Stratocumulus processing of gases and cloud condensation nuclei

1. Trajectory ensemble model

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Abstract. Aqueous-phase processing of gases and of the cloud condensation nucleus (CCN) spectrum is addressed using a trajectory ensemble model. We first derive a set of boundary layer parcel trajectories from a large-eddy simulation model (LES) and then use this trajectory set for subsequent cloud microphysical/chemical studies. We explore this approach in the stratocumulus-capped marine boundary layer and show examples of aqueous-phase processing of gases and CCN. The microphysical model is a Lagrangian parcel model that is driven by the thermodynamic and kinematic fields produced by the LES and calculates CCN deliquescence and droplet growth by condensation on a moving mass grid. It is coupled with a sulfate chemistry model that treats oxidation of S(IV) to S(VI) via ozone and hydrogen peroxide for a size-resolved droplet spectrum. The model reproduces the observed (and previously modeled) aqueous processing of particles that leads to growth of CCN and lowering of their critical supersaturations. Results show that important information on parcel in-cloud residence times and boundary layer mixing timescales can be gleaned from this approach. By averaging the results of 500 parcel trajectories, a more representative picture of CCN and gas processing is obtained compared with that derived from a single parcel simulation representing average conditions. Finally, processed CCN spectra are used as input to a coupled microphysical/dynamical cloud-resolving model, and it is suggested that cloud processing may either enhance or suppress drizzle formation, depending on the concentration and sizes of the CCN.

1. Introduction

Aqueous-phase chemistry is now recognized as having an important impact on atmospheric sulfate production [Lelieveld and Heintzenberg, 1992]. The primary means by which clouds produce sulfate is thought to be via the oxidation of sulfur dioxide principally by hydrogen peroxide and ozone. Sulfate production has an attendant impact on sulfate particle size distributions. Observations in the marine boundary layer show strong evidence of bimodal aerosol spectra [Hoppel et al., 1990] that have been attributed to in-cloud processing of the activated fraction of particles. Subsequent modeling studies [e.g., Bower and Choularton, 1993; Hegg et al., 1996], which have included calculations of oxidation of S(IV) to S(VI) (sulfate), have reproduced this bimodality and provided further credence to this theory. Through this mechanism, various aqueous-phase chemical processes deposit mass in the droplets that were formed on cloud condensation nuclei (CCN) and enhance the amount of soluble material [e.g., Hegg and Hobbs, 1982; Chameides, 1984]. On complete evaporation, each droplet produces a single particle [Mitra et al., 1992] thus increasing the mass of the particles and enhancing their potential for activation during subsequent cycles.

Another cloud processing mechanism that has been proposed is that of collection processing [Hudson, 1993; Flossmann, 1994; Feingold et al., 1996]. Via this mechanism, the total droplet population is reduced in number so that on subsequent droplet evaporation the available solute mass is redistributed amongst fewer and therefore larger particles. The collection mechanism was studied by Feingold et al. [1996] and will not be pursued further here.

This study will examine aqueous-chemistry processing of aerosol and gases in the cloudy marine boundary layer (BL). In particular, the focus will be on stratocumul-
mulus clouds because of the importance of this cloud type in the global radiation budget [e.g., Nakajima and King, 1990]. The potential for cloud processing to modify aerosol size spectra has strong implications for the BL system: (1) drop sizes and number concentrations will be affected, with concomitant impact on cloud optical properties such as optical depth, albedo, and albedo susceptibility (the change in albedo resulting from the change in drop concentration) [Twomey, 1991]; (2) modification of the CCN distribution has the potential to affect the initiation of drizzle [e.g., Albrecht, 1989]; the drizzle process removes water from the cloud and affects cloud optical properties; in addition, drizzle impacts the boundary layer dynamics that in turn impact cloud microstructure [Stevens et al., 1998]; (3) the dependence of cloud chemistry on drop size creates an additional feedback to the system; and (4) in the shortwave, cloud radiation depends strongly on droplet size, and since the dynamics of stratocumulus are forced primarily by cooling at cloud top, modifications in the CCN distribution have the potential to affect cloud dynamics.

Clearly the BL system is a closely coupled one and requires consideration of dynamics, microphysics, chemistry and radiation. Previous modeling studies have, by necessity, simplified treatment of one or more of these components. These models are rather loosely classified into three categories. We limit the survey to BL models and do not discuss mesoscale and regional models.

1.1. Models Rich in Microphysics or Chemistry but Poor in Dynamics

This category includes box models (i.e., no dynamics) [e.g., Chameides, 1984], single-parcel models with prescribed dynamics [Hegg and Larson, 1990; Twomey et al., 1989; Bower and Choularton, 1993], and one-dimensional models [Ackerman et al., 1995]. None of these models is designed to address the interaction between microphysics/chemistry and dynamics properly but rather to provide detailed treatment of microphysics/chemistry in a controlled dynamical framework. The one-dimensional model attempts to solve for dynamics but cannot resolve the BL eddy structure that is so important for the interaction with microphysics. The advantage of box models and parcel models, from the microphysical/chemical point of view, is that they solve droplet growth on a moving mass grid. The moving grid is preferred over the fixed grid for a number of reasons: (1) There is no arbitrary distinction between aerosol particle and droplet, and a continuum of growth is allowed, (2) one eliminates the numerical diffusion associated with fixed grid structures, and (3) one avoids the problem of regeneration of aerosol particles following droplet evaporation that are a feature of fixed grids [e.g., Feingold et al., 1996]. A drawback of the moving grid is that it precludes a simultaneous study of droplet coalescence, although this can be overcome by using hybrid grids [Jacobson and Turco, 1995; Cooper et al., 1997]. An additional advantage of the parcel model is that advection occurs on a Lagrangian (moving) grid, eliminating numerical problems associated with spatial advection.

