

Contributions of organic and sulfate components to CCN concentrations in a boreal forest

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The ability of atmospheric aerosols to nucleate cloud droplets is dependent on both the particle size and composition. Organic compounds significantly contribute to particle composition; thus, their ability to act as cloud condensation nuclei (CCN) is crucial for understanding cloud droplet formation. While the organic fraction can significantly alter the hygroscopicity of particles, the complexity of the organic composition makes quantifying the organic contribution to CCN activity difficult. Here we present measurements from Whistler, British Columbia (1020 masl) during May and June 2008 that were highly influenced by organic contributions from biogenic sources. Non-refractory organic mass and inorganic mass (*e.g.* sulfate, nitrate, ammonium) were measured with High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and organic functionality was quantified with Fourier Transform Infrared (FTIR) spectroscopy. Size distributions and CCN measurements were also made allowing for a Köhler theory CCN closure analysis to be performed for the one-month study. The highest agreement between modeled and measured CCN number concentrations, $CCN_{predicted}/CCN_{measured} = 0.95$ ($R=0.74$), was achieved when the organic fraction was considered insoluble. CCN activity is most sensitive to mean particle size for aerosols that contain less soluble material. Our results provide some constraints on the solubility of the oxygenated organic fraction of biogenically derived organic aerosols.

1. Introduction

Atmospheric particles influence climate by acting as cloud condensation nuclei (CCN) [Twomey, 1977; Albrecht, 1989]. Their ability to activate cloud droplets is primarily a function of their size and chemical composition [Seinfeld and Pandis, 2006]. Köhler theory describes the competing effects involved in cloud droplet activation, namely the in-

fluence of curvature (Kelvin term) and the presence of a solute (Raoult term) [Köhler, 1936]. The complex nature of ambient atmospheric aerosols makes prediction of CCN concentrations difficult. Many laboratory studies have investigated CCN activity with respect to particle chemistry. These experiments have evolved from the usage of simple soluble species, such as NaCl [Katz and Kocmond, 1973] to organic species of variable solubility [Cruz and Pandis, 2002]. Yet, it is difficult to extrapolate these studies to the actual atmosphere due to the inherent chemical oversimplification of such laboratory studies.

Organic compounds are a significant and complex constituent of atmospheric aerosols. The wealth of organic species and the varying solubilities of organic compounds makes quantifying the organic contribution to CCN activity difficult. Classifying organic composition by functional group is a useful approach to tackle this complexity since degree of oxidation and bond types relate to solubility.

Models to predict CCN concentration have been built upon previous theoretical and laboratory studies [Roberts *et al.*, 2002]. The comparison between predicted CCN and measured CCN is known as CCN closure analysis [Seinfeld and Pandis, 2006]. To “achieve closure” is to accurately predict the measured CCN. Such closure was not achieved when only limited chemical information was available [Martin *et al.*, 1994], but improved instrumentation and sufficient measurements of aerosol composition, including organic components, improves the success of closure studies [Broekhuizen *et al.*, 2005] [Hersey *et al.*, 2008]. Roberts *et al.* [2002] achieved closure when the Amazonian biogenic aerosol studied was considered insoluble. Using measurements at Whistler, BC as a case study, we show organic composition was predominately insoluble. This highlights the ability of CCN closure analysis to provide even greater detailed information of organic speciation during a period of biogenic influence.

2. Methods

During a one month campaign (May 17, 2008 to June 16, 2008) at Whistler, BC the ambient aerosol was measured using many co-located instruments. The instrumentation critical to this CCN closure analysis is described here.

2.1. Sampling Site

Whistler is located in Southwest British Columbia. Samples were collected at 1020 masl in the Whistler valley surrounded by mountains. Vancouver, 100km southwest of Whistler, is the closest large city. Whistler’s natural environment and distance from a major city is ideal for studying biogenic and/or long range transported aerosol [Leitch *et al.*, 2008]. During this study high concentrations of terpenes and isoprenes were measured, which implies a portion of the OM was biogenically derived [Sun and Ariya, 2005]. Through this CCN analysis we examine the solubility of the organic fraction of biogenic aerosol.

