



Influence of oceanic dimethyl sulfide emissions on cloud condensation nuclei concentrations and seasonality over the remote Southern Hemisphere oceans: A global model study

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[1] We use a global chemical transport model with size-resolved aerosol microphysics to investigate the sources of cloud condensation nuclei (CCN) in the Southern Hemisphere remote marine boundary layer (MBL). Long-term observations of CCN number at Cape Grim (40°41'S, 144°41'E) show a clear seasonal cycle with a 2–3 times higher concentration in summer than in winter, which has been attributed to seasonal changes in the dimethyl sulfide (DMS) ocean-to-atmosphere flux. We find that this cycle at Cape Grim and also throughout the 30°–45°S latitude band is caused mostly by changes in the regional-scale DMS ocean water concentration. In this latitude band, DMS emissions increase the simulated CCN concentrations from November to April, with a maximum effect of 46% in January (calculated at 0.23% supersaturation). Farther south, the impact of DMS on CCN is apparent only from December to February and increases the CCN concentration at most by 18% at 45°–60°S and by 40% at 60°–75°S. These model-derived contributions of DMS to Southern Ocean summertime CCN are smaller than the 80% derived from correlations between satellite-observed chlorophyll and column CCN, which we explain in terms of nonlinear behavior of CCN from the free troposphere (FT). We show that the main microphysical pathway of DMS influence on CCN number is nucleation of DMS-derived H₂SO₄ in the FT and subsequent growth of formed particles by condensation and coagulation during entrainment into the MBL. Our simulations suggest that >90% of the increase in MBL CCN when DMS is added to the model is formed in this way. The growth of ultrafine sea spray particles to CCN sizes due to condensation of DMS-derived H₂SO₄ in the MBL affects the simulated CCN concentrations by less than 6%. Overall, entrainment of nucleated sulfate aerosol into the MBL from the FT accounts for 43–65% of the summer zonal mean CCN concentrations but only 7–20% of the winter CCN over the Southern Hemisphere oceans.

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1. Introduction

[2] Oceanic dimethyl sulfide (DMS) has a global emission of 13–37 Tg(S)/a [Kettle and Andreae, 2000] and is an important contributor to the global sulfur cycle. Model studies suggest it accounts for 25–32% of the globally averaged annual SO₂ burden and 18–42% of the particle sulfate burden [Chin and Jacob, 1996; Gondwe et al., 2003; Kloster et al., 2006]. The effect of oceanic DMS on marine climate has been a topic of intense research since Charlson et al. [1987] suggested, in what has become known as the CLAW hypothesis, that DMS may have a capacity to regulate the local or regional climate through its effect on

cloud condensation nuclei (CCN) concentrations. The CLAW hypothesis states that if climate change increases oceanic DMS emissions, cloud albedo in marine environments could also increase owing to higher number concentration of DMS-derived CCN. The increased albedo in turn reduces the amount of short-wave radiation that reaches the lower levels of the atmosphere and thus causes cooling of the Earth's surface.

[3] One of the key steps in validating the CLAW hypothesis is to establish a direct link between DMS emissions and marine CCN concentrations. In theory, DMS can increase the CCN number through three pathways:

[4] 1. First, DMS and its oxidation product SO₂ transported to the free troposphere (FT) are oxidized to H₂SO₄ and can form new particles, most likely through homogeneous nucleation of sulfuric acid-water particles at FT temperatures [Kulmala et al., 1998; Vehkamäki et al.,

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2002; Spracklen *et al.*, 2005b]. The particles formed in the FT grow by condensation and coagulation and can be entrained into the marine boundary layer (MBL) by turbulent diffusion and large-scale transport. While new particle formation in the FT and entrainment of particles into the MBL have been observed frequently [Clarke, 1993; Covert *et al.*, 1996; Clarke *et al.*, 1996, 1999; Clarke and Kapustin, 2002], the importance of DMS as a source of FT H_2SO_4 has been disputed by Ito [1993], who suggests that the main sources in remote marine regions are inert, more long-lived sulfur-containing gases COS and CS_2 . However, Berresheim [1987] has shown that the lifetime of DMS at Southern Ocean latitudes can be at least 1–2 days, which is long enough for at least some of the emitted DMS to be transported into the FT. Furthermore, airborne measurements south of Australia show summertime DMS concentrations up to 2.4 ppt at 3 km altitude, that is, $\sim 5\%$ of the mixed layer concentrations [Berresheim *et al.*, 1990].

[5] 2. The second potential pathway by which DMS can influence marine CCN concentrations is through a change of the MBL particle size distribution via condensation of DMS oxidation products. DMS oxidation in the MBL produces H_2SO_4 vapor that can grow ultrafine sea spray particles to CCN sizes. The importance of this pathway was highlighted in a global model study by Pierce and Adams [2006], who found that condensation growth of ultrafine sea spray particles increases CCN concentrations south of 70°S by $\sim 14\%$.

[6] 3. The third pathway, explored in some model studies, is nucleation of new particles directly in the MBL from DMS-derived H_2SO_4 , which then grow to CCN sizes [Pandis *et al.*, 1994; Yoon and Brimblecombe, 2002]. Although particle formation events have been occasionally observed in the MBL [Clarke *et al.*, 1998; Ehn *et al.*, 2007], they seem to be relatively rare and do not necessarily occur even when the H_2SO_4 concentration is very high, even of the order of 10^8 cm^{-3} [Weber *et al.*, 2001]. Furthermore, both observations [Davison *et al.*, 1996; O'Dowd *et al.*, 1997] and some model studies [Pirjola *et al.*, 2000] indicate that even when the events do occur, they are unlikely to contribute to CCN concentrations significantly over remote regions. This is because of the sporadic nature of the events and because the small particles are quickly lost by coagulation in the absence of high concentrations of condensable vapor.

[7] Observations have clearly shown that DMS affects the marine aerosol mass and size distribution through its oxidation products SO_2 , H_2SO_4 and methanesulfonic acid (MSA). For example, Ayers *et al.* [1991] reported that their multiyear observations from Cape Grim, Tasmania ($40^\circ 41'\text{S}$, $144^\circ 41'\text{E}$), show matching seasonal cycles for atmospheric DMS and aerosol phase MSA (only source DMS) and nss-sulfate (possible sources natural and anthropogenic SO_2 and H_2SO_4). Similar results with concentration peaks in January were reported by Preunkert *et al.* [2007] for an Antarctic coastal site. During a summertime cruise in the northwestern Pacific, Ooki *et al.* [2003] found that areas of high chlorophyll concentration had on average 9 times higher nss-sulfate mass concentration and 2 times higher accumulation mode number concentration than background marine areas. Such correlations are not, however, found in all remote marine data sets, and, for example, Bates *et al.* [1992] found no significant relationship between DMS and

MSA or nss-sulfate during their late summer cruise in the Southern Hemisphere eastern Pacific Ocean. Furthermore, a correlation between DMS and the mass of its oxidation products in the aerosol does not necessarily mean that a similar correlation exists between DMS and CCN concentrations. Impactor measurements at Cape Grim show that the mass concentrations of both MSA and nss-sulfate peak in the aerosol accumulation mode diameter range of $\sim 0.25\text{--}1 \mu\text{m}$ [Andreae *et al.*, 1999], indicating that the majority of nss-sulfate mass has been formed in aqueous phase oxidation reactions of DMS-derived SO_2 . Since these reactions take place in existing cloud droplets, the sulfate formation through this mechanism does not contribute to formation of new CCN but will enable subsequent drop formation to occur at a lower supersaturation on larger particles. It is also important to notice that most of the potential CCN are at sizes smaller than 200 nm, which typically give only a minor signal in mass based measurements.

[8] Field studies looking directly for a link between DMS emissions and CCN number have had variable success. For example, during a 6-week cruise in the South Atlantic, Andreae *et al.* [1995] found DMS to explain over 60% of CN variance but to have a much weaker correlation with measured CCN. O'Dowd *et al.* [1997] failed to observe a correlation with DMS and its expected condensed oxidation products on a 2-month cruise from the Falkland Islands to Antarctica, but saw a moderate correlation between MSA and nss-sulfate CCN (measured with a volatilization technique), suggesting that there is at least a partial link between DMS and CCN. This is further supported by their observation that a spatial correlation existed between DMS and nss-sulfate CCN. On the other hand, a high correlation between DMS and CCN was found in a regression analysis of data from a northeastern Pacific cruise by Hegg *et al.* [1991], who also concluded that the relationship between the two atmospheric parameters might not be linear. One reason behind the difficulties in establishing a clear relationship between DMS emissions and CCN concentration may be that it can take several days to weeks from DMS emissions before particles large enough to act as CCN are formed. Cruise data are further complicated by the fact that having a fairly short lifetime of about 1–2 days [Berresheim, 1987], atmospheric DMS follows closely the regional seawater DMS concentrations which can change dramatically within a fairly short period of time during the cruise [Andreae *et al.*, 1995].

[9] Further support for the link between DMS and CCN comes from two marine measurement stations with long-term CCN records and from analysis of satellite data. Observations at Cape Grim, Tasmania, show very similar seasonal cycles for atmospheric DMS and CCN concentrations, with a factor of 2–3 higher CCN concentrations during the biologically active season than in midwinter [Ayers and Gras, 1991]. Short-term airborne measurements higher in the boundary layer (BL) close to the site indicate that CCN concentrations can be more than an order of magnitude higher in summer than in winter [Yum and Hudson, 2004]. These local near-surface observations are consistent with seasonal changes in cloud optical depth observed by satellite near Cape Grim [Boers *et al.*, 1994]. Several studies have indicated that while primary sea salt flux emissions are an important contributor to the surface-

level CCN in the Southern Ocean region, they cannot explain the observed seasonal variability of CCN [Andreae et al., 1999; Vallina et al., 2006]. At the Mace Head Irish coastal site (53°19'N, 9°54'W), measurements show a clear seasonal cycle of CCN in marine air masses [Reade et al., 2006]. The highest CCN concentrations are observed during the biologically active season when the DMS emissions are expected to be the highest, but a direct link between the two cannot be established because continuous DMS measurements are not made at Mace Head. Furthermore, recent data from Mace Head indicate that oceanic plankton blooms can influence the submicron aerosol distribution significantly through release of organic compounds [Cavalli et al., 2004; O'Dowd et al., 2004; Nilsson et al., 2007], which could downplay the role of DMS at this site.

