Cloud processing of aerosol as modeled by a large eddy simulation with coupled microphysics and aqueous chemistry

Graham Feingold
Environmental Technology Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA

Sonia M. Kreidenweis
Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA

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[1] Cloud processing of aerosol through both drop collision coalescence and aqueous chemistry is simulated with the aid of a large eddy simulation model and fully coupled components that represent (1) size-resolved aerosol, (2) size-resolved microphysics, and (3) the conversion of SO_2 to sulfate via aqueous chemistry. Prior work with cloud parcel models has shown that the outcome of processing in a stratocumulus-capped marine boundary layer depends strongly on the cloud liquid water content, aerosol concentrations, trace gas concentrations, and contact time with a cloud. The current model represents spatial and temporal variability of these parameters at large eddy scales on the order of a few hundred meters and timescales on the order of a few seconds. A number of scenarios are presented here: (1) a case with relatively low aerosol concentrations in which aqueous chemistry processing does not substantially affect drizzle, (2) a case with intermediate aerosol concentrations of relatively large size in which drizzle is suppressed by aqueous chemistry, and (3) a case with intermediate aerosol concentrations of relatively small size in which drizzle is enhanced by aqueous chemistry. The simulations indicate that aqueous chemistry can modify the dynamics and microphysics of stratocumulus clouds and illustrate the complexity of the coupled system. This work suggests that parameterizations of the effects of cloud processing of aerosol require careful consideration of the myriad feedbacks in the cloudy boundary layer. *INDEX TERMS:* 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3307 Meteorology and Atmospheric Dynamics: Boundary layer processes; 1610 Global Change: Atmosphere (0315, 0325); *KEYWORDS:* cloud, aerosol, aqueous chemistry, boundary layer

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1. Introduction

[2] Clouds modify aerosol size distributions through numerous mechanisms including the addition of nonvolatile sulfate mass to aerosol particles via aqueous chemistry [*Hegg and Hobbs*, 1982; *Schwartz*, 1984; *Hoppel et al.*, 1990; *Hegg and Larson*, 1990; *Bott*, 1999; *Hatzianastassiou et al.*, 1998; *Feingold et al.*, 1998; *Zhang et al.*, 1999; *Wurzler et al.*, 2000; *Krämer et al.*, 2000], drop collision coalescence [*Hudson*, 1993; *Flossmann*, 1994; *Feingold et al.*, 1996], precipitation scavenging, and homogeneous nucleation of new particles in the vicinity of clouds. The fact that aerosol particles not only affect cloud drop size distributions, but that clouds influence the size and concentration of aerosol particles has implications for aerosol-cloud interactions and related climate feedbacks. For example, aqueous addition of sulfate to aerosol particles that have been incorporated into drops provides an interesting feedback mechanism: modified aerosol size spectra can change the drop size distribution in subsequent cloud cycles, and either enhance or suppress drop number concentrations [e.g., *Bower et al.*, 1997; *Feingold and Kreidenweis*, 2000].

[3] Concurrent with aqueous sulfate production, drop collision coalescence reduces the total drop concentration with a commensurate decrease in aerosol number concentration because one aerosol particle is produced for each evaporated droplet [*Mitra et al.*, 1992]. Competing effects can therefore be identified: (1) collision coalescence steadily reduces drop and aerosol concentrations, increases particle size and activated drop size, and increases the likelihood of stronger collision-coalescence in subsequent cloud cycles; this might be conceived of as a runaway precipitation process; (2) aqueous chemistry produces more sulfate mass on the already activated particles, generates larger particles and either increases drop concentrations (and therefore suppresses drizzle) or decreases drop con-

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centrations (and enhances drizzle). In an eddy resolving cloud model, *Feingold et al.* [1996] explored the relative importance of these processes on the mean size of aerosol particles and suggested that, at low cloud liquid water content (LWC), aqueous chemistry processing might dominate, but that above some threshold LWC, collision coalescence would become more important. However, that study did not include a coupled aqueous chemistry component to clarify these conditions.

[4] The number of parameters that determine the mutual effects of aerosol on clouds is very large and includes LWC, cloud contact time (which is closely tied to boundary layer dynamics and cloud type), aerosol concentration, size and composition, gas phase concentrations of SO_2, oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2), as well as ammonia (NH_3) and nitric acid (HNO_3), which affect drop pH and therefore the oxidizing capacity of the cloud water. Given this broad range of conditions, prior numerical studies have tended to simplify certain aspects of the problem, usually by considering simple kinematic flows or adiabatic parcel models [e.g., *Hegg and Larson*, 1990; *Bower and Choularton*, 1993; *Bower et al.*, 1997; *Gurciullo and Pandis*, 1997; *Feingold et al.*, 1998; *Feingold and Kreidenweis*, 2000] so as to focus on the aerosol-cloud interface. In so doing they have separated the microphysics and chemistry from the dynamics. Others have considered Eulerian cloud models in one or two dimensions [e.g., *Flossmann*, 1994; *Bott*, 1999; *Wurzler et al.*, 2000] and, therefore, have captured the coupling between dynamics, microphysics, and chemistry. The large number of processes that need to be treated typically limits the spatial dimensions of the model and sometimes the accuracy of the resolution of the phenomenon. Like other modeling studies the current one compromises representation of some aspects of the problem (see section 2) but strives for a reasonable balance. Most importantly, it resolves coupled dynamics, radiation, microphysics, and aqueous chemistry components at the large eddy scale.

[5] The goals of this study are (1) to present the new large eddy simulation (LES) model, and (2) to illustrate the sensitivity of the coupled system to an aerosol size distribution that changes during the course of the simulation as a result of aqueous chemistry, collision coalescence, and drizzle. The model is presented in section 2; initial conditions are described in section 3; results for a three-dimensional (3-D) LES are presented in section 4, followed by a series of two-dimensional (2-D) simulations that enable us to consider far more cases because computation time is significantly reduced. These results are discussed (section 5) from the general perspective of aerosol-cloud feedbacks. We end with a brief summary in section 6.

2. Model Description

[6] The LES described by *Feingold et al.* [1994] and *Stevens et al.* [1996] has been coupled to the aqueous sulfate chemistry model described by *Feingold et al.* [1998] and *Zhang et al.* [1999]. Thus the model features coupled dynamics, radiation, microphysics, and chemistry.

2.1. Dynamics

[7] The dynamical model is the LES version of the Regional Atmospheric Modeling System (RAMS), developed at Colorado State University [*Pielke et al.*, 1992]. In this study some of the simulations are performed in two dimensions, and then it is more appropriately termed an eddy-resolving model (ERM). The model has been applied to stratocumulus studies in both LES and ERM form in a number of papers that have investigated various aspects of cloud condensation nucleus (CCN)-cloud interactions and drizzle formation [e.g., *Feingold et al.*, 1994, 1996, 1999; *Stevens et al.*, 1996, 1998]. A critical analysis of the model is given by *Stevens et al.* [1996].

[8] The grid size is $\Delta x = \Delta y = 80$ m; $\Delta z = 25$ m for LES simulations, and $\Delta x = 50$ m; $\Delta z = 25$ m for ERM simulations. The time step is 2 s for both dynamics and microphysics, with a time splitting between microphysics and aqueous chemistry. For aqueous chemistry, a variable time step is used (see section 2.3).

[9] A two-stream radiative transfer model includes short- and long-wave schemes [*Harrington et al.*, 1999] that are coupled with the rest of the model. The model has eight bands (three solar and five infrared). It treats gaseous absorption by H_2O, O_3, and CO_2 and the optical properties of the drop size distributions.

2.2. Microphysics

[10] Drop size distributions are resolved into 25 size bins covering the radius range 1.5 μm < r < 1000 μm, which is sufficient for stratocumulus that produce relatively weak precipitation. Droplet condensation, collision coalescence, sedimentation, and solute transfer between drop bins [*Feingold et al.*, 1996] are represented by using a two-moment scheme that solves for both drop mass and drop number in each of the bins and minimizes numerical diffusion [*Tzivion et al.*, 1987]. The initial aerosol, which is assumed to be composed of ammonium sulfate, is represented by 14 size bins in the range 0.01–6 μm with equations for mass and number in each bin. Activated aerosol enters droplets as separate ammonium and sulfate species. The ratio of these species may vary with time as a result of aqueous chemistry (see below), but the modification of the aerosol to a more acidic form is not considered in terms of its effect on activation of particles in subsequent cycles or on the growth of droplets.

2.3. Aqueous Chemistry

[11] The significant modifications to the model are associated with the representation of aqueous sulfate chemistry. The aqueous chemistry model considers oxidation of soluble S(IV) species to S(VI) via O_3 and H_2O_2. It does not include any treatment of gas-phase chemistry; gases are depleted by uptake on drops and aqueous chemical conversion and are not replenished by large-scale advection or chemistry. Our prior work considered aqueous chemistry in a Lagrangian cloud parcel model that used a moving grid representation of the cloud microphysics. Only five soluble species were considered, namely, SO_2, O_3, H_2O_2, NH_3, and HNO_3. Since Eulerian models dictate the use of fixed bin microphysics, the first step was to couple the sulfate chemistry module to the 25-bin microphysical scheme used in the LES. The representation of only five soluble species presents a rather formidable numerical burden in the LES. Besides dynamical equations for the gas-phase species themselves, each of these species requires an aqueous

component in each of the 25 drop-sized bins. This representation requires 5 + (5 × 25) = 130 equations in addition to the 103 equations needed to describe the cloud microphysics. This would preclude 3-D LES representations on most computing platforms.

