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Effects of anthropogenic sulfate on cloud drop nucleation and optical properties

By CATHERINE C. CHUANG* and JOYCE E. PENNER, *Global Climate Research Division, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA*

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ABSTRACT

The characteristics of the cloud drop size distribution near cloud base are initially determined by the aerosol particles that serve as cloud condensation nuclei (CCN) and the updraft velocity. Changes in CCN concentrations can change cloud drop number thereby affecting cloud optical properties and the global radiation budget. The CCN concentration depends on the composition and size distribution of the aerosol particles. Chemical reactions of the emitted gaseous sulfur compounds due to human activities will alter, through gas-to-particle conversion, the aerosol size distribution, total number, and its chemical composition. It is important to assess these changes in order to estimate the effect of anthropogenic sulfur emissions on cloud drop number concentrations. Here, we assume that the aerosol size distribution is modified, with total number unchanged, by two processes: condensation of sulfuric acid vapor (H_2SO_4) on a prescribed pre-existing particle size distribution and aqueous-phase oxidation of SO_2 followed by evaporation of the drops. We examine the relationship between the resulting anthropogenic sulfate-containing aerosol size distribution and cloud drop number concentrations. The results are used to estimate the possible change in cloud optical thickness and cloud albedo due to an increase of anthropogenic sulfate mass concentration. This work is aimed at improving the assessment of the effects of anthropogenic sulfate on cloud optical properties and the global radiation budget.

1. Introduction

Atmospheric aerosols play an important rôle in the radiation budget, either directly by scattering and absorbing solar radiation or indirectly, by influencing the microphysical properties of clouds and thereby modifying their radiative properties and lifetimes. The direct aerosol effect of climate forcing (i.e., the change in reflected solar radiation) due to scattering by anthropogenic sulfate aerosols may range from -0.3 to -1.1 W m^{-2} (Penner et al., 1994). Such forcing is comparable but of opposite sign to the greenhouse forcing by CO_2. Smoke particles from biomass burning can contribute an additional cooling of comparable magnitude to that of sulfate aerosols (Penner et al., 1992). Aerosols may also indirectly affect the radiation budget by changing the reflectivity of clouds when they act as cloud condensation nuclei (CCN), but the magnitude of the forcing associated with the indirect effect is quite uncertain. Recently, Boucher and Rodhe (1994) and Jones et al. (1994) have each developed parameterizations relating cloud drop concentration to sulfate mass or aerosol number concentration, respectively, and used them to develop estimates of the indirect forcing by anthropogenic sulfate aerosols. These parameterizations made use of measured relationships in continental and maritime clouds. However, these relationships are inherently noisy, yielding more than a factor of 2 variation in cloud drop number concentration for a given aerosol number (or for a given sulfate mass) concentration. They do not make use of information from the climate model regarding local updraft velocities, and they have had to make certain simplifying assumptions.

* Corresponding author.

In the study by Boucher and Rodhe (1994), simultaneous aerosol mass and CCN number concentration measurements were used to establish a hypothetical range of dependencies between the sulfate aerosol mass and cloud drop number concentration. However, their results of the indirect radiative forcing by sulfate aerosols are sensitive to these assumed relationships and the predicted forcing may be overestimated when comparing with observations of cloud drop radius and cloud albedo. In the study by Jones et al. (1994), aerosol number concentration was related to cloud drop number concentration based on measurements. But in converting the model-predicted sulfate mass concentrations to aerosol number concentrations for use in the parameterization, the aerosol composition and size distribution were prescribed and assumed to be universally applicable both in the case of the natural background aerosol (present prior to industrialization) and in the present-day perturbed case.

The characteristics of the cloud drop size distribution near cloud base are initially determined by the size distribution and chemical characteristics of the aerosol particles that serve as CCN and by the local updraft velocity (Lee et al., 1980; Chuang et al., 1992). Once drop concentrations at cloud base are established, measurements have shown that these remain near constant with altitude throughout the main part of the clouds, at least in the case of stratiform and stratocumulus clouds (Nicholls, 1984; Bower et al., 1994; Mitchell, DRI, private communication). Thus, ideally, it should be possible to use these fundamental properties of aerosol size, chemical composition, and updraft at cloud base to predict the effects of anthropogenic aerosols on drop number concentrations in stratiform clouds in general circulation models. However, the large spatial and temporal variabilities in the concentration, chemical characteristics, and size distribution of aerosols have made it difficult to develop such a parameterization from data.

In this paper, our focus is to develop a means for relating the predicted anthropogenic sulfate mass to cloud drop number concentration over the range of expected conditions associated with continental and marine aerosols. We start with an assumed pre-existing particle size distribution and develop an approximation of the altered distribution after addition of anthropogenic sulfate. In this calculation, we assume that anthropogenic sulfate is formed mainly through the condensation of sulfuric acid vapor (H_2SO_4) on pre-existing particles and aqueous-phase oxidation of SO_2 followed by evaporation of the drops. We thereby develop a conservative estimate of the possible change in CCN number concentration due to anthropogenic sulfate-containing aerosols and investigate its impact on cloud albedo and global average solar radiative forcing.

