

THE EFFECTS OF CLOUDS ON AEROSOL AND CHEMICAL SPECIES PROCESSING, PRODUCTION, AND DISTRIBUTION IN THE BOUNDARY LAYER AND UPPER TROPOSPHERE

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ABSTRACT

THE EFFECTS OF CLOUDS ON AEROSOL AND CHEMICAL SPECIES PROCESSING, PRODUCTION, AND DISTRIBUTION IN THE BOUNDARY LAYER AND UPPER TROPOSPHERE ABSTRACT

Clouds play important roles in boundary layer and tropospheric aerosol and chemical processes. This work addresses the aerosol and chemical species processing, production, and distribution through two important types of clouds: convective and stratocumulus clouds.

A modeling study of the effects of convection on the transformation and redistribution of chemical species and evolution and redistribution of aerosol particles in the troposphere is presented. A two-mode, two-moment aerosol evolution model is coupled with a two-dimensional, mixed-phase, two-moment microphysics, Eulerian cloud model and a sulfate cloud chemistry model [Kreidenweis *et al.*, 1997; Taylor *et al.*, 1997; Zhang *et al.*, 1998] to examine the new particle formation mechanism and the importance of different pathways for aqueous sulfate production. In the simulations, the complexation of CH_2O with S(IV) is found to be of minor importance in most of the model cloud, compared with the oxidation of S(IV) by H_2O_2 and O_3 , while Fe(III) -catalyzed oxidation plays an important role in aqueous sulfate production. Significant SO_2 is convectively transported to the mid-to-upper troposphere, where it is oxidized to gas-phase H_2SO_4 . After cloud processing, cloud condensation nuclei (CCN) particles are removed by precipitation and graupel to form a CCN-depleted region above cloud top and in the cold and humidified cloud outflow region. The new particle formation in the mid- to upper- troposphere interacts with cloud processing and transport of chemical species and aerosol particles and produces a peak of small particle concentration in the outflow region. The model results suggest that both small

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aerosols and aerosol precursors can be transported into the mid- to upper- troposphere by convective clouds, affecting vertical profiles of aerosol concentrations. The sensitivity of the S(VI) and aerosol production, SO₂ and aerosol redistribution to variations in the initial chemical and aerosol conditions and several model parameters are also examined.

A trajectory ensemble model (TEM) is used to investigate stratocumulus processing of gases and CCN in the boundary layer. The fully coupled aqueous chemistry/cloud microphysics model [Feingold *et al.*, 1998; Zhang *et al.*, 1998] is driven by a set of boundary layer parcel trajectories derived from a large eddy simulation model to study the effects of variations in the initial chemical fields and initial aerosol number concentration on chemical heterogeneity, broadening of the CCN and drop spectra, effective drop radius, and differences in the overall fractional conversion between the TEM and a single parcel experiencing mean conditions in a stratocumulus-capped marine boundary layer. It is found that the TEM offers a more representative method of describing the stratocumulus processing of aerosol and gases than does a single parcel model. In the base case simulation, the O₃ oxidation rate averaged over all parcels is larger than the H₂O₂ oxidation rate, whereas the volume-mean cloudwater pH might suggest that H₂O₂ oxidation dominates. The liquid water-weighted pH generally increases with increasing drop size, to a peak pH. The drop size at this peak corresponds to the minimum in S(VI) concentration and is located near the mode of the drop mass distribution. However, the pH dependence on drop size at larger cloud drop sizes is affected by the initial chemical conditions. Aqueous chemistry contributes to the broadening of the drop size distribution, but the magnitude of the broadening depends on the initial aerosol and chemical conditions. In cases where more mass is added onto large particles in the tail of the initial CCN spectrum, the broadening of the drop spectrum is most evident, and may even trigger the collision-coalescence process and drizzle formation in stratocumulus clouds. The change in initial CCN number concentration has the most prominent effect on the effective drop radius.

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Chapter 1

INTRODUCTION

Interest in aerosol and atmospheric chemistry has previously focused on their potential influence on visibility reduction, human health, and acid deposition. More recent motivations include the recognition that aerosol in the atmosphere plays an important role in the global climate system due to its direct and indirect effects [Charlson *et al.*, 1992; Hudson, 1993; Intergovernmental Panel on Climate Change (IPCC), 1995, 1996]. Aerosol reflects solar radiation back to space directly via particle optical properties and indirectly via affecting cloud cover, lifetime and optical properties. There are many uncertainties regarding the aerosol direct and indirect effects, and a clear understanding of the processes linking aerosol particles, aerosol precursor emissions, and radiative effects is lacking.

In this chapter, we discuss the aerosol production processes, their relation to aerosol precursors and the interactions of aerosol, clouds, and atmospheric chemistry in two types of clouds: deep convective cloud and stratocumulus. In §1.1 and 1.2 below we begin by reviewing a subset of the studies (observations and modeling) of aerosol and atmospheric chemistry that have been conducted over the years. No attempt is made to be exhaustive in our review; rather, we intend only to illustrate the direction of the progression of our understanding, and how it has led to the questions to be addressed in this dissertation. A brief synopsis of the outstanding questions that are directly addressed by this research in subsequent chapters is given in §1.3. Connections are then made to our research strategy and the primary objectives of this work (§1.4).

1.1 Preliminaries: Recent interest in aerosol and atmospheric chemistry

It has long been known that the outstanding problems in global change are those at the intersection of the various disciplines of physics, chemistry, dynamics, biology and

human intervention. Of many such phenomena, those dealing with the interactions between aerosols, clouds and atmospheric chemistry are the focus of this dissertation. The importance of studying these arises from recent developments which demonstrate their significance to global climate and chemistry.

Model studies show that the increase in anthropogenic sulfate particles, derived mainly from the emission of sulfur dioxide, is potentially a large contributor to the change in the global radiative forcing of climate, according to the IPCC report [1996]. Increases in sulfate aerosols can lead to a negative radiative forcing. Such particles cool climate directly by reflecting solar radiation or enhancing clear sky albedo and indirectly through modification of cloud formation, lifetime and radiative properties and thus the shortwave cloud forcing. The magnitude of the estimated direct radiative cooling effect of sulfate aerosols on the global scale is about -0.5 W m^{-2} with an uncertainty of 2 W m^{-2} [IPCC, 1996]. Sulfate aerosol also creates significant regional climate change regardless of its effect on globally averaged radiative forcing. The magnitude of the indirect effect, which is the modification of cloud radiation properties and cloud life time through the modification of the cloud condensation nuclei (CCN) spectrum, is estimated to be somewhere between 0 and -1.5 W m^{-2} , and has the largest uncertainty [IPCC, 1996]. Because aerosols are the largest sources of uncertainty in the total radiative forcing of climate, and they mask climate changes due to increasing greenhouse gases, aerosols now rank with cloud feedback and ocean-atmosphere interactions as the major barriers toward a reliable prediction of climate changes on decadal and longer time scales.

Other types of aerosols, *e.g.*, mineral dust and carbonaceous particles, derived mainly from biomass burning, dust storms and other natural sources, may also contribute to the global radiative forcing, and may be comparable to the sulfate effects [Andreae, 1995; Penner *et al.*, 1994]. The radiative effects of these background aerosols are also important factors for simulating the present day climate.

Much attention has been focused on sulfate aerosol, of which the anthropogenic component has increased dramatically during the past several decades. From the IPCC [1995] report, the anthropogenic annual emission of sulfur dioxide exceeded the natural flux after

1940 and continues to increase. Some fraction of the sulfur is transformed to sulfate aerosol. Sulfate ion typically comprises around 25-50% of the anthropogenic accumulation mode aerosol mass [IPCC, 1995]. The sulfur distribution between different parts and phases of the atmosphere must be assessed. Sulfate aerosol is produced from aerosol precursors through either clean air production or in-cloud production. It is essential to know what fraction of particulate sulfate is formed via SO_2 oxidation in the gas phase by $\text{OH}\cdot$ radicals, and what fraction is formed via heterogeneous processes of dissolved SO_2 (or, more generally, S(IV)) conversion to sulfate (or, more generally, S(VI)) within the aqueous phase and on haze particles. Upon cloud evaporation, the unreacted S(IV) returns to the gas phase, but nonvolatile S(VI) remains in the particle phase. Both aerosol concentration and aerosol precursor concentration are modified by clouds. In the next section, we touch on the interactions between aerosols, chemistry and clouds, and the effects of clouds on aerosol and chemical species production, processing and distribution through two important types of clouds: deep convective clouds and stratocumulus clouds.

1.2 The interactions of clouds, aerosol and chemistry

Many studies [*e.g.*, Cess *et al.*, 1990; Kiehl and Ramanathan, 1990; Ramanathan *et al.*, 1989; Randall, 1992; Stephens *et al.*, 1993] have indicated the importance of clouds for the maintenance of global climate. While clouds directly impact the global radiative energy balance, they also play significant roles in tropospheric chemistry via several mechanisms by which they influence trace gas and aerosol concentrations, chemical conversion rates, and transport. These mechanisms include the transport of species from the boundary layer to the middle and upper troposphere by convective motion, also termed cloud pumping; heterogeneous chemical reactions occurring in cloud droplets and precipitation drops; variations in gas and aerosol concentrations that occur via the effects of removal by clouds and precipitation; the drop collision-coalescence process that depletes drop number concentration; and the effects of cloud cover upon the rates of photochemical reactions, which will not be pursued in this dissertation.

Sulfur species are of particular interest because reduced sulfur compounds are oxidized to sulfate in the atmosphere and partitioned into the particle phase; sulfur-bearing

particles are generally quite soluble and hence are effective CCN. In addition, a major sulfur-to-sulfate (S(IV)-to-S(VI)) conversion pathway occurs in the aqueous phase, and thus the presence and persistence of clouds can play a large role in shaping the atmospheric aerosol size distribution. The aqueous-phase oxidation of dissolved SO_2 (as S(IV)) to sulfate proceeds rapidly in the liquid phase. It is the major oxidation pathway on the global scale and also contributes strongly to the acidity of precipitation. Langner and Rodhe [1991] estimated that over 80% of the global oxidation of sulfur to sulfate occurred in cloud. Dissolved oxidants important in S(IV) conversion include ozone, hydrogen peroxide, and oxygen, the latter catalyzed by transition metals [Barth *et al.*, 1992; Barth, 1994; Flossmann, 1994; Kitada and Lee, 1993; Roelofs, 1993; Wang and Crutzen, 1995]. Recently, in-cloud formation of hydroxymethanesulfonate (HMS) by the reaction of dissolved formaldehyde (CH_2O) and SO_2 , has received attention due to its ability to enhance the overall solubility of sulfur dioxide and to reduce sulfate production in cloudwater [Rao and Collett, 1995].

It has also been realized by observations and model studies that clouds are not chemically homogeneous, and that the chemical heterogeneity across the droplet size spectrum has its consequence for aqueous chemistry [Daum *et al.*, 1984; Hegg and Larson, 1990; Noone *et al.*, 1988; Gurciullo and Pandis, 1997; Pandis *et al.*, 1990; Twohy *et al.*, 1989]. Field studies have suggested that the chemical composition of droplets varies, depending on the sizes of the droplets [Collett *et al.*, 1993, 1994; Ogren *et al.*, 1989]. Size-dependent chemical composition of aerosol particles and droplets of different sizes experiencing different rates of water growth could both contribute to the observed chemical heterogeneity. Twohy *et al.* [1989] pointed out that the difference in diffusional growth rates between the small and large droplets results in substantial differences in solute concentration and composition with size of droplets, and the chemistry of individual droplets is not, in general, representative of the "bulk" cloud water sample. Gurciullo and Pandis [1997] suggested that the chemical conversion rates estimated for bulk solutions can be substantially different than those computed for a size-resolved droplet spectrum and size-dependent aqueous chemistry, and the difference can be as large as a factor of 30.

In-cloud sulfate production not only plays an important role in the global sulfur cycle and precipitation chemistry, but may also contribute to the enhancement of aerosol light scattering efficiency [Lelieveld and Heintzenberg, 1992] and the increase of CCN activity of aerosol particles at low supersaturation [*e.g.*, Hoppel *et al.*, 1990]. Yuen *et al.*[1994] studied continental clouds using an explicit microphysical parcel model, and found that cloud processing has an appreciable positive effect on light-scattering. A modeling study by Hegg *et al.*[1996], using a Lagrangian parcel model, also pointed out in-cloud processing had considerable impact on particle light scattering, though the impact was scenario-dependent. Kaufman and Tanre [1994] pointed out that the increase in CCN activity can, in principle, alter the microstructure of subsequent clouds which form on the processed aerosol spectra and establish an interesting feedback. Bower and Choularton [1993] studied aerosol processing in a hill cap cloud and concluded that small CCN particles activate much more readily after cloud processing, and that the droplet effective radii are lowered in the secondary cloud.

Sulfate aerosols can also be produced through clear-air production. New sulfate particle formation is thought to occur via gas-phase reaction of SO_2 with $\text{OH}\cdot$ to form $\text{H}_2\text{SO}_4(\text{g})$, a species which can participate in binary homogeneous nucleation with water vapor to produce new H_2SO_4 solution particles [Brown *et al.*, 1996; Easter and Peters, 1994; Hegg *et al.*, 1990; Kerminen and Wexler, 1996; Kreidenweis *et al.*, 1988; Kulmala *et al.*, 1995]. Hegg *et al.*[1990] observed the nucleation of new sulfate particles above cloud tops in the marine atmosphere. Hoppel *et al.*[1994] also found sporadic new particle formation in clear air in numerous locations in the marine boundary layer. A modeling study by Pirjola *et al.*[1998], using a single air parcel trajectory model and assuming homogeneous nucleation of sulfuric acid and water explains some of the new particle formation observed in arctic air masses influenced by SO_2 -pollution events.

In the next two subsections we present an outline of the current state of knowledge associated with interactions between aerosol, chemistry and clouds. In §1.2.1 we discuss the role of deep convective cloud in processing of SO_2 and other chemical species, and in convective transport of aerosol precursors from the boundary layer to the middle and upper

troposphere and its impact on new particle formation, which relates to the clear sky albedo and the aerosol direct effect on climate. In §1.2.2 we then investigate the stratocumulus processing of CCN spectra and gases and its impact on modification of cloud droplet and CCN spectra and other properties, which are associated with aerosol indirect effects.

1.2.1 Deep convection

The typical horizontal dimension of a deep convective cloud is on the order of 10 km, and its lifetime is about one hour to several hours. A deep convective cloud is optically thick. It has little impact on radiation budget due to its small areal extent, except for the highly reflective thick cirrus-anvil cloudiness which is related to deep convection. Generally, we do not directly investigate the cloud optical properties, CCN characteristic and activity, and enhanced aerosol light scattering due to in-cloud sulfate production for this type of cloud, because of its relatively high supersaturation, and permanent removal of aerosol from the atmosphere. However, deep convective clouds constitute a mechanism of intense vertical transport, as well as a site for chemical reactions in the liquid phase. From a transport point of view, convective clouds can redistribute species (unreacted chemical species and aerosol particles) from the boundary layer to the middle and upper troposphere. These redistributed gases and aerosols generally have longer lifetimes in the upper troposphere and are subject to longer-range transport, and thus their regional and global cycles can be modified by convection. Slightly insoluble species, such as ozone, are efficiently redistributed by cloud motions; whereas most chemical species and aerosols interact with cloudwater to some degree, and the effectiveness of convective systems in transporting these species and aerosol particles should therefore depend upon the cloud chemical and dynamical environment [Flossmann and Wobrock, 1996].

There is experimental evidence for the importance of cloud transport. Chatfield and Crutzen [1984] proposed that cloud transport may be important in tropical marine regions. Observations by Pickering *et al.* [1988] showed that cumulus clouds are efficient transporters of gaseous species from the boundary layer to the upper troposphere. Deep convective storms can result not only in the venting of boundary layer air, but may also entrain stratospheric air into the troposphere, as interpreted by Dickerson *et al.* [1987] from their

thunderstorm observations. Cotton *et al.*[1995] discuss a number of observational and modeling studies in their review of cloud venting by boundary layer clouds, deep convective clouds, mesoscale convective systems, and clouds embedded in extratropical cyclones. They estimate that the entire planetary boundary layer is vented about 90 times per year, and thus it is imperative that the transport of heat and moisture by such venting processes be properly represented in large-scale models. Houze and Betts [1982] reviewed convection in the Global Atmospheric Research Program's Atlantic Tropical Experiment (GATE) and pointed out that to simulate the effects of tropical convection in large-scale models a variety of phenomena must be accounted for. Since trace gases and aerosol are redistributed along with heat and moisture, the same processes must be represented in chemical transport models.

Another speculated effect of convective transport is that convective motion vents particle precursor gases (DMS, SO₂, and H₂SO₄) and cleansed air to higher, colder levels of the troposphere that have also been humidified by the cloud transport of water, and might create optimal conditions for H₂SO₄-H₂O binary homogeneous nucleation to occur. Clarke [1992] measured aerosol in the remote free troposphere over the tropical ocean and found that lowest aerosol mass concentrations were correlated with highest number concentrations of ultrafine, volatile aerosol particles, the volatility of which suggested a sulfuric acid composition. Perry and Hobbs [1994,1995] also provided observational evidence to support new particle nucleation in clean air near the top of an isolated, marine cumulus cloud. These observations provide evidence for the hypothesis of new particle production by homogeneous nucleation in clean regions in the mid-to-upper troposphere. This hypothesis is tested in detail in this dissertation.

Sulfate in cloud water and precipitation arises from impaction and nucleation scavenging of sulfate-containing aerosol particles, which can in turn be modified by processing through cloud. Although the initial transfer of sulfur species from the gas to the cloud water occurs in liquid phase cloud droplets, microphysical processes transfer sulfate into the ice phase [Wang and Chang, 1993b] and into precipitation. In addition, deep convective cloud is usually accompanied by precipitation, which could permanently remove the

CCN particles and soluble chemical species contained in precipitation drops. Chemical processes and their response to microphysics and changing initial conditions will thus impact the degree of vertical redistribution of SO_2 and aerosol particles. In cases where SO_2 is convectively transported to the middle and upper troposphere, this redistribution might set the stage for subsequent new particle nucleation, which replenishes aerosol number concentrations, and is essential in understanding tropospheric sulfate aerosol dynamics. Convective cloud thus modulates the chemical species vertical distribution and the aerosol vertical distribution and size distribution directly by scavenging processes and indirectly by sulfur-to-sulfate aqueous conversion pathway.

Both experimental and modeling studies suggest that interactions between aerosols, chemistry and clouds occur in the convective clouds, but the conditions under which these effects play an important role, the persistence of perturbations due to clouds, and the sensitivity of the mechanisms to local physical and dynamical parameters are not fully understood. We will address these in more detail in subsequent chapters.

The above-mentioned various mechanisms by which convective clouds affect chemical species and aerosol chemistry, redistribution, and production within the troposphere have been studied separately, in varying levels of detail, by a number of workers [*e.g.*, Barth, 1994; Flossmann, 1994; Flossmann and Wobrock, 1996; Taylor 1989a,b; Wang and Crutzen, 1995]. For convective clouds, in general, studies which have treated the chemistry in detail did not treat clouds in a realistic manner, particularly with respect to the horizontal and vertical transport of gases and aerosols associated with cloud formation and evolution processes. As discussed in Iribarne and Cho [1989], most cumulus cloud chemistry models have been zero- or one-dimensional. Box models [*e.g.*, Seigneur and Saxena, 1984], Lagrangian parcel models [*e.g.*, Alheit *et al.*, 1990; Hales, 1982; Hegg and Larson, 1990; Roelofs, 1993], variations involving mixed and adiabatic regions [*e.g.*, Walcek and Taylor, 1986] or the Eulerian axisymmetric model of Asai and Kasahara [1967] [*e.g.*, Lee, 1986] have also been used. Similarly, studies that consider transport aspects in great detail have usually treated aerosols simply as tracers, have highly simplified treatment of cloud chemistry, or have ignored cloud mechanisms other than convection [*e.g.*, Charlson *et al.*,

1991; Langner and Rodhe, 1991]. There have been several efforts directed toward examining the cloud/chemistry/aerosol interaction using more realistic cloud models. Taylor [1989a,b] and Cho *et al.* [1989] described midlatitude deep cumulus cloud chemistry investigations using 1.5 dimensional cloud models and a bulk microphysics parameterization. Barth [1994] examined the chemistry in a winter storm using a two-dimensional cloud model with a bulk microphysics parameterization including ice. Flossmann [1994] investigated the scavenging behaviour of gaseous and particulate sulfate by a warm marine cloud using a two-dimensional cloud model including spectral microphysics. Respondek *et al.* [1995] studied the wet removal of $(\text{NH}_4)_2\text{SO}_4$ particles by a convective cloud containing ice using a two-dimensional cloud model with spectral microphysics and without cloud chemistry. Wang and Chang [1993a,b] investigated the cloud chemistry, precipitation chemistry, and transport of pollutants using a three-dimensional cloud model with a bulk microphysics parameterization. Kreidenweis *et al.* [1997] investigated the redistribution of SO_2 by a mixed-phase continental cumulonimbus using a two-dimensional cloud model with two-moment microphysics parameterization. These very recent studies which have treated both the cloud chemistry and clouds in detail have not included an aerosol evolution model which could deal with new particle production and aerosol condensational growth processes. Further, the aqueous conversion of S(IV) to S(VI) was limited to examination of the O_3 and H_2O_2 oxidation pathways in most of the model studies discussed above.

1.2.2 Stratocumulus

Marine stratocumulus clouds play an important role in the global radiation budget because they have large areal extent and temporal persistence, may be sensitive to anthropogenic influences, and strongly influence the planetary albedo [*e.g.*, Nakajima *et al.*, 1991; Randall *et al.*, 1984; Slingo, 1990; Twomey, 1977]. Because of the generally low CCN concentrations in the marine boundary layer, stratocumulus clouds also exert a measurable influence on the abundance and characteristics of CCN, and modify the CCN spectra and cloud optical properties, thus influencing global climate [*e.g.*, Albrecht, 1989; Feingold *et al.*, 1996]. The cloud processing in maritime clouds is not really definitive for the aerosol

direct forcing issue since modeling results to date show such forcing largely confined to continental areas [Charlson *et al.*, 1991], but it is an important aspect of the global indirect forcing by sulfate aerosol since this must necessarily occur under background conditions [Twomey, 1991]. The well known hypothesis termed the Twomey effect [1974] postulates that increased anthropogenic sources of aerosol will result in greater number of CCN, and thus higher concentration of cloud droplets and more reflective clouds. This effect is also believed to have the largest impact on optically thin marine stratocumulus clouds, as confirmed by ship track phenomena [*e.g.*, Radke *et al.*, 1989; King *et al.*, 1993].

The potential for stratocumulus processing to modify aerosol size spectra has strong implications for the boundary layer system. First, the drop size and number concentrations will be affected, which in turn affect cloud optical properties, such as optical depth, albedo, and albedo susceptibility [Twomey, 1991]. Second, the initiation of drizzle will be affected through modification of the CCN distribution. The drizzle formation process can both remove water from the cloud, affecting cloud optical properties, and impact the boundary layer dynamics that in turn impact cloud microstructure [Stevens, 1996]. Cloud chemistry depends on drop size and creates an additional feedback to the system. Finally, cloud radiation in the shortwave depends strongly on droplet size, and modifications in the CCN distribution have the potential to affect cloud dynamics.

The impact of stratocumulus clouds on CCN can take place via several mechanisms. First, there is evidence that the formation of new particles from the gas phase occurs just above cloud top [Hegg *et al.*, 1990], apparently in relatively clean regions with high relative humidity. This process replenishes aerosol number concentrations, and these ultra-fine particles may eventually grow to appropriate sizes and serve as a source of CCN. Second, stratocumulus clouds serve as a medium for in-cloud sulfate production. Various aqueous phase chemical processes deposit mass in droplets and enhance the amount of soluble material. When cloud droplets evaporate, each droplet produces a single particle [Mitra *et al.*, 1992]. Thus, aqueous chemistry enhances particle mass concentrations without affecting particle number concentrations, and the regenerated CCN are on average larger and more easily activated at ambient supersaturations. Finally, the drop collision-coalescence process

significantly depletes drop number concentration. Therefore, CCN number concentration will be reduced following evaporation of cloud, and this results in an aerosol spectrum with increased mass-mean radius. The magnitude of depletion in CCN number concentration will depend upon the depletion in drop number, and upon the percentage number of CCN activated from the total aerosol population. In this dissertation, we intend to study one type of cloud processing mechanism: aqueous chemistry in cloud.

Observations and model studies in the marine boundary layer described in the literature show strong evidence of bimodal aerosol spectra due to cloud processing of aerosol via aqueous chemistry [Bower and Choularton, 1993; Hegg and Larson, 1990; Hegg *et al.*, 1996; Hoppel *et al.*, 1994]. Hoppel *et al.* [1990, 1994] interpreted the particles under the larger (CCN) mode to be the residue of evaporated cloud droplets which undergo aqueous chemistry. Trace gases are converted to nonvolatile species which are incorporated into the aerosol particle mass during multiple cycling through the non-precipitating cloud-topped marine boundary layer via aqueous chemistry, increasing the CCN mass and size. The processed aerosol spectra are then superimposed onto the interstitial aerosol size distribution and create a "Hoppel minimum" around $0.06\text{--}0.1\text{ }\mu\text{m}$ radius. Bower and Choularton [1993] used an adiabatic parcel model for a hill cap cloud and reproduced the bimodal aerosol size distribution. They concluded that the effective radius in a secondary cloud is reduced, because more CCN are activated in the secondary cloud. Albrecht [1989] pointed out that modification of the CCN distribution has the potential to affect the initiation of drizzle; the drizzle process removes water from the the cloud and affects cloud optical properties and the boundary layer dynamics. Feingold *et al.* [1998a], on the other hand, used a trajectory ensemble model (TEM) with fully coupled microphysics/chemistry, which will be discussed in detail in the next chapter, and pointed out that whether processing enhances or suppresses drizzle formation 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.

Clearly, the boundary layer system is a closely coupled one and should take dynamics, microphysics, chemistry and radiation into consideration. Previous modeling studies have,

by necessity, simplified treatment of one or more of these components. As described in Feingold *et al.*[1998a], models dealing with detailed microphysics or chemistry in a controlled dynamical framework (poor in dynamics and radiation) include box models [*e.g.*, Chameides and Stelson, 1992], single parcel models either adiabatic or with prescribed dynamics [*e.g.*, Bower and Choulaton, 1993; Hegg *et al.*, 1996; Gurciullo and Pandis, 1997], and one-dimensional models [Ackerman *et al.*, 1995]. These models do not address the interaction between microphysics/chemistry and dynamics. The large eddy simulation model (LES) is a powerful tool for simulating boundary layer dynamics. Although LES has recently been coupled with bin microphysics models [Feingold *et al.*, 1994; Kogan *et al.*, 1994; Stevens *et al.*, 1996], few attempts have been made to couple LES with size-resolving microphysics and chemistry. Models that attempt to balance dynamics and microphysics or chemistry include two-dimensional cloud resolving models. For example, Flossmann [1994] has included size resolving microphysics and chemistry in a two-dimensional cloud model of a warm marine cloud. Feingold *et al.*[1998a] present a new method for studying heterogeneous chemistry in boundary-layer clouds that achieves a balance between dynamics, microphysics and chemistry using a trajectory ensemble model.

1.3 Outstanding problems in relation to conducted research

The above sections outline the state of knowledge, in terms of observations and modeling studies, of the effects of cumulus convection and stratocumulus processing on aerosol and gases. The extreme variability of tropospheric aerosols gives rise to many problems and questions. More knowledge of the sulfur long-range transport is needed, because the sulfur large scale spreading effect is one of the key assumptions in the direct effect of the sulfate-radiative cooling hypothesis [Charlson *et al.*, 1992]. More information is needed on the physical properties of aerosols that influence radiative transfer and cloud microphysical properties, such as aerosol spectra, and the potential regional and global effects of aerosol on cloud structures and radiative properties remain uncertain. We need a firm understanding of the relevant physical and chemical processes which produce aerosols, increasingly sophisticated representations of aerosol-chemistry-cloud-climate interactions, and incorporation of these into numerical models of precipitation, acid deposition, and climate on

local, regional, and global scales. We have to develop a basis for coupling the chemical and microphysical processes and the meteorological processes to the physical properties of aerosols to quantify the aerosol influence in models of current, past, or future climate.

To ascertain the global climatological effects of aerosol it is crucial to include microphysics and aerosol chemistry in a three-dimensional global model framework. Some modeling has been done within such a framework [*e.g.*, Langner and Rodhe, 1991; Taylor and Penner, 1994; Liousse *et al.*, 1996; Chuang *et al.*, 1997] with highly simplified cloud processes. However, future global-scale studies of the interactions of aerosols, clouds, chemistry and climate will require the development of modules in which the sub-grid-scale processes and boundary layer processes have been parameterized. This is difficult since detailed cloud microphysics must be included in the development of such parameterizations because of the sensitivity of aerosol chemistry and physics to cloud properties.

After a reading of results from earlier work on cumulus convection and stratocumulus, as outlined in §1.1, 1.2.1 and 1.2.2, we note that the state of knowledge in terms of detailed model coupling of aerosol microphysics/cloud microphysics/chemistry/dynamics is sparse. In convective type of clouds, given the fact that deep convection can transport pollutants and aerosols from surface to the upper troposphere in a matter of hours, although some modeling work addresses the cloud pumping mechanism and attempts to estimate the percentage of pollutants being lifted up by convection, only two major oxidation pathways are considered, and no attempt is made to estimate the effects of the redistribution of aerosol precursors on ultrafine particle formation in the upper troposphere as observed in aircraft measurements. Further, there are few fully coupled aerosol microphysics/cloud chemistry models available to properly address the interaction between aerosol particles, aerosol precursors, cloud, and gas and aqueous phase chemistry. Thus, the mechanisms that maintain the upper troposphere aerosol abundances are still uncertain.

To examine the deep convective type of clouds, most previous studies have used Eulerian models and either a spectral drop model or a semi-spectral (two-moment) microphysics parameterization with simplified cloud chemistry. Without resolving the large eddies in the boundary layer, in stratocumulus clouds, most detailed chemistry modeling studies are still

limited to parcel models or box models, which lack dynamics. An exception is Flossmann's work [1994] that couples a two-dimensional Eulerian framework and fixed-grid microphysics with cloud chemistry. Her work compared the rate of sulfate formation due to scavenging of particles with that due to the uptake and oxidation of SO_2 . The disadvantage of the fixed-grid microphysics is that this framework does not accurately represent regeneration of aerosol particles following droplet evaporation, because details of these spectra are often lost in the transition from aerosol to droplet and vice versa [Feingold *et al.*, 1996]. The enormous computational burden of the above-mentioned model also precludes simulations in three dimensions. No studies, moreover, have addressed issues related to chemistry interactions with cloud microphysics and impacts of chemistry on droplet spectra. For cloud-scale process studies, to explore the impact of clouds on boundary layer chemistry and the extent to which chemistry interacts with cloud microphysics and affects aerosol and drop spectra, the model design must achieve a balance between dynamics, microphysics, radiation and chemistry.

1.4 Objectives of this research

The goal of this research is to attain a better understanding of several key aspects of the role of clouds on processing, production and global distribution of aerosols and chemical species, with particular attention to processes affecting the upper troposphere and lower boundary layer. As discussed earlier, the aerosol and chemical species distribution in the upper troposphere will not only have an impact on long range transport of these species, but will have an impact on the aerosol direct effect and the formation and radiative properties of upper tropospheric supercooled clouds. Particle characteristics in the boundary layer will have an impact on aerosol optical properties, the aerosol indirect effect, and boundary layer dynamics. Work examining the convective transport and boundary layer cloud processing will allow us to develop appropriate methods for scaling such processes up to the larger scales and will assist in the parameterization of these processes in regional and even global scale climate models. The objective of this research is to employ the coupled aerosol/cloud chemistry model to investigate the impact of deep convection upon the production and

distribution of tropospheric sulfate aerosol, with particular attention to the effects upon aerosol abundance in the upper troposphere. A further step is to use the fully coupled bin resolving atmospheric chemistry/microphysics TEM model to investigate the impact of stratocumulus clouds on aerosol and chemical species processing in the marine boundary layer.

1.4.1 Deep convection

In order to study the effects of clouds on the redistribution and transformation of various chemical species, and production and distribution of aerosol particle concentrations, a two-dimensional Eulerian cloud model, described in Taylor [1989a] and Taylor *et al.*[1997], an aqueous chemistry model, as in Kreidenweis *et al.*[1997] and Taylor [1989b], is coupled with an aerosol evolution bin model [Zhang *et al.*, 1998a], simple gas-phase production of H_2SO_4 , and a case study based on the dynamic simulation of the Cooperative Convective Precipitation Experiment (CCOPE) 19 July 1981 event in Miles city, Montana [Dye *et al.*, 1986]. The dynamical features of the model cloud agree well with the observations, as described in Taylor *et al.*[1997]. However, there were no data available for the chemical composition and concentration of gaseous and particulate species to compare with our model results. The approach is to treat the cloud as a representative continental case of deep convection, and to examine particle and chemical species redistribution for a range of model conditions.

To this end, both clean and polluted base cases and various sensitivity tests are simulated using the coupled aerosol/chemistry/cloud model. The effects of changes in CCN number concentration on the dynamical properties of simulated deep convective cloud and how these feed back into the transport of chemical species are explored through two base cases. The effects of changes in some model parameters, such as the resolution of the model, on the dynamical properties of simulated deep convective cloud and how these feed back into the cloud chemistry are investigated. We vary the assumed initial aerosol composition from ammonium sulfate to ammonium bisulfate, which is from near neutral to acidic, to examine how it affects the in-cloud sulfate production, sulfate budget, and how SO_2 redistribution is changed. The effects of the initial oxidant concentrations on

in-cloud sulfate production and SO_2 redistribution are also examined under normal and extreme conditions. After cloud dissipation, the magnitude of the new particle formation is determined by the available H_2SO_4 concentration, which is mainly determined by the production term and loss terms. The production of H_2SO_4 is determined by the redistributed SO_2 concentration and assumed $\text{OH}\cdot$ concentration, while the loss rates are determined by the pre-existing aerosol surface area and binary nucleation rate. We vary the initial chemical species profiles, initial H_2SO_4 mass mixing ratio, initial small particle mass mixing ratio and number concentration, and assumed nucleation rate factor to study their impacts on aerosol population and new particle formation in the middle and upper troposphere. The hypothesis of Perry and Hobbs [1994] that convective motion vents particle precursor gases and cleansed air to higher levels, creating optimal conditions for ultrafine new particle formation, is explored within the context of the modelling studies.

1.4.2 Stratocumulus

While many of the previous studies used a single parcel model to examine chemical heterogeneity, aqueous sulfate production, and modification of aerosol spectra, the interaction between microphysics/chemistry and dynamics was not properly addressed, as pointed out by Feingold *et al.* [1996, 1998a]. It is also difficult to compare the results from a single parcel model with field measurements, because a single average parcel does not account for contributions from many air parcels experiencing different dynamical, microphysical and chemical processes.

This work presents a new method for studying heterogeneous chemistry in boundary layer clouds that achieves a balance between dynamics, microphysics and chemistry. An LES model is used as a means of describing boundary layer dynamics and deriving realistic parcel trajectories for subsequent use by a fully coupled microphysics/chemistry model to study the extent of processing of gases and CCN. A set of 500 trajectories is recorded from an LES run, as described in Stevens *et al.* [1996], to drive individual coupled microphysics/chemistry parcel models [Feingold *et al.*, 1998a; Zhang *et al.*, 1998b]. The set of 500 trajectories is chosen from an LES which simulated a stratocumulus-capped marine boundary layer, as described fully in Feingold *et al.* [1998a]. The LES model is initiated

with a case study based on the dynamics of the First ISCCP Regional Experiment (FIRE) July 7, 1987 event held off the coast of California [Betts and Boers, 1990]. The July 7 case exhibits little or no precipitation, and thus eliminates the effect of precipitation removal of CCN. The LES simulation is not intended to be a case study of this event, but rather the approach taken here is to consider the LES model dynamics as representative of the stratocumulus-capped marine boundary layer and use it as a source of parcel trajectories.

The trajectories give good coverage of the whole boundary layer and represent the mixing throughout the cloudy boundary layer, including a statistical description of the time that parcels spend in cloud. Bower and Choularton [1993] used a single parcel model to examine modification of the CCN spectrum following a cloud cycle and its consequence for a secondary cloud formation. In the work presented here, some trajectories have cycled through cloud two or three times during the course of an hour, which has consequences for the CCN spectra and drop spectra. Thus the trajectory ensemble model (TEM) represents the impacts of cycling in a less constrained manner.

Within the TEM framework, because of chemical heterogeneity across the drop spectra as suggested in the literature, we first set up a control run to simulate only the microphysical effect on the chemical heterogeneity. The effects of droplet growth/evaporation and parcel trajectory history (in-cloud residence time, liquid water content, supersaturation fluctuation) on chemical heterogeneity (cloud-water pH, solute concentration) are explored. The control run also separates the effects of combined dynamics/microphysics/chemistry on the drop spectra from those merely due to dynamics and microphysics. The variation in cloud-water pH with drop radius affects the bulk estimation of oxidation and the amount of sulfate mass deposited to each drop size. We examine the relative importance of different oxidation pathways due to the different initial chemical species concentrations and how these affect the chemical heterogeneity across cloud drop spectra, modify of CCN spectra and composition, and feed back into the cloud drop mass and number distribution. The effects of CCN changes on the radiative properties of the stratocumulus cloud are also investigated.

As discussed in Feingold *et al.* [1998a], estimating the total S(IV) to S(VI) conversion assuming an average parcel experiencing mean conditions, instead of deriving a value from

the set of trajectories, would overestimate the conversion for the assumed initial chemical fields. The magnitude of this difference depends on the slope of the time-dependent $S(\text{IV})$ depletion, and on the mean in-cloud residence time. Here, we intend to investigate different initial chemical fields and variations in the $S(\text{IV})$ depletion with time from an ensemble point of view, to explore the appropriate averaging techniques, and to examine the effect upon the predicted $S(\text{VI})$ production.

The text of Chapters 2, 3, 4, and 5 has appeared in the following publications:

1. Kreidenweis, S. M., Y. Zhang, and G. Taylor, The effects of clouds on aerosol and chemical species production and distribution: II. Chemistry model description and sensitivity analysis, *J. Geophys. Res.*, **102**, 23867–23882, 1997.
2. Taylor, G. R., S. Kreidenweis, and Y. Zhang, The effects of clouds on aerosol and chemical species production and distribution: I. Cloud model dynamics and microphysics, *J. Geophys. Res.*, **102**, 23851–23865, 1997.
3. Zhang, Y., S. M. Kreidenweis, and G. R. Taylor, The effects of clouds on aerosol and chemical species production and distribution: 3. Aerosol model description and sensitivity analysis, *J. Atmos. Sci.*, **55**, 921–939, 1998a.
4. Feingold, G., S. M. Kreidenweis, and Y. Zhang, Stratocumulus processing of gases and cloud condensation nuclei: Part I: Trajectory ensemble model, in press, *J. Geophys. Res.*, 1998a.
5. Zhang, Y., S. M. Kreidenweis, and G. Feingold, Stratocumulus processing of gases and cloud condensation nuclei: Part II: Chemistry sensitivity analysis, accepted by *J. Geophys. Res.*, 1998b.

Chapter 2

METHOD

Various methods may be used to study atmospheric chemistry and aerosol physics and chemistry systems that range from the purely observational to the purely theoretical. All methods have their limitations. For instance, if the systems of interest are observable, one could simply sit down and watch it for a long time. Unfortunately, direct observations are limited by the fact that the systems are often difficult to interrogate and control, thus making it challenging to isolate the impact and behaviour of specific physical and chemical processes. Within this work, the method of numerical modelling is used to study various processes associated with aerosol and atmospheric chemistry.

The framework of numerical modelling, which consists of solving sets of equations, written down and solved with finite differencing method with a computer, provides a quasi-theoretical method for examining causal relations within complicated systems. The equations thus solved are approximated in certain ways (and some processes too computationally demanding are approximated by a method called *parameterization*) before even entering the computational framework.

The results put forth in this dissertation are obtained with both Eulerian (fixed grid) and Lagrangian (moving grid) frameworks. For the Eulerian framework, it is easier to advect different variables, although one can not avoid the numerical problems associated with spatial advection. The same is true for an aerosol sectional model, which can not avoid the numerical diffusion. For an aerosol moving grid model in the Lagrangian framework, there is no arbitrary distinction between aerosol particle and droplet, and a continuum of growth is allowed, and 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 simultaneous study of particle coagulation and

droplet coalescence. It is especially difficult to represent mixing between parcels because communication of different moving droplet and aerosol sizes in each parcel will quickly increase the number of model variables which makes it difficult to solve the whole system. The mixing can only be done effectively on a fixed size-grid; mapping of this kind would compromise the advantages of the moving mass grid used in the condensational growth equations. We elect to use an Eulerian dynamical model and a two-moment aerosol evolution model to study convective transport in a large domain for a fairly long time, while using the Lagrangian framework of the TEM and a moving mass grid to study the cloud processing during the course of an hour in the boundary layer.

2.1 The Eulerian mixed-phase cloud model

The results for the effects of cumulus convection on aerosol and chemical species production and distribution are obtained with a two-dimensional Eulerian cloud model. To fully capture cloud scale dynamics, a three-dimensional Eulerian framework is necessary, however, as has been shown by Stevens [1996], the behavior of the two-dimensional system emulates the three-dimensional results in such a fashion that the integrity of the microphysical/dynamical interactions seems to be maintained. In order to incorporate warm and ice-phase microphysics along with chemistry and aerosols on a large domain, we have elected to use a two-dimensional Eulerian grid. A complete description of the model can be found in Taylor [1989a] and Taylor *et al.*[1997]; it is only briefly summarized here.

The model is anelastic and utilizes a flux-corrected-transport [Book *et al.*, 1981] advection scheme using a modified slow flow correction [Patnaik *et al.*, 1987]. The set of equations can be found in Taylor *et al.*[1997]. Boundary conditions in the model domain may be either radiative or periodic at the lateral boundaries. For radiative lateral boundaries the boundary velocities are computed using a weighted average of the first four gravity wave modes [Hack and Schubert, 1981]. In addition, a small-dissipation filter [Shapiro, 1970] may be applied to the grid cells near the boundary. In our case, the radiative lateral boundaries are used. The upper boundary is a rigid lid with a dissipation filter applied to the upper 2.25 km in the domain. The vertical spacing is fixed at $\Delta z = 200$ m, and

the horizontal resolution varies from $\Delta x = 1000$ m to $\Delta x = 250$ m. The model domain is 150 km wide and 15 km tall. The time step is computed using a Courant number of 0.35 for the maximum advection or gravity wave velocity in the domain. For the present, the time step is 6.375 s with $\Delta x = 1000$ m. The subgrid terms are computed with a first-order closure scheme [Cotton, 1975] using the local value of the deformation tensor to compute the grid cell interface eddy flux.

2.2 Bulk microphysics of mixed-phase cloud

The bulk microphysical scheme chosen for use in the model assumes an immediate conversion of any supersaturated vapor to liquid water and any supercooled cloud droplets to snow particles, since we are interested in domains of several hundred kilometers and extended simulation times. While an explicit microphysics formulation is ultimately desirable in order to completely represent the evolution and interaction of the water, chemistry, and aerosol particle fields, the computational time requirement is quite large, even for a limited domain. For example, the spectral scheme used by Respondek *et al.* [1995] requires 12 hrs of Cray CPU time for a 130-min simulation over a 30 km by 15 km domain, while the model run simulations presented here take approximately 8 hrs on a Hewlett Packard 712/60 for 5 hrs of simulation time on a 150 km by 15 km model domain.

This microphysical parameterization is termed bulk because precipitation drop concentration and graupel concentration are assumed to have Marshall and Palmer [1948] distributions. The bulk framework includes five different bulk water fields following Taylor [1989a]: vapor (q_v), cloud droplets (q_c), precipitation drops (q_p), snow particles (q_s), and graupel (q_g). In addition, CCN concentration (N_{CCN}), cloud droplets concentration (CNU), and snow particle concentration (SNU) are explicitly calculated, which adds complexity to the model as a two-moment mixed phase microphysical parameterization. The units for mass fields in the model are mass mixing ratio [kg kg^{-1}], and for number fields are kg^{-1} . The size distributions of CCN, CNU, and SNU are assumed monodisperse. For detailed descriptions of the time evolution of number and mass concentrations of above water fields please see Taylor [1989a] and Taylor *et al.* [1997]. We will briefly discuss the evolution of CCN and cloud drop number concentration in the model.

