The relationship between DMS flux and CCN concentration in remote marine regions

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Abstract. The relationship between the steady state cloud condensation nuclei (CCN) concentration and the dimethylsulfide (DMS) emission flux in remote marine regions is investigated by modeling the principal gas-, aerosol-, and aqueous-phase processes in the marine boundary layer (MBL). Results are in reasonable quantitative agreement with the available measurements of DMS, SO_2, H_2SO_4, CCN, and condensation nuclei (CN) concentrations in remote marine regions of the globe and suggest that indeed DMS plays a major role in the particle dynamics of the MBL. For sufficiently low DMS fluxes practically all the SO_2 produced by DMS photooxidation is predicted to be heterogeneously converted to sulfate in sea-salt aerosol particles. For DMS fluxes higher than approximately 2.5 μmole m^{-2} d^{-1} a linear relationship is found to exist between the CCN number concentration and the DMS flux.

1. Introduction

To establish a causal relationship between anthropogenic emissions and global climate effects we must understand the biogeochemical processes that govern the background troposphere. Two-thirds of the earth is covered by oceans, and this relatively dark water surface could absorb over 90% of the incident solar radiation. The presence of clouds over these oceans decreases the amount of energy reaching the sea-surface. These marine clouds can influence, through their albedo, the earth's climate.

Charlson et al. [1987] have postulated the existence of a feedback relationship by which perturbations caused by anthropogenic influences may be either dampened or accelerated by interaction with dimethyl sulfide (DMS), a metabolic by-product of marine phytoplankton. According to this hypothesis, DMS is oxidized in the atmosphere and the products of these reactions contribute to cloud condensation nuclei (CCN) formation, resulting in regulation of the earth's albedo. This change in the earth's albedo alters the radiative flux to the surface which in turn may alter the production of DMS. For a given cloud liquid water content the cloud albedo is determined largely by the number of particles that can nucleate to form droplets, namely the CCN.

An essential step in demonstrating this feedback mechanism is understanding the relationship between the source strength (flux) of DMS and the number concentration of CCN in the marine boundary layer [*Fitzgerald*, 1991]. If there is such a link, there should exist a direct correlation between DMS flux and CCN

levels, at least under conditions not influenced by anthropogenic emissions. Field studies have provided some preliminary evidence of a positive correlation between DMS and CCN. *Bates et al.* [1987] demonstrated a strong correlation between DMS and condensation nuclei (CN) levels, providing indirect evidence of this link as CCN are a subset of CN. Satellite observations have provided more direct links between DMS flux and the earth's albedo, as reported by *Durkee et al.* [1991]. *Quinn et al.'s* [1993] data from the Pacific Ocean provides direct in situ evidence of a link between DMS and CCN, as they found a weak but positive correlation between particulate non-sea salt sulfate and CCN concentrations. The large number of the DMS-CCN system variables, their spatial and temporal variability, and the highly variable time constants involved, have made it difficult to quantify through field campaigns the relationship between DMS and cloud albedo.

The next step then is to probe the theoretical basis for the link between DMS emissions and CCN concentrations by constructing a model incorporating all of the appropriate chemical and physical mechanisms. As a first approximation, this gas-to-particle link can be investigated using a time-dependent nucleation and condensation model. *Kreidenweis and Seinfeld* [1988] proposed a framework for such a model using the three-variable aerosol parameterization developed by *Warren and Seinfeld* [1986], focusing on the kinetics of the H_2SO_4/MSA split, and demonstrated the primary role of H_2SO_4 as the nucleating agent under typical ambient conditions. *Hegg et al.* [1990, 1991, 1992] have adapted this model to make predictions of behavior under specific observed conditions leading to predictions of what regions of the troposphere and what ambient conditions might

foster nucleation. However, as *Raes et al.* [1992a] demonstrated, the outcome of such a prediction may be heavily dependent on the parameters chosen in the model, as the present range of uncertainty in, for example, the condensation and nucleation rates spans several orders of magnitude. The model of *Raes and Van Dingenen* [1992] is based on a computationally-rigorous multi-sectional aerosol representation and has also been used to simulate the effect of boundary layer/free troposphere interaction on CCN levels [*Raes et al.*, 1992b]. *Lin et al.* [1992, 1993] have evaluated the competing mechanisms involved in the process of CCN formation by comparing their characteristic times and have estimated that heterogeneous SO_2 conversion is not important for the growth of submicron sulfate particles. However, *Chameides and Stelson* [1992] have shown with an aqueous chemistry model that heterogeneous conversion is a significant sink for sulfur when larger, less acidic sea-salt particles are present.

Each of the above studies has focused on some aspects of the DMS/CCN system, neglecting the rest. The present study combines for the first time a description of the full system, adopting the perspective of a steady-state model to probe the underlying behavior of the DMS/CCN link. A similar approach has been followed by *Baker and Charlson* [1990], who studied the steady-state behavior of the CCN concentration together with MBL energy and total water balances. While *Baker and Charlson* [1990] lumped all the processes resulting in CCN production into a generic CCN source term, they demonstrated that a steady-state

approach can provide valuable insights into this problem. Our goal here is to integrate the present understanding concerning the individual gas-, aerosol- and aqueous-phase processes to determine the relationship between the DMS flux and the CCN number concentration. The model sensitivity to values of various parameters and to the parametrizations used in the model itself will be probed.

2. The DMS-CCN System

We focus on processes occurring in the MBL, which we assume to be well-mixed vertically. The processes considered are gas-phase chemistry, heterogeneous removal of SO_2 in sea-salt particles, heterogeneous oxidation of SO_2 in both the sea-salt aerosol particles and cloud droplets, coagulation between the interstitial aerosol and the cloud droplets, and wet and dry deposition of the gas and aerosol species to the ocean surface. The pathways for interaction among these processes are illustrated in Figure 1. The air parcel in the MBL is assumed to go through cloud condensation-evaporation cycles and also to pass through raining cloud systems.

