Arctic Aerosol Sources and Continental Organic Aerosol Hygroscopicity

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

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Hygroscopicity

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Abstract

Atmospheric particles can affect climate directly, by scattering solar radiation, or indirectly, by acting as the seed upon which cloud droplets form. These clouds can then cool the earth's surface by reflecting incoming sunlight. In order to constrain the large uncertainties in predicting the ultimate effect of aerosol on climate, the sources of atmospheric particles and their subsequent ability to turn into cloud droplets needs to be better understood. This thesis addresses two parts of this issue: the sources of Arctic aerosol and the hygroscopicity of continental organic aerosol.

Small particles were observed in Baffin Bay during September 2008 that coincided with high atmospheric and ocean surface dimethyl sulphide (DMS) concentrations suggesting that the aerosol formed from oceanic sources. An aerosol microphysics box model confirmed that local DMS could have produced the observed particles. In addition, the particle chemical composition was measured using aerosol mass spectrometry in the central Arctic Ocean in August 2008 and particles were found to be 43% organic and 46% sulphate. Factor analysis further apportioned the aerosol mass to marine biogenic and continental sources 33% and 36% of the time, respectively, with the source of the remaining mass unidentified.

The second part of the study parameterises the hygroscopicity of the ambient organic aerosol fraction (κ_{org}) at Egbert, Ontario and Whistler, British Columbia. This
was done using two methods: 1) by assuming that the oxygenated organic component was hygroscopic and that the unoxygenated organic component was non-hygroscopic, $\kappa$ of the oxygenated component was found to be $0.22 \pm 0.04$, and 2) by assuming that $\kappa_{\text{org}}$ varied linearly with the atomic oxygen to atomic carbon ratio, it could be parameterised as $\kappa_{\text{org}} = (0.29 \pm 0.05) \times (\text{O/C})$. Calculations predict that knowing $\kappa_{\text{org}}$ is important in urban, semi-urban, and remote locations whenever the inorganic mass fraction is low.
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Chapter 1

Introduction to Aerosol Sources and Hygroscopicity
1.1. Particles in the atmosphere

1.1.1. Background and Motivation

An aerosol is a suspension of either liquid or solid particles in the atmosphere and there are three broadly defined size modes: ultrafine (< 100 nm), accumulation (100 nm - 2.5 µm) and coarse (> 2.5 µm), where the sizes are the particle diameter. The smallest of the ultrafine particles (< 10 nm) are formed from nucleation, which takes place when gas phase molecules, primarily sulphuric acid, water and possibly ammonium and organics, condense together to form a particle. These particles grow by the condensation of additional gases and coagulating with other particles. Ultrafine particles can also result from the condensation of combustion products, which give rise to elemental and organic carbon constituents. Accumulation mode particles result from the growth of ultrafine particles either through coagulation and condensation, or through aqueous oxidation in droplets, followed by evaporation. Coarse mode particles are generally mechanically generated from primary sources and are usually composed of dust, soil, biological particles (e.g. pollen) and sea salt (Finlayson-Pitts and Pitts Jr. 2000).

Ambient aerosol in the ultrafine and accumulation modes are mainly composed of water; inorganic salts, such as sulphate, nitrate, ammonium and chloride; elemental carbon; and organic carbon, which includes any carbon-containing compound that is not elemental carbon (Seinfeld and Pandis 2006). These particles can age in the atmosphere from heterogeneous oxidation (George and Abbatt 2010) and condensation of less volatile species from gas phase reactions. Loss processes of atmospheric aerosol include coagulation with other particles, wet deposition through precipitation and dry deposition.

Aerosol research remains active because of particulate effects on air quality, health (Dockery et al. 1993) and climate (Solomon et al. 2007). Some of the outstanding issues being studied are: the relationship of aerosol to climate change; the sources and chemical composition of aerosol in remote environments; the contribution of biological sources, such as plants and marine organisms, to the aerosol mass and number; the radiative properties of elemental carbon; the mechanisms by which ice nuclei are formed; and the mechanisms that cause illness when people are exposed to high particle loadings. This
thesis will focus on the role that particles can play on climate through clouds and the sources of particles in the Arctic.

Anthropogenic activities are thought to have resulted in an increase in aerosol mass since 1750 with major contributions from biomass burning and fossil fuel burning (Dentener et al. 2006), affecting climate in different ways. Particles can directly affect climate by altering the incoming radiation. For example, elemental carbon and iron-containing mineral dust absorb sunlight, thus heating the atmosphere, while inorganic and organic particles scatter sunlight, causing a net cooling at the surface (Ramanathan et al. 2001). The efficiency with which light is scattered can also depend on the relative humidity (Baynard et al. 2006) and size of the aerosol, with particles between 0.1 to 1 µm scattering light most efficiently (Seinfeld and Pandis 2006).

Particles can also affect climate indirectly by acting as cloud condensation nuclei (CCN), the seed upon which cloud droplets form. With an increase in particle concentration from anthropogenic activities, cloud droplet concentrations will also increase. Assuming that the liquid water content remains constant, clouds with higher droplet concentrations will have smaller droplets compared to cleaner clouds with fewer droplets. This higher concentration of small droplets results in clouds with higher albedo and this is known as the first indirect effect of aerosol on clouds (Twomey 1977).

A second indirect effect of aerosol on clouds is that these clouds with smaller droplets are less likely to precipitate and it will therefore take longer for these more reflective clouds to dissipate (Albrecht 1989). This has been observed in intense biomass burning events, where strongly convective clouds form, leading to delayed precipitation, although the resulting storms can be quite severe (Andreae et al. 2004). However, clouds with increased particle concentration have also been observed to have higher liquid content (Ackerman et al. 2004), which has led to some controversy as to the existence of the second indirect effect.
Overall, it is estimated that the indirect effects that aerosol have on climate contribute to -0.7 (+0.4 / -1.1) W m\(^{-2}\) (Solomon et al. 2007), and it remains the term with the greatest uncertainty in the calculation of the radiative forcing from anthropogenic activities. Although many of the uncertainties are due to the fact that cloud processes occur at scales smaller than the grids used in a climate model, it is still important that we understand the sources and ageing of aerosol, as well as their composition, which affects their final ability to act as CCN. This thesis explores the sources of aerosol in the Arctic, where the effects of aerosol on climate are not as well understood, and the ability of the organic fraction of the aerosol to activate as cloud droplets. These studies have been facilitated by the rapid development of online measurements of aerosol chemical composition, which is discussed in the next section.

### 1.1.2. Advances in Aerosol Instrumentation

The advent and wide-spread use of the aerosol mass spectrometer (AMS), manufactured by Aerodyne Research (Jayne et al. 2000; Jimenez et al. 2003) in the last 5–10 years has led to an increase in understanding of aerosol chemical composition in the accumulation mode. This real-time mass spectrometer measures the size-resolved non-refractory chemical composition of particles between 80–500 nm in diameter (Liu et al. 2007). One major advance from the AMS is that it can quantify the organic aerosol component. Electron impact ionisation, which the AMS uses to ionise sample molecules, causes atmospheric organic compounds to fragment into a small number of mass-to-charge ratios that are easily quantified. The disadvantage is that individual organic compounds cannot be identified when measuring ambient air, although classes of compounds based on hydrocarbon versus oxygenated carbon functional groups can be identified from the mass spectra.

The process by which the AMS quantifies aerosol mass is collecting the bulk mass spectrum of the sample aerosol for a given time interval. The negative effect of this is that observations obtained from an internally- and externally-mixed aerosol population are identical. In contrast, mixing-state can be determined by single-particle instruments, such as those using laser ablation techniques. Because their volatilisation processes tend
to use higher energies, these instruments are also able to detect more refractory components of the aerosol. However, these instruments tend to have other disadvantages such as poor quantitation and size- and matrix-dependent sensitivities.

Non-mass spectrometric methods of measuring aerosol chemical composition use filters or particle-into-liquid sampling. These methods tend to require longer sampling times (30 min – 14 days) in order for enough mass to be collected, especially at small particle sizes where the mass is low. Analysis also requires the samples to be extracted with a solvent, which often only extracts the components of the aerosol with certain polarities. In comparison, the AMS can be operated at <1 min resolution and can quantify both organic and inorganic components of the aerosol. Nevertheless, there are several advantages to these chromatographic methods such as being able to quantify sea-salt in the aerosol, which is refractory in the AMS, but can contribute significantly to aerosol hygroscopicity. In addition, they can quantify metal cations in particles, which the AMS also cannot detect. Ideally, several techniques deployed in parallel would give the most information about the sampled aerosol population.

The high time and size resolution of the AMS and its ability to quantify the bulk organic aerosol component has made the AMS a popular instrument amongst aerosol chemists and has contributed greatly to the study of ambient organic aerosol (e.g. Zhang et al. 2007; Jimenez et al. 2009). At the beginning of the research described in this thesis, AMS measurements were relatively rare and had not been widely applied to Arctic environments or aerosol hygroscopicity studies. The projects described in this thesis are novel in the manner that the capabilities of the AMS are applied: 1) aerosol chemical composition was measured with the AMS in the central Arctic, where aerosol mass is < 1 µg m⁻³ and past filter measurements needed sampling times of 6 - 72 hours, and 2) the latest approaches in factor analysis were performed on the organic component of the mass spectrum in order to characterise the ambient organic aerosol component such that the prediction of hygroscopicity is improved. As described in the next sections, both of these topics are still active areas of research to which this work, with the higher time resolution and additional mass spectral information obtained by the AMS, contributes.
1.2. Arctic Aerosol Sources

1.2.1. Motivation

Compared to continental regions, much less is known about the polar environment. This is mostly due to the logistical difficulties involved in making measurements in polar regions: transportation is difficult and expensive and instruments need to be able to withstand cold temperatures and often need to be able to operate unattended for long periods of time. As a result, the Arctic in general, and aerosol properties and sources in particular, are poorly characterised and understood compared to continental regions. Increased interest in polar regions arose because the Arctic is extremely sensitive to climate change and is predicted to warm two times more quickly than the global mean (see Figure 1.1) (ACIA 2005). However, climate models have more trouble predicting the degree of warming in the Arctic than the rest of the world (ACIA 2005), suggesting that there are processes and climate feedbacks in the Arctic that are still not properly represented. As such, more observations are needed in order to understand this unique environment so that future changes can be better predicted.

Figure 1.1 - Predicted global and Arctic air surface temperature change from 5 models. The baseline period is 1981-2000 and the Arctic is 60-90°N (ACIA 2005).
The Arctic mostly comprises ocean covered with sea-ice that is surrounded by land. The sea-ice prevents energy and momentum transfer between the ocean and atmosphere (Tjernstrom 2005), and it also provides a high-albedo surface. This moderates the temperature by preventing the underlying ocean from absorbing solar radiation in the summer. Although the Arctic Ocean is completely covered with sea-ice over the winter, a portion of it is young, seasonal sea-ice which will melt over the summer, leaving only the thicker, multi-year ice during the summer months. With warming temperatures, even the multi-year ice is melting (Maslanik et al. 2007), allowing more open ocean to absorb sunlight, enhancing temperature increases and furthering sea-ice retreat. This effect is known as the ice-albedo feedback (Peixoto and Oort 1992).

Another difference in the Arctic is that clouds can warm the surface during both winter and summer, depending on the liquid water content in a column of air (liquid water path), surface albedo and solar zenith angle. In the dark months of winter when there is no shortwave radiation from the sun, strong temperature inversions are established and any clouds that form will be warmer than the earth's surface. Under these conditions, the clouds will warm the surface by emitting longwave radiation downwards (Shupe and Intrieri 2004). During the summer months in regions of high albedo, such as over sea-ice, incoming shortwave radiation is reflected outwards regardless of the presence of clouds. As such, clouds will again warm the surface by emitting longwave radiation, as in the winter (Tjernstrom 2005; Sedlar et al. 2010). This is generalised in Figure 1.2, which shows the minimum liquid water path necessary before the transmittance of clouds is low enough to have a net cooling effect. In regions of the Arctic where both the surface albedo and the solar zenith angle are high, the liquid water path required for cooling is much higher than the observed liquid water path, so clouds will generally have a net warming effect.
Figure 1.2 - The dependence of cloud warming on surface albedo and solar zenith angle. The contours show the liquid water path (LWP) necessary before clouds start having a net cooling effect. The box shows the region covered by the Surface Heat Budget of the Arctic (SHEBA) study, which is typical of Arctic regions. This figure shows that at these locations, clouds have a warming effect and was taken from Shupe and Intrieri (2004).

Understanding the lifecycle of clouds in the Arctic is essential for accurately predicting the future climate in the region. However, the role that clouds have on Arctic climate is opposite to observations at lower latitudes and is one example of how the Arctic is a unique environment. More observations are necessary to understand the climate of this region, including the particles that can act as CCN as well as the sources of these particles. The following sections describe what is currently known about Arctic aerosol sources and transport.

1.2.2. Arctic Aerosol Transport

Arctic haze is a phenomenon that takes place during the winter and early spring in the northern latitudes, from North America to Europe. During this time, particle loadings are 10-40 times higher than summertime values and are principally composed of sulphate and black carbon (Barrie 1986; Quinn et al. 2007). These high aerosol mass concentrations are transported from lower latitudes in Eurasia and North America into the central Arctic (Gong et al. 2010) and do not dissipate because strong temperature inversions prevent precipitation. As sunlight returns to the Arctic in the spring, the air becomes more
convective and the particles can be lost with deposition (summarised by Quinn et al. 2007).

In the summer, air in the Arctic mainly originates from the North Atlantic Ocean. Because the air masses are transported slowly, particles from lower latitudes precipitate before reaching the Arctic (Law and Stohl 2007). Low summertime aerosol loadings have been observed, for example, in Greenland (Megaw and Flyger 1973), the central Arctic Ocean (Covert et al. 1996b) and the Canadian Arctic (Li and Barrie 1993). Under these conditions, local aerosol sources become much more important because the background concentrations are so low. This is illustrated in Figure 1.3, which shows nitrate and sulphate mass at Barrow and Alert. The aerosol mass reaches a maximum during the winter months when Arctic haze occurs and a minimum during the summer months when the air is cleaner.

![Figure 1.3 - Time series of nitrate and sulphate measured at Barrow and Alert. Nitrate is dotted line and sulphate is solid line. Figure taken from Quinn et al. (2007).](image)
1.2.3. Primary Arctic Aerosol Sources

Primary sources of aerosol that have been measured in the Arctic during the summer are crustal materials from fluvial areas and sea salt (Maenhaut et al. 1996; Xie et al. 2006; Friedman et al. 2009). Anthropogenic emissions from mining and industrial sources have also been observed (Xie et al. 2006; Friedman et al. 2009) as well as ship emissions (Xie et al. 2006), which are expected to become increasingly important as the sea-ice melts and new shipping routes emerge (Peters et al. 2011).

