Modification of aerosol mass and size distribution due to aqueous-phase SO₂ oxidation in clouds: Comparisons of several models

Sonia M. Kreidenweis,1 Chris J. Walcek,2 Graham Feingold,3 Wanmin Gong,4 Mark Z. Jacobson,5 Cheol-Hee Kim,6 Xiaohong Liu,7 Joyce E. Penner,7 Athanasios Nenes,8,9 and John H. Seinfeld8

Received 25 June 2002; revised 20 September 2002; accepted 27 November 2002; published 8 April 2003.

[1] Models of aerosol scavenging and aqueous-phase oxidation of SO₂ by H₂O₂ and O₃ in a cloud updraft are compared. Bulk models considering only a single droplet size are compared with size-resolved models that explicitly simulate multiple aerosol and drop sizes. All models simulate growth of cloud drops on a lognormal ammonium bisulfate aerosol distribution, and subsequent aqueous-phase chemistry during adiabatic ascent. In agreement with earlier published studies, it is found that relative to bulk models, the size-resolved cloud chemical models consistently calculate 2–3 times more oxidation via the SO₂ + O₃ pathway, due to calculated variability of cloud water pH among cloud drops. All models calculate high scavenging of the input dry aerosol mass, but the calculated number of cloud drops formed varies from 275–358 drops cm⁻³. Differences in the calculated number of cloud drops formed result from the treatment of gaseous species uptake, solution thermodynamics, applied water condensation mass accommodation coefficient, and bin size range definitions over which the input aerosol distribution is numerically approximated. The difference in calculated cloud drop number can under many conditions propagate to appreciable variations in cloud albedo. It is found that the modifications to the aerosol size and mass spectrum are sensitive to the number of cloud drops formed, and differences in the processed aerosol spectra were found to induce up to 13% differences in calculated light extinction properties of the modified particle distributions. These significant discrepancies among cloud aerosol chemistry interaction models, even when used to simulate relatively simple conditions, suggest that parameterizations of these processes used in larger-scale cloud, regional and longer-term climate models can contain high levels of uncertainty. INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: aerosol size distribution, aqueous chemistry, sulfur oxidation, cloud chemistry


1. Introduction

[2] Atmospheric particles containing sulfate are a dominant component of acidic deposition, and also contribute to fine particle pollution associated with regional haze [Malm et al., 1994] and health problems [Health Effects Institute, 2000]. Also, sulfate aerosol pollution induces an appreciable radiative cooling impact on global climate that

1Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA.
2Atmospheric Science Research Center, State University of New York, Albany, New York, USA.
3National Oceanographic and Atmospheric Administration, Boulder, Colorado, USA.
4Meteorological Service of Canada, Downsview, Ontario, Canada.
5Department of Civil and Environmental Engineering, Stanford University, Palo Alto, California, USA.
6National Institute of Environmental Research (NIER), Seo-gu, Incheon, Korea.
7Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, Michigan, USA.
8Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, USA.
9Now at School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.
counters the potential CO$_2$-induced warming influences, but considerable uncertainties persist about quantifying the direct and indirect radiative effects of sulfate aerosols on climate [Intergovernmental Panel on Climate Change, 2001].

[Sulfate is a significant and frequently the dominant component of aerosol mass in the atmosphere, and is produced primarily from the oxidation of SO$_3$. This oxidation occurs in the gas phase through reaction with the hydroxyl radical, and the characteristic rate of the gas-phase reaction is on the order of a few percent per hour during the day [Stockwell et al., 1990]. In cloudy environments containing sufficient oxidants, SO$_2$ is rapidly oxidized by aqueous reactions with hydrogen peroxide, ozone, organic peroxides and a number of other oxidants. It is generally recognized that the dominant mechanism of sulfate formation in the troposphere is via reactions of SO$_2$ with H$_2$O$_2$ and O$_3$ in clouds [Walcek and Taylor, 1986; Barth et al., 2000; Rasch et al., 2000]. Therefore it is important for atmospheric models that include sulfate to simulate accurately the oxidation of SO$_3$ in clouds. Most larger-scale models of atmospheric sulfur simulate in-cloud SO$_2$ oxidation using a simplified “bulk” modeling approach, where oxidation rates are calculated using a single characteristic water content, droplet size and acidity level [e.g., Chang et al., 1987; Iribarne and Cho, 1989].

[Aqueous-phase addition of mass to particles has direct and indirect radiative effects. Because of the global importance of sulfur gases and sulfate aerosol, this species has been the focus of the most study in the literature. The direct radiative effects are sensitive to the details of the initial aerosol distribution and how mass is added to the aerosol spectrum [e.g., Lelieveld and Heinzenberg, 1992; Hegg et al., 1996]. In turn, aqueous chemistry depends on the cloud drop spectrum. Indirect radiative effects arise from variations in drop spectra induced by changes in the input aerosol, and subsequent changes in cloud albedo. The concept of susceptibility of warm clouds to such albedo changes was first proposed by Twomey [1991], and later studies focused specifically on the link between sulfate aerosols, cloud condensation nuclei, and cloud droplet spectra in indirect radiative effects [e.g., Hegg, 1994; Jones et al., 1994; Boucher and Lohmann, 1995].

