

Influence of water-soluble organic carbon on cloud drop number concentration

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[1] Studies published to date produce ambiguous results regarding the magnitude and even the sign of the effect of water-soluble organic carbon (WSOC) on cloud drop concentration compared to well-characterized inorganics. We present a systematic investigation of the reasons for these discrepancies by examining the ranges of physico-chemical properties of water soluble organics that most influence drop formation. We show that when considered individually, composition parameters such as low solubility, increased molecular weight, and surface tension suppression can lead to significant effects on droplet concentration, compared to the equivalent aerosol size distribution assuming properties of ammonium sulfate solutions. When considered together, these effects tend to counteract one another and produce much smaller changes. In addition, an assessment of the published literature suggests that estimates of composition effects on drop concentration based on equilibrium assumptions can be much larger than similar estimates under nonequilibrium conditions.

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1. Introduction

[2] The effect of aerosol on cloud radiative properties, also referred to as the aerosol indirect effect [Twomey, 1974], represents the largest uncertainty in estimating the impact of aerosols on climate. The ability of aerosols to take up water and thus to act as cloud condensation nuclei (CCN) depends on many factors such as the parameters of the aerosol population: size distribution (median radius r_g , geometric standard deviation σ_g), number concentration N_d ; composition: molecular weight M_s , solubility, dissociation, and surface tension σ_s ; and cloud supersaturation, which is a strong function of updraft velocity.

[3] The relative importance of both dynamical and microphysical parameters on the aerosol indirect effect has been investigated recently by Feingold [2003], who systematically analyzed sensitivities to liquid water content, particle number concentration, aerosol size distribution parameters, updraft velocity, and the amount of insoluble material on the cloud droplet effective radius for broad parameter spaces. The study did not, however, address the effect of composition in detail.

[4] It has been shown that atmospheric particles can contain major fractions of organic material [Rogge *et al.*, 1993]. Even the subset of total organic carbon mass attributable to water-soluble organic carbon (WSOC) can be composed of hundreds of different compounds with a large range of properties. Recent studies have compared the CCN activity of WSOC to different (inorganic) reference compounds for some selected organics and conditions. Table 1 compares the drop number concentrations N_d on the basis of organic or internally mixed inorganic/organic aerosols and well-characterized inorganic compounds and summarizes the conditions and organic species assumed in these studies. The predicted relative changes in drop concentration, ΔN_d , due to WSOC cover a range of -86% to $+110\%$ so that clearly, not only the magnitude, but even the sign of the change is uncertain. In order to provide a more general and systematic assessment of the importance of aerosol composition on N_d , we explore in the present study a broad parameter space of organic properties and reference predicted drop number concentrations to those predicted for the equivalent ammonium sulfate aerosol. It should be noted that although the study focuses on organic aerosol fractions, the results may be more general to the extent that the parameters considered are applicable to other species.

[5] After showing the individual effects of each property on N_d , we address combinations of properties (M_s , σ_s , and

Table 1. Compilation of Recent Model Studies That Have Addressed the Prediction of ΔN_d Due to WSOC Compared to Inorganic Aerosols

	Reference Composition	Organic Compound(s)/Properties: Molecular Weight M_s , g mol ⁻¹ ; Solubility s , g L ⁻¹ ; Surface Tension σ_s , dynes cm ⁻¹ ; Density ρ_s , g cm ⁻³	ΔN_d [%]	Conditions
Shantz et al. [2003]	(NH ₄) ₂ SO ₄	0.1% (NH ₄) ₂ SO ₄ /99.9% adipic acid ($M_s = 146$, $\nu = 1$, $s = 25$, $\rho_s = 1.36$)	-86	$w = 20$ cm s ⁻¹
Lohmann et al. [2004]	(NH ₄) ₂ SO ₄	0.1% (NH ₄) ₂ SO ₄ /99.9% adipic acid, 0.1% (NH ₄) ₂ SO ₄ /90% adipic acid/9.9% nonanoic acid ($M_s = 158$, $\sigma_{sat} = 30$, $s = 0.26$ $\rho_s = 0.905$)	-67, -35	$w = 20$ cm s ⁻¹
Ervens et al. [2004]	(NH ₄) ₂ SO ₄	adipic acid ($M_s = 146$, $\sigma_s = \sigma_{H_2O}$, $\rho_s = 1.4$), $\sigma_s = f(c)$, glutaric acid ($M_s = 132$, $\sigma_s = f(c)$, $\rho_s = 1.4$), ~70% (NH ₄) ₂ SO ₄ , ~30% organics: 90 < M_s < 146, $\nu\Phi$ based on thermodynamic model	-50, ±0, +12, ±0	$w = 10$ cm s ⁻¹
Hegg et al. [2001]	(NH ₄) ₂ SO ₄	pinonic acid ($M_s = 184$)	-40	$w \sim 200$ cm s ⁻¹ , $N_{a,ref} = 3819$ cm ⁻³ , $N_{a,org} = 5445$ cm ⁻³
Nenes et al. [2002]	(NH ₄) ₂ SO ₄	18% levoglucosan ($M_s = 162$, $\nu = 1$), 41% succinic acid ($M_s = 108$, $\nu = 3$), 41% fulvic acid ($M_s = 732$, $\nu = 5$), $\rho_s = 1.55$, 10^{-4} mol L ⁻¹ < s < 10^{-1} mol L ⁻¹ , organic fraction: 10–50%, $\sigma_s = f(c)$	-5...+25	100 cm s ⁻¹
Rissman et al. [2004]	(NH ₄) ₂ SO ₄	same as Nenes et al. [2002], $\sigma_s = f(c)$	<0, >0	10 cm s ⁻¹ < w < 500 cm s ⁻¹
Giebl et al. [2002]	(NH ₄) ₂ SO ₄	oxalic acid ($M_s = 90$), fructose ($M_s = 180$)	±0, ~-25	experimental study
Ming and Russell [2004]	50% (NH ₄) ₂ SO ₄ , 50% NH ₄ NO ₃ , ($M_s = 80$, $\nu = 2$)	40% (NH ₄) ₂ SO ₄ /40% NH ₄ NO ₃ /11% insoluble/9% WSOC (110 < M_s < 732, $\nu = 1$)	-57, -3, +6	equilibrium, kinetic approach, solute-solute interactions
Mircea et al. [2002]	26% (NH ₄) ₂ SO ₄ , 24% NH ₄ NO ₃ , 50% insoluble	26% (NH ₄) ₂ SO ₄ /24% NH ₄ NO ₃ /30% insoluble/14% diacid ($M_s = 100$, $\nu = 3$)/6% fulvic acid ($M_s = 734$, $\nu = 5$)	+110	equilibrium
Alfonso and Raga [2004]	10% (NH ₄) ₂ SO ₄ , 90% insoluble	10% (NH ₄) ₂ SO ₄ /50% insoluble/40% oxalic acid ($M_s = 90$, $\nu = 3$)	+35	$w = 100$ cm s ⁻¹
Anttila and Kerminen [2002]	80% NH ₄ HSO ₄ , 20% organic	40% NH ₄ HSO ₄ /60% organic ($M_s = 150$, $\nu = 1$, $\sigma_s = \sigma_{H_2O}$, $\rho_s = 1.2$), $\sigma_s = f(c)$	-8, +4	10 cm s ⁻¹ < w < 100 cm s ⁻¹
Bilde and Svenningsson [2004]	NaCl, ($\nu = 2$, $M_s = 58$)	11.7% NaCl/88.3% adipic acid ($M_s = 146$), 2.2% NaCl/97.8% succinic acid ($M_s = 108$)	~-30, +~30	experimental study
Facchini et al. [1999]	$\sigma_s = \sigma_{H_2O}$	$\sigma_s = 0.7 \cdot \sigma_{H_2O}$, identical ρ_s for both compositions	+20	$N_d \propto S^k \Rightarrow \Delta N_d/N_d = 3/4 \Delta \sigma_s/\sigma_s$

solubility) to represent the properties of organic aerosols in a more realistic way. On the basis of the drop growth equation we analyze which composition effects dominate drop formation and under which conditions WSOC is likely to show the highest values of ΔN_d . Our conclusions include a discussion of the results shown in Table 1 and elucidate which assumptions and model conditions lead to large variations in the predicted ΔN_d .

2. CCN Activity: Köhler Theory

[6] The Köhler equation describes the equilibrium between particles and the ambient humid air.

$$S_{eq} = \exp \left[\frac{2M_w\sigma_s}{RT\rho_w r} - \frac{\nu\Phi M_w m_s / M_s}{\frac{4}{3}\pi\rho_{particle} r^3 - (m_s + m_{insol})} \right], \quad (1)$$

where, S_{eq} = saturation ratio of water vapor at equilibrium; M_w = molecular weight of water; R = ideal gas constant; T = temperature; ρ_w = density of water; σ_s = surface tension of

solution; $\nu\Phi$ which is approximately the van't Hoff factor, i.e., the product of the number of ions (ν) and the osmotic coefficient (Φ); M_s = molecular weight of solute; $\rho_{particle}$ = density of the haze particle, m_s = soluble mass ($m_{total} - m_{insoluble}$), r = particle radius, respectively. The first term in parentheses, the Kelvin term, describes the enhancement of the vapor pressure due to droplet curvature, and the second term in parentheses, the solute term, is a measure of the solute hygroscopicity which can be defined as the ratio of water and solute molecules at a given relative humidity. Thus the Köhler equation includes four specific parameters concerning the physico-chemical properties of the solutes and/or solutions (σ_s , $\nu\Phi$, M_s , m_s). Particle growth occurs if the term $(S - S_{eq})$ (equation (2)) is greater than 0:

$$r \frac{dr}{dt} \propto (S - S_{eq}(r)), \quad (2)$$

where dr/dt is the growth rate of the particles. In a rising air parcel that expands and cools adiabatically, the saturation depends not only on the aerosol size distribution and

Table 2. Limits of Organic Properties of Common Organic Aerosol Constituents

Parameter	Limits	Example	Source
M_s , g mol ⁻¹	90 (\gg) 1000	oxalic acid humic-like substances, polymers	oxidation of aromatic or unsaturated compounds oxidative degradation and polymerization of plant and animal matter or other precursors
$\nu\Phi$	1	carboxylic acids with $pK_a > 4$, all other organic species groups	numerous chemical and physical sources
Solubility, g L ⁻¹	5 1	polycarboxylic acid with $pK_a(4) < 2$ dicarboxylic acids $C > 10$, fatty acids	existence is questionable oxidation products of long chain monoacids, anthropogenic and biogenic emissions
σ_s , dynes cm ⁻¹	1000 20 80	dicarboxylic acids $C < 6$, NH ₄ H ₂ SO ₄ long chain monoacids (fatty acids), small alcohols inorganic ionic compounds, sugars	direct emissions (e.g., exhaust) and photochemical processes too volatile to contribute to aerosol mass biomass burning

composition, but also on the updraft velocity w [e.g., Howell, 1949]

$$\frac{dS}{dt} = \psi_1 w - \psi_2 4\pi \frac{\rho_w}{\rho_a} G(T, p, \alpha) \int r n(r) [S - S_{eq}(r)] dr, \quad (3)$$

where ψ_1 and ψ_2 are constants, and ρ_w and ρ_a are the density of water and air, respectively. G is a function of the mass accommodation coefficient of water α and determines the rate of condensational growth. The mass accommodation coefficient can be reduced by orders of magnitude if the particles are covered by water-insoluble organic films [Gill *et al.*, 1983]. However, since we address water-soluble organic compounds, and because of the lack of data for α for specific organic solute surfaces, we use the same values of α usually applied for particles that contain inorganics ($\alpha = 0.042$). The general results and conclusions derived for $\alpha = 1$ are qualitatively similar to those for $\alpha = 0.042$, but for the sake of brevity we do not show both sets of results. We refer the reader to Feingold and Chuang [2002] and Xue and Feingold [2004] for discussion of the sensitivity of N_d to α .