2.2. Aerosol Composition Measurements

Organic functional group concentrations were measured by Fourier Transform Infrared (FTIR) spectroscopy. Sub-micron particles were collected on 37mm Teflon filters. Simultaneous 12 and 24 hour samples were collected to check

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for consistency. The higher resolution, approximately 12 hr samples are used for all analysis here. Duplicate back filters were analyzed to check for VOC absorption and handling artifacts. FTIR spectra were measured with a Bruker Tensor 27 spectrometer. Through use of a baselining and fitting algorithm organic functional groups including alkane, acid, alcohol, amine, organosulfate, and carbonyl concentrations are obtained as described by *Russell et al.* [2009]. Alkene and aromatic groups were below detection limit for all samples.

A High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) was co-located with FTIR filter collection. HR-ToF-AMS provides real-time measurements of non-refractory compounds including sulfate, nitrate, and organic masses [*Jayne et al.*, 2000]. For this study the sulfate concentrations were used from the HR-ToF-AMS, while the more chemically specific information obtained from FTIR was used to describe the organic fraction.

2.3. CCN Measurements

CCN number concentrations were measured at a supersaturation (SS) of 0.32% in a continuous flow chamber at five minute resolution. In the chamber CCN were counted by Aerodynamic Particle Sizer (TSI 3320). This chamber is designed to activate ammonium sulfate particles of diameter 57 nm. A correction for the flow rate was applied to all raw data. The CCN number uncertainty for the instrument has previously been estimated at $\pm 15\%$ [*Chang et al.*, 2007].

2.4. Aerosol Size Measurements

Particle size and number information was measured using a Scanning Mobility Particle Sizer (SMPS). The SMPS measures size distribution through coupled Differential Mobility Analyzer (DMA) (Model 3081) size measurements and

Condensation Particle Counter (CPC) (Model 3010) particle count measurements. Five minute averaged measurements of size distributions from 7.3 nm to 305 nm were collected.

2.5. Köhler Model

CCN number concentrations were predicted using a Köhler model designed and previously used by [*Roberts et al.*, 2002]. Their the authors present the Köhler equation used in the model:

$$S_v^{eq} = \exp\left(\frac{4\sigma' M_w}{kT\rho_w D_p} - \frac{\Phi M_w}{\frac{\phi\rho' D_p^3}{6} - \sum_i m_i} \left[\sum_i \frac{v_i m_i}{M_i}\right]\right) \quad (1)$$

where S_v^{eq} is the equilibrium saturation ratio, σ' is the surface tension of the solution, M_w is the molecular weight of water, k is then Boltzmann constant, T is the temperature, ρ_w is the density of water, D_p is the particle diameter, Φ is the osmotic coefficient, m_i is the dissolved solute mass (solute denoted by i), and v_i it the van't Hoff factor.

Parameters available to adjust were considered as two groups. 1) Size and Physical parameters: particle concentration, size distribution (mean particle diameter and standard deviation) 2) Chemical parameters: soluble fraction including different chemical components represented by their density, solubility, van't Hoff factor, and molecular weight. In section 3 the chemical parameters are examined in four case studies, while the sensitivity of the size parameters are examined in section 4. For comparison with the CCN measurements, the CCN number concentrations at SS of 0.32% were calculated. The model employs a multi-component approach, which allows for more atmospherically relevant aerosol representation since atmospheric particles are not expected to be a single component. However, the model assumes the aerosol is comprised of an internal mixture, implications of this will be discussed in section 4. For this analysis