[Here several bulk and size-resolved aerosol/cloud/chemistry models are compared under a well-defined set of conditions in order to assess the uncertainties associated with different modeling approaches. The results presented here summarize the findings of the aerosol parcel model component of the World Meteorological Organization 5th International Cloud Modeling Workshop held in Glenwood Springs, Colorado, United States, in August 2000. The problem statement was first designed and disseminated in early 2000, and discussions and revisions of results continued before and after the August 2000 workshop.

2. Models Compared

[Seven participating modeling groups submitted twelve simulations for comparison. Table 1 identifies the models divided into simpler bulk models and more sophisticated, size-resolved models. The five groups contributing size-resolved calculations also submitted bulk versions of their models, and two groups contributed only bulk calculations. In subsequent figures, each model is identified using the first letter of the name identified on Table 1, and model results are further identified as “bulk” or “size-resolved.” Many of the cloud chemistry models used here are extracted from larger-scale atmospheric models, and the references to related applications are listed in the right column of Table 1.

[Further characteristics of the size-resolved models are summarized in Table 2. All of the models employ a so-called “discrete, Lagrangian” or “moving bin” approach. Although the models represent the aerosol and drop spectra as moving (in size space), discrete points, we will use the term “bin” here when discussing these points. All of the size-resolved models also solve gas-liquid transfer simultaneously with aqueous chemistry, and all treat this transfer as a nonequilibrium process.

[All models used the identical simulation conditions presented in the next section, and differences between the models arise from different numerical integration methods, different aerosol and droplet size resolutions used by the size-resolved models, and different methods for assessing cloud drop activation and water activity. In addition, the transfer of soluble HNO$_3$ and NH$_3$ gases before and during droplet growth influences the growth calculations for the size-resolved models.

3. Comparison Conditions

[All models calculate the aqueous chemical composition of cloud water within a cloud updraft. Dissolved constituents in cloud water result from the scavenging of a specified lognormal dry aerosol size distribution and dissolution of gases, and concentrations are modified by the oxidation of SO$_2$ by H$_2$O$_2$ and O$_3$. The physical conditions simulated are listed in the top half of Table 3. The chemical composition of cloud water is simulated for an air parcel lifted adiabatically at 0.5 m s$^{-1}$ starting from a height slightly below cloud base. Cloud base is reached 196 s into the simulation, and simulations continue for an additional 2400 s (1.2 km) above cloud base. At the end of the simulation, the cloud water is evaporated and the resulting dry aerosol distributions are compared.

[The relatively unpolluted chemical conditions chosen for the simulation are listed in the bottom portion of Table 3. The initial ammonium and sulfate concentrations represent a slightly acidic ammonium bisulfate aerosol. The initial ammonia gas concentration is present in excess with respect to equilibrium with this aerosol composition, which can have consequences for aerosol-cloud interactions [Seidl, 1989], as...
discussed in section 5. Initial \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \) concentrations are well in excess of \( \text{SO}_2 \) available for oxidation.

The median diameter \( D_g = 0.08 \mu\text{m} \), the geometric standard deviation \( \sigma_g = 2 \), and the total aerosol number concentration \( N_T = 566 \text{ cm}^{-3} \). A dry particle density of 1.8 g cm\(^{-3}\) is assumed. Input mass and number concentrations expressed in absolute concentration units (\( \mu\text{g m}^{-3} \), particles cm\(^{-3}\)) are defined at the initial (\( t = 0 \)) temperature and pressure listed in Table 3. The assumption of a monomodal, single-composition aerosol is made in order to deal with as simple a system as possible when diagnosing differences among models. Many previous studies have been initialized with more realistic bimodal and externally mixed aerosol distributions and have found that model predictions vary with the relative sizes and compositions of the two modes [e.g., Ayers and Larson, 1990; Hegg et al., 1992; Yuen et al., 1994; Hoppel et al., 1996].

### 4. Sulfur Chemistry

Figure 1 shows the general meteorological and chemical conditions of the parcel as it rises. Figure 1a shows a nearly linear increase in condensed liquid water content above cloud base. All models calculate that 75–80% of the initial \( \text{SO}_2 \) is oxidized to sulfate during the 40 min period.