3. Model Description

[7] We use an adiabatic cloud parcel model to examine droplet formation on a population of aerosol particles [Feingold and Heymsfield, 1992; Ervens *et al.*, 2004]. Aerosol/cloud droplets are represented by 50 particle size classes on a moving size grid, where the initial size is determined by the particle mass at that grid point. The grid points are distributed logarithmically. The equivalent radius range is $0.01 \mu\text{m} < r_{dry} < 1.2 \mu\text{m}$ ($\rho_s = 1.769 \text{ g cm}^{-3}$). Note that we assume identical initial number concentrations and masses for each simulation, which implies that ρ_s for both (NH₄)₂SO₄ and organics is identical (even though the density of organic compounds can vary between $\sim 0.8 \text{ g cm}^{-3} < \rho_s \lesssim 2.5 \text{ g cm}^{-3}$). The size distribution of aerosols is initially lognormal with a median radius $r_g = 0.04 \mu\text{m}$ and a geometric standard deviation $\sigma_g = 2$, but results for an aerosol size distribution with $r_g = 0.06 \mu\text{m}$, $\sigma_g = 1.6$ are also shown (section 4.5.1). Aerosol number concentrations of $N_a = 100 \text{ cm}^{-3}$ and $N_a = 5000 \text{ cm}^{-3}$ are considered.

[8] The model solves equation (2) for the 50 discrete sizes, equation (3), and the standard thermodynamic equations for an adiabatic parcel model. At time zero (RH = 85%) the particles are equilibrated with the ambient relative humidity, and the simulation is run until a cloud liquid water

content of 0.3 g kg^{-1} is reached. We investigate a range of constant w from 10 cm s^{-1} to 300 cm s^{-1} . We do not consider any uptake processes of soluble trace gases into the particles. In order to cover the parameter ranges of WSOC we perform model studies for the parameter spaces which are summarized in Table 2. The number of droplets N_d is defined as all particles which have a radius of $r > 1 \mu\text{m}$ regardless of whether they have exceeded their critical size.

4. Results and Discussion

[9] In the following section we discuss the effect on N_d of the properties that determine the hygroscopicity ($\nu\Phi$, M_s , solubility) and the surface tension (σ_s) of a solute and give an overview of the parameter ranges covered by common organic aerosol constituents (Table 2). We change one parameter at a time, while the other three parameters are assumed to be equal to those for (NH₄)₂SO₄ ($M_s = 132 \text{ g mol}^{-1}$, $\nu\Phi = 3$, completely soluble, and $\sigma_s = \sigma_{\text{H}_2\text{O}}$). This approach represents a simplification since organic compounds usually differ from (NH₄)₂SO₄ in more than one of these parameters but it allows us to distinguish between each individual effect with reference to a well-studied compound. In section 4.5 we address the effects of realistic combinations of parameters that correspond to common organic aerosol compounds. We note that the dynamical nature of equation (3) creates feedbacks to calculated parameters such as S and the resulting N_d that are not simply related to changes to the composition terms of S_{eq} . Therefore linear responses of N_d to composition parameters are not anticipated.

4.1. Dissociation

[10] Ionic compounds (i.e., salts) in ideal (i.e., dilute) solutions are completely dissociated into their ions (ν). At high concentrations the solutions are not ideal, and thus their activity differs from their concentration, which is taken into account by the osmotic coefficient Φ . $\nu\Phi$ for ionic compounds is a function of the solute concentration [Low, 1969; Chylek and Wong, 1998]. In modeling studies that address prediction of N_d , a constant value of $\nu\Phi = 3$ for (NH₄)₂SO₄ is often assumed [e.g., Lohmann *et al.*, 2004; Rissman *et al.*, 2004]; we make the same approximation here.

[11] The dissociation of acids only occurs if the H⁺ concentration is low enough (i.e., high pH or very dilute solutions). Most atmospheric monocarboxylic and dicarboxylic acids have values of $pK_a \sim 4$ (or higher) for the first dissociation constants; the only marked exception is oxalic

Table 3. Critical Radii and Degree of Dissociation for an Arbitrary Organic Acid With $M_s = 150 \text{ g mol}^{-1}$ and $pK_a = 4^a$

r_{dry} , μm	r_c , μm	pH _c	ν	$\nu = 1.5$		$\nu = 2$	
				r_{dil} , μm	r_{dil}/r_c	r_{dil} , μm	r_{dil}/r_c
0.002	0.002	1.50	1.0032	0.07	37	0.42	215
0.005	0.007	1.80	1.0063	0.18	23	1.1	136
0.01	0.022	2.02	1.0105	0.36	16	2.1	96
0.05	0.24	2.56	1.0348	1.80	7	11	43
0.1	0.69	2.79	1.0578	3.60	5	21	30
0.5	7.7	3.34	1.1803	18	2	105	14
1.0	21.9	3.60	1.2835	36	1.6	211	10

^aThe last columns show the drop radii at which the acid is 50% ($\nu = 1.5$) and 100% ($\nu = 2$) dissociated, respectively, and the ratios to the critical radius r_c , defined as the radius corresponding to the maximum S in equation (1).

acid ($pK_a(1) = 1.24$) [Lide, 2000] which often represents a major fraction of the dicarboxylic acid mass. We have performed a rough estimate of the degree of dissociation in an aqueous solution of particles composed of an arbitrary pure monocarboxylic acid ($M_s = 150 \text{ g mol}^{-1}$, $pK_a = 4$, $\nu_{\max} = 2$), with the solution compositions taken to be those at the particles' critical sizes (Table 3). Only in large particles ($r_{dry} > 0.5 \mu\text{m}$) will the acids be dissociated by more than 10% ($\nu > 1.1$). In the last columns of Table 3 we show the particle sizes that are required in order to reach degrees of dissociation of 50% ($\nu = 1.5$) or 100% ($\nu = 2$), respectively. It is obvious that the assumption of complete dissociation ($\nu_{\max} = 2$ for a monocarboxylic acid) is not appropriate for any of the initial particle sizes. The result implies that species that contain more than one acid group, i.e., dicarboxylic and polycarboxylic acids, are also not dissociated in activating particles if their lowest pK_a value is ~ 4 . This estimate is based on the simplified assumptions that (1) the solutions are ideal ($\Phi = 1$) and (2) no additional (e.g., inorganic) compounds are present that control the pH in the particles and thus the dissociation of acids.

[12] Figures 1a and 1b show the change in drop number concentration ΔN_d (relative to $(\text{NH}_4)_2\text{SO}_4$) for different van't Hoff factors ($1 < \nu\Phi < 5$). We note that the choice to display results for ΔN_d in these and subsequent figures

provides a view of the percentage differences incurred by specific changes in composition relative to $(\text{NH}_4)_2\text{SO}_4$ but does not always facilitate understanding at the process level for each individual composition. Section 5 explores the temporal evolution of the various terms for individual cases and allows direct comparison between the WSOC proxy and $(\text{NH}_4)_2\text{SO}_4$, and a clearer understanding of the relative importance of the terms.

[13] As expected from equation (1), the contour lines exhibit positive values for $\nu\Phi > 3$ and negative values for $\nu\Phi < 3$. The general trend is for contour lines to have positive slope at $\nu\Phi > 3$ and negative slope at $\nu\Phi < 3$. This is explained by the fact that horizontal contour lines whose values increase with increasing $\nu\Phi$ would be expected if $\nu\Phi$ effects were dominant, while if w effects were dominant, this would result in vertical contour lines, whose values would decrease with increasing w (or increasing supersaturation/decreasing influence of composition-related terms; equation (3)). Deviations from this relatively simple picture are due to a number of factors including the resolution in van't Hoff factor and w space, which creates interpolation problems for the contouring routine. In addition, despite the rather fine mass resolution (50 points) used here, N_d shows some evidence of step increases with increasing w which is particularly evident at low updrafts where mass resolution decreases because of the logarithmic grid. The fact that these step increases in N_d does not occur synchronously for the WSOC and $(\text{NH}_4)_2\text{SO}_4$ generates some sharp features in these and subsequent contour plots, which we regard as artifacts. It is therefore important to focus on the main trends and order-of-magnitude differences.

