Closure between aerosol particles and cloud condensation nuclei at Kaashidhoo Climate Observatory

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Abstract. Predicting the cloud condensation nuclei (CCN) supersaturation spectrum from aerosol properties is a fairly straightforward matter, as long as those properties are simple. During the Indian Ocean Experiment we measured CCN spectra, size-resolved aerosol chemical composition, and aerosol number distributions and attempted to reconcile them using a modified form of Köhler theory. We obtained general agreement between our measured and modeled CCN spectra. However, the agreement was not as good during a time period when organic carbon comprised a quarter of the total mass of the aerosol in the submicron size range. The modeled concentrations overpredict those actually measured during that time period. This suggests that some component, presumably organic material, can inhibit the uptake of water by the electrolytic fraction of the mass.

1. Introduction

There is no doubt that aerosol particles exert an influence on Earth's climate through their ability to nucleate cloud droplets, but the magnitude of that effect is difficult to ascertain because of the complex linkage between the atmospheric aerosol and cloud droplet concentration. These two parameters are connected through the physical and chemical properties of the aerosol particles and updraft speed during cloud activation. The added complexities of entrainment of dry air into the cloud and turbulence can usually be neglected if the cloud condensation nuclei (CCN) spectrum, which specifies the number of particles which will activate as a function of supersaturation, is taken as the link between the aerosol number distribution and the initial cloud droplet concentration. To predict cloud droplet concentration from an aerosol number distribution, the intertwined relationships of applied supersaturation, particle chemistry, and particle size must be untangled.

The supersaturation at which an aerosol particle will activate, commonly known as the critical supersaturation, can be derived from equations describing the enhanced vapor pressure over a curved surface (the Kelvin effect) and the reduced vapor pressure due to the presence of solute in the

droplet (the Raoult effect). The relationship, first derived by *Köhler* [1936], can be written as

$$S_c = \frac{n_w}{n_w + i n_s} \exp\left(\frac{4\sigma \upsilon_l}{D_p R T}\right), \tag{1}$$

where S_c is the supersaturation at which an aerosol particle will act as a CCN, i is the van't Hoff factor which specifies approximately how electrolytes dissociate in solution, n_s is the number of moles of solute in the particle, n_w is the number of moles of water, σ is the surface tension of the solution, υ_l is the molar volume of the solution, D_p is the particle's dry diameter, R is the gas constant, and T is the temperature.

Inspection of equation (1) shows that there are three ways a chemical compound in a particle of a given diameter can affect S_c. It may be insoluble or only sparingly soluble, and, of course, the van't Hoff factor and molecular weight vary from compound to compound. The surface tension of the solution also affects S_c; insoluble substances, which are partitioned selectively to the surface, can have a significant effect. The molar volume of the solution can also vary with chemical composition.

Köhler's original theory was formulated for particles which contained only one electrolyte, and it has been verified for such situations [*Gerber et al.*, 1977]. Aerosol particles in the atmosphere contain insoluble, sparingly soluble, and surface active chemical compounds as well as soluble gases. A substantial amount of theoretical work in recent years has been devoted to adapting Köhler theory to these situations [e.g., *Laaksonen et al.*, 1998; *Gorbunov et al.*, 1998; *Shulman et al.*, 1996]. In addition to the thermodynamics, which Köhler theory treats, there are kinetic processes which may affect the activation of aerosol particles. Compounds which preferentially partition to the surface may inhibit the transfer of water from the vapor to the liquid phase. In this case, a particle may not activate in a cloud or measurement device if the duration of the applied supersaturation is not sufficient for the particle to achieve equilibrium with the vapor field.

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2. Background

Attempts to reconcile measured CCN spectra and spectra predicted from Köhler theory have shown mixed results. *Liu et al.* [1996] report agreement between the two for a site in Nova Scotia which was frequently influenced by anthropogenic sources. CCN spectra were modeled using measured aerosol distributions and chemical composition derived from one-stage filter samples. The chemical analysis included SO_4^{2-}, Na^+, Cl^-, NH_4^+, and NO_3^- as well as organic carbon. CCN spectra were derived from these measurements using Köhler theory under the assumption that the soluble fraction in the accumulation mode was the measured $(NH_4)_2SO_4$. The organic carbon was not considered since it was a small fraction of the total mass. CCN active at 0.4% supersaturation were measured with a DH Associates M1 static diffusion cloud chamber, and those active at 0.06% were measured with an isothermal haze chamber. Both CCN counters were calibrated prior to the experiment with monodisperse aerosol particles of known composition. Because of the relatively large lower limit for the aerosol number distributions, 0.135 μm, a direct comparison between modeled and measured CCN spectra was possible only at a supersaturation of 0.06%. The authors report agreement for nine cases, marginal agreement for one, and poor agreement in two cases. In the instances of marginal or poor agreement, the modeled CCN concentration was higher than the measured concentration in two of the three cases.