The aerosol size distribution in the marine boundary layer is generally observed to be bimodal with a so-called nucleation mode containing particles of diameter smaller than roughly 0.12 μm and a so-called accumulation mode containing particles of diameter from approximately 0.12 to 0.6 μm [*Quinn et al.*, 1993]. The source of the aerosol in the nucleation mode is assumed to be H_2SO_4 nucleation, and the particles are assumed to consist of a
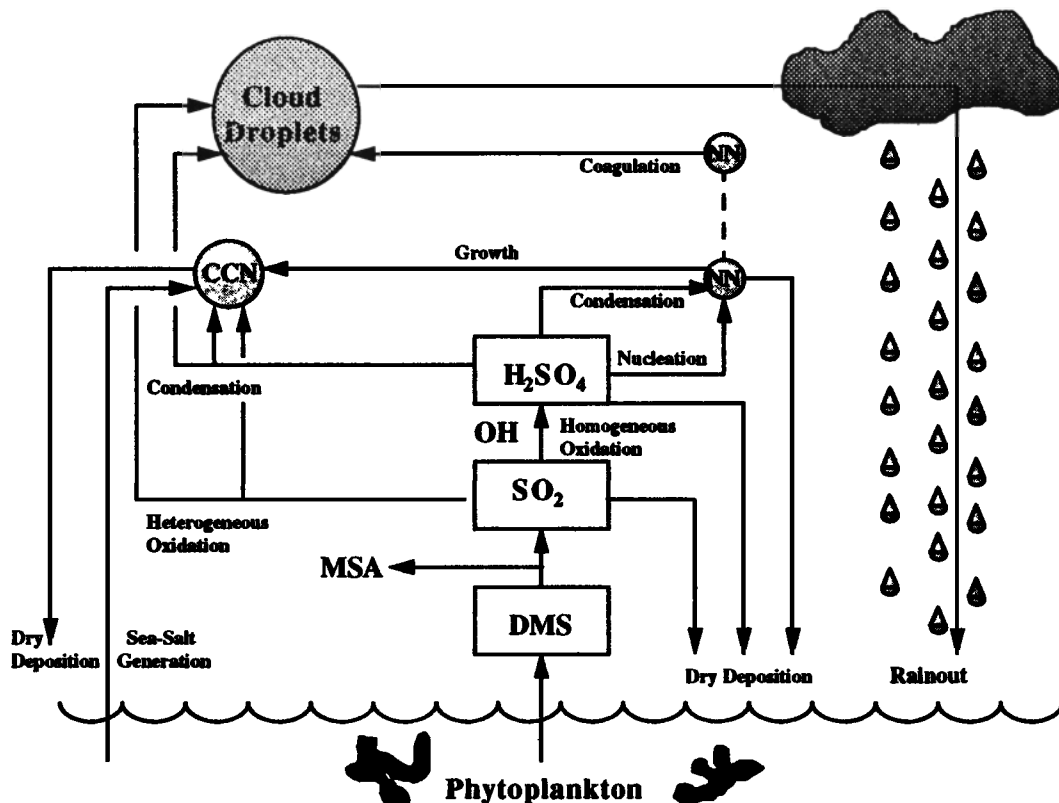

Figure 1. The DMS-CCN cycle in the remote marine boundary layer (MBL). The aerosol distribution is simulated by using two monodisperse groups of particles corresponding to the nucleation mode (NN) and to the accumulation mode (CCN). The accumulation mode particles can grow to cloud droplets, while the nuclei mode remain in the clouds as interstitial aerosol.

solution of ammonium sulfate and sulfuric acid. The particles in the accumulation mode include both the sea salt particles emitted by the ocean and the ammonium sulfate particles that have grown from the smaller mode by condensation of sulfuric acid and water. Approaches of varying complexity have been used in the past for the description of this MBL aerosol distribution. *Baker and Charlson* [1990] assumed a monodisperse CCN mode. A single mode aerosol model was also employed by *Kreidenweis and Seinfeld* [1988]. *Hegg* [1990] used a bimodal aerosol model with a monodisperse nuclei mode. *Lin et al.* [1992] grouped all particles generated during a half hour interval together and used up to 144 distinct sizes of particles. *Raes and Van Dingenen* [1992] represented the aerosol with 70 size sections. In an effort to describe the aerosol size distribution in the MBL with a modest number of parameters we will use the sectional approximation [*Warren and Seinfeld*, 1985], in which the continuous aerosol size distribution is approximated by a series of step functions. Two size sections have been used for the present work with the first corresponding to the nucleation and the second to the accumulation mode. The logarithm of the particle diameter has been selected as the independent variable for the aerosol number distribution, $n(\log_{10}D_p) = n(x)$. Five parameters are therefore required for the complete distribution description, the three sectional boundaries $(D_1, D_a,$ and $D_2)$ and the two distribution values n_1 and n_2. The definition of the size distribution function is therefore:

$$n(x) = 0, \quad x < \log_{10}(D_1)$$
$$n(x) = n_1, \quad \log_{10}(D_1) < x < \log_{10}(D_a)$$
$$n(x) = n_2, \quad \log_{10}(D_a) < x < \log_{10}(D_2)$$
$$n(x) = 0, \quad \log_{10}(D_2) < x.$$

From available measurements of aerosol size distributions in the MBL [*Quinn et al.* , 1993; *Hoppel*, 1988; *Hoppel and Frick*, 1990], we have selected $D_1 =$ 0.023 μm, $D_a = 0.1$ μm and $D_2 = 0.6$ μm. A comparison of the sectional distribution with some of the measured distributions of *Quinn et al.* (1993) is depicted in Figure 2. Accumulation mode particles with diameters larger than 0.1 μm can grow to cloud droplets for supersaturations larger than $S_c = 0.1\%$, typical of marine stratiform clouds [*Baker and Charlson*, 1990]. On the contrary, the nucleation mode particles are too small to be activated and to become cloud droplets under typical stratus supersaturations. Particles in the accumulation section are therefore defined here as CCN [*Hegg and Hobbs*, 1992].

The selection of the diameter D_a that divides the two aerosol modes is reasonable but by no means unique. Supersaturations in stratiform clouds can approach 0.5% (corresponding to an activation diameter of around 0.07 μm) and in cumuliform clouds up to 2% (activation diameter around 0.04 μm) [*Raes and Van Dingenen*, 1992]. The sensitivity of the model to this choice of the sectional boundary will be explored subsequently. The variables simulated by the model described below are the DMS, SO_2, and H_2SO_4 gas-phase concentrations and the number concentrations of the two aerosol sections N_1 and N_2. Note that
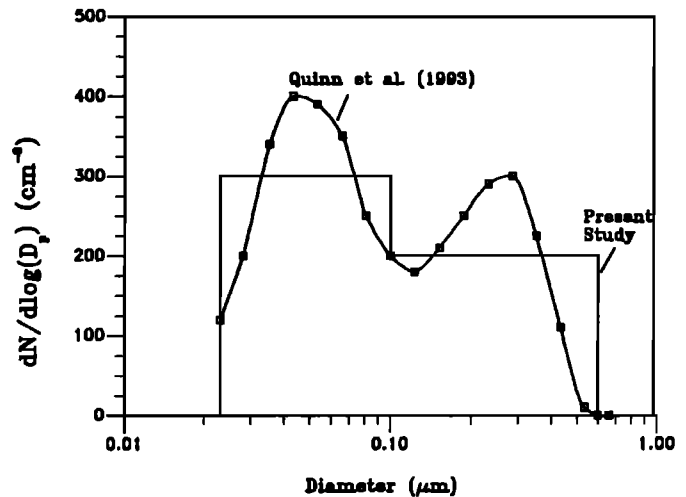

Figure 2. Modeling the remote marine aerosol size distribution with two sections. Modeled distribution vs typical measured distribution by Quinn et al. [1993].The values n_1 and n_2 of the distribution have been chosen for this example, so that total number is conserved.

$$N_1 = n_1\left(\log_{10}(D_a) - \log_{10}(D_1)\right)$$
$$N_2 = n_2\left(\log_{10}(D_2) - \log_{10}(D_a)\right).$$