[14] Figure 1a shows that the most extreme values of $\nu\Phi$ only lead to a decrease of $\Delta N_d \sim -20\%$ for $N_a = 100 \text{ cm}^{-3}$. Even though the assumption of $\nu\Phi = 5$ as a theoretical upper bound is not appropriate under atmospheric conditions (Table 2), this only leads to an error of 5–10% in the prediction of ΔN_d . The most distinct differences occur at low updraft velocities ($w < 100 \text{ cm s}^{-1}$) and high N_a (Figure 1b), i.e., under conditions for which supersaturation is small, particle growth is limited and the influence of the

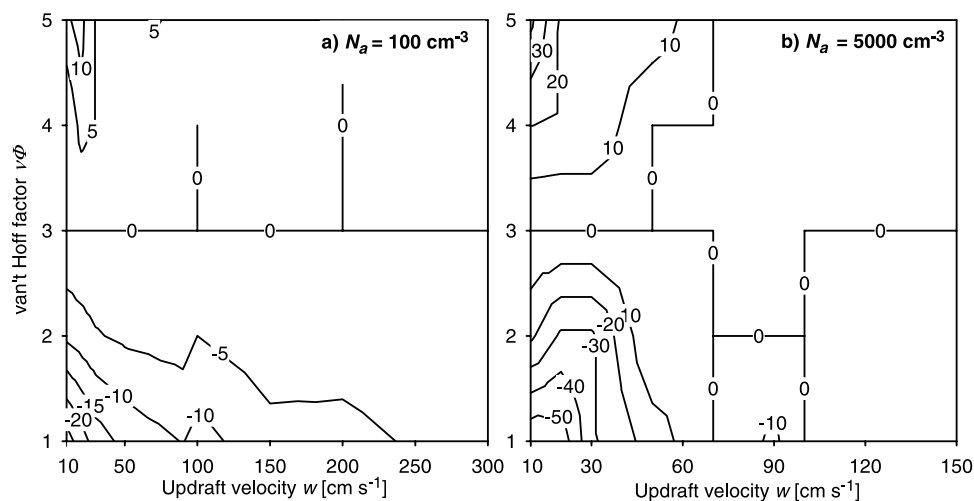


Figure 1. Relative change in drop number concentration ΔN_d [%] (compared to $(\text{NH}_4)_2\text{SO}_4$) as a function of updraft velocity w and $\nu\Phi$. Organic properties: fully soluble; $M_s = 132 \text{ g mol}^{-1}$ and $\sigma_s = \sigma_{\text{H}_2\text{O}}$. (a) $N_a = 100 \text{ cm}^{-3}$ and (b) $N_a = 5000 \text{ cm}^{-3}$.

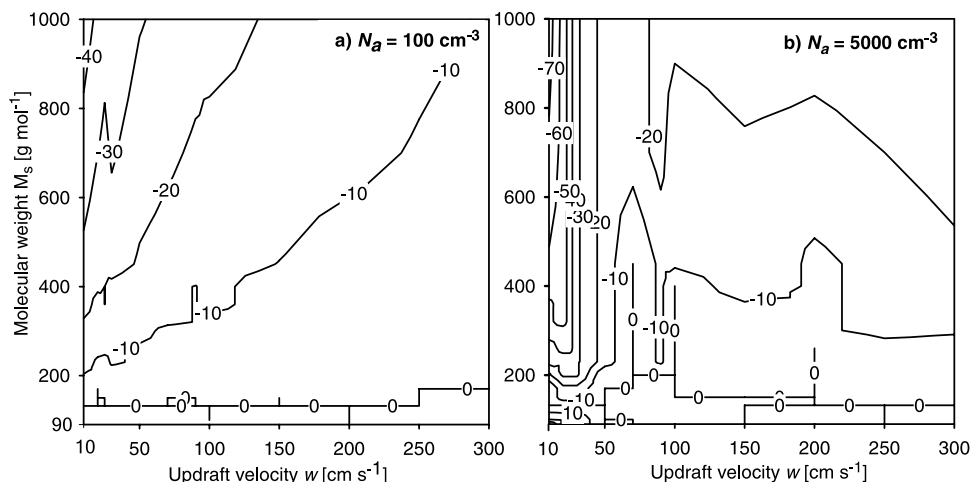


Figure 2. ΔN_d [%] as a function of w and molecular weight M_s . Organic properties: fully soluble; $\sigma_s = \sigma_{H_2O}$ and $\nu\Phi = 3$. (a) $N_a = 100 \text{ cm}^{-3}$ and (b) $N_a = 5000 \text{ cm}^{-3}$.

Kelvin and solute terms is greatest (equation (3)). For both particle concentrations ΔN_d is negligible ($\leq 10\%$) at updraft velocities of $w > 100 \text{ cm s}^{-1}$. It has been discussed in several theoretical studies that $\nu\Phi$ for inorganic compounds should be considered as a function of their aqueous concentration [Low, 1969]. However, the results in Figure 1 suggest that the assumption of a constant value (instead of a range of $\nu\Phi \pm \sim 1$) only introduces $\sim 10\%$ error in the prediction of N_d . As we have shown in Table 3, ν of pure organic acids at the critical radius is usually smaller than 1.1 so that the assumption of $\nu\Phi = 1$ for most pure organic compounds seems to be reasonable for the prediction of N_d under all model conditions.

4.2. Molecular Weight M_s

[15] An increase in molecular weight leads to a decrease in the number of moles of solute $n_s (= \nu\Phi m_s / M_s)$ for an equivalent assumed particle mass (equation (1)). M_s of organic aerosol compounds can differ by more than an order of magnitude. Oxalic acid is the smallest dicarboxylic acid ($M_s = 90 \text{ g mol}^{-1}$). All (unsubstituted) dicarboxylic acids with $C < 5$ have smaller molecular weights than $(\text{NH}_4)_2\text{SO}_4$. It has been shown that polymers with $M_s \sim 1000 \text{ g mol}^{-1}$ (or even higher) can also be major aerosol constituents [e.g., Kalberer et al., 2000].

[16] Figure 2a shows ΔN_d as a function of M_s ($90\text{--}1000 \text{ g mol}^{-1}$) and w . Small organic molecules with $M_s < 200 \text{ g mol}^{-1}$ (i.e., roughly comparable to $(\text{NH}_4)_2\text{SO}_4$, $M_s = 132 \text{ g mol}^{-1}$) do not change N_d to a significant extent. However, at the small particle number concentration ($N_a = 100 \text{ cm}^{-3}$), compounds with $M_s > 200 \text{ g mol}^{-1}$ can lead to a significant reduction of ΔN_d of up to 40% at low w .

[17] As already seen in the variation of the $\nu\Phi$ factor, the most significant changes occur at low w and high N_a (Figure 2b). Both Figures 2a and 2b suggest that aerosols composed purely of species with $M_s \leq 400 \text{ g mol}^{-1}$ do not lead to significantly different N_d compared to $(\text{NH}_4)_2\text{SO}_4$. Interestingly, below an updraft velocity of $w \sim 50 \text{ cm s}^{-1}$, species with $M_s > 400 \text{ g mol}^{-1}$ lead to ΔN_d , which is almost independent of M_s (vertical contour lines) since the relative increase in M_s at high values of M_s is lower than at low absolute values of M_s .

[18] The general trends in the contours should in principle be similar to those in Figure 1, but opposite in trend since M_s appears in the denominator of the solute term (e.g., positive contour slopes in Figure 2a). These opposite trends confirm that the ability of the particles to take up water (= hygroscopicity) is defined by the mole ratio of water to solute. The inverse term, i.e., $(\nu\Phi m_s) / M_s (m_w / M_w)$ corresponds to the solute term (equation (1)) [Rissler et al., 2004].

[19] Note, however, that the range of parameter space in M_s is much larger than for the van't Hoff factor. At high N_a , the dominance of vertical contour lines indicates the strong dependence on w in the low supersaturation environment. For reasons described above we do not place credence in the sharp contour features.

4.3. Solubility

[20] It is usually assumed that highly soluble species such as $(\text{NH}_4)_2\text{SO}_4$ are completely dissolved at ambient RH above 85% since, in the case of $(\text{NH}_4)_2\text{SO}_4$, full dissolution (deliquescence) occurs at $\text{RH} \sim 80\%$. If initially assumed to be dry, some compounds with very low solubilities (e.g., adipic and succinic acids) do not take up water below $\text{RH} \sim 98\%$. Under most atmospheric conditions the total aerosol mass exhibits higher solubilities since the fraction of soluble material (e.g., oxidized organics or inorganic ionic compounds) increases with particle age.

[21] Unlike the model simulations described above, we now assume a composition of 2% $(\text{NH}_4)_2\text{SO}_4$ and 98% organic material by mass and vary the solubility of the latter from 1 to 1000 g L^{-1} (Table 2). Unlike the treatment of $\nu\Phi$ and M_s , the dissolved mass m_s is not constant but increases rapidly if sufficient water is condensed on the particles, i.e., as water-saturated conditions are approached. Numerically, this process is treated in a way that maintains the droplet at or below saturation of the solute. We assume that the dissolution occurs instantaneously; that is, the kinetic delay that might be associated with the dissolution of the solute is neglected because of a lack of appropriate data.

[22] At solubility $\leq 20 \text{ g L}^{-1}$, Figure 3a shows similar contour morphology to Figure 1a with negative sloping contours. However, above 20 g L^{-1} , the contours tend to

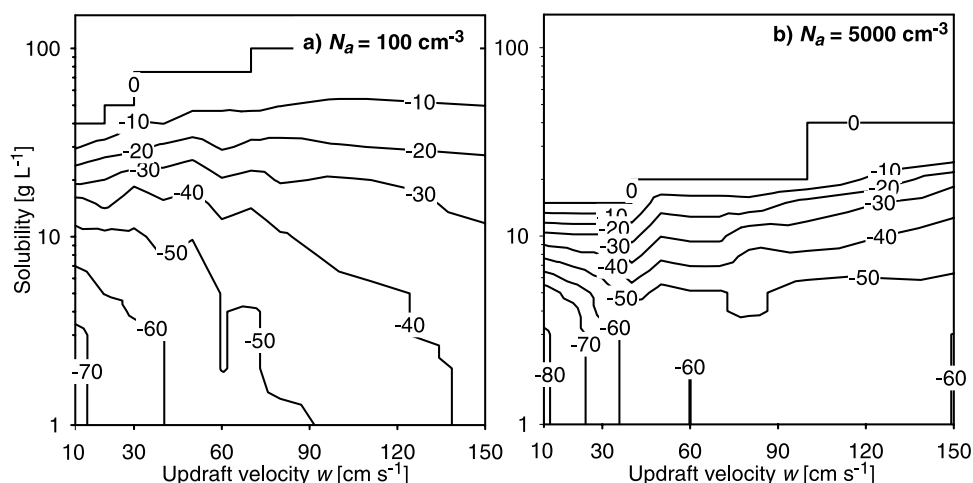


Figure 3. ΔN_d [%] as a function of w and solubility. Organic properties: $M_s = 132 \text{ g mol}^{-1}$, $\nu\Phi = 3$, and $\sigma_s = \sigma_{H_2O}$ (composition: 2% $(\text{NH}_4)_2\text{SO}_4$ /98% organics by mass). (a) $N_a = 100 \text{ cm}^{-3}$ and (b) $N_a = 5000 \text{ cm}^{-3}$.

exhibit much flatter slopes than those in Figure 1a. The assumption of 98% by mass, initially dry, low-solubility material in the aerosol implies that at low RH ($\sim 85\%$), the solute term is initially about two orders of magnitude smaller than that of pure $(\text{NH}_4)_2\text{SO}_4$, while M_s and $\nu\Phi$ affect it at most by a factor of ~ 7 and ~ 3 , respectively. Because of the broad range of expected values, a reduced solubility affects ΔN_d over the whole range of w for both values of N_a to a greater extent than M_s and $\nu\Phi$ (Figure 3). While the $\nu\Phi$, M_s , and σ_s effects are clearly dependent on N_a and w , the solubility effects exhibit weaker dependence on these parameters for solubility $\geq 20 \text{ g L}^{-1}$.