<table>
<thead>
<tr>
<th>Table 3. Cloud Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Factor</strong></td>
</tr>
<tr>
<td><strong>Physical Conditions</strong></td>
</tr>
<tr>
<td>Height above surface at ( t = 0 )</td>
</tr>
<tr>
<td>Temperature at ( t = 0 )</td>
</tr>
<tr>
<td>Relative humidity at ( t = 0 )</td>
</tr>
<tr>
<td>Pressure at ( t = 0 )</td>
</tr>
<tr>
<td>Cloud base height above surface</td>
</tr>
<tr>
<td>Cloud base pressure</td>
</tr>
<tr>
<td>Cloud base temperature</td>
</tr>
<tr>
<td>Air density at cloud base</td>
</tr>
<tr>
<td>Updraft velocity</td>
</tr>
<tr>
<td>Cloud water mixing ratio 1200 m (2400 s) above cloud base</td>
</tr>
<tr>
<td><strong>Chemical Conditions</strong></td>
</tr>
<tr>
<td>( \text{SO}_2 ) at ( t = 0 )</td>
</tr>
<tr>
<td>( \text{NH}_4\text{(g)} ) at ( t = 0 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 ) at ( t = 0 )</td>
</tr>
<tr>
<td>( \text{HNO}_3 ) at ( t = 0 )</td>
</tr>
<tr>
<td>( \text{O}_3 ) at ( t = 0 )</td>
</tr>
<tr>
<td>( \text{CO}_2 ) at ( t = 0 )</td>
</tr>
<tr>
<td>( \text{SO}_4 ) (particulate) at ( t = 0 )</td>
</tr>
<tr>
<td>( \text{NH}_4 ) (particulate) at ( t = 0 )</td>
</tr>
</tbody>
</table>
simulation (Figure 1b). In Figures 1a and 1b, the solid black and the gray lines denote the maximum and minimum of the range of quantities calculated by the 12 models.

[14] Figure 1c shows the calculated water-mass-weighted average cloud water pH as a function of distance above cloud base according to the models. Again, the two curves in Figure 1c denote the range of the 12 models’ calculations. Due to the low water content near cloud base, and the acidic nature of the aerosols, cloud water pH starts off very low, less than pH 3.6, but rapidly increases as the acidic material is diluted with increasing amounts of condensing water. Although ammonia gas is absorbed during the initial stages of cloud formation, HNO3 is also absorbed, so that the observed increase in pH is due primarily to the effects of dilution. All models calculate that greater than 97% of the initial dry aerosol mass is incorporated into the cloud water.

[15] Figure 2 plots the calculated total sulfate production as a function of the liquid-water-weighted pH 1.2 km above cloud base, showing approximately 20% range in the calculated sulfate production, and a corresponding deviation in the calculated acidity [H+] in the cloud water. The thick gray line in Figure 2 shows the slope of relationship between pH and sulfate assuming H+ is linearly related to sulfate concentration in the cloud water. This figure clearly shows that the size-resolved models disagree significantly from the bulk models, and calculate about 17% more sulfate production, leading to higher acidity and thus slightly lower average rates of the reaction between SO2 and O3 in cloud water, and the pH differences that can exist among numerous drop categories in a cloud. Any differences in pH among cloud droplets will lead to different average rates of the reaction between SO2 and O3 in clouds.

[16] Figure 3 provides a further breakdown of the calculated SO2 oxidation showing the sulfate produced by O3 and via H2O2, plotted against each other. Here there is a distinct clustering of most of the size-resolved models showing about 45 parts per trillion (ppt) more (a factor of 2–3 more) sulfate formation via the pH-dependent O3 pathway relative to the bulk models, which consistently calculate about 30 ppt sulfate production via O3 oxidation. This extra sulfate production from ozone by the size-resolved models is somewhat countered by a decrease in sulfate formation from H2O2, which is about 20–25 ppt less in the size resolved models relative to the bulk models. Generally there is an inverse relationship between the magnitude of the H2O2 versus O3 oxidation: As more sulfate is produced via the O3 reaction, less SO2 is available for the H2O2 reaction, and sulfate production from H2O2 decreases. Therefore the size-resolved models calculate less sulfate production via the H2O2 pathway, even though this reaction rate is largely independent of pH.

[17] Figures 2 and 3 demonstrate that there is a systematic and significant difference between the calculations of aqueous-phase SO2 oxidation by bulk and size-resolved models of cloud water chemistry, as has been shown previously [e.g., Hegg and Larson, 1990; Garciulio and Pandis, 1997; Ogren and Charlson, 1992]. This results primarily from the strong pH dependence of the aqueous-phase reaction between SO2 and O3 in cloud water, and the pH differences that can exist among numerous drop categories in a cloud. Any differences in pH among cloud droplets will lead to different average rates of the reaction between SO2 and O3 in clouds.