[12] A compromise was reached when we found that a two-bin representation of the aqueous chemistry can provide an excellent representation of sulfate chemistry for many reasonable conditions [*Fahey and Pandis*, 2000]. The use of two size bins for aqueous chemistry has also been used by *Bott* [1999] in a 1-D turbulence closure model. The original, moving grid representation of aqueous chemistry used in the Lagrangian parcel model was used as a standard since it is our most accurate representation of microphysics and chemistry. This model was run for initial conditions of SO_2 = 1 ppbv, H_2O_2 = 0.75 ppbv, O_3 = 40 ppbv, NH_3 = 0.1 ppbv, and HNO_3 = 0.1 ppbv along a Lagrangian trajectory with two passes through a cloud. Those results were then compared with an equivalent fixed bin microphysical model (as described in 2.2), but, for the purposes of aqueous chemistry calculations, drops were lumped into a single bin representing cloud droplets ($r \leq 20$ μm). The two simulations are remarkably close (Figure 1a) and provide confidence that representative results can be obtained with the coupled bin microphysical/aqueous chemistry model. The percentage difference between the various gas fields is insignificant for most fields. For NH_3, it is on the order of 5% although the absolute difference is small. This difference derives from the different treatments of aerosol composition in the two modeling frameworks. In the more accurate moving grid aerosol representation, aerosol composition is explicitly calculated, whereas, in the more simple form used here, the computation of aerosol properties assumes that ammonium sulfate properties apply to the aerosol regardless of the mass ratios of ammonium and sulfate. In Figure 1b comparisons of time series of pH (liquid water-weighted pH for the size-resolved model) and mean drop radius indicate excellent agreement in pH, but a slight overestimate of mean drop radius by the bin model. Differences in drop size are not surprising because each model employs a different treatment of the growth equation.

[13] In this comparison we have neglected collision coalescence and, therefore, ignore chemistry occurring in the drizzle drops. However, in the LES/ERM simulations, two bins are used, one for cloud droplets ($r \leq 20$ μm) and the other for drizzle drops ($r > 20$ μm). This study focuses on stratocumulus clouds where only a small fraction of water resides in drizzle drops [e.g., *Nicholls*, 1984]. Nevertheless, it is important to represent the transfer of soluble species to drizzle drops because drop sedimentation represents a sink of these species. It is recognized that in some cases the details of the size distribution of drops are important [e.g., *Gurciullo and Pandis*, 1997] and assumption of a single drop size may underestimate the rates of sulfate conversion. Nevertheless, the ability to reduce the number of model scalars representing aerosol, cloud, and chemistry from 233 to 97 is particularly appealing and enables simulation of a coupled system that is a useful environment for testing hypotheses. The 97 scalars represent 28 (dry) aerosol parameters (14 size bins × 2), 50 drop size bins (25 size bins × 2), 5 gas phase species, 10 soluble gas species (2 size bins × 5), and 4 dissolved aerosol species (2 size bins × 2). Table 1 summarizes the microphysical/chemical representation.

[14] Rather than assuming equilibrium between the phases, diffusion-limited mass transfer of species between the gas and liquid phases is simulated. Chemistry calculations are performed only when sufficient cloud water is present (i.e., when the mixing ratio $r_l > 1 \times 10^{-5}$ g g^{-1}). The coupled system of differential equations is solved using the Variable Ordinary Differential Equation solver (VODE) [*Brown et al.*, 1989], which adapts the chemical time step as required. Simulation time is increased by approximately 30% when chemistry is included. Three hour LESs including chemistry are manageable on a single processor 550 MHz PC operating under Linux.

3. Initial Conditions

[15] A sounding was chosen to provide a framework for investigating aerosol-cloud-chemistry feedbacks. It derives from the "First Lagrangian Experiment" associated with the Atlantic Stratocumulus Transition Experiment (ASTEX) [*Albrecht et al.*, 1995]. The case has been well documented through observations [*Bretherton et al.*, 1995] and numerical simulations [*Wyant et al.*, 1997; *Stevens et al.*, 1998]. Initial soundings are as prescribed by the GEWEX Cloud System Studies (GCSS) workshop case study [*Duynkerke et al.*, 1998]. The case study is characterized by a shallow boundary layer (cloud top ≃ 800 m) with a fairly large liquid water path, LWP ≃ 200 g m^{-2}, and a fairly moist layer above the inversion. Light drizzle was prevalent. The current model simulations compared well with observations [*Duynkerke et al.*, 1998], but this is not addressed here.

[16] The initial ammonium sulfate CCN size distributions are assumed to be lognormal with median radius (with respect to number) r_g = 0.1 μm, and geometric standard deviation σ_g = 1.5. A second set of simulations uses r_g = 0.05 μm, and σ_g = 1.8 as initial conditions. The total number concentration N_{ccn} is varied from 50 to 200 cm^{-3}.

4. Results

4.1. Large Eddy Simulations

[17] Two simulations are performed for an input CCN concentration of 100 cm^{-3}, r_g = 0.1 μm, and σ_g = 1.5; one simulation does not include chemistry, whereas the other does. Figure 2 illustrates some of the model output with snapshots of various fields 1 hour after initialization for the case that includes chemistry. The maximum cloud water mixing ratio r_l is about 0.7 g kg^{-1}. Soluble gases are depleted from their initial conditions to a degree consistent with individual parcel model calculations [*Feingold et al.*, 1998] for clouds of similar average liquid water content. Significant structure exists in these fields at scales of a few hundreds of meters; these structures are associated with similar structures in microphysical and dynamical fields. Droplet pH ranges from 2.5 near the cloud base where cloud water mixing ratio r_l is minimal to 4.7 near the cloud top where most of the cloud water resides. In general, pH contours parallel r_l contours with some exceptions. For example, at $x \simeq -1000$ m and $z \simeq 400$ m, an updraft raises air relatively rich in NH_3 (as well as SO_2, H_2O_2, and O_3) into the cloud. The result is that NH_3 (aq) is enhanced and

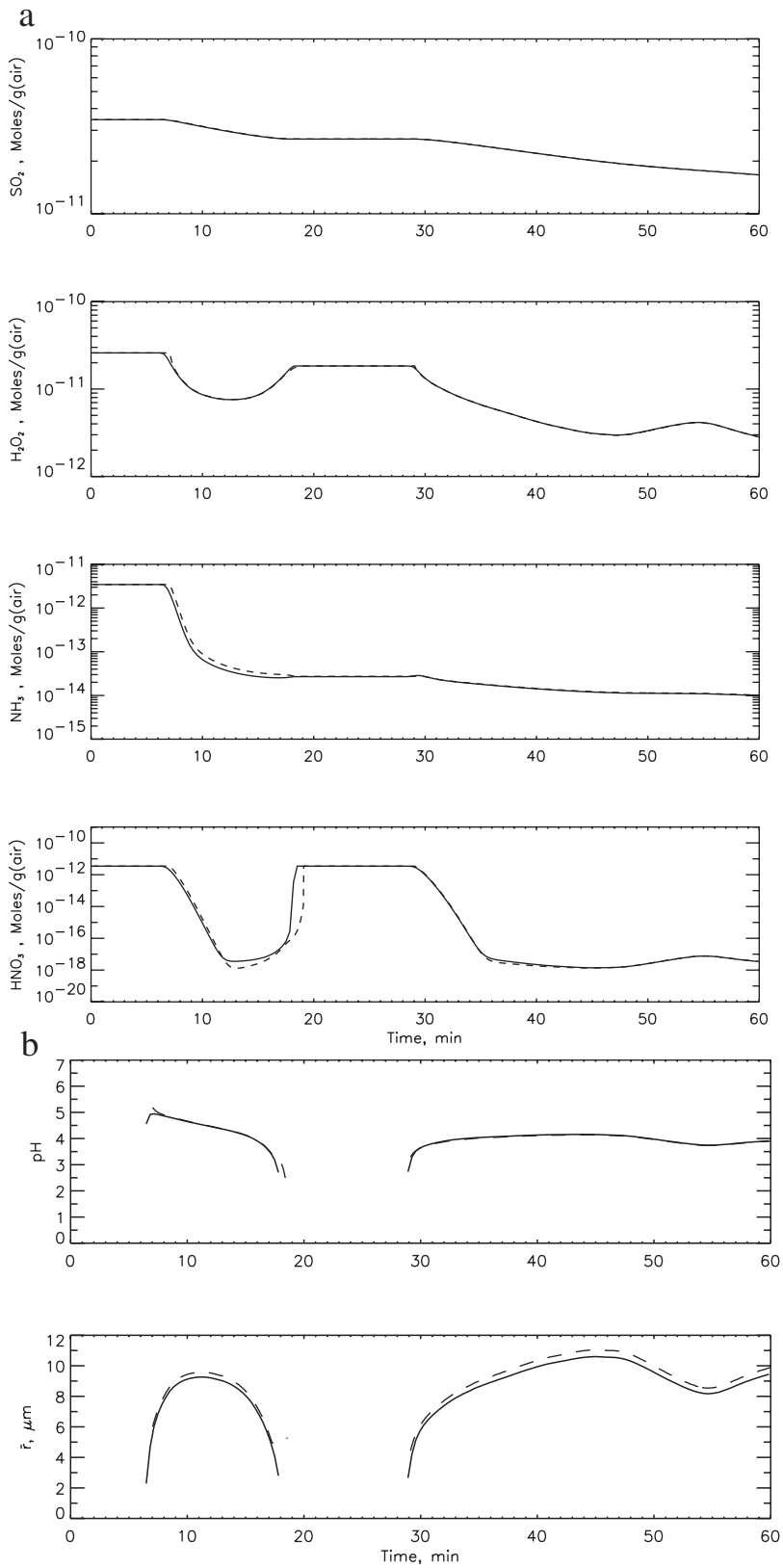


Figure 1. Comparison of two aqueous chemistry models: (a) gas phase components and (b) pH and mean drop radius $\bar{r}$. Solid line: detailed model resolving aerosol composition and aqueous chemistry in each size category. Dashed line: approximate model with simplified aerosol composition and aqueous chemistry in one size category. In the case of the detailed model, pH is calculated as a liquid-water-weighted mean value.

Table 1. Summary of the Aerosol, Cloud and Chemical Species Considered in the Model

Species	Number of Scalars	Comments
Dry aerosol	28	14 bins, mass and number in each bin
Dissolved aerosol	4	mass of NH_4^+ and SO_4^{2-} in cloud, and in drizzle
Cloud drops	50	25 bins, mass and number in each bin
Gas phase	5	SO_2, O_3, H_2O_2, NH_3, HNO_3
Aqueous chemistry	10	aqueous components of gas phase in cloud, and in drizzle

the pH is higher than implied by the r_l field in the height range $z \simeq 300$ m to $z \simeq 400$ m.