Chuang et al. [2000] did not achieve closure between measured and modeled CCN spectra during flights in the vicinity of Tenerife, Spain, during the Second Aerosol Characterization Experiment. In that case, the modeled CCN spectra were based on measured aerosol number distributions for particles with diameters between five nm and three μm. Information on the aerosol chemical composition was obtained from fine (D_p<1 μm) and coarse (D_p>1 μm) filter measurements made on Tenerife. Filters were analyzed for SO_4^{2-}, Na^+, Cl^-, NH_4^+, organic carbon, and elemental carbon. Measurements of CCN concentration at a supersaturation of 0.1% were made with the Caltech spectrometer. A regression of data from six flights resulted in the relationship, $N_{ccn, \text{ measured}} = (N_{ccn, \text{ predicted}})^{0.72}$. The predicted CCN concentrations were, on average, a factor of 2.2 higher than the measured concentrations.

Covert et al. [1998] took a slightly different approach, calculating CCN spectra from aerosol number distributions and measured hygroscopic growth factors. The growth factor is a measure of how much hygroscopic material is present in a near monodisperse portion of the aerosol number distribution, and it can be used to derive the supersaturation at which those particles will activate. This derived critical supersaturation includes the effects of soluble and insoluble mass, an effective van't Hoff factor, and the surface tension. When CCN spectra derived in this way were compared to measured CCN concentrations, the two measurements agreed within their respective errors. However, the authors concluded that closure was not reached because the direction of the disagreement was not randomly distributed. The modeled CCN concentrations were consistently 20% higher than measured concentrations.

The disparity between modeled and measured CCN spectra is almost always an overprediction: the modeled concentrations of CCN are greater than those actually measured. This systematic error indicates that there is an incomplete understanding of the activation process.

3. Experimental Setup and Data Analysis

All measurements were conducted at Kaashidhoo Climate Observatory (KCO, 4.97°N, 73.47°E) in February and March of 1999 as part of the Indian Ocean Experiment (INDOEX) intensive field phase.

3.1. Submicron Chemical Composition

A transportable aerosol time-of-flight mass spectrometer (ATOFMS) was used to obtain real-time information on the aerodynamic size and chemical composition of individual aerosol particles. Details on the function of the transportable ATOFMS instrument used in the study can be found elsewhere [*Gard et al.*, 1997]. Briefly, particles from a polydisperse aerosol are sampled directly from the ambient atmosphere through a converging nozzle. The particles are accelerated to a terminal velocity that depends on the corresponding particle aerodynamic diameter. In order to obtain the particle aerodynamic diameter from the measured particle velocity, the transportable ATOFMS is calibrated using polystyrene latex spheres (PSL, Interfacial Dynamics Corporation) of known aerodynamic diameter. After being sized, particles travel into the ion source region of a dual ion time-of-flight mass spectrometer where molecules from the particles are laser desorbed and ionized, generating ions from which chemical information can be obtained. ATOFMS provides both the positive and negative ion mass spectra for each particle.

Particles in the 0.2 to 2.5 μm aerodynamic diameter size range were classified according to the mass spectral data. A distinct break at 1.0 μm exists in the types of particles detected during the study. Below 1.0 μm, particles are composed primarily of organic species and/or elemental carbon (some of them containing potassium). In contrast, above 1.0 μm, particles are classified mostly as dust and sea salt. Sulfates are present in both submicron and supermicron particles. Positive and negative ion mass spectra of individual particles were then used to further classify the particles, taking into consideration degrees of association of different species.