The assumed pre-existing particle size distribution derives from a variety of sources, including the gas-to-particle conversion of natural emissions of non-methane hydrocarbons (primarily terpenes), aerosols from biomass burning, condensed organic species from transportation, domestic and industrial pollution, and natural and anthropogenic water-soluble inorganic species (sulfates, nitrates, ammonium) other than anthropogenic sulfate, and black carbon. The sources of these aerosols are regionally diverse; however, global scale distributions have not yet been established. Thus, the assumption of a single pre-existing distribution, as used here, is a simplifying, but necessary assumption. As noted below, the required pre-existing distribution has a component that would normally be associated with the nucleation mode. This mode could be associated with low volatility condensible organics (Novakov and Penner, 1993) or with homogeneous nucleation of sulfuric acid vapor (Kreidenweis et al., 1991). Over the oceans, the latter source of nucleation mode particles in the pre-existing distribution probably dominates. Over the continents, condensible organics from both anthropogenic and natural sources may provide the nucleation mode. To the extent that anthropogenic sulfate also contributes to a nucleation mode, we necessarily overestimate the amount of anthropogenic sulfate formed through aqueous processes or deposited by condensation. However, in the case of aerosol size distribution measured by Hoppel et al. (1990) off the coast of South Carolina, such contribution can be estimated. If the entire nucleation mode is ammonium sulfate, its total sulfate mass concentration is $\sim 0.055\ \mu g/m^3$. This is a minor fraction of the total anthropogenic sulfate shown in Lelieveld and Heintzenberg (1992) ($\sim 5\ \mu g/m^3$). In addition, Langner et al. (1992) estimated that only 6% of anthropogenic sulfate could be used for new particle formation. Hence, the neglect of homogeneous nucleation pathway

for the formation of anthropogenic sulfate appears to be reasonable.

2. Estimate the anthropogenic sulfate-containing aerosol size distribution

It has been estimated that anthropogenic sulfur emissions (mainly SO_2 from fossil fuel combustion, industrial sources, and biomass burning) dominate over natural emissions by a factor of 2 on a global average (with 90% of the anthropogenic sources in the Northern Hemisphere) (Spiro et al., 1992) and they have been significantly increased during the past several decades (Charlson et al., 1992). Model simulations (Langner et al., 1992; Penner et al., 1994) illustrate that anthropogenic sulfur emissions have caused a large increase in the mass concentration of sulfate over and around industrialized regions. Within these areas, the anthropogenic emissions are larger than natural emissions by about a factor of ten or even more (Galloway et al., 1984). How the aerosol size distribution might change as a result of these emissions is the key issue that must be addressed in order to evaluate the effects of anthropogenic sulfate on cloud optical properties.

The size distribution of anthropogenic sulfate-containing aerosols depends on the processes which form particulate sulfate. It is thought that H_2SO_4 is mainly formed during the aqueous conversion of SO_2 to $SO_4^=$ in cloud drops. H_2SO_4 is also formed in the gas phase where it may either condense onto pre-existing particles causing them to grow or form new particles through homogeneous nucleation. Homogeneous nucleation takes place only under special conditions of high sulfuric acid vapor pressure, high relative humidity, and low pre-existing particle surface area (Hoppel and Frick, 1990; Hegg et al., 1990; Kreidenweis et al., 1991; Clarke, 1993). Its contribution to the main sulfate mass distribution has been questioned because the gas phase production of H_2SO_4 is thought to be small in any case (Lelieveld and Heintzenberg, 1992) on a global basis. Here, we neglect homogeneous nucleation in determining the aerosol size distribution in order to develop a lower limit to the prediction of new CCN, and since once a certain amount of particulate surface area is available, additional gas phase mass condenses onto the existing particles instead of forming new particles (Ayers and Gras, 1991). Homogeneous nucleation of course may create new particles that eventually grow to accumulation mode size where most of the sulfate mass resides, thereby increasing total aerosol number. The effect of this process will be evaluated in a future paper.

Measurements which relate sulfate mass and aerosol number distributions are nearly non-existent, though measurements of sulfate mass and mass distribution do exist. Measurements by Stevens et al. (1978) show that sulfate accounts for about 40% of the aerosol mass for $d < 3.5\ \mu$m in urban and rural areas of the United States, and in some instances it accounts for more than 50%. Whitby (1978) estimated that the mass fraction of sulfate in the accumulation mode (mode diameter in the range 0.1 to 1 μm) was, on the average, 15–30% for continental aerosols and 30–60% for marine aerosols. Milford and Davidson (1987) reviewed the published literature on airborne mass size distributions for sulfate, which included more than 40 studies conducted over the past 20 years. Sampling locations for these studies ranged from urban centers to remote areas around the world. Most of the measured mass concentrations of sulfate over land are in the range 0–20 μg m^{-3}. Typical values in non-urban regions are on the order of 0.5–2 μg m^{-3}. High values of up to 40 μg m^{-3} are also observed near intense sources. Unfortunately, the corresponding aerosol number distribution which is the physical property most relevant to CCN determination, to the average measured sulfate mass distribution shown in Milford and Davidson (1987) is not available. Hence, we estimate number distribution of anthropogenic sulfate-containing aerosols based on the total aerosol number concentration and the amount of anthropogenic sulfate.

We begin with an assumed pre-existing particle distribution which can be expressed as the superposition of three log-normal functions,

$$\frac{dN/N_{\text{total}}}{d\log d} = \sum_{i=1}^{3} \frac{N_i}{\sqrt{2\pi}\log\sigma_i} \times \exp\left\{ -\frac{\left[\log\left(\frac{d}{D_i}\right)\right]^2}{2\log\sigma_i^2} \right\}. \quad (1)$$

Table 1. *Size distribution parameters for the pre-existing particles*

	N_i	D_i (μm)	$\log \sigma_i$
continental	0.548	0.025	0.25
	0.450	0.060	0.30
	0.002	0.750	0.35
marine	0.450	0.030	0.20
	0.540	0.150	0.15
	0.010	0.500	0.15

The assumed size distribution parameters for continental and marine pre-existing aerosols are listed in Table 1. The origin and nature of the pre-existing aerosols are not treated here. Pre-existing aerosols may consist, however, of sulfate from natural sources (Kreidenweis et al., 1991), organic aerosols (Novakov and Penner, 1993), aerosols derived from urban emissions (Hildemann et al., 1991), nitrate (Milford and Davidson, 1987), or perhaps primary and secondary biogenic aerosols (Pandis et al., 1991; Jaenicke, 1993). The main issue here is how the size distribution of pre-existing particles will change after deposition of a given amount of anthropogenic sulfate.