[18] From the perspective of aerosol-cloud interactions, the effect of aqueous chemistry on the CCN size distribution is of interest. Figure 3 illustrates the total CCN mass and number concentration for the time period corresponding to Figure 2. The increase in CCN mass in the subcloud air is significant ($\simeq$70%) so that this case can be viewed as one with strong aqueous sulfate production. CCN number is relatively unperturbed because collection has not had suffi-

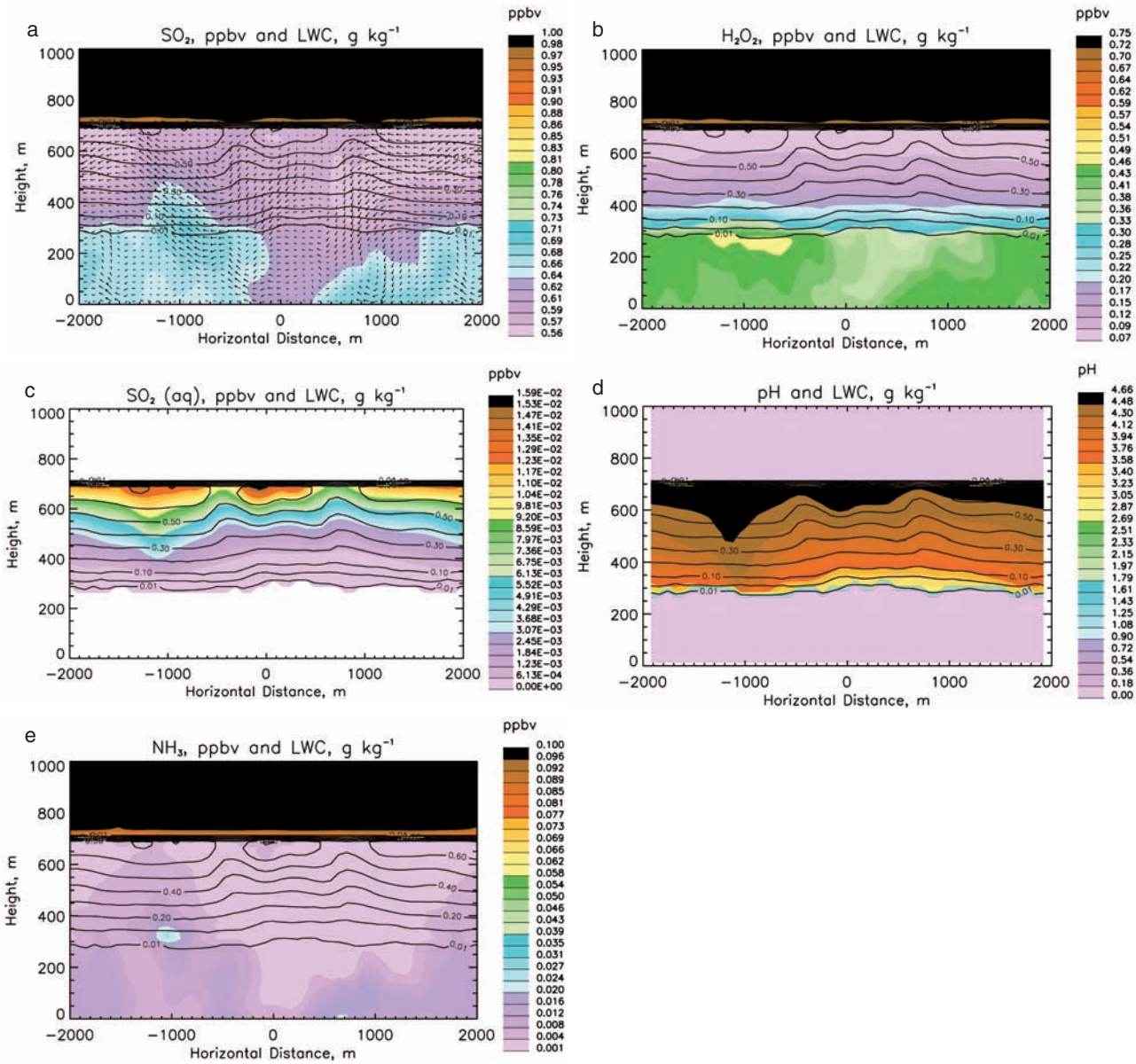


Figure 2. Cross-sections of various fields produced by the LES after 1 hour. (a) Gaseous SO_2 (color-flooded contours), cloud-water field (solid contours), and wind vectors; (b) gaseous H_2O_2 and cloud water; (c) aqueous SO_2 and cloud water; (d) cloud drop pH and cloud water (the pH is arbitrarily set to 0 outside where cloud water is negligible); and (e) gaseous NH_3 and cloud water.

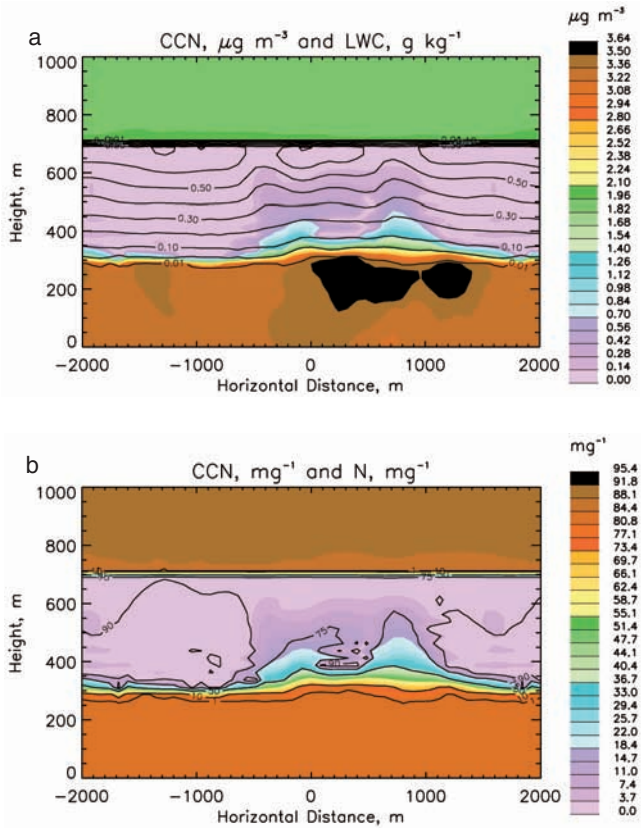


Figure 3. Cross sections of various fields produced by the LES after 1 hour. (a) Aerosol mass, CCN μg m^{-3} superimposed on the cloud water field, and (b) aerosol concentration, mg^{-1} and drop number concentration, mg^{-1}. Compare the increase in aerosol mass in the subcloud region to the initial background values (as in the air above the cloud). The aerosol number concentration is approximately the same as for the initial conditions because collection has not yet reduced it significantly.

cient time to deplete drop concentration N. Note the characteristic constant profiles of drop concentration in the updraft regions in Figure 3b. Profiles at different times also show that N is approximately constant with height.

[19] Plots similar to those in Figure 2 for later times show that the various gas fields become more homogeneous as the boundary layer mixes through, but structure in the aqueous fields tends to follow that in the r_l field. As an example we show the aqueous component of SO_2 [i.e., S(IV)] in the drizzle ($r > 20$ μm) (Figure 4). Note that the highest concentrations of S(IV) in the drizzle are not collocated with maxima in r_l or updraft w, but rather with maxima in the drizzle mixing ratio which tend to be located downwind of strong updrafts and in recirculating zones.

[20] Figure 5 shows time series of averaged quantities such as LWP, the boundary layer maximum root mean square vertical velocity w_{rms}, cloud top height, z_i, surface rainfall rate R, and integrated surface precipitation I. Note that for the given CCN input, these fields differ little in the chemistry and no-chemistry runs; the inclusion of chemistry results in minor modifications to boundary layer dynamics, but the behaviour of the system is statistically similar (at least over the 3.5 hour simulation time). Some small temporal differences in surface drizzle rates R and integrated surface drizzle I exist but, in general, the multiphase chemistry has little effect on the simulation for these conditions.

4.2. Eddy Resolving Model Simulations

4.2.1. Large Median Radius: $r_g = 0.1$ μm, $\sigma_g = 1.5$

[21] Given the large computational burden of LES, we turn to 2-D ERM simulations to enable exploration of a broader parameter space. Simulations shown in section 4.1 are repeated for the range of CCN concentrations N_{ccn} from 50 to 200 cm^{-3} with $r_g = 0.1$ μm and $\sigma_g = 1.5$. In the cases presented, simulations are terminated when the LWP is depleted by about 50% of the maximum value; therefore cases with higher N_{ccn} are run for significantly longer than those with lower N_{ccn}. Selected time series similar to Figure 5 for LWP, R, and I show (Figure 6) that, as in the case of the 3-D simulations, aqueous chemistry does not result in a significant change in these fields when $N_{ccn} = 100$ cm^{-3}. (Note that simulations in 2-D have been extended to 5.5 hours to meet the requirement that LWP be depleted to about half of its maximum.) Comparing LES and ERM simulations shows that the ERM simulations are characterized by more vigorous circulations and higher LWP because 2-D models develop larger eddies than 3-D due to the absence of energy cascading by vortex stretching. If 2-D and 3-D simulations are considered to be qualitatively similar with respect to the effect of aqueous chemistry, the results obtained by the 2-D simulations after 5.5 hours would suggest that the conclusion that aqueous chemistry does not affect drizzle based on the 3.5 hour LES simulations, is reasonable.

[22] Simulations with $N_{ccn} = 50$ or 75 cm^{-3} are similar and are therefore not shown. When $N_{ccn} = 150$ cm^{-3}, a number of trends are noteworthy (Figure 7). Measurable surface precipitation takes much longer to develop and occurs only when the cloud LWP has reached about 300 g m^{-2}. This occurs when cloud top $r_l \simeq 1$ g kg^{-1} and the cloud top effective radius $r_e = 14$ μm. There is a fairly clear trend for aqueous chemistry to enhance LWP and suppress precipitation: after 8 hours, I is 28% lower in the case with aqueous chemistry.

