

# Can Chemical Effects Rival the First Indirect Effect?

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**Abstract.** An increase in cloud droplet number concentration resulting from an increase in ambient aerosol is identified as the first indirect climatic effect of aerosols. A key question is whether chemical effects (e.g. dissolution of soluble gases) could potentially rival the first indirect effect. We assess here, using an adiabatic parcel model with explicit microphysics, the sensitivity of cloud droplet number concentration to such chemical factors. We find that numerous conditions exist, particularly for marine aerosols, for which chemical influences on cloud droplet activation can rival the first indirect effect. Our simulations suggest that estimates of the aerosol first indirect effect need to account for chemical effects, particularly when the aerosol contains surface active species, condensable gases and species that can affect water vapor condensation.

## 1. Introduction

Anthropogenic influences on cloud properties and albedo, the so-called indirect climatic effect of aerosols, could constitute a major climate forcing [*Intergovernmental Panel on Climate Change (IPCC)*, 2001]. Twomey [1977] stated that the most important parameter influencing cloud droplet number concentration is aerosol number concentration. The implicit assumption is that

varying aerosol chemical composition has a relatively minor effect on cloud droplet number concentration. This work challenges this point, and questions whether so-called chemical factors (e.g. the dissolution of a soluble gas into the growing droplets) can produce variations in cloud droplet number that can rival those of the Twomey effect itself. Through the use of simple models, we assess here the sensitivity of cloud droplet number concentration to a combined set of chemical factors as

a way to begin to evaluate their potential importance to the indirect climatic forcing of aerosols.

## 2. Chemical effects considered in this study

The chemical factors that we examine are the dissolution of soluble gases [Kulmala *et al.*, 1993] and partially soluble solutes in the growing droplet [Shulman *et al.*, 1996], surface tension depression by dissolved organic substances [Shulman *et al.*, 1996], and accommodation coefficient changes from the formation of surfactant and organic films at the droplet surface.

A water-soluble trace gas can provide enough solute to interstitial (or unactivated) cloud condensation nuclei (CCN) so that they transform into activated droplets. Of all the water soluble gas-phase species, probably the most important is nitric acid ( $\text{HNO}_3$ ) since it is ubiquitous and can be found in relatively large concentrations (e.g. Fuzzi *et al.* [1992]).

Compared to a particle containing only soluble inorganic salts, the presence of a partially soluble species can affect droplet thermodynamics in three ways: a) it can decrease droplet critical supersaturation,  $S_c$ , if the species acts to decrease bulk surface tension, b) it can increase  $S_c$  because the amount of dissolved solute tends to decrease, and c) the dissolved species can exhibit non-ideal behavior, so that critical supersaturation can either be increased or decreased. Whether cloud droplet number concentration actually increases or decreases depends strongly on the relative importance of these three competing effects. The third effect is not addressed in this study. A fourth effect that can arise from the presence of surface active species: a lowering of the water vapor accommodation (or condensation) coefficient,  $\alpha$ . This is not a thermodynamic effect, i.e. it does not influence the droplet  $S_c$ , but will be shown to strongly influence the number of activated droplets in a parcel by modifying the parcel maximum supersaturation. Substances found in the atmosphere that are partially (or completely) soluble and exhibit surfactant and bulk-surface tension lowering behavior are usually some type of water-soluble organic compound (WSOC) [Shulman *et al.*, 1996].

## 3. Description of simulations

To examine the potential importance of chemical effects on cloud droplet number, we simulate cloud droplet number concentration relative to a baseline case in which the cloud is formed from  $(\text{NH}_4)_2\text{SO}_4$  aerosol.

The "Twomey effect" is assessed by calculating the change in droplet number for a doubling of the baseline aerosol concentration. We then compare the "Twomey effect" to the change in droplet number seen, if some chemical effect would be present in the baseline aerosol (i.e. no changes in size distribution, only chemistry).

An adiabatic cloud parcel model with explicit aerosol microphysics is used for computing the activated droplet number [Nenes *et al.*, 2001]. The model utilizes a moving grid for tracking the growth of the CCN droplets. Each log-normal mode is discretized into 75 size sections of equal width in log-normal space. The minimum and maximum size for the particles are selected so that the number of aerosol particles in the bins approximates the prescribed log-normal value to within  $10^{-9}$  %. The original version [Nenes *et al.*, 2001] solved for water vapor condensation only; appropriate modifications were made to solve for the simultaneous condensation of  $\text{HNO}_3$  from the gas phase onto the droplets.

