

Chemical and dynamical effects on cloud droplet number: Implications for estimates of the aerosol indirect effect

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[1] Most aerosol-cloud-climate assessment studies use empirical aerosol number/droplet number relationships, which are subject to large variability. Historically, this variability has been attributed to unresolved variations in updraft velocity. We revisit this postulation and assess the effects of both updraft velocity and chemical composition on this variability. In doing so we utilize an inverse modeling approach. Using a detailed numerical cloud parcel model and published aerosol characteristics, with published correlations of cloud droplet versus sulfate and cloud droplet versus aerosol number as constraints, we determine a most probable size distribution and updraft velocity for polluted and clean conditions of cloud formation. A sensitivity analysis is then performed to study the variation in cloud droplet number with changes in aerosol chemistry and updraft velocities. This addresses the need to estimate the importance of chemical effects on spatial scales relevant for global climate models. Our analysis suggests that the effect of organic surfactants can introduce as much variability in cloud droplet number as the effect of expected variations in updraft velocity. In addition, the presence of organics seems to further enhance the sensitivity of droplet concentration to vertical velocity variability. The variability from organic surfactants is seen to be insensitive to variations in aerosol number concentration, implying that such effects can affect cloud droplet number consistently over large spatial scales. Our findings suggest that organics can be as important to the aerosol indirect effect as the effect of unresolved cloud dynamics, and they illustrate the potential and complex role of chemical effects on aerosol-cloud interactions. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 1610 Global Change: Atmosphere (0315, 0325); 3314 Meteorology and Atmospheric Dynamics: Convective processes; *KEYWORDS:* aerosol, clouds, indirect effect

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1. Introduction

[2] The largest uncertainty in prediction of anthropogenic influences on climate change involves the details of the hydrological cycle [Houghton *et al.*, 2001]. Water in the atmosphere has three major, competing effects on climate. Water vapor is the primary greenhouse gas in the Earth's atmosphere. Conversely, liquid water in the form of suspended cloud droplets accounts for ~30% of the Earth's albedo [Charlson *et al.*, 1987]. Water ice in the upper

troposphere absorbs infrared radiation emitted by the Earth. The mechanisms for distribution of each phase are therefore important for determining the overall effect of atmospheric water on climate. This study focuses on the formation of liquid water clouds.

[3] Cloud droplets in the atmosphere are formed from condensation of water vapor upon cloud condensation nuclei (CCN). Both the physical and chemical characteristics of a CCN population influence the number and size of cloud droplets that form. However, the physical and chemical properties of CCN vary significantly with space and time, since the sources and sinks of CCN are localized and since CCN have short atmospheric lifetimes (as compared

to the mixing timescale of the atmosphere). In addition, the cloud updraft velocity, which is highly variable within a cloud and difficult to measure [Mason, 1971], has a strong influence on the number and size of cloud droplets formed; a higher updraft provides a higher water vapor supersaturation, which is the driving force for condensational growth. The wide variability in these parameters, to which cloud droplet formation is highly sensitive, causes much of the uncertainty in cloud modeling.

[4] Most of the radiative properties of liquid water clouds can be inferred from knowledge of the cloud liquid water content and cloud droplet number concentration. Twomey [1974] suggested that increasing the number of aerosol particles increases the number of CCN, which increases the number of cloud droplets and leads to a higher cloud albedo. The increased cloud reflectivity and the associated radiative cooling are referred to as the “first indirect climate effect” of aerosols. Global climate models (GCMs) are currently incapable of providing the resolution necessary for explicitly addressing the scales involved in aerosol-cloud interactions; instead, empirical correlations between cloud droplet number and one aerosol characteristic (e.g., number concentration [Gultepe and Isaac, 1999] or sulfate mass [Boucher and Lohmann, 1995]) are often used to quantify aerosol-cloud interactions. The variability inherent in such relationships translates to a large predictive uncertainty of the indirect effect, potentially as large as the greenhouse gas radiative forcing [Houghton et al., 2001]. For example, in the Boucher and Lohmann [1995] observations the cloud droplet number concentration ranges from 60 to 600 cm^{-3} for an aerosol non-sea-salt (nss) sulfate mass of 1 $\mu\text{g m}^{-3}$. For the same liquid water path this variability in cloud droplet concentration could lead to a change in cloud reflectivity of up to $\sim 60\%$ [Seinfeld and Pandis, 1998]. This large variability shows that cloud droplet number is strongly influenced by factors other than sulfate mass but does not indicate to what the variability can be attributed.

[5] The variability in the Boucher and Lohmann [1995] and Gultepe and Isaac [1999] observations is historically attributed to variations in cloud updraft velocity [Houghton et al., 2001]. Although updraft variations may produce an order-of-magnitude range in droplet number, recent work has suggested that a variety of organic chemical effects, including reduction in surface tension and modified growth kinetics, can potentially contribute as much to the variability in cloud droplet number as updraft velocity.

[6] Several studies have shown that organic compounds can reduce the surface tension of droplets. Facchini et al. [2000] observed a decrease of up to 25% in the surface tension of polluted fog water samples as compared to the surface tension of water. The surface tension depression was shown to be a function of the bulk concentration of water-soluble organic compounds [Facchini et al., 1999]. Using Köhler theory and assuming a power law relationship between droplet number and supersaturation, Facchini et al. [1999] estimated that the maximum decrease in surface tension could lead to an $\sim 20\%$ increase in the number of cloud droplets. Li et al. [1998] found that laboratory-generated aerosol consisting of mixtures of sodium dodecyl sulfate and NaCl can lower the surface tension by up to 20% compared to the same size dry particle composed of pure

NaCl. Shulman et al. [1996] measured the solubility and surface tension of laboratory-generated aerosols, which consisted of two-component mixtures of ammonium sulfate and various difunctional organic oxygenates that have significant concentrations in the atmosphere (e.g., *cis*-pinonic acid and glutaric acid). The observed surface tension decreased by as much as 20% compared to water. It was also found that higher concentrations of ammonium sulfate actually enhanced the surface tension depression for *cis*-pinonic acid. This relatively high molecular weight organic compound is the least soluble of the model compounds studied; however, the addition of 0.5 M ammonium sulfate (which is ubiquitous in the atmosphere) allowed for the same $\sim 20\%$ reduction in surface tension at half the *cis*-pinonic acid concentration (0.02 M rather than 0.04 M).

[7] Numerous modeling studies have been performed to estimate the effect of the observed surface tension depression and gradual dissolution of organic compounds. These studies illustrate that the response in CCN concentrations to the presence of organic surfactants is often important and strongly depends on the size distribution of chemical composition and aerosol number and the local dynamical conditions of cloud formation. Nenes et al. [2002] used a numerical cloud parcel model to show that for polluted aerosol at high updraft velocities the reduction in surface tension due to organic surfactants can have a greater effect on droplet number than doubling aerosol number. For marine aerosol at low updraft the enhancement in droplet number from surfactants can be 50% of the enhancement from doubling aerosol number. Rissman et al. [2004] modified an existing parameterization by Abdul-Razzak et al. [1998] and Abdul-Razzak and Ghan [2000] to explicitly account for the effect of surface active organics on droplet number. Rissman et al. [2004] conclude that the normalized cloud droplet number sensitivity to aerosol organic mass fraction is usually between 10 and 50% of the sensitivity to updraft velocity, with the strongest relative sensitivity at higher updraft velocity. For marine aerosol, as updraft velocity increases above $\sim 0.4 \text{ m s}^{-1}$, the relative sensitivity becomes nearly constant. For continental aerosol the relative sensitivity can be negative at low updraft velocities, implying that an increase in aerosol organic mass fraction increases CCN concentration but decreases the number of cloud droplets (by decreasing the maximum supersaturation). Mircea et al. [2002] estimated that including the surface tension effects of water soluble organic compounds may increase the CCN number concentration by up to 13% for a marine aerosol, by up to 97% for a rural aerosol, and by up to 110% for an urban aerosol, under typical atmospheric supersaturations.