### Table 4. Aqueous-Phase Equilibria

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>K_{298}</th>
<th>ΔH/R</th>
<th>Accommodation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(g) ⇌ O(aq)</td>
<td>1.13 × 10^{-2}</td>
<td>2540</td>
<td>0.00053</td>
</tr>
<tr>
<td>H2O2(g) ⇌ H2O2(aq)</td>
<td>7.45 × 10^{4}</td>
<td>7300</td>
<td>0.018</td>
</tr>
<tr>
<td>HNO3(g) ⇌ HNO3(aq)</td>
<td>2.1 × 10^{-7}</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>CO2(g) ⇌ CO2(aq)</td>
<td>3.4 × 10^{-2}</td>
<td>2440</td>
<td>0.05</td>
</tr>
<tr>
<td>SO2(g) ⇌ SO2(aq)</td>
<td>1.23</td>
<td>3150</td>
<td>0.035</td>
</tr>
<tr>
<td>NH3(g) ⇌ NH3(aq)</td>
<td>62</td>
<td>4110</td>
<td>0.05</td>
</tr>
<tr>
<td>H2O2(aq) ⇌ HO2 + H2O</td>
<td>2.2 × 10^{-12}</td>
<td>-3730</td>
<td></td>
</tr>
<tr>
<td>CO2(aq) ⇌ HCO3 + H+</td>
<td>4.3 × 10^{-7}</td>
<td>-1000</td>
<td></td>
</tr>
<tr>
<td>HCO3</td>
<td>4.68 × 10^{-11}</td>
<td>-1760</td>
<td></td>
</tr>
<tr>
<td>SO2(aq) ⇌ SO3 + H+</td>
<td>1.3 × 10^{-2}</td>
<td>1960</td>
<td></td>
</tr>
<tr>
<td>HSO4</td>
<td>6.6 × 10^{-8}</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>NH3(aq) ⇌ NH4 + OH-</td>
<td>1.7 × 10^{-5}</td>
<td>-450</td>
<td></td>
</tr>
<tr>
<td>HNO3(aq) ⇌ NO3 + H+</td>
<td>15.4</td>
<td>8700</td>
<td></td>
</tr>
</tbody>
</table>

*aUnits of k are liter(water) moles\(^{-1}\) atm\(^{-1}\) or moles liter(water) \(^{-1}\) s\(^{-1}\).

*bEquilibrium for other temperatures (T) calculated as K(T) = K_{298} \times \exp[-ΔH/R(1/T-1/298)].

*cValue for HNO3(g) = NO3 + H+.

### Table 5. Aqueous-Phase Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Expression*</th>
<th>k_{298}</th>
<th>E/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3 + SO2(aq) ⇌ S(VI)b</td>
<td>k_{298}\exp[-E/R(1/T-1/298)]</td>
<td>2.4 \times 10^{4}</td>
<td>0</td>
</tr>
<tr>
<td>O3 + HSO4 ⇌ S(VI)b</td>
<td>k_{298}\exp[-E/R(1/T-1/298)]</td>
<td>3.5 \times 10^{5}</td>
<td>-5530</td>
</tr>
<tr>
<td>O3 + SO4 ⇌ S(VI)b</td>
<td>k_{298}\exp[-E/R(1/T-1/298)]</td>
<td>1.5 \times 10^{7}</td>
<td>-5280</td>
</tr>
<tr>
<td>H2O2(aq) + HSO4 ⇌ S(VI)b</td>
<td>k_{298}\exp[-E/R(1/T-1/298)]</td>
<td>7.45 \times 10^{7}</td>
<td>-4430</td>
</tr>
</tbody>
</table>

*aUnits of k are liter(water) moles\(^{-1}\) s\(^{-1}\).

*bS(VI) = SO4^{2-} + HSO4^{-}.
considerable ranges and differences, the average pH calculated by the size-resolved models agrees to within 0.03 pH units (Figure 1).

5. Cloud Drop Number Concentrations and Modification of Aerosol Size Distributions

[19] The number concentration of cloud droplets computed in each of the five size-resolved models is shown in the last row of Table 2, from 275 cm$^{-2}$ for Jacobson’s model to 358 cm$^{-2}$ for Liu’s model. This variation can be traced to a number of assumptions made in the models. Although, as shown in Table 2, different numerical solvers are used in the models, we did not find any appreciable differences in results that could be traced to the solvers, but found that other factors were important. First, while the Feingold, Jacobson, Liu, and Nenes models explicitly treat the growth of droplets by water condensation and calculate the time history of ambient water saturation ratio, the Gong model uses a parameterization as implemented in the regional model AURAMS [Gong, 2002]. This parameterization is based on a simple empirical relation between the number density of cloud condensation nuclei (and thus cloud drops) and that of the ambient atmospheric aerosols [Jones et al., 1994]. The largest particles are assumed to activate first; the smallest size of “activated” particle is determined by counting downward from the large end of the aerosol spectrum until the specified total number of CCN is accumulated. The adiabatic liquid water content, computed from thermodynamic considerations alone, is distributed evenly among the “activated” particles to determine drop size, resulting in a relatively narrow cloud droplet spectrum. Differences in drop size arise only at the large end of the drop spectrum, and originate from the chosen step size for updating LWC (60 s for this study). Despite the simplicity of this treatment, the number of drops computed in the Gong model is similar to that computed by the other models.