The number of activated cloud droplets depends on updraft velocity (cooling rate), soluble gas concentration, and aerosol size distribution and chemical characteristics. Updraft velocity influences both the transit time and the maximum  $S$  in a cloud updraft; we consider updraft velocities of 0.1, 0.3, 1, and 3 m s<sup>-1</sup>. Cloud thickness is selected to be 250 m, so that enough time is allowed for the CCN population to activate. We consider the marine (pristine) and urban tri-modal log-normal aerosol size distributions of Whitby [1978] to represent pristine and polluted aerosol, respectively. The characteristics of the distribution are given in Table 1.

In terms of the aerosol chemical composition, the aerosol is assumed to contain  $(\text{NH}_4)_2\text{SO}_4$ , and a mixture of an organic and completely insoluble substance. The organic in the aerosol is assumed to be composed of 18% (by mass) levoglucosan ( $\text{C}_6\text{H}_{10}\text{O}_5$ , molar mass = 0.162 kg mol<sup>-1</sup>, density = 1600 kg m<sup>-3</sup>, van't Hoff factor = 1), 41% (by mass) succinic acid ( $\text{C}_6\text{O}_4\text{H}_6$ , molar mass = 0.118 kg mol<sup>-1</sup>, density = 1572 kg m<sup>-3</sup>, van't Hoff factor = 3), and 41% (by mass) fulvic acid [US Geological Survey, 1979], ( $\text{C}_{33}\text{H}_{32}\text{O}_{19}$ , molar mass = 0.732 kg mol<sup>-1</sup>, density = 1500 kg m<sup>-3</sup>, van't Hoff factor = 5). This organic mixture reproduces the surface tension behavior observed in the "Po Valley 2" data in Charlson *et al.* [2001] and is used to assess the effects of surface tension lowering in cloud droplet activation. As samples from completely different environments tend to exhibit similar behavior [Charlson *et al.*, 2001], we use the "Po Valley 2" data to describe the surface tension depression for all types of aerosol that contain WSOC. The organic

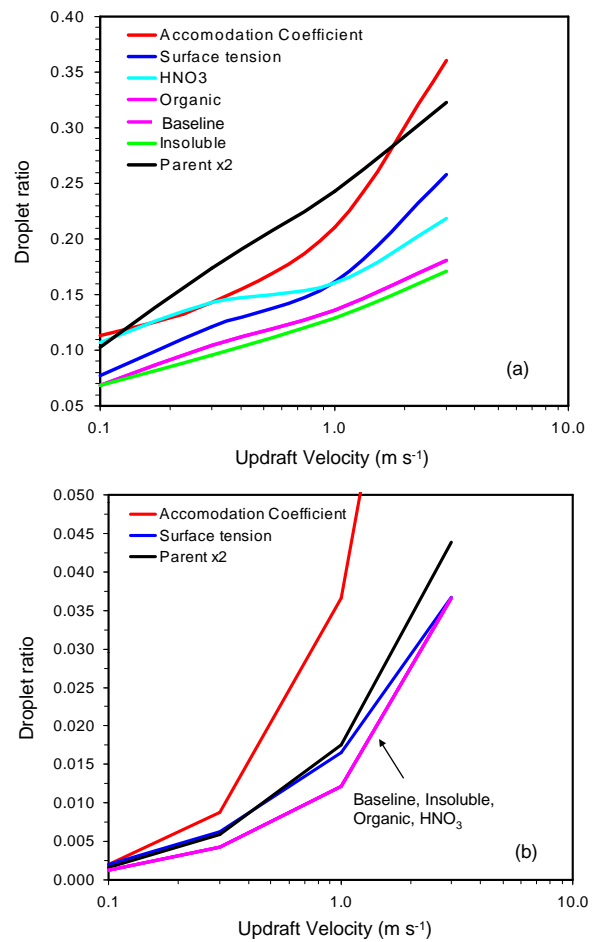
**Table 1.** Aerosol distribution parameters ( $r_{g,i}$  in  $\mu\text{m}$ ,  $N_i$  in  $\text{cm}^{-3}$ ) [Whitby, 1978]

