

Calculating CCN Activity of Ambient ATOFMS Measurements During a Period of Changing Meteorological Conditions

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Aerosols have both direct and indirect effects on climate. The direct effect is characterized by a particle's ability to scatter and absorb radiation. These particles can also nucleate cloud droplets. Once activated, these cloud condensation nuclei (CCN) can go on to form clouds, which also scatter and absorb radiation (the indirect aerosol effect). Changing aerosol size and chemistry will affect CCN activity and cloud microphysical properties. Here we show that CCN activity can change dramatically in a short amount of time due to shifting winds and changing meteorological conditions. During a study in Riverside, CA in September of 2007, single particle dual polarity Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) measurements were made that showed three time periods where the aerosol chemistry was dominated by one particle type. A large increase in salt concentration was observed when the winds were coming from the west. Then, a sudden shift to winds from the east resulted in a large concentration of elemental carbon mixed with organic carbon (ECOC), followed closely by a rise in biomass burning particles. A Kohler theory model was used to estimate the number of particles likely to activate and a ratio of activated to total particles was calculated for particles assuming the dominant particle type made up all of the particles (CCN_{pure}) and including all of the particle types (CCN_{mixed}). These calculations suggest that the salt and ECOC periods' CCN activity agreed fairly well with $CCN_{\text{mixed}}/CCN_{\text{pure}}$ of 1.00 and 0.998, respectively. The biomass period however had less agreement with $CCN_{\text{mixed}}/CCN_{\text{pure}}$ of 0.988. Our results show that local CCN activity is highly variable on a short time scale and that the dominant particle type can be used to predict CCN activity if it is 50 percent or more of the total particles.

Introduction

Clouds play an important role in the radiative balance of the Earth. Depending on cloud droplet properties, clouds can scatter or absorb solar, IR and microwave radiation resulting in a warming or cooling of the Earth's surface. Cloud droplets form on aerosols, which when activated are known as cloud condensation nuclei (CCN). The ability of a particle to serve as a CCN is based on its water solubility, chemical composition, and size, as described by the Kohler theory [Kohler, 1936]. Kohler theory models give a good approximation of the critical supersaturation necessary for a particle to activate or take up water. Aerosol chemistry and concentration vary greatly spatially and temporally, which complicate predictions of CCN activity. CCN predictions can be simplified if we can make assumptions about CCN using only the dominant particle type. The dominant particle type in a given location can change dramatically in a short amount of time due to changing meteorological conditions, thus changing the number of CCN active particles.

ATOFMS [Gard et al., 1997] has been used to measure aerosol distributions in real time. Two scattering

laser beams are used to estimate particle size utilizing the Time-of-Flight technique [Gard et al., 1997] and a Nd-YAG laser is used to ionize the particle to measure the positive and negative ions present. It has been shown [Song et al., 1999, Ferguson et al., 2001] that positive ions can be used to determine the source of the aerosol, while the negative ions can be used to estimate the amount and type of atmospheric processing or aging that has occurred.

Methods

ATOFMS was used to measure ambient air during a September 2007 field study in Riverside, CA. Changes in wind direction caused anomalous increases in particle concentrations, with the dominant particles types changing rapidly. On September 4, 2007 Santa Ana winds brought salts, likely dry lake bed salt, in from the east. Then, on September 6, 2007 the winds came from the west and a large increase in ECOC concentration was observed, followed by an increase in biomass burning particles.

