Particle growth and inferred mass accommodation coefficients for nitrate uptake on sulfate particles in an urban port region

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ABSTRACT

Particles produced by ships and other port-related emission sources near coastal communities contribute significantly to human health and climate forcing. Heterogeneous reactions on particle surfaces including uptake of inorganic acids can alter the chemical and physical properties of aerosols and thus their effects on health and climate. Particle sulfate and ammonium content are thought to control condensation of nitric acid at the air-liquid interface, however other limitations on nitric acid uptake are poorly understood. Here we show that the partitioning of inorganic acids onto particles is dependent upon both size and chemical composition. Single particle mass spectrometric measurements near the Ports of Long Beach and Los Angeles indicate that the nitrate and sulfate content vary significantly with the chemical composition and source of the primary particle. The growth of particles from the port area to an inland site was modeled for varying mass accommodation coefficient values and compared to ambient data. Comparisons between modeled growth and size distributions observed near the trajectory's end suggest that the magnitude of the mass accommodation coefficient for the polydisperse aerosol population is on the order of 10^{-1}, which is consistent with literature values of 0.15 for the uptake of nitric acid by water. Here the value is found to be closer to 0.25, which may be reflective of the particular chemical and physical properties of aerosols produced in the port region. Consideration of these aspects may necessitate the adjustment of mass accommodation coefficient values from current literature for more accurate modeling of the impacts of global and regional transport of port-related emissions to local communities.

INTRODUCTION

Ships, industries, and refineries in urban port regions produce large quantities of particulate matter that may contribute to cardio-pulmonary inflammation and mortality, as well as to radiative forcing in both coastal regions and over open ocean[1-4]. Port emissions include large quantities of SO_2, metals, and soot; particles produced in ship stacks often contain vanadium, soot, and hydrated sulfuric acid[1,3,5,6].

Particles produced in port regions are exposed to both sulfur and nitrogen gases during transport and can undergo atmospheric processes such as coagulation and condensation. The condensation of sulfuric and nitric acids onto particles is limited by their concentration of ammonium. As ammonium sulfate is the preferred form of sulfate, the addition of particulate nitrate as ammonium nitrate can be determined from the concentration of particle phase ammonia remaining after all available sulfate has combined with ammonium[13]. Heterogeneous uptake of inorganic species such as sulfate and nitrate affects particle acidity and could have important implications for particle hygroscopicity and reactivity[3].

While ship emissions themselves have been fairly well characterized, little is known about the impacts of port-related emissions on local communities. Long Beach, CA, the site of the fifth largest port center in the world, has been the site of several recent studies seeking to clarify these uncertainties. Spatial variation of particle mass and major components including sulfur and organic and elemental carbon is relatively limited[7-10,12]; some heterogeneity results from local traffic emissions, particularly among ultrafine particles. Studies with single particle mass spectrometry have investigated the mixing states of chemical fingerprints such as ammonium or carbonaceous signatures and secondary species including sulfate and nitrate. The presence of these secondary species in particle mass spectra is suggestive of atmospheric processing. Hughes et al. 2000 observed that 34% of 0.56-1.0 μm particles consisted of ammonium nitrate mixed with carbon; filter measurements taken alongside the aerosol time-of-flight mass spectrometer (ATOFMS) yielded ammonium and sulfate ion concentrations of approximately 3.5 μg·m^{-3} and 6 μg·m^{-3}, respectively[11]. A more recent ATOFMS study of Long Beach aerosol analyzed nearly four million individual particles, 51% and 36% of which were observed to contain sulfate and nitrate mass spectral signatures, respectively[12]. Ammonium was measured on 44% and 43% of sulfate- and nitrate-containing particles[12]; as the sensitivity of ATOFMS for ammonium is 70 times less than that for sodium ions, the actual ammonium content of particles is likely much higher[14]. The absence of negative ion spectra for nearly 30% of particles examined suggests that many particles have a high water content[15,16]; this is consistent with the high relative humidity (often >90%) observed and with recent speculations by Murphy et al. 2009 that the majority of particle mass emitted by ship stacks consists of hydrated sulfuric acid[12,17].