Other primary aerosols that have been observed in the Arctic are organics which are thought to be biological in origin. It has been speculated that these particles are emitted into the atmosphere from the ocean when bubbles burst through the sea surface microlayer (SML) (Bigg and Leck 2001; Russell et al. 2010). The SML is enriched in organic matter that is water insoluble (Hardy 1982), including microcolloids (Bigg et al. 2004) and exopolymer secretions (Chin et al. 1998). As the bubbles burst, these organic compounds can be transferred into the atmosphere and transported farther away.

Transmission electron microscopy of particles collected in the central Arctic has found that the atmospheric particles contain water insoluble cores that are partially soluble when exposed to xylene vapour. These organic particles can also be coated with sulphuric acid (H$_2$SO$_4$) or methane sulphonic acid (MSA) (Bigg and Leck 2001). Fourier transform infrared spectra of particles collected in the North Atlantic Ocean and Greenland Sea also detected an organic component with an alcohol functional group that correlated with sodium and wind speed, corroborating the primary nature of these particles. However, scanning transmission microscopy near edge x-ray absorption fine structure images suggest that these organic components are water soluble, since they are distributed evenly around the aerosol with potassium and other soluble ions (Russell et al. 2010).

Similar observations have been made further south, off the coast of Ireland. Ceburnis et al. (2008) used vertical gradient measurements to show that the ocean was a source of water insoluble organic mass and sea salt, but a sink for water soluble organic mass and
non sea salt sulphate. This is consistent with these water insoluble organic components being primary in nature. In general, the smaller particles are enriched in water insoluble organic mass and coincide with periods of high biological activity, suggesting that it is biological in origin (O'Dowd et al. 2004). Using nuclear magnetic resonance spectroscopy, the organic component of particles mechanically generated from sea water in the North Atlantic Ocean was identified to be similar to lipopolysaccharides (Facchini et al. 2008).

At this point, it is unclear whether this primary organic component of marine and Arctic aerosol is water soluble, since different techniques have conflicting conclusions. Nor is their chemical nature well characterised. More observations are still needed in order to understand the contribution of this source to aerosol mass and the prevalence of these compounds.

1.2.4. Secondary Arctic Aerosol Sources

One of the local sources of secondary aerosol is from marine biological input. Because the Arctic is mostly ocean, marine sources are relevant to the particle loading. As with other marine environments, the CLAW hypothesis is thought to describe at least part of the atmospheric chemistry in polar regions. Figure 1.4 shows the original negative feedback mechanism proposed by Charlson et al. in which an increase in solar radiation results in more biologically productive phytoplankton which will produce more dimethyl sulphide (DMS) in the ocean. DMS can volatilise into the atmosphere which will lead to increased sulphate particles and therefore increased CCN. This increase in CCN will result in a greater cloud albedo which will then lead to lower solar radiation and therefore stabilise the phytoplankton activity.
The CLAW hypothesis has led to active research in the past 20 years with no unified conclusion. Although each link that the hypothesis proposes does exist, they only occur under specific circumstances that are not always present at the same time (Ayers and Cainey 2007). For example, CLAW hypothesises that atmospheric DMS oxidises to form SO₂ which then further oxidises to form H₂SO₄. Sulphuric acid is a necessary precursor for particle nucleation and this increase in particle concentration is what increases cloud albedo through the first indirect effect (Charlson et al. 1987). However, DMS in the atmosphere can undergo many other reaction pathways to produce other compounds such as methane sulphonic acid or dimethylsulphoxide, both of which can condense onto existing particles (Davis et al. 1998) and would not necessarily nucleate and increase the particle number concentration (Kreidenweis et al. 1991).
One of the steps in the CLAW hypothesis is particle nucleation, which takes place when gas phase sulphuric acid molecules condense together to form a liquid particle. In general, if the existing particle concentration is high, then it is more energetically favourable for the gas phase sulphuric acid molecules to condense on the surface of the existing particles than to nucleate and form new particles. Although it is a step in the CLAW hypothesis, nucleation is rarely observed in the marine boundary layer (MBL) in non-polar regions (Kulmala and Kerminen 2008). Covert et al. (1996a) sailed 90 days in the Pacific ocean over two years from 55°N to 70°S and only observed nucleation once near Washington state (Covert et al. 1992) in an event that was attributed to subsidence of new particles formed in the free troposphere (Hegg et al. 1992). Background aerosol concentrations are generally too high and SO$_2$ concentrations too low for nucleation to be favourable in the MBL (Pirjola et al. 2000; Cainey and Harvey 2002). Instead, DMS is thought to be transported into the free troposphere where it oxidises (Davis et al. 1998). Because both the background concentrations and temperatures are lower in the free troposphere, nucleation is more likely to occur (Cainey and Harvey 2002). These nucleated particles then subside (Clarke 1993) and contribute to the stable aerosol distribution that is observed in the MBL (Raes 1995; Katoshevski et al. 1999).

In contrast, the polar MBL has lower background aerosol concentration and temperatures, making it more favourable for nucleation to occur (Pirjola et al. 2000; Cainey and Harvey 2002). Nucleation has been observed in Antarctica (Koponen et al. 2003; Asmi et al. 2010), Svalbard (Strom et al. 2009), northern Finland (Lihavainen et al. 2003) and the central Arctic Ocean (Wiedensohler et al. 1996). Although the studies in Antarctica (Koponen et al. 2003), northern Finland (Lihavainen et al. 2003) and the central Arctic (Wiedensohler et al. 1996) could be linked to air masses originating from the ocean, only in Antarctica did the authors conclude that the air had not originated from the free troposphere and no further work was done to determine whether the particles actually originated from marine emissions. As such, although nucleation is predicted to occur in the polar MBL, the question of whether it actually does occur still remains and its contribution to the Arctic aerosol loading is unknown. Continuous measurements at
polar sites could easily determine whether this was a significant contributor to Arctic aerosol mass.

A less-studied secondary aerosol source in the Arctic is from the lower volatility organic compounds formed from organic reactions. For example, isoprene, monoterpane and sesquiterpene oxidation products have been identified in aerosol samples collected at Alert, Canada (Fu et al. 2009). Isoprene is thought to have originated from more local phytoplankton emissions, while monoterpane and sesquiterpene originated from trees from more southern latitudes, although monoterpane emissions have, in other studies, been identified from phytoplankton (Yassaa et al. 2008). In another example, Ziemba et al. (2010) observed a particle growth event in Greenland which could not be reproduced using a model with sulphuric acid alone. Organic compounds, likely from the snow, were invoked to explain the additional aerosol mass.

The contribution of biological sources to Arctic aerosol is still poorly understood. Whether it is primary organic aerosol emitted directly from the ocean surface, secondary sulphur aerosol from DMS oxidation products such as H$_2$SO$_4$ or MSA, or secondary organic aerosol from the oxidation of isoprene or monoterpane emitted from phytoplankton, these sources are still inadequately characterised and their relative significance unknown. One of the goals of the research field in general is to identify the sources of Arctic aerosol and then to determine the contribution of each source to the observed aerosol. As Arctic temperatures increase, the summer sea ice will diminish and the significance of each source will change. Thus, it is important that we understand and characterise these sources now so that we can predict how they will change in the future with warmer summers.

1.2.5. Introduction to Arctic Work

To contribute towards our understanding of these issues, Chapter 2 of this thesis describes particle nucleation and growth events observed in Baffin Bay during late August to September 2008 on board the Canadian Coast Guard Ship *Amundsen*. Co-located atmospheric DMS measurements were high when nucleation-mode particles were
observed, suggesting that DMS from local marine organisms is the source that fuelled the nucleation and growth events. To test this hypothesis, an aerosol microphysics box model was initialised with parameters based on observed DMS mixing ratios and background aerosol concentrations to see if the observed particle nucleation and growth events could be reproduced. The idea was that if the model could not reproduce the measured observations, then DMS from marine organisms could not have been the only source of the particles. In this case, other sources, such as organic compounds or subsidence from the free troposphere, would need to be invoked in order to explain the observed nucleation-mode particles.

The findings from the model were that local DMS in the MBL could have been the sole source of these nucleation and growth events. This demonstrates that in the eastern Canadian Arctic, if there is sufficient atmospheric DMS and low enough background aerosol concentration, then particle nucleation and growth can take place. These findings can be contrasted to observations made in the Beaufort Sea during the fall of 2007 when no nucleation was observed. Some combination of lower solar radiation, less biological activity and different marine biology in the western Canadian Arctic inhibited particle nucleation and growth to take place. Our results are the first to link polar nucleation and growth events in the marine boundary layer to surface ocean sources and are the first observations of nucleation mode particles in the Canadian Arctic.

Another approach to learning more about aerosol sources is by measuring a time series of the chemical composition of the aerosol and then performing factor analysis or receptor modelling. Chapter 3 describes measurements made using the AMS aboard the icebreaker Oden in the central Arctic Ocean during August and early September, 2008. Positive matrix factorisation (PMF), a factor analysis technique, was performed on the entire aerosol mass spectrum and the aerosol mass was found to originate 33% from marine biogenic sources and 36% from continental sources. Although the marine biogenic factor was composed of sulphate and MSA, both of which are DMS oxidation products, it also had an organic component that was 15% of the mass. From this analysis alone, it is not possible to determine whether this organic fraction was primary or
secondary in nature and no conclusions can be drawn as to whether it is the primary organic aerosol fraction measured by other researchers, or whether it is formed from secondary processes. The remaining 31% mass was attributed to an unidentified factor that was 88% organic. This aerosol source could be either oceanic or continental and was largely independent of the inorganic aerosol levels.

These are the only AMS measurements made in the central Arctic Ocean at surface level to date. Although aircraft campaigns did occur in the Arctic free troposphere (e.g. Warneke et al. 2009), their measurements were often affected by long range transport, especially from biomass burning. In contrast, the findings from this work are more sensitive to local aerosol sources because these measurements were made in the boundary layer. The other novel aspect of this work is that PMF was performed on the entire aerosol mass spectrum, which allowed the inorganic aerosol, especially sulphate, to be apportioned to anthropogenic and biogenic sources. It also identified an organic fraction associated with each of the sources. This was necessary since both the inorganic and organic sources of Arctic aerosol are not well understood compared to continental regions where PMF is typically performed on only the organic part of the mass spectrum. This is because the inorganic sources of aerosol are already fairly well understood in continental regions compared to the organic sources (see next section).

1.3. **Continental Organic Aerosol Hygroscopicity**

In comparison to the Arctic, the sources of continental ultrafine and accumulation mode aerosol are better understood. The sources of inorganic particles, in particular, are fairly well constrained, with particulate sulphate and nitrate originating from the oxidation of anthropogenic SO₂ and NOₓ emissions, ammonium from agricultural sources and black carbon from combustion sources (Seinfeld and Pandis 2006). Primary organic aerosol sources include vehicular traffic, while secondary organic aerosol is formed from the condensation of oxidation products of volatile organic compounds originating from both anthropogenic and biogenic sources. The main focus of current aerosol research is on secondary organic aerosol because its impact on climate is the most uncertain (Kanakidou et al. 2005).
One aspect of the impact that the organic fraction of the aerosol has on climate is the ability of organic-bearing particles to activate as cloud condensation nuclei (CCN). Organic aerosol that are CCN-active, used in this thesis as particles < 200 nm in diameter that activate at a supersaturation of < 1%, could either contribute to the first indirect effect of aerosol causing cooling, or they could make the existing aerosol more easily lost to precipitation. At this point, it is unclear whether the organic component actually affects the radiation budget and if so, the relative contribution compared to inorganic aerosol. The focus of this work is to study the ability of the organic component of the aerosol to activate as CCN. This field has become much more widely researched since the commercialisation of the continuous-flow streamwise thermal gradient CCN counter by Droplet Measurement Technologies in 2006. The measurements made in this work all used a continuous-flow parallel-plate thermal gradient diffusion chamber custom built at University of Toronto, which operates slightly differently than the commercial instrument. The AMS has also helped expand this field of research since the organic aerosol component can now be quantified and incorporated into the CCN calculations. For example, aerosol chemical composition measured using an AMS to predict CCN concentrations only began in 2003 (Broekhuizen et al. 2006). However, unless the aerosol mass at sizes < 100 nm is high, the AMS is not as sensitive to border-line CCN-active particles and the composition of the smaller particles needs to be inferred from the larger-sized particles. More recent advances in factor analysis have provided the ability to characterise the chemical nature of the organic component so that its CCN-activity can be better predicted and/or parameterised. The next sections describe the theory, motivation and contribution of this research.

1.3.1. Köhler Theory

The thermodynamics of droplet activation of inorganic compounds is thought to be well understood (Pruppacher and Klett 1980) and is described using the Köhler equation (Köhler 1936), which accounts for the decrease in the equilibrium vapour pressure of water due to the presence of soluble species and the increase in the equilibrium vapour pressure of water due to the curved surface formed from a droplet. This is shown below:
\[ s = (S / 100\% + 1) = a_w \exp\left( \frac{4\sigma M_w}{\rho_w RTD} \right), \]  
(Kreidenweis et al. 2005) \textbf{Equation 1.1}

where \( s \) is the ratio of the partial pressure of water above the droplet to the equilibrium vapour pressure of water over a flat surface, or saturation ratio, and \( S \) is the supersaturation. In Equation 1.1, \( \sigma \) is the surface tension of the droplet, \( M_w \) is the molecular weight of water, \( \rho_w \) is the density of water, \( R \) the universal gas constant, \( T \) the temperature and \( D \) the diameter of the droplet. The activity of water, \( a_w \), is sometimes expressed using Raoult's Law as the mole-fraction of water \((X_w)\) as such:

\[ a_w = X_w = (1 - X_{\text{solute}}) \approx 1 - \frac{M_w}{\rho_w} \frac{n_{\text{solute}}}{\pi D^3 / 6}, \]  
\textbf{Equation 1.2}

where \( n_{\text{solute}} \) and \( X_{\text{solute}} \) are the moles and mole-fraction of the soluble species in the initial aerosol. It should be noted that Raoult's Law is only valid for ideal solutions, which is generally a good approximation by the time that the droplet has activated although perhaps not initially. A more accurate expression for \( a_w \) will be introduced in Equation 1.3. Typical supersaturations in clouds are 0.05 - 0.8 \% (Pruppacher and Klett 1980).

As the contribution of the organic component to ambient aerosol was recognised (Novakov and Penner 1993; Saxena and Hildemann 1996; Alves et al. 2002; Kiss et al. 2002; Zhang et al. 2007), the CCN-activity of model organic compounds began to be studied in the laboratory. The general conclusions from these studies were that the CCN-activity of pure organic aerosol and mixed organic / inorganic aerosol systems can be predicted if their water activities in Equation 1.1 are known (e.g. Cruz and Pandis 1997; Corrigan and Novakov 1999; Hori et al. 2003; Abbatt et al. 2005). This requires knowing the chemical composition of the aerosol as well as physical properties, such as the solubility, density and molecular weight, of all the components in order to calculate \( n_{\text{solute}} \) in Equation 1.2. Insoluble organic compounds, if effloresced (dried until the particles crystalise), are not CCN-active (Raymond and Pandis 2002; Pradeep Kumar et al. 2003; Huff Hartz et al. 2006), although the CCN-activity can greatly increase if 1-10\% by mass of a soluble inorganic compound such as ammonium sulphate or sodium chloride is
added (Raymond and Pandis 2003; Shantz et al. 2003; Bilde and Svenningsson 2004; Broekhuizen et al. 2004).