[23] Shantz *et al.* [2003] found that ΔN_d for aerosol composed of 99.9% adipic acid/0.1% $(\text{NH}_4)_2\text{SO}_4$, ΔN_d is about the same for both $w = 20 \text{ cm s}^{-1}$ and $w = 50 \text{ cm s}^{-1}$. In the same study they suggest that species with solubilities greater than 100 g L^{-1} can be treated like $(\text{NH}_4)_2\text{SO}_4$, i.e., as completely dissolved species. On the basis of our results this solubility limit seems to be lower ($\sim 40 \text{ g L}^{-1}$); however, this limit is a strong function of the assumed slightly soluble mass fraction.

[24] In addition, the relative humidities at which pure organics effloresce can be very low [e.g., Braban *et al.*, 2003], and mixtures (as usually encountered in atmospheric aerosols) exhibit lower deliquescence relative humidities (and thus a higher solubility) than the individual compounds in a pure state [e.g., Marcolli *et al.*, 2004] and likely retain water to low RH in the atmosphere. Since it is probable that atmospheric organic aerosols at ambient RH are in a (supersaturated) liquid state, these results represent an overestimate of the effects of solubility. If the initial state contains no solid organics, then the results shown in Figures 1 and 2 are applicable, regardless of the solubility of the pure organic in water.

4.4. Surface Tension σ_s

[25] In ionic solutions, anions are usually enriched at the surface [Jungwirth and Tobias, 2001]. Because of the strong interactions of the anions with the cations in the bulk,

the drop has a slightly higher surface tension ($\sigma_{(\text{NH}_4)_2\text{SO}_4} \sim 85 \text{ dynes cm}^{-1}$) than pure water ($\sigma_{H_2O} \sim 72 \text{ dynes cm}^{-1}$) [Pruppacher and Klett, 1997]. Organic molecules in aqueous solution often cause lower surface tension since their hydrophobic parts are oriented toward the surface and lead to an expansion of the droplet. A specific relationship between concentrations of organic aerosol constituents and surface tension has been given by Facchini *et al.* [1999]:

$$\sigma_s = 72.8 - 0.01877 \cdot T \cdot \ln(1 + 628.14 \cdot [C]), \quad (4)$$

where T is the temperature [K] and $[C]$ the concentration of WSOC [mol C L^{-1}]. It has been shown that its application is appropriate for high M_s organic (e.g., polycarboxylic) substances, but greatly overestimates the σ_s effect of small dicarboxylic acids [Shulman *et al.*, 1996; Ervens *et al.*, 2004].

[26] In order to show the maximum effect of σ_s on drop activation, σ_s is fixed to a constant value. Organic compounds that suppress σ_s to values as low as 30 dynes cm^{-1} throughout the activation process lead to a significant increase in N_d at $w < 100 \text{ cm s}^{-1}$ ($N_a = 100 \text{ cm}^{-3}$, Figure 4a). For $N_a = 5000 \text{ cm}^{-3}$ (Figure 4b), N_d may be more than doubled ($\Delta N_d \leq +140\%$) compared to pure $(\text{NH}_4)_2\text{SO}_4$ for surface tensions $\sigma_s < 50 \text{ dynes cm}^{-1}$. For this particle concentration a significant increase in N_d is predicted for the whole range of w . The values for ΔN_d in Figure 4 certainly represent an overestimate of the σ_s effect since it is assumed that σ_s is constant (saturated solution), which is inappropriate since the particles become progressively more dilute. In the following section we will consider the extent to which this assumption overestimates the surface tension effect.

[27] As before, the broad trends in the contours result from a combination of a horizontal contribution of decreasing magnitude, with increasing σ_s and a vertical contribution of decreasing magnitude with increasing w . The “noisy” features in the contours at low w result from the

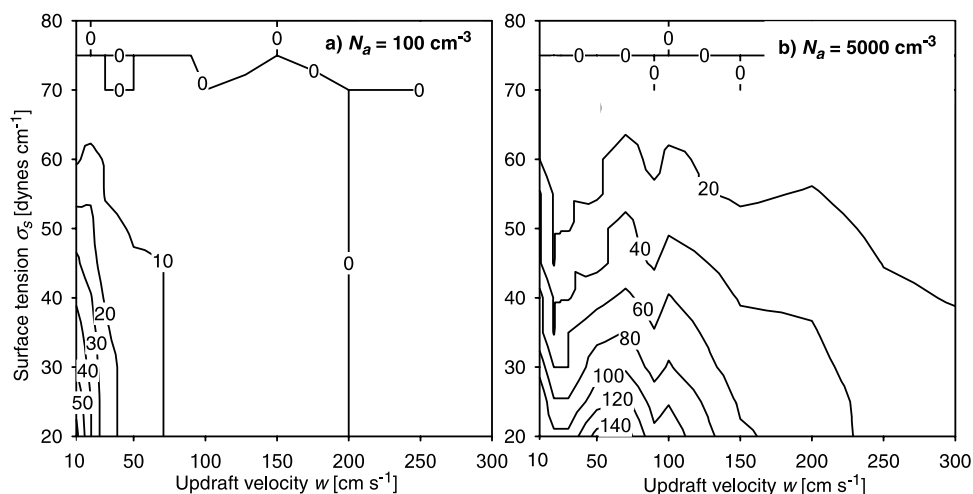


Figure 4. ΔN_d [%] as a function of w and surface tension σ_s . Organic properties: fully soluble; $M_s = 132$ g mol $^{-1}$ and $\nu\Phi = 3$. (a) $N_a = 100$ cm $^{-3}$ and (b) $N_a = 5000$ cm $^{-3}$.

discontinuous changes in N_d in the two respective results ((NH $_4$) $_2$ SO $_4$ /organics) that produce ΔN_d .

4.5. Combination of Parameters

[28] Organic aerosol constituents differ in more than one of the properties assumed in the previous sections. In order to reflect the organic aerosols in a more realistic way we consider the combined effects of M_s , σ_s and dissolved mass fraction as a function of dilution.

4.5.1. Molecular Weight and Surface Tension

[29] Zappoli *et al.* [1999] have shown that macromolecular compounds (similar to humic substances) can comprise major fractions (20–50%) of the WSOC. These acidic species are likely to be surface active and contribute to the soluble fraction of the aerosols. On the basis of equation (4), a combined approach for accounting for a simultaneous change in σ_s and M_s can be derived using

$$\sigma_s = 72.8 - 0.01877 \cdot T \cdot \ln(1 + 628.14 \cdot n_C \cdot c_{aq}), \quad (5)$$

where c_{aq} is the solute concentration [mol L $^{-1}$], n_C is the number of carbon atoms ($M_C = 12$ g mol $^{-1}$):

$$n_C = \frac{M_s}{2.2M_C}. \quad (6)$$

[30] Polycarboxylic acids exhibit an average mass ratio of $m_s/m_C \sim 2.2$ [Turpin and Lim, 2001]. (We performed some sensitivity studies that showed the choice of m_s/m_C does not have a significant influence on N_d .) It is likely that interactions of organics with other species (metal ions, H $^+$, etc.) are responsible for the strong decrease in σ_s which cannot be explained by pure organic compounds [Tuckermann and Cammenga, 2004]. Since to date no comprehensive correlation between C number and σ_s is available we use equation (5) for the full range of M_s even though it represents an upper bound for the σ_s effects. For many high M_s organic species (e.g., neutral compounds like sugars) the surface tension effects should be negligible, and thus the

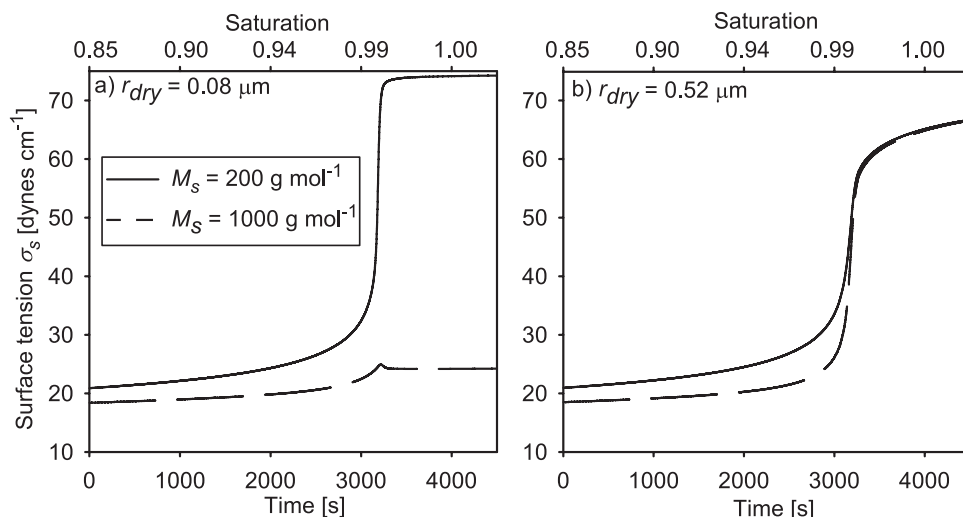


Figure 5. Temporal evolution of σ_s in two size classes ($r_{dry} = 0.08$ μm and $r_{dry} = 0.52$ μm) for two different M_s . $N_a = 100$ cm $^{-3}$ and $w = 10$ cm s $^{-1}$.