Time evolution of CCN concentration is governed by

$$\frac{\partial}{\partial t} \rho_0 N_{CCN} = -\frac{\partial}{\partial x_i} \rho_0 v_i N_{CCN} + \frac{\partial}{\partial x_i} \overline{\rho_0 v_i' N_{CCN}'} + \rho_0 S_{CCN}, \quad (2.1)$$

where S_{CCN} is the CCN source term. The source term is

$$S_{CCN} = \begin{cases} \frac{c_s}{\delta t} N_{CCN} & \text{condensation} > 0 \\ \frac{CNU + SNU}{\delta t} & \text{evaporation of cloud drops and snow} \\ -(S_c + S_p + S_s + S_g) \frac{N_{CCN}}{q_{SO4a}} & \text{impact scavenging by cloud hydrometeors} \end{cases} \quad (2.2)$$

where q_{SO4a} is the mass mixing ratio of CCN. S is the impact scavenging loss terms of aerosol particles. Subscripts c, p, s, and g denote cloud drops, precipitation drops, snow, and graupel particles, respectively. In this scheme the CCN spectra are assumed monodisperse. In order to account for the possibility of partial activation of CCN due to the variations in natural CCN size spectra, the factor c_s , called the activation efficient, is included in equation 2.2. Calculations by Jensen and Charlson [1984] for various aerosol size distributions showed that for typical continental convective clouds, the total nucleation scavenging efficiency of the aerosol mass concentration is close to 1.0 and that 75% is activated within 100 m of cloud base. Here c_s is set to 0.75 for the runs in this dissertation and results in 98.4% of the CCN activated within 500 m of cloud base and 99.9% activated within 800 m when condensation occurs. Sensitivity tests indicate the base model run is not sensitive to $0.7 \leq c_s \leq 1.0$. In the next chapter, we vary c_s to 0.55 to investigate its effect on chemistry.

Cloud droplets or snow evaporate and return particles to the CCN field when droplet or snow diameters fall below $1 \mu\text{m}$. In addition, when the precipitation or graupel mixing ratio falls below $10^{-8} \text{ kg kg}^{-1}$, the hydrometeors have fall velocities less than 0.1 m s^{-1} and are assumed to completely evaporate and return particles to the CCN field.

Cloud droplet concentration is computed in a manner similar to CCN:

$$\frac{\partial}{\partial t} \rho_0 CNU = -\frac{\partial}{\partial x_i} \rho_0 v_i CNU + \frac{\partial}{\partial x_i} \overline{\rho_0 v_i' CNU'} + \rho_0 S_{CNU}, \quad (2.3)$$

where S_{CNU} is computed from

$$S_{CNU} = \left[\alpha_c + \frac{SNU}{q_s} \beta_c - \frac{CNU}{q_c} \gamma_c \right], \quad (2.4)$$

where α_c is the CCN source term for a positive condensation rate, β_c is the snow melting rate, and γ_c includes autoconversion and collection of cloud drops, riming of snow and graupel, and freezing of cloud drops.

A consequence of a variable drop concentration is that the cloud drop diameters may sometimes exceed $50 \mu\text{m}$. Since drops larger than this will have fall velocities greater than 0.1 m s^{-1} [Pruppacher and Klett, 1978], they should be transferred to the precipitation field. Natural drop size spectra [e.g., Pruppacher and Klett, 1978] may simultaneously contain cloud drops with diameters larger and smaller than $50 \mu\text{m}$. Given a monodisperse size spectrum in the model, rather than convert all cloud drop water to precipitation when the drop diameter exceeds $50 \mu\text{m}$, only a portion is removed via an addition to the autoconversion term that reduces the cloud drop diameter to $50 \mu\text{m}$:

$$-\frac{\delta q_c}{\delta t} = \frac{\pi}{2\rho_w} CNU D_c^2 \frac{d}{dt} D_c, \quad (2.5)$$

where ρ_w is the density of liquid water, D_c is the cloud drop diameter, and

$$\frac{d}{dt} D_c = \frac{D_c - 50\mu\text{m}}{\delta t}. \quad (2.6)$$

Snow is another category in the model for which two-moments of the size spectra are predicted. Snow crystal is formed from activation of ice nuclei and cloud droplet freezing. Ice nuclei are assumed to exist at temperature below -10°C and are computed using the Meyers *et al.* [1992] expression for ice nuclei concentration. Contact freezing of cloud drops is via Brownian diffusion of ice nuclei. For detailed descriptions of these processes see Taylor *et al.* [1997].

2.3 Cloud chemistry model

In this dissertation, the sulfur species and sulfate aerosol are the primary focus, and thus relevant sulfur chemistry is included in the model; NO_x chemistry is not considered. In addition to the S(IV) to S(VI) oxidation pathways typically considered in cloud chemistry models via dissolved ozone (O_3), hydrogen peroxide (H_2O_2), oxygen catalyzed by iron (Fe) and the complexation of dissolved formaldehyde (CH_2O) with S(IV) have also been added to examine their effect on S(VI) production and on chemical species redistribution. The

Table 2.1: Chemical reactions included in the cloud chemistry model. Sources: 1, Maahs [1982]; 2, Seinfeld [1986]; 3, Martin and Damschen [1981]; 4, National Bureau of Standards [1965]; 5, Ledbury and Blair [1925]; 6, Bell [1966]; 7, Martin [1984]; 8, Martin and Hill [1987]; 9, Jacob [1986]. *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 $k = k_{298} \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right]$ for the rate coefficient.

Reaction	Rate Coefficient (k: $\text{M}^n \text{s}^{-1}$) or Equilibrium Constant (K: M or M atm^{-1})*	Source
Equilibrium Reactions		
(R3) $\text{SO}_2(g) \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O}$	$K_3(T) = 3.013 \times 10^{-5} \exp\left(\frac{3168.6}{T}\right)$	1
(R4) $\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{H}^+$	$K_4(T) = 1.820 \times 10^{-5} \exp\left(\frac{1964.2}{T}\right)$	1
(R5) $\text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+$	$K_5(T) = 1.39 \times 10^{-9} \exp\left(\frac{1122.2}{T}\right)$	2
(R6) $\text{H}_2\text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}_2(aq)$	$K_6(T) = 3.99 \times 10^{-6} \exp\left(\frac{7030}{T}\right)$	3
(R7) $\text{O}_3(g) \rightleftharpoons \text{O}_3(aq)$	$K_7(T) = 2.13 \times 10^{-6} \exp\left(\frac{2560}{T}\right)$	4
(R8) $\text{CH}_2\text{O}(g) \rightleftharpoons \text{CH}_2(\text{OH})_2(aq)$	$K_8(T) = 2.18 \times 10^{-6} \exp\left(\frac{6491.55}{T}\right)$	5
(R9) $\text{CH}_2\text{O}(aq) + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2$	$K_9(T) = 2.29 \times 10^{-3} \exp\left(\frac{4046}{T}\right)$	6
Aqueous Phase Reactions		
(R10) $\text{S(IV)} + \text{H}_2\text{O}_2 \Rightarrow \text{S(VI)} + \text{H}_2\text{O}$	$K_{10}(T) = 8 \times 10^4$	7
(R11) $\text{S(IV)} + \text{O}_3 \Rightarrow \text{S(VI)} + \text{O}_2$	$K_{11}(T) = 4.19 \times 10^5 + \frac{100}{[\text{H}^+]}$	7
(R12) $\text{S(IV)} + \text{O}_2 + \text{Fe}^{3+} \Rightarrow \text{S(VI)} + \text{Fe}^{3+} + \text{M}$	$K_{12}(T) = 5.83 \times 10^{16} \exp\left(-\frac{10970.21}{T}\right)$	8
(R13) $\text{HSO}_3^- + \text{CH}_2\text{O}(aq) \Rightarrow \text{CH}_2(\text{OH})\text{SO}_3^{2-}$	$K_{13}(T) = 1.03 \times 10^{10} \exp\left(-\frac{4881.24}{T}\right)$	9
(R14) $\text{SO}_3^{2-} + \text{CH}_2\text{O}(aq) \Rightarrow \text{CH}_2(\text{O})\text{SO}_3^{2-}$	$K_{14}(T) = 1.09 \times 10^{10} \exp\left(-\frac{1811.59}{T}\right)$	9

oxygen catalyzed by manganese (Mn) is not included in the model, since the observational data for the concentration of manganese in cloud water is not available. Also, for the combined Fe-Mn system, the rate of sulfate formation is 3 to 10 times faster than that expected from the sum of the independent rates, which is called iron/manganese synergism reaction [Seinfeld and Pandis, 1998]. Thus, we elect to add only the oxygen catalyzed by iron pathway which gives a conservative measure of the total oxygen catalyzed by trace metal pathway. The chemical reactions included in the model are summarized in Table 2.1, and the formulations for the chemical source and sink terms are discussed briefly in this section.

The SO_2 , H_2O_2 , O_3 , and CH_2O concentrations in cloud droplets and precipitation are assumed to be in equilibrium with the local gas phase concentration. Therefore, SO_2 and CH_2O concentrations in the liquid phase are carried as implicit fields, i.e., when required in

the source terms, they are computed as a function of the gas phase concentrations. These liquid phase concentrations are calculated using Henrys Law:

$$[M] = K_h p_i \quad (2.7)$$

In equation 2.7, K_h is the equilibrium constant, p_i is the partial pressure of gas species i in air, and $[M]$ is the liquid phase concentration of species i . The partial pressure of gas species i has been approximated as:

$$p_i = \frac{pq_i}{M_i/M_d + q_i} \approx pq_i \frac{M_d}{M_i}, \quad (2.8)$$

where the contribution of q_i (mass mixing ratio of species i) in the denominator has been neglected, p is the air pressure, and M_i and M_d are the molecular weights of species i and dry air, respectively. As discussed by Schwartz [1988], since oxidation is generally the rate-limiting mass transfer factor in the pH range (3–5) of the present cloud chemical calculations, the equilibrium assumption is generally appropriate. For the more soluble species, such as CH_2O and H_2O_2 , this assumption may overpredict their concentration in the aqueous phase, and in this case will maximize the conversion of S(IV) to S(VI) by H_2O_2 , producing a conservative estimate of the redistribution of SO_2 to higher levels of the atmosphere.

Two additional assumptions are used: (1) the sulfur chemistry is dominated by aqueous phase reactions on the time scales characterizing the clouds studied, and (2) aqueous-phase photochemical reactions are assumed to have little effect on sulfate production and have been ignored.

As mentioned above, the Fe(III)-catalyzed oxidation of S(IV) by molecular oxygen [Martin and Hill, 1987] is considered in our model. Trace metal Fe in particulate matter is scaled to the mass of the ammonium in aerosol particles, which varied from ammonium sulfate to ammonium bisulfate. The Fe(III) concentration is assumed to be 50% of the total Fe concentration. This gives a reasonable Fe(III) concentration in the range of 10^{-7} to 10^{-6} M [Siefert *et al.*, 1996]. The reaction mechanism for formaldehyde complexation with S(IV) is based on the work by Rao and Collett [1995] and is shown schematically in Figure 2.1.

The sum of $[\text{CH}_2(\text{OH})\text{SO}_3^-]$ and $[\text{CH}_2(\text{O})\text{SO}_3^-]$ is taken as the HMS concentration in the liquid phase. The backward reaction of HMS to S(IV) has been neglected, since the equilibrium for reactions (R13) and (R14) is displaced far to the right [Boyce and Hoffmann, 1984]. From available data, the characteristic time for the backward reaction in the aqueous phase is calculated to be approximately 4 hours. Since the simulations reported here are for times of 1 hour or less for the liquid phase, the backward reaction is unimportant.

Details of the sulfate, ammonium and H_2O_2 source terms and the pH calculation are described more fully by Taylor [1989b] and are briefly summarized here. The aerosol species (sulfate and ammonium mass concentrations and number concentrations of particles) are transferred into their aqueous forms when particles are activated to cloud droplets, and are transferred to the corresponding ice phase, precipitation, and graupel forms during the relevant microphysical transformation. No aerosol species are released during such transformations, but rather are carried with the hydrometeor species they have been transferred to. Upon evaporation of hydrometeors, the aerosol species are returned to the atmosphere; they are removed from the domain if they are incorporated into precipitation that reaches the ground. When cloud droplets transform to snow and graupel, some of the S(IV) in cloud water will be entrapped in the ice phase. We have used the temperature-dependent Chen and Lamb [1994] formulation to determine this fraction, and have also used their expression to represent the absorption of SO_2 onto ice. It is further assumed that 76% of the H_2O_2 dissolved in the cloud water will be released back to the environment due to degasification in the conversion of liquid to ice. All other gaseous species are completely degassed when ice forms.

For completeness, the following discussion follows that in Taylor [1989b] and refers to the present modifications of and additions to the source and sink terms shown in his Figure 1. The detailed schematic of sulfur chemistry diagram is shown in Figure 2.2. The new prognostic chemistry variables discussed here are advected simultaneously with the dynamic and microphysical fields. In the following, the condensation rate for cloud water is denoted by $\delta q_c / \delta t$. Variables written in all capital letters and found on the right-hand side of the equations, *e.g.*, PEVAP, refer to microphysical transitions, as described by Taylor

[1989a]. Subscripts denote the molecule-hydrometeor field; *e.g.*, q_{HMSc} is the HMS cloud water mixing ratio, $[H_c^+]$ is the hydrogen ion concentration in cloud water, and so on. The chemical fields in the model are expressed in terms of mass mixing ratio $[kg\ kg^{-1}]$ and the source terms are written in terms of $[kg\ kg^{-1}\ s^{-1}]$. When species i aqueous phase concentration is converted to the equivalent mass mixing ratio in air, a conversion factor consisting of the molecular weight of species i divided by 1000 appears.

The term PHMS1 is CH_2O in solution in cloud water. It is a sink term for CH_2O vapor, and represents the rate of formation of CH_2O in cloud water due to dissolution of CH_2O (Figure 2.1). The equilibrium constants can be found in Table 2.1. The conversion of gas-phase CH_2O into aqueous CH_2O is given by reactions (R8) and (R9).

The concentration of total CH_2O in the aqueous phase is then given by

$$[CH_2O]_T = [CH_2O] + [CH_2(OH)_2] = K_8 \left(\frac{1 + K_9}{K_9} \right) p_{CH_2O} \approx K_8 p_{CH_2O}, \quad (2.9)$$

where the approximation is valid since $K_9 \gg 1$. One thus obtains

$$PHMS1 = 0.03 K_8 p_{CH_2O} \frac{\delta q_c}{\delta t}, \quad (2.10)$$

where the factor of 0.03 results from the molecular weight conversion for CH_2O , as mentioned above.

The term PHMS2 is complexation of CH_2O with S(IV) in cloud water. It is a sink term for CH_2O and is given by a combination of reactions in cloud water. Included in this formulation are the contributions from CH_2O complexation with both HSO_3^- and SO_3^{2-} (reactions (R13) and (R14)). The complexation rate is given by

$$-\frac{d[CH_2O]}{dt} = -\frac{d[S(IV)]}{dt} = \frac{d[HMS]}{dt} = k_{13}[CH_2O][HSO_3^-] + k_{14}[CH_2O][SO_3^{2-}]. \quad (2.11)$$

With $[HSO_3^-] = \frac{K_3 K_4}{[H^+]} p_{SO_2}$ and $[SO_3^{2-}] = \frac{K_3 K_4 K_5}{[H^+]^2} p_{SO_2}$, equation 2.11 can be rewritten as

$$-\frac{d[CH_2O]}{dt} = -\frac{d[S(IV)]}{dt} = \frac{d[HMS]}{dt} = (k_{13} + k_{14} \frac{K_5}{[H_c^+]}) \frac{K_3 K_4 p_{SO_2}}{[H_c^+]} [CH_2O]. \quad (2.12)$$

One obtains:

$$PHMS2 = 0.03 q_c (k_{13} + k_{14} \frac{K_5}{[H_c^+]}) \frac{K_3 K_4 p_{SO_2}}{[H_c^+]} \frac{K_8}{1 + K_9} p_{CH_2O}. \quad (2.13)$$

The term PHMS3 represents the transfer of CH_2O to gas phase from riming ice and graupel, and cloud droplet freezing and evaporation. It is a source term for CH_2O vapor. When cloud droplets evaporate (CEVAP), freeze to form ice (CSFZ), or are collected by ice particles (riming, SRME) and graupel (GRME), CH_2O in the liquid phase is returned to the gas phase.

$$PHMS3 = 0.03[q_c CEVAP + CSFZ + SRME + GRME]K_8 p_{CH_2O}. \quad (2.14)$$

The term PHMS4 is the CH_2O complexation with S(IV) in precipitation drops. This is a sink term and is given by a combination of reactions analogous to that in cloud water (PHMS2).

$$PHMS4 = 0.03q_p(k_{13} + k_{14}\frac{K_5}{[H_p^+]})\frac{K_3K_4p_{SO_2}}{[H_c^+]}\frac{K_8}{1 + K_9}p_{CH_2O}. \quad (2.15)$$

The term PHMS5 represents the equilibrium of CH_2O in precipitation and transfer of CH_2O to gas phase from graupel. It assumes Henry's Law equilibrium between precipitation drops and CH_2O in the environment. When precipitation evaporates (PEVAP), precipitation drops freeze to form graupel (PGFZ), or graupel particles collect precipitation drops (PGCOL), CH_2O in the liquid phase is returned to the environment.

$$PHMS5 = 0.03[PEVAP + PGFZ + PGCOL]K_8 p_{CH_2O}. \quad (2.16)$$

The term PHMS6 represents the S(IV) complexation with CH_2O in cloud water. This is a sink term for SO_2 . S(IV) combines with CH_2O to form HMS in the liquid phase and thus is removed from cloud water. Since S(IV) is carried as an implicit field, the combination rate (in terms of mass mixing ratio) is

$$-\frac{dq_{SO_2V}}{dt} = -\frac{dq_{CH_2OV}}{dt}\frac{M_{SO_2}}{M_{CH_2O}}, \quad (2.17)$$

where M_{SO_2} and M_{CH_2O} represent the molecular weights of SO_2 and CH_2O , respectively. Thus the term PHMS6 is analogous to PHMS2, except the conversion factor 0.03 is changed to 0.064.

$$PHMS6 = 0.064q_c(k_{13} + k_{14}\frac{K_5}{[H_c^+]})\frac{K_3K_4p_{SO_2}}{[H_c^+]}\frac{K_8}{1 + K_9}p_{CH_2O}. \quad (2.18)$$

The term PHMS7 is the S(IV) complexation with CH₂O in precipitation drops. It is also a sink term for SO₂. As shown above for PHMS6, this term is analogous to PHMS4, except the conversion factor 0.03 is changed to 0.064.

$$PHMS7 = 0.064q_p(k_{13} + k_{14}\frac{K_5}{[H_p^+]})\frac{K_3K_4p_{SO_2}}{[H_c^+]}\frac{K_8}{1+K_9}p_{CH_2O}. \quad (2.19)$$

The term PHMS8 is the formation of HMS_c in cloud droplets. This is a source term for HMS in cloud water. The conversion factor is modified to 0.111 to be consistent with the complexation of S(IV) in cloud water.

$$PHMS8 = 0.111q_c(k_{13} + k_{14}\frac{K_5}{[H_c^+]})\frac{K_3K_4p_{SO_2}}{[H_c^+]}\frac{K_8}{1+K_9}p_{CH_2O}. \quad (2.20)$$

The term PHMS9 expresses the formation of HMS_p in precipitation drops. This is a source term for HMS in precipitation. The conversion factor is also modified to 0.111.

$$PHMS9 = 0.111q_p(k_{13} + k_{14}\frac{K_5}{[H_p^+]})\frac{K_3K_4p_{SO_2}}{[H_c^+]}\frac{K_8}{1+K_9}p_{CH_2O}. \quad (2.21)$$

The precipitation may have non-zero fall velocities. If so, the concentration of HMS in precipitation has fallout as an additional sink term. This fallout term is computed using

$$S_{p,HMS_p} = -\frac{\partial}{\partial z}(\rho_0 v_p q_{HMS_p}). \quad (2.22)$$

Iron is not created or destroyed in the iron-catalyzed S(IV) to S(VI) oxidation. This pathway consumes S(IV) in the liquid phase and produces sulfate in cloud water and precipitation. The following terms express the S(IV) sink rates due to Fe(III)-catalyzed oxidation pathway. The corresponding source terms as the S(VI) source rates have also been added into the model.

The term PION1 is the S(IV) oxidation catalyzed by Fe(III) in cloud droplets. This is a sink term for gas phase SO₂. The rate coefficient can be found in Table 2.1. The catalyzed oxidation rate is

$$\frac{d[S(VI)]}{dt} = -\frac{d[S(IV)]}{dt} = k_{12}[H^+]^{-1}[Fe^{3+}][S(IV)]. \quad (2.23)$$

We approximate $[S(IV)] \approx [HSO_3^-]$ in the pH range of cloud water, i.e., $3 \leq pH \leq 5.5$ [Martin, 1984]. Thus,

$$PION1 = 0.064\frac{k_{12}}{[H_c^+]}\frac{K_3K_4p_{SO_2}}{[H_c^+]}\frac{q_{Fe(III)}}{0.056}, \quad (2.24)$$

where the factor of 0.056 has arisen from the conversion between mixing ratio and molar concentration.

The term PION2 is the S(IV) oxidation catalyzed by Fe(III) in precipitation drops. This is also a sink term for SO₂. This reaction is analogous to the reaction taking place in cloud water:

$$PION2 = 0.064 \frac{k_{12}}{[H_p^+]} \frac{K_3 K_4 p_{SO_2}}{[H_p^+]} \frac{q_{Fe(III)}}{0.056}. \quad (2.25)$$

2.4 Aerosol evolution model

We include aerosol microphysics in the coupled chemistry/dynamics model. The aerosol part of the model includes a two-moment, two-mode (small particle (CN) mode and CCN mode) explicit aerosol evolution model, and gas phase SO₂ and sulfuric acid as particle precursors. CCN are activated to cloud droplets, but small particles are assumed to remain as interstitial particles unless scavenged by cloud droplets, when their mass is transferred to the CCN category during cloud evaporation. The aerosol model is based on that used by Kreidenweis *et al.*[1988]. Two integral modes are used to represent the two size categories. Each mode is described by its moments, total mass and number, which are treated as independent variables, and thus the mode mean size is a dependent variable. The prognostic variables carried are small particle mass mixing ratio, q_{CN} , and number concentration, N_{CN} ; CCN category mass mixing ratio, q_{SO_4a} , and number concentration, N_{CCN} ; sulfuric acid vapor mass mixing ratio, $q_{H_2SO_4}$, and SO₂ mass mixing ratio, q_{SO_2} . The subscript "a" indicates the species in the CCN particles. These prognostic variables are advected simultaneously with the dynamic, microphysical, and chemical fields. We assume the particles are initially composed of ammonium sulfate or ammonium bisulfate. Thus the mass mixing ratio of ammonium ion in CCN, q_{NH_4a} , is also carried as an independent variable. Since the composition of small particles is not altered by aqueous chemistry, the ammonium mass in the small particles is carried as an implicit field. A schematic of the aerosol model is shown in Figure 2.3, and the processes represented there are discussed further in this section.

2.4.1 Aerosol nucleation and growth

Sulfuric acid can form new particles by binary homogeneous nucleation with water vapor and can grow pre-existing particles by condensation. Since the time scale for the growth of small particles to CCN size particles is several weeks, and that for coagulation between unactivated particles in the upper troposphere is approximately one day to several days, longer than the time scales simulated in this study, these processes have not been included.

Gas-phase formation of H_2SO_4

In the gas phase, atmospheric H_2SO_4 is formed via reaction of SO_2 with $OH\cdot$ in the troposphere [Calvert and Stockwell, 1984]. The production of $OH\cdot$ is governed by photochemical reactions, and is a function of the amount of ultraviolet light reaching the troposphere. The gas-phase reaction of SO_2 and $OH\cdot$ is a chain reaction, and the ultimate product is H_2SO_4 [Stockwell and Calvert, 1983]. A single second order reaction, representing the rate-limiting step, is usually assumed [Atkinson and Lloyd, 1984]:



The rate constant is $k_{SO_2, 298K} = 1.1 \times 10^{-12} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$, and the activation energy $\frac{E_a}{R} = -231 \text{ K}$ [Yin *et al.*, 1990]. Using

$$k_{SO_2} = k_{SO_2, 298K} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right], \quad (2.27)$$

we obtain

$$k_{SO_2} = 5.06689 \times 10^{-13} \exp(231/T). \quad (2.28)$$

The production rate of H_2SO_4 (in mass mixing ratio units) is then

$$PSUS5 = k_{SO_2} q_{SO_2} [OH\cdot] \frac{98}{64}, \quad (2.29)$$

where the convention using "PSU" for such source terms conforms to that used in previous work [Taylor, 1989b; Taylor *et al.*, 1997; Kreidenweis *et al.*, 1997]. From equation 2.29, it is seen that the H_2SO_4 production rate in the upper troposphere depends on SO_2 redistribution and on $[OH\cdot]$. In the simulations discussed here, we have chosen a diurnally-averaged $[OH\cdot]$ vertical profile and keep it constant with time. Thus, variations in H_2SO_4 production rates in the upper troposphere are controlled by variations in SO_2 concentration.

Nucleation of H_2SO_4

In this model, the small particle mode is the Aitken or nucleation mode. Aerosol particles in this mode are produced by H_2SO_4 - H_2O binary homogeneous nucleation with a rate determined by temperature, relative humidity RH, and relative acidity of H_2SO_4 . The relative acidity is defined as the partial pressure of acid vapor in the gas phase divided by the vapor pressure of the pure acid at that temperature. When the small particle mode evolves, its mode mean size can change. However, we fix the size and mean mass of the newly nucleated particles to be at the lower size limit of this mode. Whenever a nucleation burst occurs, the mass flowing into the nucleation mode is the nucleation rate times the fixed mean nucleation particle mass of 6.52×10^{-21} kg particle⁻¹ (≈ 0.01 μm). The number concentration of particles flowing into this small particle mode is adjusted accordingly, using the current mean particle mass of the mode. This is a conservative estimate of the small particle number production rate, since it will always be less than or equal to that predicted. A sensitivity run in which the unadjusted number predicted by nucleation theory was input to mode 1 produced only small differences in the simulations.

The results of Jaecker-Voirol and Mirabel [1989] using hydrate theory to compute homogeneous binary nucleation rates are fit to polynomials and used to calculate nucleation rates for different temperatures, relative humidities and H_2SO_4 concentrations. These theoretical calculated nucleation rates from hydrate formation are lower than previous classical theoretical rates by a factor of 10^5 - 10^6 , and agree better with experimental results than the old theory, as pointed out by Jaecker-Voirol and Mirabel [1988]. However, uncertainty still remains in the nucleation rate calculation, as pointed out by Raes *et al.* [1992]. They used the theory of Jaecker-Voirol and Mirabel [1988] and applied the possible range of thermodynamic data, and showed that the range of uncertainty could be 10 orders of magnitude due to the uncertainty in thermodynamic data alone at 25°C and RH = 50%. They proposed a nucleation rate factor (the ratio of observed nucleation rate in their experiments to the calculated nucleation rate), t_n , to be between 10^4 and 10^7 at 25°C, and pointed out those values were close to the upper bound of the range reported in literature. In our simulations, we use $t_n = 1$ for the base cases and most sensitivity tests, and change it to

10^4 in one sensitivity simulation to investigate the effect of this parameter on the model results.

Condensational growth of particles

In our model, H_2SO_4 and water vapor can either nucleate to form new particles, or condense onto pre-existing particles. The rate of condensation, J , of H_2SO_4 onto an aerosol particle with diameter D_p is described using the modified form of the Dahneke expression [Seinfeld, 1986]:

$$J = 2\pi D D_p \beta(K_n)(p - p_0), \quad (2.30)$$

where D is the diffusivity of sulfuric acid in air, K_n is the Knudson number (the ratio of the air mean free path to the particle radius), $\beta(K_n)$ is a correction factor to the continuum profile including the sticking probability δ ,

$$\beta(K_n) = \frac{1 + K_n}{1 + 2K_n(1 + K_n)/\delta}, \quad (2.31)$$

where the sticking probability δ is assumed to be 1 in the model, p is the partial pressure of H_2SO_4 in the ambient air, and p_0 is the vapor pressure of H_2SO_4 the vapor pressure of solution. The solution vapor pressure p_0 in the condensational growth rate calculation 2.30 is assumed to be zero, as justified from the data of Bolsaitis and Elliot [1990].

The aerosol condensational growth rates are based on the wetted size of the sulfate particles. Since the relative amount of water vapor is so much greater than that of acid vapor, the growing $\text{SO}_4^{2-}\text{-H}_2\text{O}$ particles are always in equilibrium with water vapor, and the growth of particles is assumed to be controlled by the impingement rate of sulfuric acid molecules onto the particles [Kreidenweis and Seinfeld, 1988; Raes *et al.*, 1992]. The mass of water associated with the wetted particles is determined by finding the mean sulfate mass per drop ($q_{\text{SO}_4}/N_{\text{CCN}}$ or $q_{\text{CN}}/N_{\text{CN}}$) and finding the solution concentration such that the partial pressure of water vapor over the drop equals the water vapor in the surrounding gas.

Ammonium is implicitly considered in the wet particle mean size calculation by assuming ammonium sulfate or ammonium bisulfate aerosol composition. Since the dependence

of particle size on relative humidity for ammonium sulfate and ammonium bisulfate is similar, as pointed out by Tang and Munkelwitz [1994], for simplicity, we use the same coefficients to convert dry diameter to wet diameter for both aerosol compositions; the particle size on the efflorescence branch of the hysteresis curve is parameterized. After cloud processing and chemical conversion in the aqueous phase, the ratio of sulfate to ammonium will increase for those CCN regenerated from evaporating cloud droplets, in turn changing particle hygroscopicity. This will introduce some error for the dry and wet diameter calculation since the change in hygroscopicity is not accounted for. We estimated the error in the condensation rate calculation to be about 10% at 9–10 km height in the model domain, where the results are most sensitive to the computed condensation rate.

For the small particle mode, the H_2SO_4 condensation rate ($\text{kg kg}^{-1} \text{ s}^{-1}$) is

$$PSUS2 = 2\pi\alpha D\bar{D}_{p,CN}\beta(K_n)N_{CN}q_{\text{H}_2\text{SO}_4}. \quad (2.32)$$

For the CCN mode, the H_2SO_4 condensation rate is

$$PSUS3 = 2\pi\alpha D\bar{D}_{p,CCN}\beta(K_n)N_{CCN}q_{\text{H}_2\text{SO}_4}, \quad (2.33)$$

where $\bar{D}_p$ is the mass mean diameter of wet particles in each mode, N is the number concentration in each mode, subscripts denote the mode, the factor α corrects for monodispersity assumed in the integral model and is set to 0.85 for both modes [Kreidenweis *et al.*, 1991], and K_n is the Knudson number for the wet particles. PSUS2 is generally one to two orders of magnitude smaller than PSUS3. For H_2SO_4 condensation onto the unactivated CCN, we also compute an effective addition rate of NH_4^+ onto the particles. This rate is adjusted to maintain the $\text{NH}_4^+/\text{SO}_4^{2-}$ aerosol composition, and accounts for the presence of neutralizing NH_3 in the environment. Thus the ratio $\text{NH}_4^+/\text{SO}_4^{2-}$ is modified only by sulfur oxidation processes occurring in cloud, as described in Kreidenweis *et al.*[1997].

2.4.2 Aerosol-cloud interaction

Since it is so hygroscopic, we assume that sulfuric acid vapor is immediately lost to cloud hydrometeors in any cloudy grid box. The scavenging of both CCN and interstitial small particles by all the hydrometeors is also considered in the model. CCN are mainly

activated (nucleation scavenging) to form cloud droplets, and when the cloud evaporates, CCN are regenerated from cloud droplets. Due to chemical conversion inside cloud and other cloud processes, the regenerated CCN are usually different from the original CCN in size, number, and spatial distribution [Flossmann, 1994; Feingold *et al.*, 1996; Kreidenweis *et al.*, 1996]. The activation coefficient is set to 0.75 in the model, as described in Taylor *et al.*[1997]. Small particle scavenging by cloud hydrometeors is parameterized in the same way as that for CCN, except the scavenging coefficients are different. The scavenging parameterizations for the CCN mode are described in detail in Taylor *et al.*[1997].

The time rates of change of H_2SO_4 mass mixing ratio, small particle and CCN mass mixing ratio, and number concentration are as follows:

$$\begin{aligned} \frac{\partial}{\partial t} \rho_0 q_{H_2SO_4} = & -\frac{\partial}{\partial x_i} \rho_0 v_i q_{H_2SO_4} + \frac{\partial}{\partial x_i} \overline{\rho_0 v_i' q_{H_2SO_4}'} \\ & + \rho_0 (PSUS5 - R_{nucl} - PSUS2 - PSUS3 - S_{cloud}) \end{aligned} \quad (2.34)$$

$$\frac{\partial}{\partial t} \rho_0 q_{CN} = -\frac{\partial}{\partial x_i} \rho_0 v_i q_{CN} + \frac{\partial}{\partial x_i} \overline{\rho_0 v_i' q_{CN}'} + \rho_0 (PSUS2 + R_{nucl} - S'_c - S'_p - S'_s - S'_g) \quad (2.35)$$

$$\frac{\partial}{\partial t} \rho_0 N_{CN} = -\frac{\partial}{\partial x_i} \rho_0 v_i N_{CN} + \frac{\partial}{\partial x_i} \overline{\rho_0 v_i' N_{CN}'} + \rho_0 \frac{N_{CN}}{q_{CN}} (R_{nucl} - S'_c - S'_p - S'_s - S'_g) \quad (2.36)$$

$$\begin{aligned} \frac{\partial}{\partial t} \rho_0 q_{SO_4a} = & -\frac{\partial}{\partial x_i} \rho_0 v_i q_{SO_4a} + \frac{\partial}{\partial x_i} \overline{\rho_0 v_i' q_{SO_4a}'} + \rho_0 (PSUS3 - S_c - S_p - S_s - S_g \\ & - \frac{q_{SO_4a}}{N_{CCN}} ACTI + q_{SO_4c} CEVAP + q_{SO_4s} SEVAP) \end{aligned} \quad (2.37)$$

$$\begin{aligned} \frac{\partial}{\partial t} \rho_0 q_{NH_4a} = & -\frac{\partial}{\partial x_i} \rho_0 v_i q_{NH_4a} + \frac{\partial}{\partial x_i} \overline{\rho_0 v_i' q_{NH_4a}'} + \rho_0 (\frac{36}{96} PSUS3 - S''_c - S''_p - S''_s - S''_g \\ & - \frac{q_{NH_4a}}{N_{CCN}} ACTI + q_{NH_4c} CEVAP + q_{NH_4s} SEVAP) \end{aligned} \quad (2.38)$$

The time evolution of N_{CCN} is expressed in equation 2.1. Here, $-\frac{\partial}{\partial x_i} \rho_0 v_i q$ or $-\frac{\partial}{\partial x_i} \rho_0 v_i N$ is the advection of each independent variable, and subscripts denote each variable. Eddy diffusion is the turbulent diffusion term for each variable ($\frac{\partial}{\partial x_i} \overline{\rho_0 v_i' q'}$ or $\frac{\partial}{\partial x_i} \overline{\rho_0 v_i' N'}$). S' , S'' , and S are the scavenging loss terms of small particles and CCN particles, respectively. Subscripts c, p, s, g denote cloud droplets, precipitation drops, ice and graupel particles, respectively. ACTI is the activation of CCN to cloud droplets. CEVAP and SEVAP are evaporation of cloud droplets and snow, respectively, upon which their number and mass

are returned to the CCN category. CNU and SNU are the number concentration of cloud droplets and snow, respectively. R_{nucl} is the H_2SO_4 nucleation rate. $S_{cloud} = \frac{q_{H_2SO_4}}{\delta t}$ is loss term of H_2SO_4 to any cloud hydrometeors, treated as an instantaneous adjustment that removes all gas phase H_2SO_4 .

2.5 Trajectory ensemble model-TEM

The results for the stratocumulus processing of aerosol and gases are obtained with a Lagrangian trajectory ensemble model. During the course of an LES run [Feingold *et al.*, 1998a], after turbulence has developed, 500 tracer particles are released from randomly distributed points below cloud (between 200 and 450 m) and their trajectories are recorded every 2 s (the LES model time step). The trajectories include kinematic (position, vertical velocity) and thermodynamic (pressure, liquid-water potential temperature, total water mass mixing ratio) data, and the tendencies related to these variables can be calculated from the trajectories. Each of the 500 trajectories constitutes a driver for a Lagrangian parcel model simulation of size-dependent droplet growth and chemistry.

Traditionally, parcel models are run in adiabatic mode, *i.e.*, their trajectories are defined by updrafts of constant velocity producing adiabatic expansion and subsequent condensation of vapor. Here, each parcel produces non-adiabatic 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. Each Lagrangian parcel model uses time-splitting for integration of the microphysical and chemical rate equations.

2.5.1 Microphysics

The initial aerosol is assumed to have a uniform chemical composition of ammonium sulfate. For simplicity we define the aerosol size spectrum by five logarithmically spaced discrete sizes, but these can be extended to as many bins as needed. Sensitivity tests using 10 bins and 25 bins have been performed and produced similar S(IV) to S(VI) conversion. The solute mass in each size category is carried as ammonium ion mass and sulfate ion mass independently, to allow variations in the ratio of ammonium to sulfate as chemical

reactions proceed in a parcel cycling through cloud. The growth of these particles is solved on a moving mass grid.

Time t , height z , pressure p , liquid-water potential temperature θ_l , and total water mixing ratio r_t are input from the trajectories. The parcels are not assumed to be adiabatic; instead, the tendencies of non-adiabatic liquid water potential temperature $\frac{d\theta_l}{dt}$ and total water mass mixing ratio $\frac{dr_t}{dt}$ are prescribed from the trajectories, which depend on calculations in the LES host model, along with other tendencies $\frac{dz}{dt}$ and $\frac{dp}{dt}$. Independent variables temperature, T , droplet radius, r , and water vapor mixing ratio, r_v are integrated using a variable coefficient Ordinary Differential Equation solver VODE [Brown *et al.*, 1989]. The time rates of change of T and r_v are

$$\frac{dT}{dt} = \frac{T}{\theta_l} \frac{d\theta_l}{dt} + 0.286 \frac{T}{p} \frac{dp}{dt} + \frac{L}{c_p} \frac{dr_l}{dt}, \quad (2.39)$$

and

$$\frac{dr_v}{dt} = \frac{dr_t}{dt} - \frac{dr_l}{dt}. \quad (2.40)$$

Droplet growth is solved following Pruppacher and Klett [1978],

$$r \frac{dr}{dt} = \frac{s - 1 - y}{\frac{\rho_w RT}{e_s D^2 M_w} + \frac{L \rho_w}{K_a^* T} \left(\frac{LM_w}{RT} - 1 \right)}, \quad (2.41)$$

where $s = \frac{e}{e_s(T)}$, $e = \frac{r_v p}{0.622 + r_v}$, $y = \ln a_w + \frac{2\sigma_s/a M_w}{RT \rho_w a}$. The supersaturation field which drives droplet growth is calculated from T and r_v at the current time step. The water activity of the multi-component solution inside the growth equation is calculated using the Zdanovskii-Stokes-Robinson (ZSR) relation [Sangster and Lenzi, 1974]. Water activity data for the binary solutions are obtained from Chen [1994]; Kreidenweis (personal communication); Tang and Munkelwitz [1994]. The equilibrium size of unactivated particles is computed as a function of relative humidity (RH), using the water activity. For purposes of computing water activity, the solution is assumed to be a mixture of ammonium sulfate and ammonium bisulfate when the ammonium to sulfate ion molar ratio is between 1 and 2; and the solution is assumed to be a mixture of ammonium bisulfate and sulfuric acid when the ammonium to sulfate ion molar ratio is between 0 and 1.

The liquid water mixing ratio r_l is

$$\rho r_l = \sum_i \frac{\pi}{6} D_{p,i}^3 n(D_{p,i}) \rho_{s,i}. \quad (2.42)$$

Here, $\rho_{s,i}$ is the solution density of droplet size i . The time rate of change of r_l , $\frac{dr_l}{dt}$, can be derived from equation 2.42. Additional details of the microphysics used in the TEM can be found in Feingold *et al.*[1998a] and Feingold and Heymsfield [1992].

2.5.2 Size-resolved chemistry

In this application, as a first attempt, each parcel is treated as a closed system, with no gas-phase sources or replenishment so as to investigate the chemical behaviors in a controlled dynamical framework. A parcel will keep its identity in the boundary layer until five or six characteristic eddy mixing times have elapsed, as discussed in Feingold *et al.*[1998a]. Thus allowing no mixing is reasonable during a one-hour simulation. The aerosol composition is restricted to ammonium and sulfate species. Relevant sulfur chemistry is simulated in the model, including the dissolution and reaction of SO_2 , O_3 , H_2O_2 , and NH_3 .

Instead of assuming instantaneous equilibrium between the gas and aqueous phases, the mass-transfer rate of species between phases is calculated, as in Pandis and Seinfeld [1989]. The mass-transfer coefficients $K_{mt,i}$ are the same among species since we assume all species have the same diffusivity. This assumption has only a minor effect on the mass-transfer rates and little effect on the overall chemistry output. The mass-transfer coefficients also depend inversely on drop size, so that the gas phase species equilibrate more quickly with small drops than with large ones. The calculation of the mass-transfer coefficient is:

$$K_{mt,i} = \frac{3\eta D_i}{R_p^2}, \text{ and } \eta = \left(1 + \left[\frac{1.33 + 0.71K_n^{-1}}{1 + K_n^{-1}} + \frac{4(1 - a_W)}{3a_W}\right]K_n\right)^{-1}, \quad (2.43)$$

where $K_n = \frac{\lambda}{R_p}$ is the knudson number, and λ is the mean free path of species i . R_p is the drop radius. D_i is the diffusivity, the value to be $0.1 \text{ cm}^2 \text{ s}^{-1}$. a_W is the sticking coefficient and is chosen to be 0.01 in the model.

In each size category, the concentrations (in gmol g^{-1}) of gas phase SO_2 , O_3 , H_2O_2 , NH_3 , and of aqueous phase S(IV), S(VI), $\text{O}_3(\text{aq})$, $\text{H}_2\text{O}_2(\text{aq})$ and N(III) are also integrated

using VODE. The general expressions for the time rate of change of concentrations in the aqueous and gas phase can also be found in Lelieveld and Crutzen [1991] and Pandis and Seinfeld [1989].

$$\frac{dC_g}{dt} = \sum_i K_{mt,i} r_{l,i} \frac{C_{aq,i}}{H^* RT r_{l,i}} - C_g, \quad (2.44)$$

$$\frac{dC_{aq,i}}{dt} = K_{mt,i} r_{l,i} C_g - \frac{C_{aq,i}}{H^* RT r_{l,i}} + S_i, \quad (2.45)$$

where C_g is the gas phase concentration of any species, $C_{aq,i}$ is the aqueous phase concentration of any species at drop size i , $r_{l,i}$ is the water mixing ratio of drop at size i , and H^* is the effective henry's law coefficient for any species. S_i is the aqueous phase source or sink term of any species at drop size i .

The electroneutrality equation includes the positive ions H^+ , NH_4^+ and the negative ions OH^- , HSO_4^- , SO_4^{2-} , HSO_3^- and SO_3^{2-} :

$$[H^+] + [NH_4^+] = [OH^-] + [HSO_4^-] + 2[SO_4^{2-}] + [HSO_3^-] + 2[SO_3^{2-}]. \quad (2.46)$$

The S(IV) to S(VI) conversion is via the O_3 and H_2O_2 oxidation pathways [Hoffmann and Calvert, 1985]. The chemical reactions and equilibrium equations are listed in Table 2.2.

When sufficient cloud water is present ($r_l > 1 \times 10^{-6} \text{ g g}^{-1}$), chemistry calculations are performed on those droplet categories with ionic strength $< 2 \text{ M}$, which allows chemistry on some haze particles [Seinfeld, 1986]. If the ionic strengths for all five size categories are higher than 2 M , chemistry calculations are terminated, and only microphysical processes are solved for.

Table 2.2: Chemical reactions included in the TEM. ¹The 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 $k = k_{298} \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right]$ for the rate coefficient.