Another contribution that an organic component can have on CCN-activity is by partitioning from the bulk of the droplet to the surface. This could inhibit water uptake and some studies have found the droplet growth rate to be slower in the presence of organic compounds (Shantz et al. 2003; Ruehl et al. 2008; Shantz et al. 2010). It could also decrease the surface tension in the exponential term of Equation 1.1, which would result in a more CCN-active aerosol. Measurements of bulk solutions of organic compounds show a decrease in surface tension compared to water (Shulman et al. 1996; Facchini et al. 1999; Mircea et al. 2002; George et al. 2009) and CCN experiments of biomass burning aerosol have shown that the CCN-activity is greater for fractions with inorganic salt and hydrophobic fractions than for inorganic salt alone (Asa-Awuku et al. 2008). However, CCN measurements of sodium chloride / sodium dodecyl sulphate aerosol have been unable to observe such a strong effect and instead see an overall decrease in CCN-activity due to a decrease in soluble ions when the surfactant partitions to the surface (Li et al. 1998; Sorjamaa et al. 2004; Prisle et al. 2010). At this point, it is unclear how the surface tension in a droplet changes in the presence of a surface-active organic.

Although laboratory studies can predict the CCN-activation of organic compounds, they require the exact chemical composition of the aerosol. Because the organic component of ambient aerosol can consist of numerous compounds which can be difficult to identify and quantify (Saxena and Hildemann 1996; Jacobson et al. 2000), simplifying assumptions need to be made. The next section describes a modified version of Köhler theory which does not require all the physical properties of each of the aerosol components, and the section after (Section 1.3.3) describes some of the assumptions that have been made to predict the CCN-activity of the ambient organic aerosol fraction.
1.3.2. κ-Köhler Theory

In order to simplify the calculation of the activity of water for ambient aerosol, κ-Köhler theory was used in this study. In this modified Köhler theory (Petters and Kreidenweis 2007; Petters and Kreidenweis 2008), the activity of water is represented as:

\[ a_w = \frac{D^3 - D_i^3}{D^3 - D_i^3 (1 - \kappa)}, \]  

(Petters and Kreidenweis 2007) \hspace{1cm} \text{Equation 1.3}

where \( D \) is the wet droplet diameter, \( D_i \) is the initial dry particle diameter and \( \kappa \) is the hygroscopicity parameter of the aerosol. The advantage of this approach is that it incorporates the density, molecular weight and solute non-idealities of all the soluble species into the hygroscopicity parameter, making it more suitable than the original Köhler equation for incorporating into climate models. Because of its simplicity, many researchers have started to use \( \kappa \) to describe aerosol hygroscopicity for laboratory measurements (e.g. Duplissy et al. 2008; Wex et al. 2009), field measurements (e.g. Rose et al. 2008; Jimenez et al. 2009; Chang et al. 2010; Padro et al. 2010) and models (Pringle et al. 2010).

The overall \( \kappa \) of an aerosol with multiple components can be determined by finding the volume-weighted average of the \( \kappa \) of the individual components and the details of implementation will be discussed in Chapter 4 and Chapter 5. Although \( \kappa \) can be determined for inorganic components from thermodynamic tables (e.g. Clegg et al. 1996), \( \kappa \) for ambient organic aerosol is not well known and one of the goals of Chapter 4 is to better constrain it.

Because this discussion includes studies both before and after \( \kappa \) was introduced, the terms "hygroscopic" and "soluble" will both refer to CCN-active compounds (particles < 200 nm in diameter that activate at a supersaturation of < 1%), whereas the terms "non-hygroscopic" and "insoluble" will refer to CCN-inactive compounds. In reality, a compound could be soluble but non-hygroscopic (e.g. fulvic acids which are soluble but
high in molecular weight (Petters et al. 2009)), however, this will facilitate the comparison of different studies.

1.3.3. Köhler Theory for Ambient Organic Aerosol

The study of CCN under ambient conditions usually involve aerosol-CCN closure studies in which the measured CCN concentrations are compared to concentrations predicted using Köhler theory based on either assumed or measured aerosol chemical composition and size distributions. Agreement between the predicted and measured CCN concentrations is considered to validate the assumptions used in the calculation. Early studies that relied on filter analysis for chemical composition either assumed that there was no organic component (Liu et al. 1996; VanReken et al. 2003) or assumed that a fraction of the mass was made up of insoluble organics (Cantrell et al. 2001; Roberts et al. 2002) in order to achieve closure.

Later closure studies that used the AMS to measure aerosol chemical composition either assumed that the organic component was completely insoluble at polluted sites (Broekhuizen et al. 2006; Medina et al. 2007), or assumed that a constant fraction of the organic component was soluble in more remote locations (Chang et al. 2007; Wang et al. 2008; Gunthe et al. 2009). In the case of the latter studies, there was no consideration for changes in the chemical nature of the organic component.

An ongoing challenge in these types of studies is discerning the mixing state of the aerosol. Incorporating the mixing state has been found to be especially important at urban locations where the composition of particles with activation diameters that correspond to the supersaturation of the CCN counter (< 100 nm) can be quite different than the overall aerosol composition (Broekhuizen et al. 2006; Cubison et al. 2008). While in the past mixing state has been monitored using hygroscopic tandem differential mobility analysers have been used to determine the mixing state, however, recent work using a CCN counter has also been able to determine the mixing state (Rose et al. 2010).
One of the goals of Chapter 4 is to characterise the organic component in such a way that would on the one hand adequately describe its hygroscopicity but on the other would not require a detailed listing of every organic compound since this would make it computationally challenging to predict the CCN-activity. Two methods are explored in that chapter. The first method uses factor analysis on the organic component to characterise oxygenated and unoxygenated factors that are assumed to be hygroscopic and non-hygroscopic, respectively. The second method assumes a relationship between the degree of oxygenation of the organic component based on its mole ratio of atomic oxygen to atomic carbon and the organic component's hygroscopicity. Both of these methods were found to be suitable for describing the organic aerosol component's hygroscopicity even as the nature of the organic component changed throughout the study. At the time of this study, this work was the first attempt to characterise the hygroscopicity based on the organic component's oxygenation for supersaturated conditions. Since then, a laboratory study of secondary organic aerosol (Massoli et al. 2010) and an ambient study at Mexico City (Padro et al. 2010) have used similar approaches.

1.3.4. Importance of the Hygroscopicity of the Aerosol Organic Fraction

The results from early laboratory (Section 1.3.1) and field (Section 1.3.3) studies highlight two conditions under which the CCN-activity of the organic component is not important:

1) when the aerosol is mostly inorganic, since the inorganic component will dominate activation and the hygroscopicity of the organic component will not significantly affect the CCN-activity of the overall aerosol; and

2) when the organic component of the aerosol is non-hygroscopic, in which case it can be simply assumed as such. This frequently occurs in urban locations where the nucleation mode is composed of organics that are likely from primary sources and
therefore hydrocarbon-like (Zhang et al. 2005) and not CCN-active (Raymond and Pandis 2002).

Since the goal of this overall work is to observe the effect of a CCN-active organic aerosol component in an ambient aerosol, locations of study had to be chosen such that the aerosol particles were primarily composed of organic compounds that were CCN-active. To this end, studies were conducted at Egbert, Ontario, a rural site (Chapter 4) and Whistler, British Columbia, a forested site (Chapter 5). Both of these sites are influenced by organic-rich aerosol that were hygroscopic, with the aerosol originating from biogenic sources, either from the boreal forests in Ontario, or the coniferous forests in BC. In addition, Egbert is also subject to aged anthropogenic emissions, which provides a different type of organic aerosol.

Chapter 5 summarises the closure studies that have been conducted in our group and explores the importance of understanding the hygroscopicity of the ambient organic component at continental sites. While it may seem that the two conditions described above are sometimes true, Chapter 5 gives examples of locations for which the ambient aerosol is composed primarily of hygroscopic organic compounds. These locations include urban, downwind of urban and remote locations, suggesting that the importance of the hygroscopicity of the organic component is not only restricted to forested sites. These findings put all the CCN work from our group in perspective and illustrate their contribution in our understanding of organic aerosol hygroscopicity.

1.4. Summary

The overall goals of this research were to investigate the sources of Arctic aerosol and the hygroscopicity of continental organic aerosol. In particular, the questions that are addressed are:

1. Can particles nucleate in the marine boundary layer from DMS originating from the surrounding ocean in the Canadian Arctic?
2. What is the aerosol chemical composition in the central Arctic Ocean and what are their sources?
3. How can the ambient continental organic aerosol fraction be described such that its hygroscopicity can be predicted?
4. Under what conditions can the hygroscopicity of the organic fraction affect the hygroscopicity of the ambient aerosol?

The findings from the Arctic work will contribute towards our understanding of the sources of particles in this remote region of the world, whether they are locally nucleated particles, in the case of the Canadian Arctic, or transported, in the central Arctic Ocean. For the organic aerosol hygroscopicity, these studies propose a simplified method of characterising the hygroscopicity of the organic component based on its degree of oxygenation such that the exact composition of the aerosol is not needed in models. At the same time, these results determine where the hygroscopicity of the organic is important. These findings can be applied to other locations where CCN studies have not been conducted, such as the Arctic, to determine where further hygroscopicity studies are needed. All of these studies contribute to our understanding of the effects that aerosol can have on climate.

1.5. References


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Chapter 2

Relating Atmospheric and Oceanic DMS Levels to Particle Nucleation Events in the Canadian Arctic

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2.1. Introduction

Sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) is crucial to new particle formation. In continental regions H\textsubscript{2}SO\textsubscript{4} is typically formed from the oxidation of anthropogenic SO\textsubscript{2}, while in the marine boundary layer (MBL), H\textsubscript{2}SO\textsubscript{4} is thought to primarily originate from the oxidation of dimethyl sulphide (DMS) produced through the planktonic food web (Bates et al. 1987; Shaw 1989; Yin et al. 1990\textit{a}; Yin et al. 1990\textit{b}; Kreidenweis et al. 1991). However, whereas nucleation is often observed in continental and coastal regions, new particle formation is rarely observed in the MBL and is thought to be an insignificant particle source (Raes 1995; Covert et al. 1996; Katoshevski et al. 1999; Pirjola et al. 2000; Phinney et al. 2006; Kulmala and Kerminen 2008; Yu et al. 2010).

Modelling studies of low to mid-latitude marine nucleation have found that SO\textsubscript{2} concentrations are too low and condensation sinks too high for nucleation to be favourable and speculate that the primary source of marine aerosol is nucleation from DMS transported to the free troposphere (Hegg et al. 1992; Covert et al. 1996; Cainey and Harvey 2002) which subsides, resulting in the relatively constant aerosol distribution observed in the MBL (Raes 1995; Katoshevski et al. 1999). For example, Hegg et al. (1992) could only reproduce the nucleation rate observed in the MBL by Covert et al. (1992) off the coast of Washington if the higher SO\textsubscript{2} concentrations from the free troposphere were used in their model. Similarly, Cainey and Harvey (2002) used aerosol dynamics box models to model three MBL sites ranging from 1°N to 41°S and did not predict any nucleation because SO\textsubscript{2} concentrations were too low and condensation sinks too high. However, they did predict nucleation in the tropical free troposphere and possibly the Eastern Antarctic Plateau where required SO\textsubscript{2} concentrations were 2-3 orders of magnitude lower. All of these studies concluded that nucleation in the MBL did not contribute significantly to the background marine aerosol. However, our understanding of ambient nucleation has improved greatly in the last 10 years on both the modelling and observation fronts. As such, newer nucleation schemes could find that nucleation is now predicted to be favourable and significant in MBL regions of the globe.
The exception to the lack of nucleation in the MBL is in polar regions (Strom et al. 2009; Asmi et al. 2010). Examples include summertime in Alboa, Antarctica, where nucleation was observed when the air had been influenced by the coast but not when it was primarily from the continent (Koponen et al. 2003). Back trajectories from this study did not indicate any vertical motion, suggesting that the air had not subsided. Similarly, in Pallas, Finland (68°N), nucleation was only observed when clean marine air from the Arctic or North Atlantic Oceans was sampled (Lihavainen et al. 2003). Finally, Wiedensohler et al. (1996) linked ultrafine particles observed in the central Arctic Ocean pack ice to either DMS from the open ocean or from the free troposphere using principal component analysis and partial least squares regression.

A thorough study by Pirjola et al. (2000) used a Lagrangian based sectional box model and binary and ternary nucleation theory to compare nucleation under marine and polar marine conditions. This study found that nucleation is favourable under polar marine conditions where particle concentrations and temperatures are low. In these runs, the atmospheric DMS concentrations required were 100 - 400 pptv. In contrast, simulating nucleation under marine conditions at lower latitudes in the model proved to be more difficult, primarily due to the higher particle concentrations and condensation sink.

The overall effect of aerosols on climate is still highly uncertain, especially in the Arctic where particles can warm the surface, as opposed to lower latitudes where they have a net cooling effect (Shupe and Intrieri 2004). As the temperature in the Arctic is increasing twice as quickly as the rest of the earth (ACIA 2004), it is urgent that our understanding of aerosol sources and processes improves. In particular, the rapid loss of the summer multi-year and first-year sea ice (Maslanik et al. 2007), and the corresponding areal increase in ice-free waters suggest that nucleation sources that originate from oceanic precursors may increase as well with climate warming.

This study reports the first observations of nucleation mode particles (NMP) simultaneous with increased atmospheric DMS levels in the Canadian Arctic archipelago. Higher DMS concentrations in the ocean surface waters (hereafter referred to as “aqueous
DMS”) at the same time suggest that these NMP originated from marine biogenic sources. In order to test the hypothesis that these NMP formed from DMS oxidation in the MBL, we use a model of aerosol nucleation and microphysics to show that the particle formation and growth can be accounted for purely by DMS oxidation. However, we cannot exclude the possibility of other processes or species contributing to the particle formation.

2.2. Measurements

The research cruises took place on the Canadian Coast Guard Ship *Amundsen* from 29 September to 7 November 2007 and 29 August to 2 October 2008 as a part of the Canadian IPY Arctic SOLAS and CFL programs. The cruise ranged from Baffin Bay to the Beaufort Sea during 2007 while in 2008, measurements started in Gjoa Haven, Nunavut (NU) in the Eastern Canadian Archipelago and ended near Iqaluit, NU. A map of the routes can be seen in Figure 2.1. All times presented are in co-ordinated universal time (UTC).

![Figure 2.1 - Route of CCGS Amundsen during the two transits, coloured by date.](image-url)
Atmospheric instruments were housed in a shed on the top deck of the ship with an inlet that was approximately 18 m above sea level. A scanning mobility particle sizer (SMPS, TSI 3080, 3081, 3010) measured the aerosol size distributions between 10 and 500 nm with a sample time of 5 minutes and a sample flow and sheath flow of 1 L and 5 L, respectively. An ultrafine condensation particle counter (UCPC, TSI 3025A) measured the total particle concentration > 3 nm. We interpret the difference between the UCPC concentration and the total value measured by the SMPS as an indication of the presence of particles between 3 and 10 nm. Both of these aerosol instruments sampled from a stainless steel tube (9.5 mm outer diameter) with < 1.8 s residence time.