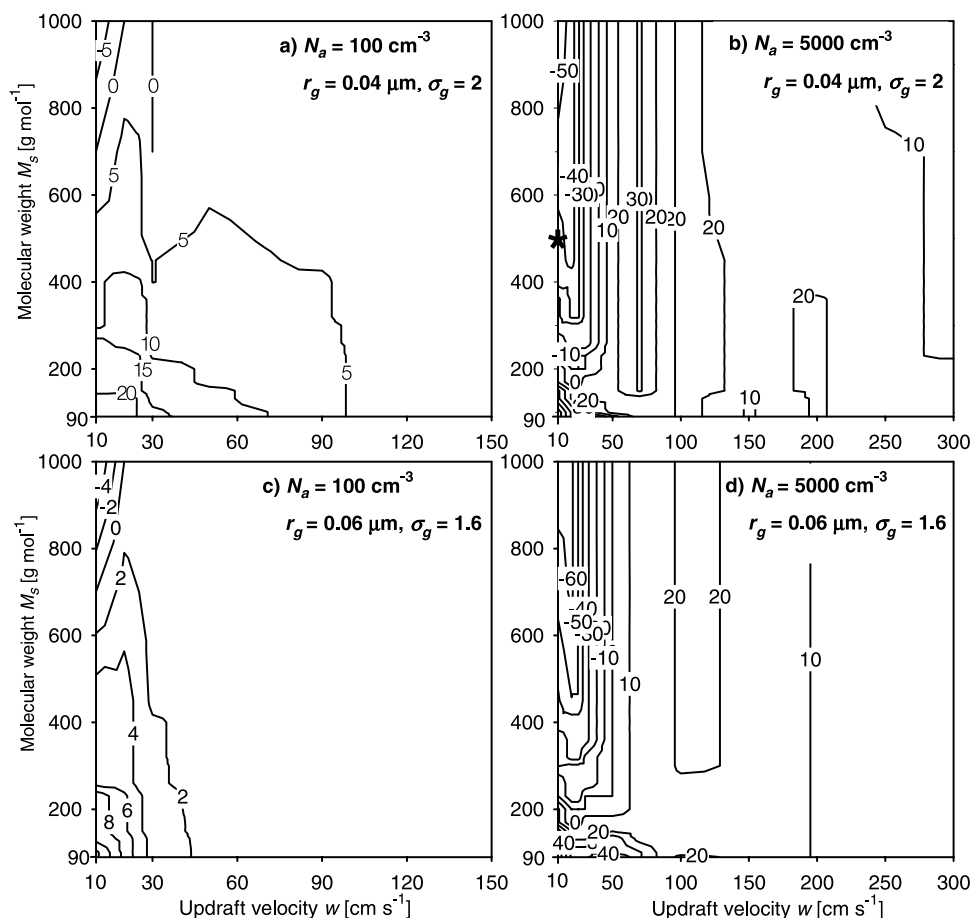


Figure 6. ΔN_d [%] as a function of w and surface tension σ_s ; $\sigma_s = f(c_{\text{aq}}, \text{carbon number})$ and carbon number = $M_s/12/2.2$. Organic properties: fully soluble; $\nu\Phi = 3$. (a–d) Conditions specified at top right of each plot.

conclusions drawn from Figure 2 with regard to the effects of M_s on N_d are more appropriate.

[31] Figure 5 shows the temporal evolution of the surface tension for two selected size classes ($r_{\text{dry}} = 0.08 \mu\text{m}$, $r_{\text{dry}} = 0.52 \mu\text{m}$) and M_s of 200 g mol^{-1} and 1000 g mol^{-1} , respectively. At low RH, i.e., if the particles are saturated solutions, σ_s is about 20 dynes cm^{-1} , which represents a lower limit for high M_s compounds. Close to the maximum supersaturation ($t \sim 3200 \text{ s}$, see section 5.2) there is a rapid increase in σ_s until $\sim 70 \text{ dynes cm}^{-1}$ ($\sim \sigma_{\text{H}_2\text{O}}$) is reached (Figure 5). The small particles which contain organic species with $M_s = 1000 \text{ g mol}^{-1}$, do not activate under these conditions and thus are not dilute enough to exhibit high σ_s .

[32] A negative relationship between M_s and σ_s leads to counteracting effects which result in smaller absolute values for ΔN_d . For a particle concentration of $N_a = 100 \text{ cm}^{-3}$, ΔN_d increases to 15% (Figure 6a), compared to -40% if surface tension effects are neglected (Figure 2a). Even at higher particle concentrations (Figure 6b) a distinct decrease in N_d can only be observed at $w < 30 \text{ cm s}^{-1}$. These simulations suggest that at $w < 50 \text{ cm s}^{-1}$ M_s tends to control N_d , while at moderate w the suppression of σ_s leads to an increase in N_d . Above $w \sim 250 \text{ cm s}^{-1}$ the composition does not cause significant change in ΔN_d ($\leq 10\%$).

[33] We performed the same calculations for a broad range of size distributions, $0.02 \mu\text{m} < r_g < 0.06 \mu\text{m}$, $1.4 < \sigma_g < 2$. For most of these size distributions we found comparable features to those shown in Figures 1–4 and 6. As an example, the results in Figures 6c and 6d ($r_g = 0.06 \mu\text{m}$, $\sigma_g = 1.6$) show good qualitative agreement with those in Figures 6a and 6b. Generally, N_a has a more significant influence on ΔN_d than the size distribution parameters r_g and σ_g . The results are quite insensitive to the geometric standard deviation σ_g . However, at very small geometric mean radii ($r_g \sim 0.02 \mu\text{m}$) the absolute values of ΔN_d and the general trend for the importance of composition to be confined to low w is not as clear as in Figures 1–4 and 6.

4.5.2. Low Solubility of High Molecular Weight, Surface Active Compounds

[34] To date, many uncertainties exist about the physical and/or chemical sources and properties of high M_s species found in aerosols. It is likely that many of them exhibit much lower solubilities than $(\text{NH}_4)_2\text{SO}_4$. In order to simulate the effect on N_d of such compounds, we show in Figure 7 two examples for the overall effects on N_d for the full set of ranges in M_s , σ and the solubility at two different w (20 cm s^{-1} , 100 cm s^{-1}) and N_a (100 cm^{-3} , 5000 cm^{-3}). At low solubilities the solubility limitation

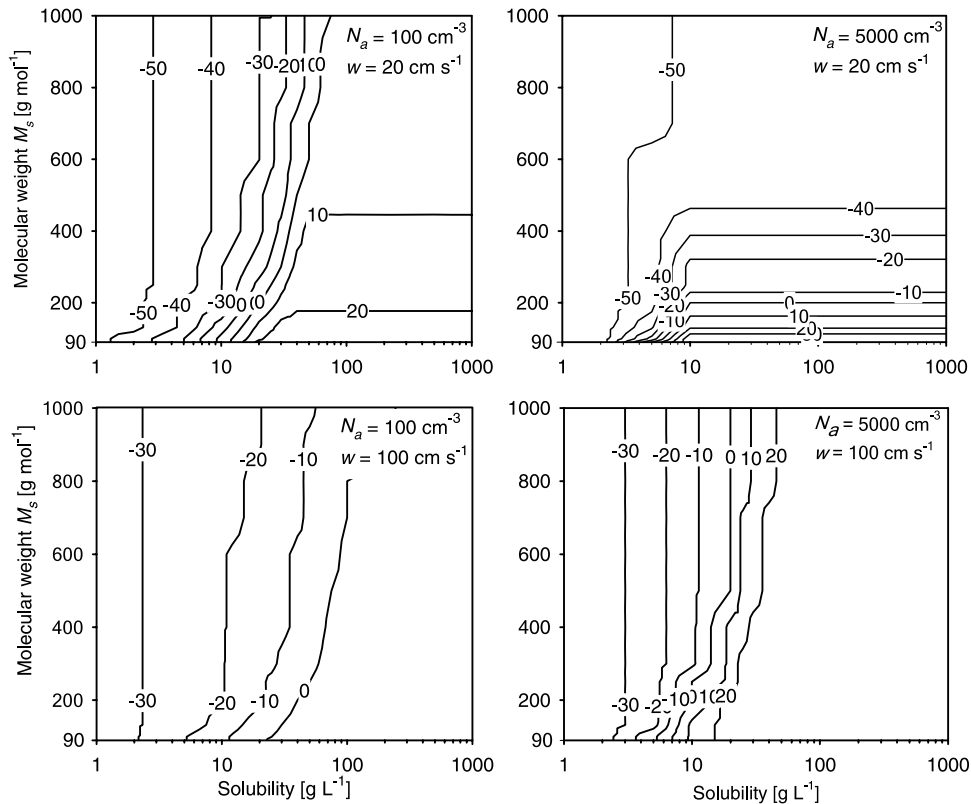


Figure 7. ΔN_d [%] as a function of solubility and surface tension σ_s ; $\sigma_s = f(c_{aq}, \text{carbon number})$ and carbon number = $M_s/12/2.2$; $\nu\Phi = 3$.

dominates and ΔN_d is affected primarily by solubility and not by M_s and σ_s (vertical contour lines). At higher solubilities, M_s has a significant influence on ΔN_d (Figures 2 and 6), and thus it dominates at high solubilities (Figure 7, horizontal contour lines at $w = 20 \text{ cm s}^{-1}$). The importance of M_s is much smaller at higher w , and thus the results at $w = 100 \text{ cm s}^{-1}$ show little dependence on M_s . The predicted increase in N_d for very low M_s , high-solubility species is likely due to the overestimate of the σ_s effect by low M_s species (e.g., dicarboxylic acids).

5. Temporal Evolution

[35] In the following section we investigate the temporal evolution of all terms that are modified by composition for a case where there is a significant change in N_d ($N_a = 5000 \text{ cm}^{-3}$; $w = 10 \text{ cm s}^{-1}$). On the basis of this analysis we glean information on the effect of the various terms on N_d within the context of the temporally evolving fields. We perform this analysis for subsaturated particles; that is, it can be assumed that solutions are dilute. Under such conditions, some assumptions can be applied and equation (1) can be simplified to [e.g., Pruppacher and Klett, 1997]

$$S_{eq} - 1 \sim \underbrace{\frac{A}{r} - \frac{B}{r^3}}_y, \quad (7)$$

where $A = (2 M_w \sigma_s)/(RT \rho_w)$ and $B = (\nu\Phi M_w m_s)/(4/3 \pi \rho_w M_s)$ (cf. equation (1)).

