci.*, **101**(23), 8537-8541, doi:10.1073.

Wingenter, O. W., and 11 co-authors (2007), Unexpected consequences of increasing CO_2 and ocean acidity on marine production of DMS and CH_2ClI: Potential climate impacts, *Geophys. Res. Lett.*, **34**, L05710, doi:10.1029/2006GL028139.

Figure 1. *Top*: Absolute difference in DMS flux (nanomoles/m^2/s) between the final decades of the 60 year CCSM simulations. Positive values indicate that the 970 ppm simulation transfers more DMS to the atmosphere than the 355 ppm case. *Bottom*: Percentage difference of DMS flux for the 970 ppm simulation relative to the 355 ppm simulation. Note: values above +150% have been clipped so that the small and moderate magnitude features can be seen.

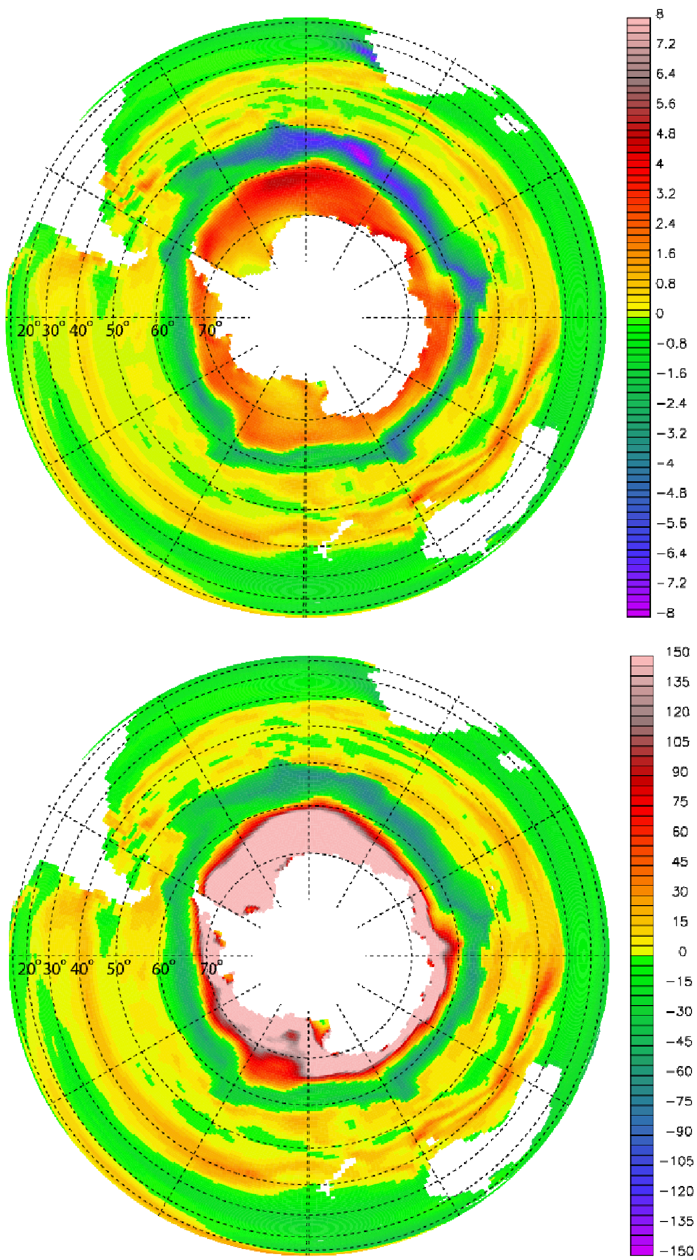

Table 1. Annual average increase in DMS flux going from a present-day climate to a future climate, in 10° latitude bands, for the models described in the auxiliary material[a].

Gener-ation	Reference	Degrees South Latitude								Interpretation
		80-70	**70-60**	**60-50**	**50-40**	**40-30**	**30-20**	**20-10**	**10-Eq**	
1st	*Gabric et al.*, 2001,03		+30		+5					Ice cover domiates
2nd	*Gabric et al.*, 2004		+50	+105	+30	+10	+5	+5	+5	ML[b] changes dominate
2nd	*Vallina et al.*, 2007	-5	0	+5	+5	0	0	+5	+5	ML[b] changes dominate, notes [c,d]
3rd	*Bopp et al.*, 2003		0	(+10)	+30	+10	(0)	(-10)	-15	See text, notes [e,f,g]
3rd	*Kloster et al.*, 2007	>+30	+10	-20	0	0	-10	-10	-10	See text, notes [e,g]
4th	This work	+170	+70	-15	+5	0	-10	-10	-10	See text.

[a]The percentage changes are taken directly from text interpretations in the original work wherever possible, and rounded to the nearest 5%.