Equilibrium Reactions	Equilibrium Constant (M or M atm ⁻¹)	$-\frac{\Delta H}{R}$, K ¹	Reference
$\text{SO}_2(\text{g}) \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O}$	1.23	3120	<i>Smith and Martell</i> [1976]
$\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{H}^+$	1.23×10^{-2}	1960	<i>Smith and Martell</i> [1976]
$\text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+$	6.61×10^{-8}	1500	<i>Smith and Martell</i> [1976]
$\text{H}_2\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}_2(\text{aq})$	7.45×10^4	6620	<i>Lind and Kok</i> [1986]
$\text{O}_3(\text{g}) \rightleftharpoons \text{O}_3(\text{aq})$	1.13×10^{-2}	2300	<i>Kozac-Channing and Heltz</i> [1983]
$\text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{OH}(\text{aq})$	75	3400	<i>Hales and Drewes</i> [1979]
$\text{NH}_4\text{OH}(\text{aq}) \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.75×10^{-5}	-450	<i>Smith and Martell</i> [1976]
$\text{H}_2\text{SO}_4(\text{aq}) \rightleftharpoons \text{HSO}_4^- + \text{H}^+$	1000		<i>Perrin</i> [1982]
$\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$	1.02×10^{-2}	2720	<i>Smith and Martell</i> [1976]
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	1.0×10^{-14}	-6710	<i>Smith and Martell</i> [1976]
Aqueous Phase Reactions	Rate Coefficient (M ⁿ s ⁻¹)	$-\frac{E}{R}$, K	Reference
$\text{S(IV)} + \text{H}_2\text{O}_2 \Rightarrow \text{S(VI)} + \text{H}_2\text{O}$	7.45×10^7	-4751	<i>Hoffmann and Calvert</i> [1985]
$\text{S(IV)} + \text{O}_3 \Rightarrow \text{S(VI)} + \text{O}_2$	2.4×10^4		
	3.7×10^5	-5533	
	1.5×10^9	-5280	<i>Hoffmann and Calvert</i> [1985]

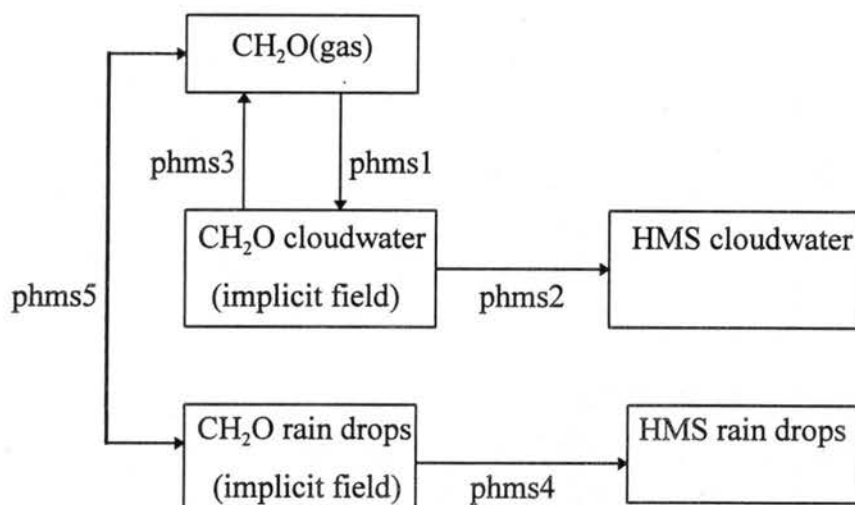


Figure 2.1: Formaldehyde reaction diagram. The arrows denote the processes related to any two fields in the box.

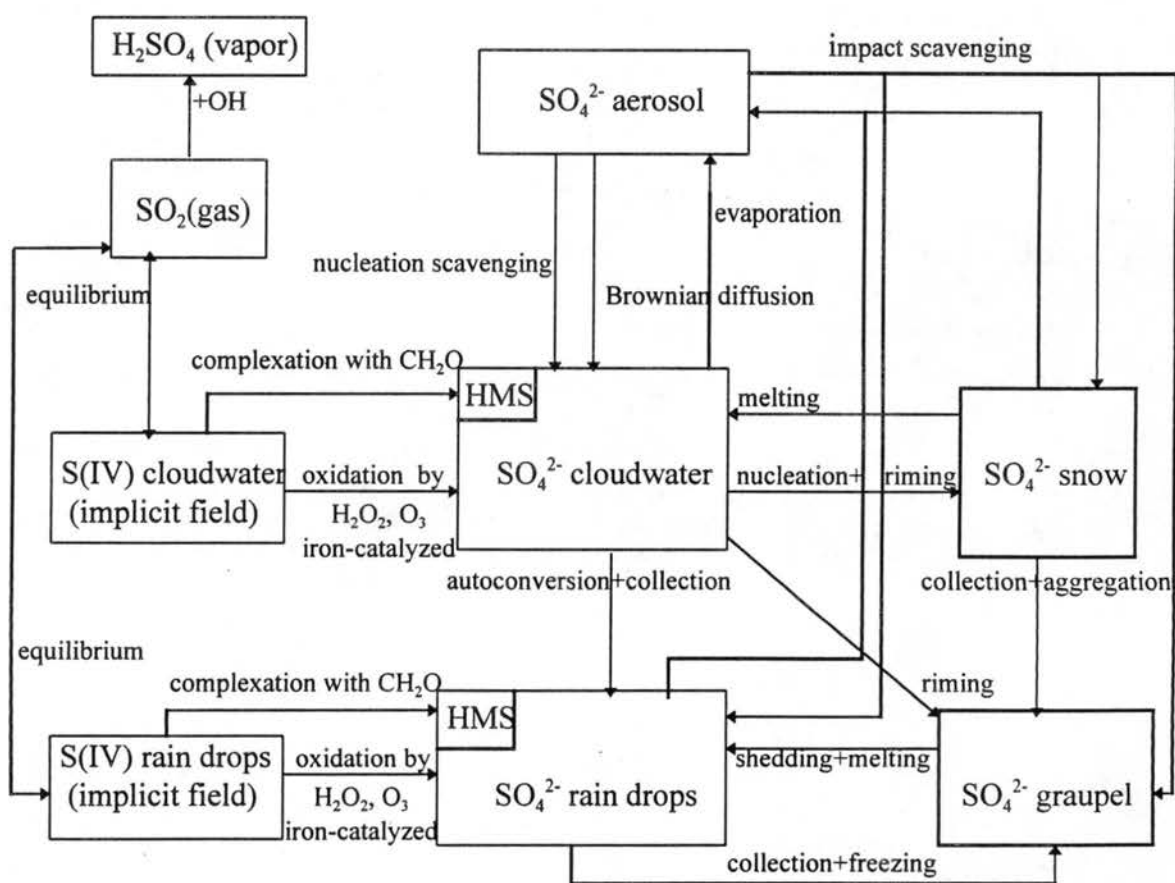
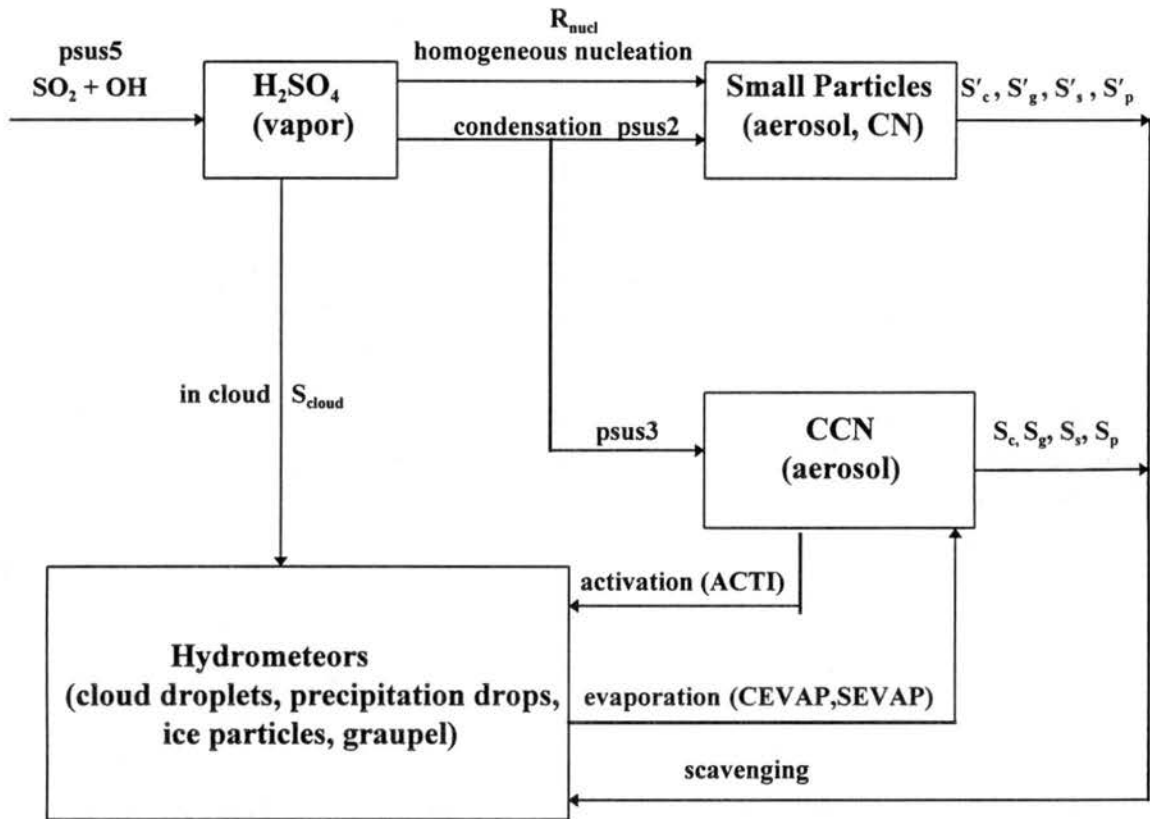


Figure 2.2 Schematic of sulfur chemistry diagram. The arrows denote the processes between any two fields in the box.



Aerosol Scheme Diagram

Figure 2.3: Aerosol scheme diagram. The arrows denote the interactions between any two fields in the box.

Chapter 3

THE EFFECTS OF DEEP CONVECTION ON IN-CLOUD SULFATE PRODUCTION AND SO₂ REDISTRIBUTION

In this chapter, we use the coupled chemistry/cloud dynamics model described in §2.1-2.3 to examine the relative importance of different oxidation pathways in cloud processing of SO₂, and to study cloud effects on the redistribution and transformation of various chemical species. The goals of this chapter include the simulation of a continental cumulus cloud based on sounding data from the CCOPE measurements. This case is characterized by deep convection accompanied by glaciation. Wang and Chang [1993a] studied the August 1 case of the CCOPE project to examine the importance of dynamic transport on redistribution of different gases with different solubility using a three-dimensional cloud chemistry model, and Respondek *et al.* [1995] studied the uptake, redistribution, and deposition of ammonium sulfate particles using the same CCOPE case as ours. Because of the lack of chemical data, our simulations are not considered to be a case study but a physical plausible arena through which various sensitivities may be explored.

3.1 Initial condition

The two-dimensional cloud model simulates a small continental cumulonimbus cloud based on sounding data. The sounding profiles of temperature and humidity from the measurements of CCOPE 19 July 1981 are used to initialize the temperature and water vapor mixing ratio fields, and are uniformly distributed in the x direction. The initial horizontal and vertical wind fields are set to be zero. The cloud is forced by a sensible heat source at 721 mbar. The two-dimensional model covers a domain of 150 km in the horizontal (x direction) and 15 km in the vertical (z direction). The grid spacing is $\Delta z = 200$ m and $\Delta x = 1000$ m, resulting 152×76 grid points, and the time step is $\delta t = 6.375$

s. The sub-cloud forcing is turned off after 1 hr 30 min to allow the boundary layer to develop. We use open lateral boundaries and a rigid lid upper boundary. The model uses flux-corrected advection scheme, and the lower boundary factor is the ratio of background value divided by current value. Boundary conditions for the sub-grid terms are specified as fluxes, and are set to zero for chemical species. The simulations start at zero model time. The total model run is 5 hours, the simulated cloud forms at 41 min with cloud base near 3 km, and the mixed-phase cloud lifetime is about 3 hours.

Two model simulations are performed, each with a different initialization of chemical fields to simulate polluted and clean atmospheres. The concentrations of different chemical species are assumed to decrease exponentially with different scale heights. Table 3.1 lists the initial surface values of different chemical species and the applied scale height. The appropriate values of SO_2 , H_2O_2 , and O_3 concentrations for clean and moderately polluted atmospheres are in agreement with observations and other model studies [Hegg *et al.*, 1986; Georgii and Meixner, 1980; Luke *et al.*, 1992; Yuen *et al.*, 1994]. The initial gas phase H_2O_2 and CH_2O concentrations are constant with altitude, and gas phase O_3 concentration is constant with time and height. The concentration of CH_2O is chosen based on continental observations by Munger *et al.*[1989].

Table 3.1: Initial chemical fields for the coupled chemistry/cloud dynamics model.

Species	Clean Case (Surface Value)	Polluted Case (Surface Value)	Scale Height (km)
SO_2	2 ppbv	10 ppbv	2.0
O_3	50 ppbv	50 ppbv	constant with time and altitude
H_2O_2	0.5 ppbv	1 ppbv	constant with altitude
CCN	900 cm^{-3}	2100 cm^{-3}	3.5
CH_2O	1 ppbv	4 ppbv	constant with altitude
NH_4^+	1.8 ppbv	9.6 ppbv	3.5
SO_4^{2-}	0.9 ppbv	4.8 ppbv	3.5

In the chemistry model, only CCN aerosol is considered, with chemical composition for the base cases assumed to be ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$. The CCN concentrations are increased by about a factor of 2.5 from clean to polluted. Appropriate values for

the CCN number concentration, aerosol sulfate and aerosol ammonium ion mass for both clean and polluted cases are based on Whitby [1978]. The moderately polluted simulation, for which cloud condensation nuclei (CCN) surface concentrations are 2100 cm^{-3} , gives cloud base CCN concentrations of about 800 cm^{-3} , is consistent with CCN measurements below cloud base obtained from the CCOPE field experiment [Jensen, 1985]. Total Fe in aerosol particles is assumed to be 6% mass of the ammonium ion concentration in aerosol, and ferric ion in solution is assumed to be 50% of the total Fe in solution. The total Fe concentration and the percentage of ferric ion in total Fe in solution are in agreement with continental observations [Cahill, 1988; Erel *et al.*, 1993; Hillamo *et al.*, 1993; Siefert *et al.*, 1996]. This gives ferric ion concentrations in cloud water and precipitation which are 3% of the NH_4^+ in the liquid phase.

In the next section, we discuss the general development of the model cloud with the coupled chemistry/dynamics model. The sections that follow address specific issues related to chemistry and cloud interactions and the effects produced.

3.2 General development of the simulated cloud

The sounding case study used is identical to that of Taylor *et al.*[1997]. Their CCN number concentration profile is the same as used here in the polluted case study. Details regarding the development of the model cloud, including two-dimensional plots of the various hydrometeor species, a discussion of the simulated transport patterns, and comparisons with observations can be found in the work by Taylor *et al.*[1997]; the salient features are mentioned here. Since the dynamics of the simulated cloud for the clean case are slightly different, these are also summarized.

For the polluted case, cloud top height rises from 3.6 km to 7.6 km during the initial stages of growth, with ice phase initiation around 1 hr 7 min. The mature stage of the simulated cloud begins at 1 hr 11 min and lasts until around 1 hr 52 min, during which the cloud top reaches its highest level of 9.6 km, with the overall maximum vertical velocity of 7.47 m s^{-1} occurring at 4.4 km at 1 hr 25 min. Significant liquid water content (q_c) starts at 41 min and lasts until 1 hr 42 min with a maximum liquid water content of 3.74 g kg^{-1} in

the entire model domain at 6.2 km at about 1 hr 11 min. The simulated cloud begins to decay at around 2 hr 2 min, and totally disappears at around 3 hr 44 min. In agreement with the model results of Respondek *et al.*[1995], the onset of significant ice formation (via vapor deposition growth of ice crystals, heterogeneous drop freezing, and riming of ice particles) initiates a decrease in the liquid water content, and ice crystals and graupel dominate the upper regions through the decay period. Also in agreement with Respondek *et al.*[1995], precipitation consists primarily of completely melted graupel; rain begins to reach the ground at 1 hr 42 min and lasts until 2 hr 18 min.

For the clean case, the cloud top height, initial and mature growth phases, and ice-phase initiation are about the same as those in the polluted case; precipitation is initiated slightly earlier. The overall maximum vertical velocity of 7.02 m s^{-1} occurs at 5.0 km and 1 hr 7 min. Significant liquid water content develops at around 41 min and lasts until 1 hr 27 min, with a maximum liquid water content of 3.08 g kg^{-1} occurring at 6.2 km at around 1 hr 8 min. The simulated cloud begins to dissipate around 1 hr 58 min, a little earlier than in the polluted case, and totally disappears around 3 hr 29 min. Rain begins to reach the ground at 1 hr 32 min and lasts until 2 hr 2 min. The total precipitation amount reaching the ground comes mainly from melted graupel, the amount of which is less in the clean case than in the polluted case. This is probably because in the clean case, the lower CCN number concentration leads to lower cloud drop number and snow particle number concentrations. The lower number concentration triggers precipitation and graupel to appear earlier, and these are on average of larger sizes, leading to a shorter sustained and less vigorous simulated cloud in the clean case.

Table 3.2 summarizes a few relevant cloud characteristics for various model times for which output is shown in the following sections. The times are chosen to represent different stages in the cloud evolution and hence in the transport patterns and the chemical composition.

3.3 Base case study

In this section simulation results for the polluted and clean base runs are discussed. First, the relative contributions to the in-cloud sulfate production from different oxidation

Table 3.2: Cloud features at selected times used to display model output.

Model Time	Cloud Features
41 min	just after initial formation of cloud
1 hr	during liquid phase cloud development
1 hr 11 min	just after initiation of ice phase; start of mature stage of cloud
1 hr 32 min	just before occurrence of precipitation (polluted case); precipitation just begins to reach the ground (clean case)
1 hr 52 min	end of mature stage of cloud; vertical motions begins to die; cloud consists mostly ice
5 hr	end of simulations; no cloud, little vertical motion

pathways and SO_2 redistribution in the simulations are discussed in terms of the difference between the polluted and clean cases. Sensitivity simulations which vary the initial chemical species concentrations and some of the dynamics model parameters are then discussed in comparison to the polluted and clean base simulations in the following section.

3.3.1 In-cloud sulfate production

Particulate matter which is scavenged into the droplets is released back into the ambient air when the cloud dissipates, when precipitation evaporates, or at the edge of the cloud, where partial evaporation occurs. In our simulations, all of the initial aerosol particles are assumed to have the same composition, and to consist solely of SO_4^{2-} and NH_4^+ species. Therefore, the ratio of $\text{SO}_4^{2-}/\text{NH}_4^+$ in both the aerosol released from evaporating cloud particles and in cloud water will be the same in the absence of in-cloud production of SO_4^{2-} . Since uptake of NH_3 is not included in our model, NH_4^+ can be used as a tracer for the scavenging of aerosol SO_4^{2-} to determine the fraction of in-cloud sulfate production, as has been often done in field studies reported in the literature [e.g., Liu *et al.*, 1993; Strapp *et al.*, 1988]. In-cloud oxidation of SO_2 will increase the ratio of $\text{SO}_4^{2-}/\text{NH}_4^+$, so that the particles which are left behind after cloud dissipation are likely to have higher $\text{SO}_4^{2-}/\text{NH}_4^+$ ratios, compared with those before cloud formation.

The percentage contribution of in-cloud sulfate production to the total cloud-water sulfate is defined as:

$$E = \frac{\text{total cloud - water } SO_4^{2-} \text{ mass} - \frac{8}{3} \times \text{cloud - water } NH_4^+ \text{ mass}}{\text{total cloud - water } SO_4^{2-} \text{ mass}} \quad (3.1)$$

where $\frac{8}{3}$ is the ratio of aerosol sulfate to aerosol ammonium before cloud formation, for the assumed ammonium sulfate composition.

Figure 3.1 shows the domain-averaged evolution of the fraction of cloud-water SO_4^{2-} produced in cloud for both the clean and polluted cases. The fraction attributed to in-cloud production is 8% to 68% in the clean case, and 7% to 52% in the polluted case. The fluctuations of in-cloud production show the inhomogeneity of cloud chemistry, nucleation scavenging, and other cloud microphysical processes. Liu *et al.*[1993] estimated the sulfate production in summer time clouds (cumuli or stratocumuli) over Ontario, Canada to be from 8% to 83%, with a median of 27% (mean 37%), using the in-cloud-water NH_4^+ as a tracer of particulate SO_4^{2-} . Burkhard *et al.*[1994] studied midwest clouds and applied aerosol selenium (Se) as the nucleation scavenging tracer to estimate that the average in-cloud oxidation accounted for up to 50% of the total SO_4^{2-} . Our model results are within the ranges of these observations. The computed differences between the clean and polluted cases demonstrate the nonlinearity of the nucleation scavenging and in-cloud production processes. That is, the initial concentrations of both aerosol sulfate and SO_2 are less in the clean case, but the ratio of initial SO_2/SO_4^{2-} is larger. This leads to a lower contribution to SO_4^{2-} from nucleation scavenging of aerosol, and higher percentage of S(IV) conversion to S(VI) in cloud water, in the clean case.

The vertical profiles of the computed rates for the different pathways for removal of S(IV) in cloud water (H_2O_2 oxidation rate, O_3 oxidation rate, iron-catalyzed oxidation rate and formaldehyde complexation rate), for the cloud core area, are shown in Figure 3.2 for the polluted case at several times during the simulation. The core area is defined as the 75–79 km domain average, and the half-domain area is defined as the 50–100 km domain average. In the polluted case, at most times, the H_2O_2 oxidation pathway dominates near cloud base, while O_3 oxidation dominates in the upper part of the cloud, since cloud-water pH is usually higher in the upper part of the cloud and hydrogen peroxide is rapidly

depleted in the upper cloud region. Iron-catalyzed oxidation is always comparable to the H_2O_2 and O_3 pathways, while the formaldehyde complexation rate is an order of magnitude smaller at most times. Barth *et al.*[1992] simulated a cold-frontal rainband and obtained similar results comparing H_2O_2 , O_3 , and iron-catalyzed oxidation, although they assumed ammonium bisulfate aerosol, which is more acidic than the neutral aerosol used in our study. The vertical profiles of the normalized (with respect to surface value) $\text{H}_2\text{O}_2(\text{g})$ mass mixing ratio in the core area during the period when liquid-phase cloud water exists are shown in Figure 3.3 and demonstrate that $\text{H}_2\text{O}_2(\text{g})$ is depleted in the cloudy region. Due to its relatively large Henry's Law constant, the amount of H_2O_2 in cloud water is largely constrained by mass balance. That is, when q_c increases, the amount of H_2O_2 in cloud water does not increase linearly, but depends on the $\text{H}_2\text{O}_2(\text{g})$ available. However, the low Henry's Law constant and assumption of constant gas-phase O_3 means that the computed O_3 amount in cloud water will increase as q_c increases. This partly explains why the H_2O_2 oxidation rate is higher initially (q_c low) and then smaller than the O_3 oxidation rate, in the upper cloud at later times as the $\text{H}_2\text{O}_2(\text{g})$ is depleted by chemical reactions. At 1 hr 32 min in Figure 3.3, most of the cloud water has been converted to ice-phase species, and the vertical transport of $\text{H}_2\text{O}_2(\text{g})$ from the boundary layer has replenished some of the $\text{H}_2\text{O}_2(\text{g})$ at higher levels in the domain.

A two-dimensional plot of the pH in cloud water for the polluted case is shown in Figure 3.4; the outermost contour indicates the approximate boundary of the $q_c = 0.1 \text{ g kg}^{-1}$ contour. The pH contours for the clean case have similar trends, except the 3.5–4 level drops out and a 5–5.5 region appears near the center of the cloud. In both cases, the highest pH values of cloud water are initially in the middle and then move to the upper regions of the cloud, with more acidic values at the cloud edges, where q_c is low and the cloud droplets are less dilute. Since the O_3 oxidation rate is pH -dependent, and increases with increasing pH value, and the H_2O_2 oxidation rate is almost pH -independent, this pH variation also contributes to higher O_3 oxidation rates in the upper cloud and higher H_2O_2 oxidation rate in the lower cloud, which is consistent with the model results of Barth *et al.*[1992].

The sources for S(VI) in cloud water, integrated over the whole model domain for the whole run time (5 hours), are summarized in the liquid-phase sulfate source budget shown in Table 3.3. In-cloud sulfate production ($\text{H}_2\text{O}_2 + \text{O}_3 + \text{iron pathways}$) is a higher percentage of the total in the clean case, consistent with the time-dependent trends in Figure 3.1. In both cases, the liquid-phase oxidation is comparable to the uptake of CCN, while impaction scavenging is negligible, as suggested by Kitada *et al.*[1993]. The budget is also consistent with the model results of Berge [1993], although he computed a slightly higher percentage due to in-cloud sulfate production. Since S(IV) to S(VI) oxidation by H_2O_2 is oxidant limited, and O_3 concentration is assumed constant in our model case study, the O_3 pathway is the major contributor to the in-cloud sulfate production, although it is less dominant in the polluted case because the cloud water is more acidic. The iron-catalyzed oxidation depends not only on the pH value of the cloud, but also on the ferric ion concentration in cloud water. The ferric ion concentration in the clean run is about one order of magnitude smaller than that in the polluted run, and the average pH value is only a little higher than that in the polluted case. These two factors offset each other, with the result that iron-catalyzed oxidation is relatively more important in the polluted case. In each case, iron catalyzed oxidation is comparable to the other two pathways and can not be neglected, as suggested by other model studies [*e.g.*, Barth *et al.*, 1992; Wang and Chang, 1993b].

Table 3.3: Liquid-phase sulfate source budget in percent contribution in the base cases.

	CCN (Nucleation scavenging)	H_2O_2	O_3	Iron	Impaction scavenging
Polluted	70.55	7.95	12.84	8.66	≈ 0
Clean	57.00	6.43	30.89	5.68	≈ 0

The reaction of CH_2O with S(IV) is expected to inhibit in-cloud sulfate production, since it binds S(IV) in an unreactive complex. In these simulations, however, complexation of S(IV) with formaldehyde plays a minor role in influencing sulfate production and in SO_2 uptake and redistribution, since the computed rates are so much lower than the other S(IV) reaction rates. The complexation reactions are highly pH dependent and are slowed by the

low cloud-water pH predicted for most times and most cloud regions; the complexation rate is highest just below cloud top, where pH is also relatively high (Figure 3.4). In situations where pH is moderated, for example, in cloud water with high buffering capacity [Rao and Collett, 1995] or regions with strong sources of neutralizing gases such as ammonia [Kruse-Plass *et al.*, 1993], the relative importance of the complexation reaction could be enhanced. Reaction with formaldehyde would then serve as a significant sink for $S(IV)$, one which does not produce $S(VI)$ and therefore competes with the oxidation reactions. The complexed $S(IV)$ is later released by the decomposition of HMS after evaporation of cloud water; thus, the redistribution pattern for SO_2 may also be altered by this reaction.

3.3.2 Redistribution of CCN and gas-phase SO_2

In this section, the effects of in-cloud $S(IV)$ oxidation on SO_2 redistribution are examined. Two conservative tracers (Tracer 1 for SO_2 mass and Tracer 2 for CCN concentration) are used in the model to estimate the effects of convective transport. This is similar to the approaches of Wang and Crutzen [1995], who present two-dimensional plots of the ratios of species concentrations from a combined chemistry and transport run to those from a transport-only model, and Flossmann and Wobrock [1996], who compared redistribution patterns and amounts for SO_2 treated as both an inert and a reactive species. In our study, Tracer 1 has the same initial mass mixing ratio and scale height as SO_2 , except it is treated as an inert gas species having no sources or sinks. Tracer 2 has the same initial number concentration and scale height as the CCN field, except it is never scavenged into hydrometeors. Figure 3.5 shows the vertical profiles of the core area Tracer 1 mass mixing ratio at 0 hr, 1 hr 11 min, and 5 hr for both the polluted and clean cases. Initially, the tracer mixing ratio decreases exponentially with height; at 1 hr 11 min in the cloudy region, the tracer mass mixing ratio is nearly constant with height in both the clean and polluted cases; at 5 hr, the tracer is depleted in the boundary layer and transported to the upper troposphere. The tracer mixing ratio profiles for the two cases are nearly the same at 1 hr 11 min (mainly liquid-phase cloud), but different at 5 hr. This is due to the fact that there is lower maximum vertical velocity in the clean case, and the ice-phase microphysics is different in the two cases. Respondek *et al.* [1995] also found that their model results were

sensitive to the treatment of the ice phase. In a sensitivity study, they purposely inhibited ice nucleation to compare the results with the simulation that included ice formation. Their case without ice had higher vertical velocity, different onset times and duration of precipitation, reached its highest level earlier, and had different cloud microstructure and precipitation chemistry.

The vertical profiles of the half-domain averaged and core area gas-phase concentrations of SO_2 at various times are shown in Figure 3.6. The uptake of SO_2 in cloud water at 1 hr 11 min is evident when Figure 3.6a is compared with the tracer profile (Figure 3.5). A higher percentage of SO_2 is dissolved into and reacts in the aqueous phase in the clean case. At 1 hr 52 min, vertical motion is still transferring SO_2 mass from the boundary layer to higher levels. At 5 hr, vertical motion is dying, and much of the SO_2 mass in the boundary layer has already been transported to the upper troposphere at the detrainment level, although the magnitude is much reduced, when compared with the tracer mass, by aqueous-phase conversion of SO_2 conversion into sulfate. Little SO_2 is redistributed to the mid-troposphere. At 5 hr, there is also a lower percentage of initial SO_2 redistributed in the clean case. This is consistent with the 1 hr 11 min plot (Figure 3.6a), which shows a higher percentage dissolution and reaction of SO_2 in the aqueous phase for that case.

The vertical profiles of CCN number and Tracer 2 concentrations at different times for the polluted case are shown in Figure 3.7. At 1 hr 11 min, CCN have been activated as cloud drops and depleted from the cloudy region, while at 5 hr, CCN concentrations have increased in the formerly cloudy regions, due to both vertical transport from the boundary layer and release from cloud droplet and ice particle evaporation. It is also noted that there is a depleted region, relative to the tracer field, in the CCN field in the upper troposphere between 7 and 10 km, where ice particles and graupel particles formerly dominated. This is the result of several processes. As the simulated cloud evolves, some of the CCN mode is scavenged into the ice phase and graupel and thus removed from the upper cloud region. Vertical motions transport the CCN depleted region (created by nucleation scavenging), which is in the middle to lower part of the cloud during the liquid water phase, upward into the upper troposphere. Although included in the simulations, the CCN source due to

release of aerosol particles from evaporation of ice particles is negligible between 7 and 10 km, since very little evaporation of ice particles occurs.

As indicated in Figure 3.6, some of the initial gas-phase SO_2 can be transported upward by cloud updrafts, while some SO_2 is trapped inside cloud and converted to S(VI) . The difference between SO_2 and Tracer 1 concentrations (both normalized with respect to their initial values) is used to determine the percentage loss due to SO_2 dissolution and subsequent chemical conversion. For both cases, the percentage of SO_2 loss reaches a maximum and then decreases after the cloud dissipates, releasing gases back into the environment. When averaged over the half domain, 5–7% of the SO_2 is lost after 5 hours; averaged over the total domain, only 1–1.5% of the SO_2 is permanently depleted. These estimates agree with the model results of Wang and Chang [1993a] and Flossmann and Wobrock [1996], who also showed that most of the SO_2 survived cloud uptake. A slightly higher percentage of SO_2 is dissolved and reacted in the aqueous phase in the clean case, and thus less is redistributed to the mid and upper troposphere.

3.4 Sensitivity tests and results

As discussed in the begin of this chapter and in the introduction, we will investigate the sensitivities of vertical redistribution of SO_2 and CCN to the chemical and physical processes which take place in-cloud and in the near environment. In addition to the simulations described in preceding section, five simulations have been performed using different initial conditions, two other simulations have been performed using a different CCN activation efficiency (0.55, modified from 0.75 in the base cases) in the bulk microphysics, and two additional simulations have been performed using smaller horizontal grid spacings, $\Delta x = 500 \text{ m}$ and $\Delta x = 750 \text{ m}$. These sensitivity studies are listed in Table 3.4.

The details of the cloud dynamics in each sensitivity simulation are slightly different, due to the differences in chemistry or in microphysics, but the overall transport is not significantly affected. Simulations 4 and 5 use NH_4HSO_4 aerosol as input, and the fractions of cloud-water sulfate due to in-cloud production in those cases are decreased compared to the base runs. This means that the in-cloud production is sensitive to the aerosol chemical

Table 3.4: Initial conditions of the model sensitivity simulations for the coupled chemistry/dynamics model.

Simulation	Dynamics and microphysics input	Chemistry input
1	same as the clean base case	clean case; no iron-catalyzed reactions
2	same as the polluted base case	polluted case; no iron-catalyzed reactions
3	same as the polluted base case	polluted case; H_2O_2 is 0.5 ppb instead of 1 ppb
4	same as the clean base case	clean case; NH_4HSO_4 aerosol
5	same as the polluted base case	polluted case; NH_4HSO_4 aerosol
6	activity efficiency 0.55	clean case
7	activity efficiency 0.55	polluted case
8	$\Delta x = 750m$	polluted case
9	$\Delta x = 500m$	polluted case

composition assumed in the model input, which is reasonable since NH_4HSO_4 aerosol is acidic when scavenged into cloud water. The oxidation of S(IV) to S(VI) is sensitive to the acidity of the cloud water; as $p\text{H}$ decreases, the Fe-catalyzed and O_3 oxidation reaction rates are suppressed, as is the solubility of SO_2 . Simulations 1 and 2 eliminate the iron-catalyzed pathway, which leads to a smaller contribution of in-cloud sulfate production to the total. Similar results are seen for Simulation 3, which reduces H_2O_2 concentration in the polluted case. The modification of the CCN activation efficiency (in Simulations 6 and 7) has the largest impact on the evolution of the simulated cloud; however, the overall fraction of cloud-water sulfate due to in-cloud production seems insensitive to this microphysical parameter.

The corresponding liquid-phase sulfate source budgets for the sensitivity simulations are shown in Table 3.5. Elimination of iron-catalyzed oxidation resulted in a 2% decrease (clean) and 4% decrease (polluted) in the contributions due to total liquid-phase oxidation. Since the total S(IV) to S(VI) conversion is decreased, the $p\text{H}$ value is expected to be a little higher in those simulations, leading to a relatively larger increase in O_3 oxidation than H_2O_2 oxidation. This is found to be the case. The O_3 contribution increases from 40.761 in the clean base run to 44.293 in Simulation 1, and from 89.528 in the polluted base run to 104.028 in Simulation 2, whereas the H_2O_2 contribution is nearly unchanged. With H_2O_2 initial concentrations decreased by a factor of 2 in Simulation 3, the H_2O_2 contribution

also decreases by almost the same factor. The increased available S(IV), enhanced due to the decrease in H_2O_2 pathway, is consumed by the O_3 and iron pathways.

Table 3.5: Liquid-phase sulfate source budget for the sensitivity simulations. Values are in grams of sulfate.

	CCN (Nucleation scavenging)	H_2O_2	O_3	Iron	Impaction scavenging	Sum
Polluted	491.769	55.443	89.528	60.354	0.0019	697.0959
Clean	75.217	8.483	40.761	7.489	0.0002	131.9502
1	75.099	8.369	44.293	0.0	0.0002	127.7612
2	475.100	57.328	104.028	0.0	0.0021	636.4581
3	481.074	28.214	96.634	68.807	0.0020	674.7310
4	75.254	9.879	40.689	1.721	0.0002	127.5432
5	472.513	55.800	70.611	6.573	0.0022	605.4992
6	76.855	8.695	41.233	8.948	0.0003	135.7313
7	479.994	59.286	89.102	64.451	0.0033	692.8363
8	412.40	51.713	93.517	59.232	0.0013	616.8630
9	365.262	41.562	86.182	47.134	0.0007	540.1410

Changing the initial aerosol chemical composition, from ammonium sulfate to ammonium bisulfate in Simulations 4 and 5, decreases the contribution from the iron-catalyzed pathway from 60.354 in the polluted base run to 6.573 in Simulation 5, and from 7.489 in the clean base run to 1.721 in Simulation 4, partly due to the decrease in ferric ion concentrations that accompany the change in NH_4^+ in cloud water. The total liquid-phase oxidation decreases by 2% (clean) to 7% (polluted). The importance of the O_3 pathway does not change much in the clean atmosphere, but decreases from 89.528 in the polluted base run to 70.611 in Simulation 5. This is because in our chemistry model, as discussed above, the H_2O_2 oxidation rate is almost independent of pH , whereas the O_3 oxidation rate decreases with decreasing pH , and increases with higher q_c ; the iron-catalyzed oxidation rate decreases more sharply with pH than the O_3 rate, and also decreases with decreasing cloud-water ammonium ion concentrations.

Simulations 6 and 7 changed the CCN activation efficiency from 0.75 to 0.55. This increases the maximum liquid water content in both the clean and polluted runs, and reduces cloud droplet evaporation. With the same initial water vapor field, the change in

activation efficiency has a larger relative impact on the cloud droplet concentration and ice-phase microphysics in the polluted case than that in the clean case, and thus affects the cloud dynamics more strongly in the polluted case. The contributions from both nucleation scavenging and liquid-phase sulfate production in the clean atmosphere are increased, with the ratio between the two mechanisms and the weights of the different oxidation pathways nearly unchanged. However, only the H_2O_2 and iron-catalyzed pathways increase, with a 2% increase in total liquid-phase oxidation in Simulation 7, compared with the polluted base run. Berge [1993] also tested the sensitivity to reducing activation efficiency, and found that the CCN scavenging pathway was reduced by 3% in his S85 case and 5% in his D88 case, which were more like our polluted base run; there was negligible sensitivity to the activation efficiency in his J88 case, which was more like our clean base run. The conclusions from our Simulation 7 agree with the results from his S85 and D88 cases, and those from Simulation 6 agree with his J88 case.

Figure 3.8 compares the redistribution of SO_2 in the core area at the end of the model run (5 hr) for the polluted (Figure 3.8a) and clean (Figure 3.8b) sensitivity simulations. The cloud dynamics plays an important role in SO_2 redistribution, in addition to the cloud chemistry, because vertical motion transports SO_2 mass out of the boundary layer to the mid to upper troposphere, while cloud processing reduces the amount being transported. The interaction between these two mechanisms determines the SO_2 redistribution, although the cloud dynamics has a less pronounced effect on in-cloud sulfate production and cloud-water sulfate source budget, as discussed above. Simulations 1 through 6 have a higher percentage SO_2 redistribution, compared with the base cases. The uptake of SO_2 to the aqueous phase is suppressed in Simulations 4 and 5, due to ammonium bisulfate aerosol being more acidic when scavenged into cloud water, and thus those two simulations obtain the highest percentage SO_2 redistribution. Wang and Crutzen [1995] also found that the redistribution of SO_2 was sensitive to the assumed acidity of the boundary layer chemical composition. Simulations 1, 2, and 3 either reduce H_2O_2 concentrations or eliminate the iron-catalyzed pathway, which both lead to decreased depletion in cloud water and increased SO_2 redistribution. Simulation 6 has a higher percentage SO_2 redistribution than

that of the clean base run, and the overall SO_2 redistribution is also higher in Simulation 7 than that of the polluted base run, although the initial chemical fields in the sensitivity runs are the same as in the base runs. These findings are mainly due to the fact that stronger updrafts in Simulations 6 and 7, created by the change in cloud dynamics related to the sensitivity to the activation efficiency, transport more SO_2 from the boundary layer to the upper levels, compared with the base cases.

The results from Simulations 8 and 9 are discussed separately from the other sensitivity simulations. These simulations repeat the polluted base case run, except that the horizontal resolution Δx is refined from 1000 m to 750 m and 500 m, respectively. The details of the cloud dynamics are somewhat sensitive to the resolution changes. The maximum vertical velocity is increased as the resolution is increased, as pointed out in Taylor *et al.*[1997]. This also affects the lifetime of the simulated cloud. The simulated cloud disappears around 3 hr 44 min for the $\Delta x = 1000$ m case, but small ice particles are still present until 5 hr for both $\Delta x = 750$ m and $\Delta x = 500$ m cases.

Figure 3.9 shows the evolution of the fraction of SO_4^{2-} produced in cloud, averaged over the whole cloudy domain, for the polluted base run and Simulations 8 and 9. The range of the percentage contribution attributed to in-cloud sulfate production is about the same for the different horizontal resolutions. Liquid cloud water disappears earlier in the $\Delta x = 500$ m case than in the other two cases, which will affect the cloud sulfate source budget (Table 3.5). The CCN nucleation scavenging pathway is decreased when the resolution is increased, which might be due to better resolution of partially cloudy regions; this result is also consistent with those of Taylor *et al.*[1997], who found that the cloud extent is smaller for $\Delta x = 500$ m. The reduction in the iron-catalyzed pathway seen in Table 3.5 is related to the decrease in the ferric ion concentration in cloud water: since Fe^{3+} has been tied to the ammonium in cloud water, and thus to the extent of aerosol nucleation scavenging, there is less catalyst available. The H_2O_2 oxidation pathway is related to its concentration in cloud water, which is in turn related to the liquid water condensation rate and cloud extent. Therefore, the H_2O_2 oxidation pathway is also reduced when the grid is refined. The efficiency of the O_3 oxidation pathway is nearly unchanged.

Since the tracer upward mass flux is decreased when the resolution is increased, the tracer transport pattern is different in all three cases, as shown in Figure 3.10a. The SO_2 redistribution for the three simulations is shown in Figure 3.10b. Due to the nonlinear interaction between chemical conversions and upward mass fluxes, the SO_2 redistribution is the highest in the $\Delta x = 1000 \text{ m}$ case. This result will be investigated in future studies of the convective transport of reactive species and aerosols.

3.5 Summary and conclusion

In this chapter a detailed sulfate chemistry model, including prognostic equations for CCN mass and number concentrations, is incorporated into a two-dimensional Eulerian cloud dynamics model to simulate the effects of convective transport on active chemical species redistribution in a small midlatitude continental cumulonimbus. Formaldehyde complexation with S(IV) and iron-catalyzed oxidation is also added to the sulfate chemistry to examine the relative importance of oxidation to complexation. Comparison of the dynamics model run with observations are discussed in Taylor *et al.*[1997], and the model yields good agreement with the observed general cloud characteristics.

For the choice of parameters used in this chapter, CH_2O complexation with S(IV) has a minor effect on the SO_2 redistribution, but this complexation process might be important in cloud processing of active chemical species, since CH_2O binds unreacted S(IV) and allows it to be redistributed. The H_2O_2 oxidation pathway is important initially, but H_2O_2 is quickly depleted from the cloudy region after several minutes; the O_3 oxidation pathway begins to dominate in most regions of the simulated cloud, while the H_2O_2 pathway still dominates near cloud base. The iron-catalyzed oxidation is comparable to the H_2O_2 and O_3 pathways.

The fraction of cloud-water S(VI) attributed to in-cloud production is less in the polluted case, and a smaller percentage of SO_2 is dissolved and reacted in the aqueous phase; therefore, a higher percentage of the initial SO_2 is redistributed in the polluted case. CCN concentrations are significantly depleted above the formerly cloudy region between 7–10 km at the end of the model run, while SO_2 is transported from the boundary layer

to the upper troposphere. This redistribution may set the stage for later gas-to-particle conversion, as SO_2 is oxidized in the gas phase to sulfuric acid [Perry and Hobbs, 1994]. The low aerosol surface area of the depleted CCN population and low temperatures in the mid-to-upper troposphere are conducive to new particle formation. This scenario will be examined in the next chapter.

The sensitivity tests show that the oxidation of S(IV) to S(VI) is sensitive to the initial aerosol composition and the acidity of the cloud water. When the cloud water is more acidic, the oxidation of S(IV) to S(VI) is suppressed, and less SO_2 is dissolved and reacted in the aqueous phase. The contribution to the cloud-water sulfate from the sum of all liquid-phase oxidation pathways is decreased, by a few percent, for reduced H_2O_2 concentration, elimination of the iron-catalyzed pathway, or increased acidity of the initial aerosol composition. The SO_2 redistribution is more sensitive to the change in the initial aerosol composition than to changes in other chemical fields, or in microphysical parameters, as also concluded by Wang and Crutzen [1995].

The contribution of in-cloud sulfate production to the total cloud-water sulfate and the total percentage SO_2 converted is only moderately sensitive to changes in the model resolution. However, the SO_2 redistribution pattern in the cloud core area is changed when the model resolution is increased. The effects of model resolution on estimates of chemical species conversion and redistribution need to be further explored.