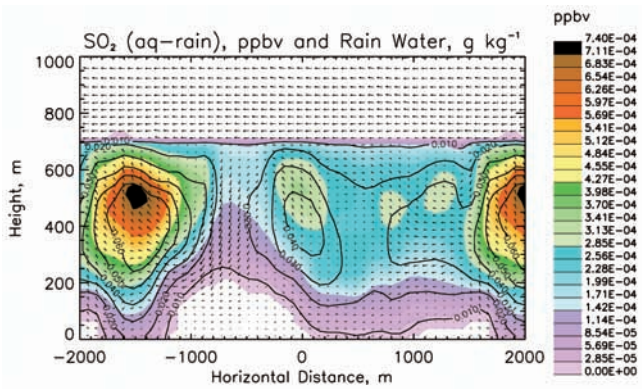


Figure 4. Cross section of aqueous SO_2 in rain drops ($r > 20$ μm) superimposed on the cloud water field and wind vectors. The highest concentrations of aqueous SO_2 are collocated with the highest concentrations of large drops and rain water. These regions tend to occur in recirculation zones and are not collocated with maximum cloud water.

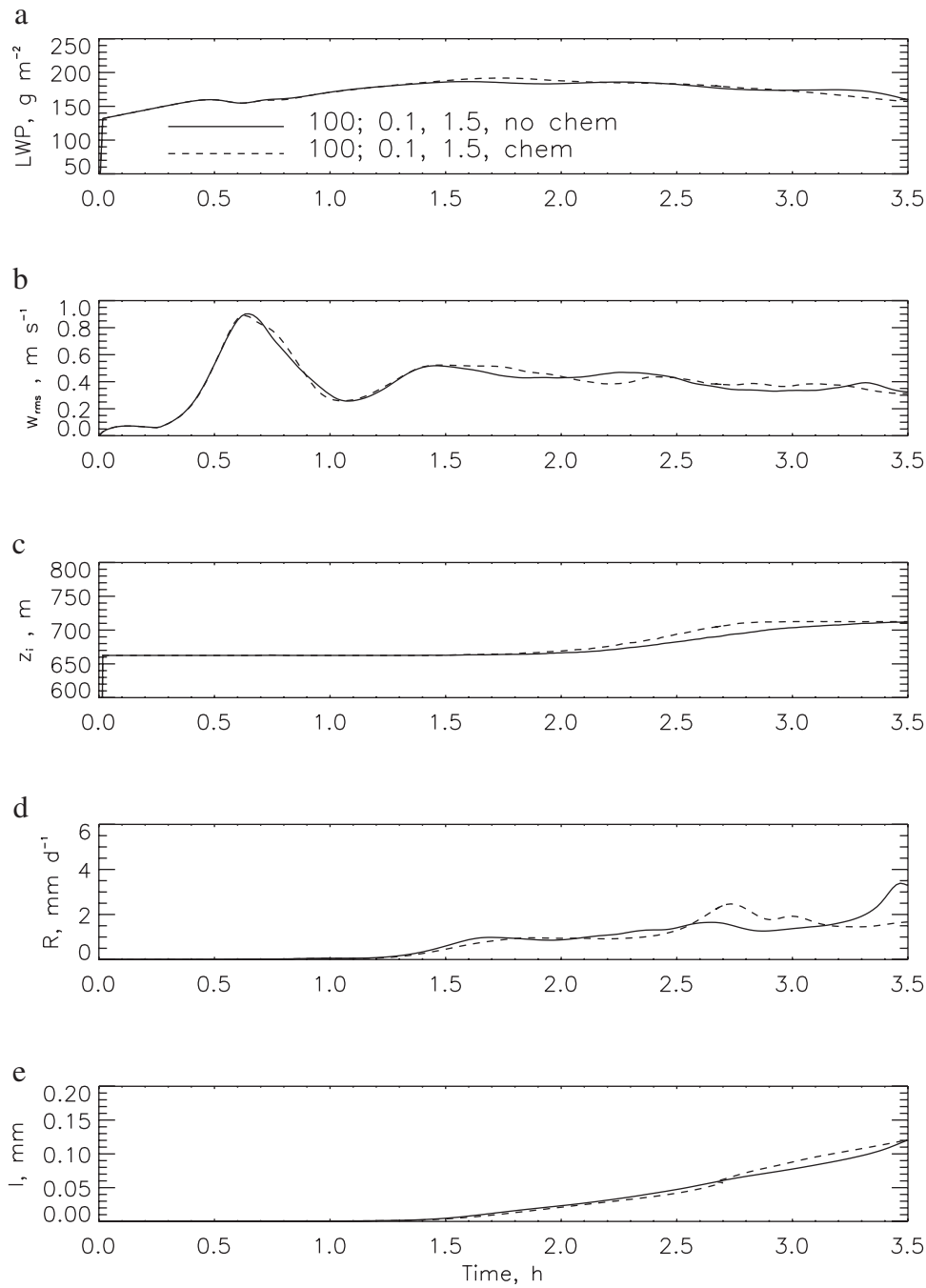


Figure 5. Time series of various fields for the two LES: (a) LWP; (b) boundary layer maximum root-mean square vertical velocity, w_{rms}; (c) boundary layer top, z_i; (d) surface precipitation rate R; and (e) accumulated surface precipitation I. Fields have been averaged over the domain. Solid lines represent the simulation without aqueous chemistry, and dashed lines represent the simulation with aqueous chemistry. Simulations are statistically very similar. Input aerosol are noted on the figures. The notation "100; 0.1; 1.5" implies N_{ccn} = 100 cm^{-3}, r_g = 0.1 μm, and σ_g = 1.5.

[23] Simulations for N_{ccn} = 200 cm^{-3} show similar trends, and therefore are only described. As expected, precipitation takes longer to develop than in the case shown in Figure 7. The R fields are well correlated, as are the w_{rms} fields, which implies that the two simulations are dynamically similar, even though the precipitation is suppressed. The suppression of drizzle is similar to that for the case of N_{ccn} = 150 cm^{-3} (Table 2).

4.2.2. Small Particles: r_g = 0.05 μm, σ_g = 1.8

[24] Because previous simulations were for a rather large median radius of 0.1 μm, the second aerosol mode created by the addition of sulfate mass, which usually resides at a

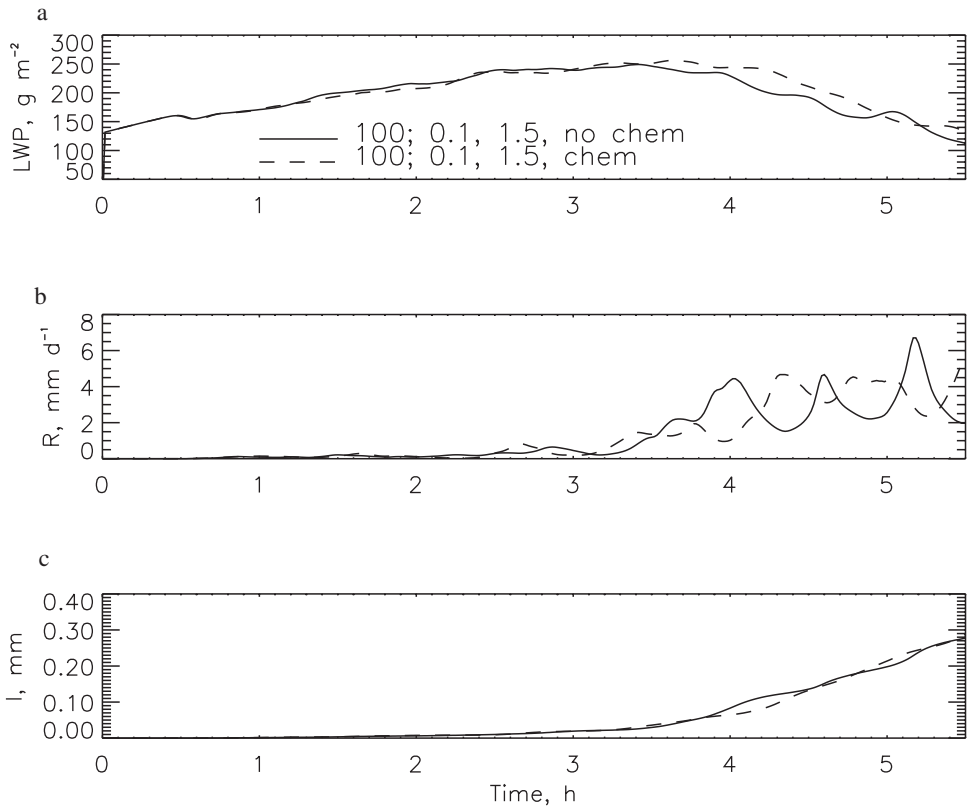


Figure 6. As in Figure 5, but for 2-D simulations. Note that the simulation time in Figure 6 is significantly longer than that in Figure 5.