[8] The presence of organic film-forming compounds (FFCs), which form a thin film over a partially deliquesced aerosol particle (with the hydrophobic side of the molecules facing outward and the hydrophilic side facing inward), has the potential to inhibit the rate of droplet growth. The condensation coefficient, which is the probability of a water vapor molecule “sticking” upon collision with an aerosol particle, may be considerably reduced when FFCs are present on the particle surface. A condensation coefficient of 0.045 is widely recognized by the cloud physics community as the typical value for atmospheric droplets (e.g., Feingold and Chuang [2002] used a value of 0.042 to

represent typical FFC-free cloud droplets), although the value varies significantly between studies [Mozurkewich, 1986; Pruppacher and Klett, 2000]. Pruppacher and Klett [2000] summarize that an aged atmospheric drop will have a condensation coefficient of ~ 0.01 , while a clean drop will have a value closer to unity. Two recent studies indicate that the condensation coefficient of pure water is even smaller than previously estimated; Shaw and Lamb [1999] estimate a value of 0.04–0.1, and Li *et al.* [2001] estimate a value of 0.17 ± 0.03 at 280 K and 0.32 ± 0.04 at 258 K.

[9] There is evidence for the existence of FFC compounds in ambient aerosol that lower the condensation coefficient to as low as 10^{-5} [Chuang, 2003]. This lower condensation coefficient indicates that at least 99.98% fewer collisions result in “capture” of a water molecule from the gas as compared to an uncoated cloud drop. The chemical composition of FFC-coated particles and the corresponding condensation coefficients are issues that need to be addressed in future studies. In addition, the distribution of FFCs within the aerosol population must be looked at carefully. The modeling study of Feingold and Chuang [2002] shows that when a minor fraction (5–10% mass) of polluted aerosol is composed of FFCs and the FFC is distributed according to surface area, modified growth kinetics can suppress the number of cloud droplets by as much as 90%. When Nenes *et al.* [2002] distributed the same organic FFC by aerosol mass, a decrease in the initial rate of condensation led to a large enough increase in cloud parcel supersaturation that the result was an increase (by 50–100%) in cloud droplet number. For marine aerosols both studies found that cloud droplet number was modestly affected by the presence of FFCs. Feingold and Chuang [2002] also did simulations in which the FFC was distributed by mass, which resulted in nearly the same droplet number as when FFCs were not present. However, Feingold and Chuang [2002] used a unimodal lognormal size distribution, whereas Nenes *et al.* [2002] used a trimodal lognormal distribution. Distributing the FFC by mass reduces the growth of larger aerosol particles, which can increase the cloud supersaturation and allow more of the smaller particles to activate. The greater number of larger aerosol in the Nenes *et al.* [2002] study may have been a significant factor enabling greater droplet activation when the condensation coefficient was decreased to 10^{-5} .

[10] These and many other studies have shown that considerable variability in cloud droplet number may be induced by different chemical effects, but the studies do not assess the potential significance of the chemical effects on scales larger than individual updrafts. The current study attempts to address the cloud system scale by using an inverse modeling approach based on an observational data set that includes cumuliform and stratiform clouds and CCN originating from both clean and polluted conditions. This unique approach uses empirical correlations of droplet number versus aerosol number and sulfate mass, observed ranges of chemical composition, cloud dynamics, and aerosol size distribution to constrain the chemical effects on cloud droplet number. We use a numerical adiabatic cloud parcel model with explicit microphysics [Nenes *et al.*, 2001] to determine the minimum updraft velocity required to produce the number of droplets described by the Boucher and Lohmann [1995] and Gultepe and Isaac [1999] corre-

lations. This representative base case updraft velocity is then used with the parcel model to estimate the sensitivity of cloud droplet number to organic chemical effects. For comparison, cloud droplet number sensitivity to updraft velocity is also evaluated.

2. Methods

[11] Not all the factors affecting the number of cloud droplets are available from the published data. To overcome this lack of information, we adopt an inverse modeling analysis to constrain key unresolved parameters. The procedure is illustrated in Figure 1. For a given aerosol number the Gultepe and Isaac [1999] correlations provide the cloud droplet number, and the Boucher and Lohmann [1995] correlations provide the aerosol sulfate mass. With information about the aerosol size distribution an updraft velocity can be determined that is consistent with the observations; these conditions are used as a “base case.” Organic mass fraction, condensation coefficient, updraft velocity, and aerosol number concentration are then varied to assess their effects on cloud droplet number. The aerosol physical characteristics (Table 1) and chemical composition (Table 2) used in the analysis are obtained from published literature.

[12] The exact procedure (Figure 1) is as follows: (1) Specify the average aerosol physical and chemical characteristic for three typical environments (polluted, continental, and marine) on the basis of published observations, (2) determine a likely droplet number concentration on the basis of the empirical correlations of Gultepe and Isaac [1999], (3) using the Boucher and Lohmann [1995] correlations, determine a representative sulfate mass concentration that corresponds to the cloud droplet concentration determined from the Gultepe and Isaac [1999] correlations, (4) determine the coarse mode sulfate mass fraction or coarse mode number concentration needed to provide this total sulfate mass, and (5) determine an updraft velocity that can produce the droplet concentration from step 2 using the numerical cloud parcel model of Nenes *et al.* [2001]. These representative updraft velocities and aerosol characteristics are referred to as the base case values. The sensitivity of cloud droplet number to chemical effects is assessed by introducing a reasonable variability in organic mass fraction and condensation coefficient. The sensitivity of cloud droplet number to updraft velocity is also computed for comparison. When varying the cloud updraft velocity, the organic mass fraction is maintained at the base case value, with a condensation coefficient of 0.045. When varying the organic mass fraction, the base case updraft velocity is maintained, with a condensation coefficient of 0.045. When varying the condensation coefficient, the base case updraft velocity and organic mass fraction are assumed.

2.1. Aerosol

[13] Aerosols are diverse in their size distribution, number concentration, and chemical composition, and they exhibit significant spatiotemporal variability. As changes in aerosol physical characteristics are known to have a significant effect on the resulting cloud droplet number, the aerosol characteristics used in this analysis must encompass this diversity.