| Aerosol type | Nuclei Mode |            |        | Accumulation Mode |            |       | Coarse Mode |            |       |
|--------------|-------------|------------|--------|-------------------|------------|-------|-------------|------------|-------|
|              | $r_{g,1}$   | $\sigma_1$ | $N_1$  | $r_{g,2}$         | $\sigma_2$ | $N_2$ | $r_{g,3}$   | $\sigma_3$ | $N_3$ |
| Marine       | 0.005       | 1.6        | 340    | 0.035             | 2.0        | 60    | 0.31        | 2.7        | 3.1   |
| Urban        | 0.007       | 1.8        | 106000 | 0.027             | 2.16       | 32000 | 0.43        | 2.21       | 5.4   |

mixture is assumed to be either completely soluble, or slightly soluble, with a solubility varying between  $10^{-4}$  and  $10^{-1}$  M. In addition, the accommodation coefficient is allowed to vary between  $10^{-3}$  and 1, but no explicit correlation to organic mass fraction, liquid water content or dry particle size is assumed. There have been studies that propose to provide a link between these quantities (e.g. *Feingold and Chuang* [2001]), but observational evidence is still pending to validate any conceptual atmospheric model. The insoluble fraction of the aerosol is assumed to have the same density as  $(\text{NH}_4)_2\text{SO}_4$ . The parcel pressure, temperature, and relative humidity are initially set at 800 mbar, 273 K, and 98%, respectively.

#### 4. Sensitivity of cloud properties to chemical effects

Figure 1 shows the ratio of activated droplet number over the baseline aerosol number concentration, as a function of updraft velocity. Figures 1a and 1b correspond to aerosol conditions quite typical of marine and urban situations, respectively. The organic mass fractions,  $\text{HNO}_3$  concentration, insoluble mass fraction, and accommodation coefficient used in these simulations are within the ranges of observed values (Table 2). The presence of insoluble material in the below-cloud aerosol can have a notable impact on cloud droplet number activated because of two competing effects: a) the number of CCN that activate at a given supersaturation decreases, because the critical supersaturation of each particle increases due to the presence of insoluble material, and b) the parcel maximum supersaturation tends to increase, because the rate of water absorption in the initial stages of cloud formation decreases as a result of the fewer activated particles (compared to the baseline); this allows for the parcel supersaturation to attain higher values before reaching a maximum. The first effect tends to decrease the droplet number, while the second exhibits the opposite trend. The marine cloud

**Figure 1.** Ratio of nucleated drops over the baseline aerosol concentration, as a function of updraft velocity, for (a) marine, and (b) urban aerosol size distributions.

**Table 2.** Conditions for the simulations in Figure 1 and Figure 3.

| Simulation                | Characteristics   |
|---------------------------|---|
| Baseline                  | Aerosol is pure $(\text{NH}_4)_2\text{SO}_4$ . $\alpha=1.0$   |
| Parent $\times 2$         | Same as "Baseline" simulation, but with aerosol concentrations doubled  |
| $\text{HNO}_3$            | Same as "Baseline" simulation, with 5 ppb $\text{HNO}_3$ in the gas phase   |
| Accommodation coefficient | Aerosol is pure $(\text{NH}_4)_2\text{SO}_4$ . $\alpha=0.01$  |
| Surface tension           | Aerosol is (by mass) 75% $(\text{NH}_4)_2\text{SO}_4$ , and 25% organic (composition given in text). $\alpha=1.0$ . Organic is completely soluble. Surface tension relationship given by <i>Charlson et al.</i> [2001]. |
| Organic                   | Same as "Surface tension" simulation, without surface tension effects.  |
| Insoluble                 | Aerosol is 75% (by mass) $(\text{NH}_4)_2\text{SO}_4$ , and 25% insoluble. $\alpha=1.0$ .   |

simulations indicate that at low updraft velocities, the two effects essentially cancel each other out. At higher updrafts, the first effect dominates. The urban simulations indicate that the presence of an insoluble substance does not strongly influence droplet number.

The presence of a WSOC, if it does not act as a surfactant or change bulk phase surface tension, alters the activation behavior of the aerosol by changing the moles of dissolved solute in the droplet. The organic mixture chosen for our simulations, if it is completely soluble, activates like  $(\text{NH}_4)_2\text{SO}_4$  (Figure 1). If a decrease in bulk phase surface tension is observed, the number of activated droplets increases regardless of updraft velocity. Furthermore, if the organic is assumed to display surfactant behavior, changing only  $\alpha$ , then the activated number of droplets can increase substantially. Perhaps counterintuitively, the number of droplets actually increase as  $\alpha$  decreases, because the rate of water absorption in the cloud decreases in the initial stages of its formation (the droplets do not grow as fast); this means that cloud supersaturation reaches higher values before enough CCN activate to start significant water vapor depletion. As a result, the parcel maximum supersaturation becomes larger (compared to if  $\alpha = 1$ ), and more droplets activate. The surface tension and condensation coefficient effects are seen to be important for both marine and urban clouds.