2.1. Dimethylsulfide (DMS)

DMS enters the boundary layer at the air-ocean interface (flux F_{DMS}) and its major sink is assumed to be its reaction with the hydroxyl (OH) radical resulting in the production of both SO_2 and methane sulfonic acid (MSA). The DMS-OH reaction rate constant, k_{DMS}, is 8×10^{-12} cm^3 $molec^{-1}$ s^{-1} at 298 K [*Atkinson et al.*, 1984]. The SO_2 and MSA yields from this reaction are not firmly established and appear to depend both on temperature and NO_x availability. Field measurements have shown that MSA yields range from 6% in tropical areas [*Saltzman et al.*, 1983] to about 20% in mid latitudes [*Berresheim et al.*, 1990] to around 30% near the polar regions [*Berresheim*, 1987]. An SO_2 yield, y_{SO2}, of 0.9 has been selected for the base case of the present calculations. Considerable uncertainty still surrounds the DMS oxidation and *Berresheim et al.* [1993] recently suggested that the dominant oxidation product of DMS may be dimethylsulfone ($DMSO_2$). Moreover *Bandy et al.* [1992] proposed that the major pathway for oxidation of DMS to H_2SO_4 was via SO_3 and not SO_2, and *Lin and Chameides* [1993] showed that such a mechanism is compatible with the MSA/non-sea-salt sulfate ratios measured in remote marine air. The implications of these alternative reaction pathways will be discussed in the sensitivity analysis section. A hydroxyl radical concentration, $(OH)_g$ of 2×10^6 molec cm^{-3} is assumed, typical of summer conditions [*Crutzen and Zimmermann*, 1991]. Nighttime nitrate radical (NO_3) concentrations are low in the remote marine atmosphere so that its reaction with DMS can be neglected in the present calculations [*Langner and Rodhe*, 1991]. Recent measurements by *Daykin and Wine* [1990] indicate that the DMS reaction with iodine oxide (IO) is very slow and can also be neglected. The ocean surface is

supersaturated with DMS and thus oceanic deposition of DMS is zero. The temporal variation of the DMS gas-phase concentration, $(DMS)_g$, is thus described by

$$\frac{d(DMS)_g}{dt} = F_{DMS} - k_{DMS}(OH)_g(DMS)_g \qquad (1)$$

MSA has been measured in marine aerosol but in concentrations not exceeding 20% of the measured non-sea-salt sulfate [Quinn et al., 1993; Fitzgerald, 1991]. MSA is incorporated in the particles by condensation and not nucleation [Kreidenweis and Seinfeld, 1988; Wyslouzil et al., 1991a, b] and therefore neglecting MSA does not influence the aerosol number concentration predicted by the model. For the purpose of the present calculations, the influence of MSA condensation in the DMS-CCN system has been neglected, resulting in an error in predicted particle diameter less than 6%.

2.2. Sulfur Dioxide (SO2)

Sulfur dioxide is produced during the DMS oxidation with a yield of y_{SO2} and is lost by reacting in the gas-phase with OH, by heterogeneous oxidation in the aerosol phase and in the cloud droplets, and finally by depositing on the ocean surface. The rate of change of its concentration, $(SO_2)_g$, is

$$\frac{d(SO_2)_g}{dt} = y_{SO_2}k_{DMS}(OH)_g(DMS)_g$$
$$- K_{dep}^{SO_2}(SO_2)_g - k_{SO_2}(OH)_g(SO_2)_g \qquad (2)$$
$$- R_{aeros} - R_{cloud}^{SO_2}$$

The deposition rate constant, K_{dep}, of a species is defined as the ratio of its deposition velocity to the mixing height (H_{mix}) of the marine boundary layer. A deposition velocity of 0.5 cm s⁻¹ is used for SO_2 in the base case corresponding to a deposition rate constant of 0.43 d⁻¹ for a mixing height of 1000 m. A reaction constant k_{SO_2} of 10^{-12} cm³ molec⁻¹ s⁻¹ is used for the SO_2 gas-phase oxidation by the OH radical [Atkinson and Lloyd, 1984].

There is considerable evidence that SO_2 can be removed from the marine boundary layer by heterogeneous reaction with O_3 in the water associated with sea-salt aerosol particles [Sievering et al., 1992]. Chameides and Stelson [1992] have shown that the amount of SO_2 removed from the atmosphere by this mechanism should be roughly equal to the flux of alkalinity that cycles through the atmosphere in sea-salt aerosols. The time scale for this removal of SO_2 is estimated by Chameides and Stelson [1992] to be less than an hour and to be essentially limited only by the rates of mass transfer of the reactants to the aerosol. The loss rate (in equivalents) of SO_2 by heterogeneous reactions in the aerosol phase, R_{aeros}, is therefore set equal to the alkalinity flux, or equivalently to the product of the sea salt mass flux [Fitzgerald, 1991; Monahan et al., 1983] and the sea water alkalinity concentration [Riley and Chester, 1971]. For a wind speed of 8 m s⁻¹ this loss rate is calculated to be 18 ppt SO_2 d⁻¹. When the DMS emission rate is sufficiently small so that the gas-phase production rate of SO_2 is less

than its heterogeneous loss rate, then the loss rate is set equal to the production rate and the steady-state SO_2 concentration is negligibly small. In this case, at steady state, all the SO_2 produced is rapidly oxidized in the sea-salt aerosol particles.

Sulfur dioxide is also depleted by oxidation in cloud droplets by dissolved H_2O_2, O_3, O_2 (catalyzed by Fe^{3+} and Mn^{2+}) [Pandis and Seinfeld, 1989]. Concentrations of $H_2O_2(g)$ in the marine atmosphere have been found to be 0.5-1.5 ppb [Ray et al., 1990], substantially exceeding the measured $SO_2(g)$ concentrations of 0.06-0.1 ppb [Luria et al., 1990]. Under these conditions all the SO_2 will be oxidized in the aqueous phase to sulfate in much less than the 2 h average residence time of the air parcel in the cloud. Therefore the average loss rate of SO_2 can be approximated by

$$R_{cloud}^{SO_2} = f_{cloud}(SO_2)_g$$

where f_{cloud} is the average frequency of cloud occurrence in the MBL assumed to be 1 d⁻¹ [Hamrud and Rodhe, 1986; Raes et al., 1992b]. The model sensitivity to this assumed cloud frequency will be examined subsequently.

2.3. Sulfuric Acid Vapor (H2SO4)

The homogeneous oxidation of SO_2 is the principal gas-phase source of sulfuric acid in the marine boundary layer. The sulfuric acid vapor formed by this reaction can nucleate with water molecules and form sulfuric acid droplets, condense on the existing aerosol particles, condense on cloud droplets, and deposit to the ocean surface. The mass loss of H_2SO_4 by nucleation is negligible compared with that from condensation on the aerosol particles because the nuclei formed have a diameter of the order of 0.001 μm and typical average nucleation rates expected in the MBL are of the order of 1000 cm⁻³ d⁻¹ or less [Hegg, 1990; Raes and Van Dingenen, 1992; Lin et al., 1992]. This assumption is also justified by the results of the present study, described in subsequent sections.

The condensation rate of H_2SO_4 to the aerosol particles is described using the modified form of the Fuchs-Sutugin equation [Hegg, 1990; Kreidenweis et al., 1991]. The condensation rate J to a particle of diameter D_p is given by:

$$J = 2\pi D D_p F(Kn)A(P - P_o)$$

where D is the diffusivity of sulfuric acid in air (set to 0.1 cm² s⁻¹), Kn is the Knudsen number (that is the ratio of the air mean free path to the particle radius), $F(Kn)$ is a coefficient correcting for free molecular effects,

$$F(Kn) = \frac{1 + Kn}{1 + 1.71Kn + 1.33Kn^2}$$

and A a coefficient correcting for the interfacial mass transport limitations described by the accommodation coefficient a_c.

$$A = \left[1 + 1.33 Kn \ F(Kn)\left(\frac{1}{a_e} - 1\right)\right]^{-1}.$$

Finally, P is the bulk H_2SO_4 vapor partial pressure and P_O is its partial pressure at the particle surface. An accommodation coefficient of 0.02 for the condensation of H_2SO_4 on the aerosol particles is assumed [Van Dingenen and Raes, 1991]; the sensitivity of the model predictions to this parameter is examined later. The vapor pressure of H_2SO_4 at the aerosol surface can be estimated from the data of Bolsaitis and Elliot [1990]. A value of 10^{-5} ppt was calculated for a relative humidity of 90% and a temperature of 293 K and therefore the surface vapor pressure of H_2SO_4 in the mass transfer calculation can be assumed to be zero.