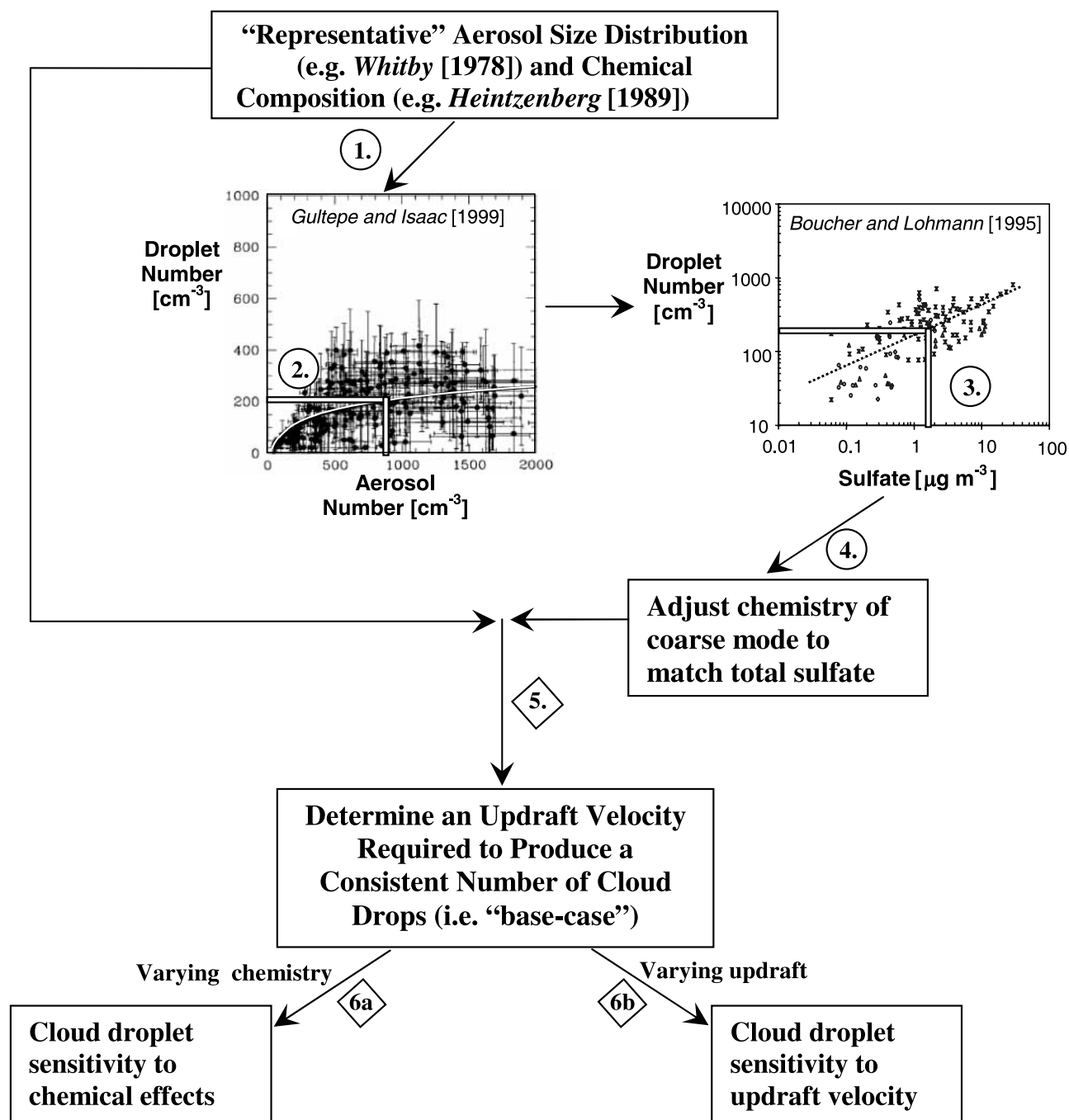


Figure 1. Flow diagram illustrating the “inverse modeling” analysis methodology used for determining cloud droplet number concentration sensitivities. Steps 1–4 (numbers in circles) involve manipulation of observational data, while the remaining steps (numbers in diamonds) employ the cloud parcel model.

[14] Regardless of the origin of the air mass, often, three distinct modes are observed in the aerosol size distribution (nuclei, accumulation, and coarse modes). The nuclei and accumulation modes together represent what are often referred to as “fine particles” (with geometric mean diameters $<0.1 \mu\text{m}$). *Whitby* [1978] characterized sulfur-containing aerosols by averaging multiple size distribution measurements made at several sites over a decade. These measurements were fit to trimodal lognormal distributions, as shown for marine, continental, and polluted aerosol in Table 1.

[15] Fine particle chemical compositions have been analyzed by *Heintzenberg* [1989], using data from 21 cities in the United States, China, Europe, and Japan; 15 nonurban continental sites in Sweden, Brazil, the United States, and the United Kingdom; and 13 locations in remote marine regions (Table 2). The fine particles mainly consist of sulfate, carbonaceous material (including elemental and organic carbon), ammonia, and nitrate. While inorganic compounds are easily resolved by chemical analysis, a substantial portion of organic matter in atmospheric aerosols has remained uncharacterized because of the wide range of

Table 1. Average Modal Size Distribution Parameters^a

Aerosol Type	Nuclei Mode			Accumulation Mode			Coarse Mode		
	\bar{D}_{g1}	σ_{g1}	N_1	\bar{D}_{g2}	σ_{g2}	N_2	\bar{D}_{g3}	σ_{g3}	N_3
Remote marine	0.01	1.6	340	0.071	2.0	60	0.62	2.7	3.1
Latitudes 60°–75°S ^b	0.018	1.4	310	0.075	1.6	70	0.58	2.49	3.1
Latitudes 15°–60°N ^b	0.020	1.47	230	0.092	1.47	176.7	0.58	2.49	3.1
Clean continental	0.016	1.6	1,000	0.067	2.1	800	0.93	2.2	0.72
Polluted	0.014	1.8	106,000	0.054	2.16	32,000	0.86	2.21	5.4

^a \bar{D}_{g_i} is given in μm , and N_i is given in cm^{-3} . Parameters are from *Whitby* [1978].

^bAverage fine marine parameters over the latitude range are from *Heintzenberg et al.* [2000], and coarse mode parameters are from *Jaenicke* [1993].

carbon numbers, functional groups, and solubilities in extraction media [*Saxena and Hildemann*, 1996]. The organic mass fraction in polluted and continental aerosol often comprises an estimated 20% of fine particle mass [*Heintzenberg*, 1989; *Ramanathan et al.*, 2001; *Neusüß et al.*, 2002]. However, the organic mass fraction may potentially be as high as 70% for a highly polluted aerosol [*Saxena and Hildemann*, 1996]. It is estimated that organic carbon (OC) can represent up to 50% of the mass of particulate matter $<10 \mu\text{m}$ in diameter (PM_{10}) over the continental United States [*Saxena and Hildemann*, 1996; *Seinfeld and Pandis*, 1998]. Given that the total organic mass can be up to 2.1 times the OC mass for nonurban aerosol [*Turpin and Lim*, 2001], organic compounds may represent up to 100% of the aerosol mass in continental aerosol. For marine aerosol the organic mass fraction may be as high as 41–67% [*Heintzenberg*, 1989].

2.2. Aerosol Used in This Study

[16] Three different aerosol (marine, continental, and polluted) are represented in this study. The trimodal log-normal size distributions used in this analysis are based on the distributions of *Whitby* [1978], scaling the modal aerosol number concentrations to be within the range of the *Gultepe and Isaac* [1999] observations (Table 3). *Heintzenberg's* [1989] observed sulfate and organic mass fractions represent the fine particle composition for these cases (Table 2). The polluted coarse mode aerosol composition is estimated by averaging mass fraction observations reported by *Ramanathan et al.* [2001], *Neusüß et al.* [2002], and *Finlayson-Pitts and Pitts* [1986]. The marine coarse mode aerosol composition estimated by *Fitzgerald* [1991] is used, and the continental coarse mode composition is assumed to be 90% insoluble and 10% ammonium sulfate. We vary the fine particle organic mass fractions from 0 to 0.41 (marine), from 0 to 0.45 (continental), and from 0 to 0.61 (polluted), which are below the ranges noted in previous studies. When the organic mass fraction is increased, the sulfate mass fraction remains as specified by *Heintzenberg* [1989], and the insoluble mass fraction is adjusted. This is an important difference from many studies [e.g., *Li et al.*, 1998], in which highly hygroscopic inorganic salts are replaced with partially soluble organic compounds.

[17] The water-soluble organic component (by a simplification of chemical composition observed in Po Valley, Italy) is assumed to be composed of (by mass) 18% levoglucosan ($\text{C}_6\text{H}_{10}\text{O}_5$, density of 1600 kg m^{-3} , and van't Hoff factor of 1), 41% succinic acid ($\text{C}_6\text{O}_4\text{H}_6$, density of 1572 kg m^{-3} , and van't Hoff factor of 3), and 41% fulvic acid ($\text{C}_{33}\text{H}_{32}\text{O}_{19}$, density of 1500 kg m^{-3} , and van't Hoff

factor of 5) [*Nenes et al.*, 2002]. The average solubility is assumed to be $0.02 \text{ kg (kg H}_2\text{O)}^{-1}$ (or $0.1 \text{ moles C L}^{-1}$).

2.3. Aerosol Number/Droplet Number Correlations

[18] The data represented by the *Boucher and Lohmann* [1995] and *Gultepe and Isaac* [1999] correlations cover a wide range of conditions of cloud formation. The *Boucher and Lohmann* [1995] correlations are based on four data sets, which include 85 observations of cloud droplet number and cloud water sulfate within stratiform and cumuliform clouds over North America [*Leitch et al.*, 1992]; 15 observations of nss sulfate and CCN active at 0.3% supersaturation at Cheeka Peak, Washington [*Berresheim et al.*, 1993; *Quinn et al.*, 1993]; 12 observations of dimethylsulfide, nss sulfate mass, and CCN active over the northeast Atlantic [*Hegg et al.*, 1993]; and 14 observations of accumulation mode particle concentrations and sulfate mass concentrations over the North Atlantic [*Van Dingenen et al.*, 1995].