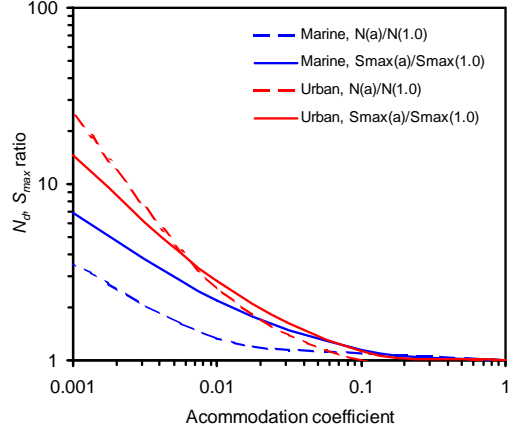
The presence of  $\text{HNO}_3$  dissolving in the droplets can substantially increase the number of activated particles. The effect is most pronounced for weak updrafts for two reasons: a) at low updrafts, when fewer droplets are formed, the available  $\text{HNO}_3$  is partitioned amongst fewer droplets, so the amount of solute per droplet is larger, and, b) at weak updraft velocities, the time scale

of the cloud activation process is longer, allowing more time for the soluble gas to dissolve in the droplets. As a result, the total amount of soluble material dissolved per droplet is larger. That the soluble gas effect is strongest for weak as opposed to strong updraft velocities is an important distinction between soluble gas and other chemical effects. In the urban cloud (Figure 1b), the effect of  $\text{HNO}_3$  on droplet number is negligible, simply because the amount of solute that is partitioned to each particle is very small. It would be too restrictive however, to state that polluted clouds are never affected by soluble gas dissolution; the combined effect of all soluble gases can still be very important [*Kulmala et al.*, 1996].

Given that the droplet number is so sensitive to changes in  $\alpha$ , it is prudent to explore the sensitivity over a range of values of  $\alpha$ . Figure 2 shows the activated droplet number and maximum supersaturation as a function of accommodation coefficient. The quantities are normalized with the values predicted for perfect accommodation ( $=1.0$ ). Red lines correspond to urban aerosol, and blue correspond to marine. Clearly the largest effects and sensitivities arise at the lowest values of  $\alpha$ .

One can see that the changes in droplet number concentration from the chemical effects in Figure 1 are similar to those of the Twomey effect. However, the extent of the Twomey and chemical effects, as expressed in Figure 1, depends on the values of organic mass fraction, and  $\alpha$  chosen for the simulation.

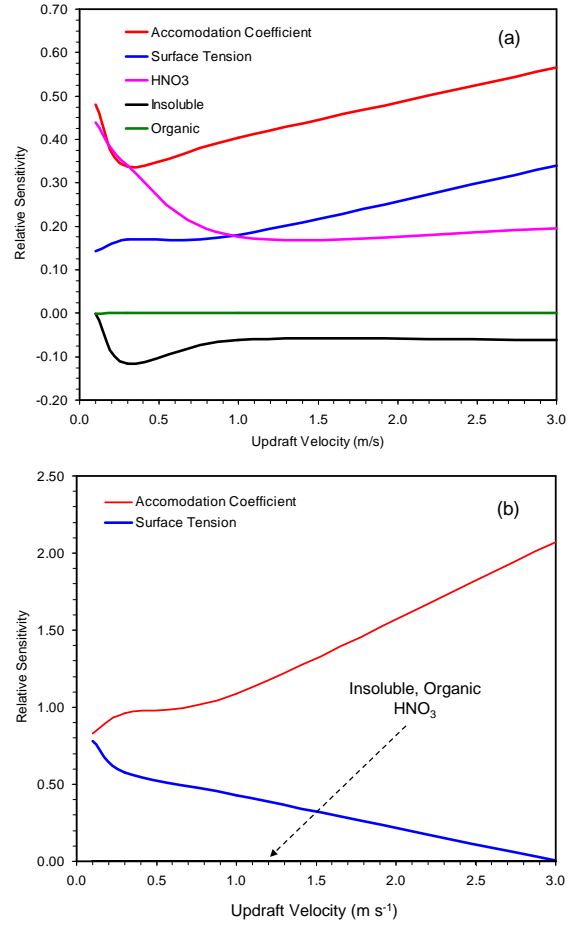
A useful representation is the relative activation sensitivity,  $\phi(x) = \left( \frac{x}{N_d} \frac{\partial N_d}{\partial x} \right) / \left( \frac{N_a}{N_d} \frac{\partial N_d}{\partial N_a} \right)$ , where  $x$  represents the organic mass fraction or  $\text{HNO}_3$  concentration,  $N_d$  is the droplet concentration, and  $N_a$  is the aerosol