Over the period February 11-26, samples for airborne particle size and chemical composition determination were collected using four microorifice uniform deposit cascade impactors (MOUDIs[*Marple et al.*, 1991]). The samplers were operated outdoors at ambient temperature and relative humidity conditions over consecutive 2-day periods. Each impactor was preceded by an AIHL cyclone separator [*John and Reischl*, 1980] designed to remove particles larger than 1.8 μm aerodynamic diameter in order to suppress particle bounce within the impactors. Particles subsequently were collected in six size ranges that span the range 1.8 to 0.056 μm particle aerodynamic diameter. In the present paper, only the data from the lowest five stages of the impactors are used, which covers the particle size range from 0.056 to 1.0 μm aerodynamic diameter. Two of the impactors were operated with Teflon impaction substrates that were analyzed for gravimetric mass, for sulfate, nitrate, and chloride by ion chromatography [*Mulik et al.*, 1976], for ammonium ion by colorimetry [*Bolleter et al.*, 1961], and for trace elements by instrumental neutron activation analysis [*Olmez*, 1989]. The samples collected on prebaked aluminum foil substrates were analyzed for elemental (black) carbon and organic carbon by the thermal-optical method of *Huntzicker et al.* [1982] as modified by *Birch and Cary* [1996] and as adapted to analysis of cascade impactor

samples by *Kleeman et al.* [1999]. Organic carbon concentrations were converted to an estimate of the mass of organic compounds present by scaling the organic carbon values upward by a factor of 1.4 in order to account for the H, O, S, and N present in organic compounds. Samples were frozen immediately after they were taken and until subsequent analysis, and all gravimetric mass determinations were made at a controlled temperature and low relative humidity (21.0 +/- 0.2 ° C; 39+/- 3% RH). A more detailed description of these experiments is presented by *Chowdhury et al.* [this issue].

3.2. CCN Spectra and Aerosol Number Distributions

CCN spectra and aerosol number distributions were sampled through the observatory aerosol manifold. The manifold consists of a 10 m high, 13 cm ID pipe through which air was drawn at a nominal flow rate of 200 liters per minute (Lpm). Sample air for individual experiments was drawn from the primary manifold flow inside the observatory. Sample air for the CCN spectra and aerosol number distributions was pulled through a 6 inch ID PVC pipe for approximately 3.3 m. The sample flow to the instruments of approximately 1.5 Lpm was drawn off the center line of the PVC tubing. The excess flow was vented out of the building. Calculated particle losses by diffusion, sedimentation, and impaction were negligible, and the data are not corrected for them.

Aerosol number distributions for particles with diameters between 20 and 600 nm were measured with a TSI (Minneapolis, Minnesota) Scanning Mobility Particle Sizer or SMPS. The Differential Mobility Analyzer within the SMPS system was operated at a 10:1 ratio between sheath and sample flows. The sheath air was dried with molecular sieve, which was changed twice daily. Number distributions were collected with a time resolution of 5 min. The SMPS system used in conjunction with the CCN measurements was set up in a manner identical to the one used for collecting the ambient number distributions with the exception of the scan times. To achieve adequate resolution in the supersaturation, distributions were sampled at a time resolution of 3 min.

The essential elements of the CCN spectrometer are a large, flow-through parallel plate thermal diffusion chamber, called the CCN Remover (CCNR), operated in series with an SMPS [*Ji et al.*, 1998]. The aerosol sample which passes through the CCNR has a residence time of approximately 1 min, which gives particles which activate time to fall out of the sample

stream. The remaining aerosol particles are counted and sized by the SMPS. Aerosol distributions (typically four to five) measured with a supersaturation of zero in the CCNR are averaged and defined as the reference *R*. Distributions measured with a temperature difference across the chamber experience some degree of supersaturation, and are defined as *D(S)*. The CCN spectrum is given by

$$CCN(S) = R - D(S). \qquad (2)$$

CCN concentrations for supersaturations below 0.1% are only qualitative since soluble particles larger than approximately 150 nm can be removed as haze droplets in the CCNR.

3.3. Calculation of CCN Spectra

The CCN supersaturation spectrum is simply the cumulative number of aerosol particles which will activate at a given supersaturation. This quantity can be easily calculated from the aerosol number distribution if the relationship between a particle's size and its critical supersaturation, S_c, is known. In theory, S_c can be calculated directly from the particles' chemical composition. However, this is generally not practical for particles of mixed composition, especially if organic material is present. Many organic compounds found in the atmosphere have not even been identified [*Yu*, 2000]; the physical properties needed to include these substances into the Köhler equation (equation (1)) are not known. Here we use a simplified definition which avoids these difficulties [*Hoppel et al.*, 1996]:

$$S_c = \frac{K}{\sqrt{\varepsilon}} \left(\frac{2}{D_p} \right)^{3/2}, \qquad (3)$$

where *K* is an amalgam of constants from equation (1) that can be calculated for a particular compound ($K = 1.71 \times 10^{-11}$ cm$^{3/2}$ for $(NH_4)_2SO_4$) and ε is the aerosol soluble fraction. The soluble fraction, which we calculate for each impactor stage, is defined as

$$\varepsilon = \frac{\text{mass of } SO_4^{2-} + NH_3^+ + NO_3^-}{\text{total mass}}. \qquad (4)$$