[20] Differences between the Feingold, Jacobson, Liu and Nenes models derive from a number of factors. The water condensation mass accommodation coefficient ($\alpha$) used in each model is shown in Table 2, and varies from 0.042 to 1. The higher the applied value of $\alpha$, the more effective is condensational growth at scavenging water vapor that would otherwise go toward activation of more droplets. The corresponding variation in droplet number concentration ($N_D$) is shown in Figure 5, where Feingold, Liu and Nenes varied the value of $\alpha$ from 1 to 0.042, resulting in 12−35% increases in $N_D$. The relationship between droplet number concentration ($N_D$) and maximum supersaturation for the Feingold, Jacobson, Liu and Nenes models, using the base-case values of $\alpha$ assumed in each as indicated on the plot, is shown in Figure 6. From this figure it is apparent that differences in treatment of water condensation cannot alone account for the differences in predicted drop number concentrations, since there should be a positive, monotonic
relationship between $S_{\text{max}}$ and $N_D$ with decreasing $a$. Those models using $a = 1$ (Nenes and Liu) did compute the lowest maximum supersaturation ($S_{\text{max}}$), but predicted higher number concentrations than the other models. The reasons for these differences are twofold: First, the droplet solution thermodynamics is treated differently among these models, and second, each model has a different bin structure. This affects the calculated $N_D$ because none of these models treat activation of partial bins.

[21] None of the models adjusted chemical reactions (except gas-liquid equilibria, and reversible liquid-liquid equilibria in the Jacobson model) for nonideal conditions under high ionic strengths. The Feingold model does not allow for transfer of gases or chemical reaction until droplets are sufficiently dilute (ionic strength <2 M). Thus the water content of drops before activation is based primarily on the initial aerosol composition. During all phases of aerosol and drop growth, the water vapor pressure over the drop is computed from a Köhler-type equation, but without the dilute approximation. Drop size is solved for iteratively, using water activity as a function of composition from the ZSR relationship, and using binary ammoniated sulfate solution data from Tang and Munkelwitz [1994]. The Jacobson, Liu, and Nenes models use the Köhler equations with the dilute approximation to compute droplet size, with the number of ions, $n$, set according to the evolving composition of the drops. These latter three models all permit gas transfer to the aqueous phase from the start of the simulation, so the aerosol in general contains more soluble material than the initial conditions suggest and is therefore easier to activate, tending to produce higher $N_D$. This explanation was confirmed by Nenes, who found drop number concentrations of 290 cm$^{-3}$ when uptake of gases was ignored, compared with 301 cm$^{-3}$ when gas transfer prior to and during activation was included. In addition, the Liu model re-equilibrates the aerosol composition with the specified initial ammonia gas concentration, so that this case has essentially a different input aerosol spectrum that leads to significantly larger $N_D$. This interpretation was borne out by a sensitivity study performed by Jacobson [2002], wherein he re-ran his model with the same initial re-equilibration assumption as used by Liu and Seidl [1998] and computed 321 drops cm$^{-3}$, compared with 275 drops cm$^{-3}$ in the model run without this assumption.

[22] The grids that are used by the various size resolving models also play a role in determining the number concentration of droplets. Figure 7 shows the superposition of initial dry aerosol size distribution, approximate critical supersaturation for this spectrum, and “bin” structure for the five size-resolved models (arbitrary y axis). The range of $S_{\text{max}}$ predicted by the models is indicated by the shaded region, and corresponds to particles with diameters from about 0.055–0.087 μm. Since the maximum supersaturations fall near the peak of the aerosol size distribution, it is clear that small deviations in predicted $S_{\text{max}}$ will translate into relatively large changes in $N_D$. Cumulative number concentrations (computed from the large end of the spectrum) vary from 375 to 235 cm$^{-3}$ between these diameters; the models have 2–4 “bins” across this range. Thus, depending on the

Figure 2. Calculated net sulfate formation plotted against cloud water pH after parcel lifted 1.2 km above cloud base according to all models. Filled squares denote bulk aqueous chemistry models. Open circles denote size-resolved aerosol/cloud water models. Gray line denotes the slope of the pH-sulfate relationship assuming H$^+$ is proportional to total sulfate. Letters next to each point refer to the first letter of the contributing model shown in Table 1. Fine stippled lines connect models of the same authors.

Figure 3. Cumulative sulfate formation via H$_2$O$_2$ versus sulfate formation via O$_3$ at 1.2 km above cloud base. Filled squares denote bulk aqueous chemistry models. Open circles denote size-resolved aerosol/cloud water models. Letters next to each point refer to the first letter of the contributing model shown in Table 1. Fine stippled lines connect models of the same authors.
model size resolution, if the predicted $S_{\text{max}}$ falls just inside or just outside one of the “bins”, a difference of 30 or more droplets cm$^{-3}$ can be computed, since these models treat the contents of each “bin” as represented by a single size particle. The effects of resolution on predicted ND are explored further in Figure 8. In most (but not all) cases, ND decreased when resolution was increased, suggesting that $S_{\text{max}}$ was falling just inside a relatively large bin in the base cases. However, it is difficult to generalize the relationship between ND and size resolution, since it depends on the maximum supersaturation, the aerosol size distribution, and the setup of the grid in diameter space.