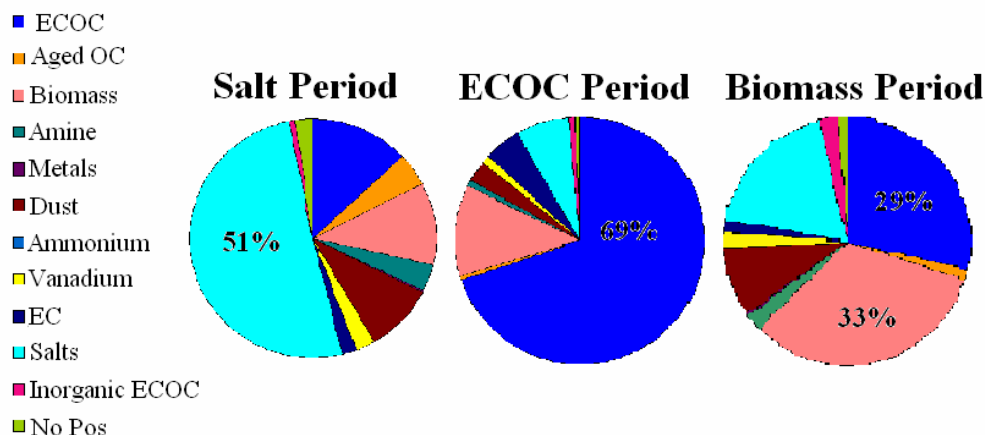


Figure 1. Relative Fraction of particle types for each time period: Salt, ECOC, and Biomass.

In this three day period, the dominant particle types changed rapidly, which according to Kohler Theory, [Kohler, 1936] would have significantly modified local CCN activity. The ATOFMS data was separated into three time periods based on the three distinct dominant particle types. Dividing the data in this way allowed an evaluation of the effects of chemical composition on CCN activity. In this study, a Kohler Theory model was used to predict an activated fraction of particles using the dominant fraction of particles as the only CCN source, which was termed CCN_{pure} , and using all of the particle types as CCN sources, termed CCN_{mixed} . The two predicted activated fractions from CCN_{pure} and CCN_{mixed} were compared to see if CCN activity can be predicted accurately using only the dominant particle type as the CCN source. This is an important question to answer because there are a lot of uncertainties in estimating aerosol indirect effects and model calculations can benefit from any simplifications that can be made. The indirect effect is characterized by aerosol influence on cloud formation and the resulting changes in radiative properties. In the submicron size range, CCN activity is influenced mostly by particle chemistry [Kohler, 1936]. Therefore, changing the chemistry of a particle will change the CCN activity and thus the type of cloud droplet that could form.

The CCN activity of the three main particle types in the study was calculated using a Kohler Theory Model developed by Gregory Roberts [Roberts et al., 2002]. The model predicts the number of particles that could activate at a given supersaturation based on chemical composition and size using equation 1 [Seinfeld and Pandis, 2006]:

$$\ln(p_w(D_p)/p^0) = (4M_w \sigma_w / RT \rho_w D_p) - (6n_s M_w / \pi \rho_w D_p^3) \quad (1)$$

Where M_w is the molecular weight of water, ρ_w is the density of water, D_p is the particle diameter, p^0 is the vapor pressure over a flat surface at a given temperature, n_s is moles of solute and σ_w is the surface tension of water.

	Salt	ECOC	Biomass
Density (g/cm ³)	2.165	1.9	1.618
Solubility (g/mL H ₂ O)	0.36	0.0052	infinite
van Hoff Factor	2	1	1
Molecular Weight (g/mol)	58.44	252	162.14
Geometric Mean Diameter (nm)	500	600	500

Table 1. Parameters used to initialize the Kohler Theory Model.

NaCl was chosen as the proxy for salt in the Kohler Theory calculations. Some of the salts observed in the study were composed of primarily sodium chloride, while others also contained calcium and magnesium. Santa Ana winds preceded the large increase in salt particles, which led to the assumption that the salts originated in dry lake beds. The sodium and chloride peaks dominated the spectra of these salts, which is why NaCl was assumed to be an accurate proxy in these calculations. Levoglucosan, a common biomass burning marker [Elias et al., 2001, Moreira dos Santos et al., 2002, Rosenørn et al., 2006, Simoneit, 2002, Simoneit and Elias, 2000, Simoneit et al., 1999] was chosen to represent the biomass burning particle types. Levoglucosan is observed in many different types of biomass burning aerosols and though it is not the only or dominant compound in biomass burning emissions, it gives a good approximation for the organics in this type of particle. Mixed Elemental Carbon and Organic Carbon (ECOC) were represented by assuming elemental

carbon was mixed with oxalic acid [Spencer and Prather, 2006]. Oxalic acid was chosen because it is an oxygenated acid and based on the mass spectra of the ECOC particles, most of these particles have undergone oxidation of some kind, making oxalic acid, an oxidized acid a good proxy for organic carbon.