1.2. Models Rich in Dynamics but Poor in Microphysics or Chemistry

In BL studies, the large eddy simulation model (LES) has emerged as a powerful tool for simulating dynamics. Earlier versions of LES [e.g., Moeng, 1986] were not concerned with microphysics, assumed simple condensation schemes to condense water, and made no attempt to resolve drop size distributions. Although LES has been coupled with bin microphysical models [Kogan et al., 1994; Feingold et al., 1994; Stevens et al., 1996], the authors are not aware of any attempts to couple LES with size-resolving microphysics and chemistry. For heterogeneous chemistry the importance of size-resolved calculations is underscored by recent studies that have shown that treating the cloud water as a bulk species, with a single pH, may introduce significant errors. Hegg and Larson [1990] demonstrated that predictions of sulfate production vary considerably between bulk and explicit (i.e., drop-size-resolved) chemistry models. Pandis et al. [1990] showed that solute species concentrations can vary widely across a fog drop size spectrum, and Pandis and Seinfeld [1991] showed that even a basic assumption such as Henry’s Law equilibrium was inaccurate for a bulk solution intended to represent a drop distribution. Clearly drop size needs to be resolved if cloud chemistry is the focus.

A problem associated with multidimensional Eulerian models is that they necessitate the use of a fixed mass grid for representation of the aerosol/cloud spectra. This framework has some disadvantages, as discussed above in section 1.1.

1.3. Models That Attempt to Balance Dynamics and Microphysics (or Chemistry)

Two-dimensional cloud resolving models are being used more frequently to couple the various components discussed in section 1.1; e.g., Flossmann [1994] has included size resolving microphysics and chemistry in two-dimensional models of BL cumulus. This approach represents a reasonable compromise, although one must bear in mind that dynamics are not correctly represented in two dimensions and that the above mentioned caveats with respect to fixed spatial and mass grids apply.

The goal of this paper is to present a new method for studying heterogeneous chemistry in boundary layer clouds that achieves a balance between dynamics, microphysics, and chemistry. A large-eddy simulation model is used as a means of describing boundary layer dynamics and deriving realistic parcel trajectories for subsequent use by a trajectory ensemble model that includes a coupled microphysical/chemical model. In section 2 we describe the methodology used in this approach. The two sub models, the LES and the trajectory ensemble model (TEM), are described in section 3. The method is applied to a theoretical case study, and results showing the extent of processing of gases
and CCN are presented in section 4. A discussion and summary follow in sections 5 and 6, respectively.

2. Method

Application of this technique includes the following steps:

1. During the course of an LES run, after turbulence is developed, 500 tracer particles are released from randomly distributed points below cloud, and their trajectories recorded. Recorded quantities include kinematic (position and velocity) and thermodynamic (liquid water potential temperature, pressure, and total water-mixing ratio) data [Stevens et al., 1996].

2. The trajectory set is used to drive 500 individual Lagrangian parcels comprising the TEM. The simulations include calculations of deliquescence, droplet activation, condensation/evaporation, and heterogeneous chemistry as described in section 3.2. The model is initialized with aerosol spectra and ambient trace-gas concentrations.

3. Output from the TEM is spatially and temporally averaged in order to facilitate examination of the effects of clouds on aerosol size distributions and trace-gas concentrations.

4. The TEM framework is applied to selected studies which examine sensitivity to input parameters. The advantages of such an approach are as follows:

   1. The dynamics are derived from a three-dimensional LES that resolves the large eddies.
   2. Size-resolved simulations of aerosol and cloud chemistry and microphysics can be performed without an enormous computational burden.
   3. Moving grids are used for both physical and mass space, eliminating the numerical diffusion associated with fixed grids.
   4. Realistic parcel in-cloud residence times and liquid water content histories are used.
   5. The approach is very amenable to process-oriented studies, which attempt to address the relationships between various key parameters. Because sensitivity experiments are easy to perform, the potential for improving our understanding of the interactions between aerosol, clouds, and chemistry is great;
   6. The approach extends the single trajectory parcel model concept to a more representative evaluation of cloud processing of aerosol and gases.

Nevertheless, there are two clear disadvantages to such an approach:

1. the model does not include feedback of microphysical and chemistry-related processes to cloud dynamics because there is currently no means to communicate these changes to the TEM. This approach therefore fails when droplets grow large enough to attain significant fall velocities that allow them to depart from air-motion trajectories. Thus the present study limits itself to non-precipitating clouds, and the collection process, which is the primary means for generating precipitation-sized droplets in liquid-phase clouds, is neglected. Nevertheless, in section 5, we examine the impact of processing on a coupled cloud model by rerunning a cloud-resolving model with the processed aerosol distribution produced by the TEM.