For the ith aerosol size section from $x_i = \log_{10}(D_i)$to $x_{i+1} = \log_{10}(D_{i+1})$ and a particle number concentration N_i the H_2SO_4 condensation rate is given by

$$J_i = K_{mt}^i N_i (H_2SO_4)_g$$

where the sectional mass transfer coefficients K_{mt}^i are calculated by

$$K_{mt}^i = \frac{2\pi D}{x_{i+1} - x_i} \int_{x_i}^{x_{i+1}} 10^x F(x)A(x)dx.$$

A deposition velocity of 1 cm s^{-1} is assumed for H_2SO_4 corresponding to a dry deposition rate constant, $K_{dep}^{H_2SO_4}$, equal to 0.86 d^{-1} for a MBL height of 1000 m. During the processing of the air parcel by clouds, the particles in the accumulation mode grow to cloud droplets of an average diameter of 20 μm. Since their corresponding surface area increases by more than three orders of magnitude, one can assume that all the sulfuric acid vapor is scavenged by the droplets in a period much shorter than that which the air parcel spends inside the cloud. The average mass transfer rate of H_2SO_4 to cloud droplets, $R_{cloud}^{H_2SO_4}$, can therefore be approximated by

$$R_{cloud}^{H_2SO_4} = f_{cloud}(H_2SO_4)_g.$$

The temporal variation of the sulfuric acid gas-phase concentration, $(H_2SO_4)_g$, is given by:

$$\frac{d(H_2SO_4)_g}{dt} = k_{SO_2}(OH)_g(SO_2)_g - L_{nucl}$$

$$- (K_{mt}^1 N_1 + K_{mt}^2 N_2)(H_2SO_4)_g \qquad (3)$$

$$- K_{dep}^{H_2SO_4}(H_2SO_4)_g - R_{cloud}^{H_2SO_4}.$$

2.4. Nucleation Mode Aerosol

Aerosol particles in the nucleation mode are produced by sulfuric acid-water nucleation with a rate J_{nucl}. This nucleation rate is primarily a function of the H_2SO_4 concentration, the temperature, and the relative humidity. The results of Jaecker-Voirol and Mirabel [1989] from hydrate theory for homogeneous binary nucleation are multiplied by an experimentally determined nucleation

factor, t_n, to produce the nucleation rate used [Raes et al., 1992a]. For a temperature of 298 K, selecting a value of t_n equal to 10^7 [Raes et al., 1992a], the nucleation rate, J_{nucl} in particles $cm^{-3} s^{-1}$, used in this study is:

$$\log_{10} J_{nucl} = 7 + [-(64.24 + 4.7RH)$$

$$+ (6.13 + 1.95RH)\log_{10}(H_2SO_4)_g] \qquad (4)$$

with the relative humidity, RH, varying from zero to one and $(H_2SO_4)_g$ the concentration of sulfuric acid vapor in molec cm^{-3}.

The deposition velocity of the aerosol particles is calculated using the theory developed by Hummelshoj et al. [1992] for dry deposition of particles to the sea surface. A deposition velocity of 0.04 cm s^{-1} for wind speed of 8 m s^{-1} is appropriate for the nucleation mode aerosol.

The condensation of sulfuric acid and water to the nucleation mode aerosol particles causes them to grow to accumulation mode particles with a growth rate of J_{growth}. At 80% RH and 298 K the equilibrium composition of a sulfuric acid solution is 25% per mass H_2SO_4 [Giauque, 1960]. Thus, the total condensation rate is assumed to be 4 times the H_2SO_4 condensation rate. The growth rate is calculated according to the theory developed by Warren and Seinfeld [1985], based on aerosol number and mass conservation during condensation. The volume concentration of the particles in section i, V_i in $\mu m^3 cm^{-3}$, is given by [Seinfeld, 1986]

$$V_i = \int_{x_i}^{x_{i+1}} \frac{1}{6}\pi D_p^3 n(x)dx =$$

$$0.0758 N_i \frac{\exp(6.908 \ x_{i+1}) - \exp(6.908 x_i)}{x_{i+1} - x_i}$$

where x_i, x_{i+1} are the sectional boundaries, and N_i the number concentration of particles in this section in cm^{-3}. Therefore, the volume concentrations for the two size sections used in this study are

$$V_1(\mu m^3 cm^{-3}) = 1.41 \times 10^{-4} N_1(cm^{-3})$$

$$V_2(\mu m^3 cm^{-3}) = 2.09 \times 10^{-2} N_2(cm^{-3}).$$

and the volume equivalent average diameters of the two sections are 0.06 and 0.34 μm correspondingly. When a volume dV of condensate (sulfuric acid and water) is added to the particles of the first section, it causes growth of dN particles to the second section. The diameter of these particles increases from $D_p (D_1 < D_p < D_a)$, to $D_a = 0.1$ μm. The corresponding volume change is

$$dV(\mu m^3 cm^{-3}) = 3.8 \times 10^{-4} dN(cm^{-3}).$$

The total condensate (H_2SO_4 and H_2O) flux J_{cond} is

$$J_{cond} = \frac{dV}{dt} = \frac{K_{mt}^1}{r_{H_2SO_4}} N_1(H_2SO_4)_g$$

where $r_{H_2SO_4}$ is the H_2SO_4 mass fraction in the aqueous solution in equilibrium with the atmosphere at 80% RH and 298 K [Giauque, 1960]. Combining the last two expressions one can show that the growth rate is

$$J_{growth} = \frac{dN}{dt} = 0.12 N_1 (H_2SO_4)_g$$

where the growth rate is expressed in particles $cm^{-3} d^{-1}$, N_1 is in particles cm^{-3} and $(H_2SO_4)_g$ is in ppt. The above method is equivalent to calculating the particle growth rate by dividing the total condensate flux (sulfuric acid and water) by the volume change of a particle growing from the volume average diameter of the first section (0.06 µm) to the minimum CCN diameter (0.1 µm). For a nucleation mode concentration of 100 cm^{-3} and a $(H_2SO_4)_g$ mixing ratio of 1 ppt, the growth rate is 12 particles $cm^{-3} d^{-1}$.