Table 1. Dry Diameters, Soluble Fractions and Critical Supersaturations Derived From the Measured Size-Segregated Chemical Composition of the Aerosol Particles[a]

Day of Year 49.56-51.47	D_p(Dry), μm	ε	S_c%	DOY 51.54-53.49 D_p (Dry)	ε	S_c	DOY 53.56-55.50 D_p (Dry)	ε	S_c
D_p(ambient)=0.44	0.350	0.244	0.05	0.328	0.386	0.04	0.320	0.453	0.04
D_p(ambient)=0.24	0.177	0.428	0.10	0.175	0.453	0.09	0.182	0.362	0.10
D_p(ambient)=0.13	0.098	0.388	0.24	0.097	0.391	0.25	0.103	0.266	0.27
D_p(ambient)=0.07	0.051	0.480	0.58	0.055	0.286	0.68	0.059	0.169	0.79
D_p(ambient)=0.04	0.034	0.163	1.84	0.039	-0.220	0.87	0.033	0.236	1.60

[a] These were used to calculate the CCN spectra shown in Figure 3 with the open triangles.

As described above, aerosol particles deposited on the impactor stages were hydrated because they were sampled at ambient relative humidity, which was near 80% at KCO. Sample air for the aerosol number distributions (see section 3.2) was dried to a relative humidity of 20% or less. To enable comparison between the two measurements, the water associated with particles on each impactor stage was calculated based on the amount of sulfate and ammonium in the measured dry mass. Using activity data from *Tang* [1996] and *Tang and Munkelwitz* [1994], this value was then used to derive the dry diameter corresponding to the lower size cut for each impactor stage.

Table 1 lists the dry lower size cut, soluble fraction, and corresponding S_c for the impactor stages for February 19-24. The lower size cut is used because it corresponds to the highest S_c for that impactor stage, which is the relevant quantity when plotting a cumulative CCN spectrum. The negative value for the soluble fraction for the smallest size range is the consequence of a very small mass loading for that particular stage on that day. We have used $\varepsilon=0.50$ in calculating S_c for that time period. The large errors bars for that data point (see Figure 3) reflect our uncertainty in the true value of the soluble fraction for that day.

4. Results and Discussion

4.1. Time Series

The time series of CCN concentrations at supersaturations of 0.3% and 0.5% and the integrated particle concentrations derived from SMPS measurements are plotted in Figure 1. The time series for SO_4^{2-}, NH_4^+, elemental carbon, and organic material are shown in Figure 2. Note that the timescales for the two plots are different; February is the only time period for which we have detailed measurements of aerosol chemical composition at KCO. (For a more complete discussion of the aerosol particle chemical composition at KCO, see *Chowdhury et al.* [this issue] and S. R. Guazzotti et al. (unpublished manuscript, 2001)). The number concentrations of CCN and aerosol particles were relatively high throughout the experiment, with the exception of a 3 day period in February and a 2 day period in March. The high concentrations, both in number and mass, reflect the polluted condition of the northern Indian Ocean and Arabian Sea during the northeast monsoon [*Cantrell et al.*, 2000; *Meywerk and Ramanathan*, 1999; *Jayaraman et al.*, 1998; *Rhoads et al.*, 1997].

The pronounced trends in number, and mass from February 19 to 24 provide an excellent opportunity to test the closure between CCN spectra and aerosol physical and chemical properties. Back trajectories indicate that the origin of the air mass changed from the Arabian Sea/western Indian coast to one more influenced by the Bay of Bengal and the eastern seaboard of India [*HYSPLIT4*, 1997]. A change in air mass implies a different aerosol chemical composition, giving us another test of aerosol-CCN closure.