The evolution of the pre-existing aerosol size distribution is primarily determined by two processes: growth by condensation of sulfuric acid vapor from OH oxidation of SO_2 and growth by in-cloud oxidation of SO_2 onto particles large enough to act as CCN followed by drop evaporation. For condensation of sulfuric acid vapor, the volume increase for a particle with radius r is taken to be proportional to the product of $r\,D'(r)$, where $D'(r)$ is the effective diffusion coefficient given by:

$$D'(r) = D\left[\frac{r}{r+\lambda} + \frac{4D}{rv}\right]^{-1}, \qquad (2)$$

and D is the diffusion coefficient for sulfuric acid vapor, λ is the mean free path, and v is the mean thermal velocity (Seinfeld, 1986; Hoppel et al., 1990). For in-cloud oxidation of SO_2, the cloud drops are assumed to be monodisperse and convert the same amount of sulfate regardless of the original size of its CCN (Lelieveld and Heintzenberg, 1992; Hoppel et al., 1990). This assumption is based on the fact that nonprecipitating clouds usually have relatively narrow drop size distributions (Pruppacher and Klett, 1978). Langner and Rodhe (1991) estimated that the amount of sulfate transformed by OH oxidation is 19%–55% of that by in-cloud oxidation. Thus, if sulfate is produced by these two pathways only, 65%–85% of sulfate would be transformed by in-cloud oxidation of SO_2; a mean value of 75% is adopted in this work. We also assume that H_2SO_4 in particulate phase is completely neutralized by reacting with NH_3 and exists as $(NH_4)_2SO_4$ (ammonium sulfate).

The number distribution of anthropogenic sulfate-containing aerosols is calculated iteratively by adding a small amount of ammonium sulfate to the pre-existing distribution until a given amount of sulfate has been accumulated. At each calculation, 25% of ammonium sulfate is distributed to all particles due to condensation, and 75% to particles which are larger than the assumed minimum size of CCN. The minimum radius of CCN is chosen in the range 0.05–0.20 μm (Lelieveld and Heintzenberg, 1992). These values correspond to variations of mean updraft velocity in nonprecipitating clouds (in the order of $\sim$10 cm/s, Cotton and Anthes, 1989) and also to variations in total aerosol number concentration and solubility. The addition of ammonium sulfate on existing particles increases the particle size from r to $r+\Delta r$, the volume of which is calculated by:

$$V(r+\Delta r) = V(r) + \Delta V_{\mathrm{con}}(r) + \Delta V_{\mathrm{aq}}(r),$$

$$\Delta V_{\mathrm{con}}(r) = 0.25\,\Delta V r\,D'(r)/\Sigma[N(r)\,r\,D'(r)] \qquad (3)$$

$$\Delta V_{\mathrm{aq}}(r) = \begin{cases} 0 & \text{if } r < r_{i,\min \mathrm{CCN}} \\ 0.75\,\Delta V/\Sigma N(r \geq r_{i,\min \mathrm{CCN}}) & \text{if } r \geq r_{i,\min \mathrm{CCN}} \end{cases},$$

where $\Delta V = V/N$ is the volume of ammonium sulfate added to existing particles at each iteration, and N is the total number of iterations. $\Delta V_{\mathrm{con}}(r)$ and $\Delta V_{\mathrm{aq}}(r)$ represent the fraction of volume distributed to a particle through condensation and aqueous processes, respectively. $r_{i,\min \mathrm{CCN}} = 0.05 + i(0.20-0.05)/N$ is the minimum radius (μm) of CCN applied to the ith iteration. The number of iterations is large enough that the resultant aerosol size distribution evolves smoothly.

Examples of the simulated anthropogenic sulfate-containing aerosol size distributions along

Tellus B/47/5-4

with comparisons to data are shown in Figs. 1, 2. The calculated size distribution will vary with the anthropogenic sulfate deposited and the total pre-existing particle concentration. However, typical values were chosen for these comparisons. Fig. 1a shows the number distribution of continental aerosols before (thick solid curve) and after (light dashed curve) the deposition of anthropogenic sulfate. Also shown for comparison is the average continental aerosol number distribution measured near the coast of Charleston, South Carolina (curve 1 of Fig. 7 in Hoppel et al., 1990). The simulated size distribution is plotted versus particle equilibrium size at a relative humidity 40 % to be consistent with measured data by Hoppel et al. (1990) (private communication). Fig. 1b presents sulfate mass distributions from simulation and measurements (see Fig. 2 in Milford and Davidson