[19] The *Gultepe and Isaac* [1999] plots of cloud droplet number concentration versus aerosol number concentration is based on five data sets, which include observations in Syracuse, New York, Ontario (Eulerian Model Evaluation Field Study (EMEFS) I and II), Nova Scotia (North Atlantic Regional Experiment (NARE)), Bay of Fundy, and central Ontario (Radiation, Aerosol, and Cloud Experiment (RACE)). There were more than 10,000 observations collected over a period of 11 years. The cloud types observed were primarily stratus and stratocumulus.

[20] These observations exhibit a high degree of variability. Thus we do not use the correlations to predict the number of droplets for individual updrafts. Rather, the correlations are used to estimate a representative updraft velocity that is required to produce the typical observed droplet concentration for cloud systems in different environments (represented by average aerosol chemical and phys-

Table 2. Modal Base Case Chemical Composition for Each Aerosol Type Used in This Study^a

Aerosol Type	Fine			Coarse			
	ϵ_{SO_4}	ϵ_o	ϵ_{ins}	ϵ_{SO_4}	ϵ_{NaCl}	ϵ_o	ϵ_{ins}
Marine	0.22	0.11	0.59	0.05	0.93	-	0.05
Clean continental	0.37	0.24	0.25	0.07	-	-	0.9
Diluted polluted	0.28	0.31	0.30	0.11	-	0.2	0.644

^aThe fine particle ($\bar{D}_{g_i} < 0.1 \mu\text{m}$) mass fractions are obtained from *Heintzenberg* [1989]. Coarse mode sulfate mass fractions are calculated using the procedure outlined in the text. The other coarse mode mass fractions are estimated from *Fitzgerald* [1991], *Ramanathan et al.* [2001], *Neusüß et al.* [2002], and *Finlayson-Pitts and Pitts* [1986].

Table 3. Base Case Modal Aerosol Number Concentrations as Obtained From the Procedure Outlined in the Text^a

Aerosol Type	Modal Number Concentration, cm ⁻³				Parameters Constrained by Droplet Correlations	
	Nuclei	Accumulation	Coarse	Total N_{ap}	N_d^b	$m_{SO_4}^c$
Marine	230	177	3.1	410	150	1.75
Clean continental	555	444	4.1	1003	299	4.46
Diluted polluted	1152	348	5.4	1505	352	6.62

^aConcentrations N_i are given in cm⁻³. The other modal size distribution parameters are given in Table 1.

^bBase case droplet number N_d , given in cm⁻³, is constrained by the *Gultepe and Isaac* [1999] correlations.

^cTotal aerosol sulfate mass m_{SO_4} , given in $\mu\text{g m}^{-3}$, is constrained by the *Boucher and Lohmann* [1995] correlations.

ical characteristics and a representative base case updraft velocity). The *Gultepe and Isaac* [1999] and *Boucher and Lohmann* [1995] correlations are currently being used in GCMs, and their inherent variability contributes to the large predictive uncertainty in the models. By evaluating the sensitivities within the context of these correlations we are providing an assessment within the framework of the current methodology.

2.4. Cloud Parcel Model

[21] The cloud parcel model [*Nenes et al.*, 2001] captures the explicit aerosol microphysics of cloud droplet formation by diffusional growth. The model simulates the evolution of liquid water cloud droplet distributions in a nonprecipitating, adiabatic updraft and has been used in numerous studies, including a successful CCN/cloud droplet number closure study using in situ observations from the NASA Cirrus Regional Study of Tropical Anvils and Cirrus Layers (CRYSTAL)–Florida Area Cirrus Experiment (FACE) mission [*Conant et al.*, 2004]. The model does not include collision-coalescence processes but rather focuses on cloud droplet activation. The presence of slightly soluble and surfactant substances in CCN is treated explicitly, using the *Facchini et al.* [1999] correlation to characterize the surface tension of the growing droplets. The model computes the time-dependent particle sizes, water vapor supersaturation, pressure, and temperature. The initial assumed parcel conditions are a relative humidity of 98%, temperature of 284.2 K, and pressure of 939 mbar. The aerosol is not initially in equilibrium with the environment. The updraft is assumed constant since we are only interested in the cloud drop activation process, which generally occurs on the order of seconds; the buoyancy of the cloud parcel does not change significantly within this time. The number of droplets is computed by finding the CCN of highest critical supersaturation that activates (i.e., with a diameter larger than its critical diameter, evaluated at cloud top). Particles larger than this characteristic CCN are considered droplets. This definition of cloud droplets includes large CCN, which have not attained their critical diameter but are as large as activated drops ($\sim 1 \mu\text{m}$), and does not include CCN that deactivate and become interstitial aerosol.

[22] A film-breaking model is used to evaluate the effect of FFCs. The model assumes that the presence of FFCs on the droplet surface decreases the condensation coefficient to 10^{-5} . The FFC is distributed among the aerosol by mass, which is appropriate for primary sources, whereas a surface area-weighted distribution would be more appropriate for secondary organics that have entered the particles via condensation [*Feingold and Chuang*, 2002]. As the droplet

grows, the film thickness decreases. At the point when a monolayer of FFC (0.5 nm thick) is achieved, the film breaks, and the condensation coefficient immediately increases to 0.045. The FFC mass fraction is assumed to be equal to the base case organic mass fraction, only for determining how long it takes the film to break. When FFCs are not present, a constant condensation coefficient of 0.045 is assumed, uniform for all particles. In addition, a simulation is performed with a constant condensation coefficient of 0.005 to represent the maximum potential effect of FFCs. A thermal accommodation coefficient of unity is assumed [*Shaw and Lamb*, 1999]. It should be noted that the structure and evolution of films, in addition to the size-resolved chemical composition of the films themselves, are so uncertain that the mechanism of the film-breaking model is highly speculative.

2.5. Empirical Correlations and Model Setup

[23] The *Boucher and Lohmann* [1995] and *Gultepe and Isaac* [1999] relationships correlate cloud droplet number concentration with different aerosol characteristics. Employing both relationships consistently limits two of three key aerosol-cloud interaction parameters (sulfate mass, aerosol, and droplet number). By specifying a total aerosol number concentration (N_{ap}) for each environment (Table 3), cloud droplet number concentration (N_d) is calculated according to the empirical best fit relationships of *Gultepe and Isaac* [1999], as shown by

$$\text{Continental and polluted} \quad N_d = -595 + 298 \log(N_{ap}) \quad (1a)$$

$$\text{Marine} \quad N_d = -273 + 162 \log(N_{ap}) \quad (1b)$$

[24] The *Gultepe and Isaac* [1999] correlation (equation (1a)) can be applied for N_{ap} up to 1000 and 1500 cm⁻³ for the continental and polluted environments, respectively, since this is the range of the observations. Because of this the continental and polluted fine particle number concentrations from *Whitby* [1978] are reduced so that the total aerosol number concentrations are 1000 and 1500 cm⁻³, respectively, while the mean diameter and mean dispersion are kept constant. Reducing the particle number concentration can be justified physically as dilution of an urban plume or vertical mixing of a continental air mass. Thus the polluted case should be thought of as “diluted polluted” and the continental as “clean continental.”

[25] The cloud droplet number concentration, computed from equation (1), is introduced into the *Boucher and*

Lohmann [1995] correlation to obtain the total aerosol sulfate mass concentration (m_{SO_4}):

$$\text{Average} \quad m_{\text{SO}_4} = 10^{\left\{ \frac{\log(N_d) - 2.21}{0.41} \right\}} \quad (2a)$$

$$\text{Maritime} \quad m_{\text{SO}_4} = 10^{\left\{ \frac{\log(N_d) - 2.06}{0.48} \right\}} \quad (2b)$$

Table 3 shows the base case droplet number (N_d) and total aerosol sulfate mass (m_{SO_4}) as constrained by these correlations.