[23] Figures 9a–9e show the modifications to the dry sulfate aerosol mass distribution calculated by the five size-resolved models. The cloud drops 1.2 km above cloud base are evaporated, and the resulting dry aerosol size distributions are compared with the initial input spectrum. Within the cloud updraft, dry aerosols are activated in the lowest several tens of meters above cloud base, and all models activate from the largest aerosols down to a cutoff size determined by the simulated maximum in-cloud supersaturation. Only aerosols larger than the cutoff size are incorporated into the cloud water and therefore only these larger particles have the potential to accumulate more sulfate due to aqueous-phase chemistry. For the conditions considered here, Figure 2 shows that the size-resolved models calculated that SO$_2$ oxidation increased total sulfate aerosol mass by 170–180 ppt from the initial 2 μg m$^{-3}$ (520 ppt), which represents a 33–35% increase in sulfate mass.
In Figure 9, aerosol size distributions are plotted on logarithmic scales (top) and linear scales (bottom) for each model, since each plotting method shows different pertinent details of the changes to the initial spectrum. Figures 9a–9e are sorted in order of increasing number of cloud drops formed at cloud base. All models calculate essentially negligible changes to the larger portion of the aerosol spectra, since the relatively small amount of added sulfate mass does not appreciably modify the diameter of the larger particles. Particles that are smaller than the smallest particle activated are also largely unmodified by cloud chemical processes, since either chemistry in unactivated particles is neglected, or only extremely small amounts of aqueous-phase sulfate formation are calculated within the small size bins.

Particles equal to and larger than the smallest particle activated show the largest increases in particle size due to the mass addition, creating a “minimum” in the processed aerosol spectrum [Hoppel et al., 1990; Yuen et al., 1994; Hoppel et al., 1994]. For the updraft speed, humidity conditions, aerosol composition, and initial size distribution used in this study, the smallest dry diameter activated ranges from 0.06–0.07 μm, in agreement with the range of maximum supersaturations shown in Figure 7. The minimum is less pronounced in the Gong model, because in that model the grown particles are re-mapped onto the original grid, creating some loss of resolution, whereas the other modelers report the grown sizes for the moving discrete points and a modified grid is constructed from that information.

[4] In Figure 9, aerosol size distributions are plotted on logarithmic scales (top) and linear scales (bottom) for each model, since each plotting method shows different pertinent details of the changes to the initial spectrum. Figures 9a–9e are sorted in order of increasing number of cloud drops formed at cloud base. All models calculate essentially negligible changes to the larger portion of the aerosol spectra, since the relatively small amount of added sulfate mass does not appreciably modify the diameter of the larger particles. Particles that are smaller than the smallest particle activated are also largely unmodified by cloud chemical processes, since either chemistry in unactivated particles is neglected, or only extremely small amounts of aqueous-phase sulfate formation are calculated within the small size bins.

[25] Particles equal to and larger than the smallest particle activated show the largest increases in particle size due to the mass addition, creating a “minimum” in the processed aerosol spectrum [Hoppel et al., 1990; Yuen et al., 1994; Hoppel et al., 1994]. For the updraft speed, humidity conditions, aerosol composition, and initial size distribution used in this study, the smallest dry diameter activated ranges from 0.06–0.07 μm, in agreement with the range of maximum supersaturations shown in Figure 7. The minimum is less pronounced in the Gong model, because in that model the grown particles are re-mapped onto the original grid, creating some loss of resolution, whereas the other modelers report the grown sizes for the moving discrete points and a modified grid is constructed from that information.

Figure 7. Superposition of initial dry aerosol number distribution, estimated critical supersaturation (Sc) as a function of particle size, and grid structure of the five size-resolved models, shown as “bin” endpoints. The shaded area indicates the size range spanned by the upper and lower estimates of critical supersaturation, according to whether ν = 2 or ν = 3 is assumed in the Köhler equation. The heavy horizontal lines show the largest and smallest maximum supersaturations computed by the five models, and define the width of the shaded area.

Figure 8. Variation of drop number concentration with number of sizes (“bins”). Applied values of water condensation mass accommodation coefficient are shown alongside each name.
The Jacobson and Gong models, forming the fewest number of cloud drops, show significant aerosol mass depletion near aerosol diameters \( \sim 0.08 \)–\( 0.12 \) \( \mu \)m, and increases in the mass concentration distribution in the size range from 0.2–0.3 \( \mu \)m diameter. In contrast, Liu’s model, forming the greatest number of cloud drops (358 \( \text{cm}^{-3} \)), induces appreciable mass concentration depletions down to 0.06 \( \mu \)m diameter, and aerosol mass increases primarily in the 0.15–0.2 \( \mu \)m diameter range.