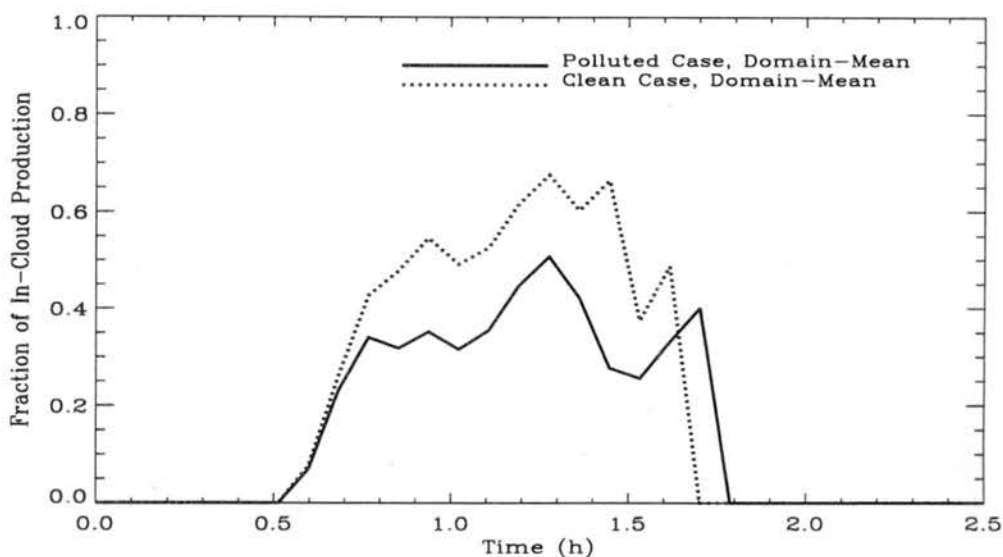


Figure 3.1: The evolution of the fraction of cloud-water SO_4^{2-} produced in cloud for both the clean and polluted cases, for the domain average.

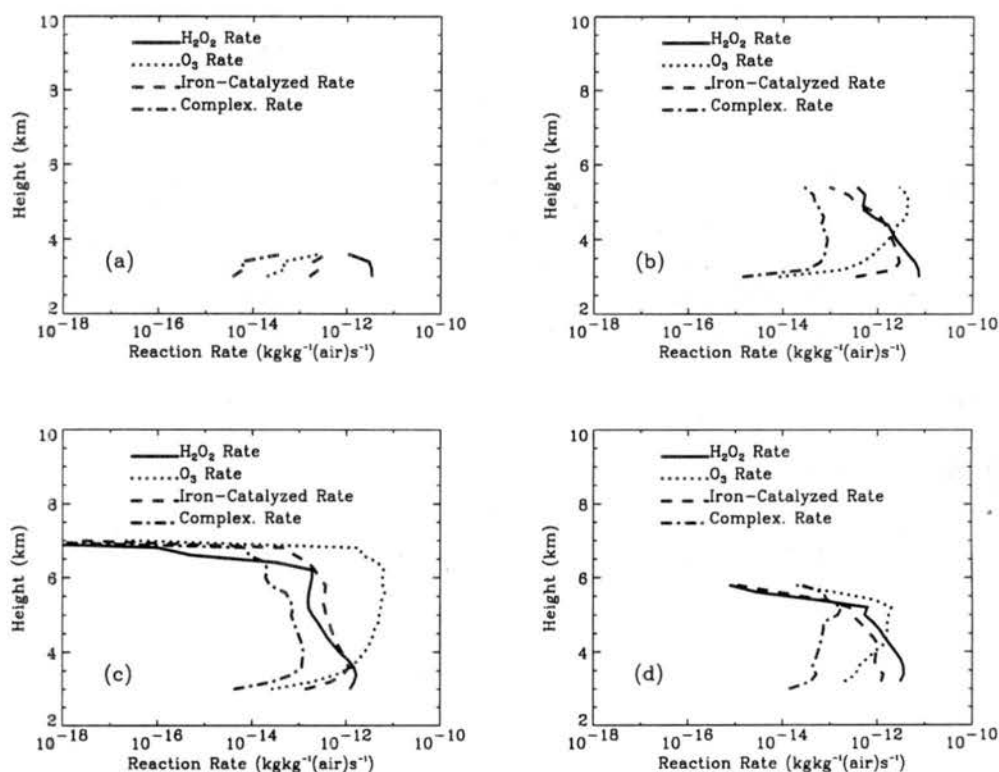


Figure 3.2: The vertical profiles of the computed rates for the different pathways for removal of S(IV) in cloud water, in the cloud core area, for the polluted base case (a) at 41 min, (b) at 1 hr, (c) at 1 hr 11 min, and (d) at 1 hr 32 min. The core area is defined as the 75–79km domain average.

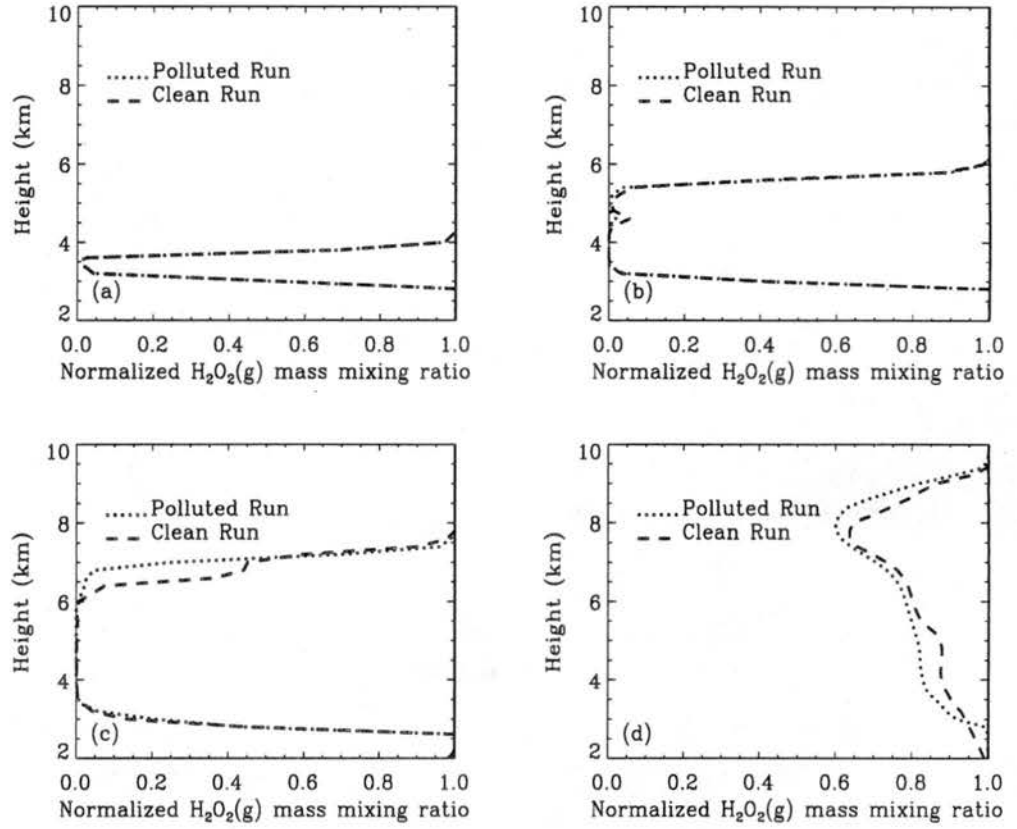


Figure 3.3: The vertical profiles of the normalized (with respect to initial surface value) $\text{H}_2\text{O}_2(\text{g})$ mass mixing ratio in the core area during the period when liquid-phase cloud water exists (a) at 41 min, (b) at 1 hr, (c) at 1 hr 11 min, and (d) at 1 hr 32 min. The initial profile of $\text{H}_2\text{O}_2(\text{g})$ is set to be constant with height and is therefore coincident with the right vertical axis.

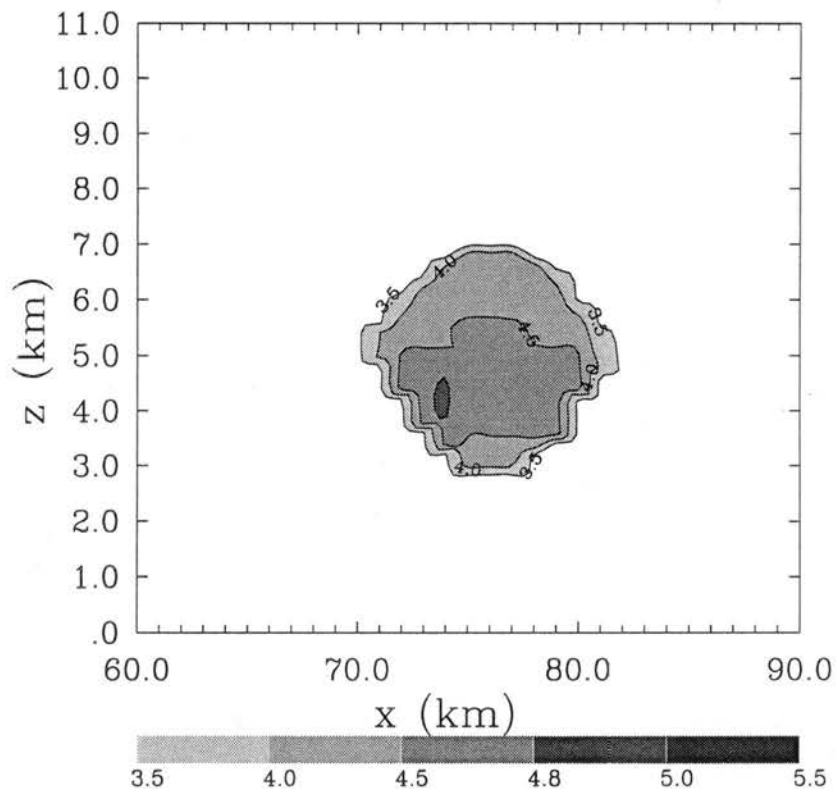


Figure 3.4: Two-dimensional pH field produced by the model for the polluted base run at 1 hr 11 min.

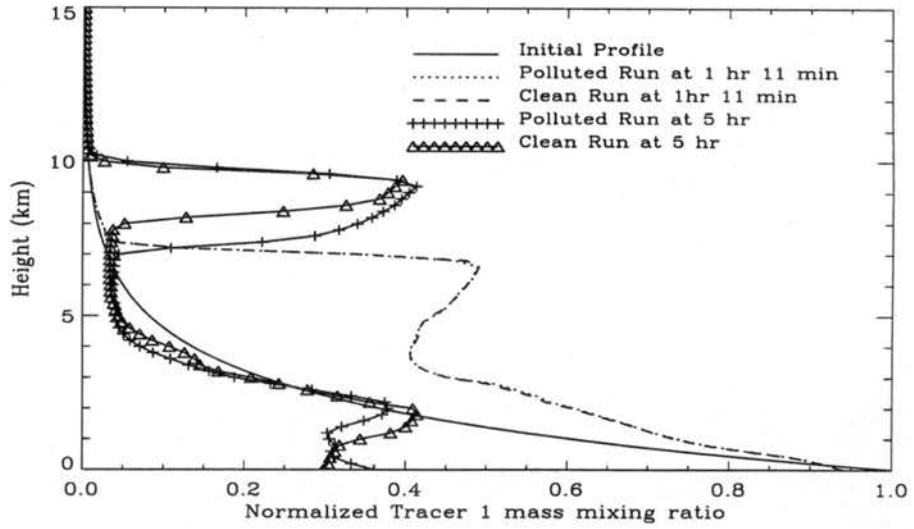


Figure 3.5: The vertical profiles of the core area normalized (with respect to initial surface value) Tracer 1 mass mixing ratio at 0 hr, 1 hr 11 min, and 5 hr for both the polluted and clean cases.

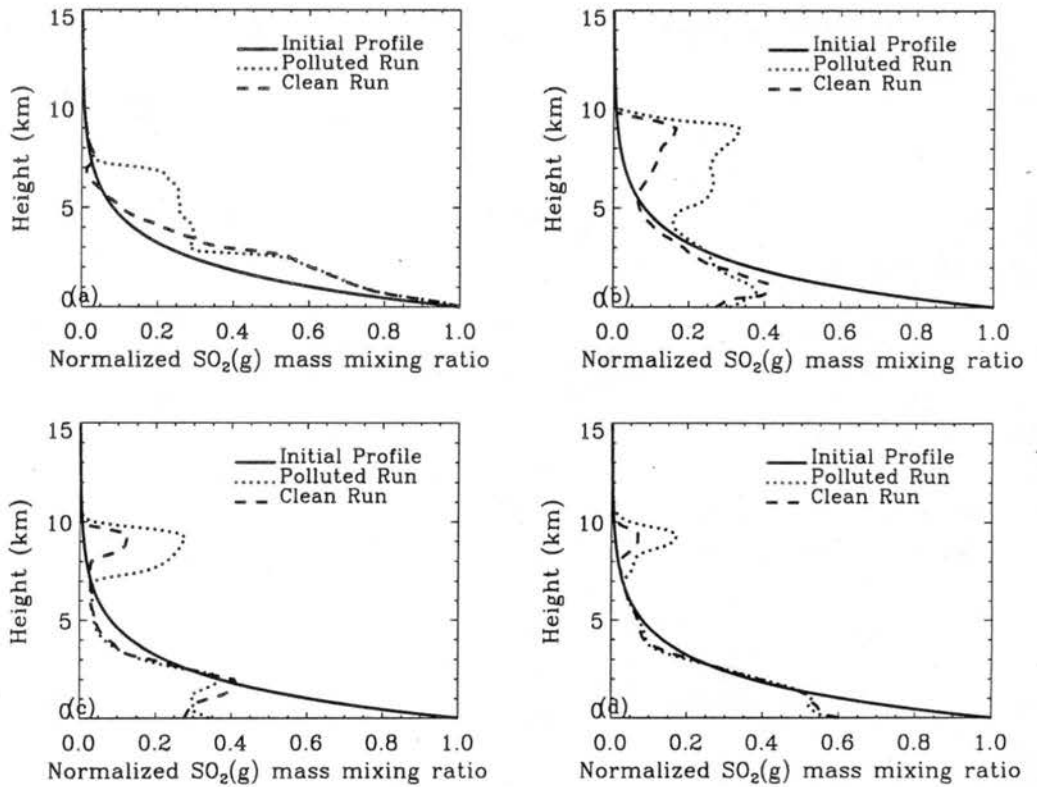


Figure 3.6: The vertical profiles of the half-domain averaged and core area gas-phase SO_2 normalized (with respect to initial surface value) mass mixing ratio at various times: (a) at 1 hr 11 min in the core area, (b) at 1 hr 52 min in the core area, (c) at 5 hr in the core area, and (d) at 5 hr for the half-domain average. The half-domain is defined as the 50–100 km domain average.

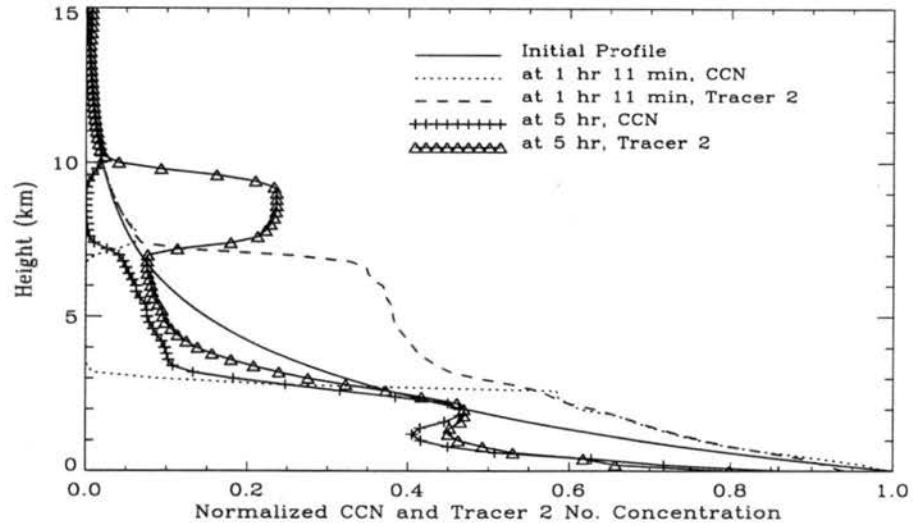


Figure 3.7: The vertical profiles of normalized (with respect to initial surface value) CCN number and Tracer 2 concentrations at different times for the polluted base case.

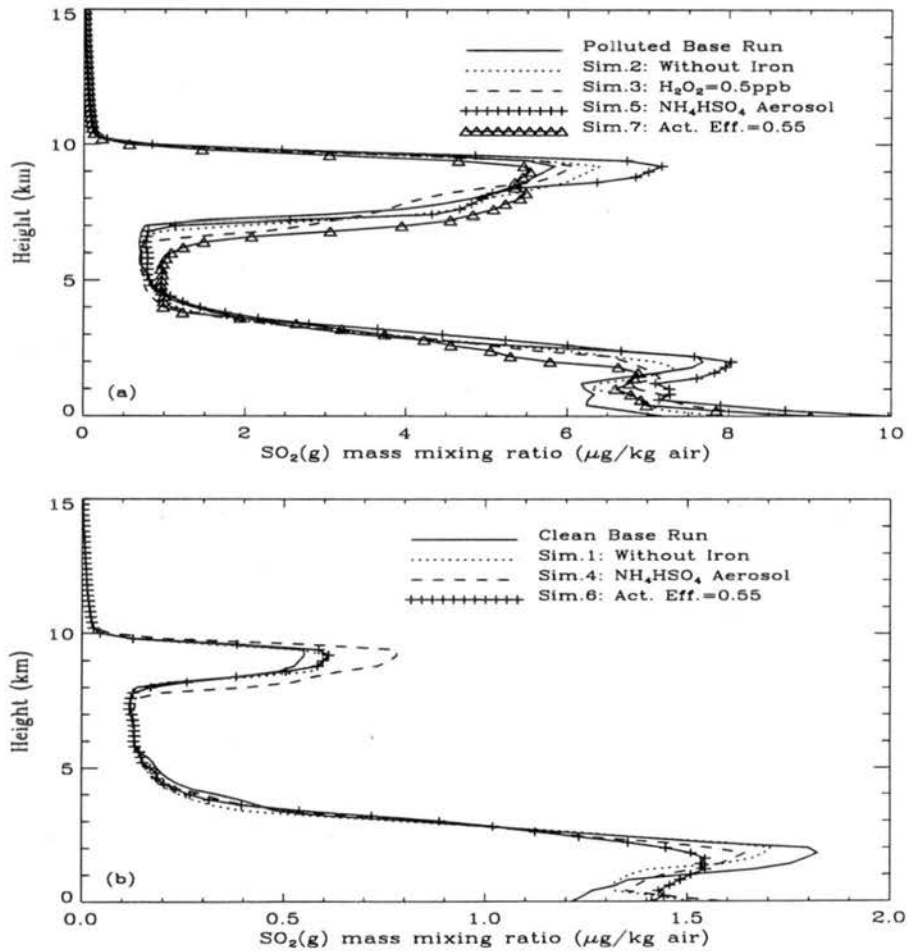


Figure 3.8: The redistribution of SO_2 in the core area at the end of the model run (5 hr) for the sensitivity simulations: (a) polluted cases, and (b) clean cases.

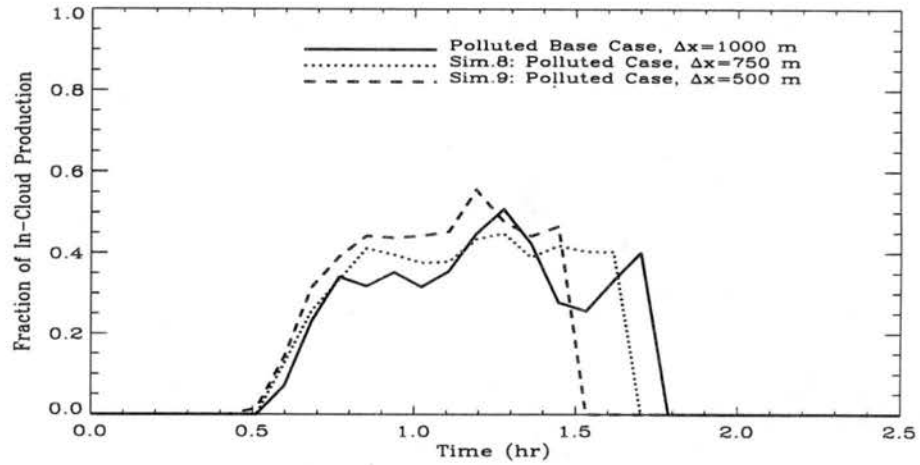


Figure 3.9: The evolution of the fraction of SO_4^{2-} produced in cloud, averaged over the whole cloudy domain, for the polluted base run and Simulations 8 and 9.

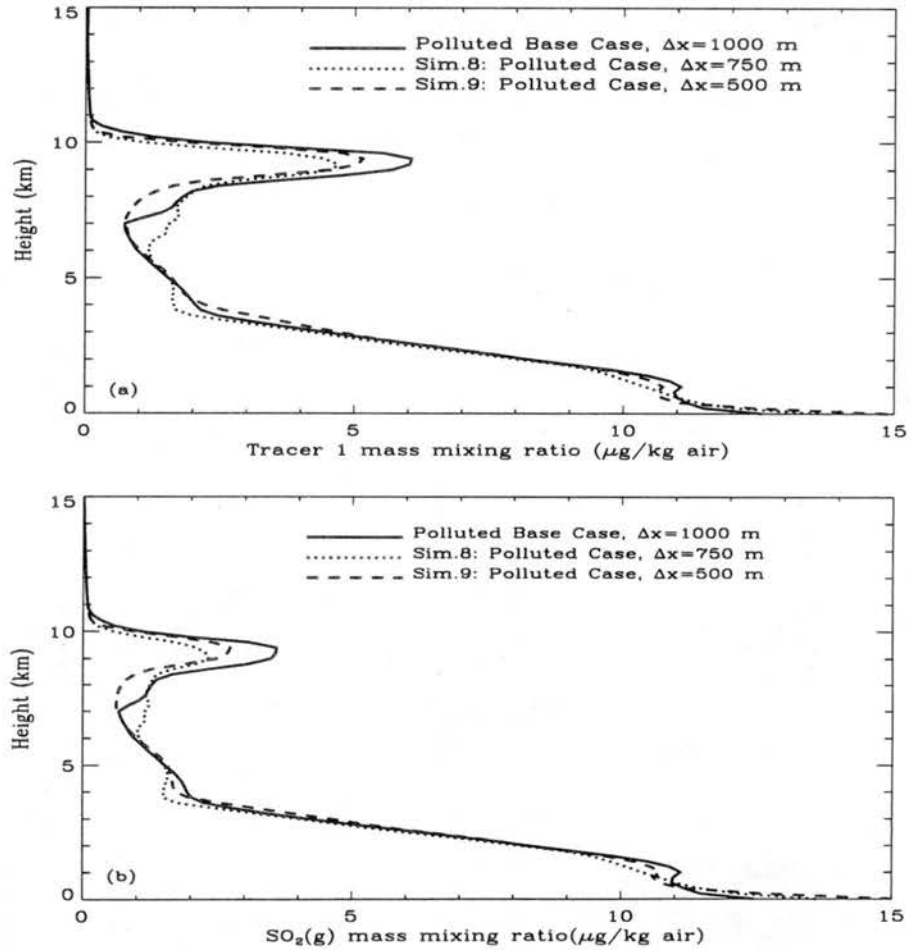


Figure 3.10: The redistribution of SO_2 and Tracer 1 mass mixing ratios at 5 hr, averaged over the half-domain, for the polluted cases: (a) Tracer 1 mass mixing ratio, and (b) SO_2 mass mixing ratio.

Chapter 4

THE EFFECTS OF CLOUD ON AEROSOL REDISTRIBUTION AND PRODUCTION IN THE UPPER TROPOSPHERE

Results in Chapter 3 show that chemically active gases are transported by convective clouds from the boundary layer to the mid-to-upper troposphere. Since depleted CCN concentrations are simultaneously predicted above the formerly cloudy region, this redistribution might set the stage for subsequent new particle formation through $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ binary homogeneous nucleation. This scenario will be further explored in this chapter. In order to study the effect of deep convection on the redistribution and production of aerosol particle concentration, in this chapter, we have used the coupled aerosol/chemistry/cloud dynamics model described in Chapter 2 to examine particle redistribution and production for a range of model conditions. The goals of this chapter include the same simulation of a continental cumulus cloud based on sounding data from the CCOPE measurement as in Chapter 3.

4.1 Initial condition

The two-dimensional cloud model is used to simulate a continental cumulus cloud based on the same CCOPE 19 July 1981 sounding data. The initializations of temperature, humidity, horizontal and vertical wind fields, domain coverage, grid spacing, heat source, and the boundary conditions are the same as the base case simulated in Chapter 3. Boundary conditions for the sub-grid terms are specified as fluxes, and are set to zero for aerosol particles. We choose grid spacings of $\Delta z = 200$ m, $\Delta x = 1000$ m, and the time step is $\delta t = 6.375$ s. The total model run is 10 hours.

The initial chemical fields are the same as in Chapter 3 for both polluted and clean atmospheres, as shown in Table 4.1. In addition to the sensitivity simulations, we also

perform a no-nucleation run, which is the polluted base case without the aerosol nucleation process (the nucleation rate is artificially set to zero), and which is used to separate the effects of the new particle formation process from vertical transport and the aerosol condensational growth process.

The initial mass mixing ratios of different chemical species are assumed to decrease exponentially with different scale heights, except for the OH·, H₂O₂, CH₂O, and O₃ fields. The OH· profile is constant during the simulation. The H₂O₂ and CH₂O are initially

Table 4.1: Initial chemical and aerosol fields for the coupled aerosol/chemistry/cloud dynamics model. ^aValue chosen from Eisele and Tanner [1993]; ^bvalue from Thompson and Stewart [1991]; ^cvalue from Munger *et al.*[1989].

Species	Clean Case (Surface Value)	Polluted Case (Surface Value)	Scale Height (km)
SO ₂	2 ppbv	10 ppbv	2.0
H ₂ SO ₄ ^a	$1 \times 10^7 \text{ cm}^{-3}$	$2 \times 10^7 \text{ cm}^{-3}$	2.0
OH· ^b	profile 1	profile 1	constant with time
O ₃	50 ppbv	50 ppbv	constant with time and altitude
H ₂ O ₂	0.5 ppbv	1 ppbv	constant with altitude
CCN	900 cm^{-3}	2100 cm^{-3}	3.5
CH ₂ O ^c	1 ppbv	4 ppbv	constant with altitude
$N_{\text{small particle}}$	$\sim 2100 \text{ cm}^{-3}$	$\sim 11000 \text{ cm}^{-3}$	3.5
N_{CCN}	900 cm^{-3}	2100 cm^{-3}	3.5
SO ₄ ²⁻ (small particle)	3.93 pptv	19.7 pptv	3.5
NH ₄ ⁺ (CCN)	1.8 ppbv	9.6 ppbv	3.5
SO ₄ ²⁻ (CCN)	0.9 ppbv	4.8 ppbv	3.5

constant with height, but are depleted by cloud scavenging and chemical reaction. The O₃ is constant throughout the simulation due to its low solubility. Table 4.1 lists the initial surface values of different chemical and aerosol species and the applied scale heights. The SO₂, H₂O₂, O₃, CH₂O, the total Fe concentration and ferric ion concentration, and CCN category mass mixing ratio and number concentration are consistent with published observations and are the same as those of the base cases studied in Kreidenweis *et al.*[1997] and in Chapter 3.

We choose two diurnally averaged OH· profiles for sensitivity studies. OH· profile 1 is from a one-dimensional clear air tropospheric photochemical model by Thompson and

Stewart [1991] for a mid-latitude continental case, and is used for both clean and polluted base cases here. $\text{OH}\cdot$ profile 2 is from the model results of Thompson *et al.*[1991] for a clean continental case, and is used as a sensitivity run. The $\text{OH}\cdot$ profiles are shown in Figure 4.1. The main difference between the $\text{OH}\cdot$ profiles is above 5 km, where $[\text{OH}\cdot]$ in profile 2 is lower by about an order of magnitude. Although a diurnally-averaged $\text{OH}\cdot$ profile is used here, the timing of SO_2 transport and diurnal $\text{OH}\cdot$ variations could affect the H_2SO_4 production rate significantly, either positively or negatively. This study does not examine such interactions but focuses on the effects of variations in SO_2 transport on H_2SO_4 production rates. Using the clear-air $\text{OH}\cdot$ profile overestimates $[\text{OH}\cdot]$ within and below cloud, and may underestimate it near cloud top or above cloud [Ruggaber *et al.*, 1994]. However, as will be shown later, this is not likely to have a significant impact on our findings, since the major impacts of the $\text{SO}_2 + \text{OH}\cdot$ reaction on the aerosol profile occurs in clear air after cloud dissipation.

In the aerosol model, we assume the small particle composition for the base cases to be ammonium sulfate. The small particle mass mixing ratio and number concentrations have the same scale height as the CCN aerosol. The small particle number concentrations are increased by a factor of 5 from the clean to the polluted cases. Appropriate values for small particle number concentration and small particle sulfate mass for the clean and polluted cases are based on Whitby [1978]. The initial H_2SO_4 surface concentration for the clean base case is $1 \times 10^7 \text{ molec cm}^{-3}$, which is in agreement with the measurements of Eisele and Tanner [1993] at a coastal site in Washington State, and is increased by a factor of 2 from clean to polluted. However, as will be shown, the model predictions are not sensitive to the choice of $\text{H}_2\text{SO}_4(\text{g})$ initial condition.

4.2 General features of the simulated cloud dynamics

The sounding case study used here is identical to that in Taylor *et al.*[1997], Kreidenweis *et al.*[1997], and Zhang *et al.*[1998]. The general development and the discussion of the simulated transport patterns of the simulated clouds for the polluted cases are described in more detail in Taylor *et al.*[1997]. As described above in Chapter 2, condensational

growth onto the aerosol will only affect the CCN sulfate and ammonium ion mass mixing ratios, but the CCN number concentration is unchanged. Since the cloud dynamics are most sensitive to the assumed CCN number concentrations, the simulated cloud in this coupled aerosol run will be only slightly different from those of the previous dynamics only and dynamics + chemistry runs discussed in Taylor *et al.*[1997] and Kreidenweis *et al.*[1997]. A two-dimensional depiction of the model cloud for the polluted base case is shown in Figure 4.2, and salient features are summarized in Table 4.2. The precipitation amount that reaches the ground is somewhat smaller in the clean base case than that in

Table 4.2: General features of the simulated cloud dynamics.

	The polluted base case	The clean base case
Cloud lifetime	41 min → 3 h 44 min	41 min → 3 h 24 min
Initial growth stage	41 min → 1 h 11 min	the same as polluted
Mature stage	1 h 11 min → 1 h 58 min	1 h min → 1 h 52 min
Decay stage	2 h 4 min → 3 h 44 min	1 h 58 min → 3 h 24 min
Cloud-top height (maximum)	9.6 km	same as the polluted
Initial growth stage	7.6 km	same as the polluted
Mature stage	9.6 km	same as the polluted
Maximum vertical velocity	7.34 (m s^{-1})	6.98 (m s^{-1})
Maximum liquid water content	3.72 (g kg^{-1})	3.01 (g kg^{-1})
Liquid phase lifetime	41 min → 1 h 42 min	41 min → 1 h 27 min
Ice phase time	1 h 6 min → 3 h 44 min	1 h 6 min → 3 h 24 min
Precipitation time	1 h 42 min → 2 h 13 min	1 h 32 min → 2 h 2 min

the polluted base case, and the sulfate mass deposited is much less in the clean case.

Table 4.3 summarizes a few relevant cloud characteristics for various model times for which output is shown in the following sections. The times are chosen to represent different stages in the cloud evolution and hence in the transport patterns, the chemical composition, and aerosol evolution.

4.3 Base case studies

4.3.1 Redistribution of CCN particles, humidity, and gases

In this subsection, the effects of convective transport and cloud processing on environmental humidity, chemical species and CCN concentration in the mid- to upper-

Table 4.3: Cloud features at selected times used to display model output in the coupled aerosol/chemistry/cloud dynamics model.

Model Time	Cloud Features
20 min	Midway between the initial time and the model cloud formation time
36 min	Just before initial formation of cloud
1 h 42 min	Precipitation just begins to reach the ground in the polluted base case
3 h 44 min	Time of cloud dissipation
4 h	Just after cloud dissipation; no cloud, little vertical motion
5 h	Some time after cloud; little vertical motion
10 h	End of simulations; clear air, little vertical motion

troposphere are examined. Cumulus convection vents unreacted chemical species to the outflow region above cloud top and produces the local maximum concentration there, as observed by Dickerson *et al.*[1987]. Cotton *et al.*[1995] discussed venting of boundary layer air to the upper troposphere by cumulus clouds. Flossmann and Wobrock [1996] simulated a medium-sized warm precipitating convective cloud that vented SO_2 from the marine boundary layer to the free troposphere, and pointed out that residual SO_2 could eventually participate in long range transport. Kreidenweis *et al.*[1997] also simulated a mid-latitude continental cumulus cloud and pointed out that cumulus clouds can redistribute some SO_2 to the upper troposphere; and one consequence of this convective transport appears to be that the aerosol precursor gas (SO_2), once it is transported to the free troposphere from the boundary layer, produces $\text{H}_2\text{SO}_4(\text{g})$ as it is oxidized by $\text{OH}\cdot$. Convection also transports cloudy, cleansed air to the upper troposphere, when CCN particles are nucleation scavenged into cloud droplets to form cloud. In this case study, the CCN source due to release of aerosol particles from evaporation of ice particles is negligible in the upper troposphere between 7 and 10 km, as pointed out by Kreidenweis *et al.*[1997], since most of the ice is ultimately precipitated. The cleansed air has a lower available aerosol surface area, allowing condensable vapor ($\text{H}_2\text{SO}_4(\text{g})$) to build up and eventually exceeds the critical concentration, and thus favoring the nucleation of new particles. Moisture is also lifted to higher altitudes by convection [Perry and Hobbs, 1996], humidifying previously dry layers; elevated humidity is another factor that favors nucleation of sulfuric acid particles.

Figure 4.3 shows the two-dimensional relative humidity fields for the polluted base case at the initial time and after cloud dissipation at 5 h. Initially, there are three maxima, with peak value of 65% at 2.2 km, peak value of 60% at 4.2 km and peak value of 71% at 7.4 km; and the RH at 9.4 km is 54%. After cloud dissipation, the water vapor reaches a maximum in the middle of the domain, where the cloud had formed, with peak RH of 85% at 5.6 km. Some moisture is also brought up by convection to the 9–10 km height; the RH at 9.4 km in the center of the domain is increased to 60%. It will be seen later that new particle formation is predicted at that location. The redistributed moisture is between 40 and 110 km in the horizontal at the end of the model run, because the initial horizontal mean wind is set to zero, and mean horizontal advection is not considered in our model study. After 5 hr, the air is a little drier around 9–10 km, which leads to a reduced half-domain mean value of RH (not shown).

Figures 4.4a-b show the CCN aerosol concentrations at different times for the polluted base case. At 1 hr 42 min (the same time as Figure 4.2), CCN are activated as cloud droplets and depleted from the cloudy region, and precipitation begins to scavenge some CCN below cloud. When CCN are nucleation scavenged into cloud droplets, some of the cloud droplets undergo microphysical transformation to precipitation drops and ice particles, and the CCN contained in these hydrometeors are permanently removed by wet deposition. The CCN-depleted air is further transported upward at 3 hr 44 min, as shown in Figure 4.4b. By the end of the simulation, the CCN concentrations in the formerly cloudy region around 4–7 km are partly recovered due to cloud droplet evaporation and diffusion processes, but the CCN-depleted region between 7–10 km, where the ice phase formed and precipitation removal of the CCN was most effective, remains.

4.3.2 Particle nucleation via $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ pathway

Particle nucleation rates via the $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ pathway are increased at lower temperature, higher humidity, and lower preexisting aerosol surface area [Hegg *et al.*, 1990; Perry and Hobbs, 1994; Weber *et al.*, 1996]. The nucleation rate is very sensitive to fluctuations of temperature and humidity [Easter and Peters, 1994; Kerminen and Wexler, 1996]. Around 9.2 km height, the initial temperature and relative humidity, RH, are -45°C and

51%, respectively. At these conditions, the nucleation rate will increase by an order of magnitude if the RH increases 8–9%, or if temperature decreases 2–3 °C. The vapor concentration needed to produce a nucleation rate of $1 \text{ cm}^{-3} \text{ s}^{-1}$ is often used as a criterion for determining onset of significant nucleation. Wexler *et al.*[1994] obtained the following empirical relation for this critical vapor concentration:

$$C_{crit,H_2SO_4} = 0.16 \exp(0.1T - 3.5RH - 27.7) \quad (4.1)$$

where T is temperature in Kelvin, the relative humidity RH is a fraction, and C_{crit,H_2SO_4} is the critical concentration of H_2SO_4 vapor in $\mu\text{g m}^{-3}$. In the simulations presented here, the initial H_2SO_4 critical concentration is about $2 \times 10^{-4} \mu\text{g m}^{-3}$ or 0.05 ppt at 9.2 km, and $0.29 \mu\text{g m}^{-3}$ or 66 ppt at the surface. The percentage differences between the critical vapor concentrations at 5 hr and 0 hr are shown in Figure 4.5. The critical vapor concentration has been reduced most in the middle of the domain where cloud is formerly present; the critical vapor concentration in most of the large region affected by convection has been reduced significantly. Since the upper regions are also where SO_2 precursor gas has been vented to, a source of H_2SO_4 is also present, enhancing the likelihood of supersaturating $H_2SO_4(g)$ and thus nucleating new particles.

In the polluted and the clean base simulations, we are focusing on the effects of the conditions initially, before cloud formation, and after cloud dissipation on particle nucleation. There is no particle nucleation inside cloud, since any $H_2SO_4(g)$ transported or produced is scavenged into cloud hydrometeors immediately. After cloud dissipation and SO_2 redistribution, the gas phase oxidation reactions must proceed for some time to build up enough $H_2SO_4(g)$ for nucleation. Thus the following results at 4 and 10 hr are discussed.

Figures 4.6a-d show the half-domain mean vertical profiles in the polluted base case of the rates of the processes affecting $H_2SO_4(g)$ mass mixing ratio: H_2SO_4 gas-phase chemical production rate, the condensation rates onto both particle modes, and the nucleation rate. The half-domain mean is defined as the 50–100 km domain average. Figures 4.6a and b show the initial conditions and conditions just before cloud formation, and Figures 4.6c and

d show conditions after cloud dissipation. Gas-phase H_2SO_4 is rapidly lost to hydrometeors in cloud, which is not shown here. Some SO_2 is redistributed to the upper troposphere by convection, as discussed in Kreidenweis *et al.*[1997]. This leads to the observed peaks in the post-cloud production rate profiles at 9–10 km. At all altitudes, nucleation and condensation processes both compete for H_2SO_4 vapor produced from $\text{SO}_2 + \text{OH}\cdot$. The loss rate due to condensation onto aerosol particles always dominates below 6 km, whereas the loss rate due to nucleation dominates around 9–10 km. By comparing the initial condition, Figure 4.6a, with that at 20 min, Figure 4.6b, we note that the imbalance between loss rates and production rates due to the choice of the initial conditions is quickly adjusted; however, the imbalance between sink rates and production rates (production rates exceed loss rates) between 6–8 km after cloud dissipation is adjusted more slowly, as shown in Figure 4.6c and d. This occurs because CCN and small particles are scavenged and removed by cloud processing, and the condensational sink rebuilds only slowly. Also, the critical $\text{H}_2\text{SO}_4(\text{g})$ concentration for nucleation is relatively high at this level, and the production rate is too slow to increase the sulfuric acid vapor to supersaturation. At 9–10 km, the condensation rate onto aerosols is two orders of magnitude smaller and insufficient to balance the $\text{H}_2\text{SO}_4(\text{g})$ production rate; therefore, the concentration of $\text{H}_2\text{SO}_4(\text{g})$ quickly builds up and triggers the nucleation, and the particle nucleation rate nearly balances the production rate around this height, as seen in Figures 4.6c and d. Between 4 and 10 hr (Figure 4.6c and d), the minimum in the condensation rate increases due to new particle production at this height, which in turn increases available aerosol surface area for condensation.

As described in Kreidenweis *et al.*[1997], we use the conservative Tracer 2 (initially set to the CCN number concentration, but without any source and sink terms) to isolate the effects of convective transport on the CCN number concentration. We do not show simulations in which the initial [CCN] or the activation parameter are changed, because the cloud dynamics are then modified and it is difficult to separate the changes in transport patterns from the changes in condensational sink rate. Instead, the condensational sink onto Tracer 2 is computed, to estimate the maximum possible condensational loss rates for

$\text{H}_2\text{SO}_4(\text{g})$, if the polluted air were vertically transported to higher levels without removal of CCN. In Figures 4.7, the calculated condensation rates onto both Tracer 2 and small particles are compared with the base case condensation rates onto the CCN and small particle modes. Although Tracer 2 is redistributed by the cloud and produces a peak around 9–10 km, the condensation rate onto Tracer 2 is still one order of magnitude smaller than the $\text{H}_2\text{SO}_4(\text{g})$ production rate, therefore, the $\text{H}_2\text{SO}_4(\text{g})$ concentration will still build up. The condensation rate is proportional to the $\text{H}_2\text{SO}_4(\text{g})$ concentration, but before the condensation rate can increase enough to balance the production, the $\text{H}_2\text{SO}_4(\text{g})$ concentration passes the critical value, which leads to new particle formation. Thus the nucleation rate, and not the condensation rate, eventually balances the production rate around 9–10 km (Figure 4.6d). Higher concentrations of unactivated particles than considered here would be needed to suppress the predicted new particle formation in the convective outflow region. Less efficient precipitation of activated particles would also suppress the new particle formation.

The comparison of H_2SO_4 nucleation rates at different times for the clean and polluted base cases is shown in Figures 4.8a-d. At 9–10 km in both cases, the nucleation rate after cloud dissipation has increased by one order of magnitude, compared to the nucleation rate before cloud formation. There is also a weak secondary nucleation rate peak around 7 km. The initial nucleation rate due to the choice of parameters used to set up the model (Figure 4.8a) is insufficient to produce the observed number of small particles at 9–10 km. For instance, at 9.4 km, the initial nucleation rate is about $30 \text{ cm}^{-3} \text{ h}^{-1}$, which could produce a maximum of about 100 cm^{-3} particles at 3 hr 44 min. However, the predicted small particle number concentration is about 1000 cm^{-3} at that time, and is mainly due to convective transport.

4.3.3 Redistribution of small particle concentration

In this subsection, the effects of new particle production and convective transport processes on small aerosol particle concentrations are examined. Convection transports interstitial particles as well as aerosol precursor gases and water vapor to the upper troposphere, regions that formerly had low particle concentrations. Thus both direct transport

and homogeneous nucleation can lead to a significant increase in the number concentration of small particles.

The small particle concentrations at different times for the polluted base case are shown in Figures 4.9a-d. At 1 hr 42 min (the same model time as Figure 4.2), small particles are vertically transported to the upper troposphere by convection, but are bounded within the cloud core area between 60–90 km in the horizontal. The precipitation scavenging of small particles by drops, ice particles, and graupel particles is evident below 3 km in the core region. In Figure 4.9b, at the time when the ice cloud disappears, the air flow containing unactivated small particles is detrained at cloud top, producing a maximum small particle concentration of about 1000 cm^{-3} in the middle of the domain. The minimum in the small particle concentration between 6–8 km is due to the scavenging of small particles by ice and graupel. In Figure 4.9c, 5 hr into the run, this small particle concentration maximum zone extends to 50–100 km in the horizontal and is intensified, with a maximum value of 1800 cm^{-3} in the core area, largely due to the new particle formation process. The new particle production zone is coincident with the height to which unreacted SO_2 is redistributed, as described in Kreidenweis *et al.*[1997], with the redistribution of water vapor, as shown in Figure 4.3, and with the lower available aerosol surface area in the cleansed air, as shown in Figure 4.4. The minimum between 6–8 km is partially replenished, also due to the new particle formation process, as shown in Figure 4.6c. A similar new particle production pattern exists to 10 hr, as shown in Figure 4.9d. The small particle concentration maximum zone has become more prominent, with peak values of 4800 cm^{-3} in the core area, and the minimum zone in the core area between 6–8 km is further replenished.

To separate the effects of the aerosol nucleation process from those from convective transport, condensation, and scavenging processes, we have simulated a no-nucleation run which sets the nucleation rate to zero. The redistribution of small particle concentration is almost unchanged from 3 hr 44 min to 5 hr and 10 hr for the no-nucleation run, suggesting most of the transport is associated with the cloud formation. At 3 hr 44 min, the polluted base case results are close to those from the no-nucleation run, demonstrating that transport contributes most to the small particle concentration profile at this time. At 5

hr and 10 hr, the peak values in the polluted base case are much larger than those in the no-nucleation run, which shows the significant effect of the nucleation process on the small particle concentration in the upper troposphere 1-6 hours after cloud dissipation.

