Hygroscopic and optical properties of organic sea salt aerosol and consequences for climate forcing

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[1] Scattering of incoming solar radiation by sea salt aerosol is strongly dependent on relative humidity (RH) since hygroscopic particles take up water at high RH. Organic compounds may constitute up to 50% of marine aerosol mass in internal mixtures. We used a detailed thermodynamic and optical model to calculate hygroscopic growth and extinction of sea salt aerosol internally mixed with a soluble organic compound. Increasing organic content from 10 to 50% suppresses growth at high RH compared to a pure NaCl particle by 4 to 20%. For a mildly absorbing organic, the scattering increase with RH is reduced by up to 32% for these mixtures, consistent with observations. Internal mixtures of 90% NaCl and 10% non-absorbing organics cause 3% less cooling than 100% NaCl particles in the visible spectrum over the clear-sky oceans. For a mildly absorbing organic compound, 10% organic content reduces radiative cooling substantially compared to 100% NaCl aerosol. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation. **Citation:** Randles, C. A., L. M. Russell, and V. Ramaswamy (2004), Hygroscopic and optical properties of organic sea salt aerosol and consequences for climate forcing, *Geophys. Res. Lett.*, *31*, L16108, doi:10.1029/2004GL020628.

1. Introduction

[2] Atmospheric aerosols scatter and absorb incoming shortwave solar radiation. Depending on the aerosol optical properties and the surface albedo, aerosols may exert a warming or cooling effect on the surface [*Chylek and Coakley*, 1974]. Aerosol optical properties are dependent on size distribution, shape, chemical composition, and mixing state, all of which are strong functions of relative humidity (RH) [*Pilinis et al.*, 1995]. The dependence of scattering on RH, quantified by the scattering growth factor $f_{RH}(\sigma_{sp}) = \sigma_{sp(85\%)}/\sigma_{sp(40\%)}$, is one of the most important parameters determining the direct aerosol effect [*Charlson et al.*, 1992].

[3] Sea salt is the most ubiquitous aerosol over the oceans and has been recognized as the dominant aerosol contributor to the clear-sky albedo over oceans [*Haywood et al.*, 1999]. Produced by the evaporation of sea spray from wind induced white caps, sea salt occurs in aerosol with diameter $D_p > 0.13$ μm [*Murphy et al.*, 1998] and therefore is an efficient scatterer in the shortwave radiation regime of $0.08 < D_p < 1$ μm [*Schwartz*, 1996]. Primarily consisting of NaCl, sea salt aerosol, like most inorganic salts, are hygroscopic and exist as dry particles at low RH. When the RH increases to the deliquescence relative humidity (DRH), salt particles abruptly take up water to form saturated droplets. Conversely, when the RH over a droplet is decreased, the particle does not crystallize at the DRH, but remains in a metastable equilibrium until a lower RH, the crystallization relative humidity (CRH). This hysteresis phenomenon has been well characterized in the laboratory for several common salts (e.g., NaCl, $(NH_4)_2SO_4$, KCl, $MgSO_4$) and combinations of these salts [*Tang*, 1996, 1997].

[4] Surface-active organic material in seawater can become incorporated into the aerosol phase during the bubble-bursting process resulting in an internal mixture of inorganic salts, organic compounds, and water. Several studies have observed organic compounds internally mixed with marine aerosol [*Dick et al.*, 2000; *Swietlicki et al.*, 2000], and organic compounds have been found to constitute up to 50% of the total fine aerosol mass in both urban and marine locations [*Middlebrook et al.*, 1998]. Organic compounds have been found to alter the amount of water absorbed by aerosol particles at sub-saturated RH [*Saxena et al.*, 1995]. Altering the hygroscopic behavior of the aerosol acts to change the aerosol composition, influencing refractive index and size, both of which determine aerosol extinction at a given wavelength. Thus, the direct radiative properties of sea salt aerosol can be significantly altered by internally mixing organic compounds with sea salt. Most studies of the direct aerosol forcing to date have either considered external mixtures of organic compounds and other species, or have not included the effect of internally mixed organic compounds on hygroscopic growth [*Penner et al.*, 1998; *Haywood et al.*, 1999]. The purpose of this study is to show that the reduced hygroscopic growth caused by organic compounds internally mixed with sea salt can cause a significant reduction in scattering (and cooling) when compared to pure sea salt aerosol over an ocean surface.

We employ a detailed organic-electrolyte thermodynamic equilibrium model [*Ming and Russell*, 2002] (hereafter MR, 2002) to study the hygroscopic growth of NaCl-organic mixtures. As an example of a water soluble organic compound (WSOC), we consider glutaric acid, a diacid observed in marine aerosol [*Decesari et al.*, 2001]. Assuming a single-mode lognormal size distribution, optical properties are calculated using Mie theory for various mixtures of NaCl and the model WSOC as a function of RH. The purpose here is to explore the sensitivity of the optical properties to organic mass fraction that results from changes in hygroscopic growth and changes in refractive index. The consequences of internal mixtures of organic compounds and sea salt are then evaluated using the *Chylek and Coakley* [1974] relation.