6. Potential Radiative Effects

In this study, the largest discrepancies among the size-resolved models are the 25–30% differences in the calculated...
number of cloud drops formed. These differences will induce appreciable microphysical and radiative impacts [e.g., Feingold and Kreidenweis, 2000; Hegg et al., 1996]. Here we crudely estimate the potential direct and indirect radiative impacts. We emphasize that although the relationships between variations in processed aerosol spectra, cloud drop number concentrations, and radiative properties have been explored in many previous studies, some of which are cited earlier, our focus in this work is to examine how differences arising from models treating an identical, simple case propagate into uncertainties in estimates of such relationships.

6.1. Indirect Radiative Effects

[27] Indirect radiative impacts of aerosols refer to the influence of aerosols on the radiative properties of clouds forming on aerosols. To examine the potential impact of model differences on indirect aerosol forcing, we consider the simple Twomey [1991] model as summarized by Seinfeld and Pandis [1998]. This model proposes that cloud optical depth is proportional to cloud depth, cloud liquid water content to the 2/3 power, and cloud drop number concentration to the 1/3 power. Therefore the range in cloud droplet number calculated in this study (275–358 drops cm\(^{-3}\)) translates into approximately a 9% range \([(358/275)^{1/3} - 1\) in calculated cloud optical depth.

[28] Twomey’s [1991] definition of the susceptibility, \(d\alpha/dN\), at constant liquid water content, shows that the cloud albedo, \(\alpha\), for optically thin clouds is most sensitive to changes in drop number concentration when cloud albedo is 0.5. Under these conditions the approximation \(\Delta\alpha \approx 0.075 \Delta\ln(N)\) is valid. Using this expression, the 25–30% spread in the calculated droplet number translates into an albedo change of 0.02 \([= 0.075 \ln(358/275)]\), which is a significant uncertainty in the influence of clouds on the atmospheric energy budget in cloudy areas.

6.2. Direct Radiative Effects

[29] Direct radiative impacts of aerosols refer to the scattering and absorption of light as it passes through an aerosol-laden atmosphere. Here we examine changes in the light scattering properties of the aerosol distributions shown in Figure 9 caused by the addition of sulfate mass by calculating radiative extinction efficiencies from the size distributions.

[30] For this extinction calculation, sulfate is assumed to be associated with ammonium bisulfate aerosol having a refractive index of 1.5, no absorption, and a dry particle density \(\rho\) of 1.8 g cm\(^{-3}\). The extinction efficiencies computed for each size distribution are normalized by the mass concentration of ammonium bisulfate aerosol. The single particle light extinction efficiency was calculated for a representative visible wavelength (530 nm) using a Mie theory model of light absorption and scattering by spherical particles [Bohren and Huffman, 1983]. Integrations are performed by numerically summing particle diameter “bins” of the size-resolved models, assuming each “bin” is represented by its midpoint diameter.

[31] Figure 10 shows the changes to the extinction efficiency induced by the addition of sulfate mass to the initial distribution by in-cloud SO\(_2\) chemistry. Extinction efficiencies are calculated for dry particles, and for those same particles under high humidity conditions \((RH = \sim 90\%)\), where the particles absorb water and swell in size and mass relative to the dry particles. Recall that all models calculate 34% sulfate mass increases from 520 ppt to 690–700 ppt. However, since the models calculate different number concentrations of droplets, the particle diameters experiencing the most significant growth by mass addition change from model to model.

[32] Under dry conditions, the initial dry lognormal aerosol distribution is calculated to have an extinction efficiency \(E = 3.23 \text{ m}^2 \text{ g}^{-1}\). According to all of the size-resolving models, the addition of sulfate mass under dry conditions decreases the normalized extinction efficiency. This effect results from the fact that all models add sulfate mass to aerosols in the 0.15–0.3 \(\mu\)m diameter range, which is smaller than the aerosol diameter that most efficiently scatters visible radiation \((\sim 0.7 \mu\text{m} \text{ diameter})\). The magnitude of this decrease ranges from less than 5% to about 13% relative to the initial lognormal distribution.

[33] Under humid conditions, a wet-to-dry particle diameter ratio of 1.8 is assumed, a reasonable approximation for ammonium bisulfate aerosol at 90% RH [Tang and Munkelwitz, 1994]. The initial and final size distributions are...
shifted by this factor, and the aerosol mass is increased by the corresponding amount of water required to increase the diameter by 1.8. The computed extinction efficiencies are again normalized by the dry ammonium bisulfate mass. The initial humidified lognormal size distribution now has \( E = 20.5 \, \text{m}^2 \, \text{g}^{-1} \), and all of the modified size distributions show 1–11\% increases over this value of \( E \). Under higher humidity conditions, the peak in the sulfate mass distribution is shifted into more optically active diameter ranges.