4.2. Closure Between Measured and Calculated CCN Spectra

Measured and calculated CCN spectra from February 19, 21, and 23 are shown in Figure 3. On February 19 the concentration of CCN was relatively high, and most of the particles were relatively large, which can be seen in the number distributions (shown in Figure 4) and in the shape of the CCN
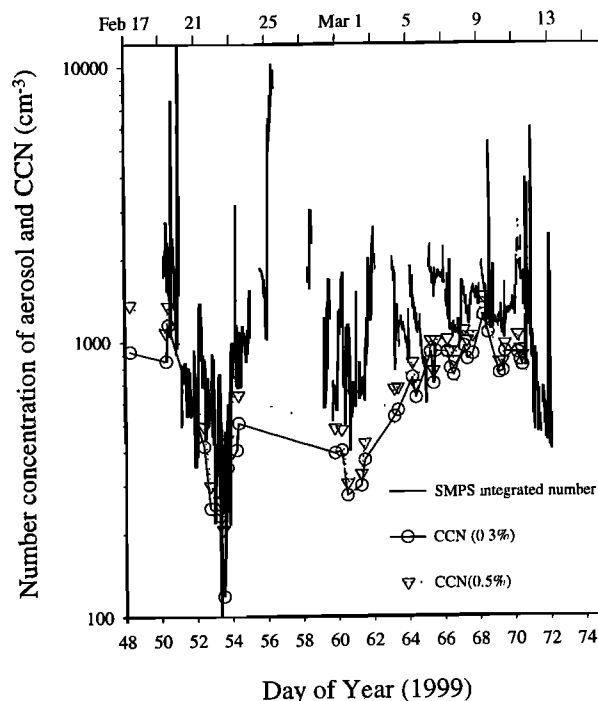

Figure 1. Time series of integrated number concentrations from the SMPS and CCN at two supersaturations.

spectrum (half of the particles activate at a supersaturation less than 0.15%). By February 21, the concentration of CCN had dropped by about a factor of 5, and the number distributions were distinctly bimodal, suggesting that the aerosol particles had been through at least one non-precipitating cloud cycle [*Hoppel et al*, 1994]. The concentration of CCN had risen again by February 23, and the number distributions had reverted to a monomodal character.

The measured CCN spectra for each day are shown with two calculated spectra. We calculate an upper limit to the CCN spectra, using the reference size distribution R and an assumed chemical composition of pure ammonium sulfate to convert particle diameter to critical supersaturation (i.e., equation (3) with $\varepsilon=1$ and $K_{(NH4)2SO4}$). The substantial discrepancy between the measured spectra and the spectra calculated from the distribution of idealized aerosol particles indicates the presence of some other substance in the aerosol particles which is either insoluble (i.e., not contributing to the Raoult term in equation (1)) or which inhibits the transfer of water from the vapor to the liquid phase by forming a film at the particles' surface.

We also calculate the CCN spectra based on the measured chemical composition and aerosol number distributions. We calculate ε for each impactor stage from equation (4), then use this value to determine S_c from equation (3). We use $K_{(NH4)2SO4}$ because nearly all of the ionic material in the submicron size range at KCO is either SO_4^{2-} or NH_4^+. The number concentrations are taken from ambient number distributions. We have assumed that particles deposited on separate impactor stages are internally mixed, which means that each impactor stage can be characterized by a single value of ε. We justify this assumption from measurements made with the ATOFMS. The single particle data show that sulfate aerosols with aerodynamic diameters between 0.2 and 2.5 µm consist exclusively
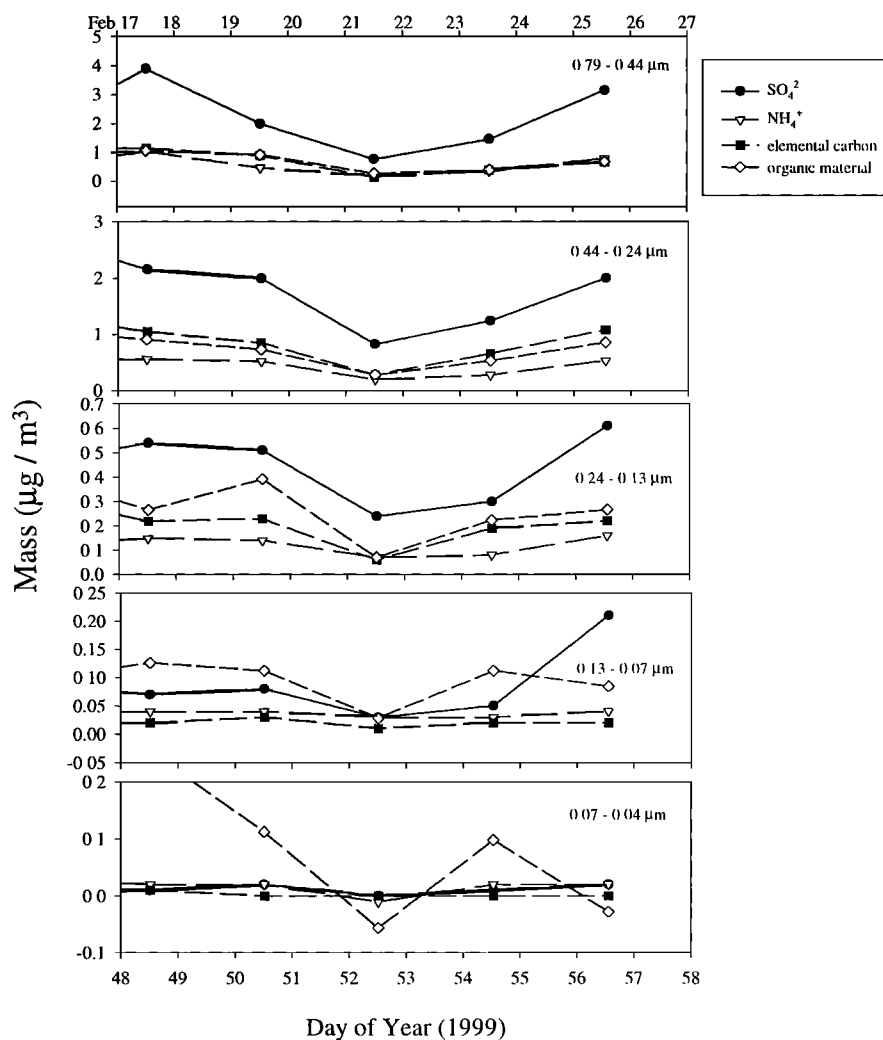
Figure 2. Time series of aerosol chemical composition.