2. Description of Models

[5] To quantify the amount of aerosol water uptake, we define the hygroscopic growth factor (HGF) as the ratio of the diameter $D_{p,RH}$ at a specified RH to the original dry diameter $D_{p,dry}$, which is at an RH lower than the CRH of all solutes present (on the lower branch of the hysteresis curve) [*Swietlicki et al.*, 2000]:

$$HGF(RH) = \frac{D_{p,RH}}{D_{p,dry}} \tag{1}$$

The organic-electrolyte model uses a semi-empirical approach to describe the phase equilibria of aerosol particles consisting of electrolytes and organic species in aqueous solution.

[6] Aerosol particles existing at relative humidities between 35% and 95% often behave nonideally; thus, in order to minimize the Gibbs free energy of the solution, the solution activity must be calculated. To calculate solution activity, three types of interactions must be considered: electrolyte-water, organic-water, and organic-electrolyte. The model combines the Pitzer-Simonson-Clegg model (electrolyte-water interactions) [*Clegg and Pitzer*, 1992] and a modified version of UNIFAC (organic-water and organic-electrolyte interactions) [*Reid et al.*, 1987] to describe solutions of ions, organic species, and water [MR, 2002].

[7] For this study, hygroscopic growth factors for dry particles consisting of NaCl and glutaric acid of various mass ratios were obtained for a dry diameter of 320 nm and applied to a single-mode lognormal size distribution for the dry aerosol with modal diameter D_{pg} = 320 nm, σ_g = 2.5, and N = 40 cm^{-3} [*Shettle and Fenn*, 1979]. For D_p > 100 nm (below which surface tension effects can affect growth), growth factors had little variation with size (<1%) [MR, 2002]. For this reason, the growth factor for 320 nm was used for the entire distribution at a given RH. With the calculated wet size distributions from hygroscopic growth factors, composite refractive indices were computed with a volume-weighted linear mixing rule. The real refractive indices used for each species (NaCl, glutaric acid, and water) at a wavelength of 0.55 μm were 1.510, 1.431, and 1.333, respectively, and the imaginary indices used were 1×10^{-7}, 6×10^{-3}, and 1.96×10^{-9} [*Erlick et al.*, 2001]. Given wet lognormal distributions and composite refractive

indices, and assuming spherical particles, Mie theory was used to calculate extinction (σ_{ep}), scattering (σ_{sp}), and absorption (σ_{ap}) coefficients, the single scattering albedo (ω), and the asymmetry factor (g) as a function of RH [*Bohren and Huffman*, 1983]. The backscattering fraction was approximated as $\beta = (1 - g)/2$ [*Sagan and Pollack*, 1967]. These results from the Mie calculations acted as inputs to the two-stream solution of *Chylek and Coakley* [1974].

3. Results

[8] Growth curves for mixtures of NaCl and glutaric acid were computed for a dry diameter of 320 nm. Other size distributions were not considered because the sensitivity of the optical properties to the assumed dry size distribution has already been explored by *Pilinis et al.* [1995]. The organic-electrolyte model correctly predicts the DRH of NaCl (75.3% [*Tang*, 1996]), and the DRH of pure glutaric acid is close to the measured value of 85(±)5% [*Cruz and Pandis*, 2000]. At high RH (75% to 90%), 10%, 30%, and 50% glutaric acid cause 4%, 12% and 20% decrease in growth, respectively, relative to pure NaCl. The decrease in DRH to 68% for these same mixtures allows for significant growth compared to pure salt below its DRH of 75%. At lower RH (68% to 75%), the mixed particles are actually larger than NaCl. Figure 1 presents the scattering coefficient as a function of RH for NaCl mixed with 0%, 10%, 30%, 50%, 75%, and 100% model WSOC (glutaric acid growth with assumed refractive indices), where percent mass refers to the dry particle consisting of only NaCl and model WSOC (i.e., prior to the addition of water). At 85% RH, the scattering coefficient is 8%, 22%, and 37% lower than the pure salt scattering coefficient for dry mixtures consisting of 10%, 30%, and 50% model WSOC, respectively. Prior to the DRH, there is negligible uptake of water, so the differences in scattering coefficient here reflect the effects of volume-weighting the refractive indices of the model WSOC and NaCl only. After deliquescence, water accounts for the majority of the aerosol volume, so the real refractive index is weighted heavily to the value of water. The changes in scattering among the WSOC/NaCl mixtures after the DRH reflect the reduced water uptake (and reduction in diameter) associated with increased organic content rather than the change in real refractive index.