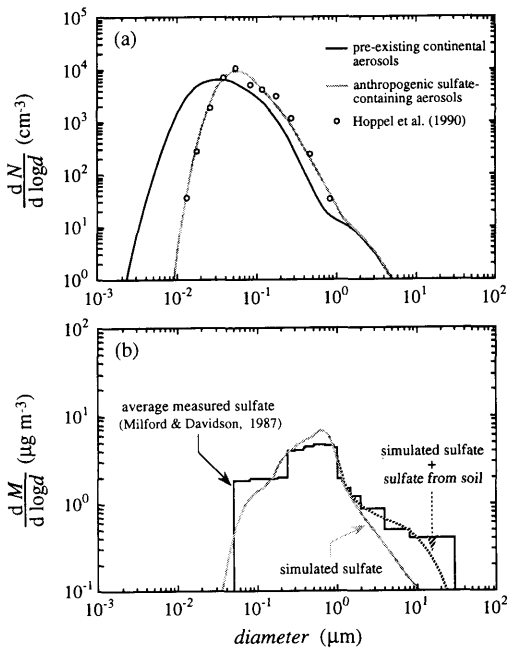

Fig. 1. (a) Number distributions of the prescribed pre-existing continental and the simulated anthropogenic sulfate-containing aerosols. The open circles show measurements by Hoppel et al. (1990). (b) Comparison of sulfate mass distributions between simulation and measurements. The pre-existing continental aerosols have number concentration 5500 cm^{-3} and natural sulfate mass 0.1 μg m^{-3}. The anthropogenic sulfate deposited is 5 μg m^{-3}. Coarse particles over continents are assumed to consist of soil dust containing 700 g of sulfur per ton.

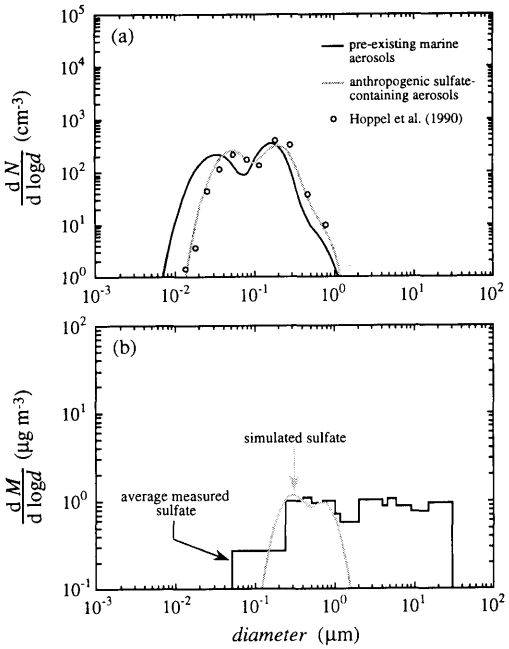

Fig. 2. Same as Fig. 1 but for marine aerosol distributions with pre-existing aerosol number concentration 250 cm^{-3}, natural sulfate 0.3 μg m^{-3}, and anthropogenic sulfate 0.5 μg m^{-3}.

(1987)). For this comparison, the anthropogenic and natural sulfate mass were assumed to be 5 and 0.1 μg m^{-3}, respectively, consistent with the calculated annual average near Charleston (Langner and Rodhe, 1991; Lelieveld and Heintzenberg, 1992; Penner et al., 1994), while the pre-existing aerosol number concentration was assumed to be 5500 cm^{-3} in keeping with that measured by Hoppel et al. (1990). In general, the simulated anthropogenic sulfate distribution through gas-to-particle conversion is in reasonable agreement with the average measured data for submicron particles. The validity of the derived size distribution for the range of particle sizes important for CCN concentration (0.1–0.7 μm) is, however, difficult to ascertain, because the resolution of the cascade impactor data, used in most observational studies is inadequate. The discrepancy in the predicted mass of sulfate in coarse particles may be explained if natural sources are responsible for the supermicron sulfate. If the pre-existing coarse particles consist primarily of soil dust and if 700 g of sulfur are contained in a ton of soil (Mason and

Moore, 1982), the total supermicron sulfate distribution agrees much better with the measurements (see Fig. 1b).

Fig. 2a shows the simulated marine aerosol number distribution as well as the average measured data over the remote tropical Atlantic ocean from Hoppel et al. (curve 4 of Fig. 7, 1990). The mass distributions for sulfate from simulation and measurements (see Fig. 3 of Milford and Davidson (1987)) are shown in Fig. 2b. The pre-existing aerosols in marine boundary layer were assumed to have a bimodal distributions as is frequently observed over the oceans. The total aerosol concentration was assumed to be 250 cm^{-3} which is typical of the remote tropical Atlantic ocean (Hoppel et al., 1990) where the natural sulfate concentrations from DMS are on the order of 0.2–0.5 $\mu g\ m^{-3}$ (Langner and Rodhe, 1991; Lelieveld and Heintzenberg, 1992; Penner et al., 1994). In this case, the anthropogenic sulfate concentration deposited on the pre-existing aerosols was assumed to be 0.5 $\mu g\ m^{-3}$, and the natural sulfate was taken to be 0.3 $\mu g\ m^{-3}$. The sulfate mass distribution data summarized by Milford of Davidson contains sea spray aerosols. Therefore, the coarse-particle sulfate is attributed to sea salt and the simulated anthropogenic sulfate distribution and the average measured sulfate data are compared only for particles $< 1\ \mu m$. It is noted that condensational growth has a considerable effect on small particles, while in-cloud oxidation of SO_2 followed by cloud evaporation can change the pre-existing CCN size distribution. Good agreement between simulated number distributions with measurements as shown in Figs. 1a and 2a indicates that the parameters listed in Table 1 may represent a reasonable "average" distribution for pre-existing particles. Note that the pre-existing distribution contains a mode near 0.01–0.03 μm for both the continental and marine cases. This indicates that nucleation must play a role in the formation of CCN. Here we assume that much of the nucleation occurs as a result of natural aerosol precursors.