Since the initial CCN and small particle profiles have the same scale heights, Tracer 2 can also be used to examine the transport patterns for small particles in the absence of scavenging losses and nucleation sources. Further, the Tracer 2 and the no- 2 and the no-nucleation run can be compared: Tracer 2 shows only the effect of conservative tracer effect of conservative tracer transport, while the no-nucleation run also simulates the processes of small particle loss to cloud hydrometeors and condensation. The Tracer 2 profiles at 3 hr 44 min, 5 hr and 10 hr are similar, since there is little air motion after the cloud disappears (eddy diffusion is a slow process after cloud dissipation). At 3 hr 44 min and 5 hr, the small particle concentration in the polluted base case is smaller than the Tracer 2 concentration, due to scavenging of small particles by cloud hydrometeors. At 5 hr, although the new particle production process has begun to influence the small particle concentrations, the elapsed time is too short for the small particle concentrations to be replenished to levels comparable to the Tracer 2 concentrations; however, at 10 hr, the small particle concentration is greater than the Tracer 2 concentration, due to sustained nucleation of new particles for a longer period. These comparisons demonstrate that the nucleation of new particles can play a significant role in the observed small particle concentration. They also demonstrate that the observed effects of convection on vertical profiles of particles will vary depending on the time at which such observations are made.

4.4 Sensitivity tests and results

As discussed in the introduction, one of the goals of this investigation is to examine the sensitivities of the vertical redistribution of gases and aerosols to the physical processes which take place in-cloud and in the near environment. We also seek to examine the extent to which findings with respect to new particle formation are general or depend on the choice of model parameters. To test these sensitivities, in addition to the simulations described above, five polluted case simulations are performed, varying the initial values

of the following variables: aerosol composition, $[\text{OH}\cdot]$ profile, aerosol mass mixing ratio, $\text{H}_2\text{SO}_4(\text{g})$ mass mixing ratio, and nucleation rate factor used in the nucleation formula, as listed in Table 4.4. Different aspects of the simulations will be discussed below. We have also varied the initial values of SO_2 and H_2O_2 concentrations for the polluted and clean cases, and discuss their effects on $\text{H}_2\text{SO}_4(\text{g})$ production. Changes in the assumed initial

Table 4.4: Initial conditions of the model sensitivity runs for the coupled aerosol/chemistry/dynamics model.

Simulation	Dynamics and microphysics input	Chemistry and aerosol input
1	same as the polluted base case	polluted case; initial aerosol composition NH_4HSO_4
2	same as the polluted base case	polluted case; $\text{OH}\cdot$ profile 2
3	same as the polluted base case	polluted case; small particle number concentration and mass mixing ratio increased by a factor of 100
4	same as the polluted base case	polluted case; initial H_2SO_4 mass mixing ratio decreased by a factor of 10
5	same as the polluted base case	polluted case; $\text{OH}\cdot$ profile 2, nucleation factor increased by a factor of 10^4
6	same as the clean base case	clean case; surface SO_2 decreased to 1 ppb and surface H_2O_2 increased to 1 ppb
7	same as the clean base case	clean case; surface SO_2 the same and surface H_2O_2 increased to 2 ppb
8	same as the polluted base case	polluted case; surface SO_2 decreased to 2 ppb and surface H_2O_2 increased to 2 ppb
9	same as the polluted base case	polluted case; surface SO_2 decreased to 5 ppb and surface H_2O_2 increased to 5 ppb

CCN vertical profiles are not directly examined, as these would change the cloud dynamics and microphysics, and thus their effects could not be isolated.

4.4.1 Effect of initial aerosol composition

In the first sensitivity simulation, S1, the initial aerosol composition is modified from fully neutralized $(\text{NH}_4)_2\text{SO}_4$ to partially neutralized NH_4HSO_4 . As discussed in detail in Kreidenweis *et al.*[1997], the predicted pH values in the base case polluted cloud were 3.5–5.5, in the range of observations; although pH values in S1 are also within this range, a change in the CCN composition from $(\text{NH}_4)_2\text{SO}_4$ to NH_4HSO_4 would suppress the

aqueous conversion of S(IV) to S(VI) by the pH-dependent O_3 and iron-catalyzed oxidation pathways, since the cloud water is initially more acidic in the latter case. This will increase SO_2 redistribution, and thus increase the nucleation rate and the small particle concentration in the outflow region above cloud top in S1, compared with those in the polluted base run. The normalized (with respect to initial surface value) half-domain mean small particle number concentration for both S1 and the polluted base case at different times are shown in Figures 4.10a and b, and the half-domain mean H_2SO_4 nucleation rates are shown in Figures 4.10c and d. The transport patterns in both cases are similar, since the tracer redistribution is similar (not shown); but the nucleation rate is larger in S1 than that in the polluted base case, since more SO_2 is redistributed. The higher concentrations of the small particles in the outflow region above cloud top in S1 (Figures 4.10a-b), are due to new particle formation from these larger nucleation rates.

4.4.2 Effect of $[OH\cdot]$ profile

The second sensitivity simulation, S2, uses a different $[OH\cdot]$ vertical profile. $OH\cdot$ profile 2 has a much lower $OH\cdot$ concentration above 3 km, as shown in Figure 4.1, and is decreased by 50% around 9 km compared to $OH\cdot$ profile 1. This will affect the rate of the $SO_2 + OH\cdot$ oxidation reaction that produces $H_2SO_4(g)$ in the mid-to-upper troposphere. The half-domain mean H_2SO_4 nucleation rates at different times are compared in Figures 4.11a-d. At the initial time, the nucleation rates for S2 and the polluted base case are the same, since initial nucleation rates depend solely on initial temperature, RH, and $H_2SO_4(g)$ concentration. Since $OH\cdot$ profile 2 has lower concentrations at upper levels and higher concentrations at lower levels, compared to $OH\cdot$ profile 1, at later times, the nucleation rates at higher levels for S2 are smaller than those in the polluted base case, due to the $H_2SO_4(g)$ production rate being smaller. This shows the model is sensitive to $[OH\cdot]$, particularly in the mid- to upper- troposphere. As we noted earlier, including diurnal variations in $[OH\cdot]$ could also have significant impacts, depending on whether maxima or minima in $[OH\cdot]$ coincide with SO_2 redistribution. The production of small particles in the model is not sensitive to the values of $[OH\cdot]$ in the boundary layer, since H_2SO_4 condensation onto preexisting aerosol particles dominates and balances the H_2SO_4 production process.

4.4.3 Effect of initial small particle profile

The condensation rates of $\text{H}_2\text{SO}_4(\text{g})$ onto aerosols depend on the surface area of pre-existing aerosols. In the simulations, most CCN aerosols are removed by cloud processing (microphysical transformation to ice phase and precipitation), and CCN-depleted air masses are brought up to 9–10 km by convection. However, small particles are not nucleation scavenged to cloud drops, but rather are lost by impaction scavenging. In this sensitivity study, S3, the initial number concentration and mass mixing ratio of small particles is increased by a factor of 100, and thus more small particles are transported to higher levels by convection. The objective is to investigate the effect of higher concentrations of redistributed small particles on the predicted nucleation rate at higher levels. Figures 4.12a-d show the half-domain mean H_2SO_4 nucleation rates at different times for S3 and the polluted base case. At the initial time, the nucleation rate is only affected by the initial H_2SO_4 concentration, temperature and RH, thus the nucleation rates for both runs are the same. For the increased initial small particle number concentrations and mass mixing ratio, the nucleation rate at 36 min (the time just before the simulated cloud formed) is suppressed by about one order of magnitude, due to the competition for vapor between condensational growth onto pre-existing particles and nucleation. This is also the case for the nucleation rates below 8 km and above 11 km at later times. However, after cloud dissipation at 5 hr and 10 hr, the nucleation peaks at 9–10 km are not affected by the condensational growth process, which is consistent with results shown in Figure 4.7. Even with increased number concentrations of small particles being transported upward, the condensational growth onto these particles and any remaining CCN at 9–10 km is still not enough to balance the $\text{H}_2\text{SO}_4(\text{g})$ production rate. This leads to a build up of $[\text{H}_2\text{SO}_4(\text{g})]$, which quickly exceeds its low critical values at the low temperatures and high RHs at that altitude, and new particle formation occurs to compensate for the production of $\text{H}_2\text{SO}_4(\text{g})$. From this study, we conclude that the predicted new particle formation at 9–10 km is not very sensitive to the increase of small particle concentration. However, larger increases than examined here could have a greater impact.

4.4.4 Effect of initial $\text{H}_2\text{SO}_4(\text{g})$ profile

We decrease the initial $\text{H}_2\text{SO}_4(\text{g})$ mass mixing ratio by an order of magnitude in Simulation 4 (S4) to test the sensitivity of post-cloud nucleation and resulting small particle concentrations to this variable. At the initial time, the nucleation rate is much smaller in Simulation 4 for the decreased initial $\text{H}_2\text{SO}_4(\text{g})$ mass mixing ratio. However, since the $\text{H}_2\text{SO}_4(\text{g})$ production rate at this height is the same in the two simulations, the $[\text{H}_2\text{SO}_4]$ quickly builds up and the nucleation rate is quickly adjusted at 9–10 km. At later times, there are only minor differences between the two simulations. Thus, the model results are not sensitive to the choice of the initial $\text{H}_2\text{SO}_4(\text{g})$ mass mixing ratio.

4.4.5 Effect of choice of nucleation rate factor

In sensitivity simulation 5 (S5), we increase the nucleation rate factor in the nucleation formula by four orders of magnitude, and choose the lower $[\text{OH}\cdot]$, which is $\text{OH}\cdot$ profile 2, to examine the impact on that case, for which lower nucleation rates are predicted. As discussed above, the production of $\text{H}_2\text{SO}_4(\text{g})$ is ultimately balanced by the $\text{H}_2\text{SO}_4(\text{g})$ loss terms, either nucleation or condensation. At 9–10 km height, the nucleation rate is constrained by the $\text{H}_2\text{SO}_4(\text{g})$ production rate, thus controlling the number of new particles formed. Since temperature, RH and the H_2SO_4 production rate are about the same in the two simulations, the increase in the nucleation rate factor will lower the threshold H_2SO_4 concentration for nucleation, and the $[\text{H}_2\text{SO}_4(\text{g})]$ has to remain at a lower concentration to achieve the same balanced nucleation rate.

Figure 4.13 compares the nucleation rates at different times for S5 and S2. At the initial time, the nucleation rate is increased in S5 due to increased nucleation rate factor (exceeds the production rate, not shown). We also noted this rate in S5 is chopped off (not increase by 10^4) between 7–10.6 km since it is limited by the maximum H_2SO_4 conversion rate ($q_{\text{H}_2\text{SO}_4}/dt$). After cloud dissipation, the nucleation rate at 9–10 km is not modified as expected (larger than that in S2), since it is bounded by the $\text{H}_2\text{SO}_4(\text{g})$ production rate (the same in two cases). Therefore, the nucleation rate peak at 9–10 km has only minor differences between S5 and S2. This result is due in part to our model constraint that

the critical size of the nucleated particles is a constant, independent of $[\text{H}_2\text{SO}_4]$. Allowing variations in the critical size would permit the rate of production of the number of particles to change, although we do not expect this to have a pronounced impact on the results.

It is a little more complicated between 6–8 km after cloud dissipation. At 5 hr, the $\text{H}_2\text{SO}_4(\text{g})$ mass mixing ratios are about the same, but the nucleation rates are larger in S5, and the secondary nucleation rate peak appears earlier in S5 than in S2, as shown in Figure 4.13c. At 10 hr, the nucleation rates between 6–8 km are about the same in S2 and S5, as shown in Figure 4.13d, when the $\text{H}_2\text{SO}_4(\text{g})$ mass mixing ratios are larger in S2. These indicate that when the nucleation rate factor is increased by 10^4 , the actual nucleation rate is not simply increased by 10^4 (by 5 at 5 hr), rather the critical concentration of $\text{H}_2\text{SO}_4(\text{g})$ is lowered, and the nucleation rate adjusts itself more quickly to the environmental changes than without the increase. However, the imbalance between production rates and loss rates still remains in S5 (not shown), which tells us that it is still difficult for the system to achieve the approximate steady state at this height.

The complexity between 6–8 km is because condensation competes with nucleation at these lower altitudes, but is not important at 9–10 km. This competition is altered by changing the nucleation rate factor. Therefore, although the nucleation rates at 9–10 km are not sensitive to the choice of the nucleation rate factor, the secondary peak of nucleation rate at lower altitudes is more sensitive to the choice of this parameter.

4.4.6 Additional sensitivities

We also perform four runs changing the initial values of both SO_2 and H_2O_2 concentrations to investigate their effects on redistribution of SO_2 and the new particle formation in the upper troposphere, summarized in Table 4.4. The relative concentrations of these two gases will strongly affect the extent to which SO_2 can be oxidized in cloud, thus determining how much can be vented to the upper troposphere. Typically, most model studies and observations [Barth *et al.*, 1992; Flossmann and Wobrock, 1996; Hegg *et al.*, 1986; Yuen *et al.*, 1994] suggested H_2O_2 to be 0.5 ppb or 1 ppb for the clean and polluted atmosphere. The runs are consistent with those presented in Chapter 3, and assume 1 ppb and 2 ppb for the SO_2 and H_2O_2 surface concentrations in the clean case (SO_2 is 2 ppb and H_2O_2

is 0.5 ppb in the clean base case), and 2 ppb and 5 ppb for the SO_2 and H_2O_2 surface concentrations in the polluted case (SO_2 is 10 ppb and H_2O_2 is 1 ppb in the polluted base case). Since the conversion of S(IV) to S(VI) in the aqueous phase via the H_2O_2 oxidation pathway is fast and increases as H_2O_2 concentration increases, the increased H_2O_2 concentration in all four cases will reduce SO_2 redistribution in the upper troposphere. In both the 1ppb clean run and 2 ppb polluted run, almost all the SO_2 is consumed in the aqueous reaction and little is left for redistribution in the upper troposphere. In these two cases, the redistribution of small particles is mainly due to convective transport, and nucleation plays a minor role. There are net losses in the whole domain for the small particle concentrations, since nucleation does not compensate the impaction scavenging loss. In S7 and S9, the air parcel residence time in the liquid-phase cloud is not enough to consume all the SO_2 . Some SO_2 survives the aqueous oxidation and is redistributed to higher levels, where it leads to nucleation of the small particles. The net increase of the small particle concentration in the whole domain in S7 is 2.7%, compared to a 3.7% increase in the clean base case. The nucleation rate after cloud dissipation is still higher than that before cloud rate, but is smaller than that of the clean base case. The net increase of the small particle concentration in S9 is 0.6% compared to a 6.8% increase in the polluted base case, and the nucleation rate peak at 9–10 km after cloud dissipation is much smaller.

4.5 Summary and conclusions

A two-moment aerosol evolution model, including condensation, nucleation, and gas-phase production of H_2SO_4 , has been incorporated into a two-dimensional cloud and sulfate chemistry model to simulate the effects of clouds on aerosol redistribution and production in a small midlatitude continental cumulonimbus cloud.

Temperature, relative humidity, pre-existing aerosol surface area, and $\text{H}_2\text{SO}_4(\text{g})$ production rate are the main factors that affect the nucleation rate. For the parameters used in this study, the critical $\text{H}_2\text{SO}_4(\text{g})$ concentration in the upper troposphere is very low, favoring the formation of new particles. When SO_2 is convectively redistributed to this high altitude in the clean and polluted base cases studied, gas phase production of sulfuric acid

vapor, although a small sink for SO_2 , significantly enhances $\text{H}_2\text{SO}_4(\text{g})$ concentration and triggers new particle formation. The nucleation rates increased by one order of magnitude after cloud dissipation compared to before cloud conditions in both the clean and polluted cases, due to convective transport of particle precursor gases, water vapor, and cleansed air to higher altitudes. The nucleation has a prominent effect on the small particle population. It doubles the small particle number concentration at 5 hr, and triples the small particle number concentration at the end of the 10 hr run. A layered structure in the small particle distribution, as observed by Hofmann [1993], also appears in some simulations.

For the choice of parameters used in this study, pre-existing aerosol surface area plays a significant role in suppressing nucleation in the lower troposphere, but only a secondary role for nucleation in a relatively thin layer in the upper troposphere, where the threshold $\text{H}_2\text{SO}_4(\text{g})$ concentration for nucleation is low. The simulations show that sulfuric acid sinks are always dominated by condensation below 6 km and by nucleation around 9–11 km.

The sensitivity tests demonstrate that the predicted small particle concentration in the upper troposphere is sensitive to initial aerosol composition and to the choice of the diurnally-averaged $[\text{OH}\cdot]$ profile. However, the contribution to the enhanced small particle concentration at 9–10 km is unchanged for increased initial small particle concentration, increased nucleation rate factor, and decreased initial $\text{H}_2\text{SO}_4(\text{g})$ concentration, primarily since the simulated nucleation rate at that level is bounded by the gas-phase $\text{H}_2\text{SO}_4(\text{g})$ production rate. A larger nucleation rate factor lowers the critical H_2SO_4 concentration and trigger the nucleation more easily at other levels. In some cases, SO_2 is almost fully consumed by aqueous reaction and is not transported to the upper troposphere. In cases where sufficient SO_2 is transported to cold and/or relatively particle-free regions, if there is a source of $\text{OH}\cdot$ and gas phase production of H_2SO_4 can proceed, nucleation is predicted to occur, leading to enhanced small particle concentration. However, the production of significant concentrations of new particles can be a slow process and may not initially be observed over the aerosol concentrations lifted convectively with the precursor gases. Thus the observation of new particle formation in convectively processed air is expected to depend strongly on the time at which observations are made.

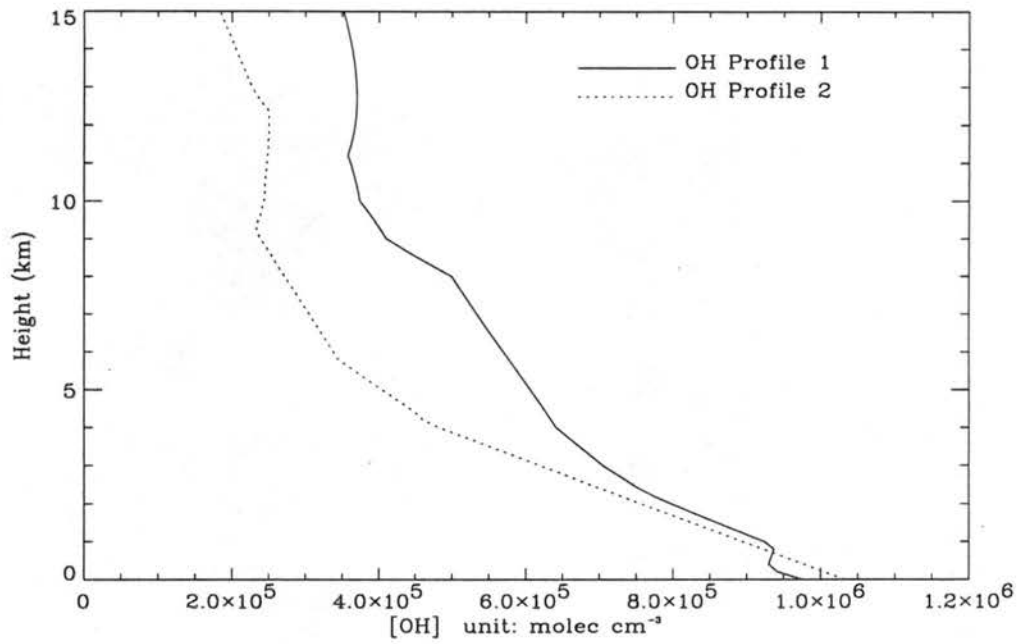


Figure 4.1: The vertical profiles of assumed $[\text{OH}\cdot]$.

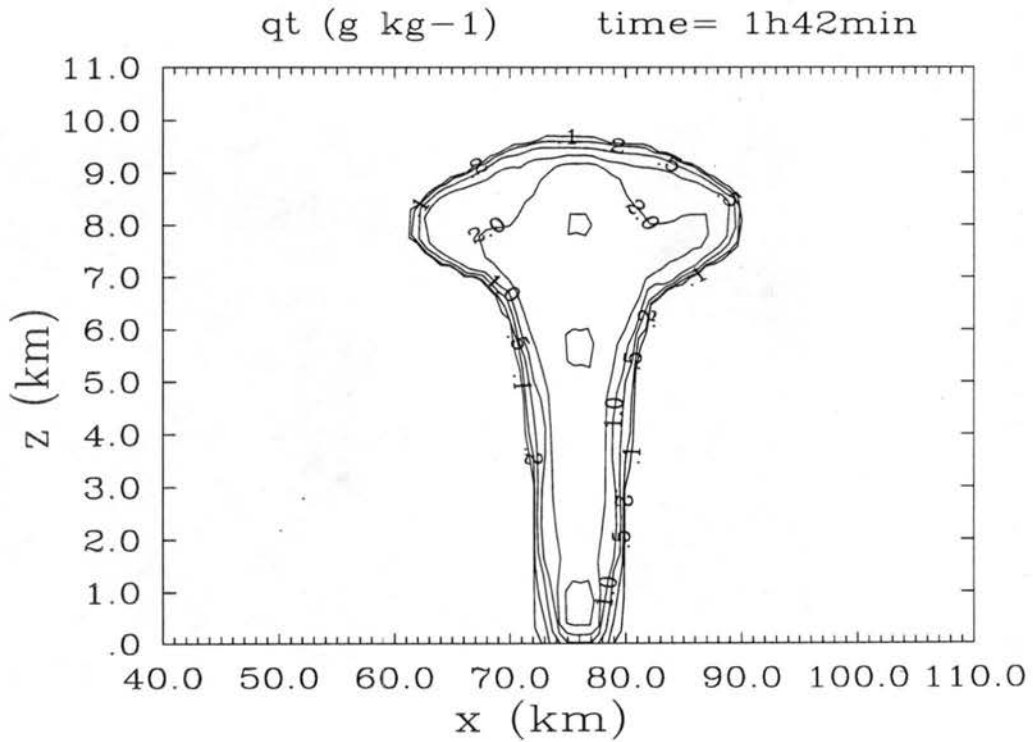


Figure 4.2: Two-dimensional depiction of the model cloud, total water (cloud drops + precipitation + ice + graupel) mixing ratio fields at 1 h 42 min for the polluted base run.

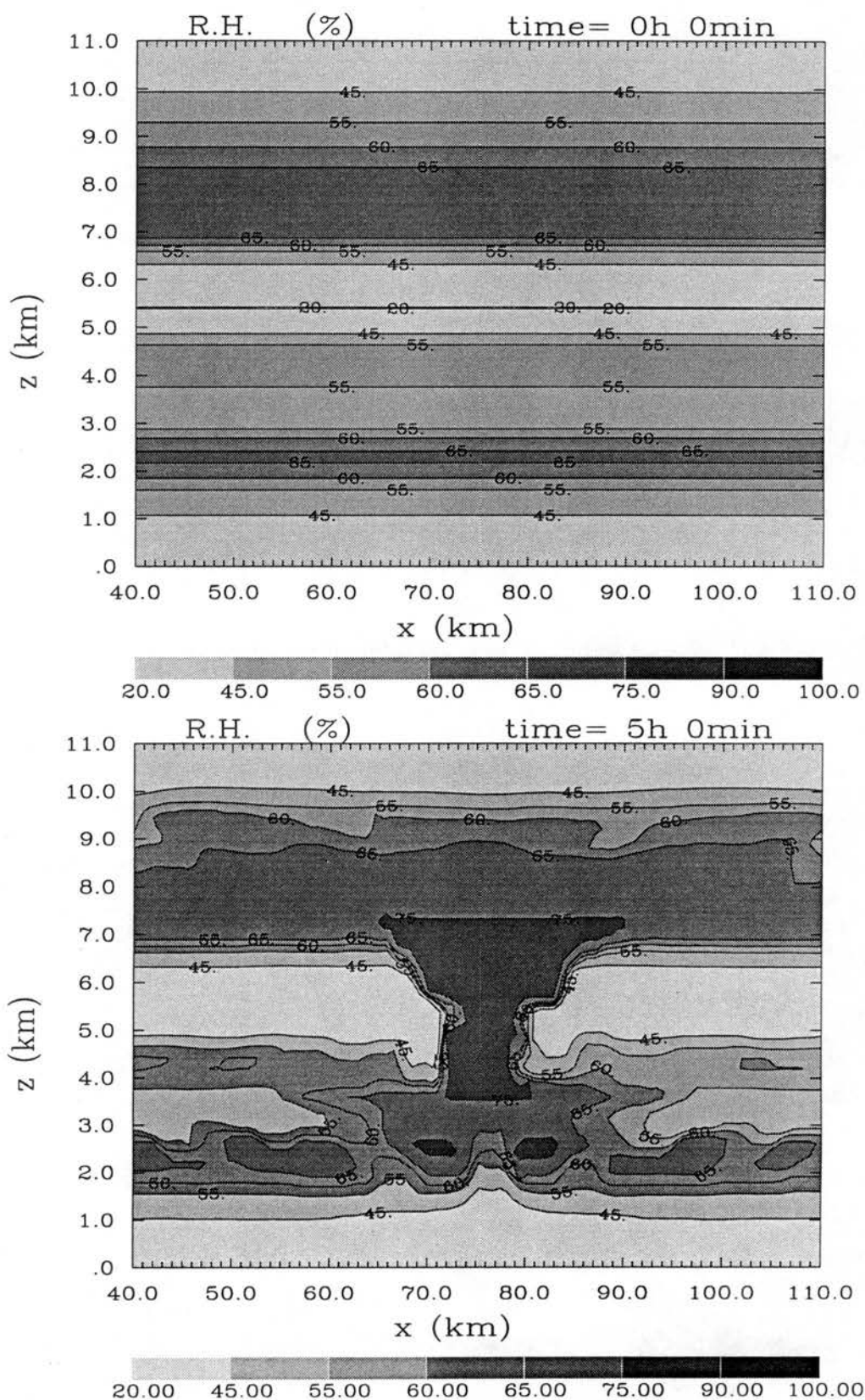


Figure 4.3: Two-dimensional relative humidity field produced by the model for the polluted base run, (a) at 0 h, (b) at 5 h.

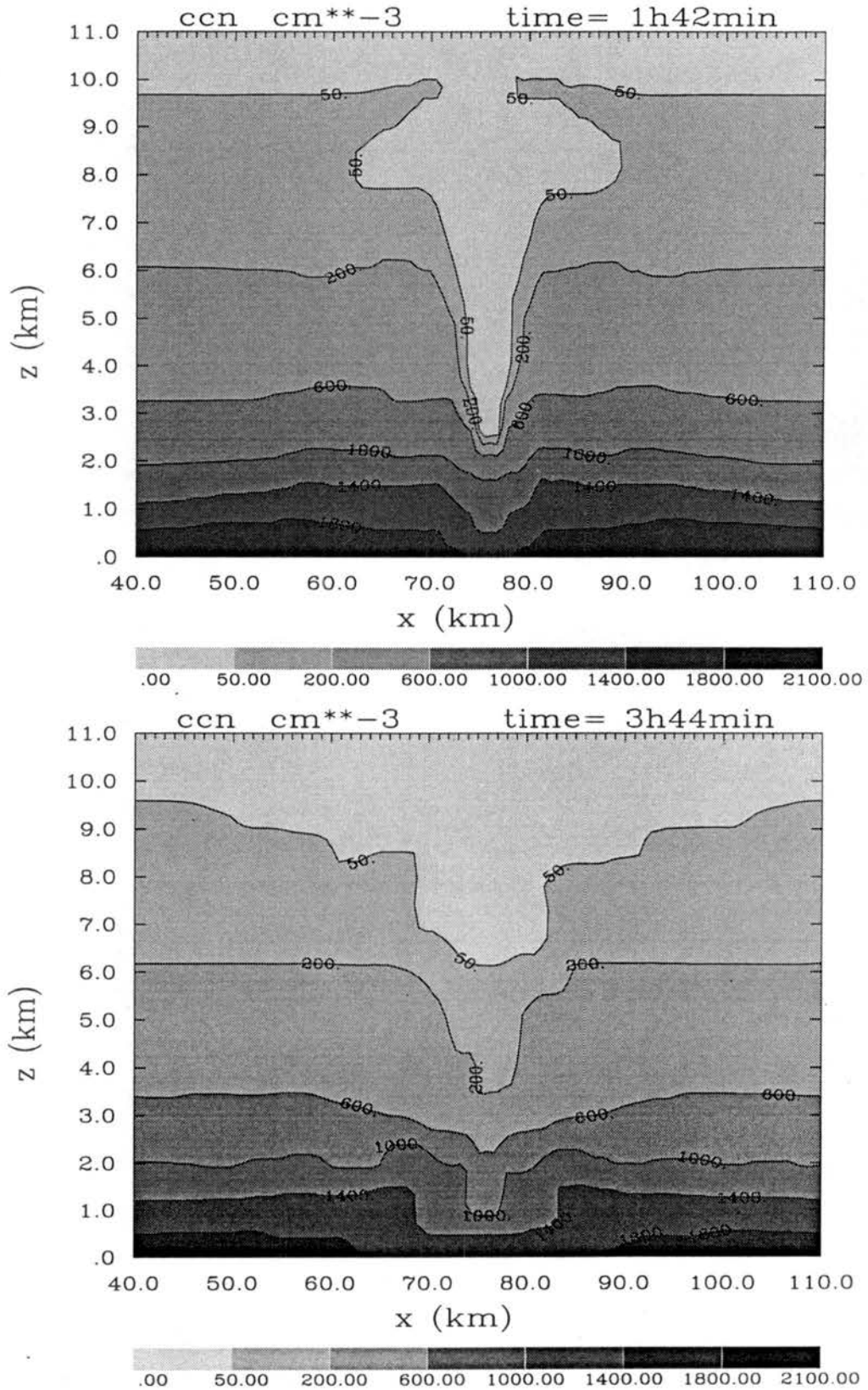


Figure 4.4: Two-dimensional depiction of CCN number concentration for the polluted base case, (a) at 1 h 42 min, (b) at 3 h 44 min.

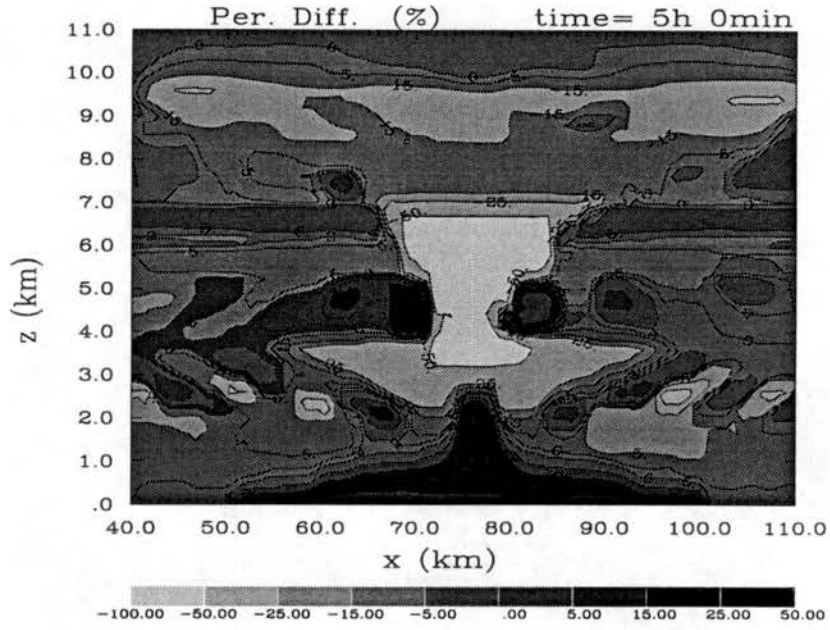


Figure 4.5: The percentage differences between the critical H_2SO_4 vapor concentrations at 5 and 0 h.

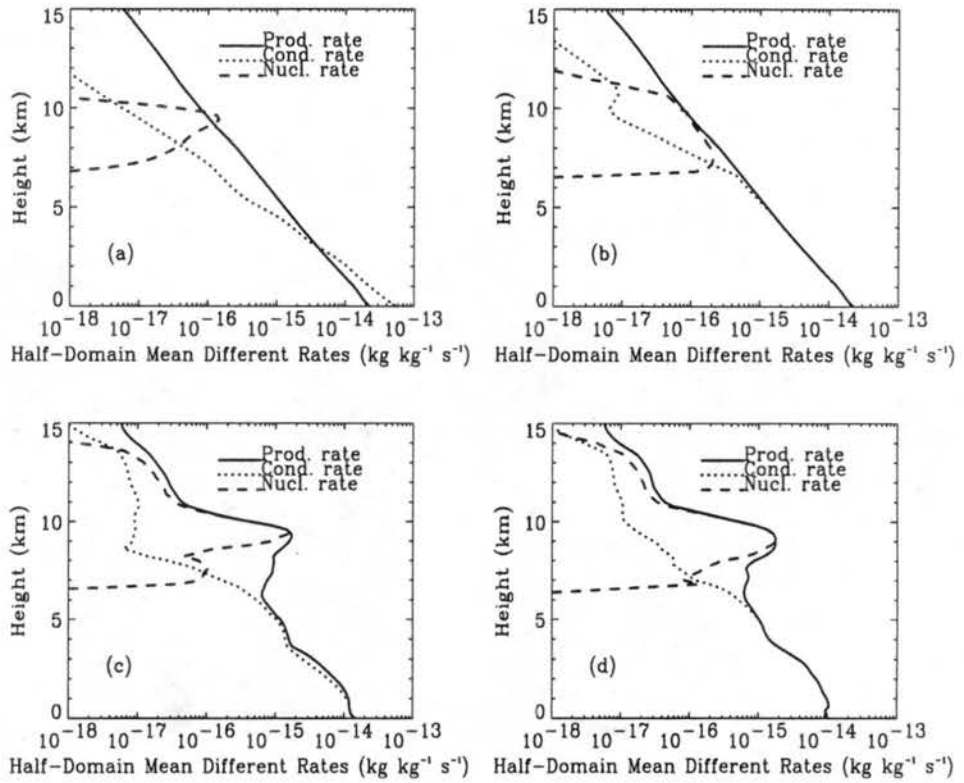


Figure 4.6: The vertical profiles of the half-domain averaged different rates that determine the $\text{H}_2\text{SO}_4(\text{g})$ mass mixing ratio, for the polluted base case, (a) at the initial time, (b) at 20 min, (c) at 4 h, and (d) at 10 h. Half-domain mean is defined as the 50–100 km domain average.

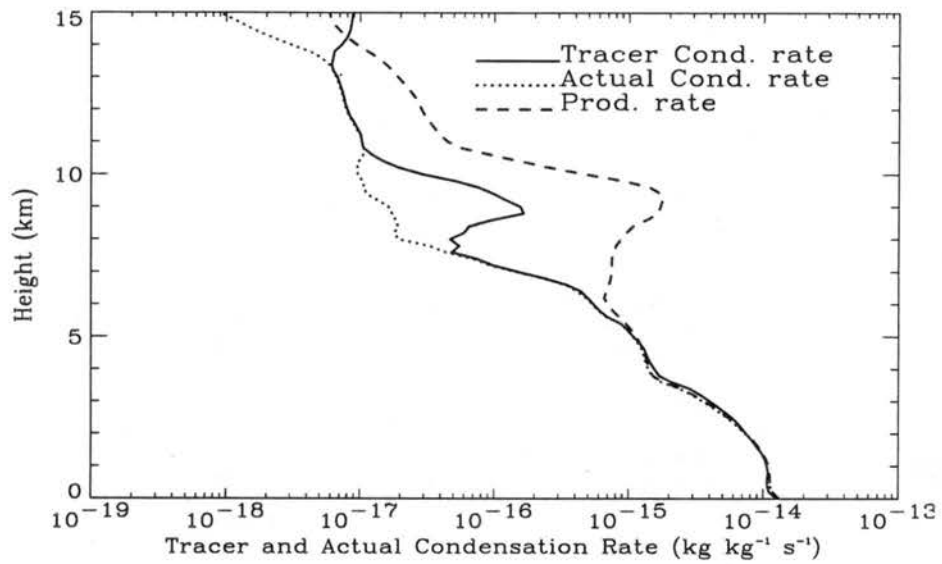


Figure 4.7: The vertical profiles of the half-domain mean actual condensation rates and computed tracer condensation rates, for the polluted base case at 5 h.

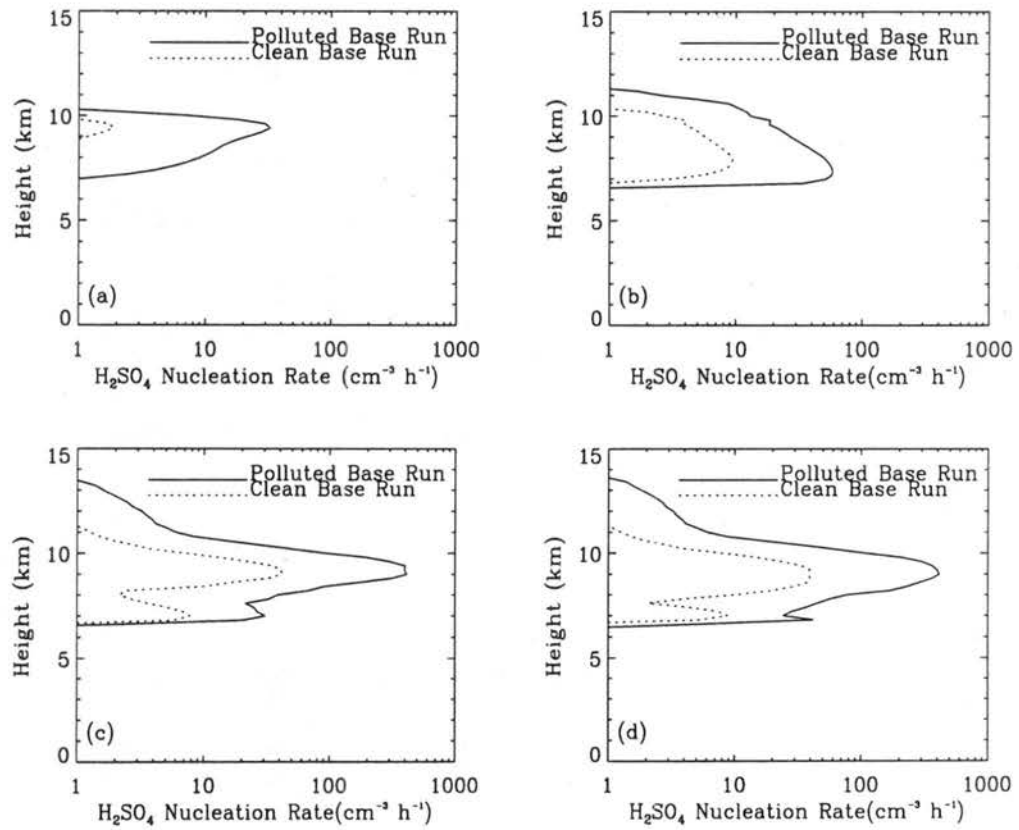
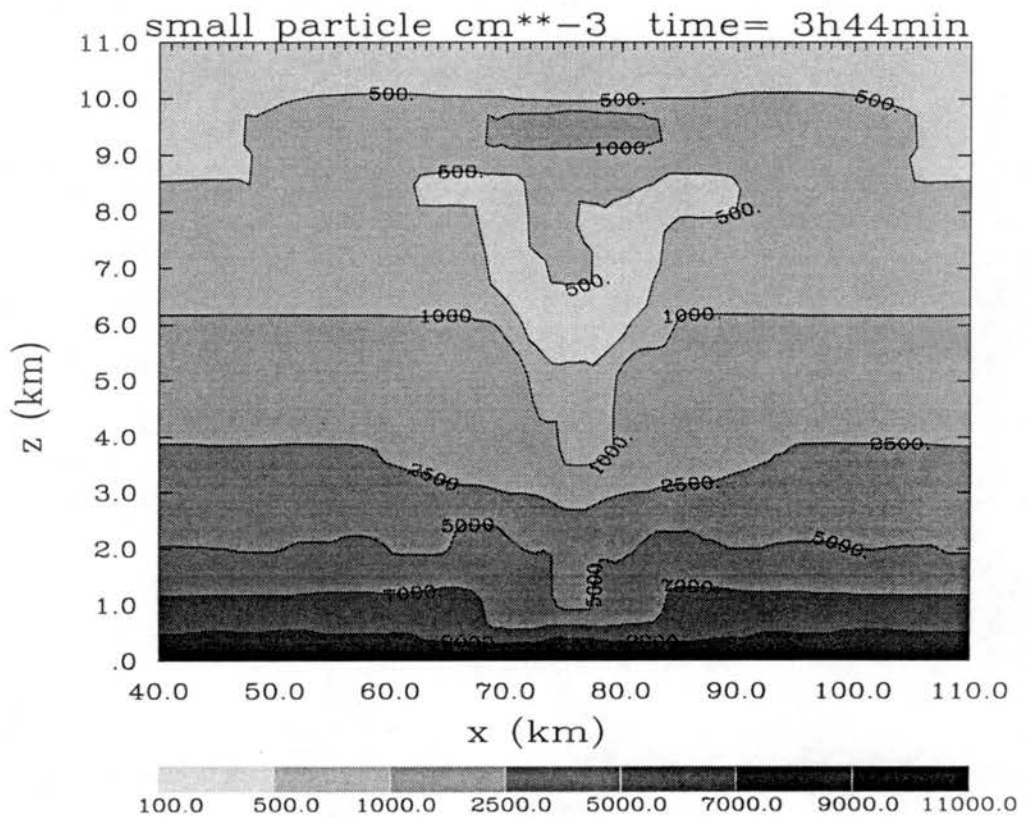
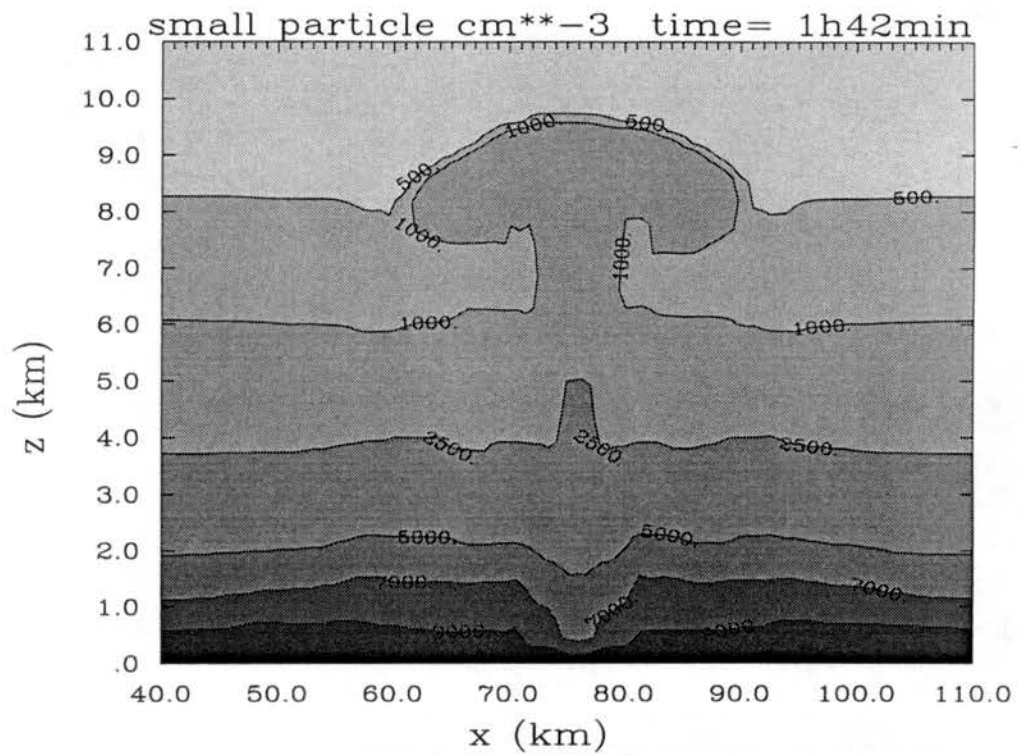


Figure 4.8: The vertical profiles of the half-domain mean $\text{H}_2\text{SO}_4(\text{g})$ nucleation rates for the clean and polluted base run, (a) at the initial time, (b) at 20 min, (c) at 5 h, and (d) at 10 h.