2. In the current configuration of the model, each parcel is considered to be closed, and there is no representation of mixing between parcels. Eddy mixing occurs on a timescale given by

\[ \tau = \left( \frac{L^2}{\epsilon} \right)^{\frac{1}{3}} \]  

where \( L \) is the eddy length scale and \( \epsilon \) is the eddy dissipation rate. The large-eddy scales in this simulation range from 300 m to about 800 m. The smaller length scale is also typical for parcels if one divides the BL volume (10 km\(^3\) in this case) by the number of parcels (500). The larger length scale is the approximate BL depth. For typical eddy dissipation rates of \( 10^{-4} \text{ m}^2 \text{s}^{-3} \), (1) yields \( \tau \approx 15 \) to 30 min. We expect that eddies will not mix completely until 3–4 timescales have elapsed. Thus we consider it reasonable to examine TEM results without exchange of information between parcels for the 1 hour simulations represented here, but recommend exercising caution before applying this approach to longer timescales. Within the TEM framework, a number of possibilities exist for communicating information between parcels. Walton et al. [1988] discuss the fact that whereas Eulerian schemes attempt to eliminate numerical diffusion, the Lagrangian approach can only be effective over long timescales if mixing (physical diffusion) is represented. This was accomplished in their Lagrangian global model by interpolating parcel information to a fixed spatial grid and then communicating grid quantities back to the parcels. A similar approach will be considered here in future work that addresses longer timescales.

3. Model Description

The individual model components are briefly described in sections 3.1 and 3.2.

3.1. LES Model

The model used in this study is the large-eddy simulation (LES) version of the Regional Atmospheric Modeling System (RAMS) model developed at Colorado State University [Pielke et al., 1982], which calculates droplet growth explicitly following the moment-conserving techniques of Tzivion et al. [1987]. It has been applied to stratocumulus studies in a number of works [Feingold et al., 1994, 1996, 1997; Stevens et al., 1996, 1998] that have investigated various aspects of CCN-cloud interactions and drizzle formation.

The model is nonhydrostatic and compressible. Predictive equations are solved for three velocity components \((u, v, w)\), liquid water potential temperature, \(\theta_l\), perturbation Exner function, \(\pi\), and total water-mixing ratio, \(r_l\). In the current study, the LES model is used only as a source of parcel trajectories describing boundary layer motions. During the course of the model
run, 500 parcels are released within the boundary layer (below cloud and between 200 and 450 m) and the kinematic and thermodynamic fields are recorded every 2 s (the model time step). Information is interpolated trilinearly from adjacent grid points (Δx = 25 m, Δy = 50 m) as described by Stevens et al. [1996].

3.2. Trajectory-Ensemble Model (TEM)

Each of the trajectories produced by the LES constitutes a driver for a Lagrangian parcel model simulation of droplet growth and chemistry. Traditionally, parcel models are run in adiabatic mode; that is, their trajectories are defined by updrafts of constant velocity producing adiabatic expansion and subsequent condensation of vapor. Here each parcel produces (typically) nonadiabatic liquid water contents that are representative of the flow experienced by that particular trajectory through the cloud. The degree of adiabaticity depends on calculations in the LES host model. Along each trajectory, microphysical and chemical calculations are performed as described in sections 3.2.1 and 3.2.2.

3.2.1. Microphysical calculations. The size distribution of CCN is initially set up on a logarithmic grid, and growth of these particles is solved on a moving mass grid. In the current calculations five size categories have been used to represent the size distribution, although this number can easily be increased without severely impacting computation time. Droplet growth is solved following Pruppacher and Klett [1997 p. 509] and assuming a condensation coefficient of 0.042 and a thermal accommodation coefficient of unity. The supersaturation field driving droplet growth is calculated from the cooling associated with expansion in the parcel updraft, constrained by the parcel temperature and vapor fields, and the simultaneous condensation of vapor onto droplets. Growth calculations are performed with the variable-coefficient ordinary differential equation solver (VODE) [Brown et al., 1989]. Further details of the microphysical model are given by Feingold and Heymsfield [1992].

3.2.2. Chemistry calculations. The chemistry model computes the uptake and reaction of SO₂, O₃, H₂O₂, NH₃ and HNO₃. A complete list of chemical reactions and their temperature dependence is given in Table 1. Mass transfer of species between the gas and liquid phases is simulated, as by Pandis and Seinfeld [1989], rather than assuming equilibrium between the phases. Chemistry calculations are only performed when sufficient cloud-water is present (cloud-water mixing ratio, \( r > 1 \times 10^{-6} \text{ g g}^{-1} \)) and when an individual droplet category has an ionic strength < 0.02 M [Bower and Choularton, 1993; Seinfeld 1986, p. 214]. Chemistry calculations are not performed in haze particles, which have ionic strengths of about unity. The CCN are initially assumed to be composed of ammonium sulfate, regardless of size. Thus we ignore the impact of sea-salt particles both as sites for aqueous conversion in haze particles [e.g., Hegg et al., 1996] and in terms of their ability to raise droplet pH and affect aqueous conversion in cloud droplets. The ammonium ion and sulfate ion concentrations are treated independently, allowing for a variable ratio between the two, which affects the water activity, and hence the calculation of droplet growth at small sizes. In the studies presented here, the reaction mechanism is rather simple, considering only the formation of S(VI) via the oxidation of S(IV) through O₃ and H₂O₂ (Table 1), although it can be modified readily to include more species and more complex chemistry, including photochemistry. As with the microphysical equations, the differential equations are solved using VODE.