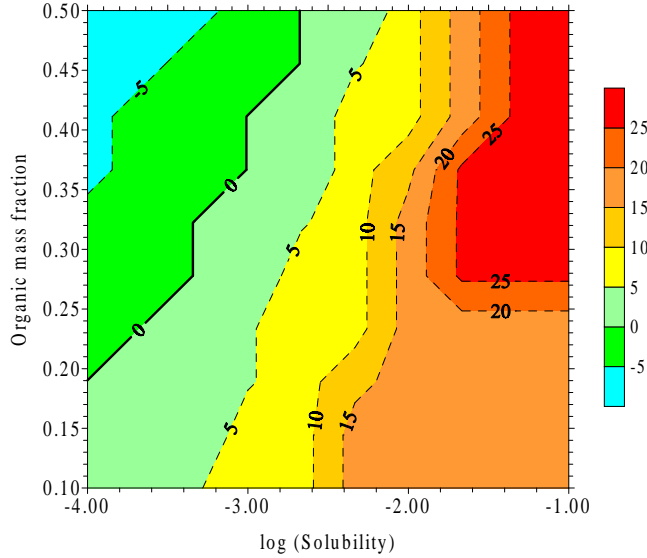
**Figure 2.** Nucleated droplet number and maximum supersaturation as a function of accommodation coefficient. The quantities are normalized by the values predicted for perfect accommodation ( $=1.0$ ). Red lines correspond to urban conditions, and blue correspond to marine.

concentration.  $\phi(x)$  expresses the ratio of the nondimensional sensitivity of droplet change due to chemical effects to the nondimensional sensitivity of droplet number concentration due to changes in aerosol number ("Twomey effect"). When  $|\phi(x)| > 1$ , the droplet population is more sensitive to chemical effects than the Twomey effect. When  $|\phi(x)| \sim 1$ , chemical effects exhibit similar sensitivity to the Twomey effect, and as  $|\phi(x)| \rightarrow 0$ , they become insignificant. The derivatives are numerically approximated from the simulations in Figure 1, and the results are shown in Figure 3. Clearly one can see that for the marine cloud, surface tension changes, soluble gas, and accommodation coefficient effects can exhibit comparable sensitivities to the Twomey effect. Similarly, for the urban cloud, surface tension and accommodation coefficient effects can rival the Twomey effect.

Up to this point, we have assumed that the WSOC is completely soluble. Equally interesting is the effect of a partially soluble WSOC on droplet number. Figure 4 shows the isopleth contours of  $\Delta N/N = \frac{(N_{WSOC} - N_b)}{N_b}$  with respect to organic mass fraction and solubility. In these simulations,  $\alpha$  is assumed to be unity, and the dissolved organic is assumed to decrease the bulk water surface tension. The surface tension change depends on the WSOC concentration when the droplet is on the verge of activation, and can be simply expressed



**Figure 3.** Relative nucleation sensitivity,  $\left( \frac{x}{N_d} \frac{\partial N_d}{\partial x} \right)$ , as a function of updraft velocity. Sensitivities for (a) marine, and (b) urban aerosol are shown. The curves correspond to the results presented in Figure 1.