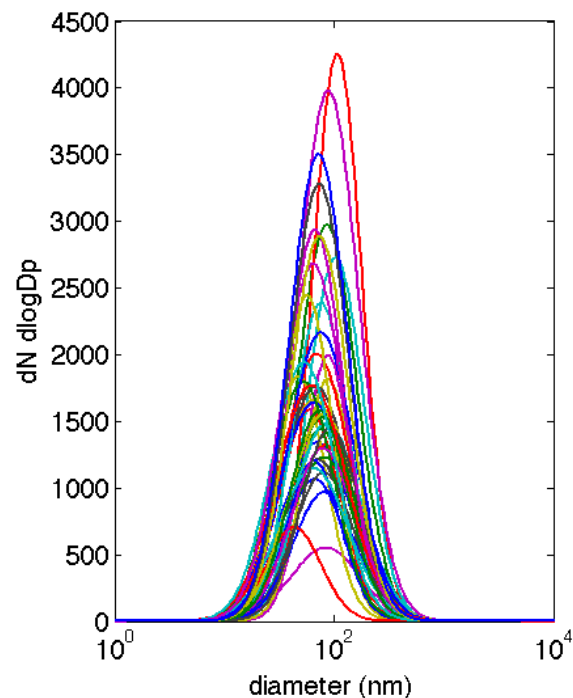


Figure 1. Size distribution of 40 sample periods determined by SMPS measurements of geometric mean diameter, geometric standard deviation and number concentration.

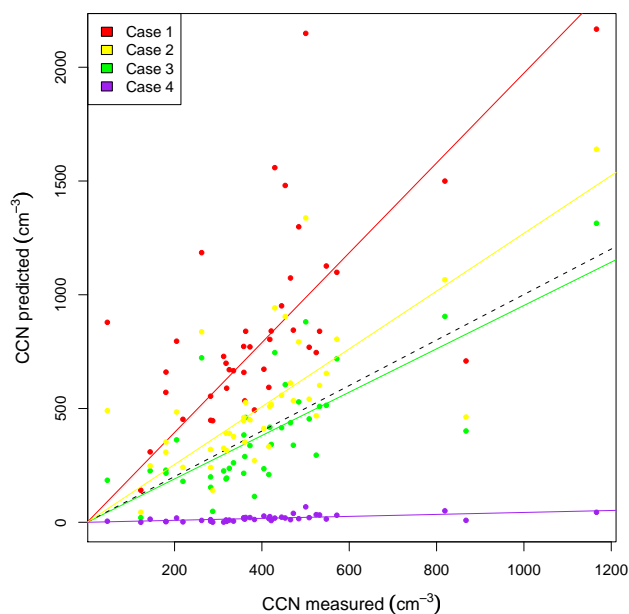


Figure 2. The comparison between predicted and measured CCN is shown for four cases in red, yellow, green, and purple for cases 1,2,3, and 4 respectively. The dashed black line shows the 1:1 line for CCN predicted equal to CCN measured.

the model was used to represent the particle composition as one component, two components, and three components.

Table 1. Range of the 40 size distribution input parameters

Size Parameter	Minimum	Mean	Maximum
Number (cm^{-3})	430.5	1297.0	2815.0
Mean Diameter (nm)	43.69	73.97	108.20
Standard Deviation	1.639	1.908	2.130

3. Results

3.1. Measurements

A total of 80 FTIR filter samples were collected from 17 May 2008 to 16 June 2008. Of these, 40 samples were used for the closure analysis that met these criteria: approximately 12 hour samples, alkane groups above detection limit, and CCN measurements were collected simultaneously. The SMPS, HR-ToF-AMS, and CCN measurements (instrument resolution discussed in section 2) were averaged over the filter collection duration. From the SMPS, a geometric mean diameter, geometric standard deviation, and number concentration were obtained for each sample.

The fitted lognormal modes for the 40 size distributions are shown in Figure 1. The figure is meant to highlight the variability and range of the samples over the month long study. The number and particle diameter varied considerably, while the standard deviation of the distribution was less variable (see Table 1).