Atmospheric DMS was measured using a proton-transfer-reaction mass spectrometer (PTR-MS, Ionicon Analytik) which sampled off a 10 m long, 6.3 mm outer diameter, Teflon line in the shed at the top of the ship. A sample residence time of \( \approx 2.5 \) s was calculated from a 3.0 L min\(^{-1}\) flow rate. This instrument ionises incoming gas-phase molecules by transferring a proton from H\(_2\)O\(^+\), which is formed through a discharge ion source. The protonated DMS is then detected using a quadrupole mass spectrometer at a mass-to-charge ratio of 63. Backgrounds were measured for 5 minutes every hour by diverting the sample air through a platinum catalyst heated to 350°C to remove ambient volatile organic compounds. A detailed description of the operation of this instrument can be found in the literature (de Gouw and Warneke 2007) as well as the specific operation during the 2008 transit (Sjostedt et al. manuscript in preparation).

Ocean surface DMS was measured by sampling seawater from Niskin-type bottles into 25 mL bottles with no headspace and hermetically sealing the bottles. DMS was concentrated using purge and trap and quantified using a gas chromatograph (Varian CP-3800) with a capillary column (CP-Sil 5CB fused silica, 30 m x 0.32 mm, 4 \( \mu \)m film thickness) and a pulsed flame photometric detector. Calibration was performed using a permeation tube standard (Kin-Tek Laboratories) at 40°C and diluted with helium. Further details of the ocean surface DMS sampling during 2007 and 2008 can be found in Luce et al. (2010) and Motard-Côté (in preparation), respectively.
Solar radiation was measured starting on 10 October in 2007 and 6 September in 2008 on the top deck of the ship using a pyranometer (Eppley, model PIR). The sensor was scanned at 2 s intervals and data stored as 1 minute averages by a micrologger (Campbell Scientific, model CR23X).

2.3. Observations

2.3.1. General Observations

Surface water DMS concentrations during the 2008 transit ranged from 0.5 to 4.8 nM and for corresponding times, loosely correlate with atmospheric DMS mixing ratios (see 2nd panel in Figure 2.2). High aqueous DMS levels show that the ocean was biologically active during the 2008 transit, suggesting that the atmospheric DMS could have originated from local sources. The ratio of DMS concentration in the air to DMS concentration in the water ranged from 0.001 to 0.008 (unitless). Since the Henry's law constant for DMS at 273 K in seawater is higher (0.028 (Wong and Wang 1997)), these results are consistent with the ocean being the source of atmospheric DMS observed during this cruise. This is supported by work done by Rempilo et al. (2011) who calculated a DMS flux of 0.2 – 1.3 μmol m$^{-2}$ d$^{-1}$ from the ocean surface during the cruise. However, it is also possible that the atmospheric DMS could have originated from more southern latitudes since it has an atmospheric lifetime against OH oxidation ranging from 2.2 - 22 days (for [OH] = 10$^{5}$ - 10$^{6}$ molecules cm$^{-3}$) (Hynes et al. 1986).
Figure 2.2 - Time Series of the 2008 Cruise.  
Cosine of the solar zenith angle and radiation (top panel), DMS air and ocean surface levels (second panel), condensation sink and concentrations of particles between 3 and 10 nm (3rd panel) and size distributions (bottom panel) during the 2008 cruise.

Figure 2.3 – Time Series of the 2007 Cruise.  
Cosine of the solar zenith angle and radiation (top panel), condensation sink and concentrations of particles between 3 and 10 nm (middle panel) and size distributions (bottom panel) during 2007.
2.3.2. Observations of Small Particle Events

Figure 2.2 and Figure 2.3 show the aerosol size distribution, atmospheric DMS mixing ratio and solar radiation for the 2008 and 2007 transits, respectively. Times when ship emissions are suspected (UCPC concentrations > 20 000 particles cm\(^{-3}\) or a maximum 1 s UCPC measurement > two times the minimum within a 5 min sampling window) are excluded. These figures also include the calculated reduced condensation sink (m\(^{-2}\)), which can be interpreted as a measure that the gas phase molecules will condense on the surface of existing particles and is given by Kerminen et al. (2004):

\[
CS' = \frac{1}{2} \sum_j \frac{d_j N_j (1 + Kn_j)}{1 + 0.377Kn_j + 1.33Kn_j(1 + Kn_j)},
\]

where \(d_j\) is the diameter of the particle at the \(j^{th}\) size bin, \(N_j\) is the particle number concentration at that size bin and \(Kn_j\) is its Knudsen number and is equal to \(2\lambda/d_j\), where \(\lambda\) is the mean free path of air, the average distance a molecule travels before colliding with another molecule.

During 2008, NMP were observed during three periods that coincided with increases in DMS mixing ratios to > 150 ppt and condensation sink < 5 m\(^{-2}\). The size of these small particles (< 30 nm) suggests that they had recently nucleated.

The first distinct period shows particle growth starting on 27 Aug 2008 12:00 and ending on 3 Sep 2008 00:00 when the ship anchored at Resolute, NU (74.72°N, 95.12°W). It was interrupted on 30 Aug 2008 12:00 when the CCGS Amundsen stopped at Kugaaruk, NU (68.52°N, 89.86°W) but resumed when it re-entered the Gulf of Boothia on 1 Sep 2008 03:00. Particle growth was observed in this time period but the smallest particles (less than 10 nm) were relatively low in concentration, probably having formed earlier in a region not sampled by the ship's path.
The second and third periods occurred at 7 Sep 2008 21:00 to 10 Sep 2008 3:00 and 19 Sep 2008 12:00 to 25 Sep 2008 6:00, respectively. During both of these periods, particles < 30 nm were observed with no evidence of further growth. In contrast to the first event, the number of particles between 3 and 10 nm also increased significantly to > 800 cm\(^{-3}\), suggesting that nucleation had recently occurred, although it was not followed by growth beyond 30 nm. Furthermore, HYSPLIT back trajectories show that the air originated from the northwest and northeast during these two periods (Draxler and Rolph 2010; Rolph 2010) when the air had passed over regions of pack ice (Figure 2.4a and c). This air was likely cleaner with lower condensation sink, allowing particle formation to occur on a local to regional scale. These back trajectories also show that the source of DMS during these periods likely originated from the surrounding ocean since the air had previously passed over more northerly, ice-covered locations.
These two periods were separated by 9 days of significantly higher levels of background aerosol with modes at 30 and 150 nm, which resulted in an increased condensation sink. In addition, the solar zenith angle throughout the cruise (Figure 2.2, top panel), calculated based on the ship's location and day of year, compared with the measured total radiation, suggests that the period between these last two nucleation events was cloudy, leading to lower OH production rates. HYSPLIT back trajectories show that the air was from the southeast (Figure 2.4b), having descended from Greenland to a large degree. This combination of potentially lower OH production and increased background aerosol likely contributed to the suppression of particle formation.

During the 2007 study, particles < 20 nm were rarely observed. The two small periods of increased particle concentration between 3 and 10 nm in size (Oct 9 and 12) maximised at roughly 100 cm$^{-3}$, low relative to the 2008 cases that gave rise to concentrations of up to 1000 cm$^{-3}$. The most likely reason for the lower prevalence of nucleation events during the 2007 cruise is that it took place one month later when solar radiation was lower resulting in lower OH production rates and lower ocean surface DMS concentrations (0.05 to 0.80 nmol L$^{-1}$ in 2007 (Luce et al. 2010) compared to 0.52 to 4.75 nmol L$^{-1}$ in 2008 (Motard-Côté et al. In preparation)). This can be seen in Figure 2.5, which shows the probability distribution function of the measured radiation for the 2007 and 2008 cruises. The 2008 transit received more insolation which should have increased the OH production rates as well as phytoplankton activity. The average radiation for the 2$^{nd}$ and 3$^{rd}$ nucleation events combined was 52 W m$^{-2}$, which is greater than 85% of the radiation measurements made during the 2007 transit. However, the sampling areas during these two studies also differed greatly. Since the oceanographic conditions of the Beaufort Sea (2007 transit) and the Baffin Bay (2008 transit) are different, the biological activity would also be expected to differ, which could also contribute to the presence of NMP.
Figure 2.5 – Probability distribution function of solar radiation for the 2007 and 2008 transits. The solar radiation during the 2007 transit (red) had a greater probability of being < 50 W m\(^{-2}\) while in 2008 (black) it had a greater probability of being > 50 W m\(^{-2}\). Dotted and dashed vertical line represents the average radiation during the 2nd and 3rd nucleation periods, respectively.

We also note that at a later time in the 2008 cruise, from 26 Sep to 1 Oct, the condensation sink was also low and yet no nucleation events were observed. However, at this time the DMS mixing ratios were especially low. These observations imply that a combination of high sunlight, low condensation sink and sufficient DMS is required for nucleation and growth events to be observed, as consistent with prior understanding.

2.4. Modelling of nucleation and growth

In order to gauge whether the NMP can be explained by the oxidation of DMS, a microphysics box model is used to address the following questions:

- Are the aerosol size distributions during the nucleation and growth events consistent with known processes involving only DMS?
- Is there a requirement for other chemical species in the nucleation and growth process, as constrained by the observations and our knowledge of the kinetics and mechanisms of these processes?
2.4.1. Model Description

To determine if the sulphate generated from DMS oxidation could potentially account for the measured nucleation and growth, we used a box-model version of the TwO-Moment Aerosol Sectional (TOMAS) microphysics algorithm (Adams and Seinfeld 2002; Pierce and Adams 2009b; Pierce and Adams 2009a; Riipinen et al. 2011). This version of TOMAS is configured to simulate the number of particles and mass of hygroscopic aerosol (e.g. sulphate, sea salt, oxidised organics) within 44 log-normally spaced size bins that span dry diameters of 0.6 nm and 10 μm. TOMAS calculates the nucleation, condensation and coagulation that shape the aerosol size distribution. The model includes gas-phase sulphur chemistry (DMS, SO₂ and H₂SO₄) based on Chin et al. (1996), which has been shown to perform well in Arctic environments compared to other schemes (Karl et al. 2007). Nucleation is modelled using activation nucleation theory (J_{nuc} = A[H₂SO₄]) where J_{nuc} is the nucleation rate and A is an empirical parameter (Sihto et al. 2006).

The A factor for activation nucleation is not known for the Arctic environment, thus we perform simulations with A factors ranging from 10^{-10} to 10^{-6} s⁻¹ (see Table 2.1). The model is initialised with a pre-existing aerosol size distribution (mode = 150 nm, σ = 2, number concentration variable to represent measured condensation sink values) and DMS mixing ratios varying across the range of measured values (Table 2.1). In this way, we can test the sensitivity of nucleation and growth to these parameters. The initial aerosol is assumed to have the properties (density and hygroscopic growth) of ammonium bisulphate. Changing the assumed aerosol density and hygroscopic properties across potential values has a much smaller effect on nucleation/growth than varying the pre-existing aerosol size distribution across the range of values we are testing. We assume that the box passes over an active plankton bloom followed by a region with zero or low DMS emissions, thus there is no source of DMS into the box after initialisation. SO₂ and H₂SO₄ vapour concentrations were assumed to be initially zero. No other condensable species other than H₂SO₄ (e.g. organics) are included in the model. The OH concentration ([OH]) was assumed to be constant, but we perform simulations with several typical diurnal-average values for the Arctic (Table 2.1) and Antarctic (Jefferson
et al. 1998). Simulations were run for 48 hours, which is representative of the longest we expect initial ambient conditions to remain relevant, especially as the ship was moving throughout the study. All possible permutations of model inputs (Table 2.1) are simulated, for a total of 180 simulations. In contrast to other modelling studies, we begin with DMS oxidation because SO$_2$ and H$_2$SO$_4$ were not measured during the two cruises.

Table 2.1 – Range that model parameters were varied independent of each other. The condensation sink was calculated from the background aerosol concentration.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tested parameter values</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (s$^{-1}$)</td>
<td>$10^{-10}$, $10^{-9}$, $10^{-8}$, $10^{-7}$, $10^{-6}$</td>
</tr>
<tr>
<td>Initial DMS mixing ratio (pptv)</td>
<td>100, 200, 400</td>
</tr>
<tr>
<td>[OH] (molecules cm$^{-3}$)</td>
<td>$1 \times 10^5$, $3 \times 10^5$, $1 \times 10^6$</td>
</tr>
<tr>
<td>Background aerosol concentration (cm$^{-3}$)</td>
<td>10 [0.70], 20 [1.41], 100 [7.0], 500 [35.2]</td>
</tr>
<tr>
<td>[Condensation Sink (m$^{-2}$)]</td>
<td></td>
</tr>
</tbody>
</table>

There are many uncertain input parameters that are varied in the model; however, the overall purpose of the model runs is to test if DMS could have driven the aerosol nucleation and growth under the conditions measured during the experiment. If under even the most favourable measured conditions for DMS-driven nucleation and growth (high DMS mixing ratios, low pre-existing aerosol concentrations, most intense solar radiation) the model cannot produce both the number of nucleated particles and their growth, another species must be contributing to the nucleation and/or growth of the aerosols, or the particles are not formed locally. On the other hand, if there are sets of input parameters that do reproduce the nucleation and growth, it is possible that DMS is the dominant species involved with the nucleation and growth. This does not, however, rule out the possibility of other species contributing due to uncertainties in the actual values of the inputs.
2.4.2. DMS Oxidation

In the atmosphere, the oxidation of DMS takes place with OH via abstraction or addition, with the former favoured at warmer temperatures (Hynes et al. 1986). Figure 2.6 shows one of the possible mechanisms by which DMS can oxidise to form H$_2$SO$_4$ via OH abstraction.

\[
\begin{align*}
\text{H}_3\text{CSCH}_3 & \xrightarrow{\text{OH}} \text{H}_3\text{CSCH}_2 & \text{O}_2 / \text{NO} & \rightarrow \text{H}_3\text{CSCH}_2 & \rightarrow \text{H}_3\text{CS} & \xrightarrow{\text{O}_2} \text{H}_3\text{CSO}_2 & \rightarrow \text{H}_3\text{C} + \text{SO}_2 \\
\text{SO}_2 & \xrightarrow{\text{OH}} \text{HSO}_3 & \text{O}_2 & \rightarrow \text{SO}_3 & \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{SO}_4 (g) & \rightarrow \text{H}_2\text{SO}_4 (p)
\end{align*}
\]

Figure 2.6 - DMS Oxidation Scheme
(Yin et al. 1990b; Davis et al. 1998; Finlayson-Pitts and Pitts Jr. 2000; Seinfeld and Pandis 2006)

SO$_2$ has also been observed in chamber studies to form from the addition of OH onto the sulphur atom in DMS (Arsene et al. 1999). In either case, the exact mechanism that takes place in the atmosphere depends on the conditions and most intermediate species can only be speculated based on the end products. The nucleation of H$_2$SO$_4$ from gas phase into particle phase in the last step is still the subject of much research.

