

Organic Functional Group Contributions to Cloud Condensation Nuclei in the Arctic During ICEALOT 2008

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Abstract. Cloud condensation nuclei (CCN) affect cloud droplet formation processes as well as number concentration. An increase in cloud droplet number concentration influences the Earth's radiative balance by increasing the reflected incoming solar radiation. Chemical composition influences the properties of the aerosol particles, which impact their ability to act as CCN. Organic functional groups in particles, such as alkanes, which are hydrophobic, and alcohol groups, that are hydrophilic, contribute differently to the CCN potential than completely soluble inorganic functional groups. Measurements of inorganic and organic aerosol were made during the ICEALOT research cruise in the North Atlantic and Arctic in March and April of 2008. Fourier Transform Infrared (FTIR) spectroscopy was used to identify and quantify the organic functional group fractions of submicron particles. The contribution of the organic fraction of internally mixed particles to the formation of CCN has not yet been well established. Here it is shown that defining the organic fraction as soluble increases the average number of percent predicted CCN by 7.92% for an initial diameter of 100nm over a base case in which the organic fraction was considered entirely insoluble. Increasing the organic fraction increases the influence of the solubility of the organic fraction on the predicted percent CCN. Determining the soluble portion of the organic fraction is important for accurate calculations of CCN.

1. Introduction

Aerosols play an active and important role in cloud formation. In the Arctic and North Atlantic marine regions, particles from polluted continental as well as clean marine sources can affect cloud formation. Particles that can activate at a given supersaturation and grow to become cloud droplets are defined as cloud condensation nuclei (CCN) [Seinfeld and Pandis, 2006]. The potential for particles to become CCN depends on both physical and chemical properties. The Köhler theory is used to describe the influence of these properties in determining the vapor pressure over an aqueous solution droplet [Köhler, 1936] and can be used to predict the ability of a particle to act as CCN. The initial aerosol composition affects the prediction of the CCN activity. According to Chan et al. [2008], the Köhler theory can be effectively used to predict CCN, even for aerosol with organic components. Two competing effects in the Köhler theory are the Kelvin and Raoult effects, which act to increase and decrease the vapor pressure of a particle, respectively [Seinfeld and Pandis, 2006]. The solute effect, or Raoult effect, dominates when the radius is small and includes solubility and hygroscopic properties. Increasing the soluble

fraction causes an increase in the wet diameter and a decrease in the supersaturation necessary to form CCN. For an internally mixed aerosol population in which particles have size-independent composition, CCN at a given supersaturation can be calculated by integrating the following equation from D_s to infinity

$$CCN(s) = \int n(D_p) dD_p \quad (1)$$

where $n(D_p)$ is the number distribution of the aerosol population and D_s is the activation diameter for a specific supersaturation (s) [Seinfeld and Pandis, 2006]. At a D_p of infinite size, all particles will be activated as CCN.

Understanding the factors that contribute to the formation of CCN is important to understanding cloud formation and properties. The largest source of uncertainty in the radiative forcing of the atmosphere is due to the indirect effect in which aerosols contribute to cloud formation by serving as CCN [IPCC Report, 2007]. An increase in CCN in a region can lead to an increase in cloud droplet formation, which can lead to an increase in cloud coverage [Twomey, 1977]. According to the IPCC Report [2007], 50-60% of the Earth's albedo is influenced by cloud coverage. An increase in albedo, from an increase in cloud coverage and the number of cloud droplets, can lead to a cooling effect through the reflection of shortwave radiation [Twomey, 1977].

Aerosol particles can be made up of multiple organic and inorganic components. Organic compounds make up a significant fraction of aerosol mass [Kanakidou, 2004]. The properties of particles depend on the functional groups that make up their composition. Both organic and inorganic functional groups affect the potential of a particle to absorb water and activate as CCN. The ability of soluble inorganic aerosols to act as a CCN is relatively well established, but the potential for organic aerosol to serve as a CCN has not been studied to such an extent [Seinfeld and Pandis, 2006].

Solubility is an important factor in determining the ability of a particle to become a CCN because the particle needs

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to absorb water to grow. Inorganic and organic functional groups range in solubility depending on their hygroscopic properties [Saxena *et al.*, 1996]. Increasing the ratio of atoms with the potential to create hydrogen bonds with the water (fluorine, oxygen, and nitrogen) to the number of carbon atoms and/or increasing the polarity increases particle solubility. Functional groups such as alkanes, have only carbons and are considered insoluble. Acids, alcohols, carbonyls, and organosulfates are more hydrophilic and partially soluble due to their polarity and higher ratio of oxygen to carbon.