**Figure 4.** Isopleth contours of cloud droplet number concentration change (%) relative to the baseline simulation, with respect to the logarithm of solubility (moles  $\text{L}^{-1}$ ) and organic mass fraction of aerosol. The surface tension effects are as described in the text. A marine convective cloud with an updraft velocity equal to  $1 \text{ m s}^{-1}$  is assumed in these calculations.

in terms of the organic solubility, organic mass fraction and dry particle size. At the  $\Delta N/N = 0$  line, the insolubility and surface tension effects exactly compensate for each other, and the aerosol behaves as if it were composed entirely of  $(\text{NH}_4)_2\text{SO}_4$ . It can be shown that the surface tension needed to achieve this for a given CCN is:

$$\sigma^* = \left[ \frac{M_s}{M_o} \frac{\nu_o \rho_o}{\nu_s \rho_s} \varepsilon_o \right] \sigma \quad (1)$$

where  $\sigma^*$  and  $\sigma$  are the surface tensions of the WSOC-containing drop and pure water, respectively,  $M_s, M_o$  are the molecular masses of  $(\text{NH}_4)_2\text{SO}_4$  and the dissolved WSOC,  $\nu_s, \nu_o$  are their corresponding van't Hoff factors,  $\rho_o, \rho_s$  are their densities, and  $\varepsilon_o$  is the WSOC mass fraction.

For a given CCN, in order to have surface tension equal to  $\sigma^*$  at activation, it can be shown that the solubility of the WSOC,  $\Gamma^*$ , ( $\text{mol L}^{-1}$ ) should satisfy:

$$\Gamma^* = \left( \frac{\rho_o}{\rho_w} \varepsilon_o \right) \left( \frac{M_s \sigma^*}{RT \nu_s \rho_s d_d} \right)^{3/2} \quad (2)$$

where  $\rho_w$  is the water density, and  $d_d$  is the dry particle diameter. From inspection of the above relationship, we see that each particle has its own "characteristic" solubility to act as a pure salt CCN, i.e.  $\Gamma^* = \Gamma^*(\varepsilon_o, d_d)$ . Assuming that the organic mass fraction is constant, we can expect that the average  $\Gamma^*$  for the CCN population would correspond to an "effective  $d_d$ " close to the peak of the activated CCN number size distribution, where most of the activated CCN are found.

To the left of the  $\Delta N/N = 0$  line (Figure 4), there is not enough dissolved organic to compensate for the decrease in inorganic solute. To the right of the line, the reverse is true. At solubilities below  $10^{-4} \text{ M}$ , the organic behaves as if it were insoluble. Depending on the organic mass fraction, at solubilities between  $10^{-4}$  and  $10^{-2} \text{ M}$ , surface tension effects substantially change cloud droplet number, inducing changes larger than 10% when the solubility exceeds around  $5 \times 10^{-3} \text{ M}$ . The largest decrease in surface tension is seen when the volume of water in the droplet is precisely that needed to completely dissolve the substance. Because of this, beyond about  $5 \times 10^{-2} \text{ M}$ , a further increase in solubility does not have an additional significant effect on cloud droplet number. This limiting solubility can be expressed by a simple mathematical criterion similar to Equation (2).

## 5. Conclusions

There are numerous conditions for which chemical effects on droplet activation can be comparable to the Twomey effect, particularly for CCN with marine-type size distributions. All activation effects exhibit strong dependence on the magnitude of updraft velocity. For the species that can affect bulk phase surface tension, it seems that the lowering of surface tension associated with a dissolving organic substance has a stronger effect on cloud properties than the fact that the substance itself is only partially soluble; thus, even though both effects should always be considered, uncertainties in the surface tension behavior of the aerosol may be more influential than uncertainties in the solute contribution alone.

The dissolution of a soluble gas like  $\text{HNO}_3$  during cloud formation can also have a large impact on cloud droplet number concentration. In contrast to other activation effects, higher updraft velocities (and, as a consequence, higher droplet concentrations) diminish the role of a soluble gas; the reason for this is that less solute is introduced per droplet, because of both increased droplet concentration and a shorter period available for

activation.

If both surface tension-lowering species and condensable gases are present, they act synergistically to increase droplet number, i.e. for dynamical conditions where one effect is negligible, the other becomes important. This is a particularly important point: given that large variability in updrafts occurs in real clouds, one would expect to see that polluted marine clouds can experience an overall enhancement of droplet activation. Furthermore, if a portion of the dissolved species acts as a surfactant, a small decrease in accommodation coefficient can be enough to substantially enhance the number of activated drops.

Atmospheric conditions vary significantly throughout the globe, so that the relative importance of each individual aerosol chemical effect on cloud droplet activation will vary locally. Together, however, the effects can have an important global impact; this implies that current estimates of the first aerosol indirect effect might be underestimated, and will continue to do so until global models include chemical effects.

**Acknowledgments.** A. Nenes and J.H. Seinfeld were supported by U.S. Office of Naval Research grant N00014-96-1-0119.

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Received N/A; revised N/A; accepted N/A.