The mechanism in the model simplifies all of this chemistry and only considers the reaction DMS + OH $\rightarrow$ SO$_2$, with a 75% efficiency for the OH addition branch and 100% efficiency of SO$_2$ formation for the abstraction branch (Chin et al. 1996). SO$_2$ then oxidises to form H$_2$SO$_4$ which is the only compound that contributes to particle nucleation and growth in the box model. To date, H$_2$SO$_4$ is still the main compound thought to drive particle nucleation in general (Kulmala and Kerminen 2008), and other products of DMS oxidation are not thought to significantly contribute to the particle nucleation process. As such, H$_2$SO$_4$ is the only species included in our model. It is possible that other oxidation products could contribute to particle growth by condensing onto the newly nucleated particle surface, however, these species are not included in our
aerosol box model for simplicity. This would affect our final predicted particle distributions by increasing the mode diameter.

2.4.3. Model Results and Discussion

A simulated nucleation event using TOMAS is shown in Figure 2.7, assuming that the initial condensation sink is 0.70 m$^{-2}$, A factor is $10^{-10}$ s$^{-1}$, DMS mixing ratio is 400 pptv and [OH] is $10^6$ molecules cm$^{-3}$. As shown in this example, it is possible, under favourable conditions, for nucleation followed by growth to 80 nm to occur. In this analysis, simulations that resulted in an increase in the number concentration of particles larger than 10 nm are classified as nucleation and growth events. All model runs that resulted in nucleation and growth are shown as coloured symbols in Figure 2.8. The vertical axis in this figure represents the number of nucleated particles at the end of the simulation (i.e. the increase in the number of particles $> 10$ nm) and the horizontal axis represents the diameter of the mode. The grey bars shown in the background are measured number concentrations and modes from the three event periods in 2008.

Figure 2.7 - Simulated aerosol size distributions (dN/dlogDp) showing nucleation and growth from the box model.

The A factor was $10^{-10}$ s$^{-1}$, initial DMS mixing ratio was 400 pptv, condensation sink was 0.70 m$^{-2}$ and [OH] was $10^6$ molecules cm$^{-3}$. 
Given the assumptions made in our model and described above, Figure 2.8 shows that there are conditions under which sulphate from DMS oxidation can account for the nucleation and growth observed during the 2008 study. In general, the conditions required are an A factor $\leq 10^{-8}$ s$^{-1}$, $[OH] \geq 3 \times 10^5$ molecules cm$^{-3}$ and background particle concentrations of $\leq 100$ cm$^{-3}$. In our simulations, higher A factors tend to promote too much nucleation and not enough growth, resulting in too many particles that are smaller than observed.
Figure 2.8 - Nucleated number concentration and modal diameter for different model runs. Closed and open symbols are for \([\text{OH}] = 10^6\) and \(3 \times 10^5\) molecules cm\(^{-3}\), respectively. The shape of the symbol represents the atmospheric DMS mixing ratio (pptv) and the colour represents different A factors (s\(^{-1}\)). Shaded gray bars represent the observed number concentration and modal diameter during the three periods, with the lighter bars representing the first event and the darker bars representing the 2nd and 3rd events. Panel a) is for a background particle concentration of 10 and 100 cm\(^{-3}\) while panel b) is for background concentrations of 20 cm\(^{-3}\).

The observations in Figure 2.8 are coloured by date, with the dark gray bars representing the second and third periods in which NMP were observed, when the particles rarely grow beyond 30 nm. For example, for a background particle concentration of 10 particles cm\(^{-3}\), the model can reproduce the observed aerosol properties if \([\text{OH}] = 3 \times 10^5\) molecules cm\(^{-3}\), the A factor \(\leq 10^{-9}\) s\(^{-1}\) and DMS(g) mixing ratio \(\leq 200\) pptv (Figure 2.8a). As can be seen from Figure 2.8a and b, there are several combinations of parameters that could result in the small particles observed. Since the SMPS has a lower cut point of 10 nm, measured particle modes of 10-15 nm may correspond to modelled cases with modes < 10 nm whose distribution extends to sizes larger than 10 nm (e.g. modelled particles with a mode of 8 nm will have a tail that extends to > 10 nm where it would be observed by the SMPS). This is supported by the difference in the UCPC and SMPS concentration (Figure 2.2, light blue dots in 2\(^{nd}\) panel), which suggests that smaller particles were present, although not detected by the SMPS. In addition, the particles may
have had < 48 hours to nucleate and grow and the observations may correspond to the initial stages of particle growth. As such, parameters that result in greater final concentrations and modal diameters, i.e. A factor of $10^{-8} - 10^{-6}$ s$^{-1}$, could also account for our observations. In contrast, in order to reproduce the growth event observed during the first period (30 Aug to 3 Sep 2008), shown in Figure 2.8 as light gray bars, background particle concentrations $\leq 20$ cm$^{-3}$, $[\text{OH}] = 10^6$ molecules cm$^{-3}$ and A factors of $10^{-10} - 10^{-9}$ s$^{-1}$ are needed.

The A factors found to fit observations are 1-4 orders of magnitude lower than observations at continental sites (Sihto et al. 2006; Riipinen et al. 2007) and laboratory experiments (Sipila et al. 2010). Korhonen et al. (2008) used an A factor of $2 \times 10^{-6}$ s$^{-1}$ for the Arctic in a global chemical transport model but also overpredicted the number concentration in the summer nucleation mode. Similarly, Yu et al. (2010) used a global model with an A factor of $10^{-6}$ s$^{-1}$ and overpredicted particles with diameters $> 4$ nm in tropical and polar oceans.

Earlier nucleation theories assumed that nucleation depended on H$_2$SO$_4$, water vapour and/or ammonium (Kulmala and Kerminen 2008) and recent research has shown that it can also depend linearly on the concentration of low-volatility oxygenated organic compounds (Metzger et al. 2010). It is likely that the overall nucleation rate is dependent on all of these gases, but that everything but H$_2$SO$_4$ is in excess in most locations, making nucleation the most sensitive to its presence. In this scenario, the A factor really represents a product of the concentration of all of these other gases and it is possible that in the Arctic, they are present in lower concentrations than at continental sites where higher A values have described nucleation rates. If, for example, the nucleation mechanisms measured by Metzger et al. (2010) are relevant in the Arctic, then smaller low-volatility organic concentrations would lead to a lower A factor. However, as Arctic nucleation mechanisms are still poorly understood, other factors that inhibit aerosol nucleation but favour growth may be present.
2.5. Conclusions and Atmospheric Implications

This study reports the observation of nucleation in the Arctic MBL coinciding with high atmospheric DMS during the summer of 2008. Elevated surface ocean DMS concentrations suggest that the local ocean was biologically active enough to be the source of atmospheric DMS. An aerosol microphysics box model including a sulphur scheme using observed DMS mixing ratios as an initial condition was run to simulate the observed nucleation and growth events. Based on our model results, we show that MBL DMS alone could explain the observed aerosol nucleation and growth. Although we cannot rule out the role of condensable organic compounds, ultrafine primary oceanic particles arising from bubble bursting, or subsidence from the free troposphere, we have no need to invoke them to explain the observations. These findings are complementary to those of Rempilo et al. (2011) who observed biogenic contributions to the sulphur in particles ≤ 10 μm during the cruise. Taken together, the results from both of these studies suggest that biogenic sulphur can affect both the small particles, by forming new particles, as well as larger particles, by contributing particle mass. Both of these effects can affect the overall radiation budget of the Arctic.

In contrast, measurements taken 10 months earlier at similar latitudes did not observe any nucleation or nucleation mode particles. This is likely due to lower solar radiation, which resulted in lower OH production rates and ocean surface DMS concentrations. As more of the Arctic marine regions become increasingly ice free over the summer, oceanic input of gaseous aerosol precursors into the atmosphere will become more important. Further measurements of the type presented in this paper are needed to document how the particle numbers in the Arctic are responding to such climate change.

2.6. Acknowledgements

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2.7. Contributions

Rachel Chang is the main author of the manuscript, made the particle measurements during the 2007 transit, interpreted the data, and ran and interpreted the aerosol microphysics model. Steven Sjostedt made the DMS and particle measurements during the 2008 transit and completed the initial data analysis. Jeffrey Pierce adapted his existing box model, assisted Rachel in running the model and interpreting the results, and provided the text in Section 2.4.1. Tim Papakyriakou provided the radiation data, and Michael Scarratt and Sonia Michaud provided the surface ocean DMS measurements. The overall study was designed by Maurice Levasseur, Richard Leaitch and Jonathan Abbatt, who all provided critical comments to the manuscript.

2.8. References

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Chapter 3

Aerosol composition and sources in the Central Arctic Ocean during ASCOS


A manuscript in preparation for submission to Atmospheric Chemistry and Physics Discussions
3.1. Introduction

The sources and chemical composition of Arctic aerosol are not as well known as for continental regions. In a recent intercomparison study of 13 models that predict Arctic aerosol mass, the majority of the models had trouble predicting the aerosol mass, especially in the summer when the aerosol mass is overpredicted at Alert, Canada (83°N, 62°W) and Ny-Ålesund, Spitsbergen (79°N, 12°E) (Shindell et al. 2008). As reviewed by Barrie (1986) and Quinn et al. (2007), Arctic haze is a phenomenon in which the aerosol mass during Arctic winter and early spring can be 10–40 times higher than in summer. Because there are few local sources, Arctic haze is dominated by aerosol mass transported from lower latitudes. In the Arctic, the winter air is stable and dry, which slows aerosol removal processes and results in the accumulation of aerosol mass (Law and Stohl 2007).

During the summer, air first passes over the North Atlantic Ocean before arriving to the Arctic. However, because the air travels more slowly and precipitation is more frequent, aerosol mass transported from the continents does not accumulate as much as in the winter (as summarised by Law and Stohl (2007)) and particle concentrations can be \(< 5 \text{ cm}^{-3}\) over the Arctic pack ice (e.g. Covert et al. 1996; Mauritsen et al. 2011). As a result, local sources of aerosol become more important. Nilsson and Leck (2002) found that over the central Arctic pack ice, sub-micron sulphur-containing particles can be efficiently scavenged by wet deposition on a timescale of 1 day, suggesting that particles observed over the pack ice beyond a 1 day travel time from the open ocean are formed from oxidation of transported gases, emitted by a local source within the pack ice, or originate from the free troposphere.

Natural primary aerosol sources observed in the Arctic summer include sea salt and crustal materials, which have been observed in measurements of total suspended particles (Xie et al. 2006) and particles \(<10 \mu\text{m}\) (Maenhaut et al. 1996; Friedman et al. 2009). However, transmission electron microscope (TEM) studies have failed to observe sea-salt in particles \(<200 \text{ nm}\) (Bigg and Leck 2001; Leck and Bigg 2005). Traditionally, biogenic
contributions to marine aerosol, including over the Arctic pack ice, have focussed on the products of dimethyl sulphide (DMS) oxidation. DMS volatilises from the ocean into the air where it is oxidised to ultimately form, among other products, sulphuric acid or methane sulphonate (MSA) (Yin et al. 1990), both of which end up in the condensed phase. Local marine biogenic sources of sulphur in aerosol have been observed at various Arctic sites such as over the Arctic pack ice (Leck and Persson 1996; Kerminen and Leck 2001), at Alert (Li and Barrie 1993a; Li and Barrie 1993b; Norman et al. 1999), at Ny-Ålesund (Heintzenberg and Leck 1994) and at Barrow, USA (71ºN, 156ºW) (as summarised by (Quinn et al. 2009)).

Recent observations, however, suggest that marine environments can also contribute an organic component to the particulate mass over the Arctic and North Atlantic oceans. It has been proposed that organic compounds found in marine particles are emitted directly from the ocean by the bursting of bubbles (e.g. O'Dowd et al. 2004; Bigg and Leck 2008; Ceburnis et al. 2008; Facchini et al. 2008; Russell et al. 2010), with conflicting reports as to whether they are soluble (Russell et al. 2010) or insoluble (O'Dowd et al. 2004; Bigg and Leck 2008; Ceburnis et al. 2008; Facchini et al. 2008). The chemical nature of these compounds also varies, with studies reporting that they are similar to lipopolysaccharides, based on nuclear magnetic resonance spectra (Facchini et al. 2008) or are similar to simple biological sugars, based on fourier transform infrared spectra (Russell et al. 2010). Specific to the Arctic Ocean pack ice, TEM images from previous expeditions have observed insoluble organic components in particles <500 nm in diameter (Bigg and Leck 2001). It is thought that these organics are formed from microcolloids (Bigg et al. 2004) that are aggregates of exopolymer secretions, which are a part of dissolved organic matter (Chin et al. 1998).

There is also evidence of secondary organic products, with the oxidation products of isoprene identified in aerosol collected at Alert (Fu et al. 2009), which could have originated from local marine organisms emitting isoprene. Aerosol growth observed at Summit, Greenland has also been attributed to organics originating from the snow (Ziemba et al. 2010). The level of scientific understanding of the biological contributions
to organic aerosols in the Arctic, as well as aerosol sources in general, is still low due to the limited amount of observational data.

The physical and chemical properties of aerosol particles determine whether they can act as cloud condensation nuclei (CCN) and nucleate cloud droplets. As such, the particle sources and aging processes in the Arctic are important since they can affect their ability to active as CCN. At low-to mid-latitudes, an increase in particle number concentration tends to result in clouds that have higher albedo and cool the surface (Twomey 1977). In the Arctic, however, because of high surface albedos and low levels of solar radiation, longwave emissions from clouds can dominate and the clouds instead warm the surface during most of the year (Shupe and Intrieri 2004; Tjernstrom 2005). Furthermore, for thin clouds under pristine conditions, as often found in the Arctic, increased particle concentrations due to pollution can lead to clouds that increase surface warming from longwave emission (Garrett et al. 2002; Garrett and Zhao 2006). Whether Arctic clouds have a net warming or cooling effect depends on the time of year and location (Garrett et al. 2002; Wang and Key 2003; Shupe and Intrieri 2004; Tjernstrom 2005; Garrett and Zhao 2006; Lubin and Vogelmann 2007). As such, it is important that cloud forcing, formation and dispersion are well understood such that the effects of future increases in temperature and particle concentration on Arctic low-level clouds and their effects on polar climate can be predicted.

This paper presents measurements of aerosol chemical composition made over the central Arctic Ocean and uses them to elucidate information about aerosol sources to contribute to our understanding of low-level cloud formation over the pack ice. Measurements were made with an aerosol mass spectrometer (AMS), which quantifies chemical composition of the non-refractory (volatile at 870 K and 10⁻⁵ Pa) component at high time-resolution from mass spectra. This is in contrast to previous studies in the high Arctic and central Arctic Ocean which relied on filter or impactor measurements collected over hours to weeks (e.g. Li and Barrie 1993a; Hillamo et al. 2001; Xie et al. 2006), and which do not measure the organic component. Although surface AMS measurements have been made at Eureka, Canada (80°N, 86°W) (Kuhn et al. 2010), to our knowledge, this is the first
time that AMS measurements have been made in the boundary layer in the central Arctic Ocean region.