Table 1. Chemical Reactions Included in the TEM

<table>
<thead>
<tr>
<th>Equilibrium Reactions</th>
<th>Equilibrium Constant, M or M atm⁻¹</th>
<th>(-\frac{\Delta H}{R^<em>}, K^</em>)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂(g) ⇌ SO₂ · H₂O</td>
<td>1</td>
<td>3120</td>
<td>Smith and Martell [1976]</td>
</tr>
<tr>
<td>SO₂ · H₂O ⇌ HSO₃⁻ + H⁺</td>
<td>1.23</td>
<td>1960</td>
<td>Smith and Martell [1976]</td>
</tr>
<tr>
<td>HSO₃⁻ ⇌ SO₃²⁻ + H⁺</td>
<td>6.61 \times 10⁻²</td>
<td>1500</td>
<td>Smith and Martell [1976]</td>
</tr>
<tr>
<td>H₂O₂(g) ⇌ H₂O₂(aq)</td>
<td>7.45 \times 10⁴</td>
<td>6620</td>
<td>Lind and Kok [1986]</td>
</tr>
<tr>
<td>O₃(g) ⇌ O₃(aq)</td>
<td>1.13 \times 10⁻²</td>
<td>2300</td>
<td>Kosac-Channing and Helzt [1983]</td>
</tr>
<tr>
<td>NH₃OH(aq) ⇌ NH₃⁺ + OH⁻</td>
<td>75</td>
<td>3400</td>
<td>Hales and Drewes [1979]</td>
</tr>
<tr>
<td>H₂SO₄(aq) ⇌ HSO₃⁻ + H⁺</td>
<td>1.0 \times 10⁻¹⁴</td>
<td>450</td>
<td>Perrin [1982]</td>
</tr>
<tr>
<td>HSO₃⁻ ⇌ SO₄⁻² + H⁺</td>
<td>1.0 \times 10⁻¹⁴</td>
<td>2720</td>
<td>Smith and Martell [1976]</td>
</tr>
<tr>
<td>H₂O ⇌ H⁺ + OH⁻</td>
<td>7.45 \times 10⁻²</td>
<td>-6710</td>
<td>Smith and Martell [1976]</td>
</tr>
<tr>
<td>S(IV) + H₂O₂ ⇌ S(VI) + H₂O</td>
<td>7.45 \times 10⁷</td>
<td>-4751</td>
<td>Hoffmann and Calvert [1985]</td>
</tr>
<tr>
<td>S(IV) + O₃ ⇌ S(VI) + O₂</td>
<td>2.4 \times 10⁴</td>
<td>-5533</td>
<td>Hoffmann and Calvert [1985]</td>
</tr>
<tr>
<td>S(IV) + O₂ ⇌ S(VI) + O₂</td>
<td>3.7 \times 10⁶</td>
<td>-5280</td>
<td>Hoffmann and Calvert [1985]</td>
</tr>
</tbody>
</table>

The temperature dependence is represented by \( K(T) = K_{298} \exp \left[ -\frac{\Delta H_{298}}{R^*} \left( \frac{1}{T} - \frac{1}{298} \right) \right] \) for the equilibrium constant and \( k = k_{298} \exp \left[ -\frac{\Delta H_{298}}{R^*} \left( \frac{1}{T} - \frac{1}{298} \right) \right] \) for the rate coefficient.
Table 2. Input data for the trajectory ensemble model

<table>
<thead>
<tr>
<th>Input Parameter</th>
<th>Value*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCN</td>
<td>$1 \times 10^{-17}$, $1 \times 10^{-11}$ g</td>
<td>mass range of particles (ammonium sulfate)</td>
</tr>
<tr>
<td></td>
<td>$r_g=0.05 \ \mu$m, $N=45 \ \text{mg}^{-1}$, $\sigma_g=1.8$</td>
<td>lognormal parameters (5 size categories)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>5</td>
<td>see part 2 for sensitivity to these values</td>
</tr>
<tr>
<td>O$_3$</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

*Gas concentrations are in parts per billion by volume, however the model uses the conservative mixing ratio units of mol g$^{-1}$ (air) to ensure that each parcel has the same initial conditions.

The computation time requirements for a set of 500 parcels is rather modest: about 3.5 hours on a workstation with a 66 MHz processor. Note that this is far shorter than the approximately 3 weeks CPU time required for the LES run with bin microphysics but no chemistry or approximately 18 hours for a similar two-dimensional simulation.

4. Results

The LES model is initiated with the July 7, 1987, sounding from the First International Satellite Cloud Climatology Project Regional Experiment (FIRE) held off the coast of California (see the stratocumulus sounding presented by Betts and Boers [1990]). This sounding has been chosen because it produces little or no precipitation for CCN concentrations of the order of 50 cm$^{-3}$ or higher and thus eliminates the effect of precipitation removal on the CCN spectrum. The LES simulation is not intended to be a case study of this event but rather to provide a physically plausible source of parcel trajectories for the TEM.