In this paper, we present the results of the application of a condensation model to polydisperse aerosol in the Long Beach port region to examine the limiting effects of sulfate and ammonium content on nitric acid condensation during one hour of particle transport.

Ambient sulfur and nitrogen gas concentrations as well as the mass accommodation coefficient are found to be important indicators of particle growth.

METHODS

A condensation model was applied to examine the growth by condensation of nitric acid over a trajectory from the port area to a site five miles inland. Particle growth was modeled by calculating a condensation rate for the continuum regime (J_c) and applying the Fuchs-Sutugin approach to adjust the rate to the transition regime (J) using a correction factor, β:

$$J=J_c \cdot \beta=2\pi\beta D_p D_g(c_\infty-c_s) \text{ where}$$
$$\beta=[0.75\alpha(1+Kn)]/[Kn^2+Kn+0.283Kn\alpha+0.75\alpha]$$

where D_p is the particle diameter, D_g is the condensing gas' diffusivity through air, c_∞ is the concentration of gas far from the particle, c_s is the vapor-phase concentration at the particle surface, Kn is the Knudsen number, and α is the mass accommodation coefficient or 'sticking probability'[13]. The ($c_\infty-c_s$) term represents the so-called "driving force" of the condensation process and is equivalent to the concentration of ammonium ions available for combination with nitrate after all available sulfate has been converted to $(NH_4)_2SO_4$ (*aq* or *s*). The maximum condensation rate was assumed for each value between 0 and 1 of α. Particles were assumed to be produced at the Ports of Long Beach and Los Angeles; the average wind speed (2.2 meters per second) and distance between ports and the sampling site used by Yandell et al. 2009 (4.5 miles) were used to determine a transport time of 3300 seconds[12]; for simplicity, particle growth was modeled over one hour.

In order to satisfy the parameterization of particle growth described above, particles were assumed to have high water content and be internally mixed. The concentration gradient, $c_\infty-c_s$, was assumed to be equal to $[HNO_3]_p= [NH_4^+]_{left}$ where $[NH_4^+]_{left} = [NH_4^+]_{total} - 2x[SO_4^{2-}]$. The ammonium and sulfate ion concentrations measured by Hughes et al. 2000 were used to define this value[11].

For simplicity, particles were assumed to follow log normal distributions among different size modes. Particles produced in the port region were treated as particles emitted by ships. Filter measurements taken onboard a cruising ship by Murphy et al. 2009 suggested a mode in particle mass concentrations between 100-180nm, corresponding to a number concentration peaking below 100nm, and measured a somewhat bimodal distribution with modes near 60 and 90nm with a differential mobility analyzer (DMA) passing through a ship plume[17]. Petzold et al. 2008 observed similar bimodality with a DMA at 15 and 50nm, but showed that this bimodality was dependent on engine load such that below 75% load, the nucleation mode was diminished while the larger mode was only minimally influenced. For the purposes of our study, we assume nucleation and condensation mode distributions analogous to those measured by Petzold et al. 2008[18]. As real size distributions are not precisely lognormal, the widths of our lognormal distributions, σ_g, are assumed to be 1.7 and 1.5 with total number concentrations of 2500 and 1000 for the nucleation and condensation modes, respectively. Accumulation and coarse mode particles are neglected in model simulations, as Petzold et al. 2008 did not observe particles below 250nm[18]. Variation of these parameters would result in slowed or hastened growth of particle distributions under the condensation model; parameters were duplicated in each simulation to limit the variables under investigation.

RESULTS

Figure 1 displays the growth of the polydisperse aerosol distribution over one hour from its starting distribution parameters with changing α. The mass accommodation coefficient is defined as the number of molecules entering the liquid phase divided by the number of collisions with the surface. The value of α varies between 0 and 1; that is, a vapor molecule can stick at the surface of a particle after every collision, after no collision, or anywhere in between. Mass accommodation coefficients cannot easily be measured directly and are generally inferred from experimental determination of an uptake coefficient, γ. The uptake coefficient is related to the flux, J, of condensing gas to a particle by

$$J=0.25 \cdot c(\infty) \cdot \hat{c} \cdot \gamma$$

where $c(\infty)$ is the concentration of gas in air and $\hat{c}$ is expressive of the kinetic collision rate per unit of particle surface area, which is readily approachable in the laboratory. γ can also be expressed with terms accounting for mass accommodation, gas-phase diffusion, interfacial transport, and aqueous diffusion, all of which limit uptake of materials at particle surfaces[13].