Cloud droplet formation over the Arctic and North Atlantic regions is important to the regional climate. Cloud droplet concentrations range from 10 to 200 cm^{-3} over oceans [Hegg and Hobbs, 1992]. Increasing the number of CCN in this area can lead to an increase in cloud droplet formation. Over the Arctic and North Atlantic, the cloud cover is mainly marine stratocumulus. Altering the CCN will change the cloud cover and impact the regional and global radiative balance. This paper works toward understanding the influence of organic functional group solubility on the ability of particles to serve as CCN.

Table 1. Species Parameters: Inputs of solubility, density, van't Hoff Factor, and molecular weight for each compound included in the Köhler theory model to calculate CCN

Species	Density (g/cm^3)	Solubility (g/mL)	van't Hoff Factor	MW (g/mol)
Sulfate	1.8	0.76	1	96
Nitrate	1.7	1.2	1	62
Ammonium	1.8	0.76	1	36
Glutaric Acid	1.42	1.1	1	132
Diethylhexyl sebacate	0.90	0.0001	1	422

2. Methods

2.1. Overall Measurements

Measurements of submicron particles using instrumentation aboard the R/V Knorr were made from March 19 to April 24, 2008. Aerosol was collected from the North Atlantic and Arctic Oceans and from the Greenland, Norwegian, and Barents Seas while the ship traveled in the area of 20-30W and 41-81N. The inlet was located at a height of 18m above sea level and consisted of a mast which extended 5m above and forward of the aerosol measurement container. The inlet was heated to dry the aerosol to a relative humidity of 25% or less, during sampling.

Sector control for the flow was used to prevent direct ship emissions from being collected. The flow of air was automatically shut off when the wind direction was from the back of the ship, near the smoke stack.

2.2. Aerosol Mass Spectrometer

A quadrupole Aerosol Mass Spectrometer (AMS) made real time measurements of submicron particle composition

averaged over five minute intervals. Non-refractory ions, chemical components that vaporize at the vaporizer temperature of 600C, such as sulfate, nitrate, and ammonium were quantified, in addition to total particle organic mass (OM) [Allan *et al.*, 2003; Jayne *et al.*, 2000].

2.3. Fourier Transform Infrared Spectroscopy

Submicron particles were collected on 37mm Teflon filters for 12 hour and 24 hour periods. After collection, the filters were frozen and transported back to San Diego for analysis by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra were analyzed using an automated algorithm that included baselining, peak-fitting, and integrating at specific peak locations to quantify organic functional group mass associated with major carbon bond types using the method outlined by Maria *et al.* [2002] and revised by Russell *et al.* [2009]. Concentrations were calculated by dividing the mass (μg) of each functional group measured for each filter by the total volume (m^3) of air pulled through the corresponding filters.

2.4. Köhler Model

The Köhler model [1936] as described by Roberts, *et al.* [2002] was used to calculate the number concentration of CCN produced from the submicron particles measured by AMS and FTIR. In order to determine the number of particles that activate to become CCN, the compositions of the particles were identified and quantified. The properties of the inorganic compounds (sulfate, ammonium, and nitrate), as exemplified by Roberts, *et al.* [2002], were used as inputs into the Köhler code, in addition to those for the organic fraction. The solubility, density, van't Hoff Factor, and molecular weight for each compound used are included in Table 1. In this calculation, it was assumed that the particles were internally mixed and that the average particle composition for each sample was not dependent on the size of the particles.

3. Results and Discussion

Submicron particles over the Arctic and North Atlantic Oceans during spring 2008 varied in their organic and inorganic functional group composition. The measurements from the AMS were averaged over the sampling periods of each 12 hour filter to get the same temporal scale as the FTIR measurements, giving thirty-seven samples. Previous analysis of OM measured by FTIR and AMS showed correlation between the two techniques for these samples. Fractional contribution of each functional group to the total OM was found by dividing the concentration of each group by the total concentration of the sample. The OM from the AMS was used to determine the organic functional group fractions of the total particle mass. This was done to normalize the OM measured by AMS and FTIR. There was a larger overall fraction of inorganic mass in the measured particles with the fraction of sulfate ranging from 30% to 78%, ammonium from 0 to 27%, and nitrate from 0 to 7%. The total OM fraction, consisting of acid, alcohol, alkane, amine,