3. Cloud drop nucleation and parameterization

An aerosol particle becomes activated as a CCN when the environmental supersaturation ratio becomes greater than its critical value. The resulting drop grows to a size much larger than the initial size of the particle due to condensation of water. The magnitude of the critical supersaturation for activation decreases with increasing particle size and mass fraction of soluble material in the aerosol particle; therefore, larger particles are activated earlier than smaller particles and activation of maritime aerosols whose composition contain a large fraction of soluble salts (Heintzenberg, 1989) is more favorable than continental particles for a given value of supersaturation. In this section, we investigate the relationship between anthropogenic sulfate-containing aerosols and cloud drop nucleation.

The detailed microphysical model described by Chuang et al. (1992) was used to compute the spectral evolution of interstitial aerosols and cloud drops. This model describes a Lagrangian air parcel which may also entrain environmental air. Here, we assumed the parcel dynamics were adiabatic because we are interested only in the initial stages of cloud development. The vertical

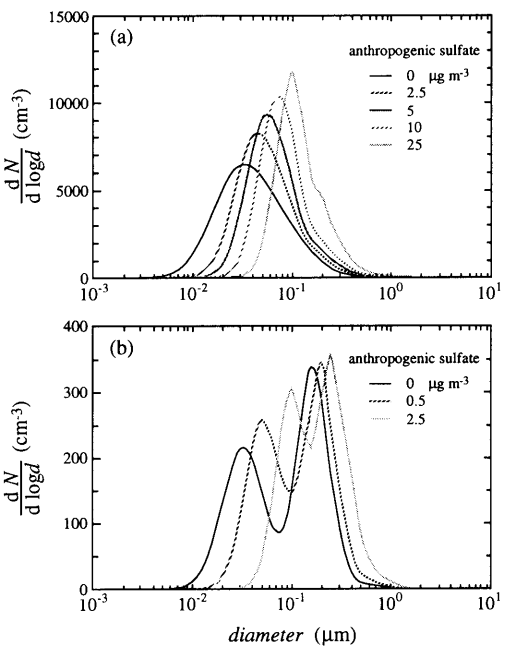

Fig. 3. Simulated size distributions with different loadings of anthropogenic sulfate for (a) continental aerosols and (b) marine aerosols. The number concentrations of pre-existing aerosols are 5500 cm^{-3} for continental case and 250 cm^{-3} for marine case.

temperature and humidity profiles were those used by Lee et al. (1980). We examine the consequence of water vapor diffusion to aerosols which are an internal mixture of sulfate and other materials (organic matter, NO_3^-, NH_4^+, ..., etc.). We also perform a series of calculations to investigate the effects of anthropogenic sulfate on aerosol size distribution. Figs. 3a, b show the simulated aerosol size distributions with different loadings of anthropogenic sulfate. The pre-existing aerosol number concentration was assumed to be 5500 cm^{-3} over land and 250 cm^{-3} over ocean, respectively. The size distribution becomes narrower with larger deposition of anthropogenic sulfate because the smaller particles increase in radius more rapidly than larger ones during the condensation of sulfate. The mass fraction of soluble material in the pre-existing aerosols was assumed to be 50% for continental case and 70% for marine case. For calculation of aerosol activation, this fraction is adjusted according to the total amount of anthropogenic sulfate added to the fine particles. The soluble material on pre-existing aerosols is also assumed to have the same properties as ammonium sulfate.

Figs. 4a, b present the relationship of the predicted cloud drop number nucleated to anthropogenic sulfate in particles. In these figures, we vary aerosol number concentration from 500–10000 cm^{-3} for continental case (Fig. 4a) and from 50–500 cm^{-3} for marine case (Fig. 4b) to cover the spatial and temporal variations expected for the concentration of pre-existing aerosols. In addition, we also consider updraft velocities ranging from 10 cm s^{-1} to 200 cm s^{-1} to cover a wide range of updrafts expected in both stratus and stratocumulus. Looking at any one curve in Fig. 4, one notes that under many circumstances the predicted cloud drop number concentration is larger on particle size distributions with a higher loading of anthropogenic sulfate even though the total number of aerosol particles is unchanged in these simulations. The concentration of cloud drops is of course also affected by both updraft velocity and total (in this case pre-existing) aerosol number. For the continental case with a moderate updraft velocity 50 cm s^{-1} and aerosol number 2000 cm^{-3}, we estimate that the number of the condensationally-produced cloud drops would increase from 350 to 560 if a typical amount of anthropogenic sulfate 2 $\mu g\ m^{-3}$ in non-urban regions were added onto the pre-existing particles. For the marine case with the same updraft velocity but much lower aerosol concentration 100 cm^{-3}, the number of cloud drops nucleated would increase from 60 to 75 for a total deposition of anthropogenic sulfate equal to 0.2 $\mu g\ m^{-3}$.

It is important to try to compare these results with all available data. Here, we compare our model results with measurements of sulfate concentration in cloud water samples (Leaitch et al., 1992). These measurements were conducted over central Ontario, Canada and over upper New York State. The observed ranges of cloud drop number concentrations with cloudwater sulfate 0.05–10 $\mu g\ m^{-3}$ are about 55–750 cm^{-3} for stratiform clouds and 160–950 cm^{-3} for cumuliform clouds (derived from eqs. (1) and (2) of Leaitch et al., 1992). For the same range of sulfate concentrations (presumably anthropogenic), our simulations show that the number concentrations of cloud drops which are nucleated on continental aerosol size distributions with total number concentrations ($>10^{-3}\ \mu m$) 500–10000 cm^{-3} are about 50–910 cm^{-3} for updraft velocities 10–50 cm s^{-1}. The predicted cloud drop numbers through nucleation on anthropogenic sulfate-containing aerosols seem to be in the right range, although direct comparison with measurements is difficult because of variabilities in updraft velocity and total aerosol number concentration. However, these measured data serve as a reference to check our model simulations with the inferred size distributions of the anthropogenic sulfate-containing aerosols.