[10] Satellite data have been used to study the influence of DMS on aerosol radiative properties mostly over the Southern Ocean. Applying a statistical linear regression analysis to satellite and model data in this region, Vallina et al. [2006] found that CCN number and the product of chlorophyll and OH radical concentrations show a seasonal dependence and that CCN number anticorrelates with primary sea salt flux, which was represented in the analysis with monthly mean wind speed. The same authors estimated that biogenic emissions account for ~80% of the summertime CCN column in the 40°–60°S latitude band, whereas their contribution in winter is ~35%. Gabric et al. [2002] presented a correlation between satellite-derived chlorophyll and aerosol optical depth (AOD), which is dominated by particles in the large CCN size range, on monthly, weekly and daily timescales over the Southern Ocean. Despite these links found between chlorophyll and aerosol properties in the Southern Hemisphere, Stefels et al. [2007] have pointed out that no straightforward global relationship exists between marine biomass parameters, such as chlorophyll, and DMS because only some of the algae species produce DMS precursors and because the physiological conditions of algal cells affect the production. Indeed, Vallina and Simó [2007] showed that globally the oceanic DMS concentrations correlates much more closely with solar radiation dose into the top mixed layer of seawater than with biomass or sea surface temperature. Using this information, Vallina et al. [2007] estimated that DMS can contribute up to 30% to globally averaged annual CCN column concentration but that the contribution is spatially highly variable and most significant over remote marine regions.

[11] While these observations give strong support to the DMS-CCN link proposed in the CLAW hypothesis, they fail to reveal the microphysical mechanism through which DMS acts and the contribution of the local DMS ocean water concentration to CCN relative to the contributions of other factors like wind speed, precipitation and long-range transport. Previous model studies have addressed some of these questions but have reached conflicting conclusions. Pandis et al. [1994] and Russell et al. [1994] studied the MBL as a closed system and suggested that MBL nucleation leads to a linear relationship between DMS emissions and CCN number at DMS fluxes higher than 2.5 $\mu\text{mol}/\text{m}^2/\text{d}$. Yoon and Brimblecombe [2002] extended such box model studies by including also entrainment of particles from the FT (implicitly assuming that none of these particles were formed by DMS oxidation) and showed that the MBL

nucleation mechanism can explain the shape of the Cape Grim CCN seasonality curve. They also concluded that DMS contributes significantly to CCN only at low wind speeds, while the dominant factors at moderate and high wind speeds are primary sea spray flux and entrainment from the FT. These model studies predicted frequent MBL concentrations of H_2SO_4 of $\sim 4 \times 10^6$ to $5 \times 10^7 \text{ cm}^{-3}$, which, although not totally unrealistic, are higher than, for example, the measured mean of $\sim 2 \times 10^6 \text{ cm}^{-3}$ during the 2006 MAP cruise off the coast of Ireland specifically targeting biologically active areas [Aufmhoff et al., 2007]. However, even H_2SO_4 concentrations as high as the modeled values rarely lead to new particle formation in the real MBL [Weber et al., 2001; Ehn et al., 2007]. Results consistent with this were reached by Lin et al. [1992], whose box model study indicated that MBL nucleation influences CCN concentrations only if the preexisting CCN number is very low, that is, $\sim 1 \text{ cm}^{-3}$ when the SO_2 concentration is 30 ppt and $\sim 10 \text{ cm}^{-3}$ for a high SO_2 concentration of 100 ppt. It should also be noted that the actual mechanism of MBL nucleation is not known and therefore the studies above have had to rely on theoretical nucleation models tuned with semiempirical multiplying factors.

[12] Other box model studies have proposed that entrainment from the FT is the major source of MBL CCN particles. Raes [1995] suggested that entrainment regulates the CCN concentration and quenches further new particle formation in the MBL. Without simulating the actual microphysical processes in the FT the author also concluded that the MBL aerosol number is mainly controlled by the amount of DMS transported into the FT and the residence time of nucleated particles in the FT. Also, Katoshevski et al. [1999] found entrainment from the FT to dominate the MBL total particle number by using a simplified description of a self-preserving FT aerosol entrained with a fixed rate. The authors concluded, however, that sea spray particles (not explicitly simulated in the study of Raes [1995]) are more likely to govern the CCN concentration owing to their larger size and more favorable cloud activation properties. The dominant role of sea spray was also stressed by Pierce and Adams [2006], whose global model study suggested that sea spray emissions increase the CCN concentrations by 150–500% over the Southern Ocean. On the other hand, a three-dimensional (3-D) model study by Lucas and Prinn [2003] indicated that binary homogeneous nucleation of DMS-derived sulphuric acid and water in the FT may be an important source of MBL aerosol and CCN.

[13] In this study, we use a global size-segregated aerosol microphysics model to investigate in detail the role of DMS emissions in the formation of CCN in the remote Southern Hemisphere MBL. We compare the model results with available long-term measurements to find out whether DMS can explain the observed seasonal cycle. We also quantify the changes in CCN sources between summer and winter, including the contribution of continental sulfur sources to MBL CCN.

2. Methods

2.1. Model Description

[14] All the model runs presented in this study were made with the global aerosol model GLOMAP, which is an

extension to the TOMCAT 3-D chemical transport model [Chipperfield, 2006; Stockwell and Chipperfield, 1999]. A detailed description of GLOMAP is given by Spracklen *et al.* [2005a]. The model is run with a T42 spectral resolution ($2.8^\circ \times 2.8^\circ$) and with 31 hybrid σ -p levels extending to 10 hPa. Large-scale atmospheric transport is specified from European Centre for Medium-Range Weather Forecasts (ECMWF) analyses at 6-hour intervals. Here the sectional version of GLOMAP, “GLOMAP-bin,” is used, which represents the aerosol size distribution with a sectional moving center scheme using 20 size sections to cover the size range of 3 nm to 25 μm . In the runs presented here, the aerosol composition is described with two internally mixed components: sulfate and sea spray. The masses of both components along with the number of particles are tracked in each size section. Our study seeks to quantify the contribution of DMS and sea spray to CCN, but we do not attempt to simulate oceanic organic emissions that may vary with ocean biological activity. While secondary organic material from this source is not expected to have a major influence on clouds [Meskhidze and Nenes, 2006, 2007], we cannot rule out the role of primary organic material [O’Dowd *et al.*, 2008; Spracklen *et al.*, 2008].

[15] Oceanic DMS emissions are calculated using monthly mean seawater concentrations from Kettle and Andreae [2000] and the sea-to-air transfer velocity of Nightingale *et al.* [2000]. Other simulated sources of sulfur species are anthropogenic SO_2 emissions from Cofala *et al.* [2005] and volcanic SO_2 emissions based on the work of Andres and Kasgnoc [1998] and Halmer *et al.* [2002]. We assume that 2.5% of SO_2 from these continental sources is emitted as primary sulfate particles at particle sizes proposed by Stier *et al.* [2005]. The primary sea spray emission flux is simulated according to Mårtensson *et al.* [2003] for particles smaller than 2 μm in dry diameter and according to Monahan *et al.* [1986] for sizes larger than 2 μm . The Mårtensson *et al.* [2003] sea spray flux parameterization is based on controlled laboratory experiments on synthetic seawater at different wind speeds and water temperatures, and covers the ultrafine size range (<100 nm) that Pierce and Adams [2006] found in their global model simulations to increase CCN concentrations over the Southern Ocean by up to 50%. Although direct validations of this parameterization against field measurements are not available in cold water temperatures, it has been shown to reproduce observations well in temperate and tropical waters [Nilsson *et al.*, 2007], and to give a good general agreement with measured particle size distributions in latitudes 45° – 75°S [Pierce and Adams, 2006].

[16] The sea surface temperature is taken from ECMWF analyses. The aerosol processes simulated in the baseline run are binary homogeneous nucleation of H_2SO_4 and H_2O according to Kulmala *et al.* [1998], condensation of H_2SO_4 , hygroscopic growth, coagulation, wet and dry deposition, transport, and cloud processing (SO_2 oxidation by hydrogen peroxide).

[17] Monthly mean boundary layer clouds are from the International Satellite Cloud Climatology Project (ISCCP) archive. Cloud drop activation in these clouds is calculated according to the mechanistic scheme of Nenes and Seinfeld [2003] using a random up-draught velocity in the range 15–30 cm/s and the activated drops are assumed to grow to 40

times their dry diameter. Aqueous phase H_2SO_4 forms in these BL clouds through the reaction of SO_2 and H_2O_2 . Oxidation of SO_2 by O_3 in freshly emitted alkaline sea spray particles is not simulated in the baseline run, but we examine the influence of this process in a set of sensitivity simulations. Precipitation scavenging of particles and water-soluble gases is considered only for higher-level convective and frontal clouds as diagnosed every 6 hours in the host model TOMCAT from the ECMWF analyses (and thus separately from ISCCP boundary layer clouds). Sea ice coverage follows monthly mean data taken from British Atmospheric Data Centre database [Rayner *et al.*, 2003].

2.2. Observations

[18] The only long-term record of CCN in the Southern Ocean comes from Cape Grim, northwestern Tasmania ($40^\circ 41'\text{S}$, $144^\circ 41'\text{E}$, 94 m above sea level). This site hosted frequent CCN measurements in the period 1981–1989 and has also continuous records of SO_2 and DMS measurements. The CCN data used in this study are taken from the study of Ayers and Gras [1991], which reports climatological monthly means over the 9-year period of measurements as well as median values for individual months at supersaturations 0.23% and 1.2%. Our results show that a global (or at least hemispheric) model is required to interpret observations from this single site.