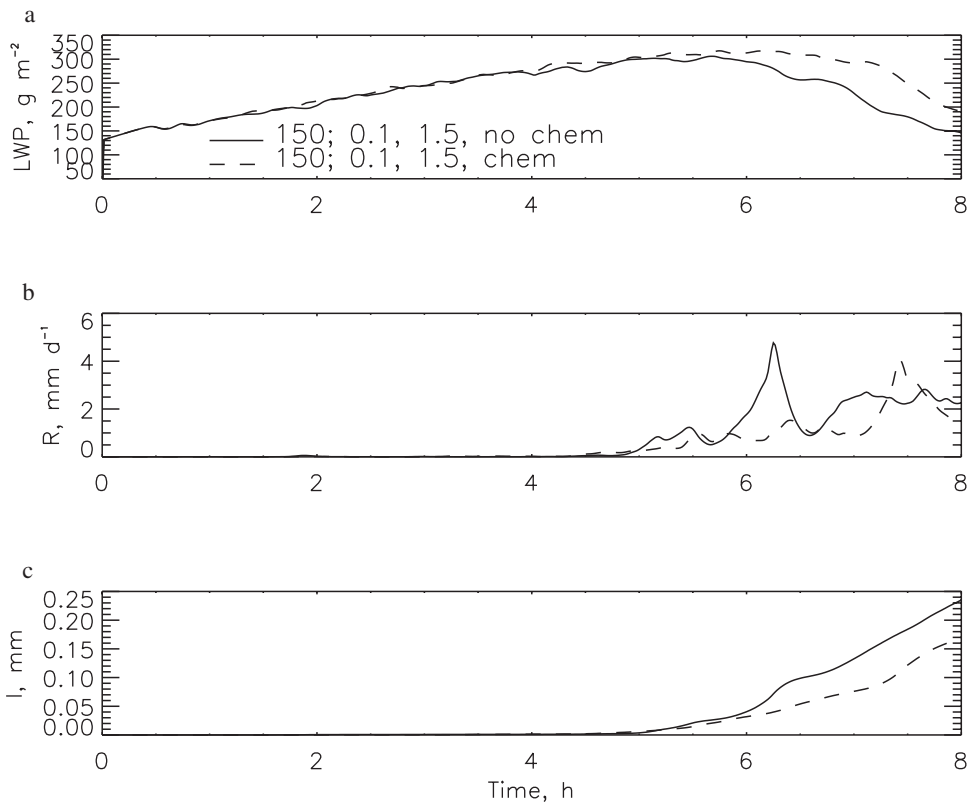


Figure 7. As in Figure 6 but for aerosol concentrations of 150 cm^{-3}. Aqueous chemistry results in a suppression of precipitation.

Table 2. Summary of Increases in Mean Aerosol Mass and Radius (at Maximum LWP) and Changes in Integrated Surface Precipitation Amount (at the End of the Simulation)[a]

(N_{ccn}; r_g; σ_g)	Initial Mass, μg m^{-3}	Mass Added, % (at Maximum LWP)	Increase in $\bar{r}$, % (at Maximum LWP)	ΔI, % (Final)
(150; 0.1; 1.5)	2.64	134	40	−28
(150; 0.05; 1.8)	0.746	436	90	+37
(200; 0.1; 1.5)	3.50	100	31	−21
(200; 0.05; 1.5)	0.994	321	!73	+39

[a]A plus (minus) sign indicates an increase (decrease) in precipitation relative to the case without aqueous chemistry. N_{ccn} is in cm^{-3}, r_g in μm, and σ_g is unitless.

similar radius [*Hoppel et al.*, 1990] will not be separated substantially from the original aerosol mode. A subset of simulations is now repeated for r_g = 0.05 μm and σ_g = 1.8. Results for N_{ccn} = 100 cm^{-3} (not shown) again indicate only slight differences in precipitation between the two simulations. Figure 8 shows time series of key fields for N_{ccn} = 150 cm^{-3}. In contrast to Figure 7, where precipitation was suppressed by aqueous chemistry, here precipitation is increased by as much as 37% after 8 hours. The increased precipitation is accompanied by a slightly lower z_i and higher LWP. *Stevens et al.* [1998] showed that precipitation results in reduced cloud turbulence and reduced entrainment. They hypothesized that small amounts of drizzle may sustain higher LWP by reducing entrainment drying. The current simulation is consistent with that hypothesis.

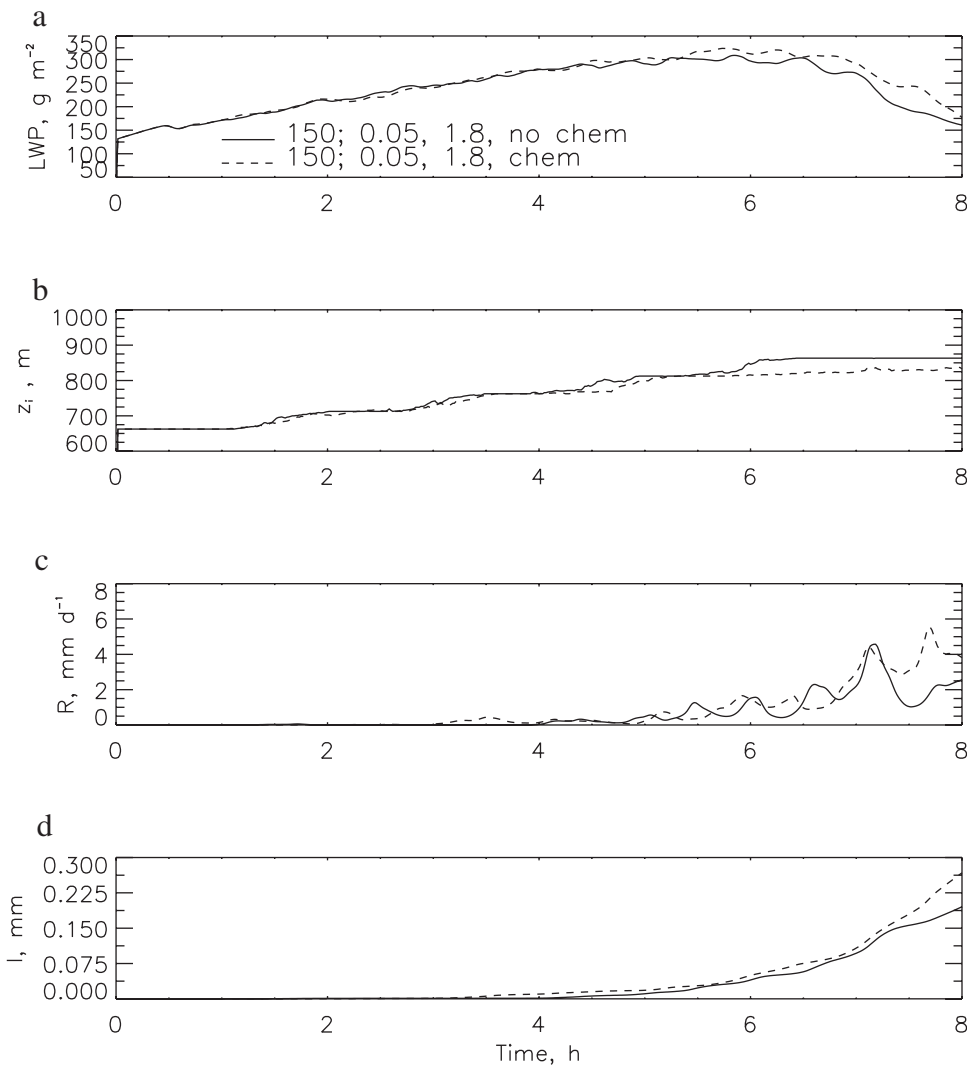


Figure 8. As in Figure 7 but for an aerosol size distribution comprising smaller particles. Aqueous chemistry results in an enhancement of precipitation.

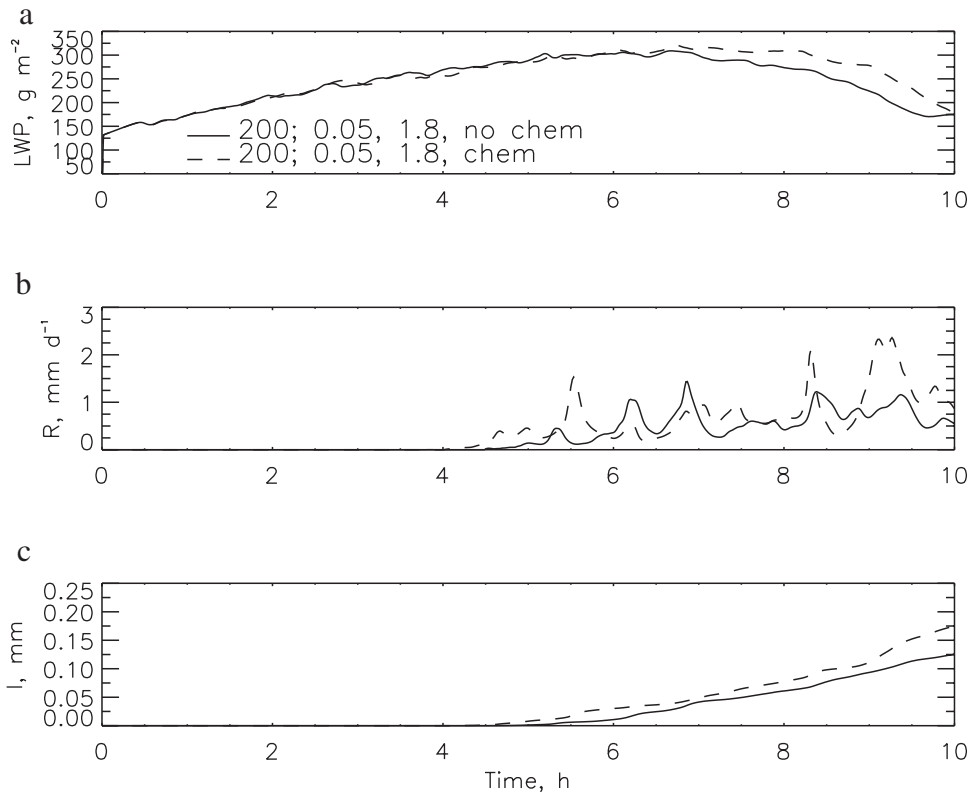


Figure 9. As in Figure 8 but for a higher concentration of aerosol particles (N_{ccn} = 200 cm^{-3}).

[25] Results for N_{ccn} = 200 cm^{-3} (Figure 9) again indicate sustained enhancement in precipitation rates and LWP, and they are qualitatively similar to results for N_{ccn} = 150 cm^{-3}. Surface precipitation takes much longer to develop and is noticable only when LWP reaches levels that allow drizzle-sized drops to grow. Surface precipitation increases by 39% by the end of the 10 hour simulation (Table 2).