5.1. Definition of Mean Parameters

[36] We define mean terms for r and y that represent the general behavior of the aerosol population according to the approach of Feingold and Heymsfield [1992]:

$$\bar{r} = \frac{\int r n(r) dr}{\int n(r) dr} = \frac{\int r n(r) dr}{N_a} \quad (8)$$

$$\bar{y} = \frac{\int y(r) n(r) dr}{\int n(r) dr}, \quad (9)$$

where $n(r)$ is the number concentration of the size class with the radius r . The weighting of y with $r n(r)$ follows from equation (3). Similarly, we define a mean Kelvin and solute term as

$$\overline{\left(\frac{A(r)}{r}\right)} = \frac{\int \frac{A(r)}{r} n(r) dr}{\bar{r} N_a} = \frac{\int A(r) n(r) dr}{\bar{r} N_a} \quad (10)$$

$$\overline{\left(\frac{B(r)}{r^3}\right)} = \frac{\int \frac{B(r)}{r^3} n(r) dr}{\bar{r} N_a} = \frac{\int \frac{B(r)}{r^3} n(r) dr}{\bar{r} N_a}. \quad (11)$$

[37] We do not show the terms for all 50 individual size classes. However, we have checked that the average terms reflect the behavior of the individual terms reasonably well and allow a reliable interpretation of different properties that directly or indirectly influence both terms. This seems an

appropriate level of detail given that we seek a general assessment of the various terms.

[38] High particle concentrations provide a large surface area for condensation (all else being equal), which leads to suppressed S so that the importance of y on $(S - y)$ is greater at high N_a . Therefore the highest sensitivity of ΔN_d to the composition is seen for $N_a = 5000 \text{ cm}^{-3}$ (Figures 1–4). We perform the analysis for the following data set which is marked by an asterisk in Figure 6b: $N_a = 5000 \text{ cm}^{-3}$, $w = 10 \text{ cm s}^{-1}$, $M_s = 500 \text{ g mol}^{-1}$, $\Delta N_d \sim -50\%$.

[39] In order to separate the individual composition effects we compare five different cases:

[40] 1. Case I uses $(\text{NH}_4)_2\text{SO}_4$ as a reference compound.

[41] 2. Case II uses an organic compound with the following properties: $M_s = 500 \text{ g mol}^{-1}$ and $\sigma_s = \sigma_{\text{H}_2\text{O}}$.

[42] 3. Case III uses an organic compound with the following properties: $M_s = 132 \text{ g mol}^{-1}$ and $\sigma_s = f(c_{\text{aq}})$ for the description of the surface tension (equation (5)). We assume the identical σ_s as in case IV (σ_s based on $M_s = 500 \text{ g mol}^{-1}$).

[43] 4. Case IV uses an organic compound with the following properties: $M_s = 500 \text{ g mol}^{-1}$ and $\sigma_s = f(c_{\text{aq}})$ (equation (5)).

[44] 5. Case V is the same as case IV, with solubility 5 g L^{-1} .

5.2. Temporal Evolution of Individual Terms for $w = 10 \text{ cm s}^{-1}$

5.2.1. Kelvin (A/r) and Solute (B/r^3) Terms, and Composition Term y

[45] The various composition effects result in fairly distinct differences in the evolution of these terms that reflect both the changes in composition-related parameters as well as the dynamical feedbacks associated with the modified particle radius. For example, a smaller solute term due to high M_s (case II), and/or low solubility (case V) leads to smaller particle sizes and, as a result of negative feedbacks, to larger solute and Kelvin terms. For reference, vertical lines are drawn in Figure 8 at $t_{S=1}$ and $t_{S_{\text{max}}}$ for case V; however, the corresponding lines for the other cases are very similar ($< \pm 40 \text{ s}$). In all five cases, the solute term exceeds the corresponding Kelvin term at $S < 1$. As water saturation increases, the particles grow efficiently causing a decrease in both terms which is more pronounced for the solute term ($\propto r^{-3}$). The decrease in B/r^3 for case V (effect of solubility) is stronger than in the other cases because the increase of the soluble fraction leads to a rapid increase of the particle size. Shortly after water saturation is reached, y becomes positive ($A/r > B/r^3$). The crossover from a solute effect dominance to a Kelvin effect dominance is expedited for cases with lower surface tension (compare cases III and I) and occurs also sooner for higher M_s (compare cases II and I). During the stage of rapid drop growth ($S \geq 1$), the particles become dilute and the differences in the various parameters shown in Figures 8a–8e become less distinct. All potential modifications to the drop concentration due to aerosol composition factors are determined over a relatively short window of time.

5.2.2. Driving Force of Drop Growth ($S - y$) and Resulting Saturation S

[46] Particle growth is determined by $(S - y)$ (equations (2) and (7)). An increase in y leads to reduced drop growth

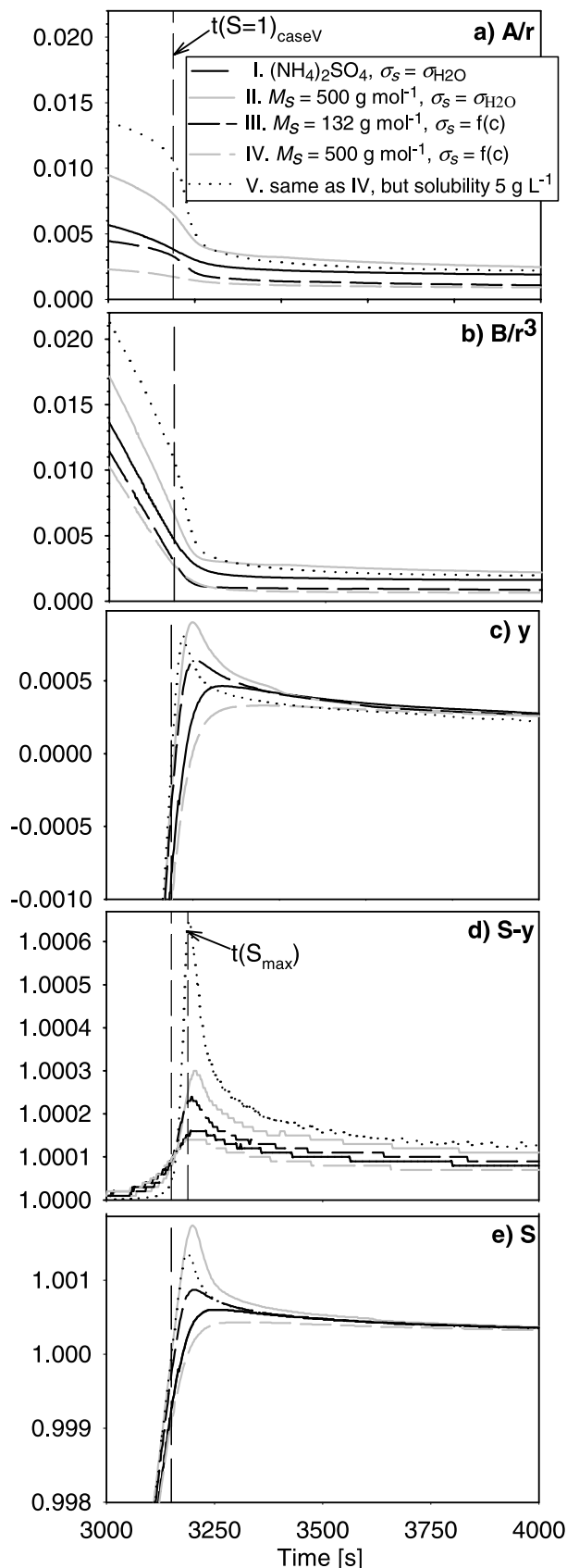


Figure 8. Temporal evolution of (a) Kelvin term A/r , (b) solute term B/r^3 , (c) $y = A/r - B/r^3$, (d) $(S - y)$, and (e) S . Aerosol size distribution: $r_g = 0.04 \mu\text{m}$, $\sigma_g = 2$, and $N_a = 5000 \text{ cm}^{-3}$.

as clearly seen for case V prior to $S = 1$. Because of the relatively small number of growing droplets and low growth rates in cases II and V, the ambient supersaturation increases and creates sharper peaks in $(S - \gamma)$ at supersaturated conditions than for the other cases. The different values of $(S - \gamma)$ are generally reflected in changes in S_{\max} (Figure 8e); the highest $(S - \gamma)$ tend to have the highest S_{\max} . However, this is not always the case (compare cases II and V) since the supersaturation is a result of subtle feedbacks of the water vapor supply, available surface area, and composition-dependent condensation.

5.2.3. Drop Number Concentration N_d

[47] Changes in S_{\max} and $(S - \gamma)$ have direct influence on N_d (Figure 9a). Between $t_{S=1}$ and $t_{S_{\max}}$ there is a steep increase in the drop number for all cases. In general, the temporal evolution of N_d follows the corresponding $(S - \gamma)$ terms. Note that cases II and V differ in their surface tension (V having a lower surface tension) as well as in their solubility (V having a lower solubility). The fact that N_d is the same for these cases reflects the countering effects of lower surface tension, which tends to increase N_d , and lower solubility which tends to decrease N_d . It is also noted that the maximum drop concentration does not always occur at S_{\max} . After $t_{S_{\max}}$ chemical effects can cause the smallest activated droplets to evaporate because $(S - \gamma)$ becomes negative. (The transition to negative γ is not visible in Figure 8e because we have calculated the population mean $(S - \gamma)$, equation (9)).

[48] For comparison, in Figure 9b we show N_d for $w = 300 \text{ cm s}^{-1}$. At high w the time period during which the γ term can influence dS/dt , and thus drop formation, is much smaller, resulting in smaller relative differences in N_d than for $w = 10 \text{ cm s}^{-1}$.

6. Comparison With the Literature

[49] While the data in Table 1 show a scattering of $-86\% < \Delta N_d < 110\%$, this work predicts much smaller values ($-60\% < \Delta N_d < +20\%$; Figures 6 and 7) for organic aerosols whose composition characteristics vary over realistic ranges. The absence of a general conclusion regarding the influence of WSOC on N_d has to be considered within the context of the limited set of model conditions and species, and the assumed values of various composition-related parameters employed in the various studies (Table 1). In this section we clarify the assumptions that have been made in these studies and explain the range of ΔN_d against the background of our analysis of the influence of individual organic properties.