[b]ML stands for 'mixed layer'.

[c]No zonal integrations presented so that samples were taken along meridians central to the Pacific, Atlantic and Indian basins.

[d]Their run duration was fifty years, which therefore had less greenhouse gas buildup than the other models (see table S1).

[e]Zonal average flux perturbations reported most directly in the text.

[f]Parenthetical values indicate interpolation.

[g]Checks performed against zonal concentration integrations.

Auxiliary Material

Model Descriptions

In the first generation model of *Gabric et al*. [2001, 2003], coupled but coarse general circulation modeling was used to force simulations of a decoupled nitrogen cycle, which in turn controlled sulfate fixation into the reduced precursor DMSP (dimethyl sulfoniopropionate). Kinetic limits on the sulfur concentration of surface layers were imposed by means of time constants representing microbial oxidation, and sea-air transfer was computed using parameterizations for generic marine trace gases. The model was used for a series of simulations extending from Tasmania to the Antarctic coast. Because the mechanisms were nitrogen decoupled such that the full evolution of nutrient fields could not be captured, major effects on the reduced sulfur flux were restricted to wind/temperature functionality of the piston velocity and to reductions in ice cover. In these simulations the effect on DMS concentration of a warmer world was positive and of order tens of percent, as shown in Table 1.

Under contemporary climate it is possible to model the DMS distribution as a multivariate correlation over a wide range of oceanographic drivers fitted to the climatology of *Kettle and Andreae* [2000]. This was the basis for the second generation of models. In one of these, DMS was considered a function of both local chlorophyll and mixed layer depth [*Gabric et al*., 2004]. Positive flux changes due to climate change are apparent across the hemisphere, and beneath winds representative of 50S the mixed layer effect was extreme. Only annual averages are included in Table 1, but it is noteworthy that seasonal increases in DMS release were of order hundreds of percent in summer.

A particularly simple relationship can be demonstrated in the present day between DMS and light dose. *Vallina et al.* [2007] extended this concept to climate change by estimating the evolution of total mixed layer radiation exposure for a fixed average chlorophyll density to create their second generation model. Since their penetration scale depth was constant, integrated wattages and DMS are both dependent mainly on season and mixed layer depth. *Vallina et al*. calculate and plot only sulfur concentration changes. We converted these to flux changes, for comparison to the other models in table 1, using the *Elliott* [2009] transfer constants and modeled temperature/wind fields. The emission changes of *Vallina et al.* are consistently a few percent positive. The low magnitude follows in part from their run duration of just fifty years, which therefore had less greenhouse gas buildup.

Bopp et al. [2003] included both the marine phosphorus and silicon cycles then represented sulfur release as a function of the local diatom fraction, including taxonomic variation of intracellular DMSP. Shortly thereafter, *Kloster et al*. [2007] performed similar experiments with a more detailed sulfur mechanism, for which parameters were determined in advance through formal optimization against climatology. In these third generation models, ten percent level reductions occurred at low latitudes, with large increases in polar seas. Within the seasonal ice domain, *Kloster et al*. [2007] offer the interpretation that loss of coverage leads to enhanced biological production while simultaneously enabling sea air transfer.

These third generation models essentially agree that, within a given region, multiple agents of sulfur cycle alteration may be intensely coupled because: 1.) stratification reduces resource inputs and hence overall production, 2.) resource restrictions shift taxonomic structures away from the diatoms, which are relatively low in sulfur, 3.) maximum mixing depths alter the degree of winter nutrient injection, while 4.) later in the year the summer minimum modulates the efficiency of radiation uptake, and 5.) the phasing of seasonal thermocline formation dictates growing season length.

The DMS mechanism used in the current work was developed and validated by Elliott [2009] for global flux studies, and can be briefly described as follows. Working from CCSM ecosystem variables, several reduced sulfur specialists are separated out from the carbon-cycle ecosystem groups in which they had previously been lumped. In particular, cyanobacteria (which produce no DMSP) are parameterized according to the pigment simulations of *Gregg et al*. [2003], and *Phaeocystis* (strong producers of DMSP) are given habitat characteristics from *Schoemann et al*. [2005]. For *P. Antarctica*, and related species, these mainly involve a preference for waters below a few degrees centigrade, as reflected in biogeographic identification data and growth rate functions. A fuzzy logic representation of the demethylation fraction is included [*Stefels et al*., 2007] along with heterotrophic bacterial densities functionalized to the autotrophs and reproducing biological uptake rate measurements. Average sulfur ecosystem flow rate was adjusted post hoc to match the documented global burden [*Kettle and Andreae*, 2000]. Further optimization was conducted following the stepwise regression procedures outlined in *Gunst and Mason* [1980], applied in order of increasing area across the ecological provinces [*Longhurst*, 1998]. While several piston velocity schemes were investigated by *Elliott* [2009], the one most consistent with direct flux measurements was selected for the present study. Its main distinguishing feature is lack of the traditional bubble bypass. Though still highly parameterized, this DMS mechanism constitutes a steady advance in detail, even relative to the latest studies, and we consider it to be a fourth generation model.