The TEM input is tabulated in Table 2. The gas phase conditions mimic those used by Bower and Choularton [1993] for their run 1. The adequate concentrations of SO$_2$, as well as copious amounts of oxidant, ensure strong aqueous-phase oxidation of SO$_2$. Nevertheless, droplet pH tends to fall below 5 (see section 4.4), despite the absence of nitric acid, so that oxidation via ozone is limited.

4.1. Parcel Trajectories and Mean Profiles of Cloud Properties

Figure 1 shows a time history of a random sample of 50 of the 500 trajectories produced by the LES and illustrates the propagation of these trajectories in the vertical domain. During the first few minutes, the trajectories are confined to their range of initialization, but they fill the domain fairly rapidly. The output values of cloud-water mixing ratio, $r_w$, and drop number, $N$, for the TEM (all 500 parcels) are averaged temporally over the course of the hour and spatially by binning into 10 m height intervals. The resulting profiles (Figure 2) indicate a cloud layer between 500 and 750 m, exhibiting the commonly observed triangular $r_w$ profile [e.g., Noonkester, 1984], and constant $N$ profile associated with nonprecipitating stratocumulus in weakly sheared environments. The peak water mixing ratio is about 0.3 g kg$^{-1}$ and $N$ is of the order of 40 mg$^{-1}$. These average profiles are similar to those obtained by horizontally averaging the LES output, as discussed by Stevens et al. [1996].

4.2. Gaseous Species

Figure 3 displays snapshots of the gaseous concentrations and sulfate derived from individual parcels at three different times (5, 20, and 60 min). Note that each point represents an individual parcel so that there are 500 points on each plot. The figures show a progressive depletion of SO$_2$, H$_2$O$_2$, and NH$_3$ and an increase in S(VI) with increasing time, particularly within the cloud layer. Below cloud, most of the points initially lie close to or at their initial concentrations; however, as time progresses, more and more parcels that have been cycled through the cloud and depleted in gases contribute to a decrease in the below-cloud concentrations. In this simulation the SO$_2$ concentration does not drop below about $1.6 \times 10^{-10}$ mol g$^{-1}$ because the chemistry slows significantly after 10–15 min when H$_2$O$_2$ and NH$_3$ have been substantially depleted.

Over the course of the 1 hour simulation period, 1800 samples are recorded at 2 s intervals. If all 1800 samples...
are superimposed, one obtains a picture of the range of expected values at any given point in space (Figure 4). The mean profile, obtained by sorting data into 20 m height bins and averaging over the 1 hour period (solid line) indicates that depletion is fairly constant with height in the well-mixed subcloud region and much stronger in cloud, where it appears to be related to cloud liquid water $r_l$ (cf Figure 2). This is because some of the dissolved gas in the cloud water will be released upon evaporation of the cloud water, but the gaseous concentration within the cloud layer is reduced because of its solubility.

An important parameter determining the extent of chemical conversion is the time available for processing or in-cloud residence time, $\tau_c$ [Chameides, 1984]. Here $\tau_c$ is calculated as the total time spent in cloud, regardless of whether a parcel has exited and reentered the cloud. Concentrations of the various gases at the end of the hour, plotted as a function of $\tau_c$ (Figure 5), indicate that for $\tau_c < 10-15$ min, there is a rapid depletion in $\text{SO}_2$, $\text{NH}_3$ and $\text{H}_2\text{O}_2$ with increasing $\tau_c$. The primary oxidant, $\text{H}_2\text{O}_2$, is rapidly exhausted within 15 min. The lowering of the pH due to sulfate production is initially mitigated by the uptake of $\text{NH}_3$, but as the available $\text{NH}_3$ is depleted the reduction in pH ensures that oxidation via $\text{O}_3$ is limited. Another important parameter is the cloud-water content [Chameides, 1984]. In this case, a related parameter is the mean $r_l$ (calculated over those periods for which $r_l > 10^{-5}$ g kg$^{-1}$). Gases tend to be rapidly depleted with increasing $r_l$ (Figure 6), especially for $r_l < 5 \times 10^{-4}$ g kg$^{-1}$. The dependence of gaseous depletion on mean $r_l$ shows a fair amount of variability. This can be partially explained in situations in which parcels experience similar mean $r_l$, but each has quite different $\tau_c$. However, much of the variability is probably related to the controls provided by the chemistry. For example, $\text{H}_2\text{O}_2$ shows progressive depletion with increasing height above cloud base, and some parts of the cloud might be sufficiently depleted such that $\text{S(IV)}$ can no longer be efficiently converted to $\text{S(VI)}$. Also, $\text{NH}_3$ shows progressive depletion with height (Figure 3c) so that near cloud top the drop pH is low enough that $\text{O}_3$ is not an effective oxidant (see section 4.4). Thus parcels that experience different trajectories through the cloud may have the same mean $r_l$ but might well have experienced different levels of depletion as they have traversed parts of the cloud where gases are depleted to varying extents.