3.2. Predicted and Measured Comparison

The model was run for a number of cases in which the size parameters were fixed while chemical composition was the experimental variable of interest. Four of those cases are highlighted here. In case 1, 100% of the particles were considered as ammonium sulfate. In case 2, the oxygenated organic fraction was considered to be adipic acid while the remainder of the organic fraction remained as insoluble. In case 3, the organic fraction was considered completely insoluble. In case 4, 100% of the particles were considered as adipic acid. A few differences in the four cases are emphasized. These are highlighted as varying representations of the organic fraction from very soluble to completely insoluble. While in case 4 the importance of ammonium sulfate is tested. They also represent varying interpretations of the organic fraction. In case 1, the whole particle is treated as ammonium sulfate, thus organics are considered as soluble as ammonium sulfate. In case 3 all organics are considered as insoluble (although the richness of organic species is well known), while in case 2 the oxygenated groups and non-oxygenated groups are subdivided. In case 4 even the known ammonium sulfate fraction is considered to be partially soluble, represented as adipic acid. Lastly, for the model they depict a one component (case 1 and 4), a two component, and a three component representation.

FTIR analysis is essential for the chemical characterization of oxygenated organic components. In this analysis, acid, alcohol, carbonyl, and organosulfate groups are considered as the oxygenated groups, while alkane and amine groups are the non-oxygenated groups. The solubilities of ammonium sulfate, adipic acid, and “insoluble” components are 0.764, 0.06, and 0 respectively.

The comparisons between predicted CCN number concentrations and measured CCN number concentrations are shown in Figure 2. The fits and slope ($CCN_{predicted}/CCN_{measured}$) of the lines shown in Figure

Table 2. Fit parameters of four closure cases shown in Fig. 1.

Fit	Description	Correlation (R)	Slope
Case 1	100% ammonium sulfate	0.64	1.97
Case 2	Oxygenated organic fraction: adipic acid, remaining organics: insoluble	0.70	1.27
Case 3	Organic fraction: insoluble	0.74	0.95
Case 4	100% adipic acid	0.70	0.04

1 are summarized in Table 2. For case 1, there is a large over-prediction of CCN. There is still an over-prediction of the modeled CCN with respect to the measured CCN, although it is substantially reduced in case 2. Case 3 when the organic fraction is considered completely insoluble slightly under-predicts relative to the measured CCN. Case 4 shows a dramatic under-prediction of CCN. Of the three cases the comparison is considered best in case 3, with a slope of 0.95 and a Pearson’s correlation (R) of 0.74.

4. Discussion

Noting that there is a 15% uncertainty in the CCN measurements, it is shown that a good closure is achieved when the organic fraction is modeled as insoluble. The closure provided further knowledge about the ambient organic fraction. Adipic acid, a dicarboxylic acid, was chosen to represent the oxygenated organic fraction because it is a known constituent of atmospheric aerosols [Sun and Ariya, 2005]. There is a slight under-prediction when the organic fraction is represented as insoluble, and a slightly greater over-prediction when the oxygenated organic is considered as soluble as adipic acid. Thus, the oxygenated organic fraction, though partially soluble is not as soluble as adipic acid. The very large over-prediction of CCN in case 1 is expected since the ambient aerosol was very rich in organics. The organic fraction ranged from 67 to 96 % of the particle composition and mean organic fraction throughout the 40 samples was 85 % (where total particle composition was assumed to be the sum of ammonium sulfate fraction and organic components). Case 4 demonstrates the crucial role even a small amount of soluble ammonium sulfate plays in CCN activity. When this small ammonium sulfate fraction was ignored a major under-prediction of CCN resulted. Other studies have noted this non-linearity effect for organic rich biogenic aerosols [Roberts *et al.*, 2002]. The results suggest that the small soluble fraction in predominately insoluble aerosols drive activation [Broekhuizen *et al.*, 2005].