[26] Aerosol mass is often dominated by the larger particles, while number is dominated by smaller particles. Because of this we need to be careful in how the sulfate is distributed throughout the size distribution. The sulfate mass determined by the Boucher and Lohmann [1995] correlation (m_{SO_4}) is equal to the sum of the sulfate mass within each lognormal mode. The sulfate mass concentration of each lognormal mode ($m_{\text{SO}_{4i}}$) is calculated according to equations (3)–(5):

$$m_{\text{SO}_{4i}} = \varepsilon_{\text{SO}_{4i}} \rho_{\text{ap}_i} V_i, \quad (3)$$

where

$$\rho_{\text{ap}_i} = \frac{1}{\frac{\varepsilon_{o_i}}{\rho_{o_i}} + \frac{\varepsilon_{s_i}}{\rho_{s_i}} + \frac{\varepsilon_{\text{ins}_i}}{\rho_{\text{ins}_i}}}, \quad (4)$$

where the subscripts are as follows: s denotes properties of the soluble component, o stands for the organic component (which is slightly soluble), and ins stands for the insoluble component, with subscript i indicating the modes (nuclei, accumulation, and coarse). In the absence of other soluble compounds the sulfate mass fraction ($\varepsilon_{\text{SO}_{4i}}$) is related to the soluble mass fraction (ε_{s_i}) by the ratio of their molecular weights (M_{SO_4}/M_s), where M_s is the molecular weight of ammonium sulfate. For the marine coarse aerosol the addition of NaCl yields $\varepsilon_{s_i} = \varepsilon_{(\text{NH}_4)_2\text{SO}_{4i}} + \varepsilon_{\text{NaCl}_i}$, where $\varepsilon_{(\text{NH}_4)_2\text{SO}_{4i}} = \varepsilon_{\text{SO}_{4i}} (M_{(\text{NH}_4)_2\text{SO}_4}/M_{\text{SO}_4})$. The volume concentration (V_i) is calculated from the number concentration (N_i), geometric mean diameter (\bar{D}_{g_i}), and geometric standard deviation (σ_{g_i}) for each mode, according to

$$V_i = N_i \left(\frac{\pi}{6} \right) \exp \left(3 \ln \bar{D}_{g_i} + \frac{9}{2} \ln^2 \sigma_{g_i} \right). \quad (5)$$

[27] Given that a variety of combinations of $m_{\text{SO}_{4i}}$ can give m_{SO_4} , we consider values that are consistent with observations. In this study, we set the fine particle mass fractions to the values reported by Heintzenberg [1989] (Table 2) and then compute the coarse mode sulfate mass fraction from the constraint $\sum m_{\text{SO}_{4i}} = m_{\text{SO}_4}$. If the computed coarse mode sulfate mass fraction is not within observed values, then we instead assume an observed coarse mode sulfate fraction and adjust the coarse mode number concentration so that $\sum m_{\text{SO}_{4i}} = m_{\text{SO}_4}$.

[28] Adjustment of the chemical composition or number concentration of the coarse mode can be justified in two ways. First, coarse mode measurements are often the least certain of the three modes because of limitations in the

instrumentation [Baron and Willeke, 2001]. Second, the contribution of the coarse mode particles to cloud droplet number is negligible, on the order of $1\text{--}10 \text{ cm}^{-3}$. Therefore, given that the coarse particle sulfate mass fraction can strongly influence sulfate mass burden, it is preferable to first assign the sulfate mass for the fine particles and then to attribute the remaining sulfate mass, given by the Boucher and Lohmann [1995] correlations, to the coarse particles.

[29] Using the procedure outlined above, coarse mode sulfate mass fractions are calculated for the marine and polluted aerosol (keeping coarse mode number concentrations constant). The calculated coarse mode sulfate mass fraction for the polluted aerosol is 0.11, midway between the observed range, 0.02–0.25 [Ramanathan et al., 2001; Neusüß et al., 2002; Finlayson-Pitts and Pitts, 1986]. Coarse mode particles in the marine boundary layer are primarily composed of sea salt, with much smaller amounts of nitrates and mineral dust [Fitzgerald, 1991]. Sea salt consists of $\sim 7.68\%$ (by mass) sulfate [Seinfeld and Pandis, 1998], so that in the absence of other mechanisms the coarse mode mass fraction of sulfate should be < 0.08 for the marine aerosol. Our analysis yields a coarse mode sulfate mass fraction of 0.01, which is slightly lower than expected.

[30] The continental aerosol distribution used lacks sufficient coarse mode particles to yield an m_{SO_4} consistent with the Boucher and Lohmann [1995] correlation. Increasing the coarse mode number concentration from 0.72 to 4.1 cm^{-3} satisfies the constraint $\sum m_{\text{SO}_{4i}} = m_{\text{SO}_4}$. This change has a negligible impact on CCN and droplet number concentrations.

3. Results

3.1. Base Case Updraft Velocity

[31] Ensuring that the aerosol chemistry and size distribution are consistent with observations is a necessary but not sufficient condition for the plausibility of our analysis. The base case updraft velocity must also be consistent with observations; otherwise, the sensitivities calculated may not be representative of the ambient atmosphere, as they have been shown to be strong functions of updraft velocity and chemical composition [e.g., Rissman et al., 2004]. The base case updraft velocity is inferred, rather than prescribed, because updraft is highly uncertain; it is both difficult to measure and highly variable.

[32] Coalescence and entrainment may have in reality affected observations of droplet number, although these processes are not explicitly addressed within the parcel model. However, these processes can only reduce droplet number. Thus the calculated base case updraft velocity actually represents the minimum cooling rate required to produce the number of cloud droplets that are predicted by the empirical correlations. Where entrainment does exist, this means that a greater updraft velocity is required to produce the observed number of droplets. A higher updraft is expected to enhance the relative sensitivity of cloud droplet number to surface tension effects [Rissman et al., 2004].

[33] The base case updraft velocity is determined iteratively. Updraft velocity is varied until cloud droplet number calculated from the cloud parcel model matches the Gultepe and Isaac [1999] and Boucher and Lohmann [1995] corre-

lations. The resulting base case updraft velocities are ~ 0.7 – 1.5 m s^{-1} for the continental case and ~ 2 – 3.5 m s^{-1} for the polluted case, which are within the expected range (e.g., 0 – 1 m s^{-1} for stratiform and ~ 1 – 17 m s^{-1} for continental cumulus clouds [Seinfeld and Pandis, 1998]). Mason [1971] found that updrafts in nonprecipitating continental cumulus clouds are typically no greater than 5 – 7 m s^{-1} . The maximum parcel supersaturations for the continental and polluted base cases are 0.7 – 0.8% and 1.2 – 1.4% , respectively. Supersaturations in the ambient atmosphere are usually $<1\%$ and almost never exceed 2% [Seinfeld and Pandis, 1998]. Although the base case updraft velocities and maximum supersaturations are higher than average values measured in situ, this is expected. Within a single cloud the higher end of the updraft velocity spectrum is expected to control the total number of cloud droplets formed. Thus, when a single updraft is used to represent the production of cloud droplets, its intensity is expected to be larger than average but still within the observed range. Thus the base case aerosol size distribution and chemical composition are reasonable representations of the ambient aerosol for the continental and polluted cases.

[34] Surface tension depression from the presence of the organics is not considered for the base case calculations. If surfactants were considered, the base case updraft velocities would be cut in half and the maximum supersaturations would be reduced to 0.4 – 0.5% and 0.8 – 0.9% for the continental and polluted cases, respectively.

[35] If the condensation coefficient were increased from 0.045 to 1.0 , the maximum supersaturation for the base case does not change significantly, but the base case updraft velocity doubles for both the continental and polluted cases. With a higher condensation coefficient an increased rate of condensation in the initial stages of cloud formation leads to a lower cloud supersaturation and thus a lower cloud droplet number. Since the droplet number is constrained, the required updraft velocity must increase in order to provide the same driving force for condensational growth.

[36] The updraft velocity for the marine environment is expected to be lower than updraft velocities over continents. However, using the Whitby [1978] distribution, the base case updraft velocity for the marine case is $\sim 13 \text{ m s}^{-1}$ (neglecting surface tension effects), which is apparently greatly overestimated. If we use a different size distribution from Heintzenberg *et al.* [2000] and Jaenicke [1993] (Table 1), the base case updraft velocity is reduced to 0.1 – 0.35 m s^{-1} . While the total number of aerosol particles remains nearly the same as the number given by Whitby [1978] (within 2%), this alternative particle size distribution has a larger proportion of particles in the accumulation mode, where the majority of CCN are found. The maximum parcel supersaturation for this new base case is $<0.5\%$, whereas using the Whitby [1978] remote marine distribution, the maximum supersaturation was $>5\%$, which is not realistic for the atmosphere. Thus we use the Heintzenberg *et al.* [2000] and Jaenicke [1993] aerosol size distribution for the marine case in our analysis.