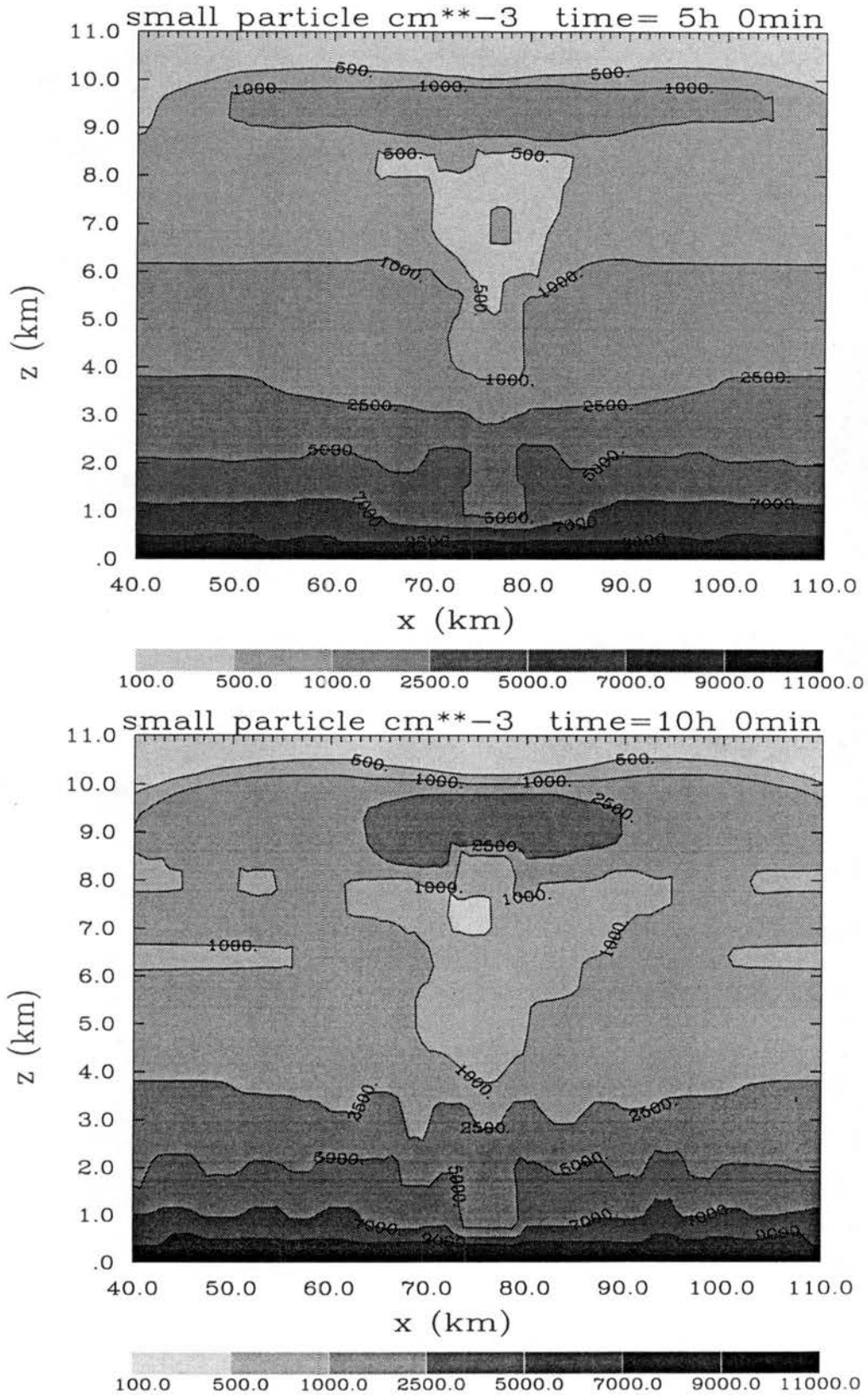


Figure 4.9: Two-dimensional depiction of small particle number concentration for the polluted base case, (a) at 1 h 42 min, (b) at 3 h 44 min, (c) at 5 h, and (d) at 10 h.

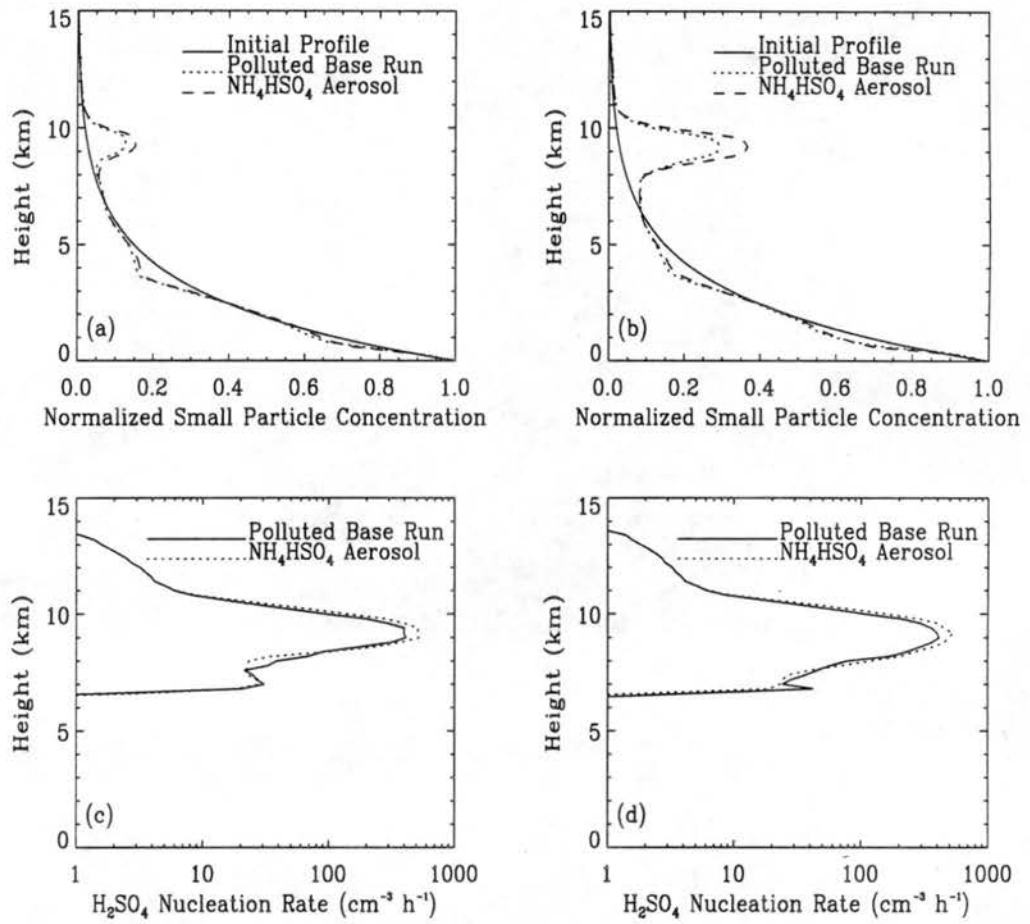


Figure 4.10: The vertical profiles of the normalized (with respect to initial surface value) half-domain mean small particle number concentration, and the half-domain mean H_2SO_4 nucleation rates, for the polluted base case and S1, (a) small particle number concentration at 5 h, (b) small particle number concentration at 10 h, (c) H_2SO_4 nucleation rate at 5 h, and (d) H_2SO_4 nucleation rate at 10 h.

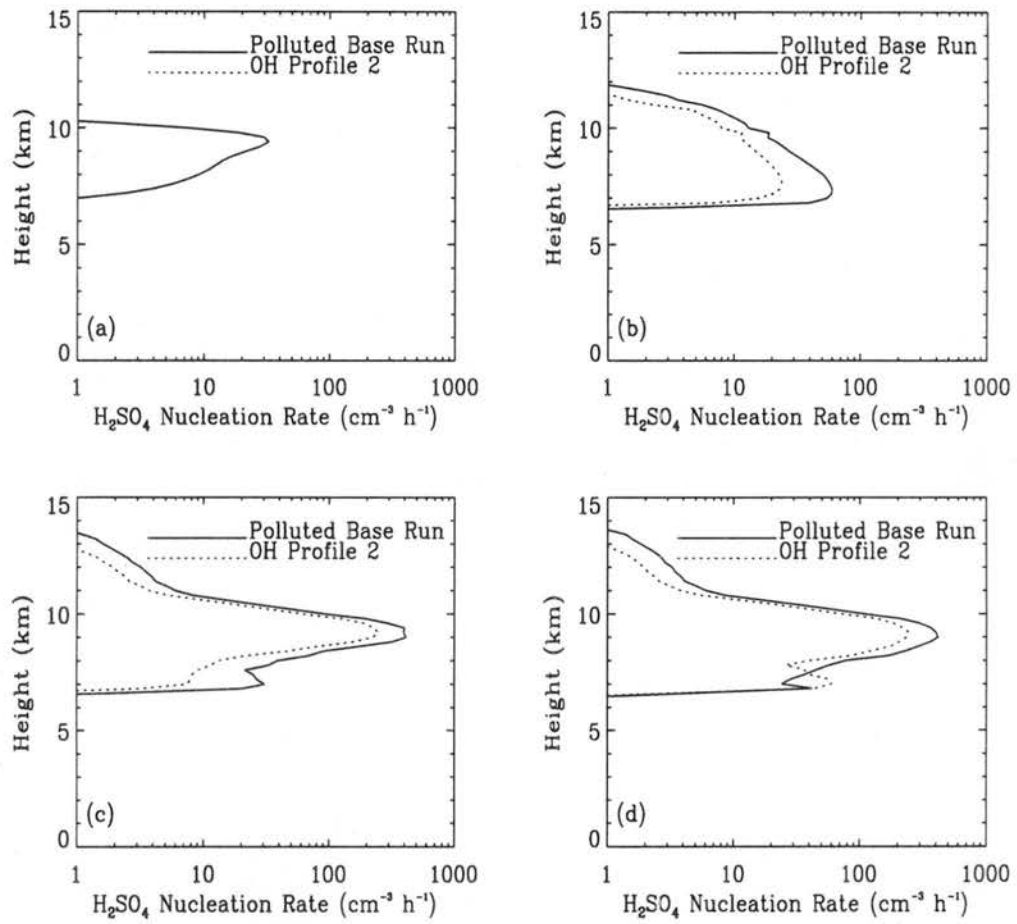


Figure 4.11: The vertical profiles of the half-domain mean H_2SO_4 nucleation rates, for the polluted base case and S2, (a) at the initial time, (b) at 36 min, (c) at 5 h, and (d) at 10h.

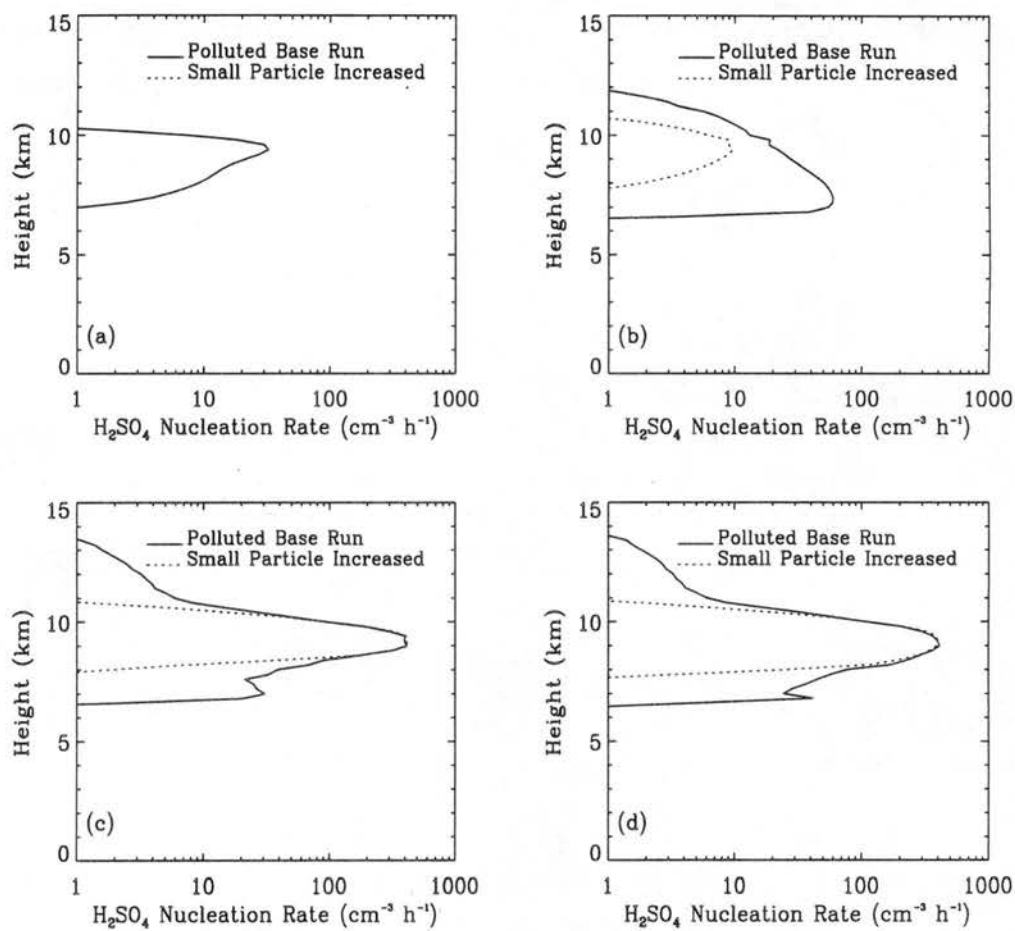


Figure 4.12: The vertical profiles of the half-domain mean H_2SO_4 nucleation rates, for the polluted base case and S3, (a) at the initial time, (b) at 36 min, (c) at 5 h, and (d) at 10h.

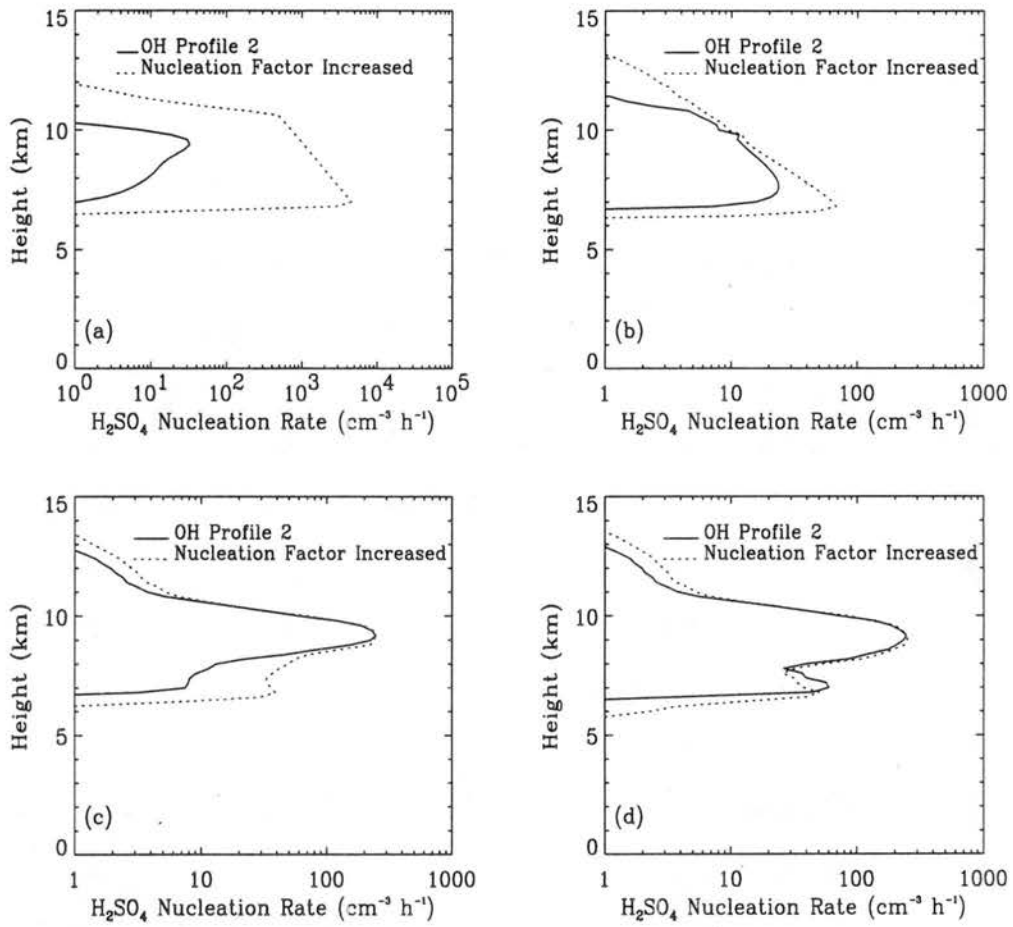


Figure 4.13: The vertical profiles of the half-domain mean H_2SO_4 nucleation rates, for both S2 and S5, (a) at the initial time, (b) at 36 min, (c) at 5 h, and (d) at 10h.

Chapter 5

CLOUD PROCESSING OF AEROSOL AND GASES IN STRATOCUMULUS CLOUDS

In the chapter we focus on the stratocumulus processing of aerosol and gases. Here, we use the TEM framework as a novel approach to study the interaction of chemistry and cloud and the effects of aqueous chemistry on the modification of CCN and drop spectra. The change in effective cloud drop radius and the chemical heterogeneity (cloud-water pH, S(VI) concentration, and composition variation) across the drop spectrum is also examined. We should note that the value of the TEM lies in the ability to accurately simulate chemical and microphysical effects without the attendant difficulties related to cloud dynamical feedbacks.

This chapter is organized in the following manner. In the first section we discuss the initial chemical species and aerosol conditions. The results from the base case and the control run are discussed thereafter. The following section includes a set of sensitivity simulations and the discussion of the effects of variation of initial chemical conditions on the cloud properties and on the difference between a single mean parcel and the TEM of the estimation of S(IV) to S(VI) conversion. The final section of this chapter includes the summary for the TEM work.

5.1 Base case study

5.1.1 Initial conditions

The trajectory set and the initial aerosol size distribution and composition are identical to those used in Feingold *et al.*[1998a]. A time history of a sample of 50 of the 500 trajectories produced by the LES is shown in Figure 5.1. It illustrates the propagation of

Table 5.1: Initial chemical and aerosol fields for the TEM.

Species	base case (H ₂ O ₂ limited)	Sensitivity Test 1 (SO ₂ limited)	Sensitivity Test 2 (NH ₃ /SO ₂ >2)	Sensitivity Test 3 (Initial CCN=150 cm ⁻³)
SO ₂	2 ppb	2ppb	2 ppb	2 ppb
H ₂ O ₂	0.3 ppb	2.5 ppb	0.3 ppb	0.3 ppb
O ₃	30 ppb	30 pb	30 ppb	30 ppb
NH ₃	1 ppb	1 ppb	4.05 ppb	1 ppb
HNO ₃	0 ppb	0 ppb	0 ppb	0 ppb
aerosol	$N_{CCN}=50 \text{ cm}^{-3}$, $r_g = 0.05 \text{ } \mu\text{m}$, $\sigma_g = 1.8$, lognormal, (NH ₄) ₂ SO ₄ , mass range: $1 \times 10^{-17} \sim 1 \times 10^{-11} \text{ g}$, 5 size categories: 1 2 3 4 5 initial r (μm) 0.011 0.035 0.11 0.35 1.1 number (cm ⁻³) 2.5 33.26 9.54 0.06 0.79×10^{-5} initial mass (g) 1×10^{-17} 3.16×10^{-16} 1×10^{-14} 3.16×10^{-13} 1×10^{-11}			$N_{CCN}=150 \text{ cm}^{-3}$, the other parameters the same as the base case

these 50 trajectories in the vertical domain. During the first few minutes, the trajectories are confined to their range of initialization, but fill the domain fairly rapidly.

The aerosol population is assumed lognormal with $r_g = 0.05 \text{ } \mu\text{m}$, $N = 50 \text{ cm}^{-3}$ and $\sigma_g = 1.8$, and consists of particles with dry radii of $0.011 \text{ } \mu\text{m}$, $0.035 \text{ } \mu\text{m}$, $0.11 \text{ } \mu\text{m}$, $0.35 \text{ } \mu\text{m}$, and $1.1 \text{ } \mu\text{m}$, respectively. The corresponding initial dry sulfate ion mass concentrations in each size category are $\sim 0.005 \text{ ppt}$, 2.3 ppt , 21 ppt , 4.1 ppt , and 0.02 ppt , respectively. The initial gas-phase chemical fields are different from those used in Feingold *et al.* [1998a] for polluted marine air. We choose Case 5 from Bower and Choularton [1993] as our base case, to simulate a moderately polluted marine environment. The S(IV) to S(VI) conversion in the base case is H₂O₂ limited, where oxidation by O₃ and H₂O₂ both play a role in the S(IV) to S(VI) conversion. In the sensitivity cases discussed later, we simulate a SO₂ limited case, where oxidation by H₂O₂ dominates the S(IV) to S(VI) conversion, and we also simulate a case where the initial ratio NH₃/SO₂>2, in which oxidation by O₃ boosts and dominates the overall S(IV) to S(VI) conversion. The initial values of gas phase SO₂, H₂O₂ and O₃ concentrations for the base case and the sensitivity simulations are in agreement with observations and other model studies [Bower and Choularton, 1993; Macdonald *et al.*, 1995; Müller and Mauersberger, 1994]. The initial aerosol and gas phase concentrations are shown in Table 5.1.

The output values of cloud-water mixing ratio r_l , and volume-mean drop radius for the TEM (all 500 parcels) for the base case are averaged temporally over the course of the

hour and spatially by binning into 10 m height intervals. The resulting profiles (Figure 5.2) indicate a cloud layer between 500 m and 750 m, exhibiting the commonly observed triangular r_l profile [e.g., Noonkester, 1984]. The volume-mean drop radius also increases with increasing height, implying a constant N profile (not shown) associated with non-precipitating stratocumulus in weakly sheared environments. The peak water mixing ratio is about 0.3 g kg^{-1} and volume-mean drop radius is around $12 \text{ }\mu\text{m}$. These average profiles are similar to those obtained by horizontally averaging the LES output, as discussed by Stevens *et al.* [1996].

5.1.2 pH calculations and drop spectra

Droplets of different sizes experience different gas mass-transfer rates, chemical conversion rates, water growth, and water evaporation rates. Droplets in different parcels also experience different cloud histories (supersaturations, in-cloud residence times, liquid water contents). These differences lead to chemical heterogeneities in the drop population. Some previous modeling studies have assumed size-dependent composition for the initial aerosol population. Those simulations suggest that larger drops tend to have higher pH compared to small drops, mainly because the composition of the particles on which those larger drops formed is more basic (e.g., sea salt) [Hegg and Larson, 1990; Hegg *et al.*, 1996; Gurciullo and Pandis, 1997]. In contrast, here we assume a size-independent initial aerosol composition. Thus, pH differences between larger and smaller drops are due to the contributions from dilution (droplet diffusional growth) or evaporation, size-dependent gas uptake and chemical conversion, and parcel in-cloud time history. To separate the contributions from microphysical and chemical processes to the pH inhomogeneity among the droplets, we perform a control run which simulates only the effect of microphysical processes on pH by setting to zero all the chemical reaction rates and gas and aqueous phase exchange of chemical species. However, the incomplete dissociation of N(III) and S(VI) in the aqueous phase is computed.

The computed pH values averaged over the last 10 minutes of the control run simulation are plotted as a function of drop size in different cloudy layers in Figure 5.3a. The

cloud top is slightly above 735 m, and the cloud base is slightly below 510 m in this simulation (Figure 5.2a). Therefore all layer averages are taken in cloud. To ensure collection of a sufficient sample for the large droplets, we sample to a drop-size grid that triples the mass from one grid point to the next and covers the range from 2 μm to 37 μm in twelve size bins. Those drops with radius greater than 37 μm are sampled to the largest sampling bin, from 25 to 37 μm . The pH values are calculated as liquid water-weighted mean values ($-\log_{10}[\frac{\sum r_{l,i} \times [H^+]_i}{\sum r_{l,i}}]$) over the last 10 minutes of the simulation, and over each 75 m height interval, and plotted at the mid-point of each sampling bin. Thus each data point represents an average pertaining to those drops that fall into the given size and height range. Only averages having mean $r_l > 0.9 \times 10^{-11} \text{ g g}^{-1}$ are included. The average S(VI) concentration (proportional to solution molarity) for each size interval is plotted on the right axis in Figure 5.3a. In Figure 5.3b, the average dr_l/dr (i.e., the total water collected in that size interval divided by the number of parcels sampled and the bin width) is plotted against drop size. Because the control run only simulates microphysical processes, Figures 5.3a and b demonstrate the effects of droplet growth, evaporation, and microphysical environment on the pH calculation and drop spectra.

The pH and solute concentration are inversely related (Figure 5.3a). The higher the pH, the lower is the S(VI) concentration, and the mode of the pH is correlated with the mode of S(VI) concentration at each cloud layer. The S(VI) concentration versus drop size generally shows a "U" shape, except that at the lowest layer, the S(VI) concentration in the largest drop interval decreases with size, and at the cloud top layer, the right hand side of the "U" shape flattens. The increase in pH and decrease in S(VI) concentration with increasing drop sizes before the r_l mode size has been pointed out in previous single parcel modeling studies [Pandis *et al.*, 1989; Roelofs, 1992]. In the work of Pandis *et al.* [1989], the solute concentration was plotted against both particle and drop sizes, and their smaller size end of the "U" shape was due to evaporating droplets and haze particles. In Roelofs' [1992] study with an entraining parcel model, the decrease of aerosol sulfate concentration with increasing drop size for the smallest drops was due to the activation of entrained aerosol particles. In contrast, in Figure 5.3a, where the S(VI) concentration is plotted

against cloud drop radius, the smaller droplets come from both growing activated particles and evaporating drops and are present because of the differences in parcel histories that have been compiled into the averages reported. Unactivated particles do not contribute to the points in Figure 5.3a since only in-cloud parcels have been sampled and haze particles are smaller than the smallest sampling grid ($2\text{ }\mu\text{m}$).

Comparing Figures 5.3a and b, the minimum in the S(VI) concentration is found in mid-sized drops, near the drop radius where r_l is the highest. The first peak in pH and the minimum in S(VI) concentration tend to locate near the mode of the droplet mass distribution (Figure 5.3b). The "U" shape shifts downward and to larger drop sizes as height increases (Figure 5.3a). This shift corresponds to the height dependence of the droplet mean size (Figure 5.2b). In Figure 5.3b, the maximum r_l also increases with height (as shown in Figure 5.2a).

Both ascending and descending parcels contribute to the in-cloud pH , S(VI) concentration and drop spectra calculations. For a parcel experiencing water supersaturation, the pH in each activated size category decreases with increasing drop size, and the solute concentration decreases more slowly for larger droplets, because larger drops dilute more slowly than smaller drops, as pointed out in other parcel model studies [Gurciullo and Pandis, 1997; Müller and Mauersberger, 1994; Pandis *et al.*, 1990; Twohy, *et al.*, 1989]. For a strongly subsaturated parcel, the smaller droplets evaporate faster than larger drops, so that the pH in smaller drop categories decreases faster, and the solute concentration increases faster for smaller drops. However, for those parcels lingering in slightly subsaturated conditions, the solution effect might be of similar magnitude but opposite in sign to the water subsaturation ratio so that the behavior of each parcel will be different. Thus, the combined effects of dilution and/or evaporation on the pH calculation across the drop spectrum require a fresh interpretation when the drop-size-dependent pH is computed for the ensemble of 500 parcels.

In the control run, although the N(III)/S(VI) ratio is always 2, due to the incomplete dissociation of S(VI) and N(III) species, the pH of the solution is high when the S(VI) concentration is low (or the solution is more dilute), and is low when the S(VI) concentration is high (or the solution is more concentrated). Through analysis of the contribution

to each sampling grid from all parcels and all CCN categories, it is found that the solute sorting affects the pH dependence on drop size at each layer, where smaller drops are usually formed on smaller CCN particles, larger drops are usually formed on larger CCN particles, and the droplets near the dr_t/dt mode size have a combined contribution. This is in part reflects the sampling of drop pH and spectra inside cloud only, where the water saturation is approximately 1; evaporating drops never experience dry enough conditions for the larger drops to shrink to $2\text{ }\mu\text{m}$ size. For example, the equilibrium size for a $1.1\text{ }\mu\text{m}$ dry particle (category 5) is about $2\text{ }\mu\text{m}$ at 90% relative humidity.

In each sampling grid up to the r_t mode, the pH is determined mainly by those drops formed on CCN categories 2 and 3 (which carry the most number of CCN particles) in a growing or evaporating status; thus, the pH increases and $S(VI)$ concentration decreases with drop radius. Most of the drops larger than the r_t mode size have been formed on CCN particles from categories 4 and 5 (which are larger than the CCN number mode size). The pH of cloud drops formed on categories 2 or 3 near the mode should be higher than that formed on categories 4 and 5 and sampled in the next sampling grid. The pH peak thus occurs near the r_t mode, because the drops formed on CCN categories 2 and 3 are more dilute than the larger drops (one to two orders of solute mass difference versus water mass tripling).

There is an anomalous feature in Figures 5.3a and b that bears further explanation. In the lowest layer, the pH of droplets near $15\text{ }\mu\text{m}$ is higher than that of drops near $10\text{ }\mu\text{m}$. This is traced to the influence of one parcel (Parcel 142), which descends through the cloud from the top layer during the last 10 minutes of the simulation. In most parcels CCN categories 2 through 5 are activated, but in Parcel 142, only categories 3 through 5 form droplets. With smaller numbers of activated particles, these drops therefore grow larger ($\sim 15\text{ }\mu\text{m}$, compared with category 3 usually at the mode of the distribution, $\sim 10\text{ }\mu\text{m}$) and thus more dilute. Since CCN category 3 contains more particles than categories 4 and 5, this produces unusually larger number concentrations of larger drops. The contributions from Parcel 142 dominate the pH and $S(VI)$ calculations in the lowest layer, because relatively few parcels with $\sim 15\text{ }\mu\text{m}$ droplets are encountered at that height. In the top

layer, the category 3 particles in Parcel 142 have grown to $\sim 22 \mu\text{m}$ and dominate the calculations at the largest sizes; other parcels have contributions only from categories 4 and 5 at these drop sizes. Although Parcel 142 also contributes to the averages taken over the middle layer, its impact there is masked by the contributions from many other parcels with drops formed on CCN categories 4 and 5 that have $p\text{H}$ and S(VI) concentrations that conform to the general trends discussed above.

Drop spectra have been calculated by averaging the contributions to specific size and height bins from the subset of the 500 parcels that enter cloud during the last 10 min of the simulation. Thus, the average spectrum comprises drop spectra that have had a variety of different growth histories and supersaturation fluctuations. Mazin [1968] showed that turbulent mixing of these drop spectra causes spectral broadening, whereas Korolev [1995] showed that a single parcel that is cycled through cloud numerous times can develop spectral broadening as a result of the irreversibility of the droplet growth equation in the presence of solute and curvature effects. Korolev [1995] concluded that spectra cycled in this manner are broader than their counterparts that have had a single traverse through cloud. The drop spectra in Figure 5.3b appear to be broader than what would be expected from adiabatic growth, and it is possible that the contributions from the numerous cycling parcels are sources of broadening. However, some broadening is due to the 75-m height bin used in the averaging; spectra near the base of a height bin tend to have smaller droplets, while those at the top of the height bin have larger drops so that the average spectrum is broader than the individual component spectra. The presence of parcels with less CCN categories activated will also have the potential to broaden the tail of the drop spectra.

We now look at the combined microphysical and chemical effects in the base case, including gas exchange and reactions, on the chemical heterogeneity of cloud drops. The total r_l for the base case is approximately the same as that in the control run (less than 2% difference). Figure 5.4 is similar to Figure 5.3 but considers both microphysics and chemistry (base case). The cloud-water $p\text{H}$ and S(VI) concentration have a slight height dependence (Figure 5.4a). The $p\text{H}$ values in each size interval generally decrease and S(VI) concentrations increase with increasing height for smaller drops, and reverse these trends

for larger drops. For the combined chemistry/microphysics run, at smaller drop sizes, the lowest cloud layer always has newly activated parcels with higher pH : parcels just entering the cloud for the first time during this period initially have high NH_3 gas concentrations, and contribute to the higher pH values in the lowest cloudy layer. As parcels penetrate further into cloud and S(IV) to S(VI) conversion continues, the pH decreases. In contrast, for larger drop sizes which probably formed on larger CCN particles, since the mean drop size increases with increasing height, as shown in Figure 5.2b, and r_l is the lowest in the lowest cloudy layer, for the same sampling bin, there are the least contributions from CCN categories 4 and 5 in the lowest layer than the other two layers. Thus, those big drops in the lowest cloud layer are more concentrated than their counterparts in the middle and upmost layer, their pH values are lower, and their S(VI) concentrations are higher in the lowest cloudy layer than in the other two layers.

In each cloud layer, the cloud-water pH generally increases with drop size to a maximum, and then decreases with further increases in size, due to solute sorting effect. The pH peak has a tendency to shift to larger drop sizes at higher levels in cloud, and the S(VI) concentration "U" shape tends to shift to larger drop sizes and to have a lower minimum closer to cloud top, in agreement with the control run results (Figure 5.3). Note that the pH peak for each layer has shifted to the next sampling interval, compared with the radius at the pH peak in the control run. This is because chemical reactions are faster at the larger r_l , which counters the effects of dilution and lowers the pH . As in Figure 5.3, the cloud-water pH dependence on droplet size generally agrees well with the solute concentration (or the molarity of cloud water), but is opposite in trend; however, we do not expect a one-to-one relationship as in the control run, due to the fluctuation of N(III) to S(VI) molar ratios. In the base case, the S(VI) concentrations have also increased by one or two orders of magnitude over that in the control run, due to aqueous chemistry.

Drop spectra for the base case are shown in Figure 5.4b. In comparison with the control run, the drop spectra are a little narrower in the lowest and topmost cloud layers at larger drop sizes. This is because parcel 142, which is responsible for the broadened tail in the control run, does not play a role here. In the base case, parcel 142 has category

2–5 activated, instead of 3–5 in the control run, due to the change in the supersaturation field. With the controlled available total r_l for this parcel, all activated CCN categories will compete for water vapor and grow fewer large drops than in the control run.

5.1.3 N(III)/S(VI) ratios

The snapshots of the computed N(III)/S(VI) ratios, where $N(\text{III}) = \text{NH}_3(\text{aq}) + \text{NH}_4^+$, and $S(\text{VI}) = \text{H}_2\text{SO}_4(\text{aq}) + \text{SO}_4^{2-} + \text{HSO}_4^-$, for the drop size range from 8–12 μm , are plotted at different times for three different cloudy layer intervals in Figure 5.5. At a specific time, values are the molar ratios of average N(III) to average S(VI) in each height interval, so that one data point represents all parcels found in that height interval. Data points with less than 10 parcels found in the height interval are filtered out. The liquid water-weighted $p\text{H}$ values are plotted on the right axis. Initially, the N(III)/S(VI) ratios are greater than 2, because gaseous NH_3 dissolves into the aqueous phase more quickly than S(IV) is converted to S(VI). After some time has elapsed, these ratios tend to be between 1.6 and 2. In the lowest cloudy layer, ratios greater than 2 and correspondingly high $p\text{H}$ values appear periodically, showing the strong signals of parcels entering cloud for the first time. Generally, N(III)/S(VI) ratios are the largest, and have the highest variability, in the lowest cloudy layer. This is in part because all the parcels are originally released below cloud between 200 m and 450 m. When parcels enter cloud, NH_3 gas quickly dissolves into the aqueous phase and maintains the O_3 oxidation for several minutes; as S(IV) to S(VI) conversion proceeds in parcels staying in cloud, producing more S(VI) in the aqueous phase, the ratios of N(III) to S(VI) decrease with height. The lowest cloudy layer also has the lowest liquid water content, which restricts the chemical conversions that tend to lower cloud-water $p\text{H}$ and decrease N(III) to S(VI) ratios. In each layer, the decrease in N(III)/S(VI) ratios generally corresponds to the decrease in the $p\text{H}$ values.

The raw unaveraged $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios in each particle size category are plotted as functions of dry particle radius at three different times, and three different 75 m height intervals below the cloud, as shown in Figure 5.6. The particles that have never been activated generally have $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios of 2. In most parcels, the smallest particle size category 1 is never activated. There is some conversion performed on these haze particles

in some parcels, if the ionic strength of these haze particles < 2 M, so that the molar ratios are below 2; however, the slow chemistry on these haze particles with negligible liquid water content has little effect on the addition of S(VI) mass or change of particle size. One parcel at 20 min between 435–510 m, three parcels at 60 min between 360–435 m, and two parcels at 50 min between 285–360 m have all size categories activated, and produce the lowest $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio in the smallest size category in that same parcel. Generally, the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios in small activated particles have large variability and the lowest values, since the added sulfate mass has a more prominent effect on the composition of small particles than on that of large particles. In the base case, particles that have grown to 0.2 and 0.3 μm radius are those for which aqueous phase chemistry has added the most sulfate mass or produced the most pronounced effects on composition and size. In particular, Figure 5.6 suggests that processed particles in the size range 0.1–1 μm are more acidic than larger particles and those smaller particles that have not been processed in cloud.

5.1.4 Oxidation rates and gas depletion rates

From the above discussion the control run and the base case, aqueous chemistry has an impact on drop spectra and chemical heterogeneity. Aqueous chemistry also exerts a measurable influence on CCN spectra, and this will be discussed in sensitivity tests in the next section. Oxidation by H_2O_2 and O_3 pathways contributes to the aqueous sulfur-to-sulfate conversion. It is of interest to examine the relative importance of these two pathways, which depend on the initial chemical species concentration and cloud-water pH.

Figure 5.7a shows the time when each of the 500 parcels first enters the cloud. It is interesting to note that there are almost always new parcels entering the cloud. There are only some small gaps in time, indicating the absence of parcels with first entries into cloud. In Figures 5.7b–d, the oxidation rates contributed by the H_2O_2 and O_3 pathways in the base case are plotted against time for Parcels 2, 39, and 232, chosen randomly from parcels entering cloud during the first 10 min, between 10–50 min, and during the last 10 min, respectively. The times corresponding to these three parcels are also marked in Figure 5.7a with solid diamonds. The oxidation rate for each pathway is the sum of the contributions from each droplet size category. The common feature for each parcel is that the oxidation

rate from the O_3 pathway is always one to two orders of magnitude larger than that from the H_2O_2 pathway for the first several minutes, but then oxidation is dominated by the H_2O_2 pathway for the rest of the in-cloud residence time, regardless of the time of second entry into the cloud. This is because the initial pH is relatively high as gaseous NH_3 dissolves into the cloud droplets, enhancing the O_3 pathway. As chemical conversion proceeds and sulfate is produced, the buffering capacity from the available NH_3 is quickly lost, pH drops, and the O_3 oxidation rate is significantly reduced. In contrast, the H_2O_2 oxidation is insensitive to pH and changes very little, except during the entry into and exit from cloud, as the H_2O_2 is absorbed or outgassed. In the first few minutes in cloud, the H_2O_2 oxidation rate increases with time, since the time scale for the dissolved H_2O_2 to reach equilibrium with its gas phase is much longer than for O_3 . The H_2O_2 oxidation rate decreases slightly with time as reagents are depleted. However, when parcels reenter the cloud for the second time, the H_2O_2 oxidation rate is immediately much higher than the O_3 pathway and remains dominant, since the available buffering agent, NH_3 gas, has already been consumed in the first cycle through cloud, as illustrated in Figure 5.8 for Parcel 2.

Interestingly, when the oxidation rates are averaged over all 500 parcels, the dominance of the H_2O_2 reaction is not evident. Figure 5.7e shows the ensemble averaged H_2O_2 and O_3 oxidation rates over time. For each pathway, we first take the sum of the contributions from each drop size category, and then average over all the parcels in cloud at a given time. Initially, when the mean cloud-water pH is still relatively high (around 5–6), the O_3 pathway is about two orders of magnitude larger than the H_2O_2 pathway; after 20 minutes, the volume-mean pH drops to around 4.5. This low cloud-water pH at the gas-phase concentrations selected for the base case might suggest that the O_3 oxidation is not important. However, from Figure 5.7e, it is seen that the averaged O_3 oxidation rate is in fact always larger than the averaged H_2O_2 oxidation rate, although they converge to the same order of magnitude at later times. Again, this result is explained by the fact that there are almost always new parcels entering the cloud for the first time (Figure 5.7a), and the contributions to the O_3 oxidation from these fresh parcels are superimposed on the

ones with lower O_3 oxidation rates. Thus, the O_3 oxidation is important throughout the simulation in the base case, despite the low volume-mean pH over most of the simulation.

The percentage depletion of gaseous concentrations and the increase in $S(VI)$ relative to initial values are plotted as functions of time in Figure 5.9. These values are calculated from the 500 parcel average, including those parcels that never enter cloud. At the end of the hour, there is a 22% depletion in SO_2 , 1% depletion in O_3 , 39% depletion in H_2O_2 , and 71% depletion in NH_3 ; the sulfate amount is 16 times larger than the original value for the initial CCN spectrum used here. These values and depletion patterns will vary with changes in the initial chemical fields and will in turn affect the total conversion rates, as discussed below.

5.2 Sensitivity simulations and discussion

To investigate the potential for stratocumulus processing to modify aerosol size spectra and drop spectra, we have performed several sensitivity tests to examine the effects of different initial chemical conditions and of different oxidation pathways on the modification of aerosol and drop spectra. To this end, we choose a SO_2 limited case (Sensitivity Test 1, S1), and $NH_3/SO_2 > 2$ case (Sensitivity Test 2, S2), to compare with the base case. An additional sensitivity test is the change in the initial CCN number concentration from 50 to 150 cm^{-3} (Sensitivity Test 3, S3), which affects the drop size dependent pH , because the drop size distribution is different. It could also affect the computed light scattering properties of the stratocumulus cloud and impact subsequent cloud formation on the processed CCN spectrum [Feingold *et al.*, 1998a; Hegg *et al.*, 1996].

The initial chemical and aerosol fields for the sensitivity simulations selected to demonstrate these differences are listed in Table 5.1. In the H_2O_2 limited case (base case), the O_3 and H_2O_2 oxidation pathways both play roles in aqueous conversion; in S1, excess H_2O_2 exists, and the H_2O_2 oxidation pathway dominates; whereas in S2, the excess NH_3 boosts the O_3 oxidation rate. The base case and S2 have common features in that O_3 plays a significant role in the aqueous chemistry. The overall $S(IV)$ to $S(VI)$ conversion in S3 is similar to that in the base case.

As mentioned above and in Chapter 1, one of the goals of this work is to investigate the effects of different initial chemical and aerosol conditions on the differences between an “average” parcel and the ensemble-averaged results. We will discuss these differences later in subsection §5.2.5.

5.2.1 Effects of varying initial H_2O_2 concentration on pH and cloud drop spectra

We vary the initial H_2O_2 gas concentration in S1 such that it is in excess of the initial H_2O_2 . The computed liquid water-weighted pH , mean S(VI) concentration, and mean dr_l/dr are plotted as functions of drop radius in Figure 5.10, which may be compared to the base case shown in Figure 5.4. For smaller droplets, which have probably formed on processed smaller particles through either evaporation or growth, the pH dependence on drop sizes agrees qualitatively with the base case, although the pH is almost a unit lower in S1 due to more S(IV) to S(VI) conversion. However, at larger drop sizes the pH dependence on drop sizes is flattened. This effect is due to the growth of smaller particles to larger drops, which are dilute and contribute to the higher pH , as supported by the low S(VI) concentrations.

Figure 5.10b shows the average drop mass density dr_l/dr as functions of drop radius. A broadened cloud drop spectrum compared to that in the base case (Figure 5.4b) is evident, with significant r_l in drops greater than $20\text{ }\mu\text{m}$ in each cloudy layer(not shown). In the top two layers for S1, the number distribution for the giant cloud drops (larger than $20\text{ }\mu\text{m}$) is greater than $0.001\text{ mg}^{-1}\text{ }\mu\text{m}^{-1}$, and this could play a significant role in triggering the collision-coalescence process and drizzle formation in stratocumulus clouds [Pruppacher and Klett, 1978; Feingold *et al.*, 1998b].

To shed light on this, the unaveraged CCN spectra at three different 75 m height intervals below the cloud, at $t = 50\text{ min}$, are shown in Figure 5.11 for the base case, S1, and S2 (discussed later). Note that what appears to be a single unprocessed size spectrum actually consists of many identical superimposed spectra. In S1, with excess H_2O_2 available and the S(VI) production limited only by SO_2 and the rate of reaction, gaseous SO_2 dissolves into the aqueous phase and is converted to S(VI) whenever parcels

enter cloud. Because the initial H_2O_2 is increased by a factor of 8.3 in S1 compared to the base case, more SO_2 is converted to S(VI) after 50 minutes in S1, resulting in enhanced processing.

In each individual parcel, the largest particles activate first, but their ionic strength is too high initially and little chemistry proceeds in those drops formed on larger particles. Since the environmental gaseous NH_3 concentration is already very low, as these drops grow larger and the ionic strength become smaller, the N(III) inside some larger drops is outgassed as the aqueous and gas phases equilibrate. This quickly brings down the pH values in those drops. Thus, the O_3 oxidation pathway is not favored on the drops formed on larger particles, due to the strong pH dependence of that mechanism.

In S1, H_2O_2 plays a more significant role than O_3 , since the H_2O_2 rate is not strongly pH-dependent. The produced sulfate is thus distributed more evenly across the drop size spectrum, which adds more sulfate mass to the large tail of the initial CCN spectrum than in the base case. This in turn tends to broaden the processed CCN spectrum. The broadened tail of the processed CCN spectrum in S1 allows growth of large cloud drops in each cloudy layer and contributes to the broadening of the cloud drop spectrum. These larger cloud drops are relatively dilute, compared with the base case, which keeps their pH relatively high and their S(VI) concentration relatively low (Figure 5.10a). In the base case, with little sulfate mass added to the large tail of the initial CCN spectrum, dr_l/dr at larger drop sizes is much lower (Figure 5.4b).