4.3. CCN Size Spectra

The raw unaveraged CCN spectra at three different times and three different 100 m height intervals below the cloud are shown in Figure 7. After 5 min, none of the below-cloud spectra indicate any processing because any parcels that have entered the cloud have not had sufficient time to mix down to these levels. Note that what appears to be a single size spectrum actually consists of many identical superimposed spectra. By 20 min a significant number of parcels that experienced processing have had time to mix down to lower levels, and there is strong evidence of a second peak at about 0.25 μm; after 1 hour even more parcels contribute to this peak. The position of this peak is closely related to the input gas concentrations and CCN spectrum. For equivalent gas input, an increase in the CCN concentration means that approximately the same additional sulfate mass is distributed over more particles so that the shift in radius and hence the position of the peak is less marked. Varying the gas concentrations in the initial conditions also affects the processing, as discussed by Y. Zhang et al. (Stratocumulus processing of gases and cloud condensation nuclei; 2, Chemistry sensitivity analysis) (herein referred to as part 2).

Hoppel et al.'s [1990] observations show a minimum at approximately 0.06 μm. In this study, all aerosol are hygroscopic. The superimposed spectra in Figure 7 indicate that after all parcels have entered cloud, two peaks separated by a minimum will be created; one peak represents unactivated particles (here a single point at 0.01 μm) and the other consists of processed CCN at $r > 0.1$ μm. Because of the coarse size resolution, there are no CCN particles between these sizes, so that the exact position of the minimum between these two categories is poorly defined. The position of the minimum could be better resolved by simulating a mixture of hy-
Figure 3. Snapshots of vertical profiles of SO$_2$, S(VI) (particles plus aqueous addition), H$_2$O$_2$, and NH$_3$ at (a) 5 min, (b) 20 min and (c) 60 min. Note the linear scale for SO$_2$ and logarithmic scales for S(VI), H$_2$O$_2$, and NH$_3$. Each data point represents one parcel.
groscopic and nonhygroscopic particles and increasing the resolution of the aerosol spectrum.

As was the case for gaseous depletion, CCN processing is also positively correlated with \( r_e \) and mean \( r_i \) (Figures 8 and 9). Initially the mass mean radius \( r_m \) of the processed spectrum increases rapidly with increasing \( r_e \), but after about 10 min further increase is slow. This is closely related to the slow down in gaseous depletion that shuts off the conversion process, which is the source of the increase in \( r_m \). As in Figure 6, dependence of \( r_m \) is a strong function of \( r_i \) for \( r_i < 5 \times 10^{-4} \text{ g kg}^{-1} \), but there is little increase above this value. Variability in \( r_m \) can be explained by similar arguments applied to Figures 5 and 6 for variability in gaseous depletion.

4.4. Calculations of pH

Computed values of pH for a number of drop size ranges (2–5 \( \mu \text{m} \), 5–8 \( \mu \text{m} \), 8–12 \( \mu \text{m} \) and 12–17 \( \mu \text{m} \)) are plotted as a function of time for three different height intervals (510–585 m, 585–660 m, and 660–735 m) in Figure 10. For a given size range, values are averaged in each height interval so that one data point represents all parcels found in the height interval at a given time. The average is performed by weighting the \( \text{H}^+ \) ion concentration in individual samples by their liquid-water contribution and normalising by the total liquid water. Figure 10 shows that after sufficient time has elapsed, smaller drops are more acidic than larger drops. This is due in part to the effect of droplet dilution through condensational growth and in part to mass transfer limitations since larger drops are less efficient at taking up the reactive gases than smaller drops [Flossmann, 1994]. On the other hand, for the first 5 or 10 min, small drops tend to be less acidic than larger ones; small drops start out with high pH of the order of 5.8, but pH falls rapidly for the first 15 min as conversion ensues. Larger drops start out with lower pH values because by the time they have grown from the small-drop population, some conversion has occurred and reduced the pH. The pH tends to decrease with increasing height for smaller drop-size ranges, although as time progresses the differences disappear. The decrease in pH with height is attributed to the fact that \( \text{NH}_3 \) depletion increases with height (and \( r_i \)), so that higher up in the cloud the drops have no buffering capacity. At larger drop sizes, there is virtually no dependence of pH on height and very little dependence on time after 15 min.

In the lowest height bin, there is a fair amount of variability in pH; this results from the intrusion of previously unprocessed parcels, rich in \( \text{NH}_3 \), into the cloud base region. A closer look at the data indicates a high correlation of the \( \text{NH}_3^+ / \text{SO}_4^{2-} \) ratio with pH in this layer. (Data not shown.) On the other hand, the upper two height bins (upper 150 m of the cloud) show much less variability, and their differences as a function
Figure 4. Vertical profiles of $\text{SO}_2$, S(VI), $\text{H}_2\text{O}_2$, and $\text{NH}_3$ collected during the course of 1 hour. The thick line through the data represents the mean profile. Some “noise” in the mean profile derives from the 10 m height bins used to obtain the average.

5. Discussion

The results shown in section 4 are just a small sample of what the TEM can produce. Rather than show extensive analyses, we have chosen to introduce the concept of the TEM model for cloud-chemistry modeling and show some examples of its potential. Further tests are undertaken in part 2 of this series. The results have underscored a number of interesting aspects of this approach.