The effect of anthropogenic sulfate accumulation on pre-existing aerosols has a significant influence on cloud drop number concentration; therefore, it should be represented in climate models. However, it is not practical to apply a detailed microphysical model in a global climate model because of the large increase in computational time required for the detailed treatment of nucleation at each grid point. An alternative is to parameterize the cloud drop nucleation and then apply this parameterization in climate models. Here, we parameterize the nucleation of cloud drops onto anthropogenic sulfate-containing aerosols based on the results from a detailed microphysical model. The cloud drop number nucleated (cm^{-3}) is expressed in the form $N_d = wN_a/(w + cN_a)$ as suggested by Ghan et al. (1993),

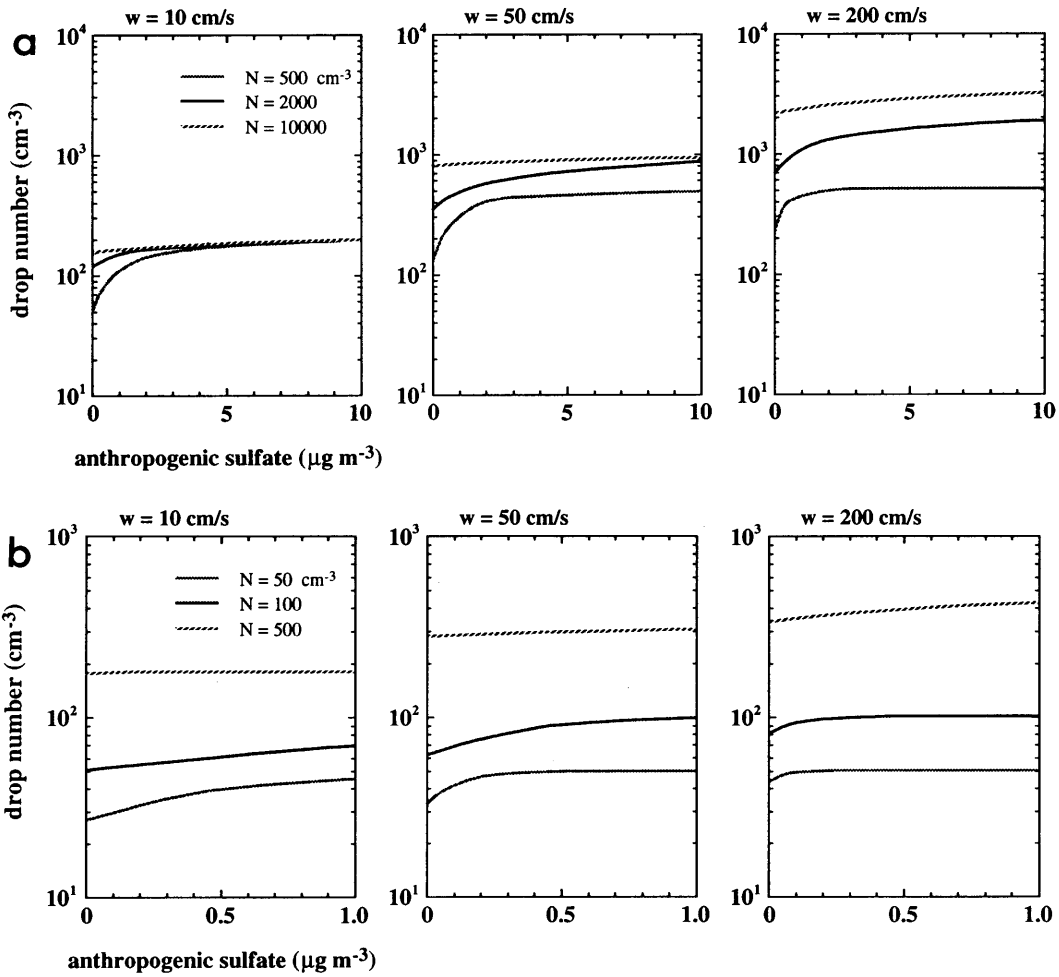

Fig. 4. (a) Predicted cloud drop number nucleated versus anthropogenic sulfate in continental particles. Aerosol number concentrations are from 500–10000 cm^{-3}. (b) Same as (a) but for marine aerosols with number concentrations from 50–500 cm^{-3}.

where N_a (cm^{-3}) is the background aerosol number concentration, and w is the updraft velocity in cm s^{-1}. In Ghan et al., a look-up table was used for scaling the value of c such that the parameterized drop concentrations match the simulated values from a detailed microphysical model. In this paper, we derive the coefficient c directly from the results of the microphysical model. From the regression curve, c may be expressed as follows

over land:

$$c = 0.03659 + 22.739X_L \quad (4)$$

over ocean:

$$c = 0.03643 - 0.3616X_O + 3.5767X_O^2, \quad (5)$$

where $X_L = \log w[1 - \log w(0.5 + \gamma)/\log N_a^{5+\gamma}$, and $X_O = \log w[1 - \log w(0.5 + 0.2\gamma)/\log N_a^{2}]/\log N_a^{2+0.1\gamma}$. γ is referred to as the shape parameter for the sulfate-containing aerosol distribution and is defined as the ratio of anthropogenic sulfate loading ($\mu g\, m^{-3}$) to the total aerosol number (1000 cm^{-3}). It is noted that the anthropogenic sulfate-containing aerosol size distributions produced through condensation and in-cloud oxidation as prescribed in Section 2