[19] In the model the particle dry diameters corresponding to these supersaturations are calculated for an internal mixture of sulfate and sea salt according to Köhler theory [e.g., Seinfeld and Pandis, 1998] and are typically found to be ~ 66 nm and ~ 22 nm, respectively. The measured CCN concentrations show a clear correlation with the observed atmospheric DMS at both of these supersaturations, although the relationship is much clearer for the higher (atmospherically less relevant) supersaturation.

2.3. Description of the Model Runs

[20] We have carried out a series of simulations starting with a baseline simulation incorporating all the processes listed in section 2.1. In the sensitivity simulations, we have switched off or added to the model one process or emission at a time in order to investigate its influence to the CCN concentrations. The sensitivity simulations made are briefly as follows:

[21] 1. All oceanic DMS emissions were switched off. Comparing the obtained results to the baseline run gives an estimate of the contribution of DMS to CCN.

[22] 2. DMS water concentration was decreased by 50%. The run gives an estimate of the sensitivity of our results to uncertainties in the DMS source.

[23] 3. Binary homogeneous nucleation was switched off. In this run the only CCN sources are direct sea spray emissions and the growth of ultrafine sea spray due to condensation of H_2SO_4 (both DMS-derived and continental). Comparison with the baseline simulation gives an estimate of the importance of FT nucleation as a CCN source.

[24] 4. Condensation of H_2SO_4 in the BL was switched off. The only sources of CCN are direct sea spray emissions at CCN sizes and FT nucleation. Comparison with the baseline simulation gives an estimate of the importance of sea spray particle growth as a CCN source.

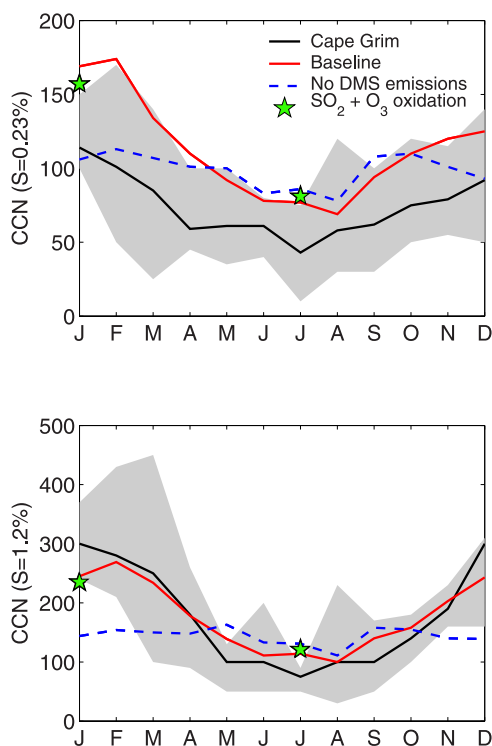


Figure 1. Observed and modeled monthly mean cloud condensation nuclei (CCN) concentrations at Cape Grim, Tasmania, at supersaturations (top) 0.23% and (bottom) 1.2%. The observed climatological mean (black line) and the range of monthly median values for years 1981–1989 (shaded grey area) are taken from *Ayers and Gras* [1991]. Details of the model simulations are given in the text.

[25] 5. Continental sulfur emissions were switched off. Comparison with the baseline run gives an estimate how much the results (and CCN observations in the studied region) are affected by anthropogenic and volcanic sources.

[26] 6. Oxidation of SO_2 by O_3 on sea spray particles was included. Comparing to the baseline run gives an upper limit estimate of the bias made in the baseline simulation by neglecting this oxidation mechanism.

[27] For the baseline simulation and the simulation without DMS emissions the model is spun up for 2 months (November and December 1999), and the actual runs are made for the following 14 months (January 2000 to February 2001). All the other sensitivity simulations are made for one summer and/or one winter month with a 2-month spin-up period.

3. Results and Discussion

3.1. Effect of DMS on the Seasonal Cycle of CCN Concentrations

3.1.1. Comparison of Model Results With Observations at Cape Grim

[28] Figure 1 presents the monthly mean simulated and measured CCN concentrations at Cape Grim, Tasmania, for supersaturations 0.23% and 1.2% (hereinafter denoted as $\text{CCN}(0.23\%)$ and $\text{CCN}(1.2\%)$). The observations show a clear seasonal cycle with 1.9 and 3.2 times higher mean concentrations in summer (December to February) than in

winter (June to August) at the two supersaturations, respectively. The simulation (hereinafter referred to as the baseline) reproduces the relative month-to-month variations and the overall amplitude of the seasonal cycle fairly well, predicting concentrations of $\text{CCN}(0.23\%)$ and $\text{CCN}(1.2\%)$ higher in summer than in winter by factors 2.1 and 2.3, respectively. Modeled monthly mean $\text{CCN}(1.2\%)$ compare very well with measured monthly mean concentrations (Figure 1, bottom) giving a correlation coefficient 0.97. A possible reason for the lower January than February value for predicted $\text{CCN}(1.2\%)$ number is that GLOMAP tends to underestimate the atmospheric DMS concentrations at Cape Grim in January while it predicts the rest of the annual cycle correctly [*Spracklen et al.*, 2005a]. The correlation coefficient of simulated and measured $\text{CCN}(0.23\%)$ is also high ($R = 0.93$). However, the simulated $\text{CCN}(0.23\%)$ concentrations are clearly higher than the observed mean values for each of the months, although 7 out of 12 months predict values just within the observed range (Figure 1, top). Although the model captures the absolute $\text{CCN}(1.2\%)$ numbers better than the $\text{CCN}(0.23\%)$ numbers at Cape Grim, we use primarily the latter, more atmospherically relevant, value in our analysis below.

[29] The effect of DMS on CCN concentrations is examined by comparing the simulated CCN concentrations in the above baseline run with a simulation in which DMS emissions are switched off (dashed blue line in Figure 1). In the no-DMS simulation the only possible sources of CCN are sea spray particles and long-range transport of primary and secondary continental sulfate aerosol from anthropogenic and volcanic emissions. Changes in CCN in this run will be driven by meteorological factors such as local surface wind speed (which determines the ocean-to-atmosphere flux of sea spray), precipitation scavenging of aerosol, and transport of aerosol from the continents. Figure 1 shows that in the no-DMS run, the simulated monthly mean CCN number remains fairly constant all year although it does show slightly lower concentrations in winter than in summer. The correlation coefficients of the simulated and observed $\text{CCN}(0.23\%)$ and $\text{CCN}(1.2\%)$ concentrations are 0.56 and 0.19, respectively. On the basis of this run, it is clear that the seasonal changes in meteorology are not large enough to explain the observed seasonal CCN cycle or the high CCN concentrations in the summer months.

[30] By comparing the baseline simulation (Figure 1, red line) with the no-DMS run (Figure 1, blue line), we find that oceanic DMS increases CCN concentrations at Cape Grim from November to April. The peak effect is in January and February when the baseline run predicts 59% and 54% higher $\text{CCN}(0.23\%)$ concentrations, respectively. In winter from May to September the model suggests that DMS emissions cause a slight decrease in the CCN concentration. This “inverse-CLAW” effect in the model is caused by a combination of aerosol processing in clouds and wet scavenging: While the wintertime DMS emissions are too low to form many new CCN, they still produce SO_2 which is oxidized to sulfate in cloud drops. This cloud processing increases the size of activated aerosol particles and makes them more susceptible to in-cloud precipitation scavenging, which, in the model, removes all particles inside a precipitating cloud that are larger than 200 nm in wet diameter. (Note that in-cloud loss of small activated drops during

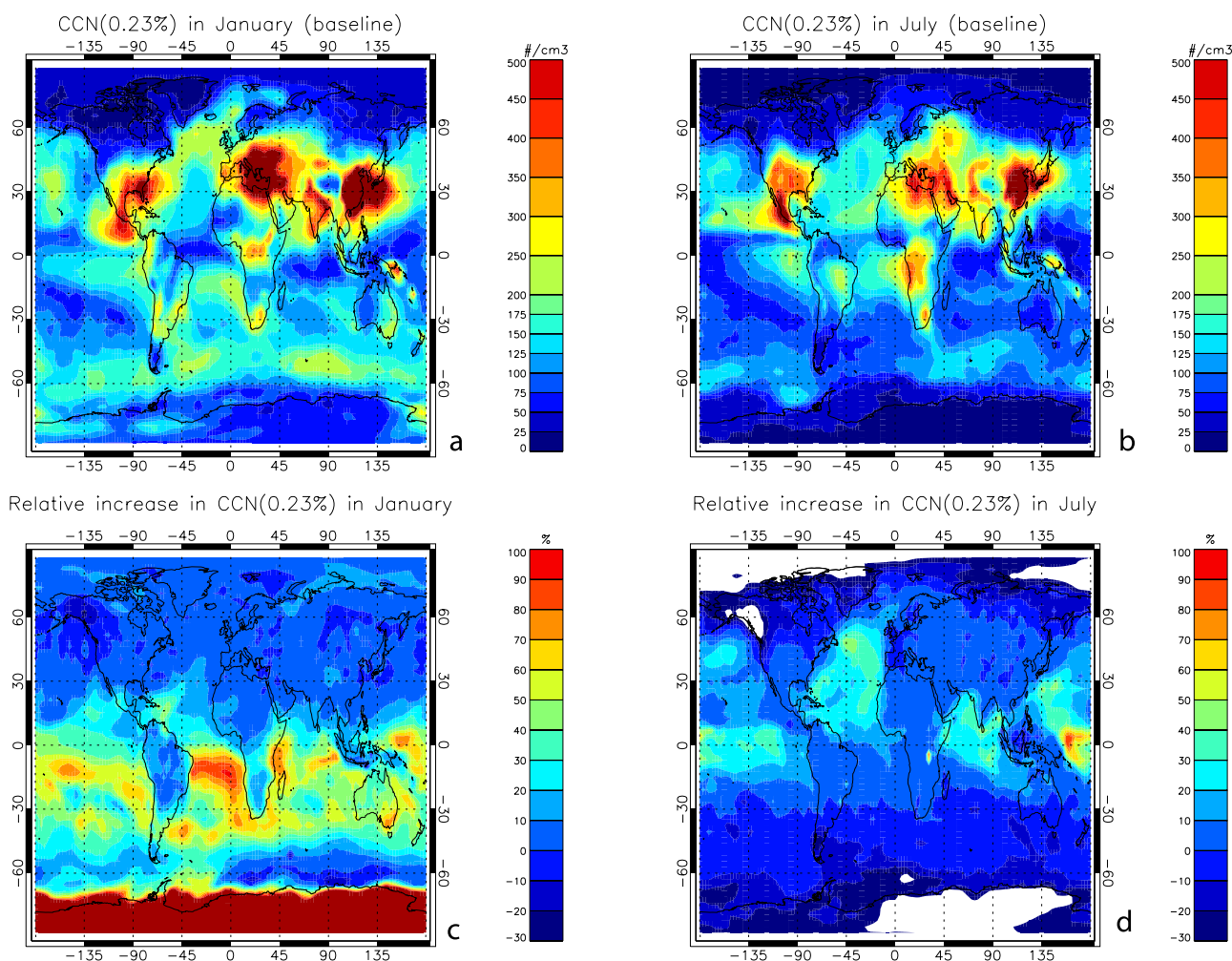


Figure 2. (a and b) Simulated global monthly mean CCN(0.23%) concentration in January and July in the baseline simulation. (Note that in the continental regions the predicted CCN number may be underestimated since we exclude primary organic and black carbon, secondary organic aerosol, and mineral dust.) (c and d) Relative increase in CCN(0.23%) concentration when dimethyl sulfide (DMS) emissions are included in the model in January and July (compared to simulation without DMS emissions).