Mass accommodation coefficients have been investigated in great detail for water vapor uptake by water due in part to the relevance of this process in cloud formation[19]; multiple sources report a mass accommodation coefficient value of 0.15 for uptake of nitric acid by water at 273K [19,23]. Using a range of values for α (α=0.01, 0.05, 0.15, 0.25, 1.00), it is apparent from Figure 1 that both the nucleation and condensation modes shift to higher modes at faster rates with increasing α. Each mode was observed to grow

Table 1. Summary of nucleation and condensation mode shifts with increasing sticking probability.

Nucleation Mode		Condensation Mode	
α	Mode (nm)	α	Mode (nm)
0.01	14	0.01	48
0.05	23	0.05	71
0.15	45	0.15	125
0.25	66	0.25	172
1.00	168	1.00	340
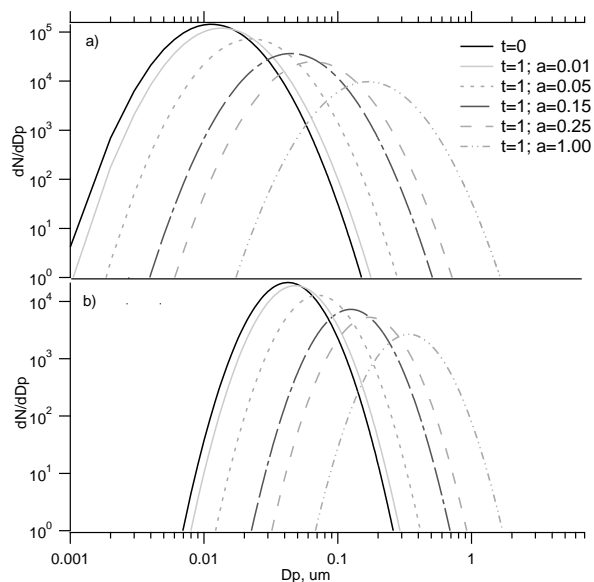
Figure 1. Changes in the size distribution mode, D_{pg}, over time with increasing α for a) nucleation and b) condensation modes. Above, t=time and a=α.

separately; for simplicity, the entire distributions were made to shift and the widths to remain constant, though realistically over time the multi-modal distribution might be expected to become more monodisperse with a change in both mode and distribution width. Assuming a constant nitric acid concentration of 2E10 molecules·cm^{-3}, the size distribution of the nucleation mode was observed to shift from a starting mode of 0.015μm to a maximum value of 0.168μm with a unity mass accommodation coefficient. The condensation mode shifted from its starting value of 0.050μm to a maximum value of 0.340μm. Size distribution mode shifts are summarized in Table 1. The condensation mode increased by a factor of 6.8 with a unity mass accommodation coefficient, while the nucleation mode increased by a factor of 11.2, demonstrating that smaller particles are more susceptible to condensation processes than larger particles. This follows from the larger surface area to volume ratios of the smallest particles.

Comparison of the modeled particle distributions and ambient particle size distributions can provide insight into the effectiveness of the model and the chemical and physical processes impacting particle growth. Particle size distributions measured with a scanning mobility particle sizer (SMPS) correspond to electrical mobility diameters rather than the aerodynamic diameters (D_{va}) utilized in this study. Electrical mobility diameters measured in a recent study were converted to aerodynamic diameters according to the procedure and assumptions outlined by Reinard et al 2007 [20]. Size distributions indicate a unimodal distribution with a mode at 63.2nm D_{va} and a mean value of 176.nm D_{va}[12]. The values and unimodality observed are consistent with

size distributions measured previously in the Long Beach community[21]. Model results are not directly comparable to SMPS size distributions because the model did not account for nucleation, deposition, coagulation, or condensation processes with vapors other than nitric acid. Despite these exclusions, rough values may be comparable. Comparing the modeled size distribution modes obtained with different values of α to the SMPS mode of 63.2nm from Yandell et al. 2009 suggests that the mass accommodation coefficient for the polydisperse aerosol modeled is on the order of 10^{-1} and may be closest to 0.25. This is consistent with available literature values[3].