Table 2. Description of test cases pertaining to the organic fraction of total particle mass

Case	Soluble Groups	Insoluble Groups
1	None	All
2	Organosulfate	Acid, Alcohol, Alkane, Amine, Carbonyl
3	Organosulfate*	Acid, Alcohol, Alkane, Amine, Carbonyl
4	Alcohol, Organosulfate, Acid, Carbonyl	Alkane, Amine
5	All	None
6	Half of OM	Half of OM

*Assigned as sulfate

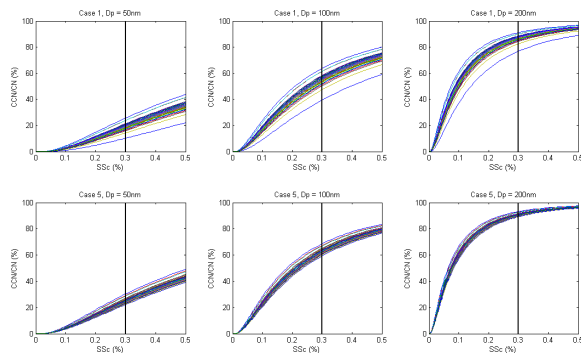


Figure 1. Percent of initial particles activated to CCN as a function of supersaturation for Cases 1 (top row) and Case 5 (bottom row) for the three initial particle diameters. Supersaturation at 0.3% is marked with a vertical black line.

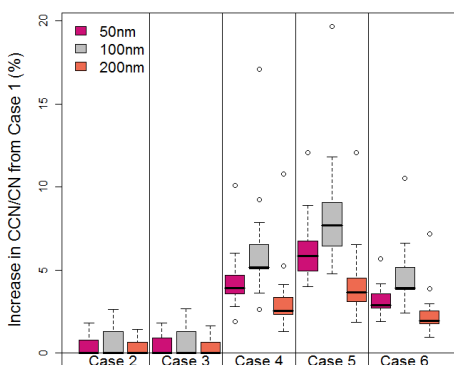


Figure 2. Range of increases in CCN/CN (%) from Case 1 for the three initial diameters. The bar is the mean value and the extending dashed lines show the range.

carbonyl, and organosulfate functional groups, was less than the inorganic fraction and ranged from 21% to 60%.

Six cases, described in Table 2, were used to determine if the assigned composition and solubility of the organic fraction affects the overall percent of particles activated to CCN. The percent of activated particles for each of the thirty-eight samples was calculated using the Köhler model for each of the six cases. Using the parameters described in Table 2, each fraction of total mass was assigned to its corresponding compound in Table 1. The soluble organic group, except in Case 3, was assigned as glutaric acid which has a solubility of 1.0g/mL of water and completely dissociates upon activation [Kumar *et al.*, 2003; Sun *et al.*, 2006]. Diethylhexyl sebacate, which has a low solubility represented as 0.0001g/mL of water was used for the insoluble group [Barton, 1990]. Because organosulfate has a similar structure to a sulfate group, it was considered to have the same properties as inorganic sulfate, in Case 3.

The percent of initial particles that activate to CCN was calculated to remove the dependence on the number distribution. A lognormal size distribution was used, so increasing the number concentration of initial particles evenly increased the amount of particles in each size range. An

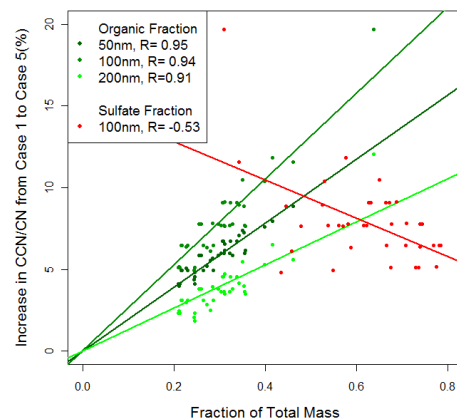


Figure 3. Correlations between the organic and sulfate fractions of total mass and the increase in CCN/CN (%) from Case 1 to Case 5.

initial particle number concentration of $1000/cm^3$ was used throughout these calculations. The percents of initial particles that serve as CCN were determined at the supersaturation of 0.3% for each sample in each case. This is the low end of the supersaturation range for marine stratocumulus clouds, as observed in this region [Pruppacher and Klett, 1997].