References for Auxiliary material

Bopp, L., O. Aumont, S. Belviso, and P. Monfray (2003), Potential impact of climate change on marine dimethyl sulfide emissions, *Tellus*, **55B**, 11-22.

Elliott, S. (2009), Dependence of DMS global sea-air flux distribution on transfer velocity and concentration field type, *J. Geophys. Res. (Biogeosci.*), 114, G02001, doi:10.1029/2008JG000710.

Gabric, A., P.H. Whetton, and R. Cropp (2001), Dimethylsulphide in the Subantarctic Southern Ocean under enhanced greenhouse conditions, *Tellus*, **53B**, 273-287.

Gabric, A., R. Cropp, T. Hirst, and H. Marchant (2003), The sensitivity of dimethyl sulfide production to simulated climate change in the eastern Antarctic Southern Ocean, *Tellus*, **55B**, 966-981.

Gabric, A., R. Simo, R.A. Cropp, A.C. Hirst, and J. Dachs (2004), Modeling estimates of the global emission of dimethylsulfide under enhanced greenhouse conditions, *Global Biogeochem. Cycles*, **18**, GB002183.

Gregg, W. W., P. Ginoux, and N. W. Casey (2003), Phytoplankton and iron: a global three dimensional biogeochemical model, *Deep Sea Res. II,* **50** 3143-3169.

Gunst, R.F. and Mason, R.L. (1980) *Regression Analysis and its Applications*, Marcel Dekker, New York.

Kettle, A. J. and M. O. Andreae (2000), Flux of dimethyl sulfide from the oceans: A comparison of updated data sets and flux models, *J. Geophys. Res*., **105**, 26793-26808.

Kloster, S. and 7 others (2007), Response of dimethylsulfide (DMS) in the ocean and atmosphere to global warming, *J. Geophys. Res.*, **112**, doi:10.1029/2006JG000224.

Longhurst, A. (1998), *Ecological Geography of the Sea*, Academic, San Diego, California.

Schoemann, V., and 5 others (2005), *Phaeocystis* blooms in the global ocean and controlling mechanisms: A review, *J. Sea Research*, **53**, 43-66.

Stefels, J., M. Steinke, S. Turner, G. Malin and S. Belviso (2007), Environmental constraints on the production and removal of the climatically active gas dimethylsulphide, *Biogeochemistry*, **83**, 245-275.

Vallina, S. M., R. Simo, and M. Manizza (2007), Weak response of oceanic dimethylsuflide to upper mixing shoaling induced by global warming, *PNAS*, **104**, 16004-16009.

Table S1. Published models that simulate evolution of the Southern marine sulfur cycle[a].

Gener-ation	Reference	Standard Geocycles	Sulfur Scheme	Domain	Model type & resolution	Initial CO_2	Final CO_2
1st	*Gabric et al.* 2001,03	Fix nitrogen, optimized[b]	One generic phytotaxon	Australian sector	Offline 3-5° OAGCM	1960-1970	x3
2nd	*Gabric et al.* 2004	Fix nitrogen, optimized[b]	Correlate ML and Chl	Global	Offline 3-5° OAGCM	1960-1970	x3
2nd	*Vallina et al*. 2007	Decoupled except ML	Correlate radiation	Global	Offline IPSL	Present	x1.5
3rd	*Bopp et al*. 2003	NPZ	Silicon segregation	Global	Offline 2° OAGCM	1995	x2
3rd	*Kloster et al*. 2007	NPZ plus Fe	Si, CaCO3 segregation	Global	Offline 2° OAGCM	1860	2100
4th	This work	N, Si, Fe, C, Ca, Chl	Multiple specialists	Global	Online 1° OAGCM	1995	x3

[a]See auxiliary text for description of generations. Abbreviations: Chl = chlorophyll. OAGCM = coupled ocean atmosphere general circulation model. ML = mixed layer. IPSL = Institute Pierre-Simone Laplace Earth system model. NPZ = nitrogen or phosphorus currency nutrient-phytoplankton-zooplankton reaction set. The 'final CO_2' column gives the approximate scaling factor for the ending CO_2 concentration relative to the initial concentration, or the final year of the simulation.

[b]Optimized to match satellite ocean color observations.

Figure S1. *Top*: Southern Ocean surface DMS concentration (nanomolar) averaged over the final decade of the 60 year CCSM simulation with an atmospheric CO_2 concentration of 355 ppm. *Bottom*: The corresponding plot from the simulation with 970 ppm atmospheric CO_2.