autoconversion is not taken into account in the model. This might lead to slight overestimation of their concentration when the cloud evaporates.) Analysis of size distributions and wet deposited sulfate mass (not shown) in the baseline run and the run without DMS emissions supports this explanation of the apparent “inverse-CLAW” effect.

[31] It is impossible to say whether the “inverse-CLAW” effect occurs in the real atmosphere where the link between activated aerosol particles and their precipitation scavenging is more complex than in the model. If it does, our baseline simulation is very likely to overpredict the effect as it neglects the oxidation of SO_2 by O_3 in freshly emitted alkaline sea spray particles. We estimate the maximum potential effect of this reaction on CCN by making a sensitivity run which assumes that aqueous phase SO_2 oxidation takes place in all MBL particles that have at least 50% sea salt mass at a rate that is limited only by SO_2 mass transfer rate, which is a reasonable assumption in remote MBL [Hoppel and Caffrey, 2005]. Clearly this assumption overestimates the oxidation rate since it does not take into

account the decreasing pH of the particles as sulfate formation proceeds. A detailed treatment of the reactions is not possible as the baseline version of the model does not track O_3 and treats sulfate and sea salt as an internal mixture at all particle sizes. However, we are mainly interested in how large an error neglecting this reaction in the baseline simulation can potentially cause, and the approach described above gives an upper limit estimate of the error.

[32] Including SO_2 oxidation on sea spray particles reduces the simulated SO_2 concentrations in the MBL significantly. At Cape Grim, the model predicts SO_2 concentrations of ~ 10 ppt in January (~ 50 ppt in the baseline simulation) and ~ 1 ppt in July (~ 20 ppt in baseline simulation), both in good agreement with monthly mean measured values at the site (9 ppt in January and 2 ppt in July [Ayers *et al.*, 1997]) and greatly improving the comparison originally presented by Spracklen *et al.* [2005a]. In July this sea spray chemistry reduces cloud processing and wet removal of activated particles and therefore increases the predicted CCN(0.23%) concentration by 5% from the

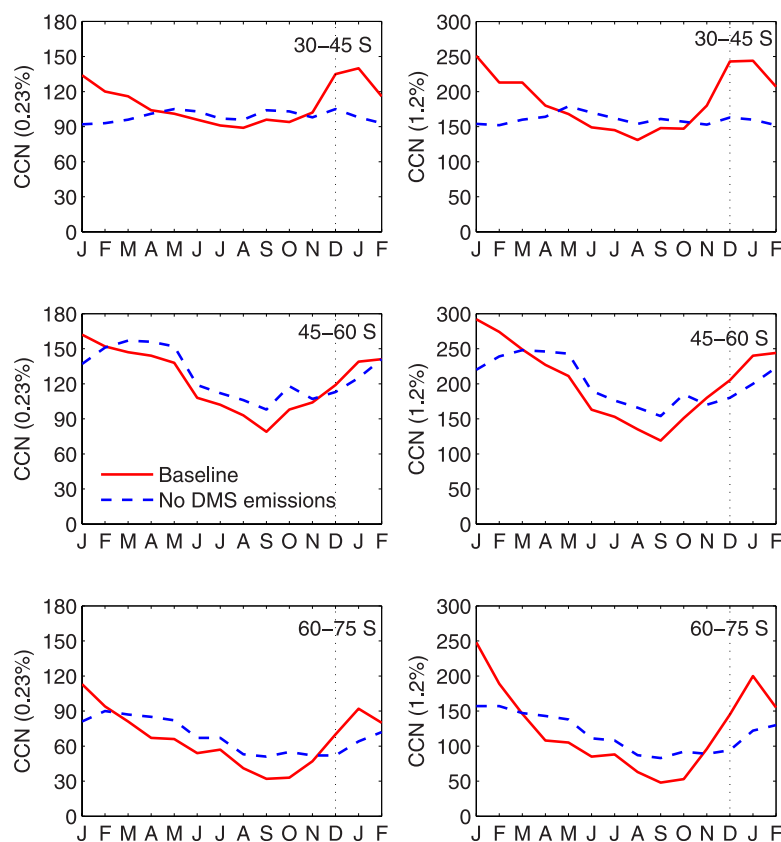


Figure 3. Simulated zonal monthly mean CCN concentrations (January 2000 to February 2001) for latitude bands 30° – 45° S, 45° – 60° S, and 60° – 75° S at supersaturations 0.23% and 1.2%. The dotted vertical lines indicate the end of year 2000.

baseline value (green star in Figure 1). This in turn decreases the “inverse-CLAW” effect, as expected. In contrast, the additional oxidation reaction decreases the simulated January concentration of CCN(0.23%) by 7% compared to the baseline simulation. While these changes in CCN concentration are not negligible, they do represent the upper limit of the expected impact of SO_2 oxidation on sea spray particles. Furthermore, the overall effect on the simulated CCN seasonality and summer peak concentrations is small and thus the missing SO_2 oxidation reaction does not affect our conclusions regarding the role of DMS on CCN formation at Cape Grim.

3.1.2. Zonal Variations in Seasonal CCN

[33] Figures 2a and 2b show that the CCN(0.23%) concentration is much higher in summer than in winter over all marine regions south of 30° S. However, the relative contribution of DMS to the summer maximum CCN differs significantly from region to region (Figure 2c). On the other hand, in winter months DMS does not increase CCN(0.23%) in any region of the Southern Hemisphere oceans (Figure 2d). Figure 2 also shows that it is justifiable to investigate the CCN seasonality and the role of DMS over this region in terms of zonal mean values. (Note that CCN concentrations shown in Figures 2a and 2b are likely to be too low in most continental regions north of 30° S since we exclude primary organic and black carbon, secondary organic aerosol, and mineral dust, which all can be important CCN sources.)

[34] Figure 3 presents the simulated seasonal cycle of marine CCN concentrations for three latitude bands over the Southern Hemisphere oceans for January 2000 to February 2001.

3.1.2.1. Band 30° – 45° S

[35] The northernmost band 30° – 45° S shows seasonality similar to that observed and simulated at Cape Grim (which is also located in this latitude band). The summertime maximum is reached in December–January when the CCN(0.23%) is 1.5 times and CCN(1.2%) 1.9 times higher than in August. By comparing the runs with and without DMS emissions it is clear that DMS contributes significantly to CCN from November to April but is not the main driver of CCN from May to October. The contribution of DMS to the CCN seasonal cycle is driven by changes in its seawater concentration rather than changes in the sea-air transfer velocity due to changes in wind speed: DMS seawater concentrations in this latitude band are about a factor 5 higher in December–January than in June–July, while monthly mean wind speed peaks from June to September when CCN concentrations are lowest (Figure 4). The peak contribution of DMS to CCN is in January when the baseline zonal mean CCN(0.23%) concentration is 46% higher than in the no-DMS run (this is somewhat lower than the 59% enhancement simulated at Cape Grim).

3.1.2.2. Band 45° – 60° S

[36] The modeled zonal and monthly mean CCN at 45° – 60° S shows quite different variation through the year, with an apparent general decrease imposed on a seasonal cycle

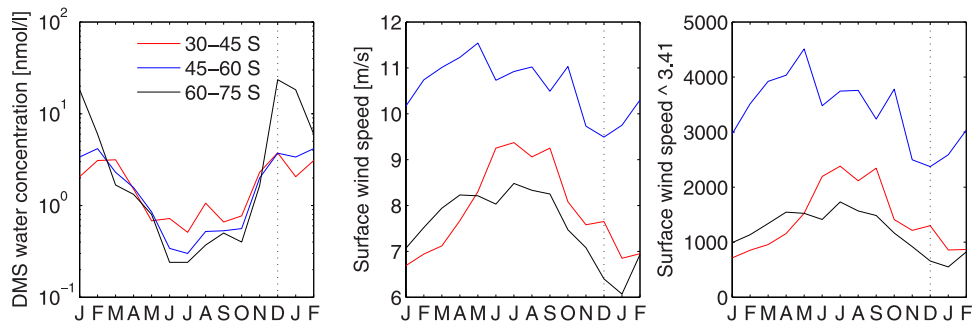


Figure 4. (left) Seasonal variation of marine zonal monthly mean DMS ocean water concentration (from the *Kettle and Andreae* [2000] database), (middle) modeled surface wind speed, and (right) modeled surface wind speed to the power of 3.41 (representing wind speed dependence of sea spray and DMS emission fluxes).