[50] About half of the studies compare N_d of WSOC and pure $(\text{NH}_4)_2\text{SO}_4$ aerosols. However, even this comparison is not straightforward; all studies listed in Table 1 are based on comparisons of identical radius, which leads to different initial masses, whereas we have performed comparisons on a mass basis which also corresponds to identical initial radii because of our assumption of identical ρ_s for all solutes. We have performed a few model simulations initialized with the same initial radii but assuming densities over the range $1.2 \text{ g cm}^{-3} < \rho_{\text{sol}} < 2 \text{ g cm}^{-3}$, i.e., similar to the range of values assumed in Table 1. The differences in N_d between our standard simulation for ammonium sulfate ($\rho_s = 1.769 \text{ g cm}^{-3}$) and an identical simulation that assumes $\rho_s = 1.2 \text{ g}$

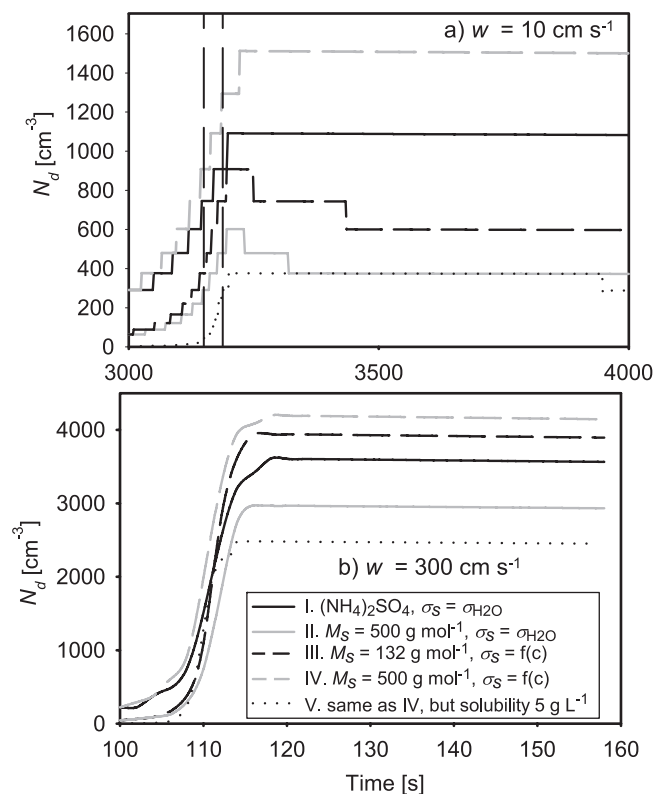


Figure 9. Temporal evolution of N_d . Aerosol size distribution: $r_g = 0.04 \mu\text{m}$, $\sigma_g = 2$, and $N_q = 5000 \text{ cm}^{-3}$; (a) $w = 10 \text{ cm s}^{-1}$ and (b) $w = 300 \text{ cm s}^{-1}$.

cm^{-3} is -20% ; conversely, when $\rho_s = 2.0 \text{ g cm}^{-3}$ is assumed, the difference is $+20\%$.

[51] Shantz *et al.* [2003] and Lohmann *et al.* [2004] modeled a comparison of the CCN activity of particles that were composed of 99.9% adipic acid and 0.1% $(\text{NH}_4)_2\text{SO}_4$ and found a significant reduction in N_d for very low w (-67% and -86%). The addition of a surface active compound, such as nonanoic acid, led to an increase in ΔN_d [Lohmann *et al.*, 2004]. These findings confirm results from our previous model study [Ervens *et al.*, 2004], where we found that a mixture of 90% adipic acid/10% $(\text{NH}_4)_2\text{SO}_4$ leads to a significant reduction in N_d . These aforementioned model as well as the present study assumed initially dry organic aerosols which might be inappropriate for atmospheric aerosols that exist as metastable solutions and thus behave more like completely dissolved particles. If even the small σ_s effect of adipic acid is considered, these differences are canceled. If glutaric acid aerosols are considered, the lower solute term is more than compensated by the σ_s effect, leading to a positive ΔN_d . The more realistic assumption of a dicarboxylic acid/ $(\text{NH}_4)_2\text{SO}_4$ mixture (with oxalic acid being the dominant organic) gives $\Delta N_d \sim 0$. These findings agree well with the experimental study by Giebl *et al.* [2002] who found that the CCN activity of oxalic acid is identical to that of $(\text{NH}_4)_2\text{SO}_4$. Hegg *et al.* [2001] predicted a significantly smaller N_d for pinonic acid compared to $(\text{NH}_4)_2\text{SO}_4$, even though the M_s of both solutes are quite similar. However, their modeling study was performed to interpret laboratory

measurements and the comparison was based on two different sets of N_d , r_g , and σ_g for $(\text{NH}_4)_2\text{SO}_4$ and pinonic acid particles, respectively.

[52] *Nenes et al.* [2002] and *Rissman et al.* [2004] assumed a complex composition of WSOC. In the first study the consideration of organic fraction, solubility, and surface tension effects led to quite a broad range in ΔN_d . The latter study did not report absolute values of ΔN_d , but predicted negative ΔN_d if hygroscopicity effects alone were considered and positive values if σ_s effects were included. Both estimates are likely to be overestimates of N_d since the initialization of the WSOC composition includes the assumption of fully dissociated organic acids (i.e., ν as high as $\nu = 3$ (diacid) and $\nu = 5$ (fulvic acid)).

[53] The reference composition chosen by *Ming and Russell* [2004] (50% $(\text{NH}_4)_2\text{SO}_4$ /50% NH_4NO_3) is comparable to pure $(\text{NH}_4)_2\text{SO}_4$ since, to a first approximation, the solute term ($\propto \nu/M_s$) of NH_4NO_3 is comparable to that of $(\text{NH}_4)_2\text{SO}_4$. Their first approach for the prediction of ΔN_d is based on the Köhler equation (equation (1)), i.e., equilibrium conditions. In this approach they determined N_d as the number of particles that have exceeded their critical sizes at a given supersaturation. They showed that under equilibrium assumptions, $\Delta N_d = 57\%$, whereas solving dynamical equations such as equations (2) and (3) yielded $\Delta N_d = 3\%$. This large overestimate of the importance of composition follows because under equilibrium assumptions, particle size is dictated by composition (equation (1)) and feedbacks to S (equation (3)), as well as kinetic limitations to particle growth (equation (2)) are not allowed. This result is an extension of the results of *Phinney et al.* [2003], who showed that for a fixed composition, N_d is underestimated when calculated on the basis of equilibrium assumptions because the equilibrium size assumption greatly enhances the sizes of the largest particles, reduces S , and suppresses activation of the smaller, more numerous particles. In addition, *Ming and Russell* [2004] included possible interactions of organic and inorganics in internally mixed aerosols, i.e., the detailed consideration of the activity coefficients of all solutes. Such interactions lead to higher solubilities, and thus the soluble mass is increased which, in turn, leads to a larger solute term. Such effects can counteract other composition effects so that a positive value for ΔN_d is predicted ($\Delta N_d = +6\%$).

[54] While the results discussed up to now allow a direct comparison of the CCN activity by inorganics and organics, *Mircea et al.* [2002] and *Alfonso and Raga* [2004] predicted an increase in CCN activity if insoluble material is replaced by WSOC. *Mircea et al.* [2002] estimated the effects on the basis of equilibrium conditions; however, this approach represents an overestimate of ΔN_d as qualitatively shown by *Ming and Russell* [2004]. The organic proxy chosen by *Alfonso and Raga* [2004], oxalic acid, has the smallest M_s among common organic aerosol constituents which leads to the highest solute term based on any organic M_s . In addition, in these two aforementioned studies $\nu = 3$ and $\nu = 5$ (and $\Phi = 1$) are applied for organic diacids or polyacids, respectively. However, we have shown that $\nu\Phi = 1$ is a more appropriate assumption; thus higher values of $\nu\Phi$ will overpredict N_d .

[55] *Anttila and Kerminen* [2002] predict more moderate changes in N_d due to WSOC. However, their simulations compare aerosols that differ only slightly in the organic fraction (20% versus 60%) and they use an organic proxy that has similar properties to $(\text{NH}_4)_2\text{SO}_4$ in terms of solubility and M_s (but $\nu\Phi = 1$). The study by *Bilde and Svenningsson* [2004] showed that only small amounts (<5% by mass) of highly soluble material (NaCl) are required in order to overcome the Kelvin effect and to provide a sufficient amount of water to allow the complete dissolution of slightly soluble organics (e.g., succinic or adipic acid). However, it is likely that in their experimental study the aerosol achieved an equilibrium state and ΔN_d might be smaller if dynamic aspects (i.e., kinetic limitations to growth in an updraft) had been taken into account.

[56] A simplified approach for the estimate of ΔN_d due to surface activity of organic properties was chosen by *Facchini et al.* [1999]. They compared the Kelvin terms for reduced σ_s and pure water and obtained S according to equation (1). A relationship between N_d and S was given by *Twomey* [1959]:

$$N_d \propto S^k, \quad (12)$$

where k is an empirical constant ($0.3 < k < 1.3$ [*Pruppacher and Klett*, 1997]). On the basis of equation (12), *Facchini et al.* [1999] derived the following expression

$$\frac{\Delta N_d}{N_d} = -\frac{3}{4} \frac{\Delta \sigma_s}{\sigma_s} \quad (13)$$

which leads to $\Delta N_d = +20\%$ for a reduction of 30% in σ_s ($\sigma_s \sim 50 \text{ dynes cm}^{-1}$). However, this estimate is based on equilibrium conditions and implies that even close to activation particles are saturated solutions.

[57] In summary, a detailed analysis of the numerous conditions and assumptions that have been made in the studies in Table 1 suggests that inappropriate assumptions such as equilibrium conditions, or very small soluble mass fractions, can explain the very broad range of predicted ΔN_d . In addition, the use of high van't Hoff factors ($\nu\Phi = 3-5$) will result in overestimates of N_d . The results presented here suggest that for moderate updraft velocities ($w > 20 \text{ cm s}^{-1}$) WSOC leads to ΔN_d of $\pm 15\%$ compared to $(\text{NH}_4)_2\text{SO}_4$.

7. Conclusions

[58] In the present study we have performed a systematic investigation of composition effects on the ability of aerosol particles to form cloud droplets. Although we have focused on organic aerosols and explored the effects of M_s , solubility, $\nu\Phi$, and σ_s on their CCN ability, relative to the equivalent ammonium sulfate particle, these results are of broad interest for species that fall into similar parameter spaces. If the individual properties are considered separately, ΔN_d can cover a range of $-70\% < \Delta N_d < +140\%$. However, if parameter combinations representative of realistic organic compounds are applied, the absolute values for ΔN_d are

reduced (on a mass-for-mass basis, and considering the same initial aerosol size distribution). The following primary results emerge:

[59] 1. For organic compounds the description of the solution water activity, which includes the van't Hoff factor, can be simplified by using $\nu\Phi = 1$ since the degree of dissociation of most pure organic acids at their critical radii can be neglected.