of sulfates associated with sea salt, dust, elemental carbon, or organic matter. No single particles consisting of pure sulfuric acid, ammonium sulfate, or sodium sulfate were detected over the specified size range during the field study.

Figure 3 shows that the CCN spectra calculated on the basis of measured aerosol number distributions and measured, size-segregated chemical composition generally agree with the measured spectra for all three days. On February 19 the modeled spectrum is conspicuously greater than the measured one at the supersaturation of 0.6%. The agreement improves as the concentration decreases on February 20, but does not degrade as the concentration rises again on February 23. We conclude that the activity of the electrolytic mass fraction can be used to predict aerosol particles' activation characteristics for this data set with the caveat that modeled CCN concentrations noticeably overpredict the measured concentrations for February 19.

It is significant that the modeled CCN spectra on February 19 overpredict the measured spectra. We can conclude that the nonelectrolytic mass on that day is not simply inert. Some component of the aerosol particles is evidently inhibiting the uptake of water by the electrolytes. A likely component is the organic compounds. Elemental carbon is largely inert. It contributes to a particle's size, which affects the Kelvin term

in the Köhler equation, but it has little effect on surface tension; neither does it dissolve into solution. Mineral dust and fly ash can also be excluded by the same reasoning.

Figure 5 is a plot of the ratio of organic material to dry mass for February 19-25. The percentage of organic material decreases as the total mass concentration decreases. During the clean period on February 21 and 22, organic compounds comprised only 10 to 15% of the total particle mass, down from near 40% on February 19. When number and mass concentrations increased again on February 23, the fraction of organic material increased, but only to 15-20%. Single-particle analysis, shown in Figure 6, also shows that the concentration of particles which contained both sulfate and organic material peaked early in the day on February 20 and declined significantly to a minimum on February 21 and 22. We do not currently have detailed molecular information on the organic component of the mass so we can only speculate that the changing organic fraction influenced the aerosol particles' activation characteristics.