5. Discussion

5.1. Suppression or Enhancement of Precipitation?

[26] The results suggest that even for a case with rather strong aqueous production of sulfate, the effects on boundary layer dynamics, cloud microphysics, and precipitation are likely to be felt over a limited range of conditions. For the simulation presented here, in which N_{ccn} is relatively small (<100 cm^{-3}), the collection process is quite efficient, and aqueous production of sulfate does not appear to be able to modify this process. We express this view with caution because in the fixed aerosol/drop bin framework, the modified CCN size distribution is not as accurately presented as in moving grid representations of the CCN distribution [e.g., *Feingold and Kreidenweis*, 2000] or as in the 2-D treatment of drop spectra [*Bott*, 1999] where each drop bin includes a multitude of CCN size categories. Nevertheless, the current treatment conserves the mass and number of CCN (at least within the accuracy of the assumption of an ammonium sulfate aerosol) and as shown by *Feingold et al.* [1996], shows the shift in aerosol size due to cloud processing.

[27] The simulations indicate that when N_{ccn} > 150 cm^{-3} and the CCN size distribution has a relatively large median size, the addition of sulfate suppresses precipitation. Here the net effect of aqueous chemistry is to increase the number concentration of CCN and therefore of cloud drops [e.g., *Bower and Choularton*, 1993; *Feingold and Kreidenweis*, 2000]. Under these conditions, the contrast between the mode of the original CCN size distribution and the mode associated with the mass addition is small, and aqueous chemistry does not change the size of particles sufficiently to generate a significant number of larger drops.

[28] When the CCN size distribution has a relatively small median size, the contrast is much larger, and the particles that are produced are able to produce higher concentrations of larger drops (relative to the initial size distribution) that help initiate collection. Thus two competing effects can be identified in these processing scenarios: (1) larger particles are more easily activated and the resulting higher drop concentrations mean that the available water is distributed amongst smaller drops thus suppressing drizzle; and (2) the larger particles generated by aqueous chemistry can generate larger drops that may accelerate the drizzle process. When the contrast between the median radius of the original size distribution and the processed distribution is small, the former dominates, whereas when the contrast is large, the latter dominates.

[29] Table 2 summarizes the results for higher concentration simulations and verifies that the percent increase in mean aerosol radius is substantially higher for the (r_g; σ_g) = (0.05 μm; 1.8) cases. It also shows that the higher the

aerosol concentration, the smaller the percent increase in aerosol radius because a similar mass of sulfate produced in the aqueous phase is distributed amongst a larger number of particles.

[30] Further illustrations of the effect on aerosol size spectra $n(r)$ are shown in Figure 10; processed CCN size distributions as well as the background distributions are displayed for the N_{ccn} = 150 cm^{-3} cases and (r_g; σ_g) = either (0.1 μm; 1.5) or (0.05 μm; 1.8). The processed size spectra are horizontally averaged at a height of 300 m and at a simulation time of 2 hours. The larger percent increase in mean radius for the (0.05 μm; 1.8) case is again apparent. Although the size spectra lack detail, they do show the creation of a mode at ≃0.1 to 0.2 μm and do represent the feedback of aqueous chemistry processing to the microphysical/dynamical model.

[31] Figure 11 shows the effect that these modified size distributions have on cloud microphysics, as represented by cloud-averaged drop number concentration and effective radius. One can see that when (r_g; σ_g) = (0.1 μm; 1.5) N is enhanced and r_e reduced as a result of aqueous chemistry. For the time period t > 3 hours, the mean increase in N is 13% and the mean decrease in r_e is 11%. These rather strong changes maintain a more colloidally stable cloud and suppress the drizzle process. When (r_g; σ_g) = (0.05 μm; 1.8), r_e increases and N decreases as a result of aqueous chemistry. For the time period t > 3 hours, the mean decrease in N is 3%, and the mean increase in r_e is 5%. These perturbations are significantly smaller than those for the (r_g; σ_g) = (0.1 μm; 1.5) case, and yet the perturbation in surface precipitation is larger (Table 2). Closer analysis of this simulation shows that at $t \simeq 3.5$ hours, which happens to coincide with the onset of surface drizzle (see Figure 8), the simulation with aqueous chemistry has a mean r_e of 17 μm, whereas the simulation without aqueous chemistry has a mean r_e of 10 μm. Recalling that an r_e of 14 μm is usually regarded as a threshold for drizzle initiation, this is clear evidence of initiation of a strong drizzle process that persists for the duration of the simulation. The system is colloidally unstable, and because the collision coalescence process is highly nonlinear in r_l and r_e, even small differences in r_e result in significant enhancement in surface precipitation. The possibility that aqueous chemistry feedbacks to cloud microphysics and dynamics may modify the amount of precipitation in a cloud system has various implications:

1. The same pollutants (aerosol and trace gases) that are implicated as being potentially able to modify precipitation will be influenced by wet deposition. Enhancement in precipitation represents a means of cleaning the atmosphere of pollutants that might have been expected to create clouds with smaller drops and higher albedo. Suppression of precipitation follows along the lines of the classical "indirect effect," which states that clouds will have higher albedo (1) because of smaller drop sizes [*Twomey*, 1974, 1977] and (2) because of suppressed precipitation [*Albrecht*, 1989].

2. Enhancement or suppression of precipitation in stratocumulus clouds may change the nature and extent of cloud cover, although the simulations presented here do not illustrate this. In a study that looked at the same case under consideration here, *Stevens et al.* [1998] showed that heavily precipitating clouds tend to create boundary layers with penetrating cumuli that feed stratocumulus decks. When precipitation is very high, cloud decks may break up and the boundary layer may become very shallow. To the extent that aqueous chemistry is capable of changing the amount of precipitation, commensurate feedbacks to boundary layer dynamics and cloudiness can be expected. If clouds do break up due to drizzle, then the boundary layer

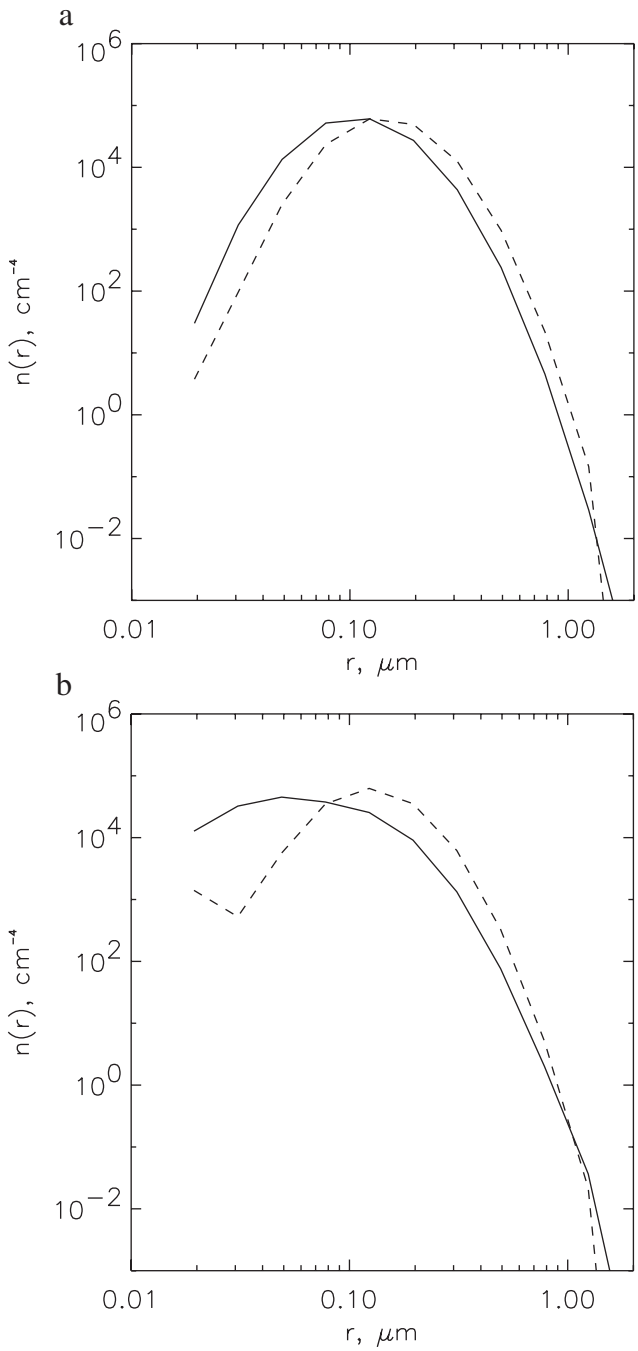


Figure 10. Aerosol size distributions $n(r)$ at a height of 375 m derived from 2-D simulations: (a) for initial conditions N_{ccn} = 150 cm^{-3}, r_g = 0.1 μm, and σ_g = 1.5, and (b) for initial conditions N_{ccn} = 150 cm^{-3}, r_g = 0.05 μm, and σ_g = 1.8. Solid line: initial condition; dashed line: modified aerosol distribution.