The particles in the nuclei mode coagulate with themselves, with particles in the accumulation mode, and with cloud droplets. Lin et al. [1992] demonstrated that the growth of nuclei by coagulation with other aerosol particles in the remote marine atmosphere is a relatively inefficient process over the time scales of interest and can be neglected when compared to other processes influencing their concentration. On the contrary, the removal of these particles by collisions with cloud droplets during the processing of the air parcel by clouds is significant [Flossmann et al., 1985]. The coagulation coefficient for the nucleation mode aerosol with 20 µm diameter cloud droplets is $2 \times 10^{-3} cm^3 d^{-1}$ [Seinfeld, 1986]. The fact that the air parcel spends, on average, 2 h per day in a cloud environment [Raes et al., 1992b], has been factored in the above value. The evolution of the number concentration of the nuclei mode aerosol, N_1, is therefore described by:

$$\frac{dN_1}{dt} = J_{nucl} - K_{dep}^1 N_1 - J_{growth} - K_{coag} N_1 N_2 . \quad (5)$$

2.5. Accumulation Mode Aerosol

Aerosol particles in the accumulation mode are either sea-salt particles that have been directly emitted to the MBL or nuclei mode particles that have grown by vapor condensation to this mode. The number emission rate (particles $cm^{-3} d^{-1}$) of sea salt particles is calculated after Monahan et al. [1983] to be

$$J_{salt} = \frac{2.5 U^{3.41}}{H_{mix}}$$

where the mixing height, H_{mix}, is in m, and U is the wind speed in m s^{-1}. The deposition velocity of the accumulation mode aerosol for a wind speed of 8 m s^{-1} is 0.06 cm s^{-1} [Hummelshoj et al., 1992] and the corresponding deposition constant K_{dep}^2 is 0.05 d^{-1}.

The periods that the air parcel spends in non-precipitating clouds are assumed not to affect directly the number of accumulation mode particles, but the processing of the air parcel by raining clouds depletes the MBL of these particles. If f_{precip} is the frequency of processing of the parcel by raining clouds (a value of 0.1

d^{-1} is assumed in the base case), e_p is the CCN rainout efficiency, and the rainout rate of these particles is equal to $f_{precip} e_p N_2$. The rainout efficiency is expected, in general, to depend on the number of CCN and the raindrop size distribution [Pruppacher and Klett, 1980]. Following Raes et al. [1992b] a rainout efficiency of 1.0 is assumed. This choice results effectively in the linearization of the nonlinear rainout process; the sensitivity of the model to this choice will be examined subsequently.

The number concentration of the accumulation mode particles is thus governed by:

$$\frac{dN_2}{dt} = J_{salt} + J_{growth} - K_{dep}^2 N_2 - f_{precip} e_p N_2 . \quad (6)$$

3. The System in Steady-State

Valuable insights about the interactions of the various components of the system can be gained by studying its steady-state behavior. While the system is characterized by a diurnal variation [Raes et al., 1992b], a pseudo-steady state can be envisioned as a sufficiently long-term average. Such an approach is supported by the available experimental evidence suggesting that aerosol concentrations are remarkably constant in the remote marine boundary layer [Baker and Charlson, 1990].

The timescales for reaching such a pseudo-steady state for the system can be estimated from the corresponding equations. They are:

$$\tau_{DMS} = \left(k_{DMS}(OH)_g \right)^{-1} \approx 1 \text{ d}$$

$$\tau_{SO_2} = \left(K_{dep}^{SO_2} + k_{SO_2}(OH)_g + f_{cloud} \right)^{-1} \approx 1 \text{ d}$$

$$\tau_{H_2SO_4} = \left(K_{mt}^1 N_1 + K_{mt}^2 N_2 + K_{dep}^{H_2SO_4} + f_{cloud} \right)^{-1} < 1 \text{ d}$$

The timescales for the two modes of the aerosol distribution reaching their corresponding steady-states are approximately:

$$\tau_{N_1} = \left(K_{dep}^1 + 0.12(H_2SO_4)_g + K_{coag} N_2 \right)^{-1} \approx 3 \text{ d}$$

$$\tau_{N_2} = \left(K_{dep}^2 + f_{precip} \right)^{-1} \approx 6 \text{ d}$$

where values of $(H_2SO_4)_g=1$ ppt, and $N_2 = 100$ cm^{-3} have been used (see results of base case simulation below). These calculations indicate that the gas-phase species are expected to reach their pseudo-steady state concentrations in around one day, while the aerosol distribution requires significantly more time. The six days necessary for the aerosol distribution to attain its pseudo-steady state are significantly less than the time that a typical air parcel spends in the marine atmosphere [Hamrud and Rodhe, 1986; Savoie et al., 1992; Ellis et al., 1993]. Hence, the pseudo-steady state is consistent with the time available for the trip of the air parcel in the marine atmosphere, before being influenced by anthropogenic sources. The time scales calculated above for approach to the pseudo-steady state are sensitive to a series of selected variables.
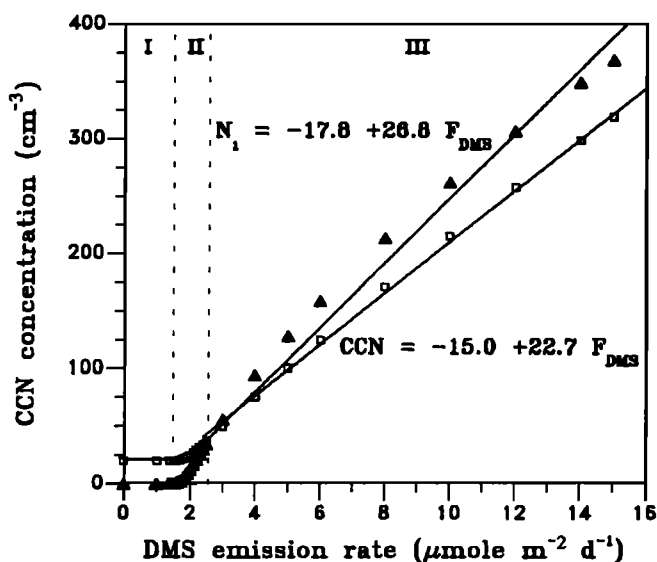
Figure 3. Predicted nuclei (N_1) and accumulation mode (CCN) concentration versus DMS emission flux for the base case meteorological conditions. The three DMS flux regimes are indicated.
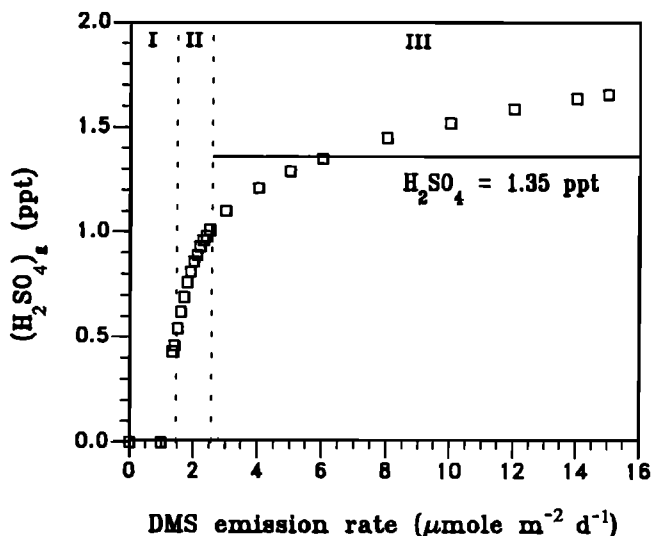

Figure 4. Predicted sulfuric acid vapor concentration versus DMS emission flux for the base case meteorological conditions. The three DMS flux regimes are indicated.

For example, increasing the rainout frequency from 0.1 d^{-1} to 0.3 d^{-1} results in a reduction of the τ_{N_2} timescale from six to three days.

The present steady-state model is obtained by setting the right hand sides of equations (1), (2), (3), (5) and (6) to zero. This model is expected to approximate the average conditions in the remote MBL, that is, after the air parcel has spent several days over the ocean and the aerosol distribution has relaxed to its pseudo-steady state form. This simplified approach provides valuable insights into the interdependencies among critical MBL processes.