[60] 2. Only high molecular weight species ($M_s > 400 \text{ g mol}^{-1}$) influence ΔN_d significantly.

[61] 3. Slightly soluble particles, if initially in their dry state, might lead to significantly smaller N_d . However, under atmospheric conditions, aged particles always contain a significant fraction of soluble material which provides sufficiently high water uptake and allows the dissolution of low-solubility material prior to saturated conditions. In addition, it is likely that atmospheric aerosols often exist as metastable solutions.

[62] 4. Both the dissolved mass fraction and σ_s are a function of the water mass, and thus composition effects caused by surface activity or reduced solubility steadily decrease in importance as activation size is approached.

[63] 5. At subsaturated conditions, drop growth rates are mainly influenced by modifications in the solute term, i.e., M_s , m_s , and/or $\nu\Phi$.

[64] 6. The largest values of ΔN_d occur at low w and high N_a , i.e., conditions under which S is small and composition effects become important (equations (2) and (3)). Under these conditions, kinetic effects on growth are important and the assumption that the particles are always in thermodynamic equilibrium with the ambient gas phase leads to an overestimate of the composition effects.

[65] Our analysis explains the large variability in predicted ΔN_d (Table 1) and confirms the results of these recent studies which have shown that at $w > 20 \text{ cm s}^{-1}$ common WSOC compounds such as (mixtures of) dicarboxylic acids, sugars, or organic polymers appear to cause $\Delta N_d \pm \sim 15\%$, compared to $(\text{NH}_4)_2\text{SO}_4$. These findings imply that the relationship between N_d and aerosol composition that usually comprises complex mixtures of inorganics and organics can be greatly simplified by only considering soluble and insoluble mass fractions. The change in shortwave cloud radiative forcing for highly idealized clouds is proportional to ΔN_d [Seinfeld and Pandis, 1997, p. 1176] and for typical conditions, $\Delta N_d = +15\%$ results in a change in shortwave forcing of about -0.5 W m^{-2} . Only organic aerosols composed purely of WSOC with more extreme properties might lead to a variability of $-50\% < \Delta N_d < +20\%$, compared to $(\text{NH}_4)_2\text{SO}_4$, with equivalent shortwave forcings of $+1.8 \text{ W m}^{-2}$ and -0.7 W m^{-2} , respectively.

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References

- Alfonso, L., and G. B. Raga (2004), The influence of organic compounds in the development of precipitation acidity in maritime clouds, *Atmos. Chem. Phys.*, *4*, 1097–1111.
- Anttila, T., and V. Kerminen (2002), Influence of organic compounds on the cloud droplet activation: A model investigation considering the volatility, water solubility, and surface activity of organic matter, *J. Geophys. Res.*, *107*(D22), 4662, doi:10.1029/2001JD001482.
- Bilde, M., and B. Svenningsson (2004), CCN activation of slightly soluble organics: The importance of small amounts of inorganic salt and particle phase, *Tellus, Ser. B*, *56*, 128–134.
- Braban, C. F., M. C. Carroll, S. A. Styler, and J. P. D. Abbatt (2003), Phase transitions of malonic and oxalic acid aerosols, *J. Phys. Chem. A*, *107*, 6594–6602.
- Chylek, P., and J. G. D. Wong (1998), Erroneous use of the modified Köhler equation in cloud and aerosol physics applications, *J. Atmos. Sci.*, *55*, 1473–1477.
- Ervens, B., G. Feingold, S. M. Kreidenweis, and S. L. Clegg (2004), A modeling study of aqueous production of dicarboxylic acids: 2. Implications for cloud microphysics, *J. Geophys. Res.*, *109*, D15206, doi:10.1029/2004JD004575.
- Facchini, M. C., M. Mircea, S. Fuzzi, and R. J. Charlson (1999), Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, *401*, 257–259.
- Feingold, G. (2003), Modeling of the first indirect effect: Analysis of measurement requirements, *Geophys. Res. Lett.*, *30*(19), 1997, doi:10.1029/2003GL017967.
- Feingold, G., and P. Y. Chuang (2002), Analysis of the influence of film-forming compounds on droplet growth: Implications for cloud microphysical processes and climate, *J. Atmos. Sci.*, *59*, 2006–2018.
- Feingold, G., and A. J. Heymsfield (1992), Parameterizations of condensational growth of droplets for use in general circulation models, *J. Atmos. Sci.*, *49*, 2325–2342.
- Giebl, H., A. Berner, G. Reischl, H. Puxbaum, A. Kasper-Giebl, and R. Hitznerberger (2002), CCN activation of oxalic and malonic acid test aerosols with the University of Vienna cloud condensation nuclei counter, *J. Aerosol Sci.*, *33*, 1623–1634.
- Gill, P. S., T. E. Graedel, and C. J. Weschler (1983), Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snow flakes, *Rev. Geophys.*, *21*(4), 903–920.
- Hegg, D. A., S. Gao, W. Hoppel, G. Frick, P. Caffrey, W. R. Leitch, N. Shantz, J. Ambrusko, and T. Albrechtschinski (2001), Laboratory studies of the efficiency of selected organic aerosols as CCN, *Atmos. Res.*, *58*, 155–166.
- Howell, W. E. (1949), The growth of cloud drops in uniformly cooled air, *J. Meteorol.*, *6*, 134–149.
- Jungwirth, P., and D. J. Tobias (2001), Molecular structure of salt solutions: A new view of the interface with implications for heterogeneous atmospheric chemistry, *J. Phys. Chem. B*, *105*, 10,468–10,472.
- Kalberer, M., J. Yu, D. R. Cocker, R. C. Flagan, and J. H. Seinfeld (2000), Aerosol formation in the cyclohexene-ozone system, *Environ. Sci. Technol.*, *34*, 4894–4901.
- Lide, D. R. (Ed.) (2000), *Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, Fla.
- Lohmann, U., K. Broekhuizen, R. Leitch, N. Shantz, and J. Abbatt (2004), How efficient is cloud droplet formation of organic aerosols?, *Geophys. Res. Lett.*, *31*, L05108, doi:10.1029/2003GL018999.
- Low, R. D. H. (1969), A generalized equation for the solution effect in droplet growth, *J. Atmos. Sci.*, *26*, 608–611.
- Marcollì, C., B. Luo, and T. Peter (2004), Mixing of organic aerosol fractions: Liquids as the thermodynamically stable phases, *J. Phys. Chem. A*, *108*, 2216–2224.
- Ming, Y., and L. M. Russell (2004), Organic aerosol effects of fog droplet spectra, *J. Geophys. Res.*, *109*, D10206, doi:10.1029/2003JD004427.
- Mircea, M., M. C. Facchini, S. Decesari, S. Fuzzi, and R. J. Charlson (2002), The influence of the organic aerosol component on CCN supersaturation spectra for different aerosol types, *Tellus, Ser. B*, *54*, 74–81.
- Nenes, A., R. J. Charlson, M. C. Facchini, M. Kulmala, A. Laaksonen, and J. H. Seinfeld (2002), Can chemical effects on cloud droplet number rival the first indirect effect?, *Geophys. Res. Lett.*, *29*(17), 1848, doi:10.1029/2002GL015295.
- Phinney, L. A., U. Lohmann, and W. R. Leitch (2003), Limitations using an equilibrium approximation in an aerosol activation parameterization, *J. Geophys. Res.*, *108*(D12), 4371, doi:10.1029/2002JD002391.
- Pruppacher, H. R., and J. D. Klett (1997), *Microphysics of Clouds and Precipitation*, Springer, New York.
- Rissler, J., E. Swietlicki, J. Zhou, G. Roberts, M. O. Andreae, L. V. Gatti, and P. Artaxo (2004), Physical properties of the sub-micrometer aerosol over the Amazon rain forest during the wet-to-dry transition—Comparison of modeled and measured CCN concentrations, *Atmos. Chem. Phys.*, *4*, 2119–2143.
- Rissman, T. A., A. Nenes, and J. H. Seinfeld (2004), Chemical amplification (or dampening) of the Twomey effect: Conditions derived from droplet activation theory, *J. Atmos. Sci.*, *61*, 1919–1930.
- Rogge, W. F., M. A. Mazurek, L. M. Hildemann, G. R. Cass, and B. R. T. Simoneit (1993), Quantification of urban organic aerosols at a molecular

- level: Identification, abundance and seasonal variation, *Atmos. Environ.*, *27A*, 1309–1330.
- Seinfeld, J. H., and S. N. Pandis (1997), *Atmospheric Chemistry and Physics*, Wiley-Interscience, Hoboken, N. J.
- Shantz, N. C., W. R. Leitch, and P. Caffrey (2003), Effect of organics of low solubility on the growth rate of cloud droplets, *J. Geophys. Res.*, *108*(D5), 4168, doi:10.1029/2002JD002540.
- Shulman, M. L., M. C. Jacobson, R. J. Carlson, R. E. Synovec, and T. E. Young (1996), Dissolution behaviour and surface tension effects of organic compounds in nucleating droplets, *Geophys. Res. Lett.*, *23*(3), 277–280.
- Tuckermann, R., and H. K. Cammenga (2004), The surface tension of aqueous solutions of some atmospheric water-soluble organic compounds, *Atmos. Environ.*, *38*, 6135–6138.
- Turpin, B. J., and H. Lim (2001), Species contributions to PM_{2.5} mass concentrations: Revisiting common assumptions for estimating organic mass, *Aerosol Sci. Technol.*, *35*, 602–610.
- Twomey, S. (1959), The nuclei of natural cloud formation, part II: The supersaturation in natural clouds and the variation of cloud droplet concentration, *Geofis. Pura Appl.*, *43*, 243–249.
- Twomey, S. (1974), Pollution and the planetary albedo, *Atmos. Environ.*, *8*, 1251–1256.
- Xue, H., and G. Feingold (2004), A modeling study of the effect of nitric acid on cloud properties, *J. Geophys. Res.*, *109*, D18204, doi:10.1029/2004JD004750.
- Zappoli, S., et al. (1999), Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, *Atmos. Environ.*, *33*, 2733–2743.

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