[37] Heintzenberg *et al.* [2000] grouped a total of 64 independent observations of marine fine aerosol size distributions from all over the world according to latitude (Table 1). Interestingly, the Whitby [1978] size distribution most closely approximates the latitude range 60° – 75°S in

terms of the proportion of aerosol in the nuclei and accumulation modes. This latitude range is very remote, and in fact, Whitby [1978] actually describes the observations as representative of a “remote marine” environment. By comparison, the 24 independent observations of fine aerosol size distribution that are listed within the latitude range 15° – 60°N by Heintzenberg *et al.* [2000] are likely influenced by anthropogenic activities. Since the Boucher and Lohmann [1995] and Gultepe and Isaac [1999] observations are from the Northern Hemisphere, we take an average of the size distribution parameters in the latitude range 15° – 60°N from Heintzenberg *et al.* [2000] to represent the fine marine aerosol in our analysis. The Jaenicke [1993] distribution is used to represent sea salt aerosol, which closely resembles the Whitby [1978] marine coarse mode aerosol distribution. With this new marine size distribution the calculated coarse mode sulfate mass fraction increases from 0.01 to 0.05 , which is closer to the expected value of ~ 0.08 .

3.2. Sensitivity of Droplet Number to Updraft Velocity

[38] The observations covered by the correlations include both stratiform and cumuliform data sets. For this reason, we consider a range of updrafts between 0.1 and 5 m s^{-1} for the continental and polluted cases and between 0.05 and 3 m s^{-1} for the marine case to cover the expected variability of droplet number from dynamical effects in both cloud types [Mason, 1971].

[39] For the updraft velocity sensitivity analysis the cloud parcel model is run twice (first at a high updraft velocity and then at a low updraft velocity) for each of the three aerosol number concentrations (1.0 , 0.75 , and 0.50 times the base case aerosol number concentration) and for each of the three environments (marine, continental, and polluted). In these simulations the organic component of the aerosol is not considered a surfactant, meaning that the surface tension remains constant as the droplet grows.

[40] For the marine base case (using the Heintzenberg *et al.* [2000] and Jaenicke [1993] distribution), cloud droplet number varies from 91 to 336 cm^{-3} as a result of changes in updraft velocity (Figure 2). The maximum parcel supersaturation corresponding to the 3 m s^{-1} updraft velocity for this case is 1.25 – 1.5% , which is on the high end of observations. This either indicates that the high updraft is very unlikely or indicates the presence of an aerosol with a chemical composition and/or size distribution that differs significantly from the average. Increasing the condensation coefficient to 1.0 decreases the maximum supersaturation for 3 m s^{-1} updrafts to 0.9 – 1.1% . However, the number of droplets also decreases by 11 – 18% .

[41] For the continental base case, cloud droplet number varies from 112 to 510 cm^{-3} (Figure 3), and for the polluted base case, cloud droplet number varies from 91 to 495 cm^{-3} as a result of changes in updraft velocity (Figure 4). For the continental case this variability ($\sim 400 \text{ cm}^{-3}$) encompasses a majority of the scatter in the observations. However, for the polluted case a significant fraction of the observations appear to be unexplained by the very large updraft variability.

[42] The maximum parcel supersaturations within 5 m s^{-1} updrafts are 1.6 – 1.9% and 1.7 – 2.0% for the continental and polluted cases, respectively. Changing the condensation

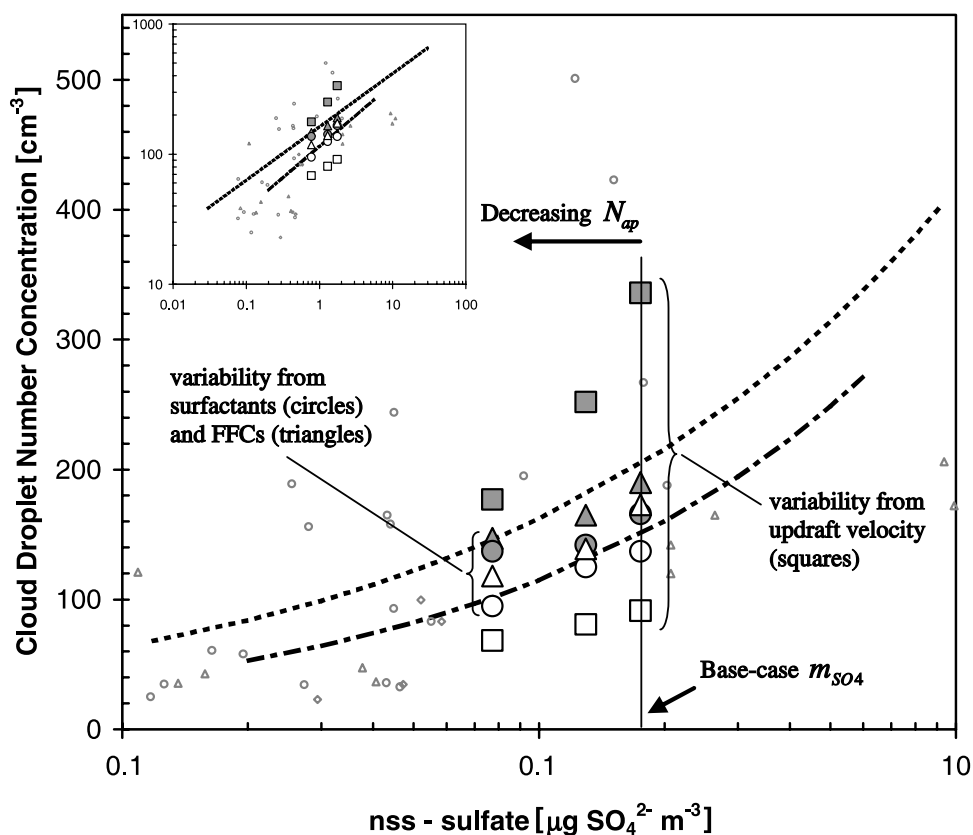


Figure 2. Marine cloud droplet number sensitivity to updraft velocity and chemical effects (using the Heintzenberg *et al.* [2000] and Jaenicke [1993] size distribution). Maritime observations, average correlation (dotted line), and maritime correlation (dash-dotted line) are from Boucher and Lohmann [1995]. Marine case cloud parcel model results for high updraft velocity (shaded squares), low updraft velocity (open squares), high organic mass fraction (shaded circles), low organic mass fraction (open circles), constant condensation coefficient (0.005, shaded triangles), and changing condensation coefficient (10^{-5} –0.045, open triangles) are overlaid on the observational data. The values of organic mass fraction and updraft velocity for each simulation point are given in Table 4. The condensation coefficient is 0.045, except where otherwise specified. The inset shows the full range of the observations on a log-log scale.

coefficient to 1.0 changes the maximum supersaturations to 1–1.4% and 1.2–1.5% for the continental and polluted cases, respectively. However, the number of droplets decreases with this higher condensation coefficient by 18–19% and 20–27% for the continental and polluted cases, respectively. Including the surface tension effect would also slightly decrease the maximum supersaturation within 5 m s^{-1} updrafts but would result in an increase in cloud droplet number by up to 39%.

3.3. Sensitivity of Droplet Number to Chemical Effects

[43] The cloud parcel model is run twice (high and low organic mass fractions specified in Table 4) for each of the three number concentrations and for each of the three aerosol types to determine the sensitivity of cloud droplet number to surfactants. Only the fine particle organic mass fractions (which contribute the most to the CCN) are manipulated. These simulations utilize a constant condensation coefficient of 0.045 under the base case updraft conditions.