4.   The Dependence of CCN on DMS Flux

Erickson et al. [1990] have suggested that the DMS flux varies with time and latitude from 0-15 μmole m^{-2} d^{-1}. Varying the DMS flux and solving the above steady-state model produces the CCN (accumulation mode) number concentration variation shown in Figure 3. The predicted CCN number concentration varies between roughly 20 and 350 particles cm^{-3}. This figure suggests that there are three distinct regimes of functional dependence of CCN on DMS for the flux range shown. When the DMS emission flux is smaller than 1.3 μmole m^{-2} d^{-1}, the CCN concentration is predicted to be essentially constant at 20 particles cm^{-3}. In this regime all the SO_2 produced by the DMS oxidation is oxidized to sulfate in the available sea-salt aerosol particles and the concentration of H_2SO_4 vapor is effectively zero. The only available CCN source is the sea salt emitted by the ocean, and the steady-state CCN concentration is determined by a balance between the wind-dependent emission rate and the dry and wet deposition rates. In the second DMS emission regime, extending between 1.3 and 2.3 μmole m^{-2} d^{-1}, most of the SO_2, but not all, is consumed by heterogeneous reaction and only a few particles per day can grow and become CCN. The CCN
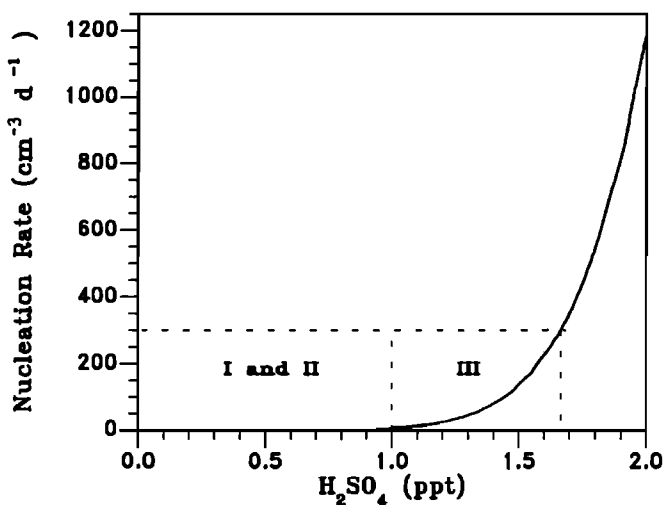
Figure 5. Nucleation rate as a function of the H_2SO_4 concentration for a relative humidity of 80% and a temperature of 298 K. The three DMS flux regimes are indicated.

concentration increases slowly (by 10 particles cm^{-3}) as the DMS emission rate increases in this regime. The third region corresponds to DMS emission fluxes larger than 2.3 μmole m^{-2} d^{-1}; despite the extreme nonlinearity of the system, the CCN concentration in this regime is a surprisingly linear function of the DMS flux.

The explanation of this unexpected behavior lies in the predicted sulfuric acid concentrations (Figure 4). In region I, as expected, the H_2SO_4 concentration is essentially zero. In the transition region II, the H_2SO_4 concentration rises sharply from zero to about 1 ppt as the DMS flux increases. However, the nucleation rate (Figure 5) is still practically zero in this region. The inability of the system to create any appreciable number of new nuclei in this region results in a very small increase of the CCN concentration. When the DMS flux exceeds 2.3 μmole

m^{-2} d^{-1}, sulfuric acid exceeds the threshold value of 1 ppt and appreciable nucleation commences. Interestingly enough, the H_2SO_4 does not need to change very much (from 1 to 1.6 ppt) to produce the relevant range of nucleation rates (Figure 5) for the system (from 0 to 300 particles cm^{-3} d^{-1}); furthermore, in region III, that concentration is nearly constant at about 1.35 ppt (within 30%). This small variation of the sulfuric acid vapor concentration is the key to the linear dependence of the CCN on DMS flux.

Equation (1) suggests that the DMS steady-state gas-phase concentration increases linearly with increasing DMS emission rate. Replacing $(DMS)_g$ with a linear function of the the DMS emission rate in equation (2), one can show that the SO_2 steady-state gas-phase concentration is also a linear function of the DMS emission rate. The linear dependence of the DMS and SO_2 concentrations on the DMS flux, F_{DMS}, is described by:

$$(DMS)_g = 17.7F_{DMS} \text{ (regions I, II \& III)}$$

$$(SO_2)_g = -12.2 + 13.7F_{DMS} \text{ (regions II \& III)}$$

Using this linearity together with the fact that $(H_2SO_4)_g$ is practically constant at 1.35 ppt in region III, equation (3) in steady-state can be rewritten as

$$k_{SO_2}(OH)_g(-12.2 + 13.7F_{DMS}) + 13K_{dep}^{H_2SO_4}$$

$$+1.35f_{cloud} = 1.35K_{mt}^1N_1 + 1.35K_{mt}^2N_2$$

Therefore, a linear combination of N_1 and N_2, corresponding to the H_2SO_4 condensation flux, is a linear function of the DMS emission rate. Similarly the steady-state form of equation (6) is equivalent to

$$J_{salt} = -0.12N_1 1.35 + K_{dep}^2N_2 + f_{precip}e_pN_2$$

suggesting that a linear combination of N_1 and N_2 is a constant independent of the DMS flux. These last two relationships show that indeed both N_1 and N_2 are expected to depend linearly on the DMS rate for DMS emission fluxes in region III. From a physical point of view, the requirement of a H_2SO_4 steady state results in a linear variation of the H_2SO_4 condensation flux to the marine aerosol with the DMS flux, or that for constant sectional boundaries the total number of aerosol particles should increase linearly with the DMS flux. The CCN steady state requires the nuclei mode particle concentration, that is the main CCN source, to vary similarly to the CCN concentration. These two requirements can only be satisfied if both aerosol mode particle concentrations vary linearly with the DMS flux.

5. Comparison With Available Measurements

Measured DMS gas-phase concentrations vary from 25 to 300 ppt [Andreae, 1985; Andreae and Raemdock, 1983; Putaud et al., 1992; Saltzman and Cooper, 1988] with a mean concentration around 100 ppt [Andreae, 1985; Berresheim, 1987]. The predictions of the steady-state

model vary from zero to 270 ppt with a value of 100 ppt corresponding to the reasonable average DMS flux of around 5 µmole m^{-2} d^{-1}. A wide variation of SO_2 gas-phase concentrations has been reported in the remote MBL varying from a few ppt to 100 ppt with averages around 40 ppt [Andreae et al., 1988; Berresheim et al., 1990; Quinn et al., 1990; 1980; Nguyen et al., 1983; Bonsang et al., 1980; Delmas and Servant, 1980; Putaud et al., 1992]. The range of the predicted steady state SO_2 concentrations is from zero to 190 ppt, in satisfactory agreement with the above measurements, although with a tendency of overprediction. For the average DMS flux of 5 µmole m^{-2} d^{-1} an SO_2 concentration of 57 ppt is predicted.