Saxena et al. [1995] found that organic species in an urban airshed seemed to inhibit uptake of water by electrolytes. They attributed this to a film coating the particles' surface or to thermodynamic effects, wherein the electrolytes and organic species form a complex matrix, the properties of which are
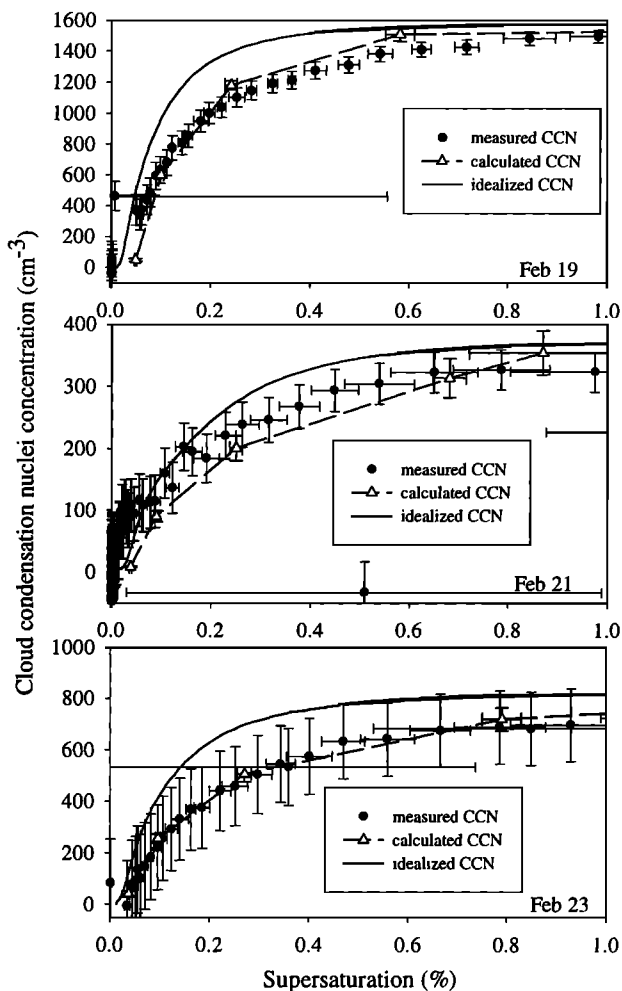
Figure 3. Measured CCN spectra shown with calculated CCN spectra. The solid black lines provide an upper limit to the CCN spectra based on idealized aerosol particles of pure ammonium sulfate. The open triangles are calculated from measured, size-segregated chemical composition and measured aerosol number distributions.

Figure 4. Ambient aerosol number distributions collected concurrent with the CCN spectra in Figure 3.

[*Shaw and Lamb*, 2000], the aerosol particles fell out of the sample stream when exposed to the critical supersaturation for that particular size and soluble fraction (i.e., they were counted as CCN since they were removed). We systematically decreased the water accommodation coefficient, simulating the effect of a hydrophobic film on the particles' surface, until the particles just traversed the CCN Remover's chamber, meaning they would not be counted as CCN. The critical value of the water accommodation coefficient was 10^{-4}. Any larger coefficient resulted in the particles being counted as CCN, any smaller and they are not. If the discrepancy between the measured CCN spectra and the CCN spectra modeled on the basis of measured chemical composition and aerosol number distributions is the result of a kinetic process at the liq-

largely unknown. We cannot attribute our results to either one or the other as we have no way to determine particle morphology.

However, if the effect is kinetic, it implies a substantial reduction in the mass accommodation coefficient of water. In that case, the particles' critical supersaturation is unchanged, but by reducing the water accommodation coefficient, the time required for the particle to reach equilibrium with the vapor field is increased. Its growth rate is slowed. Since our CCN counter is sensitive to the particles' growth rate, this effect shows up as an apparently higher critical supersaturation. In other words, the particles have activated, but grow so slowly that they do not fall out of the sample stream, which is our criteria for aerosol particles which become CCN at an applied supersaturation. Using a model of the chamber [*Cantrell*, 1999] and the measured chemical characteristics of the aerosol particles, we can estimate how much the water accommodation coefficient would have to be decreased to explain our results from February 19. When the model was initialized with recently measured mass and thermal accommodation coefficients for water, 0.06 and 0.7, respectively
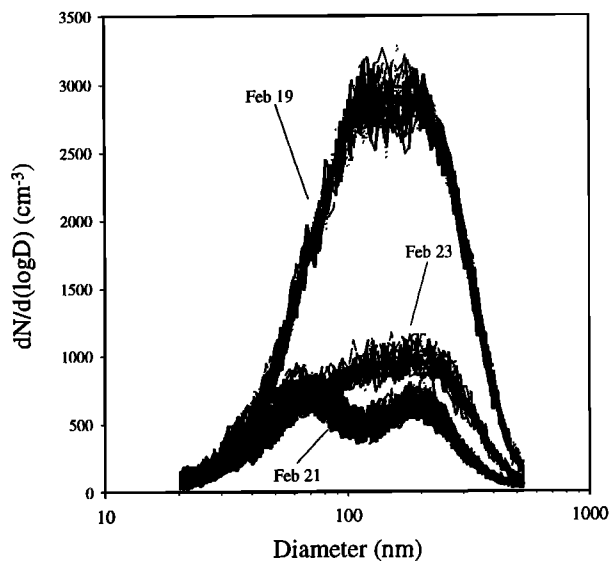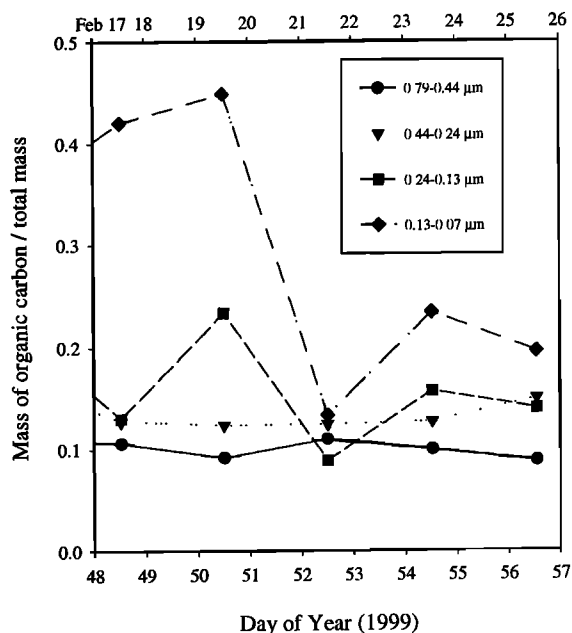