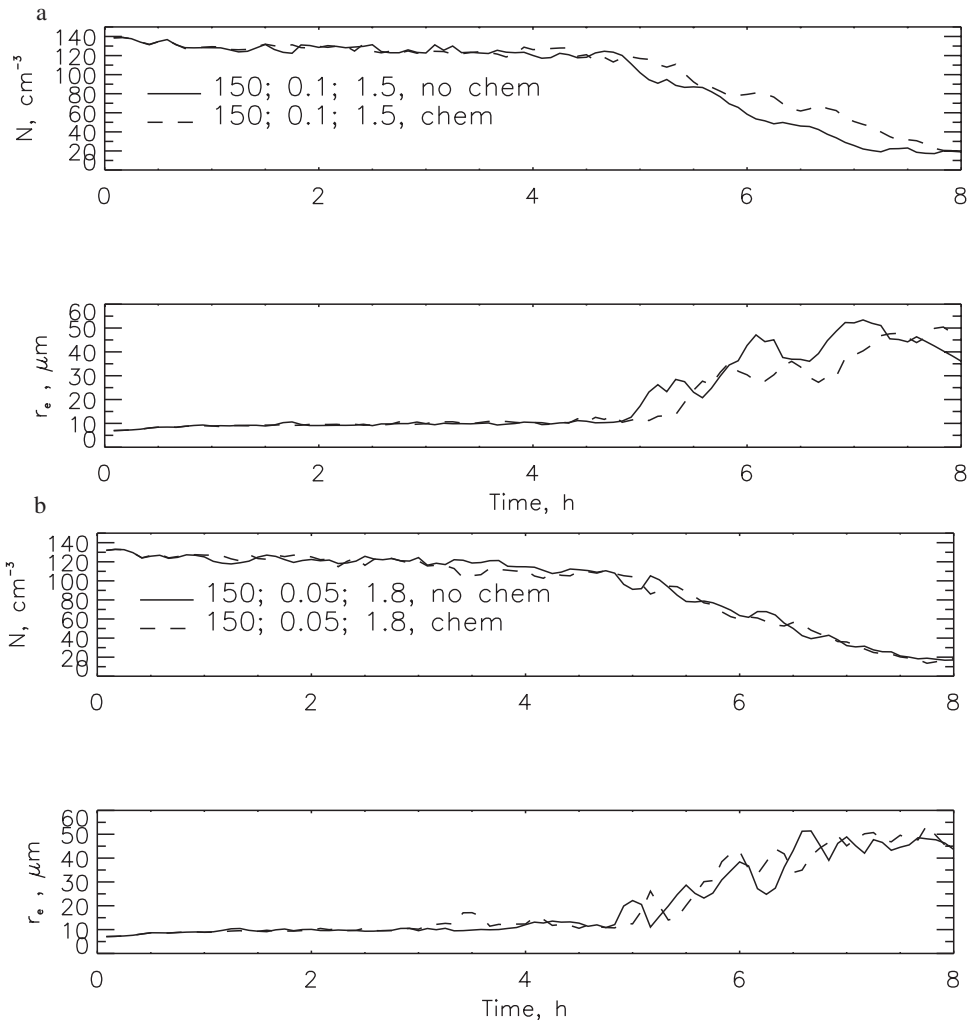
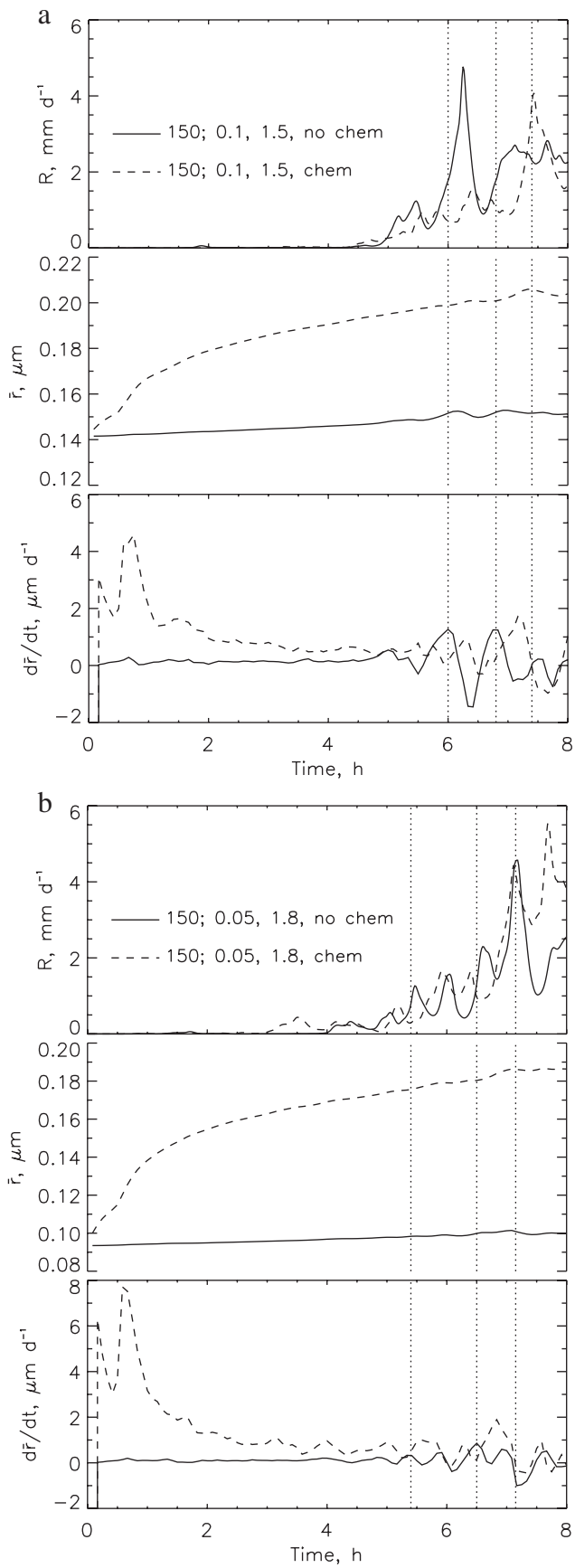


Figure 11. Time series of cloud-averaged drop number concentration and cloud-averaged drop effective radius r_e (a) for initial conditions N_{ccn} = 150 cm^{-3}, r_g = 0.1 μm, and σ_g = 1.5, and (b) for initial conditions N_{ccn} = 150 cm^{-3}, r_g = 0.05 μm, and σ_g = 1.8. In Figure 11a, aqueous chemistry results in a higher drop concentration and a smaller effective radius. In Figure 11b, aqueous chemistry results in a lower drop concentration and a larger effective radius.

is not only cleansed of pollutants, but the aqueous source of sulfate aerosol (the clouds themselves) is effectively reduced.

5.2. Collision Coalescence Processing Versus Aqueous Chemistry Processing

[32] Although only one chemical scenario has been explored, and this effectively sets the extent of chemical processing, it is of interest to compare the effects of the two processing mechanisms on the mean aerosol particle size. Boundary layer average values of aerosol mass and number concentration are calculated for simulations that include aqueous chemistry and compared with those that do not simulate aqueous chemistry. Figure 12a shows time series of the mean CCN radius $\bar{r}$, and the rate of change of mean CCN radius ($d\bar{r}/dt$), together with surface rain rate R (from Figure 7) for N_{ccn} = 150 cm^{-3}, r_g = 0.1 μm and σ_g = 1.5. Figure 12b is a similar figure but for N_{ccn} = 150 cm^{-3}, r_g = 0.05 μm and σ_g = 1.8. One can see that for the case under discussion, the CCN mass increase due to aqueous chemistry results in significantly higher mean aerosol radii. The rate of change of CCN radius is always greater for the run with aqueous chemistry for the first 5 hours of the simulation when SO_2 and oxidants are still plentiful and when collection has not yet been able to reduce drop concentrations significantly. The earlier stages of the simulation might be applicable to conditions of fresh emissions of pollutants, and under these conditions, aqueous chemistry processing should dominate particle growth. Once significant collection rates are established (as indicated by the appearance of surface drizzle), $d\bar{r}/dt$ can be correlated to the surface drizzle rates, although with some time lag: as R builds up, so does the mean radius, however at some point before R peaks, $d\bar{r}/dt$ begins to decrease, reflecting the fact that precipitation preferentially removes the larger aerosol (incorporated in the drops) from the boundary layer. The periodic nature of drizzle means that after R subsides, cloud water builds up again, collection increases, as does $d\bar{r}/dt$. The times at which $d\bar{r}/dt$ for the simulation without chemistry exceeds that for the simulation with chemistry indi-



cates that at these stages of the simulation, cloud processing is dominated by collection rather than by aqueous chemistry. These conditions might be applicable to cleaner marine boundary layers. Analysis of other pairs of simulations indicate qualitative behavior similar to that in Figure 12, although the timing and relative importance of the processes is different.

5.3. Comparison With Other Work

[33] Although prior research has addressed similar issues to those addressed here, comparison is somewhat difficult (1) because the models involved have treated different cloud types, (2) because they have addressed different chemical scenarios, and (3) the models have not always coupled microphysics and chemistry in a 2- or 3-D framework. Thus the studies have addressed clouds with different potential for both microphysical and chemical processing and their feedback to dynamics. In spite of this some general comparisons and inferences can be made. *Hatzianastassiou et al.* [1998] suggested that for a relatively low SO_2 concentration of 0.5 ppbv in combination with H_2O_2 = 0.5 ppbv and O_3 = 30 ppbv, sulfate chemistry does not play an important role, but that collection is the dominant aerosol growth mechanism. A similar conclusion was arrived at by *Feingold et al.* [1996]. The current work is in general agreement with those studies when CCN concentration is low (<100 cm^{-3}) and collection is efficient. However, it is difficult to make a definitive comparison of the relative effects of aqueous chemistry and collection for the current case. If our simulations with no aqueous chemistry were to be compared with ones that included aqueous chemistry but not collection, results would be unrealistic. By suppressing collection and therefore precipitation formation, spuriously thick clouds would develop, and to the extent that aqueous sulfate production is determined by the LWC, results would be biased toward higher sulfate production. Moreover, there would be no mechanism in place to scavenge aerosol and gases through precipitation. Ultimately, the relative importance of these processes is case dependent. The current study has identified some of the important parameters but clearly others need to be considered. Possible parameters include (1) gas phase chemistry (which has not been considered here), (2) fresh gaseous emissions (e.g., from ship plumes), (3) the stage of development of the cloud relative to the timing of intrusion of fresh emissions, (4) the existence of giant CCN

Figure 12. (opposite) Time series of surface rain rate R, mean aerosol radius $\bar{r}$, and time rate of change of mean aerosol radius for (a) for initial conditions N_{ccn} = 150 cm^{-3}, r_g = 0.1 μm, and σ_g = 1.5 and (b) initial conditions N_{ccn} = 150 cm^{-3}, r_g = 0.05 μm, and σ_g = 1.8. Solid line: collection processing only; dashed line: aqueous chemistry and collection processing. Aqueous chemistry dominates the increase in mean radius. For the first 5 hours the rate of increase in mean radius due to aqueous chemistry and collection is always greater than that due to collection alone. After 5 hours and the onset of significant precipitation, collection dominates, as indicated by the correlation between R and $d\bar{r}/dt$. See text for details.

that enhance collection beyond the rates suggested in this study [e.g., *Feingold et al.*, 1999].