5.1. In-cloud Residence Time, $\tau_c$

The TEM approach provides valuable information on $\tau_c$. The probability density function (PDF) for the set of trajectories (Figure 11) indicates that the majority of parcels spend of the order of 12–15 min/h in the cloud. Note that for the period analyzed, 123 of the 500 parcels (nearly 25%) did not enter cloud at all; this explains the presence of numerous unprocessed spectra in Figure 7. The mean value for this PDF (including parcels with zero $\tau_c$) is 14 min. The PDF of $\tau_c$ places one constraint on the amount of processing of gases and particles; however, in the case under discussion here, most of the processing is completed in under 15 min, so that a shift in the PDF to larger times would not produce any further processing. This might not be true in a case where processing is not oxidant limited.

Another rough measure of $\tau_c$ can be obtained by considering the volume of the BL occupied by cloud. Figure 2 indicates that the cloud occupies $250/750=1/3$ of the boundary layer, so that in a well-mixed BL, one might deduce that during the course of 1 hour, parcels spend on average 1/3 hour or 20 min in cloud. This in-cloud residence time may be experienced over timescales longer than the hour considered here.

5.2. Mixing Timescales

An indication of the mixing timescale for the simulated boundary layer can be gleaned from Figure 12, where the fraction of parcels depleted in $\text{SO}_2$ reaching
Figure 5. Concentrations of SO$_2$, O$_3$, H$_2$O$_2$, and NH$_3$ as a function of in-cloud residence time, $\tau_c$. Scales are as in Figure 3.

Figure 6. Concentrations of SO$_2$, O$_3$, H$_2$O$_2$, and NH$_3$ as a function of mean liquid water mixing ratio $r_l$ for the duration of cloud penetrations.
Figure 7. Snapshots of CCN size spectra on a moving mass grid at three time intervals (5, 20, and 60 min) and three height intervals (below cloud). The 5 min panel shows the unprocessed CCN spectrum. The creation of a second mode at about 0.3 μm is evident in the spectra at 20 min and 60 min.

Figure 8. Mass-mean radius, \( r_m \), of the CCN spectra calculated as a function of in-cloud residence time, \( \tau_c \).
calculation is indicative of mixing timescales, it suggests that it would take longer than 1 hour for mixing to occur all the way through the boundary layer. However, close to 25% of parcels never enter the cloud, and if only those parcels that did enter the cloud are considered, the value of 70% at the end of the hour in Figure 12 is adjusted to about 95%, suggesting that almost all parcels that entered the cloud have had sufficient time to mix down to the lower level of the BL.

5.3. Calculations Using Average Conditions

Prior work has indicated the pitfalls of using average values of various parameters when evaluating heterogeneous chemistry. For example, use of a bulk-water model for estimating conversion rates can result in significant underestimation of sulfate production compared with drop-size-resolved calculations [e.g.

Figure 9. Mass-mean radius, $r_m$, of the CCN spectra calculated as a function of mean liquid water mixing ratio, $r_l$, for the duration of cloud penetrations.

Figure 10. Calculations of pH as a function of time for 4 size-bins: (a) 2–5 μm, (b) 5–8 μm, (c) 8–12 μm, and (d) 12–17 μm. Calculations are performed at three different 75 m height intervals as indicated.
It has been argued here that the TEM affords a more representative evaluation of processing of aerosol and gases than can be obtained by a single-parcel trajectory. This hypothesis is put to the test by considering an "average" parcel or a parcel that experiences the average conditions. This parcel is defined as one that experiences the mean $v_t = 0.18$ g kg$^{-1}$ and mean $N = 43$ mg$^{-1}$ for the mean $r_c = 14$ min. A representative drop-size spectrum constrained by these values of $v_t$ and $N$ is chosen. A calculation of the percent conversion of S(IV) to S(VI) shows that this average parcel produces a conversion of $22.5\% \ h^{-1}$ compared to a value of $15.5\% \ h^{-1}$ for the full TEM; a difference of 45%. The differences between the average parcel and the TEM are explored further and reported for a range of conditions in part 2.

5.4. Impact of Processing on Cloud Evolution

As noted in section 2, the TEM approach does not enable a coupling of the microphysical/chemical model with the dynamical model. Nevertheless, some indication of the impact of cloud processing of aerosol on subsequent cloud evolution can be obtained by examining the differences between coupled LES model simulations that differ only in the input of the CCN spectrum. To expedite these experiments they have been performed in a two-dimensional version of the LES or cloud-resolving model. Although the cloud resolving model does not represent the eddy structure correctly compared with the LES, it does include the essential interactions between large eddies and size-resolved aerosol and cloud microphysics [Feingold et al., 1996].

The cloud resolving model has been run on a case that produces drizzle on a timescale of a few hours (depending on the CCN spectrum). This is the "First Lagrangian" case from the Atlantic Stratocumulus Transition Experiment (ASTEX) that has been simulated by a number of groups within the framework of the 3rd (Global Energy and Water Cycle Experiment) Cloud System Studies (GCSS) workshop and analyzed by Duynkerke et al. [1995]. Two simulations have been performed; the first uses as input the unprocessed CCN...
Figure 13. Cloud resolving model results indicating total number concentration (CCN + cloud drops). In the absence of collection and wet deposition, this value is conserved; the depletion is indicative of the extent of drizzle formation. Unprocessed CCN spectrum used as input to the cloud resolving model (solid line) is shown; Mean “processed” spectrum from Figure 7 (upper right) used as input to the cloud resolving model (dashed line) is shown.