To observe the effect of initial particle size on the percent of activated particles, the geometric mean diameter of the particle distributions was varied. Three diameters were selected to represent the size distributions observed in the Arctic regions. The diameters chosen were 100nm, which is the mean diameter observed in the monodisperse number distribution of the Arctic [Ito and Iwai, 1981], and 50nm and 200nm, which have been observed in the springtime Arctic haze in which these samples were taken [Covert and Heintzenberg, 1993]. The six case analyses were done for each initial particle diameter.

The distribution of activated particles and critical supersaturation values for Cases 1 and 5 for the three different initial diameters are shown in Figure 1. Even though there is variability in the composition fractions between the samples, all thirty-eight were plotted for two cases to show the overall trend. Increasing the initial particle diameter increased the percent of CCN predicted at 0.3% supersaturation, as seen in Figure 1. At larger initial diameters, the particles have to grow less to become activated.

To determine the influence of changing the properties of the organic fractions, the differences between Case 1 and the other cases were determined and are shown in Table 3.

Table 3. Increase in predicted CCN/CN (%) from Case 1 for three initial particle diameters

Initial Diameter (nm)	Case 2	Case 3	Case 4	Case 5	Case 6
50	0.27	0.36	4.28	6.02	2.98
100	0.39	0.53	5.80	7.92	4.15
200	0.21	0.29	2.93	3.89	2.15

Considering all of the organic fraction as insoluble (Case 1) predicted the lowest percent of CCN. There was the largest increase when all of the organic fraction was considered soluble (Case 5). This was consistent for all three size ranges, as shown in Table 3. Figure 2 shows that regardless of initial particle diameter, the solubility of the organic fraction affects the predicted percent of CCN. Determining the soluble portion of the organic fraction is important

for determining the CCN. For an initial particle diameter of 100nm, there was an average increase in CCN of 8.2% when the organic fraction was considered all soluble over all insoluble.

The impact of the solubility of the organosulfate functional group was determined by comparing Cases 1, 2, and 3. From Case 1 to Case 2, there was an average increase in predicted CCN of 0.39% when all samples were considered and 1.03% when only those with an organosulfate fraction greater than 0 were considered. This small increase shows that the fraction of organosulfate does not have a significant role in the prediction of percent CCN. The increase in the percent of predicted CCN from Case 1 to Case 3 is only 0.38% greater than the increase from Case 1 to Case 2. Changing the solubility of the organosulfate fraction from that of glutaric acid (Case 2) to that of sulfate (Case 3) had a negligible effect, as shown in Figure 2. This shows that representing the fraction of organosulfate as soluble rather than insoluble has a larger impact on the percent of CCN than slightly increasing the fraction of sulfate by considering organosulfate fraction to be included with sulfate.

The increase in CCN when considering half of the organic fraction as soluble was comparable to considering the oxygenated fractions as soluble with an average increase from the insoluble organic case of 4.3% and 3.1%, respectively, averaged for the three different initial diameters.

Increasing the fraction of OM increased the influence of the solubility upon the predicted percent of CCN. This is consistent for all three initial diameters, as shown in Figure 3. The increase in predicted percent CCN from Case 1 to Case 5 is anticorrelated with the fraction of sulfate. According to Wang *et al.* [2008], the solubility of the organic fraction influences the predicted CCN only for OM fractions greater than 70%. This is inconsistent with the current findings which show an increase in predicted percent CCN from Case 1 to Case 5, shown in Figure 3, for an OM fraction of as low as 20%. Consistent with Wang *et al.* [2008], though, is the increase in the dependence of the predicted percent CCN on the solubility of the OM fraction with an increase in OM fraction.

4. Conclusions

Organic functional groups make up a significant fraction of particle mass. In the North Atlantic and Arctic oceans, as studied in ICEALOT 2008, the composition of the fraction of OM influences the ability of aerosol to serve as CCN. Correctly assigning the solubility of the organic fraction of particle mass is important in predicting the percent of particles that activate as CCN because the organic fraction can have a significant impact. Considering the organic fraction as soluble organic creates an average increase of 7.9% in percent CCN relative to considering the organic fraction insoluble. There was a greater influence on predicted percent CCN when considering organosulfate as soluble in general rather than changing the solubility from that of glutaric acid to that of sulfate. The fraction of soluble OM affects the percent predicted CCN at all diameters, but there is the greatest impact at 100nm. Increasing the organic fraction increases the influence of the soluble and insoluble fractions of OM on percent CCN, which is true for all three initial diameters. Altering the solubility of the organic fraction impacts the predicted percent CCN. This effect increases with a greater fraction of organic mass.

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