6. Summary

[34] A large eddy simulation of the marine boundary layer that includes size-resolved treatment of aerosol and cloud drop size distributions, and a coupled aqueous chemistry component has been presented. The model has been used to simulate a stratocumulus cloud deck from a case study based on the ASTEX first Lagrangian experiment.

[35] First, the new model is presented and its strengths and weaknesses highlighted. Although cloud microphysical processes are treated in 25 size bins to keep the computation time to a reasonable level, the model calculates aqueous chemistry in two size categories: cloud drops with radius $\leq$20 μm and drops with radii >20 μm [e.g., *Bott*, 1999]. Although this may bias the rates of aqueous production of sulfate in some scenarios [*Gurciullo and Pandis*, 1997], for the gas phase input used here, we have shown that the simpler aqueous chemistry model performs adequately.

[36] Twin LES are performed for a relatively low CCN concentration of 100 cm^{-3}. In one case, aqueous chemistry is included, whereas in the second it is not. For the conditions studied here, although aqueous chemistry produces a higher sulfate mass, it is not sufficient to modify the amount of precipitation produced by the cloud, apparently because at low CCN concentrations there is a fairly active collection process. However, a series of 2-D simulations for a wider range of CCN concentrations suggests that aqueous chemistry may either enhance or suppress drizzle. Precipitation may be enhanced when the initial CCN size distribution has a relatively small mode. In this case, the larger particles produced by aqueous chemistry (about 0.1 μm radius) are more easily activated, tend to generate larger drops, and therefore enhance drizzle production. Suppression of drizzle occurs when the input CCN size distribution has a larger mode that is similar to that at which sulfate is produced by clouds. In this case the added sulfate mass translates to higher drop concentrations, smaller drops, and reduced collection.

[37] Although the simulations presented here cover only a handful of scenarios and only one set of aqueous chemistry conditions, the study has demonstrated that aqueous chemistry may, under some conditions, modify drop concentrations, cloud optical properties, and drizzle formation in stratocumulus. It suggests that the myriad feedbacks that exist in the aerosol-cloud-chemistry system present a formidable challenge to our attempts to quantify the aerosol indirect effect. Future work will explore these feedbacks in greater detail.

[38] **Acknowledgments.** Assistance from Hongli Jiang is gratefully acknowledged. Sonia Kreidenweis received support from NOAA Office of Global Programs grant NA17RJ1228.

References

Albrecht, B. A., Aerosols, cloud microphysics, and fractional cloudiness, *Science*, *245*, 1227–1230, 1989.

Albrecht, B. A., C. S. Bretherton, D. Johnson, W. H. Schubert, and A. S. Frisch, The Atlantic Stratocumulus Transition Experiment–ASTEX, *Bull. Am. Meteorol. Soc.*, *76*, 889–904, 1995.

Bott, A., A numerical model of the cloud-topped planetary boundary-layer: Chemistry in marine stratus and the effects on aerosol particles, *Atmos. Environ.*, *33*, 1921–1936, 1999.

Bower, K. N., and T. W. Choularton, Cloud processing of the cloud condensation nucleus spectrum and its climatological consequences, *Q. J. R. Meteorol. Soc.*, *119*, 655–679, 1993.

Bower, K. N., et al., Observations and modelling of the processing of aerosol by a hill cap cloud, *Atmos. Environ.*, *31*, 2527–2543, 1997.

Bretherton, C. S., P. Austin, and S. T. Siems, Cloudiness and marine boundary layer dynamics in the ASTEX Lagrangian experiment, II, Drizzle, surface fluxes, and entrainment, *J. Atmos. Sci.*, *52*, 2724–2735, 1995.

Brown, P. N., G. D. Byrne, and A. C. Hindmarsh, VODE: A variable coefficient ODE solver, *SIAM J. Sci. Statist. Comput.*, *10*, 1038–1051, 1989.

Duynkerke, P. G., et al., Simulation of a stratocumulus-topped atmospheric boundary layer: A comparison of models and observations, in *4th International Cloud Modelling Workshop, Clermont-Ferrand, France, 12–16 August 1996*, *WMP Rep. 29*, pp. 23–30, World Meteorol. Org., Geneva, Switzerland, 1998.

Fahey, K. M., and S. Pandis, The effects of variable droplet size distribution on the predictive ability of atmospheric aqueous-phase chemistry models, paper presented at 19th Annual Conference, Am. Assoc. of Aerosol Res., St. Louis, Mo., 2000.

Feingold, G., and S. M. Kreidenweis, Does heterogeneous processing of aerosol increase the number of cloud droplets?, *J. Geophys. Res.,*, *105*, 24,351–24,361, 2000.

Feingold, G., B. Stevens, W. R. Cotton, and R. L. Walko, An explicit microphysics/LES model designed to simulate the Twomey Effect, *Atmos. Res.*, *33*, 207–233, 1994.

Feingold, G., S. M. Kreidenweis, B. Stevens, and W. R. Cotton, Numerical simulation of stratocumulus processing of cloud condensation nuclei through collision-coalescence, *J. Geophys. Res.*, *101*, 21,391–21,402, 1996.

Feingold, G., S. M. Kreidenweis, and Y. Zhang, Stratocumulus processing of gases and cloud condensation nuclei, I, Trajectory ensemble model, *J. Geophys. Res.*, *103*, 19,527–19,542, 1998.

Feingold, G., W. R. Cotton, S. M. Kreidenweis, and J. T. Davis, Impact of giant cloud condensation nuclei on drizzle formation in marine stratocumulus: Implications for cloud radiative properties, *J. Atmos. Sci.*, *56*, 4100–4117, 1999.

Flossmann, A. I., A 2-D spectral model simulation of the scavenging of gaseous and particulate sulfate by a warm marine cloud, *Atmos. Res.*, *32*, 233–248, 1994.

Gurciullo, C. S., and S. N. Pandis, Effect of composition variations in cloud droplet populations on aqueous-phase chemistry, *J. Geophys. Res.*, *102*, 9375–9385, 1997.

Harrington, J. Y., T. Reisin, W. R. Cotton, and S. M. Kreidenweis, Cloud resolving simulations of Arctic stratus, II, Transition-season clouds, *Atmos. Res.*, *51*, 45–75, 1999.

Hatzianastassiou, N., W. Wobrock, and A. I. Flossmann, The effect of cloud-processing of aerosol particles on clouds and radiation, *Tellus, Ser. B*, *50*, 478–490, 1998.

Hegg, D. A., and P. V. Hobbs, Measurements of sulfate production in natural clouds, *Atmos. Environ.*, *16*, 2663–2668, 1982.

Hegg, D. A., and T. V. Larson, The effects of microphysical parameterization on model predictions of sulfate production in clouds, *Tellus, Ser. B*, *42*, 272–284, 1990.

Hoppel, W. A., J. W. Fitzgerald, G. M. Frick, and R. E. Larson, Aerosol size distributions and optical properties found in the marine boundary layer over the Atlantic Ocean, *J. Geophys. Res.*, *95*, 3659–3686, 1990.

Hudson, J. G., Cloud condensation nuclei near marine cumulus, *J. Geophys. Res.*, *98*, 2693–2702, 1993.

Krämer, M., N. Beltz, D. Schell, L. Schütz, C. Sprengard-Eichel, and S. Wurzler, Cloud processing of continental aerosol particles: Experimental investigations for different drop sizes, *J. Geophys. Res.*, *105*, 11,739–11,752, 2000.

Mitra, S. K., H. R. Pruppacher, and J. Brinkmann, A windtunnel study on the drop-to-particle conversion, *J. Aerosol Sci.*, *23*, 245–256, 1992.

Nicholls, S., The dynamics of stratocumulus, *Q. J. R. Meteorol. Soc.*, *110*, 821–845, 1984.

Pielke, R. A., et al., A comprehensive meteorological modeling system–RAMS, *Meteorol. Atmos. Phys.*, *49*, 69–91, 1992.

Schwartz, S. E., Gas-aqueous reactions of sulfur and nitrogen oxides in liquid water clouds, in *SO_2, NO, and NO_2 Oxidation Mechanisms: Atmospheric Considerations, Acid Precip. Ser.*, vol. 3, edited by J. G. Calvert, pp. 173–209, Butterworth-Heinemann, Woburn, Mass., 1984.

Stevens, B., G. Feingold, W. R. Cotton, and R. L. Walko, On elements of the microphysical structure of numerically simulated stratocumulus, *J. Atmos. Sci.*, *53*, 980–1006, 1996.

Stevens, B., W. R. Cotton, G. Feingold, and C.-H. Moeng, Large-eddy simulations of strongly precipitating, shallow, stratocumulus-topped boundary layers, *J. Atmos. Sci.*, *55*, 3616–3638, 1998.

Twomey, S., Pollution and the planetary albedo, *Atmos. Environ.*, *8*, 1251–1256, 1974.

Twomey, S., The influence of pollution on the short wave albedo of clouds, *J. Atmos. Sci.*, *34*, 1149–1152, 1977.

Tzivion, S., G. Feingold, and Z. Levin, An efficient numerical solution to the stochastic collection equation, *J. Atmos. Sci.*, *44*, 3139–3149, 1987.

Wurzler, S., T. G. Reisin, and Z. Levin, Modification of mineral dust particles by cloud processing and subsequent effects on drop size distributions, *J. Geophys. Res.*, *105*, 4501–4512, 2000.

Wyant, M. C., C. S. Bretherton, H. Rand, and D. Stevens, Numerical simulations and conceptual model of the stratocumulus to trade cumulus transition, *J. Atmos. Sci.*, *54*, 168–192, 1997.

Zhang, Y., S. M. Kreidenweis, and G. Feingold, Stratocumulus processing of gases and cloud condensation nuclei, II, Chemistry sensitivity analysis, *J. Geophys. Res.*, *104*, 16,601–16,080, 1999.

G. Feingold, Environmental Technology Laboratory, NOAA, 325 Broadway, Boulder, CO 80305, USA. (Graham.Feingold@noaa.gov)

S. M. Kreidenweis, Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA. (sonia@chem.atmos.colostate.edu)