(Figure 3). In contrast to band 30°–45°S the CCN in the run without DMS emissions also shows strong seasonality, with higher concentrations in January than July even without DMS. These results indicate that not all of the seasonal

variation is due to DMS-derived aerosol at these latitudes. The impact of DMS on CCN is apparent over a shorter summer period (December to February) than at 30°–45°S and it increases the CCN(0.23%) concentration by a max-

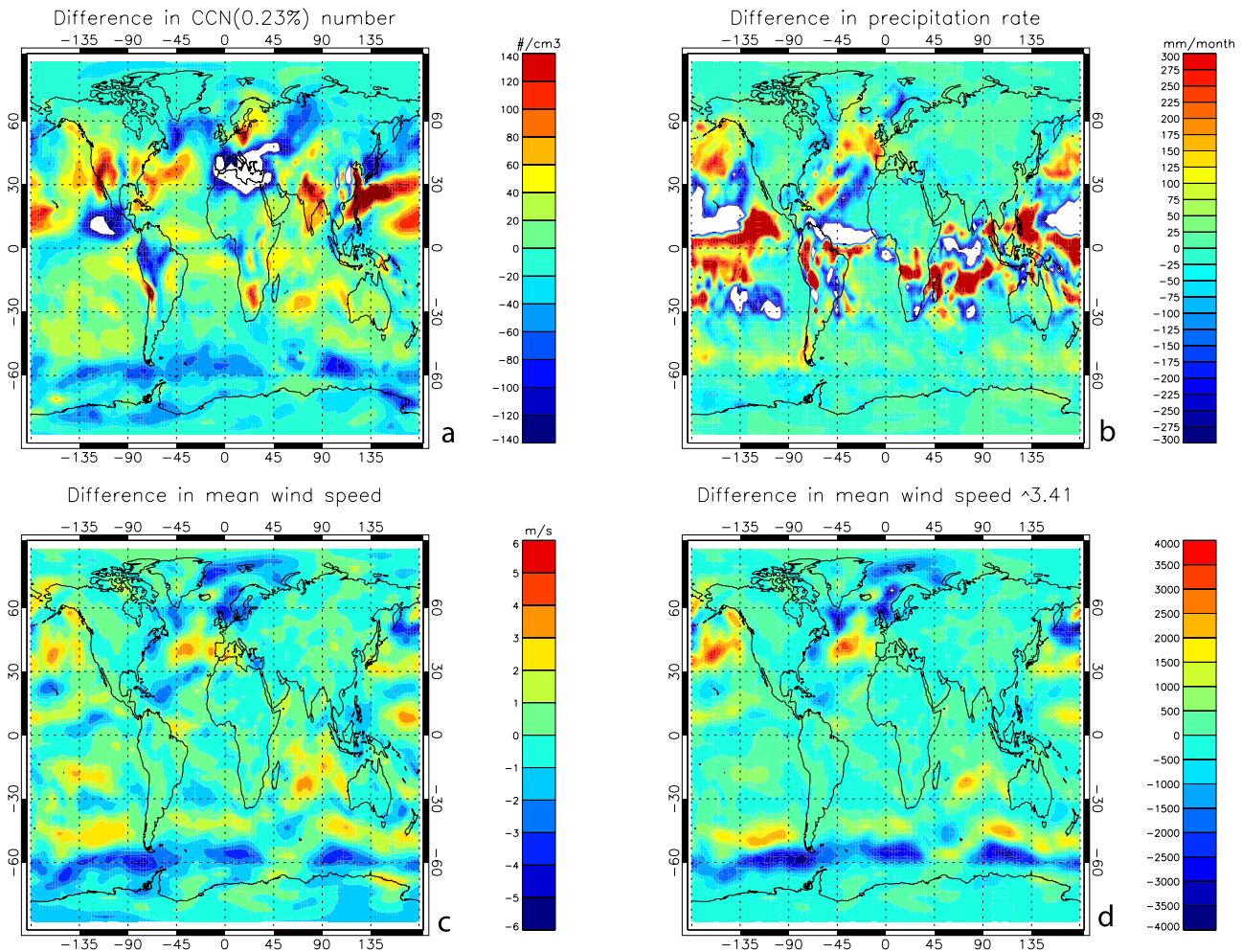


Figure 5. Differences in simulated monthly mean CCN concentrations and meteorological parameters between January 2000 and January 2001. The values are given as a change from January 2000 to January 2001. Shown are the differences in (a) CCN(0.23%) number concentration, (b) total precipitation rate, (c) mean surface wind speed, and (d) mean surface wind speed to the power of 3.41, which represents the wind speed dependence of sea spray and DMS emission fluxes.

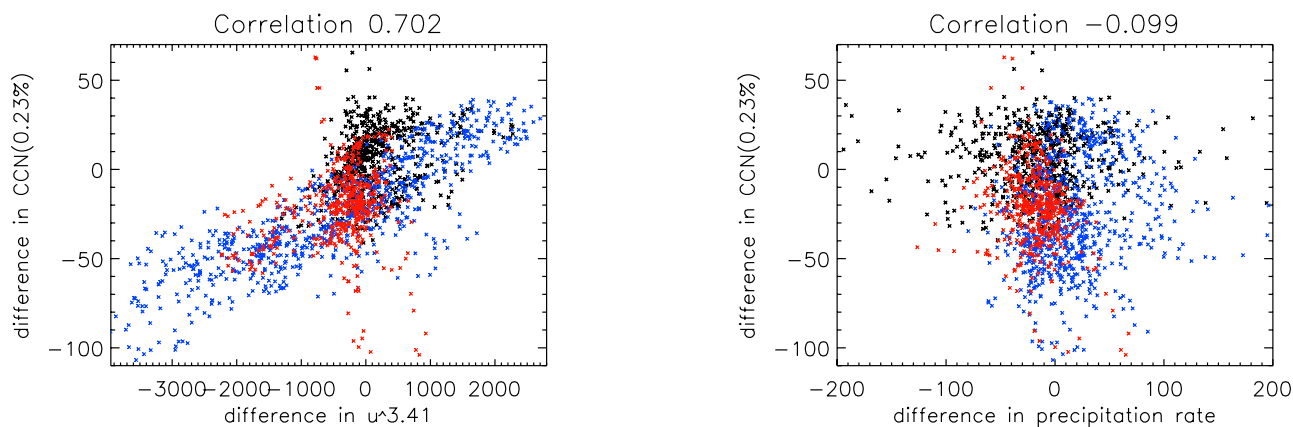


Figure 6. Difference in simulated January 2000 and January 2001 monthly mean CCN(0.23%) concentrations plotted against meteorological parameters for each model marine grid box in latitude bands 30° – 45° S (black), 45° – 60° S (blue), and 60° – 75° S (red). The left-hand plot shows change in CCN against change in mean surface wind speed to the power of 3.41. The right-hand plot shows change in CCN against change in total precipitation rate (this plot excludes 12 outlying values with larger than 200 mm/month absolute difference in precipitation rate, which have been taken into account when calculating the correlation coefficient). The correlations given are the overall correlations for all marine grid boxes in latitudes 30° – 75° S.

imum of only 11% in January 2000 and 18% in January 2001, with almost no effect (0–1%) in February.

[37] One reason for the smaller fractional contribution of DMS to CCN in summer at 45° – 60° S compared to 30° – 45° S is the different contribution of sea spray. Wind speeds are very high at 45° – 60° S, with typical monthly mean values ~ 9 – 15 m/s. As the sea spray source function is proportional to $u_{10}^{3.41}$ (where u_{10} is the wind speed at 10 m altitude), even relatively small changes in surface wind speed in this region cause significant changes in the sea spray flux. The summertime sea spray flux at 45° – 60° S is approximately a factor 3.75 higher than at 30° – 45° S (Figure 4) so the fractional contribution of DMS to CCN will be less. This sea spray source also shows large interannual variability, which is illustrated by comparing results for January and February 2001 with the same months in 2000. Using the same seawater DMS as in 2000, the January/February 2001 CCN(0.23%) concentrations are 7–14% lower than in corresponding months in 2000. Figures 5 and 6 show that this difference correlates spatially with the differences in wind speed in the two years ($R = 0.85$). In contrast, Figure 6 shows that the correlation of wind speed and CCN at 30° – 45° S is very low. Changes in precipitation rate do not show clear correlation with spatial changes in CCN concentrations at any of the latitudes (Figures 5a and 5b and Figure 6, right). This is because precipitation removes mainly particles ~ 150 nm and larger (dry diameter), whereas the CCN number is dominated by particles smaller than that. The role of wind speed as a major controlling factor of CCN cycle at 45° – 60° S is evident also by comparing Figures 3 and 4, which show that month-to-month changes in zonal mean wind speed correlate well with changes in zonal mean CCN in most of the months from May to November.

[38] A further complicating factor at 45° – 60° S is that the absolute increase in CCN due to DMS is different in Januaries 2000 (25 cm^{-3}) and 2001 (14 cm^{-3}), while at

30° – 45° S the difference is less than 1 cm^{-3} . This interannual difference can be caused either by lower DMS emission fluxes due to lower wind speeds in 2001, or by interannual changes in large-scale transport. The relative effect of these two is difficult to quantify. Nevertheless, despite interannual variability, it is clear that the peak summertime increase in CCN(0.23%) due to DMS in January is much less at 45° – 60° S (11–18%) than at 30° – 45° S ($\sim 46\%$), mainly because of the higher sea spray contribution at the higher latitudes. In section 3.2 we also show that a component of the seasonality is driven by sulfate aerosol from non-DMS sources.

3.1.2.3. Band 60° – 75° S

[39] At 60° – 75° S wind speeds are lower than at 45° – 60° S so sea spray makes a smaller contribution to CCN in summer. The correlation between wind speed and CCN anomalies in January 2000 and 2001 (Figure 6) is also weak ($R = 0.326$). Consequently, DMS increases the CCN significantly in January (by 40–44%) and February (by 4–11%). Outside these summer months the seasonal cycle of CCN is dominated by a minimum in winter when wind speeds are highest. However, at these high latitudes it is the winter increase in sea ice that drives a decreasing sea spray source and explains the modeled variations in CCN.