[44] Two additional simulations are performed to address the sensitivity of droplet number to a delayed

condensational growth rate that may result from the presence of FFCs on the droplet surface. Surface tension effects are neglected for these simulations. First, the condensation coefficient is decreased by ~ 1 order of magnitude (from 0.045 to 0.005). Then, a nonconstant condensation coefficient is assessed using a film-breaking model, for which the lowered condensation coefficient (10^{-5}) changes to 0.045 when the film breaks. Three different aerosol number concentrations and three different aerosol types are assessed at the base case updraft velocity and base case organic mass fraction.

[45] For the marine base case, increasing the organic mass fraction from 0 to 0.41 increases the number of cloud droplets from 137 to 166 cm^{-3} (Figure 2). This increase ($\sim 30 \text{ cm}^{-3}$) is mainly due to the effect of surface tension depression by the organic species but is also influenced by the replacement of insoluble compounds with slightly soluble compounds. For the constant 0.005 condensation coefficient the number of cloud droplets for the marine base case increases further to 190 cm^{-3} . Using the film-breaking model yields a droplet number of 173 cm^{-3} . Thus the overall sensitivity of

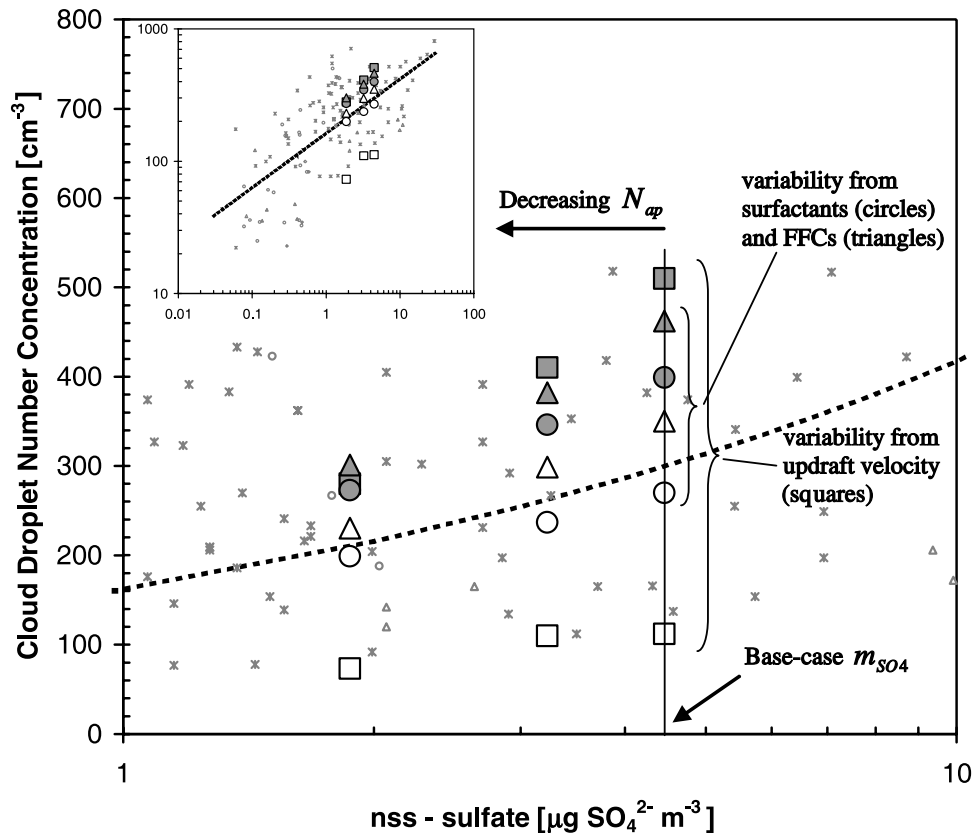


Figure 3. Same as Figure 2 but for continental aerosol with the average correlation and including all observations from *Boucher and Lohmann* [1995].

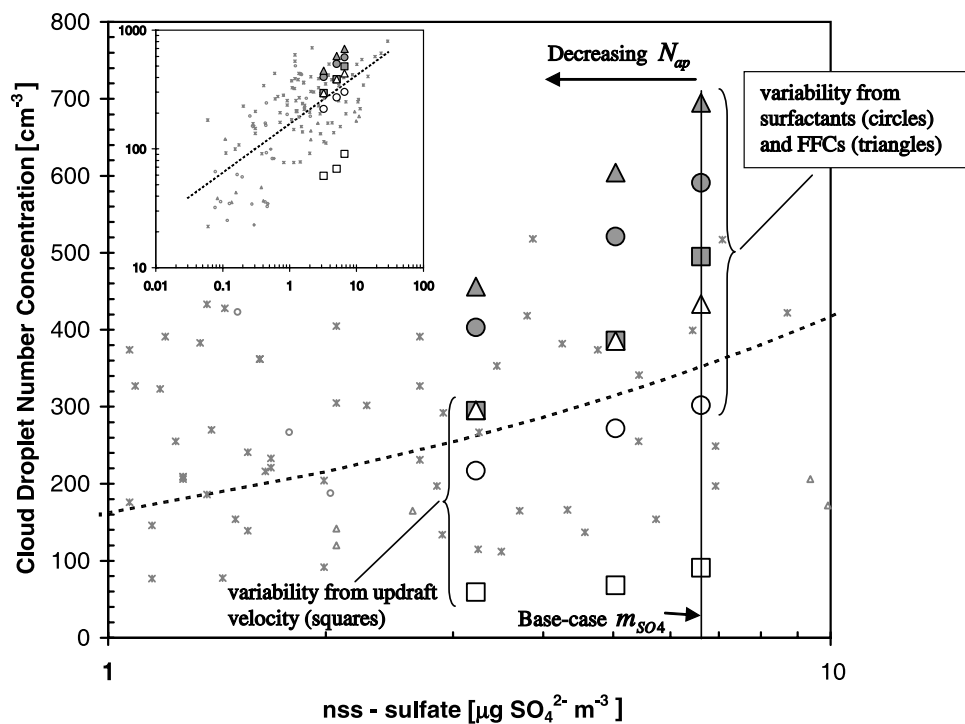


Figure 4. Same as Figure 3 but for polluted aerosol.

Table 4. Base Case, Lower, and Upper Limit Values for Updraft Velocity and Fine Particle Organic Mass Fractions Used for Assessing the Sensitivity to Dynamical and Chemical Effects, Respectively^a

Aerosol Type	Updraft Velocity, m s ⁻¹			Fine Particle Organic Mass Fraction		
	Base	Lower	Upper	Base	Lower	Upper
Marine	0.1, 0.16, 0.35	0.05	3	0.11	0	0.41
Clean continental	0.7, 1.0, 1.5	0.1	5	0.24	0	0.45
Diluted polluted	2.0, 3.0, 3.5	0.1	5	0.31	0	0.61

^aThe range of base case updraft velocities for each aerosol type is for each of the three different aerosol number concentrations (100%, 75%, and 50% of the base case N_{ap} given in Table 3). The base case fine particle organic mass fraction is from *Heintzenberg* [1989], and the upper limit in organic mass fraction is estimated from *Seinfeld and Pandis* [1998].

droplet number to chemical effects for the marine base case is ~ 50 cm⁻³. This is $\sim 20\%$ of the cloud droplet sensitivity from updraft variability.

[46] As a result of surface tension effects, increasing the organic mass fraction increases the number of droplets from 270 to 399 cm⁻³ (continental base case) and from 302 to 591 cm⁻³ (polluted base case). The constant 0.005 condensation coefficient simulation increases the number of droplets further to 462 and 695 cm⁻³ for the continental and polluted base cases, respectively. Thus the cloud droplet number sensitivity to surfactants is 32–36% (continental) and 79–96% (polluted) of the sensitivity induced by updraft variability. However, it is important to note that the number of droplets resulting from surface tension effects can be much greater than the droplet number resulting from high updraft velocity. In other words, surface tension effects shift the variability to higher droplet concentrations. This is typically the case for the polluted aerosol.

[47] Surface tension effects increased the number of cloud droplets by 9–35% (marine), 30–33% (continental), and 54–68% (polluted) from the base case. *Mircea et al.* [2002] also found that the change in droplet number resulting from replacing insoluble compounds with surfactants was greater for the urban aerosol (110% increase in droplet number from the base case) and rural aerosol (97% increase) than for marine aerosol (13% increase).