[34] In Figure 10 one additional simplified calculation (labeled “LogNrml”) is included. In this case, the additional sulfate mass is uniformly added to the initial distribution in a manner that preserves the lognormal shape of the mass distribution. Such simplifications are often employed in larger-scale models where an aerosol size distribution shape is assumed. The extinction efficiencies computed under this assumption increase under both dry and humid conditions, since mass is added to all particle sizes including those particles that are in the size range of high extinction efficiency. Clearly the assumption of a fixed aerosol size distribution shape limits the ability to accurately characterize radiative impacts associated with changes in mass of the aerosol distribution; in this study, even the sign of the changes in the extinction properties could not be reproduced. This dependence of the scattering efficiency of secondary sulfate on the initial aerosol spectrum, and on the mechanism producing the sulfate, has been pointed out by a number of authors [e.g., Lelieveld and Heintzenberg, 1992; Hegg et al., 1993; Tang, 1996; Hegg et al., 1996]. Here, we have shown that model-to-model variations for a simple case study, for which all models predicted similar total sulfate formation, can also contribute to variations in computed scattering efficiencies.

7. Conclusions

[35] Larger-scale atmospheric chemistry models that include the formation of sulfate usually use a simplified “bulk” approach to account for aqueous-phase SO₂ oxidation. Results for the simple case simulated here indicate a 15–25\% difference in the calculated sulfate formation between bulk and size-resolving models. These findings are in agreement with prior measurement and modeling work that showed that there is considerable uncertainty introduced in quantifying the oxidation of SO₂ by ozone, induced by pH variations among different cloud drops [Collett et al., 1994; Reilly et al., 2001; Pandis et al., 1990; Gurciullo and Pandis, 1997; Yuen et al., 1996; Zhang et al., 1999]. This study extends this analysis to explore differences among modeling approaches as an element of the total uncertainty. Among models of the same type (bulk or size-resolved), the <4\% differences in total SO₂-to-sulfate conversion are not very large and would certainly be acceptable in estimates of the contribution of aqueous-phase chemistry to the global sulfur cycle. For the conditions considered here, the underestimate of the SO₂ + O₃ reaction induces only a minor change in total sulfate formation despite a factor of 3 underestimate of the SO₂ + O₃ contribution. Under other atmospheric conditions, the O₃ reaction may be much more important than in this study.

[36] Detailed analysis of the size-resolved aerosol/cloud chemistry models suggests appreciable uncertainty in the number of dry aerosols that are scavenged in a cloud updraft, even for the relatively simple ammonium bisulfate aerosol distribution considered here. All models calculate approximately consistent and high scavenging of the input dry aerosol mass, but the calculated number of cloud drops formed varies from 275–358 drops cm⁻³. These differences were found to depend on different treatments of uptake of gases, assumptions regarding solution water content, and different values of water condensation mass accommodation coefficient. Among these, the value of the water condensation mass accommodation coefficient appears to be the single largest source of uncertainty that could be addressed experimentally; in a recent study, Shaw and Lamb [1999] report a value of 0.05 as the best fit to their data. Another important factor is the model resolution in diameter space, especially in the critical size range near the smallest particles activated, which is generally not known a priori from updraft and dry aerosol size distribution information. Finally, unlike the conditions chosen for this study, the composition of ambient aerosol is extremely variable, and is an additional source of uncertainty in \( N_D \). It is most likely the largest source of uncertainty in regions affected by anthropogenic pollution, where particles are not as hygroscopic as in more pristine regions.

[37] Using a simple model of cloud radiative properties, the cloud drop number deviations among models were estimated to induce a 9\% change in calculated cloud optical depths, and a corresponding change in absolute cloud albedo of up to 2\%. For optically thin clouds, this represents an appreciable relative change in cloud albedo. Furthermore, such discrepancies arising in a simple parcel model with well-characterized aerosol composition suggest that radiative and microphysical processes within clouds are highly uncertain within more complex atmospheric cloud models, regional-scale meteorological models, and longer-term climate models where many factors in addition to the uncertainties shown here can arise.

[38] The direct radiative effects of aerosols are also sensitive to how mass is added to an initial aerosol spectrum. Using a simple extinction calculation, we show that the changes to the radiative extinction efficiency, relevant to direct aerosol radiative forcing estimates, can be as large as 13\% among model simulations of the same case.

[39] The simulation carried out in this study is inherently limited in scope. Only a single chemical and aerosol condition is specified, with one updraft velocity and vertical displacement. Clearly more general conclusions can only be arrived at with a much wider range of physical and chemical conditions. Variations such as polluted versus clean, oxidant limited versus oxidant rich, overall acidity level and updraft speed are all factors that will influence the results presented here. However, a key factor regulating the magnitudes of the differences found is the relatively large variation in absolute number of cloud drops formed. This discrepancy would probably occur under many environmental conditions, given the reasons leading to it that were diagnosed from this study. This work suggests that an important next step in a cloud-aerosol model comparison series would be a more focused study of the cloud drop activation behavior in the lowest few tens of meters above cloud base in a cloud updraft.
References