These measurements were made as a part of the Arctic Summer Cloud Ocean Study (ASCOS), whose overall purpose was to study the formation, structure, and dispersion of low-level stratiform clouds during the late Arctic summer and transition to autumn freeze-up conditions. This question is multifaceted and the interdisciplinary team included meteorologists, oceanographers, atmospheric chemists, aerosol scientists and marine biologists. ASCOS continues some observations carried out in a series of three previous international ice-breaker expeditions to the high Arctic in the summers of 1991 (IAOE-91) (Leck and Persson 1996), 1996 (AOE-96) (Leck et al. 2001) and 2001 (AOE-2001) (Leck et al. 2004; Tjernstrom 2005).

3.2. Description of measurements

3.2.1. Arctic Summer Cloud Ocean Study

The ASCOS expedition (www.ascos.se) took place on the Swedish icebreaker Oden from 2 August to 9 September 2008. The research cruise began at Longyearbyen on Spitsbergen, with an open water station (OW1) on 3 August 2008 0:00 to 12:00 (78.2°N, 7.5°E) followed by a 24 h station in the marginal ice zone (MIZ1) starting 4 August 2008 12:00 (79.9°N, 6.1°E). Afterwards, the ship headed north through the Arctic Ocean drifting pack ice as far as 87.5°N, 1.5°W on 12 August 2008 when an ice camp was established on an ≈ 3 km × 6 km ice floe. The Oden drifted with the ice for 21 days and departed on 2 September 2008 to return southwards. A second marginal ice zone station (MIZ2) took place 6 September 2008 09:00 to 7 September 2008 04:00 (80.7°N, 8.9°E) immediately followed by a final 12 h open water station (OW2) ending 7 September 2008 16:00 (80.4°N, 10.1°E). All times are in UTC. Overall, the cruise ranged in location from 77.9° to 87.5°N and 11.1°W to 9.6°E. A map of the route with the ice drift highlighted is shown in Figure 3.1.
3.2.2. Aerosol Mass Spectrometer

A unit-mass resolution compact time-of-flight (C-ToF) aerosol mass spectrometer (Aerodyne Research Inc.) measured the submicron aerosol non-refractory chemical composition. The instrument was located in the aerosol sampling container on the 4th deck of the *Oden* and sampled from an inlet with an impactor whose 50% cutoff diameter was 10 µm (PM$_{10}$). The inlet was located approximately 27 m above sea level and the total flow through this 9 cm inner diameter pipe was $\approx 1100$ L min$^{-1}$. This resulted in a residence time of $<1.4$ s, while the secondary line from which the AMS sampled (10 mm OD $\times$ 7 m) had a residence time of $<4$ s. Since the room temperature was at least 20 K warmer than ambient, the RH of the measured aerosols was assumed to be $<30$% throughout the study. The PM$_{10}$ inlet was identical to the one used during IAOE-91, AOE-96 and AOE-2001 and further details on its location and design can be found in Leck et al. (2001).
Particles between 70 to 700 nm in diameter are transmitted into the AMS through a 100 µm critical orifice at 270 Pa and pass through a series of aerodynamic lenses which both focus the particles into a beam and accelerate them into a vacuum chamber. Particles impact on a resistively heated ceramic oven, which flash vapourises the components of the aerosol that are non-refractory (volatile) at 870 K and 1.33×10^{-5} Pa. The resulting gaseous compounds are ionised by electron impact (70 eV) and detected with a time-of-flight mass spectrometer. The results presented here are only for the average bulk aerosol composition, which was averaged over 5 min intervals. Further details on the general operation of the AMS can be found in the literature (Jayne et al. 2000; Jimenez et al. 2003; Drewnick et al. 2005; Canagaratna et al. 2007).

The fragmentation table, used to identify the different contributors to the spectrum, was modified from the standard table (Allan et al. 2004) according to Langley et al. (2010) to include MSA. Airbeam correction was applied to account for small changes in the inlet flow throughout the study, although the signal at mass-to-charge ratio (m/z) 40 was used due to non-linearities in the signal at m/z 28. An ionisation efficiency calibration with ammonium nitrate was performed at least once each week. The sample flow rate was ≈100 cm³ s⁻¹ (STP) and was calibrated throughout the study with a bubble flow meter. Finally, a filter was put in line twice every day for blank measurements.

3.2.3. **Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer**

DMS, toluene and benzene were measured using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF) built at Innsbruck University. The PTR-MS technique is a well-established method for fast online VOC analysis (Lindinger et al. 1998; de Gouw and Warneke 2007) in the atmosphere. The instrument used in this study (employing a TOF-MS instead of a quadrupole mass analyser) was described in detail by Graus et al. (2010). The PTR-TOF was calibrated by applying a dynamically diluted VOC gas standard (Apel & Riemer Environmental Inc, Denver, CO, USA) and zero-calibrations were performed every two to six hours using catalytically scrubbed air. The PTR-TOF
co-sampled next to the aerosol inlet through a Teflon filter and a heated 6.4 mm Sulfinert® (Restek Performance Coating) tubing with a residence time of <3 s. The PTR-TOF spectra were analyzed with routines as described by Graus et al. (2010) and Müller et al. (2010).

### 3.2.4. $^{222}$Rn

$^{222}$Rn is often used as a tracer for air that had contact with land (e.g. Russell et al. 2010) and was measured every hour using a U.S. Department of Homeland Security, Environmental Measurements Laboratory instrument based on the in-growth and subsequent alpha counting of short-lived $^{222}$Rn progeny. The sample air was pumped through a HEPA filter which removed all the radionuclides, including short-lived $^{222}$Rn progeny attached to aerosol particles. However, $^{222}$Rn, being a noble gas, passed through this filter. Next the air entered a 500 L delay chamber where part of the $^{222}$Rn decayed to its short-lived daughter nuclides. These nuclides are heavy metals and were trapped by a second filter. The alpha particles emitted by the collected daughter nuclides were then counted with a scintillation detector (Hutter et al. 1995).

### 3.2.5. $^{210}$Pb

$^{210}$Pb is a radioactive decay product of $^{222}$Rn and can be used to indicate the age of the air since it was last in contact with land. High-volume aerosol samples were collected onto glass fibre filters (Munktell MGA) on the 7th deck of the *Oden*. The sample air flow rate was $\approx 140$ m$^3$ h$^{-1}$ and the sampling time 24 h. In the laboratory the exposed filters and the field blanks were assayed for $^{210}$Pb six months after the sampling with an automatic alpha/beta analyser (Mattsson et al. 1996). $^{210}$Pb activity content of the filters was calculated from the in-grown $^{210}$Po activity which was assayed with alpha counting.
3.2.6. Positive matrix factorisation

Positive matrix factorisation (PMF) is a statistical model that uses weighted least-square fitting for factor analysis (Paatero and Tapper 1994; Paatero 1997). It uses a bilinear model

\[ X = GF + E, \]  

Equation 3.1

where \( X \) is a matrix of the measured values, and \( G \) and \( F \) are matrices computed by the model and represent the scores and loading, respectively. For AMS data, each row in \( X \) is a mass spectrum measured at a given time, with the columns representing the signal at a given \( m/z \). In this case, \( G \) represents the time series and \( F \) the profile mass spectrum for the \( p \) factors computed by the algorithm. \( E \) is the difference between the measured signal and that reconstructed by the product of \( G \) and \( F \) and is made up of the elements \( e_{ij} \). The model adjusts \( G \) and \( F \) in order to reduce the object function \( Q \), where

\[ Q = \sum_{i} \sum_{j} \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2, \]

and \( \sigma_{ij} \) is the uncertainty for each element in the matrix \( X \).

In continental regions, where the sources of inorganic aerosol are well understood, PMF is typically only performed on the organic mass spectrum (e.g. Lanz et al. 2007; Ulbrich et al. 2009a) in order to learn more about the sources and transformation processes of organic aerosol. However, in the Arctic, our understanding of both inorganic and organic sources is limited. In particular, sulphate, which is an anthropogenic constituent in continental regions, also has a biogenic source in marine areas. As such, PMF was performed on the entire aerosol mass spectrum in order to gain understanding on the sources and processes of the entire aerosol. This also allows us to associate organic fractions to both anthropogenic and biogenic aerosols. The PMF2 program (Paatero 1997) was used to analyse these data in robust mode with an outlier distance of 4 and no model error. The PMF evaluation tool kit (PET) (Ulbrich et al. 2009a) was used to prepare the data and error, execute PMF and evaluate the results. The data matrix was calculated by taking the entire aerosol mass spectrum (“All”) and subtracting species that were 1) not of interest (i.e. air and water) and 2) unreliable due to high background and
low signal (i.e. chloride and ammonium). The error matrix ($\sigma_{ij}$) was calculated by adding in quadrature the errors calculated for the entire aerosol mass spectrum to those of the subtracted species (Allan et al. 2003) and a minimum counting error of one ion was applied, as described by Ulbrich et al. (2009a). All of these calculations were done in nitrate equivalent mass, which includes all the calculations required to convert between raw ion count and aerosol mass except for the relative ionisation efficiency of each species. In this way, the PMF algorithm determined the contribution of each species based on the raw ion count.

All ambient data points were kept in the data matrix, as well as the majority of the times when the sample was influenced by the Oden’s own pollution. However, in order to avoid overweighting these pollution events, times when the total AMS mass exceeded 1 $\mu$g m$^{-3}$ were removed, since this was much greater than the background aerosol mass. In total, 168 m/z, ranging from 13 to 200, were included in the analysis, with peaks removed due to known interference (e.g. 18, 28, 32); being constantly negative, which the algorithm would be unable to fit (e.g. 33, 34); or due to difficulty fitting (e.g. 35, 36).

### 3.2.7. Potential Source Contribution Function

To identify potential source areas of the observed aerosol chemical mass at the location of the ice breaker a receptor model called potential source contribution function (PSCF) was used. The PSCF model combines meteorological information, combining air parcel back trajectories, with the AMS data, in an attempt to produce probability fields for potential source regions for the observed data.

To reconstruct the air parcel movement, three dimensional back trajectory data was calculated from the re-analysis data library using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Rolph 2010); (Rolph 2010). The meteorological data originated from the American National Weather Service’s National Centres for Environmental Prediction Global Data Assimilation System and model vertical velocities were used.
Five-day back trajectories from 5 August to 8 September 2008 were calculated hourly during the expedition arriving in the boundary layer, 100 m above Oden’s position. Each trajectory described the air parcel movement by segment endpoint co-ordinates in terms of latitude and longitude of the endpoint of each hourly-segment of the trajectory. Then, to produce the PSCF analyses, each trajectory and its corresponding segment endpoints were associated with the measured 1h-median AMS aerosol or factor data.

In this study, the northern hemisphere was divided into 18º × 2.5º grid cells. Trajectories with segment endpoints in cell $ij$ were counted as $n_{ij}$ and assumed to collect the chemical mass emitted from that cell. The probability that air from a particular grid had been transported along the trajectory to Oden’s position is then given by $P_{ij}(A) = \frac{n_{ij}}{N}$, where $N$ is the total number of trajectory segment endpoints. If the aerosol sample connected to the trajectory has a concentration higher than a selected criterion value (here the 75th percentile of the measured aerosol mass concentration is used) it is set as high, and all segments of this trajectory are considered to be high. The probability that air from a particular grid, $ij$, has a high aerosol concentration, $m_{ij}$, is then given by $P_{ij}(B) = \frac{m_{ij}}{N}$. The conditional probability that the air passing through the $ij^{th}$ cell had a high aerosol concentration when arriving to Oden is then given by the ratio of these two probabilities $PSCF_{ij} = \frac{P_{ij}(A)}{P_{ij}(B)} = \frac{n_{ij}}{m_{ij}}$.

To avoid errors when the total number of endpoints in a cell is low, only cells with at least 10 endpoints or more are used, and the PSCF values are multiplied with a weighting function $W(n_{ij}) = \begin{cases} 1.0 & \text{when } 50 \leq n_{ij}; \\ 0.8 & \text{when } 10 \leq n_{ij} < 50; \text{ and} \\ 0 & \text{when } n_{ij} < 10. \end{cases}$
Similar approaches have been used in other PSCF studies (Hopke et al. 1995; Yli-Tuomi et al. 2003; Zhang et al. 2010).

### 3.2.8. FLEXPART

The study of air mass transport to the ship and identification of aerosol source regions was based on simulations with the Lagrangian particle dispersion model FLEXPART (Stohl et al. 1998; Stohl et al. 2005) in backward mode. So-called retro-plumes (Stohl et al. 2003) were initialized at hourly time intervals or when the ship had changed position by more than 0.2° longitude or latitude since the last calculation. The simulations are based on operational data from the European Centre for Medium-Range Weather Forecasts (ECMWF) with a horizontal resolution of 0.5° and a time resolution of 3 hours. Each simulation consists of the trajectories of 60 000 “virtual” particles released in the volume of air sampled and tracked for 20 days backward in time. Stochastic fluctuations, obtained by solving Langevin equations, are superimposed on the grid-scale winds to represent transport by turbulent eddies (Stohl et al. 2005). A convection scheme is used to represent convective transport (Forster et al. 2007).

The backward simulations yield an emission sensitivity which is proportional to the residence times of the air parcels in a particular 3-D grid cell and was calculated for a passive tracer. The value of this emission sensitivity is a measure for the simulated mixing ratio in the receptor volume that a source of unit strength in the respective grid cell would produce. The emission sensitivity of the passive tracer can also be used to display the transport history. By multiplying the emission sensitivity near the ground with an emission flux from an appropriate inventory, maps of source contributions are obtained, which can be used to identify pollution sources. Spatial integration of the source contributions yields the simulated mixing ratios of the passive and aerosol-like tracers along the ship track. For emission information, the EDGAR V3.2FT2000 anthropogenic emissions inventory (Olivier and Berdowski 2001) was used outside of North America and Europe where regional emission information was used. Emissions from biomass burning were modeled as described by Stohl et al. (2007) using fire
locations detected by the moderate-resolution imaging spectrometer (MODIS) on the Aqua and Terra satellites and a land-cover vegetation classification.

### 3.3. Results and Discussion

#### 3.3.1. General AMS results

Mass concentrations for the non-refractory species in aerosol measured by the AMS are shown in Figure 3.2, with the shaded areas showing the times of the stations. These data have been corrected to STP using room temperature and pressure measurements. They are only for ambient Arctic aerosol and exclude times when influence from local emissions (e.g. ship, helicopter, snowmobile) is suspected. Possible contamination events were determined by particle number concentration measured by an ultrafine condensation particle counter, toluene mixing levels measured by the PTR-TOFMS, and by wind direction (±90°, relative to the bow) and wind speed (<2 m s⁻¹ or variable). Table 3.1 shows basic descriptive statistics for the study as well as median values for the stations during which the AMS measured. Due to technical difficulties, the AMS was not operational during OW1. Detection limits were calculated for each blank filter measurement as 3 times the standard deviation for each species, and the average of these values was used as the detection limit for the entire campaign. These are also included in Table 3.1. Although ammonium can be measured by the AMS, it is not included here since it was below its detection limit of 0.03 µg m⁻³ 86% of the time. The collection efficiency for this study was determined to be 0.6 ± 0.2 and the details can be found in Section 3.5.