[9] To compare with measurements, we have computed the scattering growth factor $f_{RH}(\sigma_{sp}) = \sigma_{sp(RH)}/\sigma_{sp(40\%)}$ where RH = 40% is considered dry (CRH of NaCl is approximately 50% [*Andrews and Larson*, 1993]). Figure 2 presents $f_{RH}(\sigma_{sp})$ as a function of RH for the mixtures considered in this study. Also presented are the results of *McInnes et al.* [1998] who measured $f_{RH}(\sigma_{sp})$ on Sable Island, Canada, with a tandem humidified nephelometer system for marine and continentally influenced air masses. Individual particle chemical analysis revealed that differences in the measured $f_{RH}(\sigma_{sp})$ were due to differences in aerosol composition, not due to differences in the particle size distributions. The modeled $f_{RH}(\sigma_{sp})$ for the different mixtures show that, as the organic mass fraction increases, $f_{RH}(\sigma_{sp})$ decreases relative to pure NaCl. For example, at 85% RH, the value of $f_{RH}(\sigma_{sp})$ for the 10%, 30%, and 50% model WSOC mixtures is 6%, 19%, and 32% lower
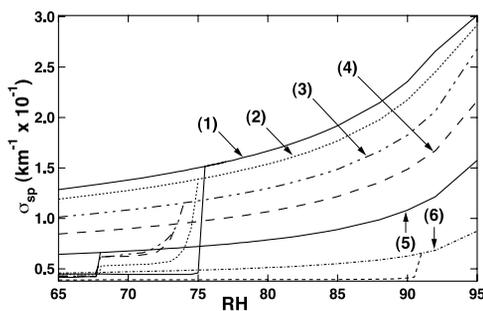
Figure 1. Scattering coefficient for lognormal distribution of particles (D_p = 320 nm, σ_g = 2.5, N = 40 cm^{-3}), with a dry composition consisting of NaCl and model WSOC (glutaric acid hygroscopic behavior with assumed refractive indices). Lines represent: (1) 100% NaCl, (2) 90% NaCl, 10% model WSOC, (3) 70% NaCl, 30% model WSOC (4) 50% NaCl, 50% model WSOC (5) 25% NaCl, 75% model WSOC, and (6) 100% model WSOC.

Figure 2. Predicted (lines) and measured (dots) scattering growth factors $f_{RH}(\sigma_{sp}) = \sigma_{sp(RH)}/\sigma_{sp(40\%)}$ for the scattering coefficients and line numbers in Figure 1. Measured scattering growth factors are for marine (open circles) and anthropogenically influenced/polluted (closed circles) cases [*McInnes et al.*, 1998].

than the value of $f_{RH}(\sigma_{sp})$ for pure NaCl. These results suggest that the reduction in growth caused by the presence of the WSOC, and the resulting reduction in scattering coefficient could be responsible for the observed reduction in $f_{RH}(\sigma_{sp})$ when going from a clean marine to a polluted continental air mass. This interpretation is consistent with the suggestion of *McInnes et al.* [1998] that the growth of sea salt aerosol may be suppressed, allowing for limited growth by organic aerosol and other aerosol types. Also note that the observed values of $f_{RH}(\sigma_{sp})$ for the clean marine case are lower than the $f_{RH}(\sigma_{sp})$ values calculated for pure NaCl, suggesting that even clean marine air may contain sea salt internally mixed with WSOC, though the potential for compounds other than organic compounds to cause the same behavior is not ruled out.

[10] Radiative implications resulting from the reduction in growth of the sea salt particle caused by the substitution of a WSOC for salt are explored with the two-stream approximation for λ = 0.55 μm. Under the assumptions of a plane-parallel atmosphere and global-average conditions, the critical ratio of absorption cross-section to average backscattering cross-section is given by *Chylek and Coakley* [1974]:

$$\frac{(1 - \omega)}{\omega\beta} = \frac{(1 - a)^2}{2a} \qquad (2)$$

where a is the albedo of the earth-atmosphere system, ω is the single scattering albedo (the fraction of radiation scattered), and $\omega\beta$ is the fraction of radiation scattered into the backward hemisphere. When $(1 - \omega)/\omega\beta > (1 - a)^2/2a$, heating of the earth-atmosphere system occurs, and when $(1 - \omega)/\omega\beta < (1 - a)^2/2a$, cooling occurs [*Chylek and Coakley*, 1974]. The critical ratios at 85% RH for the considered mixtures are plotted in Figure 3. Because we are considering sea salt aerosol over an ocean surface, we focus on the results with a surface albedo of approximately 0.1. The pure NaCl aerosol produces a strong cooling effect over the oceans. However, even with the addition of just 10% model WSOC to the dry mass, there is a marked reduction in this cooling effect (3 orders of magnitude reduction
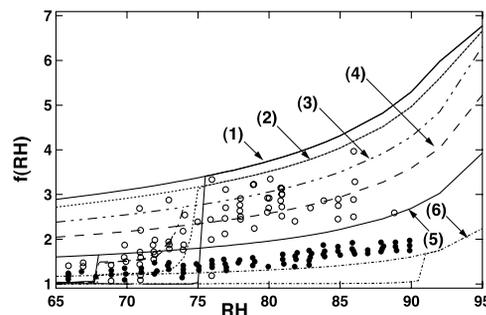
compared to pure NaCl). If we consider higher reflecting surfaces, the presence of the mildly absorbing organic aerosol allows the aerosol to even cause a warming effect. However, if the organic is considered to be non-absorbing (i.e., imaginary index the same as water), 10% model WSOC in the dry mixture causes a 3% reduction in cooling and 50% model WSOC causes a 25% reduction in cooling compared to pure NaCl. Both a non-absorbing and a mildly absorbing organic will reduce cooling when compared to pure NaCl because the WSOC will reduce the size of the aerosol at high RH typical over oceans. A mildly absorbing WSOC will significantly increase this reduction in cooling because it will both reduce the hygroscopic growth and add an absorbing material.

4. Conclusions

[11] Organic carbon can have a significant effect on the ability of hygroscopic salt aerosol to cause a cooling of the earth-atmosphere system because organic compounds can suppress hygroscopic growth of particles. As a result of this size suppression, less of the aerosol size distribution shifts into the optically active range, and less scattering results. The lowering of water uptake leads to lower values of the
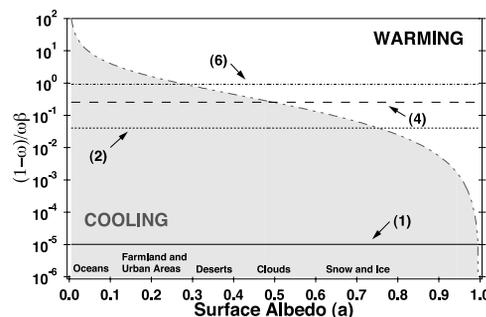
Figure 3. Critical ratio as a function of surface albedo at 85% RH for the size distribution, line numbers in Figure 1, and a mildly absorbing organic compound (m = 1.431 − 6 × 10^{-3}). Relative differences between sea salt and mixtures persist at higher RH, but magnitudes are even larger. The thick dashed line represents the equality in equation (2) such that radiative warming of the earth-atmosphere system occurs above and cooling below this line.

scattering growth factor $f_{RH}(\sigma_{sp})$, which implies that at least some of the reduction in $f_{RH}(\sigma_{sp})$ observed in moving from a marine to continentally influenced air mass results from the presence of organic compounds.

[12] The hysteresis in the hygroscopic growth behavior means that the diameter of these aerosols may differ by 40% to 90% and scattering may vary by a factor of 3 depending on whether the particles are wetting (on the stable lower branch, going from low to high RH) or drying (on the metastable upper branch). Recent evidence has shown that some organic compounds may be mildly absorbing [Gelencser et al., 2003]. When considering a mildly absorbing WSOC, not only is the mass of water within the aerosol reduced, but the aerosol is now absorbing as well. This causes an even more significant reduction in radiative cooling over the clear-sky oceans, and, if higher reflecting surfaces are considered, could also lead to a radiative warming of the column. Use of higher-order mixing rules (e.g., Maxwell-Garnett) often results in even higher imaginary indices than linear mixing when absorbing components are present [Chylek et al., 1984; Erlick et al., 1998], leading to an even greater reduction in radiative cooling over oceans than seen here. In fact, these considerations concerning organic aerosols, as inferred in this work, could enable an even better agreement of the simulated clear-sky reflected solar radiation over oceans with satellite observations [Haywood et al., 1999]. Since the refractive indices of individual organic species are largely unknown, it can be seen from this study that it is important to know whether organic components absorb, how much they absorb, and their mixing state with other constituents for the determination of composite aerosol optical parameters [Lesins et al., 2002].

[13] Organic carbon in sea salt aerosol may be produced from the surfactant layer on the sea surface or from the aging process due to condensation from the gas phase. This second mechanism will grow the dry size distribution and reduce the hygroscopic growth. Organic compounds also can become associated with sulfate particles in a similar manner. Sulfate experiences deliquescent behavior similar to sea salt, and organic compounds cause a reduction in hygroscopic growth at high humidity for sulfates as well, reducing reflection caused by sulfates. It is likely that if WSOC are associated with sulfates and sea salt, the global radiative cooling associated with organic compounds is overestimated because of inadequate accounting of their hygroscopic growth and absorption effects, thus making it imperative that evaluations of aerosol climate effects consider these physical processes explicitly.

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