5.2.2 Effects of varying initial NH_3 gas concentration on pH and cloud drop spectra

In S2, the initial gaseous NH_3 concentration is increased to 4.05 ppb, so that the initial NH_3/SO_2 ratio is slightly greater than 2. As will be shown later in Figure 5.16 in subsection §5.2.5, this sensitivity test case has a conversion slope similar to that in the base case, with the S(IV) to S(VI) conversion increases sharply in less than 10 minutes. In S2, O_3 plays a more prominent role in the aqueous chemistry due to the excess available buffering agent, NH_3 gas, and in-cloud N(III) to S(VI) ratios are maintained at a value around 2 as time elapses. The overall conversion of SO_2 for the 500 parcels ensemble is

64%, compared to 21% for the base case and 45% for S1. However, the drop spectra are not broadened. As in Figure 5.10, Figure 5.12 shows the mean liquid water-weighted pH , the mean $S(VI)$ concentration, and the average drop mass spectra dr_l/dr for S2. We find that the pH dependence on drop size and drop spectra are similar to the base case, and they are different than S1.

To understand this, the averaged modified CCN radii are plotted against size category at 50 min over the layer immediately under cloud (435–510 m) for the base case, S1, and S2 in Figure 5.13. Categories 1 and 5 have little change and are not shown in the plot. Particles in categories 2 and 3 are substantially increased in size through the mass addition of $S(VI)$ and SO_4^{2-} , with the largest increases in S2 since more $S(VI)$ production occurs in that case. However, category 4, initially $0.35\ \mu m$, is grown the most in S1, although the overall $S(IV)$ conversion is the highest in S2. In S1, the excess H_2O_2 allows conversion to proceed more evenly over the entire drop spectra, while in the base case and S2, oxidation which is dominated by O_3 pathway, is suppressed in the relatively concentrated, low pH large drops, which formed on the larger CCN particles.

As discussed above, those large drops formed on larger particles have little aqueous chemistry due to their high ionic strength, and NH_3 and SO_2 are primarily consumed in drops at the mode size of the spectrum, which have been formed on small particles. When the ionic strength in those drops formed on the largest particles is reduced, almost all gaseous SO_2 and NH_3 have already been consumed, the $N(III)$ in the larger drops is outgassed, and their pH decreases, reducing the effectiveness of the O_3 pathway.

This implies that the sulfate production occurs most strongly near the mode of the initial CCN spectrum in S2, since this is where most of the r_l exists and small particles reside, as is the case in Figure 5.13. Since most of the sulfate mass is added to the mode of the initial CCN spectrum in S2, the relatively large additional mass results in a stronger shift in the mode of the processed CCN spectrum towards larger sizes than in S1 (Figure 5.11 and Figure 5.13), with less mass added onto the tail of the initial CCN spectrum. This strengthened CCN mode size will favor the growth of categories 2 and 3, and inhibit the growth of categories 4 and 5 under certain available r_l , and produce narrow

drop spectra. On the other hand, the broadened tail of the processed CCN spectrum in S1 allows growth of large cloud drops in each cloudy layer and contributes to the broadening of the cloud drop spectra. From the comparison between S1 and S2 one may conclude that the broadening of the processed CCN spectrum and cloud drop spectrum in subsequent cloud cycles will depend not only on the total sulfate produced, but also on the distribution of the sulfate mass across the size spectrum.

5.2.3 Effects of varying initial CCN concentration on pH and cloud drop spectra

In S3, the initial CCN concentration is increased to 150 cm^{-3} with the same initial dry aerosol sizes in the five categories. As in the base case, most CCN are activated, except the smallest particle size category with relatively small number concentration. With approximately the same r_l available, we would expect the mean drop radius to decrease by about $3^{1/3}$ in each cloudy layer; in the top cloudy layer, $r = 8 \text{ }\mu\text{m}$ compared to $r = 12 \text{ }\mu\text{m}$ in the base case. Although the overall S(IV) to S(VI) fractional conversion changes little, the pH dependence on drop size is affected because of the modified drop distribution.

Figure 5.14 shows the computed volume-weighted pH, S(VI) concentration, and dr_l/dr as functions of drop radius for the last 10 minutes. The first pH peak has shifted to a smaller size than that in the base case, as expected, as has the "U" shape of the S(VI) concentration. The pH dependence on drop radius generally has a similar pattern as that in the base case, with the pH peak shifted to smaller sizes. The drop spectrum has also shifted to smaller sizes. There is more liquid water in the larger drop side of the drop spectrum in S3 than that in the base case, for example, more liquid water in sampling interval 6 in S3 than that in sampling interval 7 in the base case, due to the fact that there are tripled numbers of drops in each size category.

5.2.4 Comparison of effective cloud drop radius

The above discussion demonstrates that stratocumulus processing of aerosol and gases has a strong impact upon aerosol and cloud droplet spectra. Here, we investigate the change in cloud optical properties, as represented by cloud droplet effective radius, of

marine stratocumulus clouds, due to the modification of cloud droplet spectra via the aqueous chemistry mechanism.

Figure 5.15 shows the comparison of the time series of the average effective drop radius at the cloud top layer (715–735 m) for different cases. In S3, the initial CCN number concentration is increased to 150 cm^{-3} with the same initial dry aerosol sizes in the five categories. As in the base case, most CCN are activated, except the smallest particle size category with relatively small number concentration. In the same controlled dynamic framework, with approximately the same r_l available, the overall SO_2 depletion barely changes, and the mean drop radius is decreased by about $3^{1/3}$ in each cloudy layer, as pointed out in §5.2.3. In Figure 5.15, the average effective drop radius in the cloud top layer fluctuates between $8.3 \mu\text{m}$ and $12.8 \mu\text{m}$ in the base case, and the ratio of mean effective drop radius in the base case to that in S3 fluctuates around $3^{1/3}$. The comparison between S3 and the base case supports Twomey's hypothesis [1974, 1977] that increased anthropogenic sources of aerosol will result in the presence of greater numbers of CCN, which will produce higher concentrations of cloud droplets and, consequently, more reflective clouds.

With the same initial CCN number concentration input in the base case, control run, S1, and S2, the mean effective drop radius changes little from case to case, which implies that the aqueous chemistry has little direct effect on effective drop radius calculation, since there is no interaction between chemistry and dynamics and the collision and coalescence process is not included in the TEM. In the cases where there is significant collision-coalescence process or drizzle formation due to the modification of CCN spectrum via aqueous chemistry, the boundary layer dynamics and drop number and size distribution will change dramatically, and this conclusion may be different.

5.2.5 The overall percentage conversion of S(IV) to S(VI): TEM vs a single parcel experiencing mean conditions

The TEM offers a more representative description of the processing of aerosol and gases than can be obtained by a single parcel model, as discussed above in §5.1.2 and §5.1.4. Here, we explore further the difference between the TEM and an averaged parcel experiencing mean conditions of the cloudy boundary layer for different chemical initializations. As

Table 5.2: The overall S(IV) to S(VI) fractional conversion (%) computed via various methods, as discussed in the text.

Simulations	TEM (%)	weightd by PDF of in-cloud residence time at mean LWC from Eqn. 5.1		calculated from mean in-cloud residence time at mean LWC			
			%difference	Method 1	%error	Method 2	%error
base case	21.04	22.54	7 %	29.69	41%	23.24	10%
Sensitivity Test 1	45.34	50.53	11 %	65.59	45%	54.07	19%
Sensitivity Test 2	64.29	68.94	7 %	93.02	45%	70.17	9%
Sensitivity Test 3	21.13	22.78	8 %	29.94	42%	23.47	11%

discussed in Feingold *et al.*[1998a], different slopes in S(IV) depletion and different mean in-cloud residence times could affect the difference between “mean parcel” and TEM results.

Although stratocumulus decks can persist for hours or even days, the relevant timescale for aqueous chemistry is the time that a typical air-parcel trajectory spends in cloud. The choice of sensitivity studies is related to the relationship of the time-dependent aqueous conversion to the mean in-cloud residence time, and to differences in the slopes of the time-dependent S(IV) conversion, shown in Figure 5.16 for the average parcel experiencing mean conditions.

The mean conditions are derived from the 500 parcels and are as follows: $T = 280$ K; mean haze and drop sizes of $0.02 \mu\text{m}$, $9.6 \mu\text{m}$, $11 \mu\text{m}$, $14 \mu\text{m}$ and $15.5 \mu\text{m}$ in radius; and mean $r_l = 0.18 \text{ g kg}^{-1}\text{air}$. As shown in Figure 5.16, in the base case, the gaseous SO_2 depletion slows down after 10 minutes; in S1, the gaseous SO_2 depletion steadily increases; whereas in S2, the gaseous SO_2 is nearly depleted within 10 minutes. The base case and S2 have common features in that O_3 plays a significant role in the aqueous chemistry, and they have similar conversion slopes. There is little difference in the S(IV) conversion in the base case and S3.

The results from the average parcel and TEM are illustrated in Table 5.2. The TEM approach determines the overall chemical conversion in cloud by averaging the r_l -, drop size-, and pH- dependent conversion rate c from the ensemble of 500 parcels. It is also possible to estimate the overall conversion by performing the weighting directly [Feingold *et al.*, 1996], using

$$\bar{C} = \frac{\int c(t)f(t)dt}{\int f(t)dt}, \quad (5.1)$$

where $f(t)$ is the in-cloud residence time distribution, called the Probability Distribution Function (PDF) of in-cloud residence time, which expresses the frequency of occurrence of parcels spending time t in cloud during the course of an hour and can be determined by diagnosing the 500 parcels, and $c(t)$ is the time-dependent conversion rate from the mean parcel. This conversion rate cannot be easily determined without some simplifying assumptions. For example, the time-dependent conversions shown in Figure 5.16 are computed for the “mean parcel” conditions, which assume a constant, average r_l , the average drop size spectrum, and a constant mean temperature. Using Equation 5.1 and Figure 5.16, we computed the overall fractional conversions shown in the third column of Table 5.2, which generally compare quite favorably (within 11%) with those derived from the full TEM.

Another method for computing the overall conversion is to diagnose the conversion that occurs after a time τ_c , where τ_c is the mean residence time, defined as

$$\tau_c = \frac{\int t f(t) dt}{\int f(t) dt}. \quad (5.2)$$

Since about 26% of the 500 parcels never enter cloud during the 1-hr simulation time, there are two ways to calculate the overall conversion. Method 1 is to include the 26% out-of-cloud parcels with $t = 0$ in the PDF calculation to obtain the mean residence time. In Method 2, only the fraction of in-cloud parcels is included in the PDF calculation, and this PDF is used to calculate the mean in-cloud residence time for those in-cloud parcels (which should be larger than that calculated from Method 1). The 26% non-cloudy parcels are then accounted for in the overall fractional conversion. The PDFs of in-cloud residence time for Methods 1 and 2 are shown in Figure 5.17, and have been computed using the following:

$$\text{Method 1 : } f(t) = 0.26\delta(0) + N(t)/500 = 0.26\delta(0) + 0.74N(t)/372, \quad (5.3)$$

$$\text{Method 2 : } f'(t) = N(t)/372. \quad (5.4)$$

where $N(t)$ is the number of parcels spending a total time t in cloud, and is obtained by applying the 500 parcel time histories. The mean in-cloud residence time for 500 parcels for Method 1 is $\tau_c = 14$ min, and for Method 2 is $\tau'_c = 18$ min. Note that τ_c is for the entire

boundary layer, whereas τ_c' is only for parcels entering cloud at least once. The fractional conversion $\bar{C}$ inferred from a single size-resolving parcel experiencing mean conditions, using the mean in-cloud residence time from Method 1, is:

$$\bar{C} = c(\tau_c), \quad (5.5)$$

where $c(\tau_c)$ is the conversion rate at time τ_c for the average parcel; for Method 2,

$$\bar{C} = \frac{372}{500} c(\tau_c') = 0.74 c(\tau_c'). \quad (5.6)$$

As also shown in Feingold *et al.*[1998a], using the fractional conversion at the average in-cloud residence time overestimates the extent of cloud processing. The PDF-weighted fractional conversion is the closest to the TEM results, with 7–11% errors, while Method 1 gives the largest errors, up to 45% (Table 5.2). Using Method 2 to calculate the fractional conversion for the mean τ_l gives closer results to the TEM than Method 1. It seems more reasonable to count only in-cloud parcels in calculating the mean in-cloud residence time and the overall chemistry for those parcels, and then to account for both in-cloud and out-of-cloud parcels to get the final fractional conversion, as done in Method 2, since chemistry is only happening in those in-cloud parcels. Note that the steadily increasing conversion slope for S1 (compared to S2, S3, and the base case, for which the conversion flattens before or near the mean in-cloud residence time) results in the largest error when using the single parcel estimation compared with the TEM. We anticipate that the difference between the single parcel estimate and the TEM will get larger for cases in which the mean in-cloud residence time for 500 parcels is shorter than 10 minutes, which is on the fast conversion side of the slope.

It is interesting to note that the differences in estimated chemical conversion discussed above with respect to in-cloud residence times are computed using a size-resolved model of droplet chemistry. As discussed in detail by Gurciullo and Pandis [1997], size-resolved reaction rates are generally higher than those computed for bulk cloud water, and the overall conversions predicted by the two methods can differ by as much as 30. The errors introduced by computing overall conversion assuming a mean in-cloud residence time must

be considered in addition to the differences between size-resolved and bulk cloud-water chemistry. The overall error will depend upon the composition of the aerosol spectrum, the pH dependence of the aqueous pathways, and the relationships of the in-cloud residence time distribution to the time-dependent conversion rates.

5.3 Summary of results

In this chapter, we have utilized the TEM discussed in Chapter 2 to simulate coupled aqueous chemistry and cloud microphysics, and have investigated the effects of variations in the initial chemical fields and initial aerosol number concentration on the chemical heterogeneities across the cloud drop sizes, the broadening of the CCN and drop spectra, the change in the effective cloud drop radius, and the differences in the overall fractional conversion between the TEM and a single parcel experiencing mean conditions. The TEM offers a more representative method of describing the stratocumulus processing of aerosol and gases than does a single parcel model. It is found that the O_3 oxidation rate is always larger than the H_2O_2 oxidation rate in the base case, whereas the volume-mean pH might suggest that H_2O_2 oxidation dominates. Dilution effects usually result in increases in the liquid water-weighted pH with increasing drop size, to a peak pH . The drop size at this peak corresponds to the mode in $S(VI)$ concentration, and is located near the mode of the cloud drop spectrum. In the combined chemistry/microphysics run, the pH peak is shifted to larger sizes than in the control run because of the addition of solute mass.

Both supersaturation fluctuations and aqueous chemistry contribute to the broadening of the drop size distribution. The broadened CCN spectrum that is created by aqueous chemistry in the previous cloud cycle reenters the cloud and produces a broadened drop spectrum, but the magnitude of the broadening depends on the initial chemical conditions. The H_2O_2 oxidation pathway adds sulfate mass evenly and continuously across the drop sizes, while the O_3 oxidation pathway adds sulfate mass near the mode of the CCN spectrum over a relatively short time. The different behaviors of the O_3 oxidation and H_2O_2 oxidation in turn affect the pH dependence on the drop sizes and the magnitude of the broadening of the cloud drop spectrum. In cases where more mass is added onto the large

tail of the initial CCN spectrum, the broadening of the drop spectrum is most evident, and may even trigger the collision-coalescence process and drizzle formation.

An increase in the initial CCN number concentration decreases the volume-mean drop radius, since the available water vapor must be distributed over a greater number of drops. This shifts the mode of r_l and pH peak to smaller cloud drop sizes, which reduces potential drizzle formation. It also has the most prominent effect on the effective cloud drop radius under approximately the same r_l condition.

A single parcel experiencing mean conditions overestimates the fractional conversion of S(IV) compared to the TEM results. Different shapes of the time-dependent conversion and the regions of overlap with the mean in-cloud residence time will affect the magnitudes of the difference between a single mean parcel and the TEM, with the steadily increasing conversion with time inducing the largest error. Including only processed parcels in the fractional conversion calculation for those in-cloud parcels, which then weighted by the non-cloudy parcels, results in less error in the overall fractional conversion than including both processed and unprocessed parcels in the mean in-cloud residence time calculation. The fractional conversion estimated using the distribution of in-cloud residence times convoluted with the time-dependent conversion gives the closest results to the TEM.

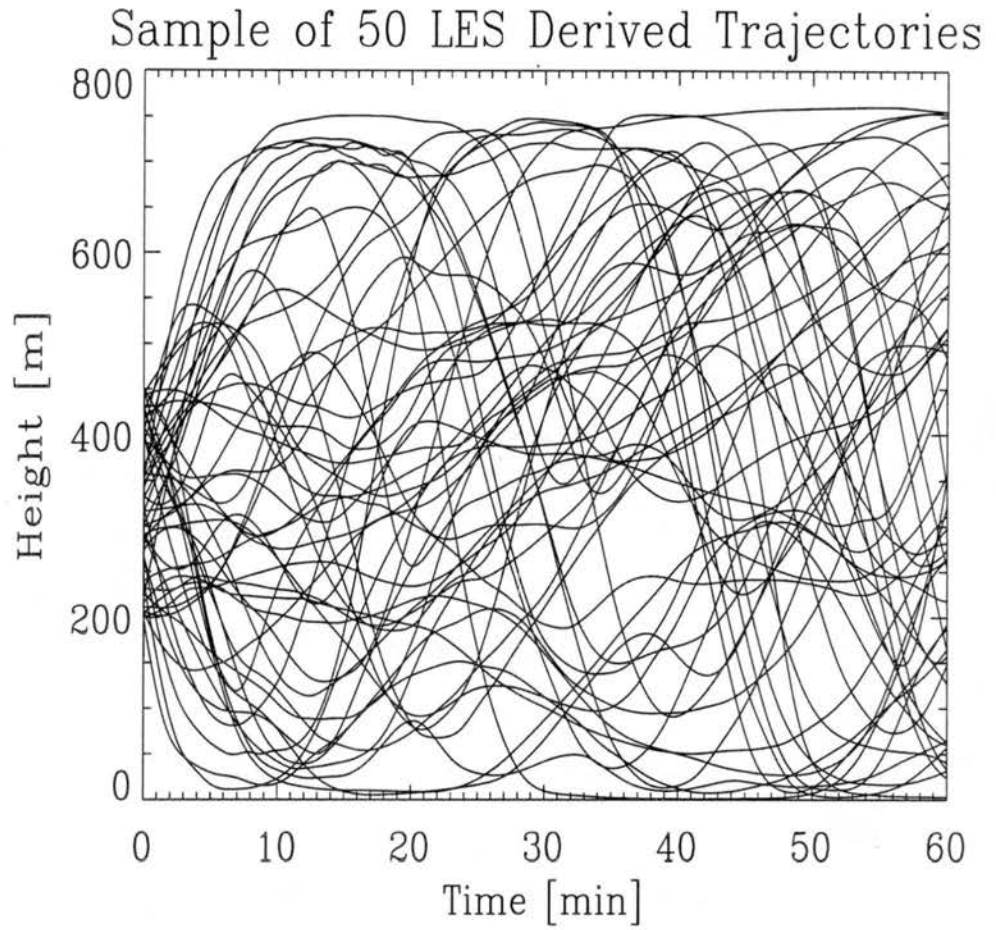


Figure 5.1: The sample of 50 of the 500 parcel trajectories.

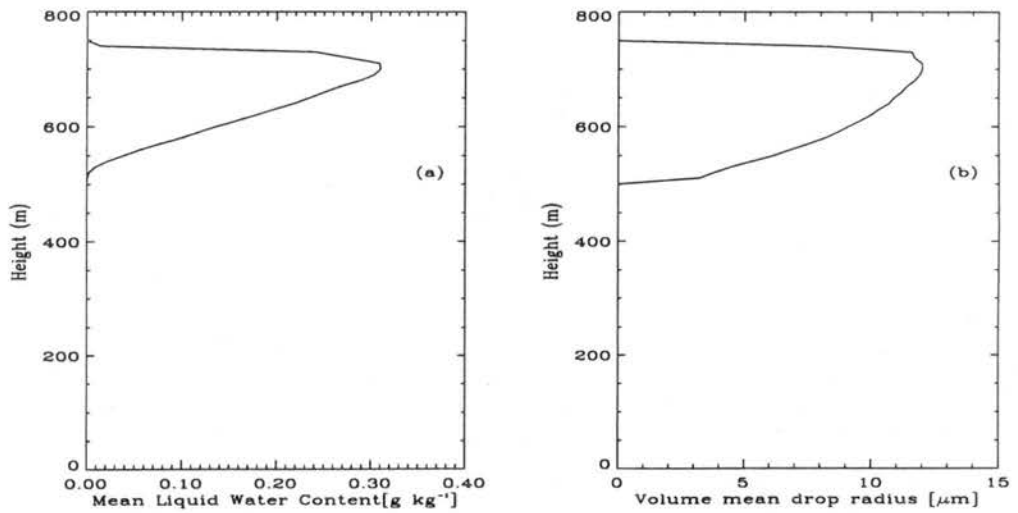


Figure 5.2: The vertical profiles of (a) mean τ_l , (b) volume-mean cloud drop radius for the base case.

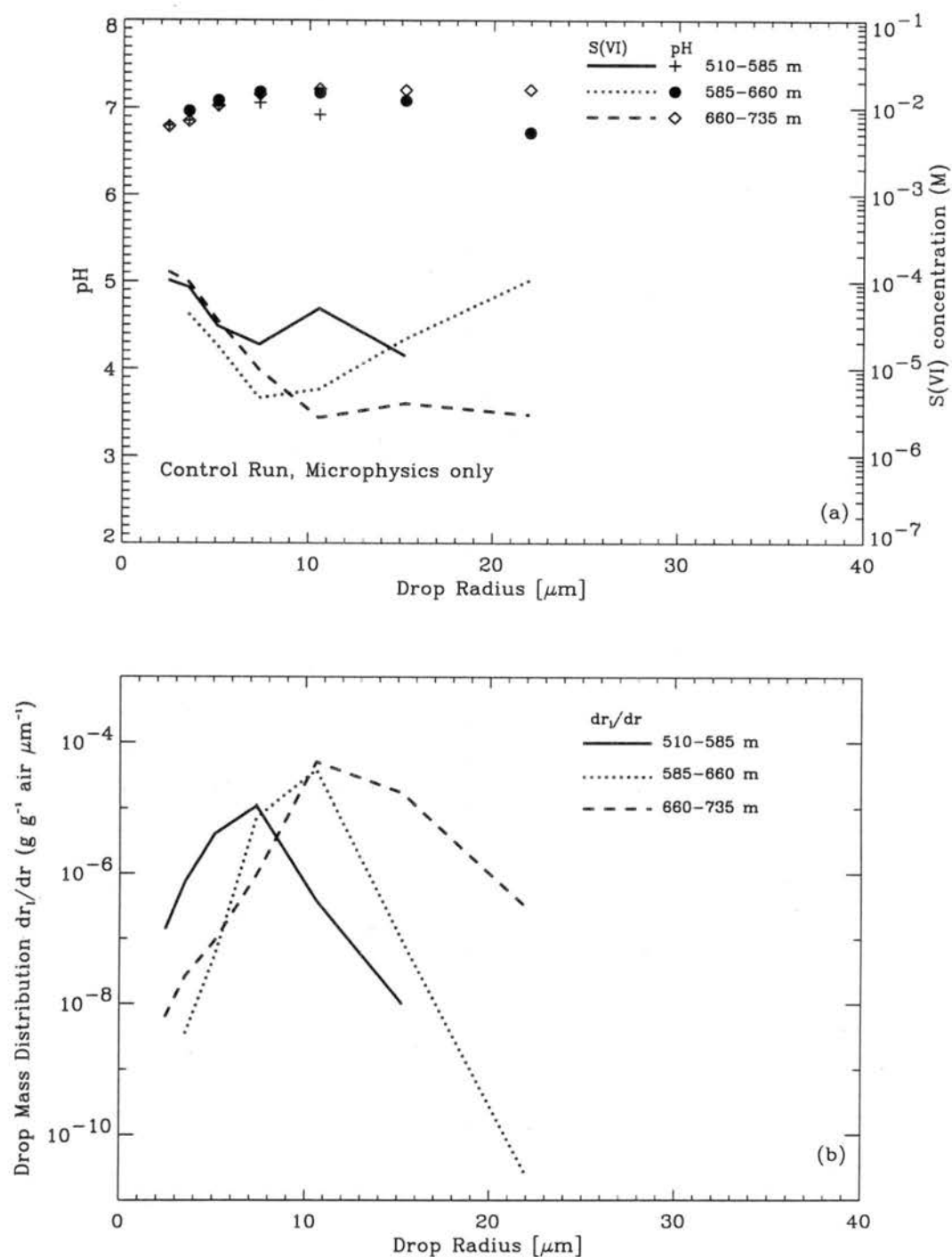


Figure 5.3: (a) The calculated liquid water-weighted mean pH as a function of drop radius for the last 10 minutes for the control run. The right-hand coordinate is S(VI) concentration in each size interval; (b) the drop mass distribution dr_l/dr . Calculations are performed for mass tripling sampling intervals at three different 75 m height intervals (in cloud) as indicated. The lines are for S(VI) concentration or dr_l/dr in each size interval, and the symbols are for pH values in each size interval.

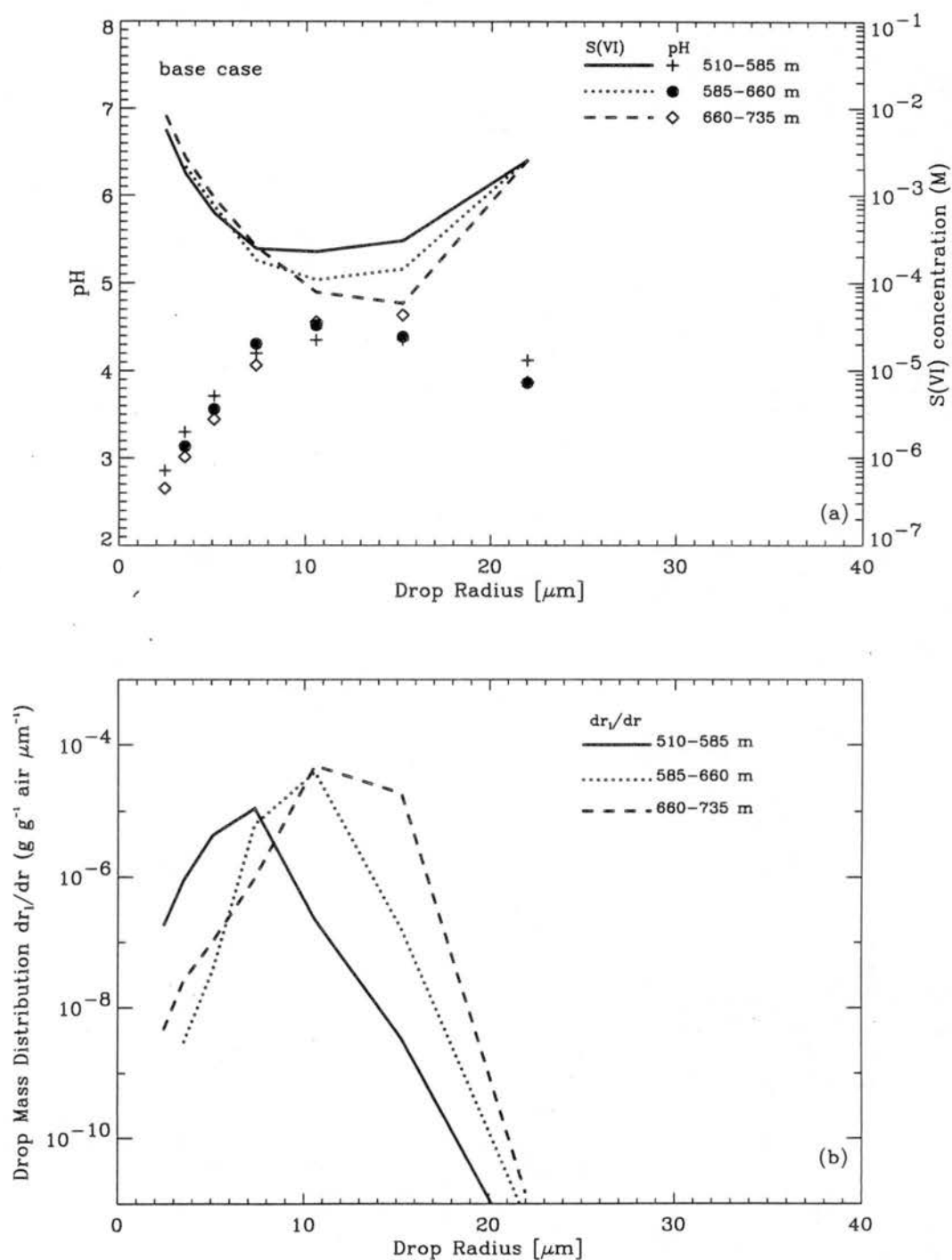


Figure 5.4: As in Figure 5.3, but for the coupled chemistry/microphysics run for the base case.

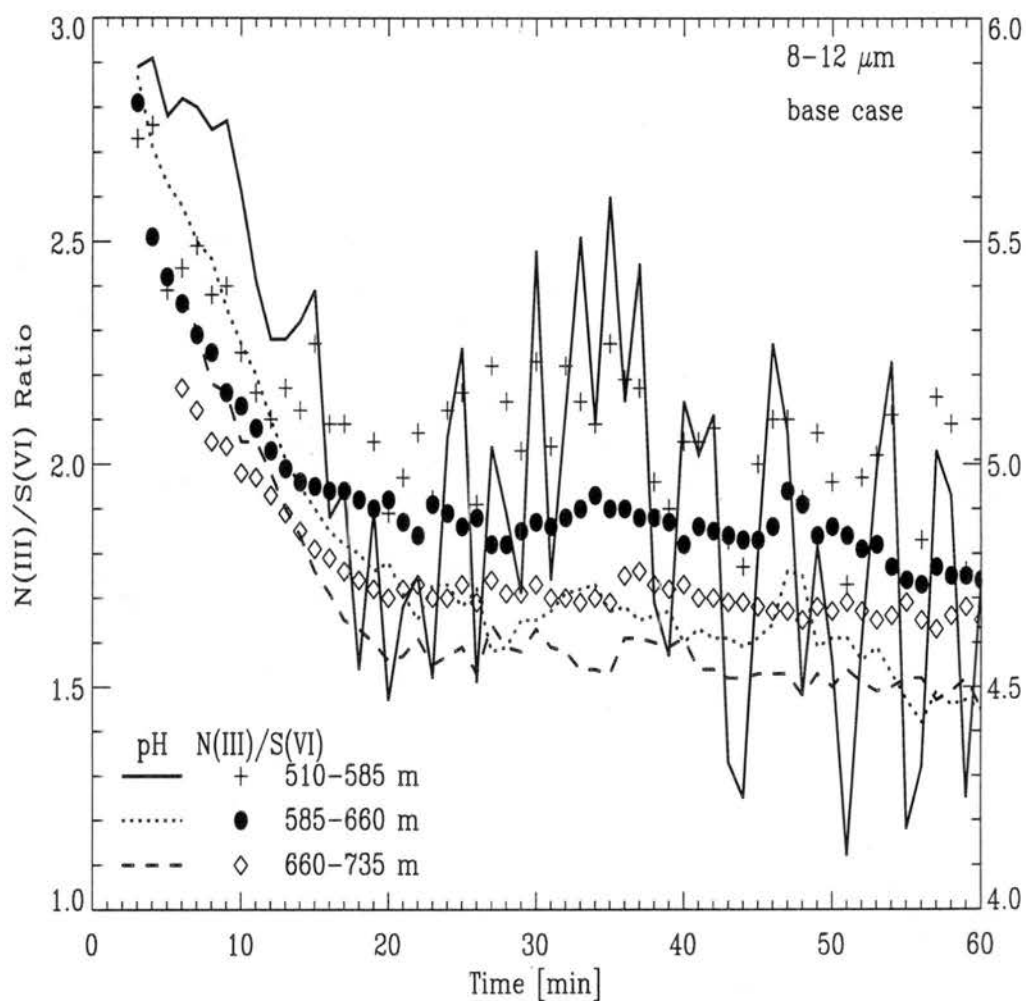


Figure 5.5: Snapshots of the computed N(III) to S(VI) molar ratios and liquid water-weighted $p\text{H}$ for the drop size range 8-12 μm for the base case. Calculations are performed at three different 75 m height intervals as indicated. The lines are for the liquid water-weighted $p\text{H}$, and the symbols are for the N(III) to S(VI) molar ratios.

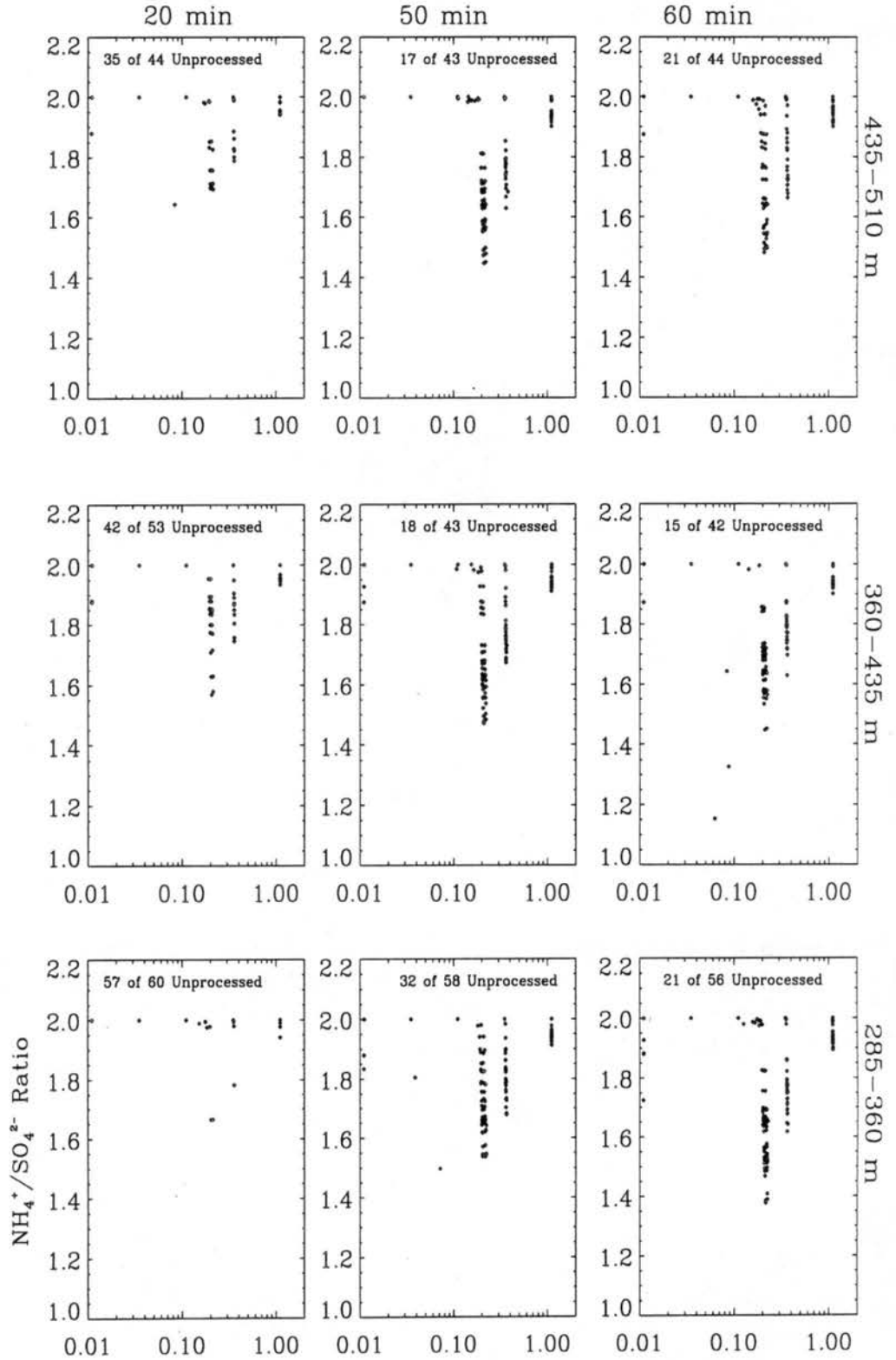


Figure 5.6: Snapshots of the unaveraged $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios in each particle size category as functions of dry particle radius at 20 min, 50 min, and 60 min, and at three different 75 m height intervals below cloud for the base case.

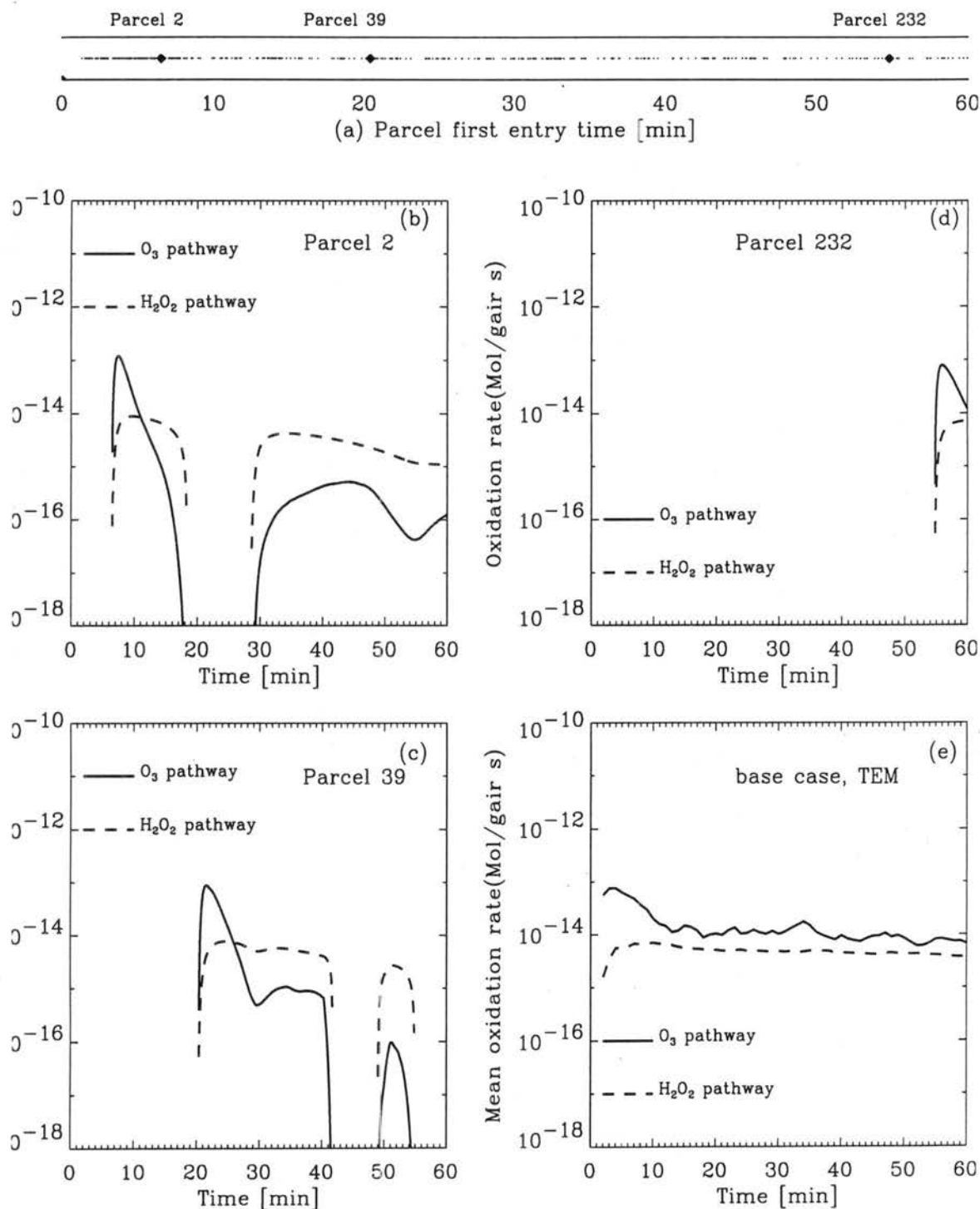


Figure 5.7: (a) Time of first entry into cloud for each of the 500 parcels. The three diamonds indicate time of entry for Parcel 2 during 10 minutes, Parcel 39 between 10–50 minutes, and Parcel 232 during last 10 minutes, respectively. Lower panels show the contribution from all drop categories to the oxidation rates via the H_2O_2 and O_3 pathways as a function of time: (b) Parcel 2; (c) Parcel 39; (d) Parcel 232; (e) TEM. The calculations for the TEM are averaged from 500 parcels.

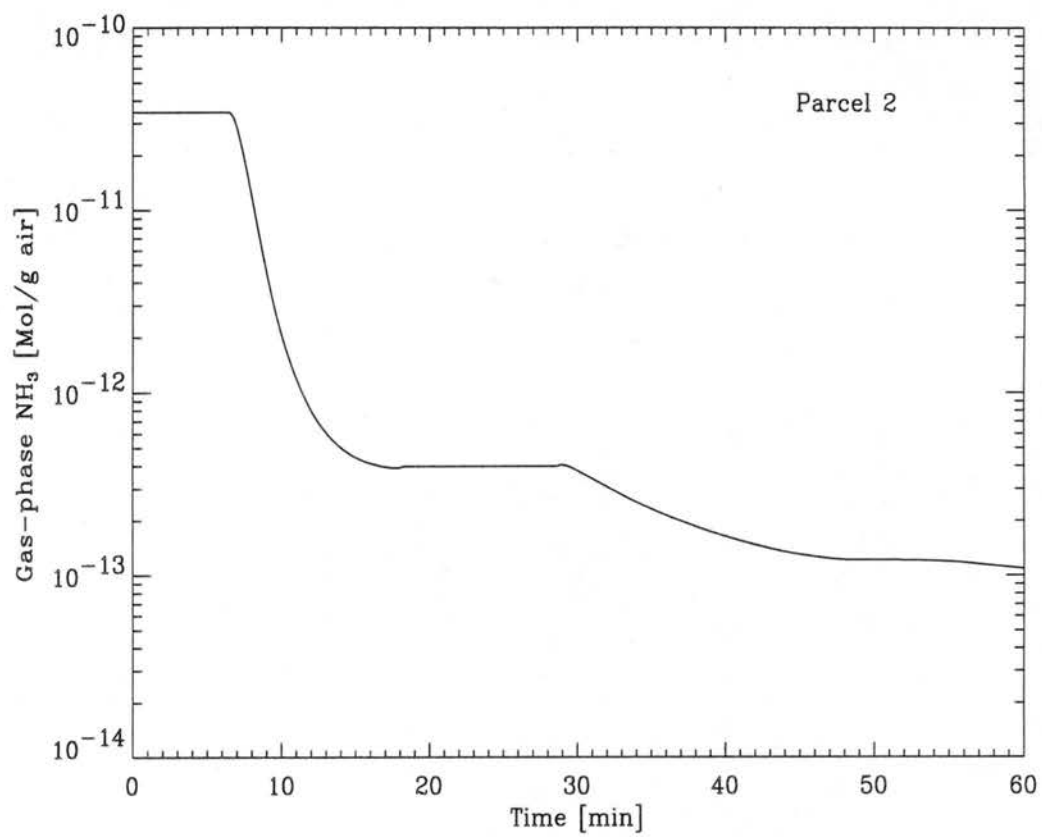


Figure 5.8: The depletion of gaseous NH_3 as a function of time for Parcel 2.