<table>
<thead>
<tr>
<th></th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>MIZ1</th>
<th>IF</th>
<th>MIZ2</th>
<th>OW2</th>
<th>Det. Lim.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td>0.01</td>
<td>0.05</td>
<td>0.08</td>
<td>0.11</td>
<td>0.04</td>
<td>0.09</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0.016</td>
<td>0.042</td>
<td>0.082</td>
<td>0.070</td>
<td>0.037</td>
<td>0.099</td>
<td>0.050</td>
<td>0.006</td>
</tr>
<tr>
<td>MSA</td>
<td>0.003</td>
<td>0.007</td>
<td>0.012</td>
<td>0.016</td>
<td>0.006</td>
<td>0.015</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.002</td>
<td>0.004</td>
<td>0.006</td>
<td>0.005</td>
<td>0.003</td>
<td>0.008</td>
<td>0.005</td>
<td>0.006</td>
</tr>
</tbody>
</table>

*Table 3.1 - 1st, 2nd and 3rd quartiles of AMS measurements. Also included are median concentrations for the four stations (see text) and detection limits. All units in µg m⁻³.*
Figure 3.2 - AMS Time Series.
Organic, sulphate, MSA and nitrate mass concentrations (solid lines) and detection limits (dashed lines) during ASCOS. Blue, yellow and gray regions represent marginal ice zone, ice floe and open water stations, respectively.

On average, sulphate and organics contributed 45 and 43% of the ambient aerosol mass measured by the AMS, respectively, with an average MSA contribution of 8%. The values for sulphate reported in this study are of non-sea salt sulphate, since sodium sulphate (Na$_2$SO$_4$), found in sea salt, has a melting point of 1150 K (Weast et al. 1983) and would be refractory in the AMS. Refractory components normally found in ambient aerosol, such as black carbon, mineral dust and sea salt, are thought to be minimal in the submicron aerosol during this study and as such, these measurements are thought to be representative of the overall aerosol. The range of sulphate ($\leq 0.35 \text{ µg m}^{-3}$) and MSA ($\leq 0.07 \text{ µg m}^{-3}$) in this study is generally in agreement with values measured at other polar sites in the summer (see Table 3.2).
Table 3.2 - Summertime sulphate and MSA concentrations at various Polar locations

<table>
<thead>
<tr>
<th>Location or Study</th>
<th>Sulphate (µg m⁻³)</th>
<th>MSA (µg m⁻³)</th>
<th>MSA / SO₄⁻²</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAOE-0.91</td>
<td>0.0027-0.66</td>
<td>0.0002-0.13</td>
<td>0.22</td>
<td>Leck and Persson (1996)</td>
</tr>
<tr>
<td>AOE-96</td>
<td>0.0036-1.185</td>
<td>0.002-0.104</td>
<td>0.22</td>
<td>Kerminen and Leck (2004)</td>
</tr>
<tr>
<td>Alert, Canada</td>
<td>0.03-0.22</td>
<td>0.03-0.05</td>
<td>0.39±0.21</td>
<td>Li and Barrie (1993a)</td>
</tr>
<tr>
<td>Ny-Ålesund, Spitsburgen</td>
<td>0.39</td>
<td>0.018</td>
<td></td>
<td>Norman et al. (1999)</td>
</tr>
<tr>
<td>Palmer Station</td>
<td>≤0.1</td>
<td>0.0001-0.065</td>
<td>0.61</td>
<td>Heintzenberg and Leck (1994)</td>
</tr>
<tr>
<td>Halley Station</td>
<td>0.075</td>
<td>0.042</td>
<td>0.65±0.13</td>
<td>Berresheim et al. (1998)</td>
</tr>
<tr>
<td>ASCOS</td>
<td>≤0.35</td>
<td>≤0.07</td>
<td>0.25±0.02</td>
<td>Read et al. (2008)</td>
</tr>
</tbody>
</table>

In general, the two MIZ stations had higher aerosol loadings in all species than both the IF and OW2 stations. Aerosol MSA mass measured at the two MIZ stations did not show any changes, suggesting that marine biology was still active at the beginning of September. This is in contrast to the findings from Leck and Persson (1996), although their study extended into October when biological activity would have decreased. Care should be taken in interpreting statistics from the non-ice floe stations since the sampling time at the two MIZ stations and the OW station were limited to ≈3% and 1% of the total sampling time, respectively.

3.3.2. PMF Results

A four-factor solution was chosen to best represent the variations in the aerosol mass for this data set. The time series and profiles of the factors are shown in Figure 3.3 and Figure 3.4, respectively. In this solution, there are three ambient factors that describe the local background air in the central Arctic: a Marine Biogenic factor, a Continental factor, and an Organic factor. In addition, a fourth factor describes emissions from the Oden itself. These will be described in more detail below.
Figure 3.3 - Time series of the PMF factors. The solid trace is the solution for an $f_{Peak}$ of -0.75 and the shaded regions the range for $f_{Peaks}$ of -1.5 to 0.
Figure 3.4 - Mass spectra of the PMF factors.
The diamond represents the solution for an \( f_{Peak} \) of -0.75, and the light and solid bars the range for \( f_{Peaks} \) of -1.5 to 0. The signal is adjusted so that the sum of the signal for each mass spectrum is one.

Finding the best PMF solution for a data set can be subjective. The number of factors in the solution, the robustness of these factors, and rotational ambiguities, all affect how well the variations are represented. The rotational ambiguities will be discussed here, while the details describing other solutions and robustness can be found in the Section 3.6.

PMF solutions can have rotational ambiguity, with \( X = G'F' + E \), where \( G' = GT \) and \( F' = T^{-1}F \) (where \( G \) and \( F \) are from the initial solution of Equation 3.1). These solutions
are explored in the PMF algorithm by varying the $f_{\text{Peak}}$ parameter. Past AMS studies that only perform PMF on the organic component can distinguish the $f_{\text{Peak}}$ by comparing the factor time series to the time series of the AMS inorganic compounds. However, in this analysis, because the entire mass spectrum is used and there are few external time traces with which to corroborate the time series for a certain PMF solution, the best $f_{\text{Peak}}$ can be difficult to determine. Instead, a range of $f_{\text{Peak}}$ values (-1.5 to 0) was found to give physically reasonable mass spectra and time series, while remaining reasonably robust. The $Q/Q_{\text{exp}}$ also varied by $<1\%$ over this range of $f_{\text{Peak}}$, demonstrating that these solutions are acceptable. As such, the results shown here are for an $f_{\text{Peak}}$ of -0.75, with the minimum and maximum of this range included to show uncertainties in the solution. In general, this uncertainty was greater than that from the robustness runs, and is considered to be more representative of the overall uncertainties.

The composition of the factors was determined by applying the fragmentation table to the profile mass spectrum of each factor. Values for an $f_{\text{Peak}}$ of -0.75 are shown in Table 3.3, and the range due to changes in $f_{\text{Peak}}$ from -1.5 to 0 can be found in Section 3.6. This calculation was corrected for the relative ionisation efficiencies of the different species but not for collection efficiency. It also assumes that there are no other components in the aerosol besides organic, sulphate, MSA and nitrate, and does not account for any organonitrogen or organosulphur compounds that may be present. The overall contribution of each factor to the ambient aerosol mass is also given in Table 3.3, excluding the Ship Emission factor. We see that the three ambient factors contribute approximately equally throughout the study. The next sections describe the characteristics of each factor.
Table 3.3 - Composition and percent contribution of factors from the four-factor solution for an $f_{\text{Peak}}$ of -0.75. See Figure 3.18 and Figure 3.19 for uncertainties. O/C calculated using the method from Aiken et al. (2008).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic (%)</td>
<td>15</td>
<td>35</td>
<td>88</td>
<td>97</td>
</tr>
<tr>
<td>Sulphate (%)</td>
<td>65</td>
<td>60</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>MSA (%)</td>
<td>16</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Nitrate (%)</td>
<td>4</td>
<td>2</td>
<td>5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>F44</td>
<td>0.09</td>
<td>0.25</td>
<td>0.17</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>O/C</td>
<td>0.42</td>
<td>1.1</td>
<td>0.71</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>% of ambient air</td>
<td>33</td>
<td>36</td>
<td>31</td>
<td>–</td>
</tr>
</tbody>
</table>

3.3.2.1. Marine Biogenic Factor

This factor was dominated by sulphate peaks ($m/z$ 48, 64, 80, 81, 98) as well as MSA peaks ($m/z$ 79 and 96). Since MSA is only significantly formed via DMS from products of biological activity (Seinfeld and Pandis, 2006), and 71% of the MSA mass was found in this factor, it was attributed to marine biogenic sources. The time series correlates to some degree with that of DMS (see Figure 3.5), but the correlation improves if we exclude the last week of the study when the Oden neared the marginal ice zone and open waters ($r = 0.36$, inset of Figure 3.5). It is not to be expected that the particulate and gas phase products of biological activity correlate so tightly since DMS is a precursor for both sulphate and MSA and the loss processes over the pack ice are expected to be slower for gases ($\tau \approx 3$ d) than particles ($\tau \approx 1$ d) (Nilsson and Leck 2002). While the concentration of DMS and its oxidation product SO$_2$ behave similarly on a seasonal and synoptic time scale, correlation on shorter time scales is not necessarily expected (Kerminen et al. 2004). Furthermore, previous studies in the Antarctic have found no correlation between DMS and its oxidation products (Berresheim et al. 1998; Read et al. 2008). We speculate that the measured air passed over productive waters that had both gas phase DMS and intermediate species which eventually oxidised to MSA and sulphate.
by the time they reached the measurement site, but that DMS had insufficient time to entirely react away. This is consistent with DMS concentrations increasing in the last week of the study while the time trace of the Marine Biogenic factor only increases slightly. As the *Oden* neared the open water source region, the particulate MSA and sulphate would not have had enough time to form from recent DMS emissions (Kerminen and Leck 2001; Karl et al. 2007).

**Figure 3.5 - Time series of the Marine Biogenic factor and DMS.**
The inset is a scatter plot of these two quantities excluding (black) and including (red) the last week of the study.

In particular, trajectories for 10 and 11 August showed that the air had passed over the open ocean ≈1 d before reaching the *Oden*. To generalise this, Figure 3.6a shows the PSCF analysis on this Marine Biogenic factor, which suggests that the air originated from the Barents sea, which, during August 2008, was ice free and biologically productive (up to 3 mg of chlorophyll a m$^{-3}$ (Feldman and McClain 2008)). This is supported by PSCF of MSA / SO$_2^{-4}$ calculated by mass for the entire aerosol (Figure 3.7a), which shows that this ratio is highest when the air originated from the Barents and Kara seas.
The MSA / SO$_4^{2-}$ ratio calculated by mass from the Marine Biogenic factor was 0.25 ± 0.02, with the uncertainties calculated from changes in the PMF $f_{Peak}$. Table 3.2, which lists other summertime values measured in polar regions, shows that our value is similar to that calculated from submicrometre filter measurements during IAOE-91 (Leck and Persson 1996) for marine biogenic times, excluding the influence of fog (0.22). It is also within the lower bounds of uncertainty found by Norman et al. (1999) for Alert, Canada.
in July and August of 1993 and 1994 (0.39 ± 0.21), although lower than the 10 year record reported by Li and Barrie (1993a) in August also at Alert (0.6 ± 0.3). Finally, it is within the range of values calculated from a box model for conditions from AOE-96 (0.32 mean, Karl et al. 2007), although lower than that predicted by a chemical transport model (0.38-0.65, Gondwe et al. 2004). Higher MSA / SO$_4^{2-}$ ratios have previously been observed in the coarse mode compared to the fine mode in the Antarctic (Jefferson et al. 1998; Read et al. 2008) and in the Pacific (Phinney et al. 2006), which is thought to occur because sulphuric acid nucleates to form the smaller particles, causing MSA, a weaker acid to condense on the neutral coarse mode aerosols (Jefferson et al. 1998). This would be consistent with the higher ratios measured at Alert, which are of total suspended particles, whereas our measurements are for submicron particles. However, some Arctic measurements do not see a size-dependent MSA / SO$_4^{2-}$ (Leck and Persson 1996).

It is interesting to note that the Marine Biogenic aerosol had an organic component that was approximately equal in mass to the amount of MSA in the aerosol. Based on this analysis alone, it is unclear whether this organic component is formed from secondary processes (e.g. oxidation of isoprene emitted from phytoplankton) or whether it is emitted directly from the ocean through a mechanism such as bubble bursting. The degree of oxygenation of the organic component of this factor is quite variable, with the fraction of the organic signal at $m/z$ 44 (F44) ranging from 0–0.12, depending on the $f_{Peak}$ used. A higher F44 usually suggests that the organic component is formed from secondary processes, although it is also possible that this organic mass is emitted as a primary aerosol that is already oxygenated, such as exopolymer secretion particulate matter, a mono or polysaccharide (Leck and Bigg 2007), or a simple biological sugar (Russell et al. 2010).

3.3.2.2. Continental Factor

The main feature of the time series of this factor is high signal between 26-30 August, which coincided with a period of high pressure. As seen in Figure 3.8, the time series correlates with the $^{210}$Pb signal ($r = 0.655$), which is a radioactive decay product of $^{222}$Rn.
The latter is often used as a tracer for air that has been in contact with soil, lending strong support that the air originated from a continental source. Furthermore, the composition of this factor, 60% sulphate and 35% organic, is similar to typical aerosols measured in continental regions (Zhang et al. 2007). Finally, this factor contains only 3% MSA, suggesting that it had little influence from marine sources.

![Graph showing time series of the Continental Factor and $^{210}$Pb. Inset shows scatterplot of these two quantities.](image)

PSCF analysis using 5-day back trajectories at 100 m reveals no specific source regions for this air (not shown). However, this is not unexpected since there was little correlation between the time series and $^{222}$Rn ($r = -0.05$, data not shown), which has a half-life of approximately 3.8 days (Weast et al., 1983), suggesting that this factor represents air that had not been in contact with land for at least a week. The organic component of this factor is aged, with an F44 of 0.25, which is comparable to the largest value previously reported (Ng et al. 2010), consistent with aerosol that has been extensively oxidised in the
atmosphere with a long residence time. In sum, this factor is consistent with very aged continentally-influenced air that has been transported to the central Arctic in the summer.