Once particles reach supermicron sizes their CCN activity is dictated by their size, with only minimal solubility effects [Kohler, 1936]. For this reason only submicron particles were considered in this study. A size distribution was measured using the Time-of-Flight technique in the ATOFMS instrument. An adaptive resonance theory-based neural network (ART-2a) was used to group particles into clusters of similar mass-to-charge ratios and to assign sizes to particle clusters [Song et al., 1999]. Then, the clusters were manually classified and grouped according to chemical composition. Relative fractions were calculated by taking the number of particle counts for a given particle type divided by the total amount of particles. The geometric mean diameter

was calculated for each time period, salt, ECOC, and biomass. The geometric mean diameters were 500 nm, 600 nm, and 500 nm, respectively. The Kohler Theory model calculations were carried out at these calculated geometric mean diameters.

Results and Discussion

Using the Kohler Theory model, CCN activity was calculated for each time period at their respective geometric mean diameters and, as expected, the salt period had the highest activated fraction for all supersaturations, followed closely by the biomass period and finally the ECOC period. Activated fraction (CCN over total particles) was calculated for each period for the pure dominant particle type (CCN_{pure}) and for the mixed particle types (CCN_{mixed}). Figure 2 shows a comparison of $CCN_{\text{mixed}}/\text{total}$ particles and $CCN_{\text{pure}}/\text{total}$ particles for each time period.