DISCUSSION

Several factors may affect the model's accuracy. Particles were assumed to have accumulated sulfate prior to the start of the model, however this may not be realistic in an urban coastal region where gases may be well-mixed such that particles are exposed to nitric acid prior to sulfuric acid, etc. The mechanism of particle condensation assumed, in which the formation of ammonium sulfate limits nitrate uptake ability, is widely accepted, but it is not the only mechanism for particulate nitrate formation. Pathak et al. 2009 observed highly acidic aqueous aerosol in Chinese cities with $[NH_4^+]/[SO_4^{2-}]$ ratios less than 1. The authors proposed that hydrolysis of N_2O_5 on particle surfaces under these conditions resulted in the high nitrate concentrations measured[22]. The same process may also contribute to nitrate formation in the Long Beach region, where many particles are observed to have high sulfate concentrations (implying high acidity) and relative humidity exceeds 80% on many summer days[12]. Thus, the model employed may not adequately model nitrate uptake by Long Beach particulate matter.

Mass accommodation values should increase with decreasing temperature[19]; at ambient temperature, 298K, we might expect α<0.15 for aqueous particles. The value of α determined through comparisons between model results and ambient particle size distributions seemingly contradicts this trend. Due to the many approximations used in the model and the neglecting of processes such as coagulation and the condensation of gases other than nitric acid, it is likely that little quantitative value beyond the order of magnitude for α can be taken from the model. The temperature dependence of α will thus not be discussed further.

Solubility constraints at particle surfaces reflective of entropic and surface tension effects may also impact the value of the mass accommodation coefficient. Solubility constraints in a real droplet may result in the determination of a value of α that is lower than an experimentally determined value which avoids buildup of materials at the surface through reactive sinks or water cycling[19]. Alternatively, the presence of some dissolved species might enhance the solubility of a condensate into

the particle, leading to a larger value of α. The Henry's Law constant for nitric acid is very high at 2×10^{-6} mol·kg^{-1}·bar^{-1}; thus, solubility constraints may be less important for nitric acid condensation than for the condensation of other species with more limited solubility. The precise aqueous character of Long Beach aerosol is unknown: if water content is lower than expected, species may exist in a saturated solution that would be reluctant to take up further material. The physical structure of the particle may also be a limiting factor for nitric acid condensation. Freshly emitted particles, particularly soot particles, may be fractal in nature rather than spherical[24], potentially enhancing surface area for heterogeneous reactions and providing different mechanism for uptake of secondary species. Particles rich in vanadium and nickel may have similar effects. The sequestering of water in certain regions of the particle may also affect surface area and water available to uptake nitric acid. A more thorough investigation of these physical and chemical effects is necessary to improve the approximation of α.

Considerations for future model inputs include modeling the growth of specific size bins rather than a lognormal distribution to minimize assumptions made by the model's designers and improve its accuracy. Real size information could be obtained by measuring particle size distributions with SMPS or other methods at the start of the model trajectory; analogous measurements at the trajectory endpoint would enable verification of model results and a more refined determination of the mass accommodation coefficient for the polydisperse aerosol of interest.

CONCLUSION

A simple condensation model was applied to model the shift in lognormal size distribution mode over a five mile, one hour trajectory. Starting particle distributions were inferred from measurements taken aboard cruising ships. Particles were assumed to be polydisperse, have high water content, and to not participate in other atmospheric processes. The mass accommodation coefficient was varied between 0 and 1; the maximum growth of nucleation and condensation mode distributions was observed to be by factors of 11.2 and 6.8, respectively. Comparisons with SMPS size distributions taken at the trajectory's endpoint indicate that the average α for the polydisperse aerosol population may be close to 0.25.

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