In addition, the sensitivity of predicted CCN to the particle size distribution was examined. The samples with the maximum, mean and minimum D_{pg} of the 40 samples were selected. The fraction of particles activating to CCN (CCN/CN) for the varying effective solubilities of the four cases are shown in Figure 3. Between the three curves it can be seen that a change in chemistry from one case to the next can have a variable effect on CCN activity; that is the slope between the two cases differ for the different sizes. The

Table 3. Slopes for lines shown in Fig 3 and the standard deviation of the slopes for the different mean particle sizes.

Case Slope	Min D_{pg}	Mean D_{pg}	Max D_{pg}	Stdev
Case 4 to 3	0.41	1.56	3.44	1.53
Case 3 to 2	0.20	0.18	0.52	0.19
Case 2 to 1	0.37	0.52	0.37	0.09

difference in the slopes among the three curves is greatest in the change from case 4 to case 3, and smallest from case 2 to 1 (see Table 3). This means that CCN activity is most sensitive to size when there is less soluble material present.

The correlations for the four cases range from 0.64 to 0.74 and improve as the slopes move toward the expected 1 to 1 line. These are reasonably high correlations considering the complexity of ambient measurements, yet a few reasons why these are not closer to 1 are considered. The model employed up to three components and assumes internally mixed aerosol mass. Although this may most likely be the case, predicted and measured CCN concentrations wouldn't be expected to match for an external mixture. Further, the oxygenated organic fraction was considered as acid, alcohol, carbonyl, and organosulfate groups, but these functional groups would be expected to have varying solubilities, and the oxygenated fraction could be further subdivided. Although surface tension effects were not examined independently as found to be important by Roberts *et al.* [2002], surface tension effects are implicit in these calculations since the surface tension of adipic acid is 5% lower than that for ammonium sulfate.

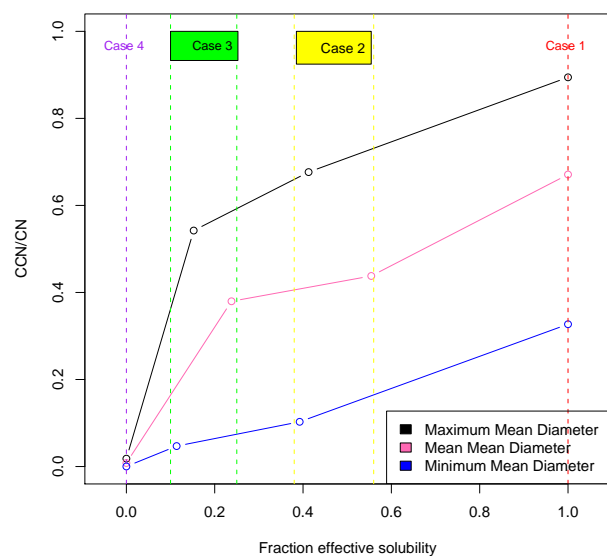


Figure 3. Fraction of CCN/CN for the varying solubilities represented by the four cases are shown. The three lines in black, pink and blue are for the samples with the maximum, mean, and minimum mean geometric diameter of the 40 samples, respectively.

5. Conclusion

Size, chemical, and CCN measurements were made for ambient atmospheric aerosols with a biogenic influence in a mid-mountain forest. The aerosols were predominately organic in composition. Out of three cases in which the organic fraction was considered: (1) completely soluble, (2) oxygenated organics partially soluble and the remaining organics insoluble, and (3) completely insoluble. The comparison between predicted and measured CCN was best in case 3 when the organic fraction was considered insoluble

($R=0.74$). Roberts *et al.* [2002] came to a similar conclusion for organic rich biogenic aerosols from the Amazon. Particle size plays the most important role when the soluble fraction is small. Case 4 (100% adipic acid) under-predicts CCN considerably demonstrating the important contribution of highly soluble components (*e.g.* ammonium sulfate) to CCN activity. From a three component CCN prediction, it is determined that although the oxygenated organic fraction is partially soluble it is less so than the partially soluble proxy of adipic acid. This study provides some constraints on the solubility of the oxygenated organic fraction of organic biogenic aerosols.

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