3.1.3. The Effect of Uncertainty in the DMS Source

[40] In addition to the *Kettle and Andreae* [2000] data set, which is used in this study, several other climatologies exist for DMS seawater concentrations. These climatologies have been obtained either by applying different interpolation techniques to the original *Kettle et al.* [1999] data set [Anderson et al., 2001; Simó and Dachs, 2002] or by using indirect quantities such as satellite-detected chlorophyll concentrations or biogeochemical models [Belviso et al., 2004; Aumont et al., 2002; Chu et al., 2003]. In addition to this, several parameterizations exist for the sea-air flux of DMS [Liss and Merlivat, 1986; Wanninkhof, 1992; Nightingale et al., 2000]. Because of the uncertainties that

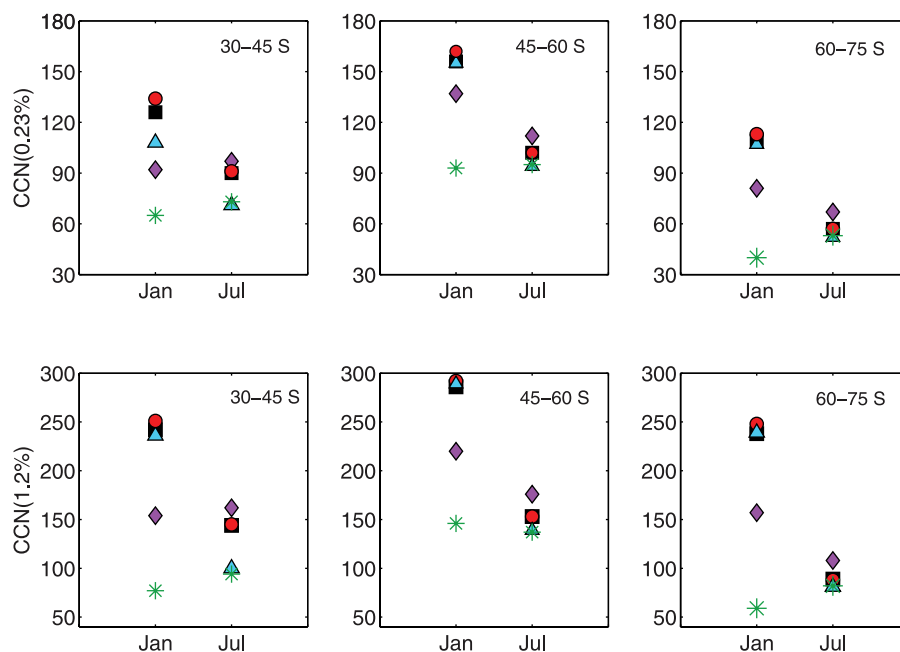


Figure 7. Simulated zonal monthly mean CCN concentrations (cm^{-3}) in latitude bands 30° – 45° S, 45° – 60° S, and 60° – 75° S. The simulations shown are as follows: red circles, baseline; purple diamonds, runs without DMS emissions; green asterisks, runs without binary homogeneous nucleation; blue triangles, runs without continental sulfur emissions; black squares, runs without boundary layer condensation of DMS-derived H_2SO_4 vapor.

using any one climatology or parameterization causes on the simulation results, we have made a sensitivity run (referred to as DMS50 below) in which the DMS water concentration was reduced by 50% from the baseline value in all oceanic regions. This sensitivity simulation was made only for January 2000 as the effect of DMS on CCN is at its largest in the summer months.

[41] By comparing the DMS50 run to the run without DMS emissions, we find that the strength of the DMS source has a large effect on the simulated CCN concentrations. In latitude band 30° – 45° S, the zonal mean $\text{CCN}(0.23\%)$ increases by 17% in the DMS50 simulation (relative to the run without DMS), while it increased by 46% in the baseline (100% DMS) run. At Cape Grim, $\text{CCN}(0.23\%)$ increases by 35% in the DMS50 run and 59% in the baseline DMS100 run. In latitude bands 45° – 60° S and 60° – 75° S zonal mean $\text{CCN}(0.23\%)$ concentrations increase by 3% and 14% in the DMS50 run, respectively (compared with 18% and 40% increases, respectively, in the baseline simulation). These simulations show that CCN in different latitude bands do not respond in similar ways to changes in DMS emission. Future work is needed to identify oceanic regions where uncertainties in DMS have the largest effect on CCN.

3.2. Sources of Surface-Level CCN

[42] The model runs with and without DMS show a clear impact of DMS on CCN. However, they do not allow us to determine the production mechanism of the additional CCN. In this section we perform a number of model sensitivity runs to understand the mechanistic link between DMS and CCN. Figure 7 summarizes the results.

3.2.1. Condensation Growth of Sea Spray Particles

[43] DMS oxidation products (SO_2 and H_2SO_4) can increase CCN owing to growth of sea spray particles. A model run in which condensation of H_2SO_4 does not add to aerosol mass in the MBL (but loss of gas phase H_2SO_4 due to condensation is still simulated) indicates that almost all of the sea spray particles acting as CCN are emitted into the atmosphere at cloud active sizes: The zonal mean $\text{CCN}(0.23\%)$ decreases by only 4–6% in summer and 0–1% in winter when condensation of H_2SO_4 onto sea spray particles (including those emitted at sizes below ~ 66 nm) is switched off (black squares in Figure 7). These values are much lower than in the global model study of *Pierce and Adams* [2006], who found that including ultrafine sea spray emissions in their model leads to 40% increase in the primary emission flux of CCN sized particles but to 60% increase in the predicted concentration of CCN. Assuming that the addition of ultrafine particles does not affect the microphysics of particles in or close to the CCN size range, one can calculate that condensation growth of ultrafine sea spray adds $\sim 14\%$ to the CCN number south of 70° S in their study. It should be noted, however, that because of differences in the model set-up, the results from *Pierce and Adams* [2006] and those obtained in this study cannot be directly compared. The higher contribution in their study compared to the current one is likely to be caused by a different definition of the CCN size (80 nm versus 66 nm) and the fact that the model of *Pierce and Adams* [2006] predicts much lower FT nucleation rates than GLOMAP owing to its different numerical treatment of condensation and nucleation [*Trivittayanurak et al.*, 2007]. On the other

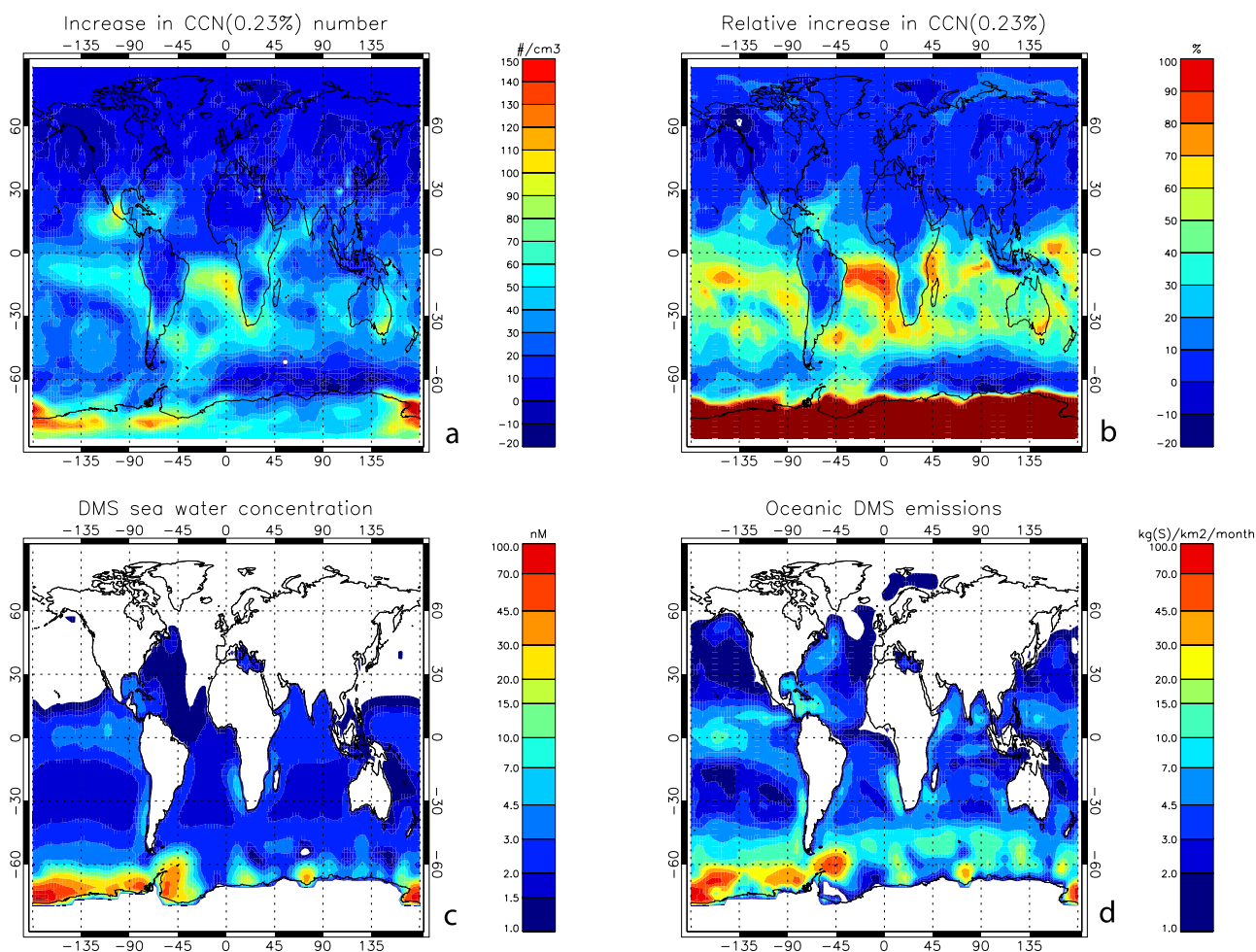


Figure 8. The effect of DMS emissions on surface level CCN(0.23%) concentrations in January 2000. (a) Simulated increase in absolute CCN(0.23%) number concentration due to DMS emissions. (b) Simulated relative increase in CCN(0.23%) number concentration (given as percent increase) due to DMS emissions. (c) DMS water concentration [Kettle and Andreae, 2000]. (d) Simulated monthly DMS emissions (given as kg(S)/km^2).

hand, uncertainties in the binary nucleation rate have been shown to have only a minor effect on the simulated properties of the MBL aerosol in GLOMAP [Spracklen *et al.*, 2005b].