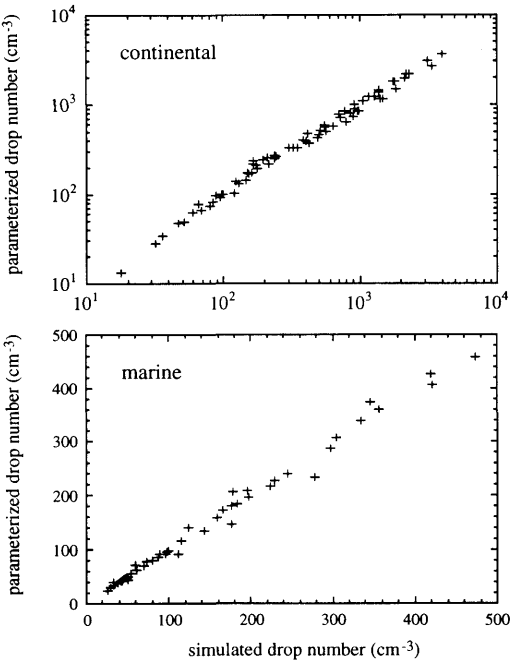

Fig. 5. Scatter diagrams of the cloud drop number concentrations from the parameterization versus the values simulated in the microphysical model.

should preserve their shape characteristics for a given value of γ. Scatter diagrams of the cloud drop number concentrations predicted from the parameterization versus the simulated values from the microphysical model are shown in Fig. 5. Since the scatter in these figures is small, we expect that the use of the parameterized number in climate models should be adequate to estimate the effect of anthropogenic sulfate-containing aerosols on initial cloud drop concentrations.

4. Optical properties of clouds

In previous sections, we examined the change in the aerosol size distribution due to deposition of anthropogenic sulfate and calculated its effect on cloud drop nucleation. In this section, we will investigate how these changes in cloud drop number concentration influence the optical properties of clouds. According to Twomey (1977), the optical thickness of a cloud (τ) with narrow drop size distribution can be approximated by

$$\tau = h\left[\frac{9\pi w_L^2 N_d}{2\rho^2}\right]^{1/3}, \tag{6}$$

where h is the cloud vertical extent, ρ is the density of liquid water, w_L is the cloud liquid water content, and N_d is the cloud drop number concentration. Furthermore, the cloud albedo α_c of a nonabsorbing, horizontally homogeneous cloud can be parameterized in terms of cloud optical thickness (Lacis and Hansen, 1974)

$$\alpha_c = \frac{\tau}{7.7+\tau}. \tag{7}$$

Since the optical thickness of a cloud is proportional to the cube root of cloud drop number concentration, this implies that an increase in the number of cloud drops will result in an increase in the optical thickness and thus an increase in the cloud albedo. Based on eqs. (6) and (7), the sensitivity of cloud albedo to an increase of cloud drop number, for constant liquid water content, may be expressed by

$$\frac{\partial \alpha_c}{\partial \ln N_d} = \frac{\alpha_c(1-\alpha_c)}{3} \tag{8}$$

(Twomey, 1991). This relation indicates that cloud albedo is most sensitive to a change in cloud drop concentration when $\alpha_c = 0.5$. Fig. 6 demonstrates the dependence of cloud albedo on drop number concentration for different cloud thicknesses. Drop

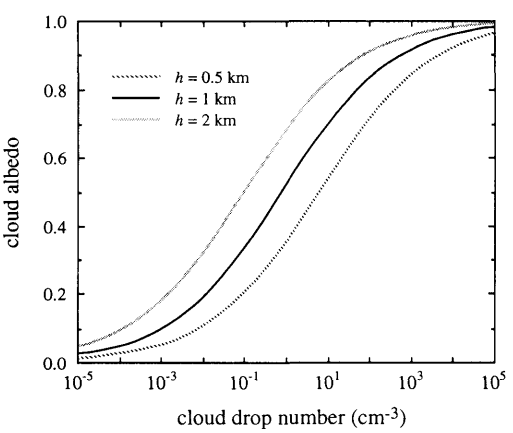

Fig. 6. The dependence of cloud albedo on drop number concentration for different cloud thickness (h). The liquid water content is assumed to be 0.2 g m^{-3}.

numbers in water clouds usually range from 10 cm^{-3} in fairly clean maritime conditions to several thousand cm^{-3} in polluted continental regions. For this range of number concentrations, an increase in the drop number has the greatest effect on cloud albedo when the cloud is thin (compare $h = 0.5$ km to $h = 2$ km).

If the fraction of cloud over the global surface, A_{cloud}, remains unchanged by the increase in cloud drop number concentration, the change of reflected solar radiation at the top of atmosphere may be approximated by an equation derived from the analysis of Charlson et al. (1992):

$$\Delta F_{cloud} = -\tfrac{1}{4} F_T A_{cloud} [0.8\, \Delta\alpha_c], \quad (9)$$

where $\frac{1}{4}F_T$ is the global average top of the atmosphere radiative flux, $F_T = 1370$ W m^{-2}, $\Delta\alpha_c$, is the change of cloud albedo.