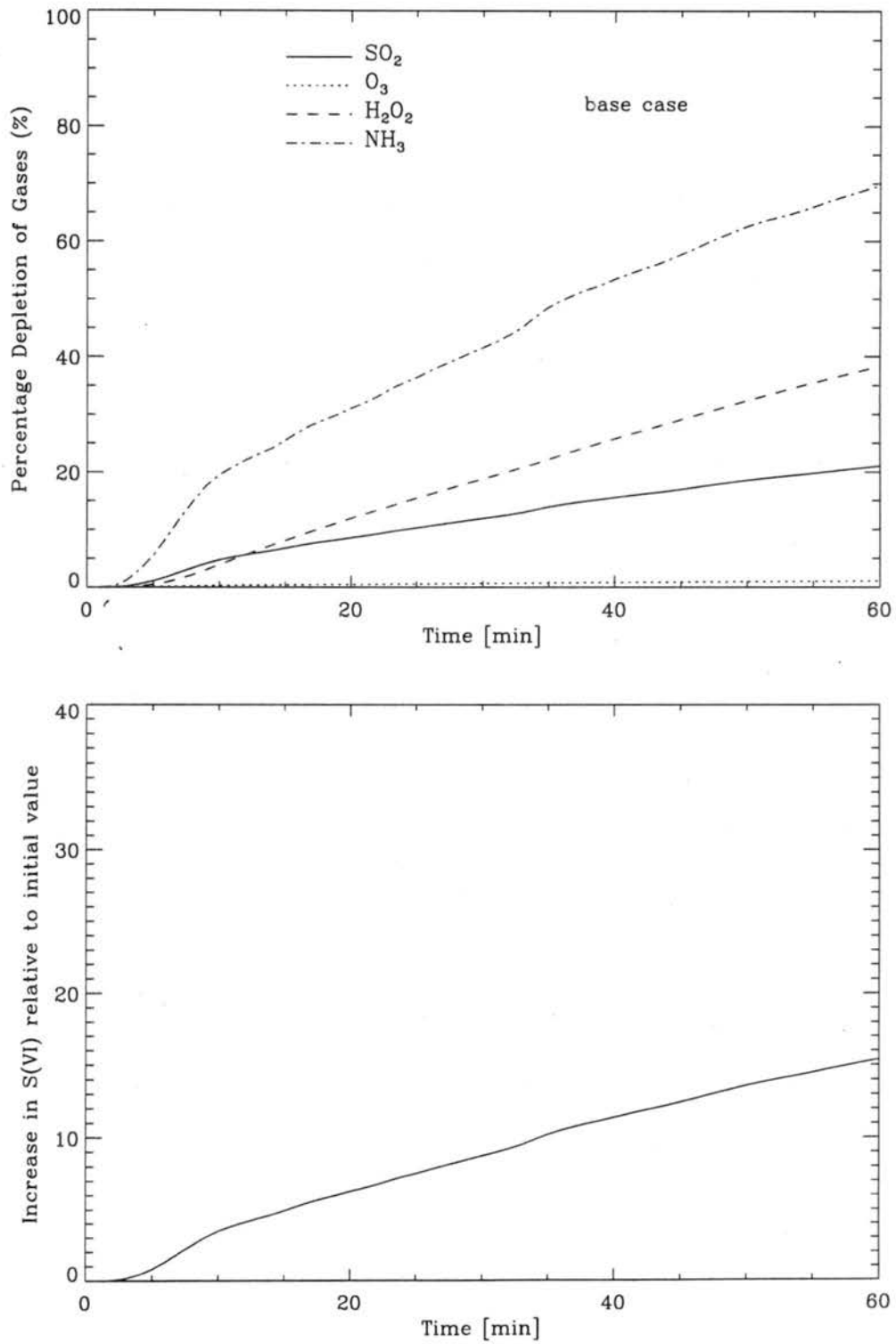


Figure 5.9: The percentage depletions of gaseous concentrations and increase in S(VI) relative to the initial values plotted as functions of time. Calculations are from the 500-parcel average.

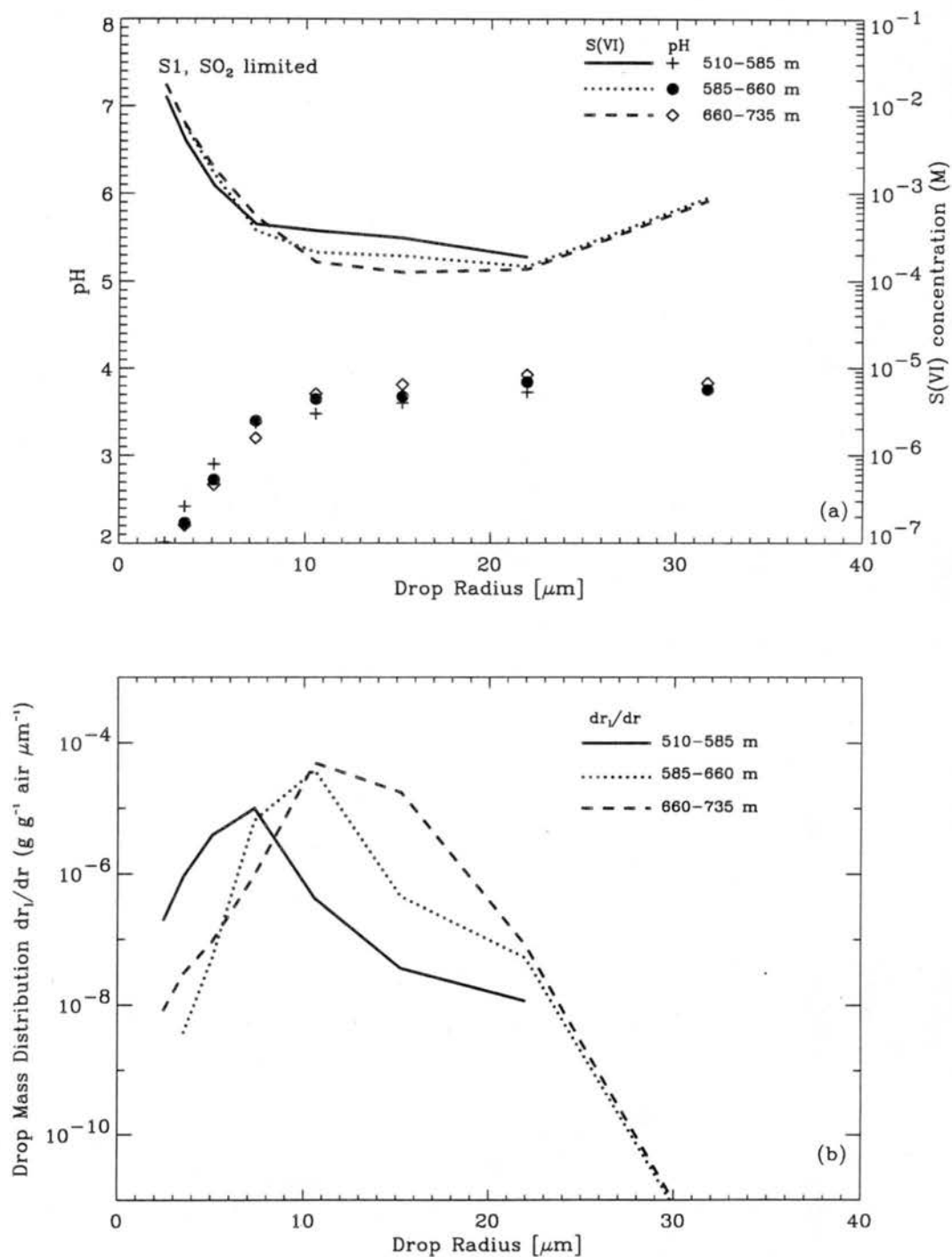


Figure 5.10: As in Figure 5.3, but for sensitivity experiment S1.

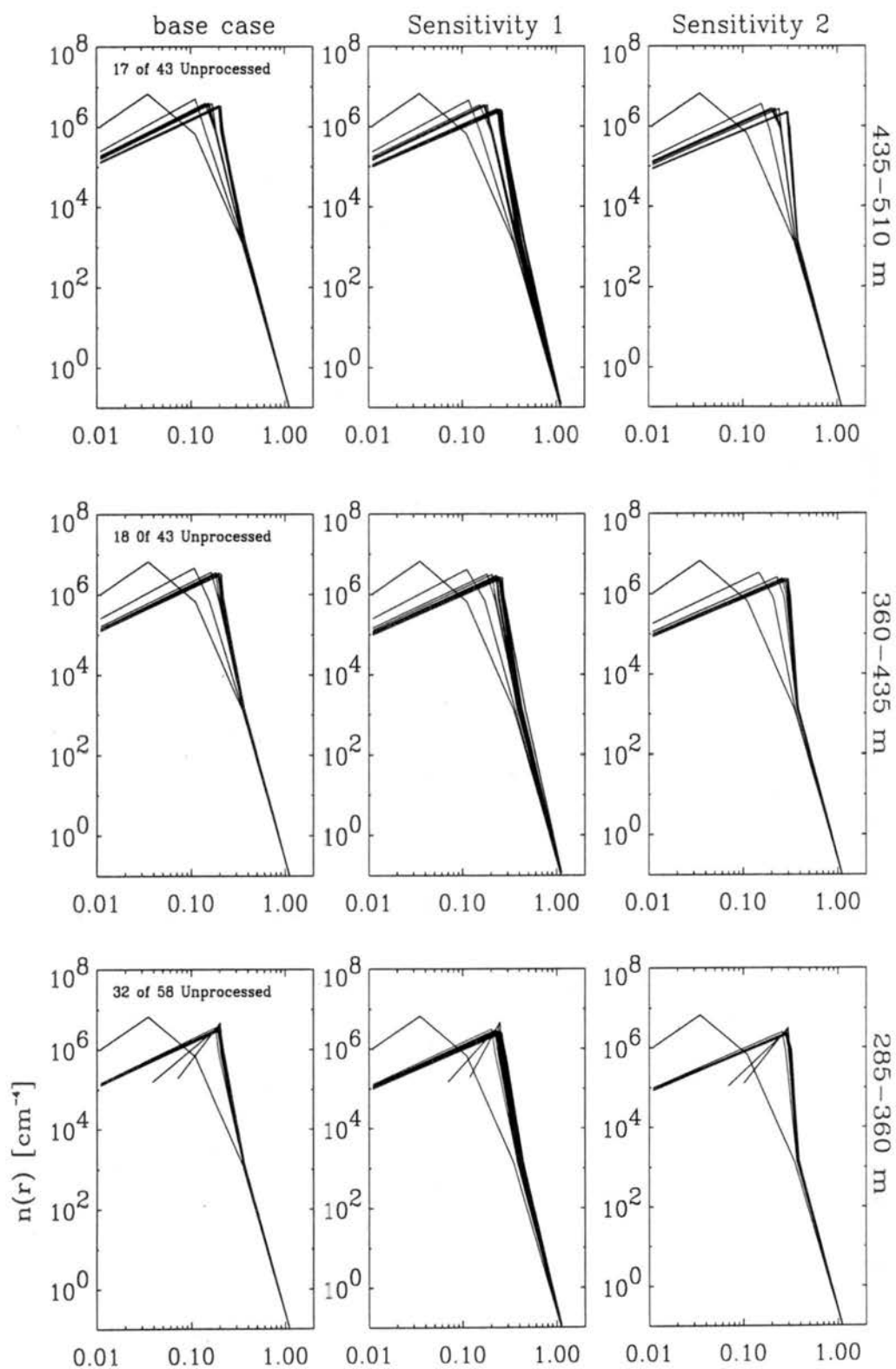


Figure 5.11: A comparison of the snapshots at 50 min of the unaveraged CCN size spectra on a moving mass-grid at three different 75 m height intervals below cloud for the base case, S1, and S2.

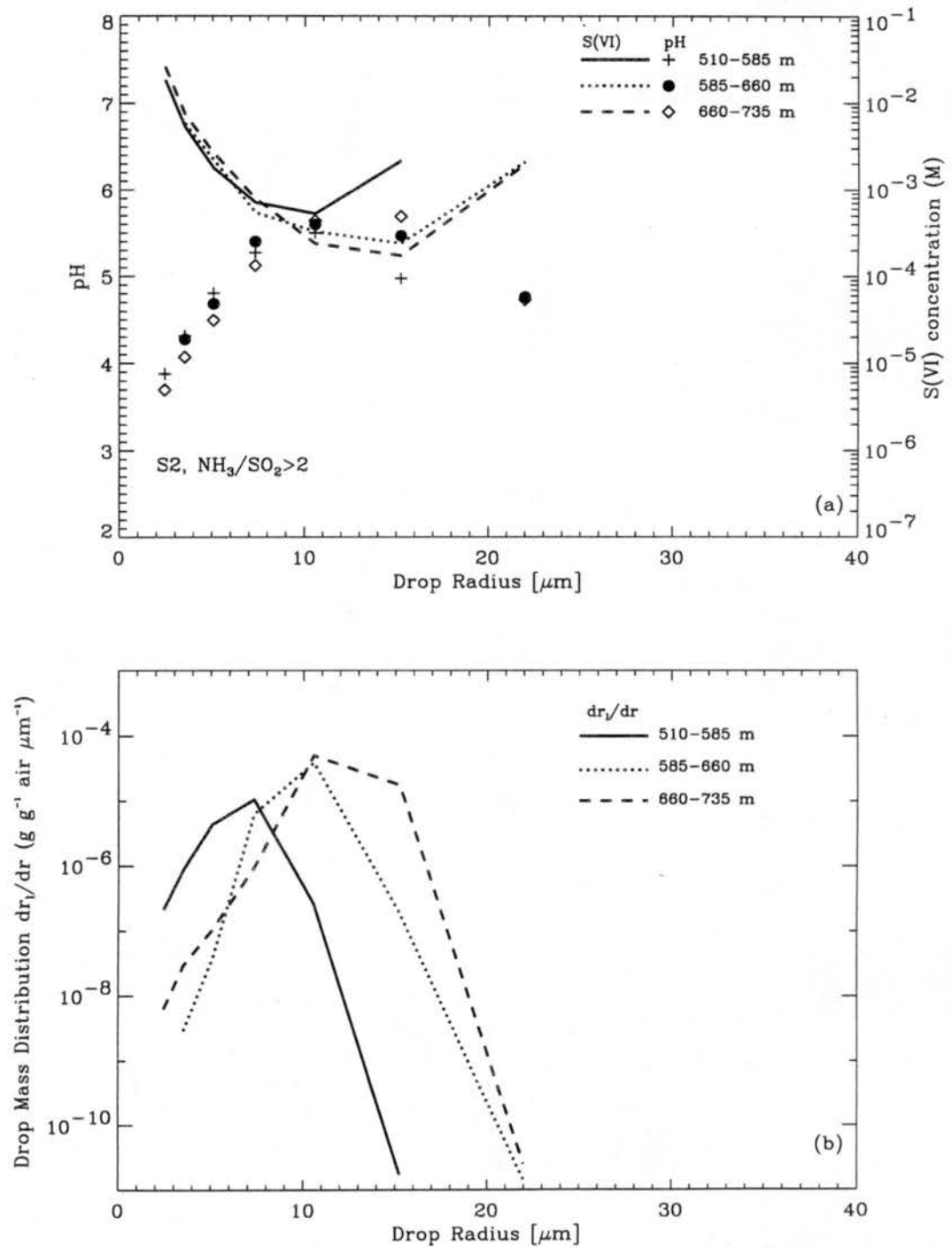


Figure 5.12: As in Figure 5.3, but for sensitivity experiment S2.

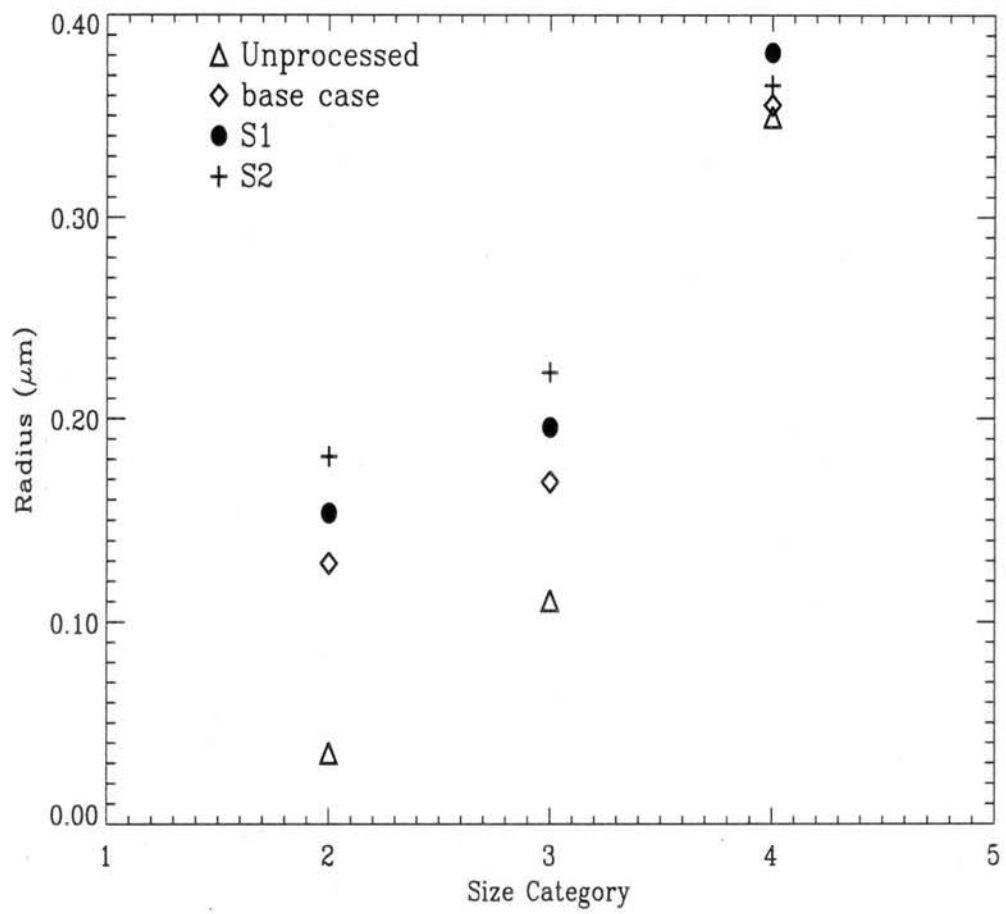


Figure 5.13: A comparison of the averaged dry CCN size for category 2, 3, and 4 at 50 min for the base case, S1, and S2.

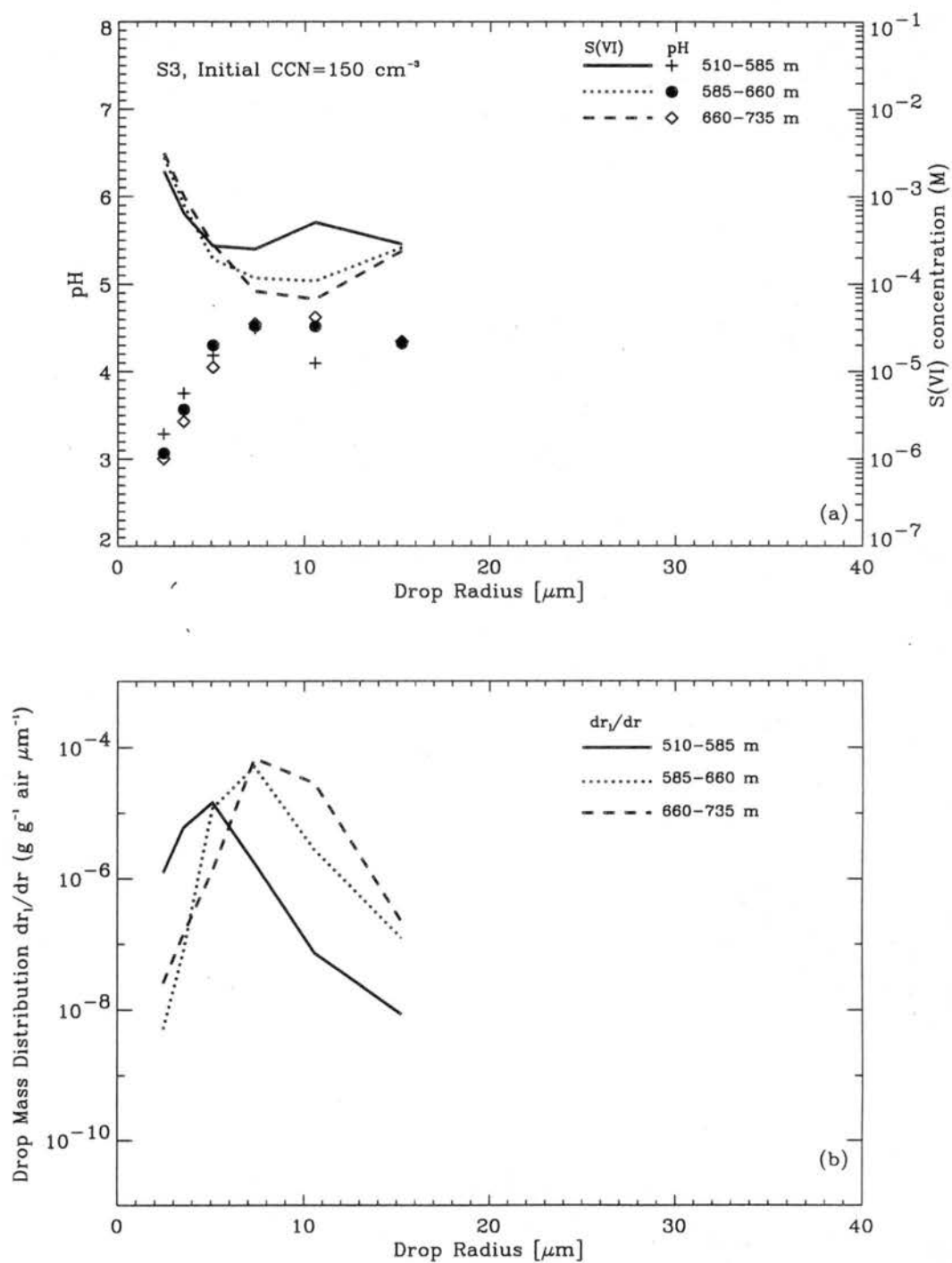


Figure 5.14: As in Figure 5.3, but for sensitivity experiment S3.

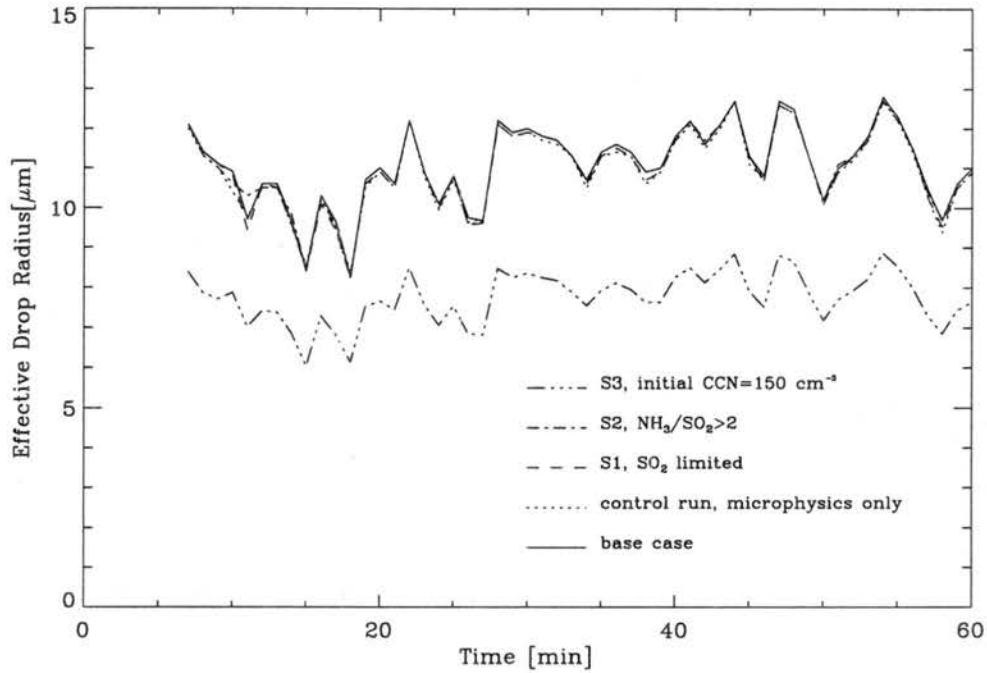


Figure 5.15: The comparison of effective cloud drop radius for different cases. Solid line: base case; dotted line: control run; dashed line: S1; dash-dotted line: S2; dash-dot-dot-dotted line: S3.

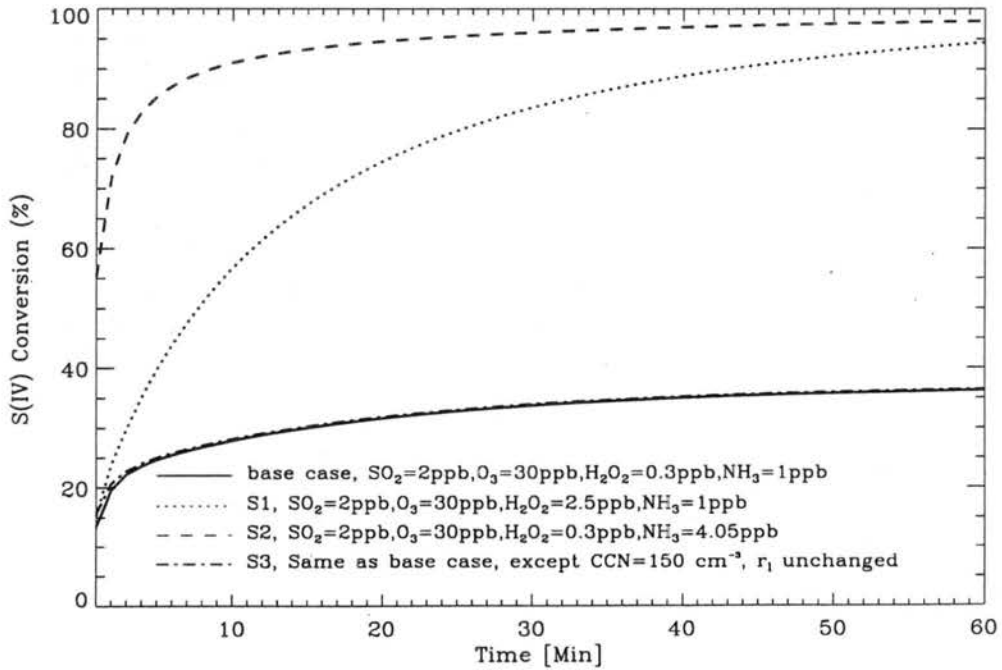


Figure 5.16: The fractional conversion of S(IV) from a single parcel experiencing mean conditions for the base case and sensitivity runs. Solid line: base case; dashed line: S1; dotted line: S2; dash-dotted line: S3.

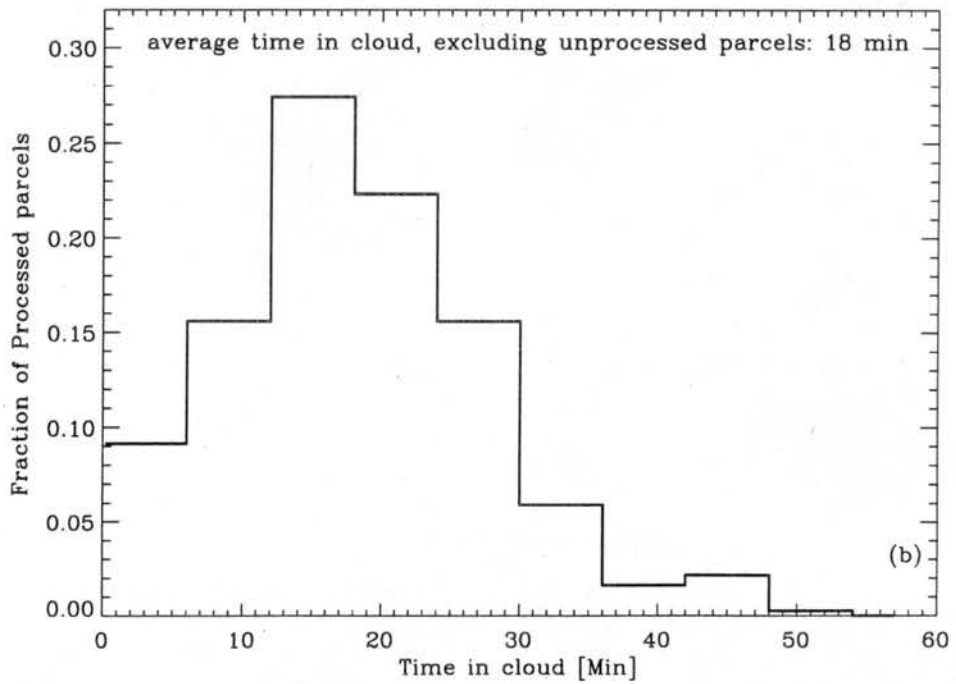
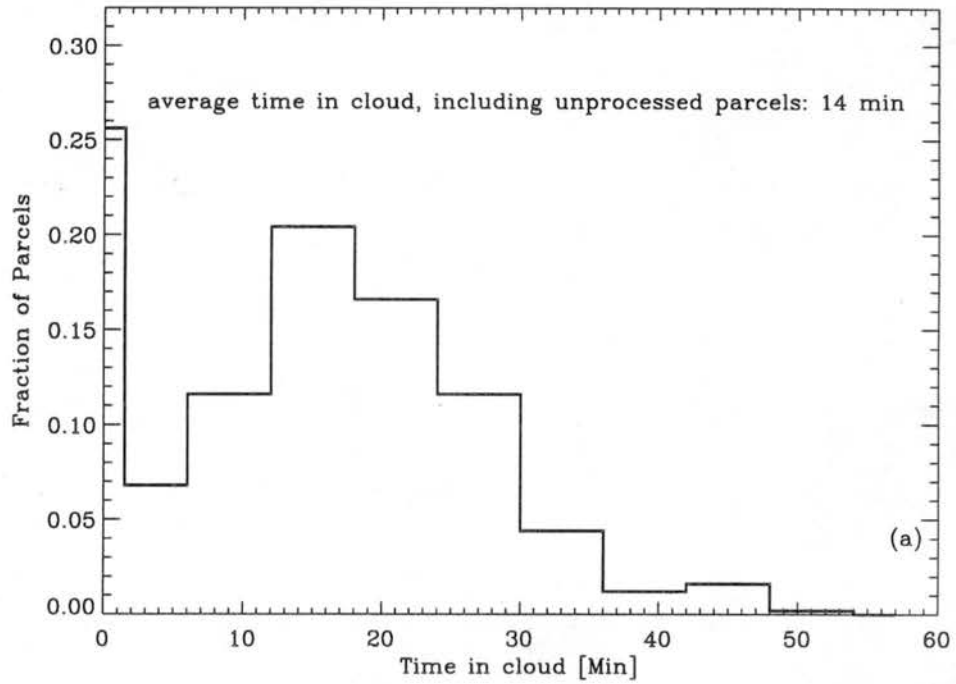


Figure 5.17: The Probability Distribution Function of in-cloud residence time. (a) Method 1, the average time in cloud is 14 min, including all 500 parcels, (b) Method 2, the average time in cloud is 18 min, including only processed in-cloud parcels.

Chapter 6

SUMMARY, CONCLUSIONS AND FUTURE WORK

The effects of clouds on chemical species and aerosol processing, redistribution, and production are examined in two frameworks, the first being a coupled aerosol/chemistry/cloud dynamics model and the second being a trajectory ensemble model. Here, we will emphasize how different results combine to form a coherent “picture”, and discuss how this picture differs or agrees with previous observations and investigations, instead of reviewing every result. We offer a brief summary of what our work suggests are the essential ingredients of aerosol direct and indirect climatic effects. At the end, we will review some limitations of our study and offer suggestions for future work.

6.1 Summary and conclusions

6.1.1 Deep convection

A two-moment, two-category aerosol evolution model, including condensation, nucleation, and gas-phase production of H_2SO_4 , has been incorporated into a two-dimensional, two-moment microphysical, and mixed-phase cloud dynamics and detailed sulfate chemistry model to study the cloud transport aspect and the interaction of aerosol, chemistry, and cloud in a small midlatitude continental cumulonimbus cloud. To the best of our knowledge, this is the first time an aerosol microphysical model has been coupled to a complicated cloud model, which is able to simulate the aerosol dynamics in the upper troposphere.

The dynamical and microphysical features of the small cumulonimbus cloud simulated with the coupled model compared well with the observations [Taylor *et al.*, 1997]. During the recent First Aerosol Characterization Experiment (ACE-1), Clarke *et al.* [1998] found enhanced layers of “new” particles in the free troposphere that corresponded to nearby

cloud top height and exhibited concentrations that exceeded those in the marine boundary layer air by about 1000 to 10,000 cm^{-3} . Many layers were associated with enhanced concentrations of water vapor and sulfuric acid. Their focused cloud experiments demonstrated that the new particles were recently formed and originated in the outflow region of clouds preferentially after late morning when photochemical processes had become sufficiently active. Other ACE-1 measurements made in transit near equatorial convection also revealed significant numbers of new nuclei formed aloft in various cloud outflow regions, where nucleation was favored when existing surface areas approach or drop below about 5–10 $\mu\text{m}^2 \text{cm}^{-3}$. These experiments are supportive of our model results, which show that in most daytime cases, when SO_2 is convectively transported to the mid-to-upper troposphere, where low aerosol surface area and water vapor are simultaneously transported, new particle formation is favored and contributes significantly to the background aerosol CN population.

Although this study largely set out to address the hypothesis of Clarke [1993] and Perry and Hobbs [1994], our results are relevant to a larger body of work. Our model studies aim to investigate the cloud transformation process of chemical species and aerosol production processes, which is the basic step in an effort to accurately quantify the aerosol influence in models of current, past, or future climate. Important points brought out by this research include:

- The cloud is chemically heterogeneous. The H_2O_2 oxidation pathway is important initially, but H_2O_2 is quickly depleted from the cloudy domain after several minutes, and the O_3 oxidation pathway begins to dominate in most regions of the cloud. The inhomogeneous distribution of cloud-water pH and sulfate to ammonium molar ratio brings complexity to parameterizations of aqueous chemistry in larger-scale models, since these basically assume a fixed pH value for the whole cloud. Recent efforts by Feichter *et al.* [1996] to explicitly calculate cloud-water pH in a global climate model treated cloud transformation processes and precipitation scavenging in a more realistic manner, though they fixed the molar ratio between sulfate and ammonium to be 1, which could favor the H_2O_2 oxidation pathway and inhibit the O_3 oxidation pathway in the first place.

- The iron-catalyzed oxidation pathway is comparable to the H_2O_2 and O_3 pathways, and has the potential to convert more SO_2 to sulfate in cloud; however, this pathway is neglected in current general circulation models (GCM) of the sulfur cycle [e.g., Chin and Jacob, 1996; Chuang *et al.*, 1997; Feichter *et al.*, 1997]. Since it could play a role in the global distribution of anthropogenic sulfate aerosol, it thus could have an impact on the estimation of the aerosol direct effect.
- The redistribution of SO_2 is related to the in-cloud sulfate production. The more SO_2 that is consumed in the liquid phase, the less is redistributed to the higher levels. In-cloud sulfate production is sensitive to initial aerosol composition and the acidity of cloud water, and moderately sensitive to changes in the model resolution. These are ignored in most global and regional S models.
- Temperature, relative humidity, pre-existing aerosol surface area, and $\text{H}_2\text{SO}_4(\text{g})$ production rate are the main factors which affect the new particle formation rate. When SO_2 is convectively redistributed to high altitude, the elevated humidity and cleansed air is simultaneously redistributed to the same region. During daytime, in the presence of $\text{OH}\cdot$, gas phase production of sulfuric acid vapor, although a small sink for SO_2 , significantly enhances $\text{H}_2\text{SO}_4(\text{g})$ concentration and triggers new particle formation. This process has a prominent effect on the small particle population. A layered structure in the small particle distribution, as observed by Hofmann [1993] and Clarke *et al.*[1998], also appears in some simulations.
- Pre-existing aerosol surface area plays a significant role in suppressing nucleation in the lower troposphere, but only a secondary role for nucleation in a relatively thin layer in the upper troposphere, where the threshold $\text{H}_2\text{SO}_4(\text{g})$ concentration for nucleation is low, also in agreement with Clarke *et al.*[1998] ACE-1 measurements. They found no particle sources in the boundary layer, but did observe new particle formation in the free troposphere in cloud outflow regions.
- The sensitivity tests demonstrate that the predicted small particle concentration in the upper troposphere is sensitive to the amount of redistributed SO_2 and the

available $\text{OH}\cdot$ source. However, the contribution to the enhanced small particle concentration at 9–10 km is unchanged for increased initial small particle concentration, increased nucleation rate factor, and decreased initial $\text{H}_2\text{SO}_4(\text{g})$ concentration, primarily since the simulated nucleation rate at that level is bounded by the gas-phase $\text{H}_2\text{SO}_4(\text{g})$ production rate. Increased nucleation rate factor would lower the critical H_2SO_4 concentration and trigger the nucleation more easily at other levels.

- The production of significant concentrations of new particles can be a slow process, and may not initially be observed over the aerosol concentrations lifted convectively with the precursor gases. Thus the observation of new particle formation in convectively processed air is expected to depend strongly on the time at which observations are made. The new particle formation process has a prominent effect on the small particle population on the time scale of hours, in agreement with Clarke *et al.* [1998] measurements of time scales of hours to a day.

In this study, in most cases SO_2 is redistributed to the upper troposphere where it could participate in long range transport to affect remote regions. It is necessary to incorporate the chemical processes which are the source of climate forcing aerosols into hemispheric and global scale models. The new particle formation process in the upper troposphere as a source to maintain the abundance of CN particles, and the possibility of these nuclei evolving to CCN particles, are also needed in such models.

6.1.2 Stratocumulus

In this dissertation, we have utilized the TEM to simulate coupled aqueous chemistry and cloud microphysics in a stratocumulus cloud. The TEM is driven with 500 parcels generated during one hour of the FIRE LES runs. Bower and Choulaton [1993] used a single parcel model to examine modification of the CCN spectrum in a hill cap cloud following a cloud cycle and its consequence for the secondary cloud formation. Here, some trajectories in the TEM have cycled through cloud 2 or 3 times during the course of an hour, which has consequences for the CCN spectra and drop spectra. Thus the TEM represents the impact of cycling in a less constrained manner. We have investigated the interaction

between chemistry and cloud and the effects of aqueous chemistry on the modification of CCN spectra and drop spectra. We have also investigated the effects of variations in the initial chemical fields and initial aerosol number concentration on the chemical heterogeneities (cloud-water pH, S(VI) concentration, and ammonium to sulfate molar ratio) across the cloud drop sizes, the cloud-top effective drop radius, and the differences in the overall fractional conversion between the TEM and a single parcel experiencing mean conditions. The TEM offers a more representative method of describing the stratocumulus processing of aerosol and gases than does a single parcel model. Important points brought out by this research include:

- It is found that the O_3 oxidation rate is always larger than the H_2O_2 oxidation rate in the base case, whereas the volume-mean pH might suggest that H_2O_2 oxidation dominates. This implies that not only the mean aqueous chemistry but also the size-dependent chemistry information should be incorporated into larger-scale models.
- Dilution effects usually result in increases in the liquid water-weighted pH with increasing drop size to a maximum, then decreases with further increasing drop size; whereas the S(VI) concentration decreases with increasing drop size to a minimum, and then increases with further increasing drop size. The drop size at the pH peak is located near the mode of the cloud drop spectrum. The addition of solute mass due to aqueous chemistry will counter the effect of dilution and lower the pH, and shift the pH peak to larger sizes.
- Both supersaturation fluctuations and aqueous chemistry contribute to the broadening of the drop size distribution. The magnitude of the broadening of CCN spectra and cloud drop spectra will depend not only on the total sulfate mass produced, but also on the distribution of the sulfate mass across the size spectrum. In cases where more mass is added onto the large tail of the initial CCN spectrum, the broadening of the drop spectrum is most evident, and may even trigger the collision-coalescence process and drizzle formation.

- The H_2O_2 oxidation pathway adds sulfate mass evenly and continuously across the drop sizes, while the O_3 oxidation pathway adds sulfate mass near the mode of the CCN spectrum over a relatively short time. The different behaviors of the O_3 oxidation and H_2O_2 oxidation in turn affect the pH dependence on the drop sizes and the magnitude of the broadening of the cloud drop spectrum.
- An increase in the initial CCN number concentration decreases the volume-mean drop radius, and shifts the mode of r_l and pH peak to smaller cloud drop sizes. This will likely suppress the drizzle formation.
- Under the same liquid water content, the increase in CCN number will result in a decrease in cloud-top effective radius.
- A single parcel experiencing mean conditions overestimates the fractional conversion of S(IV) compared to the TEM results. Different shapes of the time-dependent conversion and the regions of overlap with the mean in-cloud residence time will affect the magnitudes of the difference between a single mean parcel and the TEM, with the steadily increasing conversion with time inducing the largest error. Deriving the conversion from in-cloud parcels and then weighting by the in-cloud residence time distribution will give closer result to the TEM than deducing the conversion from mean in-cloud residence time for the whole boundary layer.

The indirect sulfate aerosol effect on climate has been studied with many GCMs [*e.g.*, Boucher and Lohmann, 1995; Feichter *et al.*, 1997; Jones *et al.*, 1994; Lohmann and Feichter, 1997]. In GCMs, sulfur chemistry and cloud microphysics have to be parameterized. Most frequently, cloud drop number concentration is empirically related to the mass of sulfate aerosols [*e.g.*, Feichter *et al.*, 1997]. The more sulfate mass, the higher the predicted cloud drop number concentration. In this study, we find that for approximately the same liquid water content, the cloud drop spectrum depends not only on the sulfate mass produced in cloud, but also on the size distribution of this sulfate mass, with sulfate mass distributed to the larger size end of the aerosol size spectrum leading to the most broadened spectrum which could have an increased efficiency of drizzle production. This implies

that with the same sulfate mass and cloud drop number concentration, the autoconversion rate will be different for different initial chemical conditions, which will in turn affect the calculation of indirect aerosol effect. The size-dependent chemistry is thus adding another aspect to the already complicated interaction of chemistry, cloud, and radiation.

6.2 Limitations and future research

While this dissertation has addressed many issues related to chemical and aerosol chemical and microphysical processes in the upper troposphere and the boundary layer, it has many limitations. The limitations of the chemical-microphysical-dynamical framework, and the limitations of time leave many questions to future studies.

A chief limitation of the upper tropospheric work is the poor representation of many physical and chemical processes. The primary physical limitation of our study of aerosol dynamics is the limited discrete sizes in our aerosol evolution model, though a two-moment representation across a size bin results in less numerical diffusion than a one-moment sectional model [Gelbard *et al.*, 1998]. To fully capture the aerosol size distribution evolution, Raes and Dingenen [1992] used up to 70 discrete sizes in a box model, and Fitzgerald *et al.* [1998] used an improved multicomponent sectional model (MAEROS) in a one-dimensional model, with a maximum number of sections of 39.

As discussed in Chapter 3, we neglect nitrate chemistry in the sulfate chemistry model, which could lower the cloud-water pH calculation. On the other hand, a neutralizing agent, NH_3 gas, is omitted, which could increase the cloud-water buffering capacity. Also, as discussed in Chapter 3, the representation of partial cloudiness is a potential weakness in the relatively coarse resolution cloud model presented here. Consequently, further studies with refined resolution are needed. In addition, the fact that all results are derived on the basis of two-dimensional integrations, leaves many issues for further investigation.

In our study, when SO_2 is convectively transported to cold and/or humid environment, new particle formation is predicted to occur in most cases during daytime. The evolution of the small particles is unknown. The SO_2 residue and enhanced concentration of small particles may participate in long-range transport to affect remote regions. Aircraft

measurements in the vicinity of deep convective clouds need to be undertaken to identify the source regions for new particles in the mid- to upper- troposphere. This is crucial for testing the direct effect of the sulfate-radiative cooling hypothesis [Charlson *et al.*, 1992] which relies on the assumptions that a fraction of the SO_2 emitted is converted to new particles by gas-to-particle conversion and that sulfur species is transported to regions far away from the source.

A major limitation in the stratocumulus work is the limited time simulation of the boundary layer cloud. The mixing between parcels is not included in the TEM framework. Though valid for the one-hour simulations represented here, caution must be exercised when applying this approach to longer time scales. Within the TEM framework, a number of possibilities exist for communicating information between parcels. Walton *et al.*[1988] interpolated parcel information to a fixed spatial grid in their Lagrangian global model and then communicated grid quantities back to the parcels. A similar approach will be considered in future work that addresses longer time scales.

Another drawback of the TEM approach is that feedback of microphysical and chemistry-related processes to cloud dynamics is not included in the TEM because there is currently no means to communicate these changes to the TEM. This approach therefore 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. However, we could examine the impact of processing on a coupled cloud model by re-running a cloud resolving model with the processed aerosol distribution produced by the TEM, which has been done by Feingold *et al.*[1998a] for a different set of initial chemical conditions.

In the chemical part of the TEM, an initial aerosol composition of $(\text{NH}_4)_2\text{SO}_4$ is assumed, and sea-salt particles are neglected. This omission is serious in applying the model to maritime boundary layers. Future work includes the development of a multi-component aerosol model for the TEM.

Lastly, we have completely neglected the radiative effects on droplet growth in the TEM, which limits our simulations to nocturnal cases.

In the TEM, we find that spectral broadening occurs in one of our sensitivity simulations due to the spectral addition of sulfate mass. Whether or not this spectral broadening

occurs in real clouds is not known. Simultaneous measurements of cloud microphysics and drop size-dependent chemistry may be able to shed light on this.

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