Figure 5. Time series of the ratio of the mass of organic compounds to total mass.
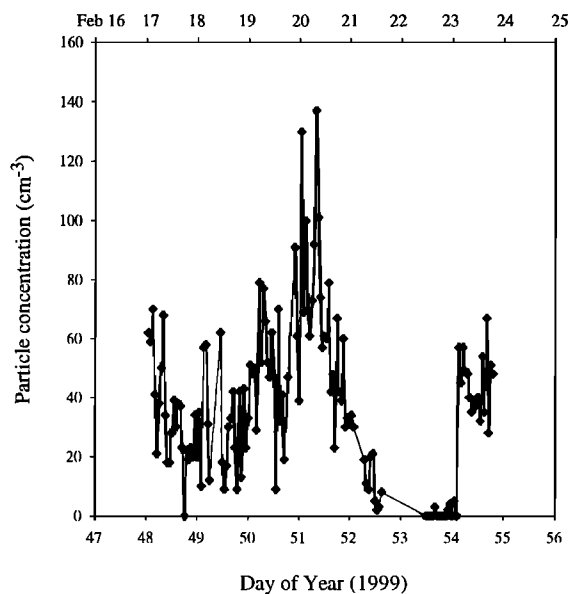
Figure 6. Temporal evolution of carbon containing particles with sulfates detected with the ATOFMS.

uid/vapor interface, the water accommodation coefficient would have to be reduced by 3 orders of magnitude.

5. Conclusions

In an experiment conducted on the island of Kaashidhoo during the Indian Ocean Experiment, we measured CCN supersaturation spectra, aerosol number distributions, and size-segregated chemical composition of the aerosol particles. Consistently high concentrations in all three parameters indicated the generally polluted condition of the northern Indian Ocean during the northeast monsoon.

We were able to achieve closure between measured CCN spectra and the CCN spectra calculated on the basis of measured aerosol number distributions and a soluble fraction derived from measured chemical composition. For eight of the 10 cases the agreement between calculated and measured CCN spectra was good. In the two cases where the agreement was not as good (February 19), modeled CCN spectra over-predicted the measured spectra, suggesting that some portion of the aerosol mass is inhibiting the uptake of water by the electrolytes. We surmise that this is due to organic material internally mixed with the electrolytic compounds. The organic material could inhibit the electrolytes' uptake of water through two competing, though not mutually exclusive mechanisms. It could form a film at the particle's surface, impeding the transfer of vapor to the liquid phase, or it could form a complex matrix with the electrolytic mass, which might have properties such that the water activity could be substantially lower. We cannot discriminate between the two mechanisms on the basis of our data.

However, if the process is kinetic (i.e., the film hypothesis), we can place a limit on how much the water accommodation coefficient would decrease. On the basis of the measured fraction of electrolytic mass and the residence time required for a particle of a particular size and chemical composition to fall out of our CCN measurement device (if a particle falls out of the chamber, it is counted as a CCN), we estimate that the

water accommodation coefficient would have to be reduced from 0.06 to approximately 10^{-4}.

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