3.2.2. Input of Aerosol From the Free Troposphere

[44] The magnitude of the midsummer increase in CCN(0.23%) due to DMS emissions varies significantly over the Southern Hemisphere oceans and does not always correlate with DMS seawater concentrations (Figure 8). The largest contribution of DMS-derived particles to absolute CCN number (up to 150 cm^{-3} increase compared to the run without DMS) is seen close to the Antarctic coast (Figure 8a) where also the DMS seawater concentration and sea-to-air flux are the highest (Figures 8c and 8d). On the other hand, very little increase in CCN concentration is simulated in most regions between 50° and 65°S despite the high DMS emissions, while large effects in absolute CCN number (up to over 50 cm^{-3} increase) and relative CCN number (up to 70–100% increase) are seen in the latitudes 30° – 50°S where DMS emissions are generally low. These results suggest that the main mechanism behind the link between DMS and CCN is not local in nature but involves

transport of DMS oxidation products or DMS-derived particles over hundreds or even thousands of kilometers.

[45] Timescales from several days to weeks associated with this scale of transport are consistent with the hypothesis that DMS oxidation products nucleate to form nanometer-sized particles that grow to CCN sizes by condensation and coagulation. We test this hypothesis with a model run in which binary homogeneous nucleation is switched off. In the baseline simulation the model predicted no nucleation in the BL, so the additional run gives an estimate of the importance of new particle formation in the FT and the subsequent entrainment of the particles into the MBL. Although most of the FT H_2SO_4 is from DMS oxidation in remote marine regions, over some remote marine regions also H_2SO_4 from anthropogenic and volcanic sources can contribute to nucleation in the FT so we have also done further sensitivity tests to isolate the continental influence. The simulation without binary homogeneous nucleation shuts down FT nucleation from both sulfur sources, and the only sources of CCN are sea spray (either emitted at or grown by condensation to CCN sizes) and primary sulfate particles, although the latter are important only close to the continents.

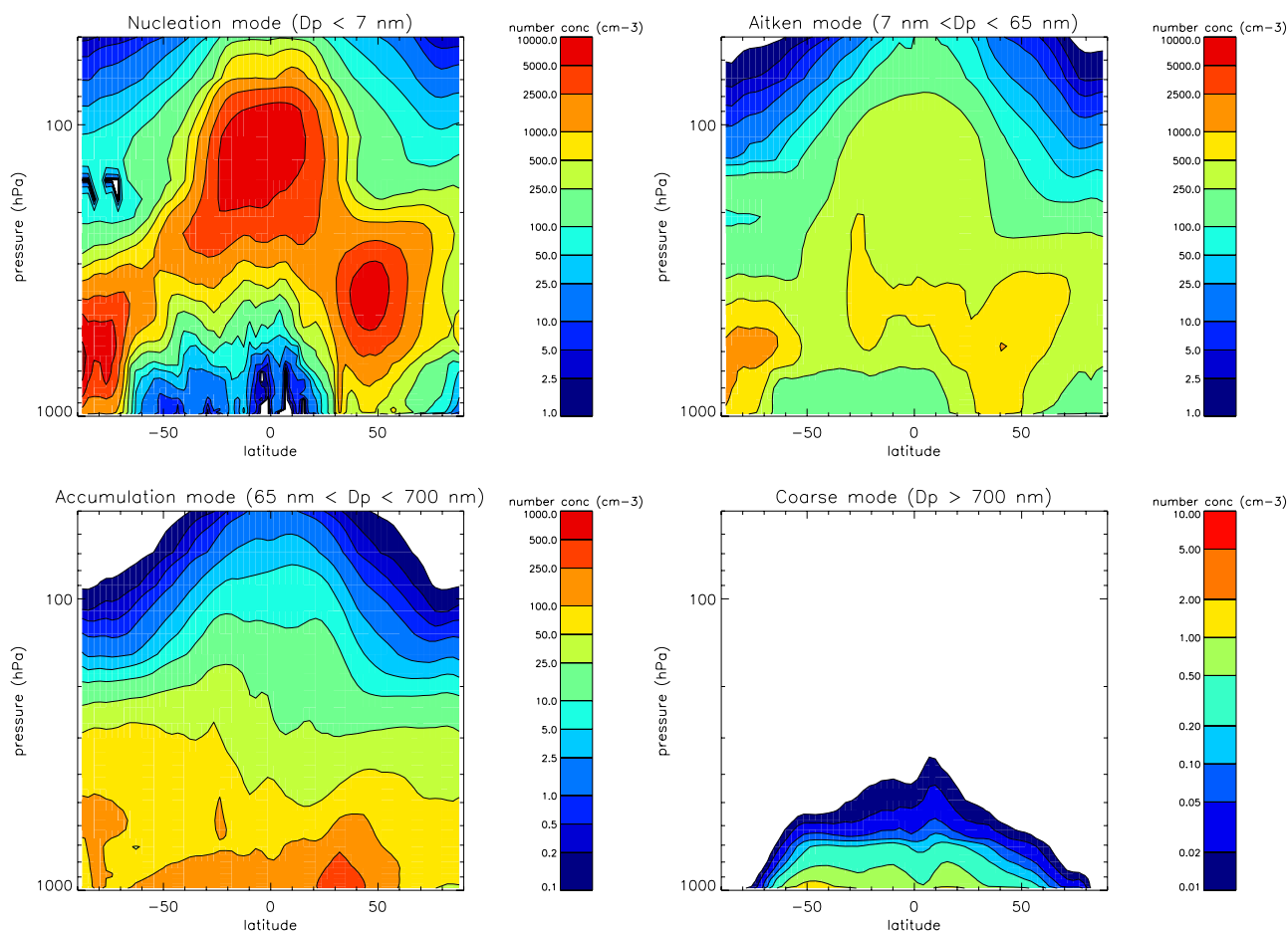


Figure 9. Modeled latitude-altitude profiles of particle concentrations in the baseline simulation. The profiles are given for four size ranges.

[46] In terms of mean zonal absolute CCN(0.23%) in the MBL, the summertime contribution of FT nucleation is fairly constant over the Southern Hemisphere oceans: It adds 69, 69, and 73 cm^{-3} to zonal averages in the three latitude bands 30° – 45° S, 45° – 60° S, and 60° – 75° S, respectively (Figure 7). Owing to differences in other CCN sources, mainly sea spray source flux, the relative contribution of the FT to CCN(0.23%) is highest (65%) in the 60° – 75° S and lowest (43%) in the 45° – 60° S latitude band. The contribution of FT nucleation to CCN at 1.2% supersaturation is even higher (Figure 7), indicating that many of the entrained particles are too small to be cloud active at realistic MBL supersaturations. In winter the contribution of FT particles is much smaller (20% of CCN(0.23%) in July at 30° – 45° S and only 7% farther south). Without the input of aerosol from the FT the model predicts a small increase in CCN from summer to winter at all latitudes, consistent with the change in wind speeds and qualitatively consistent with the observations of *Andreae et al.* [1999] of a wintertime increase in sea salt contribution to CCN at Cape Grim.

[47] The difference between the baseline run and the run without FT nucleation tells us the contribution to MBL CCN of sulfate particles nucleated and grown in the FT: approximately 70 cm^{-3} . We now show that different sulfur sources combine nonlinearly to control the number concentration of these entrained CCN. Figure 7 shows CCN

concentrations from two further simulations: one with DMS emissions but no continental emissions (blue triangles) and one with continental emissions but no DMS (purple diamonds), the latter being the same as in Figure 3. Removing continental sulfur sources reduces summertime CCN(0.23%) by $\sim 25 \text{ cm}^{-3}$ at 30° – 45° S close to the continents, but by less than 8 cm^{-3} farther south. In contrast, removing DMS emissions but retaining continental emissions leads to CCN concentrations that are still substantially higher (by 20 – 45 cm^{-3} at 0.23%) than in the run without any FT aerosol production.

[48] It is clear that the decrease in CCN when switching off FT nucleation is not the sum of decreases in runs without DMS and without continental sulfur. This is because the particle number entrained into the boundary layer from the FT is not very sensitive to the details of the nucleation process in the upper troposphere [*Spracklen et al.*, 2005b], a process often referred to as the generation of a self-preserving aerosol population as aerosol descends and coagulates through the free troposphere [*Raes*, 1995]. Of smaller influence are other processes, such as scavenging and coagulation of particles, which change slightly when one process is switched off. This result is also consistent with the finding of *Spracklen et al.* [2007] that over a part of the Southern Hemisphere ocean, anthropogenic sulfate is