Eisele and Tanner [1993] recently reported gas-phase H_2SO_4 concentrations in relatively clean air masses varying from 0.01 to 1 ppt. These measurements are in qualitative agreement with 0 to 1.7 ppt predicted. The number concentration of aerosol particles in the nuclei mode in the remote marine boundary layer has been measured to be from around 50 to roughly 500 cm^{-3} [Quinn et al, 1993; Gras, 1989; Hegg et al., 1991; Hoppel and Frick, 1990]. We predict concentrations from zero to around 350 particles cm^{-3}, with a concentration of 120 particles corresponding to the average DMS flux.

As predicted here, all available studies point to the existence of nonzero minimum accumulation mode aerosol number concentration around 40 particles cm^{-3} [Hegg et al., 1991]. Sea-salt particles emitted even when the DMS emission flux is too low to result in the production of any additional aerosol lead to a predicted concentration around 20 particles cm^{-3}. The highest accumulation mode aerosol concentrations measured in the clean MBL are around 250 particles cm^{-3} [Quinn et al, 1993; Hegg et al., 1991; Hoppel and Frick, 1990], in good agreement with the 300 particles cm^{-3} predicted in the present study.

The role of sea-salt particles as CCN has received little attention. Charlson et al. [1987] suggested that observed sea-salt particle concentrations at cloud height are typically of the order of 1 cm^{-3}, so the sea itself cannot be the main source of CCN. Blanchard and Cipriano [1987] argued that the actual sea-salt particle concentration is much higher, around 20cm^{-3} at cloud height. Latham and Smith [1990] calculated that for wind speeds around 8 m s^{-1} about 3 sea-salt particles cm^{-3} should be present, while the study of Blanchard and Woodcock [1980] had suggested 20-30 cm^{-3}. In the most recent study O'Dowd and Smith [1993] measured at ship level sea-salt particles at concentrations representing 20% of the accumulation mode number, and in high winds (17 m s^{-1}) the percentage increased to 75%. The present model suggests a sea-salt particle concentration of 20cm^{-3}, that, for low DMS fluxes, represents almost 100% of the accumulation mode aerosol number concentration and, for the average DMS flux of 5 µmoles m^{-2} d^{-1}, represents 20% of the total CCN accumulation mode number in agreement with the O'Dowd and Smith measurements [1993]. This model prediction is also in agreement with the conclusion of Ayers and Gras [1991] that at low DMS and MSA concentrations there was another source of CCN apart from DMS, probably sea-salt. These particles also indirectly influence the CCN number concentration by

providing the necessary alkalinity for the heterogeneous oxidation of SO_2.

A notable feature of the remote MBL is the constancy of the aerosol concentrations; in summer, the total particle concentration varies around 300-500 cm^{-3} with CCN being more than 20% of the total aerosol number concentration [Raes et al., 1992b]. Hoppel and Frick [1990] reported 100-300 cm^{-3} in the trade wind region and 25-1000 cm^{-3} south of trade wind region. Other measurements have indicated concentrations from 60-450 cm^{-3} [Hoppel et al., 1989; Parungo et al., 1987; Kim et al., 1990] The model predictions of total particle concentrations from 20-700 cm^{-3} are in good agreement with the above observations.

Raes et al. [1992b] suggest as a major test of MBL models that the predicted CCN concentrations should be more than 20% of the total aerosol number concentration. Measurements have indicated ratios of 40-60% [Quinn et al., 1993; Gras, 1989] and 20% [Hegg et al., 1991]. The model predicts for region III that accumulation mode particles represent from 40 to 50% of the total number concentration with this value increasing to almost 100% as the DMS flux approaches zero.

Bates et al. [1987] attempted to reconstruct the CN to DMS flux relationship using field measurements that unfortunately were not concurrent in space or time. The suggested relationship was CN = -16.9 + 77 F_{DMS}, which agrees within 30% with that predicted here, CN = -32.8 + 50 F_{DMS}. A similar set of relationships has been proposed by Hegg et al. [1991] between the CCN number concentration at various supersaturations and the DMS gas-phase concentration

$$CCN(1\% \text{ supersaturation}) = 23 + 0.86(DMS)_g$$

$$CCN(0.3\% \text{ supersaturation}) = 50 + 0.4(DMS)_g$$

The corresponding relationship predicted by the present model is CCN $(D_p > 0.1 \mu m) = 15 + 1.28 (DMS)_g$. Note that for an average DMS concentration of 100 ppt, the model predicts 143 cm^{-3}, while the two relationships by Hegg at al. [1991] predict 109 cm^{-3} and 90 cm^{-3}, respectively.

The above comparison indicates that the steady-state model reproduces the main features of gas/aerosol phenomena in the MBL.

6. Sensitivity Analysis

To investigate the effect of the choices of model parameters on the reported base case results, a detailed sensitivity analysis of the model has been performed (Table I). The change in CCN number has been calculated relative to a DMS flux of 5 μmoles m^{-2} d^{-1}.

6.1. Meteorological Conditions

The particle nucleation rate depends exponentially on the MBL relative humidity and changes of 10% in RH result in significant changes in the predicted CCN concentration. The relative humidity also influences the amount of water that condenses together with sulfuric acid vapor, enhancing the growth of small particles to CCN. An increase of the MBL height results in dilution of the

DMS emission flux and to lower DMS, H_2SO_4, and sulfate concentrations. This results in a decrease of the CCN levels that is partially offset by smaller losses to the ocean surfaces of all species involved. Wind speed increases, under constant DMS flux, lead to two opposing effects, increase of the sea-salt particle production, but also higher heterogeneous oxidation rates for SO_2 in the same particles. Therefore, for higher wind speeds, the sea-salt number concentration increases, but the total CCN number concentration is predicted to decrease.

6.2. Cloud Processing

The period that the air parcel spends between consecutive cloud processing is one of the most important model parameters. When this time (equal to $1/f_{cloud}$)is 16 h the predicted CCN concentration is 69 cm^{-3}; for 24 h it increases to 100 cm^{-3} and for 48 h it reaches 153 cm^{-3}. Every time that the air parcel passes through such a system, all the available $(SO_2)_g$ is assumed to be lost because of heterogeneous reaction with H_2O_2 and the available $(H_2SO_4)_g$ condenses on the droplets. The processing of the air parcel by raining clouds is less important as, even if rainout were to deplete the MBL of CCN entirely, this event occurs relatively infrequently (only once in 10 days in the base case). Doubling the rainout frequency results in a 10% reduction of the predicted CCN concentration. If one assumes that the rainout efficiency is not unity, but just 50%, this is equivalent to doubling the time between rainout events (equation 6). Expressing this rainout efficiency as a function of the CCN number concentration has little qualitative effect on the predicted linearity of the DMS-CCN relationship for efficiency values ranging from 50% to 100%.

Processing of the air parcel by clouds and the consequent in-cloud oxidation of SO_2, scavenging of H_2SO_4 by cloud droplets, and CCN rainout have been treated as continuous processes in the present model. In reality, the air parcel spends most of the time outside the cloud layer and is processed by clouds for a limited time per day. This assumption of continuous cloud processing is expected to result in underestimation of the maximum H_2SO_4 vapor concentration and consequently of the nucleation rate. Hence, use of this assumption is expected to result in lower predicted concentrations of the nuclei and accumulation particle concentrations. In a series of sensitivity simulations the continuous cloud processing assumption has been relaxed and the corresponding variation of the system variables has been studied. Use of this assumption was indeed found to result in an underprediction of the CCN concentration by 50%, but did not change the linearity of the DMS/CCN relationship. These dynamic simulations will be discussed in detail in a forthcoming publication.