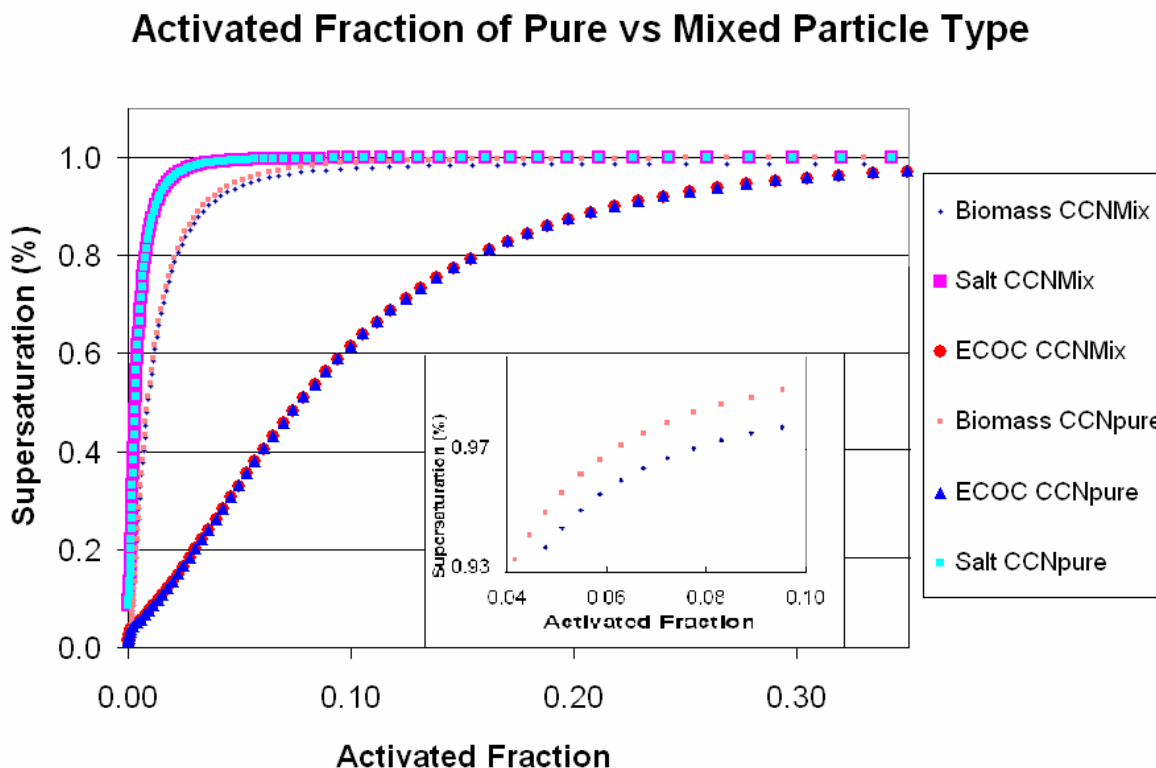


Figure 2. Activated fraction of pure and mixed particle types for each time period. The inset shows the difference between biomass CCN_{mixed} and CCN_{pure} .

For the Salt and ECOC periods, the pure and mixed CCN predictions were comparable (the lines are on top of each other). The biomass period was in good agreement, but there was some deviation from the pure estimations (see Figure 2 enlargement). The CCN

calculations which included all of the chemical species present in the time period (CCN_{mixed}) were comparable to the CCN calculations for the pure particle types (CCN_{pure}) in all cases (See Figure 2). Agreement between the mixed and pure activated fraction was very good for

the salt and ECOC periods with $CCN_{\text{mix}}/CCN_{\text{pure}}$ at 1.0 and 0.998, respectively. However, the biomass $CCN_{\text{mix}}/CCN_{\text{pure}}$ was slightly lower at 0.988 (See Figure 2 inset). The discrepancy in activated fraction is likely due to the fact that even though biomass was the dominant particle type for the time period it only made up 33 percent of the total particle counts (See Figure 1 for relative fraction of particles). The salt and ECOC time periods, on the other hand, were dominated by salt with 51 percent of total and ECOC with 69 percent of total, respectively. During the biomass period, ECOC was the second most abundant particle type, comprising 29 percent of the total particle count. The biomass CCN_{mixed} had a lower amount of activated particles than the biomass CCN_{pure} most likely due to the differences in solubilities between levoglucosan, the biomass proxy, and ECOC. The agreement between the two biomass activated fractions is still good and could possibly be explained by the degree of uncertainty in the calculations. A transmission bias on our instrument limits the size of particles we can analyze and we assume a spherical shape for all particles resulting in an inaccurate size distribution, which will alter the mean diameter used for the calculations. Using the same geometric diameter for CCN_{mix} and CCN_{pure} should help eliminate this as a major source of uncertainty. Another source of uncertainty is the choice of proxies. Changing the proxy will change the solubility of the particle and thus the CCN activity. The difference in calculated activated

fraction between CCN_{mix} and CCN_{pure} could become larger when different particle types are used, but from these observations it can be concluded that CCN activity can be accurately estimated using only the dominant particle type when that type comprises 50 percent or more of the total particle count. When the dominant particle type is less than 50 percent, the second most abundant particle type should be included to get more accurate CCN predictions.

Conclusion

A Kohler theory model was used to calculate activated fractions of particles for three time periods with distinct particle types. These calculations show that a dominant particle type is likely to control CCN activity in an air parcel when that dominant particle type is 50 percent or more of the total particle count. These predictions cannot be verified, as we do not have CCN data from this time period, and future work should include a comparison to measured CCN activated fraction.

These results could help simplify CCN predictions by allowing CCN calculations to be carried out using only properties related to the dominant particle type, if that dominant particle type is 50 percent or more of the total particles, instead of carrying out multiple calculations for each particle type present. Any simplifications that can be made to GCMs and other models will help in understanding and quantifying the aerosol indirect effect.

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