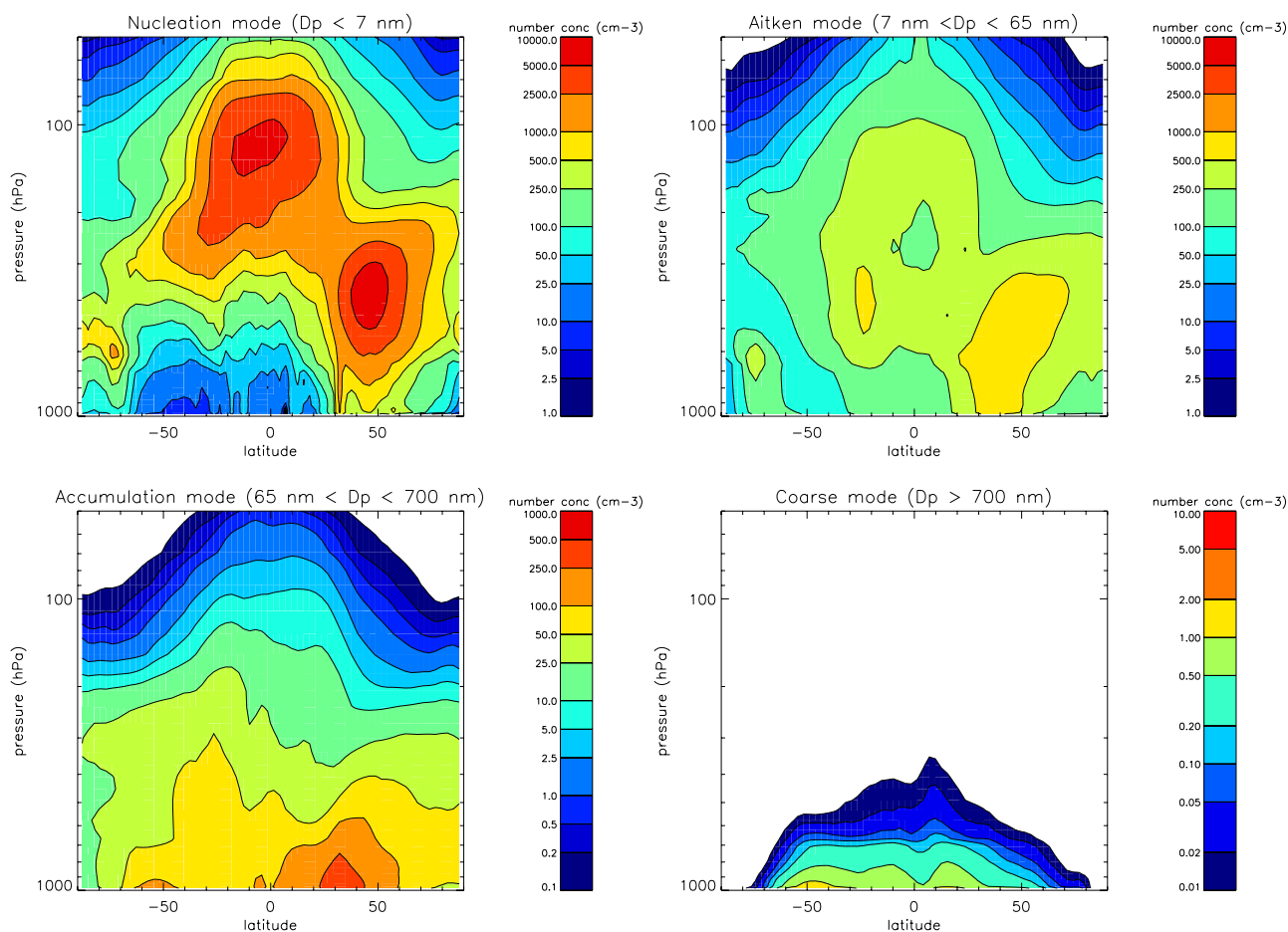


Figure 10. Modeled latitude-altitude profiles of particle concentrations in the no-DMS run. The profiles are given for four size ranges.

much more abundant at CCN sizes than in the larger particles that carry most of the sulfate mass.

[49] Figures 9 and 10 show altitude-latitude profiles of particle number through the free troposphere in four size ranges for the baseline run and the run without DMS emissions, respectively. These vertical profiles show how insensitive the FT aerosol is to changes in sulfur emission. Although there are changes in nucleation mode concentration approaching a factor 10 in the upper troposphere when DMS emissions are removed, changes in Aitken and accumulation mode-sized particles lower in the atmosphere are considerably smaller. The calculated contribution of continental sources to MBL particles in our model is much greater than estimated in an early global study by *Erickson et al.* [1991]. However, they made assumptions about the size of particles created from the emissions (100 nm) rather than calculating the nucleation and growth of particles in the FT as we do. Their model would therefore not capture the nonlinearities that we find here.

[50] These sensitivity tests explain why, even without DMS, the model predicts a higher CCN concentration in summer than winter at some latitudes, even though sea spray sources of CCN are higher in winter. The continental sulfur source, although small, makes a large contribution to summertime CCN in an atmosphere without the dominant sulfur source from DMS. The nonlinearity in particle

formation in the FT, however, means that with DMS emissions, the continental sulfur source appears to contribute only a small number of additional CCN.

4. Summary and Conclusions

[51] We have used an offline global aerosol microphysics and chemistry model to study the effect of DMS on CCN concentrations and seasonality in the Southern Hemisphere remote MBL. This study presents results of a 14-month period from January 2000 to February 2001 for latitudes 30° – 75° S. We simulate the full aerosol size distribution from 3 nm to $25 \mu\text{m}$, which enables us to investigate the microphysical processes through which DMS acts on the aerosol size distribution and CCN number. To our knowledge, this is the first attempt to simulate DMS-derived CCN formation in a size-resolved 3-D aerosol model with realistic descriptions of vertical and long-range atmospheric transport of DMS, its oxidation products and aerosol particles.

[52] At 30° – 45° S DMS produces a seasonal cycle of CCN with a summertime peak, while in a model without any DMS emissions CCN number increases from summer to winter driven primarily by an increased sea spray source. This conclusion is consistent with *Andreae et al.* [1999] and *Vallina et al.* [2006]. With seasonally varying DMS seawater concentrations CCN(0.23 μm) number is increased by 43–

46% in summer and decreases slightly in winter. The simulations reproduce the observed seasonal cycle of CCN at Cape Grim, Tasmania (40°41'S, 144°41'E), only when DMS emissions are included in the model.

[53] At 45°–60°S the impact of DMS on the seasonal cycle is much weaker (11–18%) despite the much higher seawater DMS concentrations at these latitudes. There are two reasons for this weaker impact at 45°–60°S. First, the sea spray source is higher at these latitudes than at 30°–45°S so the relative change when DMS is added to the model is simply less. Second, the model suggests that the even without DMS a large number of CCN are still entrained from the summertime free troposphere from distant continental (anthropogenic and volcanic) sources.

[54] The mechanism by which atmospheric sulfur alters aerosol microphysics is important for the summer-winter differences in CCN abundance due to DMS. We have shown that most of the summertime increase in CCN from DMS emissions comes from particles nucleated in the FT and only a small fraction (<6%) is due to growth of small sea spray particles to CCN sizes. The model simulations show that CCN production from this FT source depends nonlinearly on atmospheric sulfur. When DMS emissions are removed, CCN concentrations fall at all latitudes but a large number of CCN-sized particles remain in the FT, and are entrained into the MBL, from continental sulfur sources (Figures 9 and 10). The model shows that $\sim 70 \text{ cm}^{-3}$ sulfate CCN(0.23%) are entrained into the MBL from the FT when all sulfur sources are included, but when DMS is removed this number falls by only 43, 24, and 32 cm^{-3} at 30°–45°S, 45°–60°S, and 60°–75°S, respectively. This nonlinearity weakens the dependence of MBL CCN on DMS compared to what would be expected on the basis of the DMS contribution to total sulfate mass.

[55] Vallina *et al.* [2006] showed that satellite-derived CCN and chlorophyll were strongly correlated and estimated from these correlations a contribution of DMS to CCN of 80% in summer (averaged over 40°–60°S). Our modeled CCN over the whole Southern Ocean varies strongly with season (red lines in Figure 3) so we also see a strong correlation between imposed DMS and modeled CCN. However, we estimate a smaller contribution of DMS to CCN (increase in CCN concentration varies from 11–18% at 45°–60°S to 46% at 30°–45°S when DMS is added to the model) than that of Vallina *et al.* [2006]. The difference is most likely due to what is assumed about non-DMS contributions to CCN: The previous work assumed that continental sources made a negligible contribution to CCN over the Southern Ocean, while our model suggests that eliminating DMS leaves a background of CCN from continental sources. Because the CCN from continental sources also follow a seasonal cycle driven by photochemistry, they also contribute to the apparent correlation of CCN with chlorophyll.

[56] Our results show that CCN from different sources cannot simply be added together because of the nonlinear dependence of FT particle number on sulfur loading. We found that with DMS emissions switched on, continental sources had a small impact on MBL CCN, but when DMS emissions were switched off the continental sulfur on its own was able to produce lots of CCN. This nonadditivity of contributions to CCN is important for how our results are

cited. The increase of summertime CCN due to DMS (46% at 30°–45°S, 11–18% at 45°–60°S, and 40% at 60°–75°S) cannot be used to infer the contribution from sea spray. The best estimate of the sea spray contribution is obtained from the difference between the baseline run (with all sulfur sources) and the run without FT particle nucleation. These give January sea spray CCN(0.23%) contributions of 48% at 30°–45°S, 58% at 45°–60°S, and 35% at 60°–75°S. The wintertime contribution of sea spray is estimated to be >80% at 30°–45°S and >90% farther south. These values are also larger than those inferred from observations by Vallina *et al.* [2006] but comparable with the global aerosol microphysics model of Pierce and Adams [2006].

[57] Our simulations also show that the largest effects of DMS on CCN are not necessarily seen over regions that have the highest DMS emission fluxes. This is because the predominant microphysical mechanism behind the DMS influence takes place in the FT, where DMS-derived H_2SO_4 nucleates to form new particles, and involves condensation and coagulation growth of nanometer sizes clusters to CCN sizes which can take several days to over a week. By the time the CCN sized particles are entrained into the BL they may have traveled hundreds or even thousands of kilometers from the site of the original DMS emissions. This long-range transport of marine CCN offers an explanation why some experimental field studies [e.g., Andreae *et al.*, 1995; O'Dowd *et al.*, 1997] have failed to establish a link between DMS and CCN concentrations.

[58] This work has focused on biological control of secondary CCN through oxidation of DMS. Future work should be directed toward understanding the impact of biological processes on primary organic carbon aerosol, which will also vary seasonally [O'Dowd *et al.*, 2004; Spracklen *et al.*, 2008]. As we have shown here, primary CCN enhancements will be localized over high wind speed regions, while secondary DMS-derived CCN are spread over wide regions. These primary organic contributions, if important, will also contribute to correlations between chlorophyll and CCN and may change the experimentally derived contribution of DMS. The climatic importance of these two sources depends on how the spread of produced CCN correlates with cloud cover.

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