6.3. Gas Phase Chemistry

The parameters involved in the descriptions of the gas-phase reactions leading to the H_2SO_4 production influence significantly the model results. Reduction of the OH radical concentration to half its assumed base case value results in a 50% reduction of the predicted CCN concentration. The SO_2 yield during the DMS oxidation is

Table 1.   Parameter Variation in Steady State DMS/CCN Model for MBL

	Base Case Value	Test Values	Percent Change in CCN Number
Relative humidity	0.8	0.7	-26
		0.9	+37
Mixing height (m)	1000	500	+40
		1500	-23
Wind speed (m s⁻¹)	8	4	+15
		12	-21
Cloud frequency (d⁻¹)	1	0.5	+53
		1.5	-31
Precipitation frequency (d⁻¹)	0.1	0.05	+9
		0.20	-10
Coagulation coefficient (cm³d⁻¹)	0.002	0.001	+5
		0.00	-3
$(OH)_g$ (molec cm⁻³)	2x10⁶	1x10⁶	-50
		3x10⁶	+43
DMS to SO₂ yield	0.9	0.7	-27
SO₂ deposition velocity (cm s⁻¹)	0.5	0.25	+16
		1.00	-22
Sea salt mass flux (g m⁻²d⁻¹)	0.06	0.03	+10
		0.12	-20
Sea salt number flux (cm⁻³d⁻¹)	3	6	+4
Alkalinity flux (μg Ca m⁻³d⁻¹)	0.03	0.015	+11
		0.060	-20
Accommodation coefficient	0.02	0.05	-45
D_1 (μm)	0.03	0.001	-12
D_2 (μm)	0.6	1.2	-72
D_{CCN} (μm)	0.1	0.05	+40
$(H_2SO_4)_g$ deposition velocity (cm s⁻¹)	1.0	0.5	+6
		1.5	-5
Nuclei deposition velocity (cm s⁻¹)	0.04	0.02	+1
		0.06	-1
CCN deposition velocity (cm s⁻¹)	0.06	0.1	-4
H_2SO_4 condensate fraction	0.26	0.13	+8
Nucleation factor	1x10⁷	1x10⁴	-60

The effect of varying parameters in the steady-state DMS/CCN model of the marine boundary layer is calculated as percent change in predicted CCN number concentration relative to a base case DMS Flux of 5 μmole m⁻²d⁻¹.

of similar importance. A reduction of this yield by 28% resulted in a 27% reduction of the CCN concentration. If H_2SO_4 is not the major final product of the DMS oxidation, the proposed DMS-CCN link will weaken considerably. Alternative pathways not involving SO₂ as an intermediate product (e.g. involving SO₃) could actually strengthen this link [Lin and Chameides, 1992].

6.4. MBL-Ocean Surface Interaction

The predicted CCN concentration changes corresponding to 50% changes in the selected deposition velocities for H_2SO_4 and the two aerosol modes is less than 10%, while for SO₂ the predicted CCN level increases to 20%. Changes of CCN concentrations around 20% are also the result of 50% variation of the sea-salt flux variables.

6.5. Aerosol Distribution

The selected sectional boundaries, D_1, D_2, and D_a are reasonable but by no means unique. If a much smaller lower boundary of the distribution is selected, e.g. 0.001 μm, the changes in predicted variables are not dramatic. The steady state CCN concentration is reduced by 12% mainly because the nucleation mode particles cannot compete as effectively for the condensing sulfuric acid vapor. In this case, however, the number of these particles increases by a factor of three. The model is more sensitive to the selection of the activation diameter. Selecting a diameter $D_a = 0.05$ μm, resulted in a 40% increase of the CCN concentration. The choice of the upper distribution boundary D_2 is also important because it determines the surface area of the accumulation mode particles. Selecting a rather extreme value of 1.2 μm resulted in a 71% decrease in the CCN concentration, because of the effectiveness of these CCN as H_2SO_4 condensation sites. Changes in the growth expression used can be expressed as equivalent changes in the sectional boundaries.

The above sensitivity analysis (Table I) indicates that the predicted CCN concentrations are sensitive to the meteorological conditions (especially the RH), to the OH concentration levels, to the SO_2 yield during DMS oxidation, to the H_2SO_4 mass transport accommodation coefficient, to the activation diameter, to the size of the particles in the accumulation mode, and to the nucleation rate. An independent variation of most model parameters by a factor of two or more resulted in CCN concentration changes of generally less than 50%. A similar surprisingly small change was observed during variations of the nucleation rate by 3 orders of magnitude. Variables like the precipitation frequency, coagulation coefficient, sea salt number flux, the size of the nuclei mode particles, the H_2SO_4 and aerosol dry deposition velocities, and the species (e.g. NH_3) that condense with H_2SO_4 appear to have a secondary effect on the CCN concentration levels for a typical DMS flux.

7. Discussion

The present study suggests that under constant meteorological conditions (temperature, relative humidity, wind speed and mixing height) the CCN number concentration is expected to vary almost linearly with the DMS emission flux. It is important to note the weaknesses of the system of equations (1), (2), (3), (5), and (6) as a representation of the remote marine boundary layer. The model assumes that the MBL remains homogeneous. *Hegg et al.* [1990] proposed, for example, that new particle production can occur in the vicinity of marine clouds, and, while temporally and spatially inhomogeneous, this source could be significant.

One of the main assumptions we have made is that the diameters of the two aerosol modes are fixed and do not change significantly for this region of the DMS fluxes. The diameter D_2 of the CCN particles seems to be the most important parameter. We have relaxed this assumption, adding to the set of equations the mass balances of the two aerosol modes, calculating explicitly the diameter D_2. This diameter indeed increases with increasing DMS flux but the change is small enough not to affect the presented conclusions beyond the sensitivity analysis values of Table I. Another problem of the

specific representation of the aerosol distribution used is numerical diffusion. When a group of particles are created, the model automatically distributes them over the first section and artificially 'diffuses' them. This numerical artifact allows faster growth to the second section. When a similar group of particles grows to the second section the same numerical smearing occurs. In this case, this numerical error results in an increased condensation of H_2SO_4 in this section and prevents more CCN growing. Therefore, this numerical error from the one side accelerates and from the other decelerates the CCN growth.

Baker and Charlson [1990] proposed that two stable CCN concentration regimes exist, one corresponding to the low concentration observed over the oceans and the other to the higher continental concentrations. The first steady state results from the balancing of the CCN source by the rainout sink and corresponds to the steady-state discussed in this study. The second steady-state proposed by *Baker and Charlson* [1990] was the result of the interaction of the CCN concentration with the MBL structure in their model. This interaction between the aerosol concentration and the MBL structure has not been included in the present study and therefore only one steady state is predicted by the present model. *Baker and Charlson* [1990] proposed that at high CCN levels, the precipitation sink ceases and coagulation becomes the main sink, allowing a much higher CCN steady-state concentration.

Lin et al. [1992] and *Raes et al.* [1992b] have raised some questions about the ability of the MBL to sustain a reasonable CCN concentration and have suggested that new CCN can be produced only under special conditions (very low CCN levels) or in the free troposphere by oxidation of DMS that escapes the MBL. The above models have generally been initialized with zero nucleation mode particles and used for the simulation of one cloud cycle (usually a few days). The simulations were terminated long before a steady state was reached, thus precluding direct comparison with the results of this study.

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