To estimate the effect of anthropogenic sulfate-containing aerosols on climate as cloud condensation nuclei, we approximate N_d in eq. (6) by the concentration of cloud drops formed through the nucleation processes near cloud base. In reality, the drop number concentration in clouds is not a constant and subject to changes by coalescence and broadening processes such as the entrainment and mixing of dry air. However, measurements have shown that drop number concentrations are nearly constant as a function of altitude through the main part of stratiform clouds (Nicholls, 1984; Bower et al., 1994; Mitchell, DRI, private communication). Larger changes are observed for the cumulus clouds and in the area very near cloud top.

Local anthropogenic sulfur emissions over continents could affect the cloud drop number concentration dramatically as shown in Figs. 4a, b, leading to a significant regional climate change. If the average increase in anthropogenic sulfate concentration over continents is assumed to be 2 $\mu g\, m^{-3}$ (see, Lelieveld and Heintzenberg, 1992) and the average pre-existing particle number concentration is 4000 cm^{-3}, the enhancement in the cloud drop number concentration would be about 36% (from 227 to 309 cm^{-3}) for an average updraft velocity of 20 cm s^{-1}. This would result in an increase of cloud albedo from 0.868 to 0.879 for a cloud with thickness 1 km and liquid water content 0.2 g m^{-3}. For an assumed 40% cloud cover (i.e., $A_{cloud} = 0.113$), the estimated change in the global average solar radiative forcing is about -0.34 W m^{-2}. A similar calculation can be applied to the marine atmosphere but with average aerosol number concentration 200 cm^{-3}, anthropogenic sulfate 0.2 $\mu g\, m^{-3}$, and $A_{cloud} = 0.287$. In this case, a 16% increase of cloud drop number concentration (from 89 to 103 cm^{-3}) would change the cloud albedo from 0.827 to 0.834 for $h = 1$ km and $w_L = 0.2\, \mu g\, m^{-3}$ and decrease global average solar radiative forcing by about 0.55 W m^{-2}. One notes that the global radiation balance is more sensitive to the change of cloud drop concentration over ocean because marine clouds are relatively optically thin. In addition, the large extent of marine stratus and stratocumulus clouds is an important factor in determining the net change in reflected solar radiation. One also notes that the parameterization of cloud drop nucleation we developed in last section is related to the processes that form particulate sulfate. Hence, the estimated change of solar radiative forcing would be smaller if a higher fraction ($>75\%$) of anthropogenic sulfate is transformed by aqueous pathway.

5. Conclusions

Cloud drops are formed through the condensation of water vapor on aerosol particles which serve as cloud condensation nuclei. The drop concentration at cloud base is determined primarily by the aerosol characteristics of size and chemical composition as well as the updraft velocity. In this paper, we used a detailed microphysical parcel model to investigate the relationship between anthropogenic sulfate-containing aerosols and the condensationally produced cloud drops. The changes in aerosol size distribution associated with anthropogenic sulfur emissions may increase the number of cloud drops with subsequent influence on cloud albedo and climate. It has been suggested that the increase in CCN in industrial regions might explain why the Northern Hemisphere has not been warming as rapidly as the Southern Hemisphere over the last 50 years (Wigley, 1989).

In reality, the aerosol size distribution is the result of processes working simultaneously and continuously with such sources as sulfur, soot, particulate organic carbon, nitrate, ammonium, etc. Instead of applying a complete aerosol model

to investigate the effect of anthropogenic sulfur emissions on the aerosol size distribution, we simply derived the anthropogenic sulfate-containing aerosol distribution by assuming that 75% of the anthropogenic sulfate was formed through aqueous-phase oxidation and the remaining 25% condensed onto a prescribed pre-existing particle distribution. Uncertainties may arise from the assumed fraction of sulfate produced by condensation and in-cloud oxidation. In addition, new particle formation through homogeneous nucleation of H_2SO_4/H_2O is ignored in this paper; however, it could be important in the upper troposphere where surface area of existing particles is relatively low (Clarke, 1993) or in regions recently scavenged by cloud (Hoppel and Frick, 1990) or in the proximity of clouds (Hegg et al., 1990). Uncertainties can also arise from the assumed "pre-existing particle size distribution" which must result from a variety of processes (e.g., homogeneous nucleation, condensation, coagulation, dry and wet deposition) and sources involving the entire suite of aerosol types (Penner et al., 1994). The prescribed pre-existing size distribution was chosen to represent an "average" particle distribution where no anthropogenic sulfate was present. Although it may remain questionable whether the pre-existing distribution is independent of anthropogenic sulfate and can be treated separately, we believe that the approach used in this study provides a useful first attempt to quantify the relation between anthropogenic sulfur emissions and cloud drop nucleation.

The impact of anthropogenic sulfate on climate change is important in studying the Earth's radiation budget, since the radiative cooling associated with anthropogenic sulfate can mask to some extent the greenhouse warming. In this study, we estimate the effect of anthropogenic sulfate-containing aerosols on climate as cloud condensation nuclei under some given conditions. However, this estimated radiative cooling could be uncertain due to the large spatial and temporal variabilities in the concentration and size distribution of aerosols. As a matter of fact, these aerosol effects, which have not been included in past climate model simulations, can not be quantified without coupling a climate model with a chemistry model which treats the global-scale transport, transformation, and removal of trace species and aerosols. In future work, we will apply the results from this study to parameterize the number concentration of cloud drops in a climate model to improve the assessment of the anthropogenic sulfate-containing aerosol indirect effects on the global radiation budget.

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