[48] The constant 0.005 condensation coefficient simulations produce the greatest number of cloud droplets resulting from chemical effects. One of the interesting results is that the highest sensitivity of cloud droplet number to condensation coefficient appears to be at or near typical observations of cloud droplet condensation coefficient (i.e., 0.045). Decreasing the condensation coefficient further (below 10^{-3}) has an almost negligible effect on droplet number, as most of the aerosol particles have already activated by this point. As mentioned previously, condensation coefficients on the order of 10^{-5} have been suggested for atmospheric aerosol influenced by FFCs. When the film-breaking model is introduced, the effect on droplet number is less pronounced than with a constant condensation coefficient; using the film-breaking model produces 91% (marine), 76% (continental), and 62% (polluted) of the droplet number resulting from the constant condensation coefficient simulation. Nevertheless, for the polluted case the increase in droplet number using the film-breaking

model is nearly equivalent to the effect from a 5 m s⁻¹ updraft.

3.4. Chemical and Dynamical Effects for Variable Aerosol Number

[49] It is instructive to examine the variability from chemical and dynamical effects for other values of the aerosol number concentration. The striking feature for all three aerosol is the remarkable robustness of the variability; chemical effects remain significant, even when decreasing the aerosol number concentration by 25 and 50%. Since the *Gultepe and Isaac* [1999] observations of aerosol concentration only go up to 1000 cm⁻³ (for continental aerosol) and 1500 cm⁻³ (for the polluted aerosol), the correlations cannot be used to extrapolate the base case updraft velocity and we cannot assess the sensitivity for higher concentration plumes, although there are indications that the sensitivity may change under such conditions [*Rissman et al.*, 2004].

[50] In general, the relative sensitivity of cloud droplet number to surfactants increases as the aerosol number concentration decreases. This is most important for the marine case (Figure 2), while it appears negligible for the continental and polluted cases (Figures 3 and 4). For the marine case the sensitivity of droplet number to surfactants increases from 15 to 35% when the aerosol number concentration is reduced by 50% from the base case. The marine base case updraft velocities are on the most sensitive region of the relative organic surfactant sensitivity plot of *Rissman et al.* [2004]. At the lower aerosol number concentration a higher base case updraft is required. As updraft velocity increases (0.1 m s⁻¹ for the base case N_{ap} , 0.16 m s⁻¹ with 75% N_{ap} , and 0.35 m s⁻¹ with 50% N_{ap}), surface tension effects have a larger relative effect on droplet number, as expected from the results of *Rissman et al.* [2004]. Conversely, the continental base case updraft velocities are within a stable regime on the *Rissman et al.* [2004] relative sensitivity plot, and an increase in the base case updraft velocities causes only a slight increase in the relative sensitivity of droplet number to surfactants.

4. Implications for the Aerosol Indirect Effect

[51] The first indirect effect is related to changes in cloud reflectivity, which can be characterized fairly well by two of the following three parameters: cloud liquid water content, effective radius, and droplet number. By assuming a constant liquid water content (q_c) a change in droplet number (N_d) can be roughly related to a change in cloud reflectivity (R_c). The approximation $\Delta R_c \sim 0.075 \Delta \ln(N_d)$ is valid within 10% for an initial cloud reflectivity between 0.28 and 0.72 [*Seinfeld and Pandis*, 1998]. We assume an initial R_c of 0.5 and plot the average percent change in R_c resulting from changes in cloud droplet number from updraft variability and chemical effects (Figure 5). This rough approximation shows that chemical effects, which include both surface tension effects and changes in the condensation coefficient, may enhance cloud reflectivity by 4–10%, with respect to the base case cloud droplet number. Comparatively, variations in updraft velocity are expected to enhance cloud reflectivity by 2–12%.

[52] The second indirect effect, which is related to cloud lifetime, is an even greater challenge to quantify. We look at

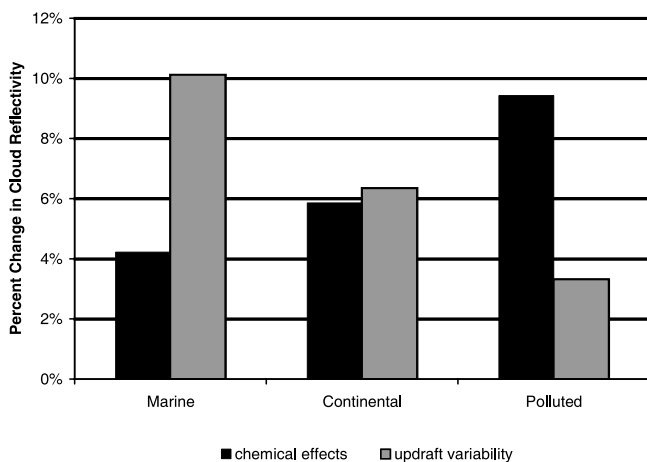


Figure 5. Estimated percent change in cloud reflectivity resulting from increases in droplet number from chemical effects and updraft variability, assuming a constant liquid water content and using a parameterization from *Seinfeld and Pandis* [1998]. An initial cloud reflectivity of 0.5 is assumed.

the rate of autoconversion (Q_{aut}) to represent the second indirect effect, since autoconversion is the rate of initial generation of rain/drizzle from cloud water, which has direct implications for cloud lifetime. The *Khairoutdinov and Kogan* [2000] parameterization describes Q_{aut} as a function of droplet number and cloud liquid water content, $Q_{\text{aut}} = 1350q_c^{2.47}N_d^{-1.79}$. Assuming constant liquid water content, the increase in droplet number resulting from chemical effects suggests that Q_{aut} may decrease by 34–63%. This is due to the smaller sizes of the droplets, which have smaller settling velocities, thereby decreasing their rate of collision. For comparison, a high updraft velocity may decrease Q_{aut} by 19–76%.

5. Conclusions

[53] This study assesses the variability in cloud droplet number that may result from the effect of organic species on surface tension and from the effect of film-forming compounds on the water vapor condensation coefficient. The cloud droplet number variability is compared to the variability caused by uncertainties in updraft velocity. An inverse modeling approach is employed for this task. Using a detailed numerical cloud parcel model, observed aerosol characteristics, and correlations of cloud droplet versus sulfate and cloud droplet versus aerosol number, a most probable size distribution and updraft velocity for polluted and clean conditions are obtained. The variation in cloud droplet number from expected variations in aerosol chemistry and updraft velocity is then compared to the observed cloud droplet number scatter in the empirical aerosol sulfate-cloud droplet number correlation.

[54] Three important results come out of this study. First, chemical effects can potentially have a significant effect on cloud droplet number concentration for conditions ranging from marine to polluted in the regions surrounding the North American continent and Atlantic Ocean. Chemical effects may account for an average of 28% (marine), 49%

(continental), and >100% (polluted) of the variability in cloud droplet number, as compared to the variability from updraft velocity. This underlines the importance of including chemical effects within GCM assessments of the aerosol indirect effect and challenges the common belief that the variability seen in empirical aerosol number/cloud droplet number relationships is primarily from the highly variable cloud dynamics.

[55] Another important finding is that surface tension effects may enhance the sensitivity of droplet number to variations in updraft velocity. Thus the microphysical characteristics of clouds originating from organic CCN are likely more sensitive to the shape of the updraft velocity spectrum than are the characteristics of clouds composed of purely inorganic CCN. Including surface tension effects increases the number of cloud droplets formed in 5 m s^{-1} updrafts by 55–63% for the polluted case and 30–39% for the continental case and increases the number of cloud droplets formed in 3 m s^{-1} updrafts by 14–16% for the marine case. Thus surface tension effects could help to explain the high end of the measured cloud droplet number variability.

[56] The other significant finding is that the relative effect of organic species on cloud droplet number appears relatively insensitive to the aerosol number concentration for a wide range of aerosol and updraft conditions typically found in GCM simulations. This suggests that the relative importance of chemical effects on cloud droplet number may not be masked by fluctuations in aerosol number concentration expected on the spatial scale of a typical GCM grid cell.

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