Calculations of the total particle concentration \( N \) (CCN + drop), a parameter that is conserved in the absence of collection and/or wet deposition, are performed for the “unprocessed” case and the “processed” case and displayed in Figure 13. One sees that although the two time series are very similar, there is a tendency for the processed spectrum to deplete \( N \), below that of the unprocessed case, indicating a slight enhancement in collection and/or wet deposition. This is further corroborated by Figure 14, where time series of the integrated surface rainfall \( I \) [millimeter] for the two cases are compared; again, it is evident that there is a slight enhancement in surface precipitation for the processed case.

At first sight, this result is at odds with those from prior studies: Bower and Choularton [1993] used both unprocessed and processed CCN spectra as input to an adiabatic parcel model and found that the processed spectra produced smaller drop effective radii. This result was explained by the fact that conversion increases the size of small particles substantially and therefore increases the number of particles that are effective as CCN in the processed spectrum, resulting in higher drop concentrations.

In the current case, almost all CCN are activated, so that the cloud-processed spectrum produces approximately the same number of drops; however, some fraction of these is larger than the drops obtained in the absence of processing, and this enhances drizzle formation slightly. Clearly, whether processing enhances or suppresses drizzle will depend on both the number concentration and size distribution of the unprocessed and processed spectra, as well as the magnitude of supersaturation in subsequent cloud cycles. If processing increases \( N \) sufficiently, then there will be a tendency for drizzle to be suppressed. However, if \( N \) is mostly unchanged but the number of larger particles is sufficiently increased, then drizzle may be enhanced. Quantifying these two relative effects is a subject of broad scope and cannot be pursued in this paper. Nevertheless, it is interesting that in the event that cloud processing does enhance wet deposition, cloud lifetimes will be limited and background concentrations of aerosol will be strongly reduced. However, if processing suppresses drizzle, then clouds will have longer lifetimes and become more reflective as drop numbers increase. The ultimate impact on reflectance and shortwave heating, resulting from the increase in \( N \), is unclear. Olsun et al. [1998] suggested that the cloud might loose its vigor and be prone to dissipation. If this were the case, it would leave behind a BL with much higher concentrations of CCN than the one in which drizzle forms.

6. Summary and Conclusions

A large-eddy simulation model has been used as a means of describing boundary layer dynamics and deriving realistic parcel trajectories for subsequent use by a trajectory ensemble model that includes a coupled microphysical/chemical model. The philosophy
behind this approach is that it provides a balance in the representation of dynamics, microphysics, and chemistry without the computational burden of coupling the chemistry model to the LES and that it eliminates numerical diffusion associated with fixed spatial grids and fixed mass grids. Its main drawbacks are that the microphysics and chemistry are not coupled to the dynamics and that droplets must follow parcel trajectories. Consequently, the technique is applied only to nonprecipitating clouds. In addition, because mixing between parcels is not represented, the technique is applicable to short timescales (of the order of 1 hour).

The trajectory ensemble model has been applied to a nonprecipitating stratocumulus case. Calculations of CCN deliquescence and droplet growth are performed along each of the 500 parcels, together with nonequilibrium mass transfer between the gas and liquid phases, and reaction of SO2, O3, and H2O2. Initial gas concentrations and aerosol size distributions have been assumed for illustrative purposes. The CCN has been assumed to have homogeneous composition; inclusion of more chemically complex aerosol is postponed for a future study.

The results indicate a strong sensitivity of gas and aerosol processing to parcel in-cloud residence time, $\tau_c$, and to cloud liquid water. However, the assumed gas concentrations also provide strong constraints on processing. For the case simulated here, the production of sulfate is oxidant limited and, beyond a $\tau_c$ of about 15 min, processing is negligible. The NH3 is strongly depleted, and equilibrium pH values range from about 2.5 (small drops) to 4 (large drops), effectively shutting off oxidation via the O3 pathway.

The LES/TEM approach is useful for obtaining estimates of boundary layer mixing timescales and probability density functions of time available for heterogeneous chemistry. It also includes the temporal/spatial variability of liquid water content encountered by the parcels. Thus it provides a more comprehensive picture of the conditions likely to be experienced by an ensemble of parcels than can be obtained by simulations with a single parcel. In a comparison of the mean conversion rate of S(IV) for all 500 parcels compared with that derived from a single parcel experiencing mean conditions, it is found that for the case simulated here, the single parcel overestimates conversion by 45%. This modeling approach is being applied to a range of initial conditions, and results will be reported in part 2.

Finally, the impact of the cloud processing of aerosol on cloud evolution has been evaluated within a twodimensional Eulerian eddy-resolving model for an ASTEX case that readily produces precipitation. For the case modeled here, the processed spectrum produces drizzle more rapidly than does the unprocessed spectrum. The results suggest that drizzle may either be enhanced or suppressed depending on the concentration of CCN particles, the initial particle size spectrum, and the extent of processing.

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References


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