3.3.2.3. Organic Factor

This factor was thus named because it is 88% organic. It is fairly robust, present in the factor solution when there are at least three factors in the solution. However, it does not correlate with any measured external tracers, making its source difficult to identify. PSCF analysis (Figure 3.6b) shows contributions from west of the Queen Elizabeth Islands, north of the Beaufort sea, as well as the area around the Kara sea, both of which were ice free at this time. The mass spectrum of the entire factor, and in particular the organic component (Figure 3.10), resembles that of oxygenated organic aerosol (OOA) often found from factor analysis of organic aerosol at continental sites (see Section 3.3.3 for comparisons). OOA typically forms from the chemical aging of gaseous emissions originating from anthropogenic sources (e.g. Zhang et al. 2007; Ng et al. 2010) and biogenic sources (e.g. Chen et al. 2009; Slowik et al. 2010) as well as aging of biomass burning aerosol (Capes et al. 2008). In particular, based on the time series of the CO fire tracer from FLEXPART, the signal at the end of the study (4–6 September, DOY 248–250) was likely due to biomass burning in Europe and North America (see Figure 3.9, which illustrates the modelled contribution of biomass burning to the air sampled on 4 September). The agreement is not as good for the remainder of the study, suggesting that this factor is not uniquely from biomass burning and instead represents background organic aerosol, potentially from a variety of sources, that was transported to the Arctic, but whose original source cannot be identified. On the other hand, primary biogenic sources of aerosol from bubble bursting, as suggested by, for example, Leck et al. (2002), cannot be ruled out. It is interesting to note that this factor has very little inorganic component, suggesting that there is a source of Arctic organic aerosol that is not associated with sulphate. The organic component of this factor is fairly oxidised, with an F44 of 0.17, and will be further discussed in Section 3.3.3.
Figure 3.9 - FLEXPART CO contribution from biomass burning for 4 September 2008 12:37.

3.3.2.4. Ship Emission Factor

The time series for this factor is characterised by low signals for most of this campaign with intermittent periods of high loading which coincide with times when the pollution record, comprised of toluene, benzene and particle concentrations, indicated that the air was at risk of being contaminated by ship exhaust. The mass spectrum resembles that of ship fumigation periods measured by Phinney et al. (2006), qualitatively, as well as hydrocarbon-like organic aerosol from Pittsburgh ($r = 0.98$) (Zhang et al. 2005; Ulbrich et al. 2009b) and Switzerland ($r = 0.93$) (Lanz et al. 2007; Ulbrich et al. 2009b) which are thought to be primary aerosols emitted from vehicular traffic in cities and whose mass spectra are similar to that of lubricating oil ($r = 0.98$) (Canagaratna et al. 2004; Ulbrich et al. 2009b). This factor helped identify when the aerosol was affected by ship emissions and by excluding it, allows us to consider the ambient high Arctic aerosol without interference. However, there are some spikes in the Continental and Organic factors that coincide with signal in the Ship Emission factor, which suggests that the separation was not perfect.
3.3.3. Discussion of organic component

To summarise the nature of the organic aerosol sampled, Figure 3.10 shows the organic mass spectra of the four factors. The Continental and Organic factors resemble that of the oxygenated organic aerosol (OOA) factor found in continental urban sites (Zhang et al. 2005; Ulbrich et al. 2009b) ($r$ of 0.73 and 0.85, respectively). As shown in Table 3.3, these organic fractions appear quite aged compared to measurements made at continental sites (Ng et al. 2010), with an F44 of 0.25 and 0.17, respectively, corresponding to an atomic oxygen to carbon ratio (O/C) of 1.1 and 0.7, using the relationship in Aiken et al. (2008). Care should be taken in interpreting these numbers, since the fragmentation table is normally applied to a full mass spectrum and not to a PMF factor profile. Nevertheless, the degree of oxygenation of the Continental factor appears to be comparable to the most aged continental aerosol observed (Ng et al. 2010) and is consistent with it being the most aged out of all the factors found in this study.

![Figure 3.10 - Mass Spectra of the Organic Components of the PMF Factors.](image)

The diamond represents the solution for an $f_{Peak}$ of -0.75, and the light and solid bars the range for $f_{Peaks}$ of -1.5 and 0. The signal is adjusted so that the sum of the entire signal for each mass spectrum, not just the organics, is one.
The organic component of the Marine Biogenic factor also resembles that of OOA from Pittsburgh (\( r \) of 0.62) (Zhang et al. 2005; Ulbrich et al. 2009b). Although F44 is quite variable depending on the \( f_{\text{Peak}} \) of the solution (see Section 3.6), it is lower than those of the other factors, demonstrating that it is different than the organics found in the other two ambient factors. If the organics in the Marine Biogenic factor were indeed formed from secondary processes, then they would be the least aged of the ambient aerosol observed.

The average F44 for the entire study, as calculated from the bulk mass spectrum, was 0.18 ± 0.05. PSCF analysis on F44 (Figure 3.7b) shows that it is highest north of Greenland and west of the Queen Elizabeth Islands, suggesting that aerosol originating from these sources were the most processed, and lowest from the Kara sea, suggesting that this air was least processed, if we only consider atmospheric processing. However, as discussed in Section 3.3.2.1, it is possible that organic aerosol emitted directly from the ocean could have a high F44, and they are originating from west of the Queen Elizabeth Islands. PMF was also performed on only the organic mass spectrum and compared to the solutions from the entire mass spectrum. However, because the organic components of the ambient factors tend to resemble OOA, the results did not yield as much information and the solution is generally in agreement with the results from PMF of the entire mass spectrum.

**3.4. Conclusions**

During August to the beginning of September 2008, submicron aerosol particles over the central Arctic Ocean were composed of approximately equal amounts of organic and sulphate components. These particles were influenced by both marine biogenic and continental sources (33% and 36% of the sampled ambient aerosol mass, respectively), both of which had a predominant sulphate component and were separated using PMF. The sulphate measured was apportioned 47% to marine biogenic sources and 48% to continental sources. However, there also appears to be aerosol that was almost purely
organic (31% by mass), although it was not possible to identify a single source for this aerosol at this time. These results show that up to 1/3 to 2/3 of the Arctic submicron aerosol mass is formed from regional marine sources and that Arctic models that only include aerosol transport from anthropogenic sources could be neglecting a significant mass. This is in contrast to the Arctic free troposphere which can at times be heavily influenced by biomass burning (Brock et al. 2011).

In general, the organic component of all ambient aerosols measured was as oxidised as, if not more than, the OOA component observed at ground-based continental sites. The organic component of air influenced by continental sources was also found to be more oxidised than that of marine biogenic sources. This is consistent with long transport of these particles. Although the degree of oxygenation of the organic component of the Marine Biogenic and Organic factors would normally be interpreted as being atmospherically processed, it is possible that under polar marine environments, primary oxygenated organic aerosol are emitted directly into the atmosphere, as suggested by previous findings over the pack ice (Leck and Bigg 2005). In contrast to previous analyses of AMS observations, this study used PMF on the entire mass spectrum, which allowed the inorganics from different sources to be separated, along with their associated organic component.

3.5. Appendix A: Verifying the AMS Mass

Not all particles that enter the AMS are detected, with some particles being lost in the transmission through the aerodynamic lens, depending on the transmission efficiency, and some particles bouncing out of the oven instead of vapourising when they impact on the oven. This latter effect is accounted for by the collection efficiency (CE), while the transmission efficiency is thought to be 100% for particles between 150 and 500 nm in diameter (see Figure 3.11 for size-dependent transmission efficiency). The CE is usually determined by comparing the mass measured by the AMS with that measured by other instruments. For this study, three methods of comparison are used, as described below.
3.5.1. Comparison with particle size distributions

The first method involved comparing the total mass measured by the AMS with mass calculated from the number distributions measured by a differential mobility particle sizer (DMPS) that also sampled from the PM$_{10}$ inlet. This system consisted of two Hauke-type differential mobility analyser (DMA) run in tandem to cover a particle size range of 3 – 800 nm in diameter. The smaller DMA was run with sheath and sample flows of 20 and 2 L min$^{-1}$, respectively, and the larger DMA at 5 and 1 L min$^{-1}$, respectively (Birmili et al. 1999).

Number size distributions were converted to mass distributions by assuming a density based on the AMS chemical composition (sulphate, nitrate, MSA and organic with densities of 1770, 1730, 1480 and 1500 kg m$^{-3}$, respectively (Weast et al. 1983; Kostenidou et al. 2007)). These numbers were corrected for the size-dependent transmission efficiency (Liu et al. 2007), and then compared to the total AMS mass. As can be seen from Figure 3.12, the linear fit results in a CE of 0.435, which is lower than the commonly used value of 0.5 (Canagaratna et al. 2007). This could be due to a systematic error in the DMPS or the AMS, or it could be due to additional refractory material that the AMS does not measure.
3.5.2. **Comparison with stages of a cascade impactor**

The second approach compared the AMS measurements of sulphate and MSA with the submicron stages of cascade impactors. Duplicate five-stage Berner cascade impactors (BCI) (Berner et al. 1979) were used to collect particles at a sampling flow rate of approximately 80 L min$^{-1}$. Pre-cleaned Tedlar® polyvinyl fluoride films (DuPont) were used as particle impaction substrates for the four largest stages. The Tedlar films for the fifth (largest) stage were greased with a thin layer of Apiezon L- vacuum grease to prevent particle bouncing. Millipore Fluoropore membrane filters (pore size 1.0µm; diameter 47 mm) were used for the smallest stage. Sampling duration ranged from 6 h to 12 h depending on the level of aerosol concentration during the cruise. Field blanks were obtained by setting the impactors/filter holders with loaded substrates/filters at the sampling site with the same sampling period without air passing through. Handling (loading/unloading) of substrates and filters was carefully operated in a glove box (free from particles, ammonia and sulphur dioxide).
The chemical composition was analysed by extracting the substrates with 5 mL Milli Q water (resistivity = 18.2 MΩ cm). Aliquots of the extracted solution were then analyzed for major cations and anions using ion chromatography. Details of the analytical procedure were presented by Leck et al. (2002).

The size ranges of the impactor stages, in aerodynamic diameter, were: 1) <0.161 µm, 2) 0.161-0.665 µm, 3) 0.665-2.12 µm 4) 2.12-5.0 µm, and 5) 5.0-10 µm, where the bounds are for 50% cut-off efficiency at 50% relative humidity (RH). In order to compare these numbers to other instruments, the corresponding geometric diameters for a dry aerosol were calculated. This was done by:

1. determining the water volume of the aerosol at 50% RH by inputting Na⁺, Cl⁻, SO₄²⁻, NH₄⁺ and NO₃⁻ concentrations measured by ion chromatography, and balancing the charge using H⁺ and OH⁻, into the aerosol inorganic model (AIM, http://www.aim.env.uea.ac.uk/aim/aim.php/) (Clegg et al. 1998; Wexler and Clegg 2002);
2. calculating the density of the wet aerosol at 50% RH (ρ_wet) assuming volume additivity;
3. converting the vacuum aerodynamic diameter (D_{va}) to a geometric diameter (D_p) using the two relationships: $D_p^2 \times C_e(D_p) \times \rho_{wet} = D_{va}^2 \times C_e(D_{va}) \times \rho_o \times \chi$, and $C_e = 1 + \frac{\lambda}{0.001 \times D} \left( 2.514 + 0.8 \times \exp \left( -0.55 \times \frac{D}{\lambda} \right) \right)$, where D is in µm, λ is the mean free path of air (0.0664 µm), $\rho_o = 1$ g cm⁻³ and $\chi = 1$. These equations are solved iteratively for D_p; and
4. removing the water content in the aerosol to convert the wet geometric diameter (D_{wet}) into a dry geometric diameter (D_{dry}) using the relationship $D_{dry}^3 = D_{wet}^3 \frac{\rho_{wet} m_{dry}}{\rho_{dry} m_{wet}}$, where the density of the dry aerosol ($\rho_{dry}$) and dry and wet masses (m_{dry} and m_{wet}) were inferred from the masses from AIM.

In this way, the dry geometric ranges for the cascade impactors were determined to be: 1) <0.099 µm, 2) 0.097-0.422 µm, 3) 0.422-1.37 µm 4) 1.36-3.22 µm, and 5) 3.21-6.44 µm.
In order to compare the mass measured by the impactors with the AMS, both the lowest two and the lowest three stages were used, with the mass representative of the AMS assumed to lie between these two. The results can be seen in Figure 3.13 and Figure 3.14. Depending on the statistic used to average the AMS mass (mean, geometric mean, median), the slope varied from 0.5 to 1. Overall, 0.8 is representative of the CE from this comparison.

Figure 3.13 - Comparing mean AMS and cascade impactor sulphate mass.

Figure 3.14 - Comparing mean AMS and cascade impactor MSA mass.
3.5.3. Comparison with PM$_1$ filters

A third approach compared the AMS mass with the sulphate and MSA mass measured by filters that sampled particles < 1 \( \mu \text{m} \) in diameter (PM$_1$). These particles were collected on Teflon filters using a filter cassette system. The sampling flow rate was about 90 L min$^{-1}$ and the sampling time ranged from 12 h to 24 h depending on the level of aerosol concentration on real time. Filters were extracted in 5.0 mL of deionised water by short manual shaking followed by 15 min of gentle rotation. The ions were measured using ion chromatography coupled with a quadrupole mass spectrometer. The results from this comparison can be seen in Figure 3.15 and Figure 3.16 for sulphate and MSA, respectively. The slopes suggest a CE for the AMS of approximately 0.75.

\[
\begin{align*}
\text{Sulphate} \\
y &= (0.8 \pm 0.1)x - 0.005 \pm 0.006 \\
r &= 0.851
\end{align*}
\]
AMS Mass, CE = 1 (µg m
-3
)

FMI PM1 Mass (µg m
-3
)

Figure 3.16 - Comparing mean AMS and PM1 MSA mass.

3.5.4. Summary

If the particles are internally-mixed, then the particle bounce in the vapouriser should affect all the components equally. As such, based on these three comparisons, the average AMS CE was determined to be 0.6 ± 0.2.

3.6. Appendix B: Discussion of solutions from positive matrix factorisation

For this study, a four factor solution was determined to best represent the measured aerosol. A two factor solution separates the Ship Emissions factor from the ambient background aerosol, while a three factor solution includes the Organic factor. It is only with four factors that the Marine Biogenic factor is separated from the Continental factor. Additional factors either identify instrumental noise, or split the existing factors. Figure 3.17 shows the decrease in \( Q/Q_{exp} \) as additional factors are included, where \( Q_{exp} \) is the expected \( Q \), the object function (see Section 3.2.6). We see that including a 5th factor decreases \( Q/Q_{exp} \) by identifying instrumental noise, while additional factors only serve to capture episodic events, often coinciding with ship emissions. Even though \( Q/Q_{exp} \)
decreased slightly from 3.36 for four factors down to 3.06 for 10 factors, including more factors did not contribute additional information about the measured aerosol. As such, the four factor solution was deemed to give the most information about the measured aerosol.

Figure 3.17 - The decrease in $Q/Q_{exp}$ as additional factors are included in the PMF solution.

The robustness of the solution can be explored by either varying the initial seed, which changes the set of pseudorandom values used for the initial point (Paatero 1997), or by using bootstrapping analysis, in which the rows of $X$ are randomly sampled and PMF is executed on the new dataset (as described by Reff et al. 2007). Both of these methods were used and the four factor solution at $f_{Peak} = -0.75$ was found to be robust: 100 values for the initial seed parameter in the PMF2 program resulted in 90 of the cases giving the solution presented here, while 100 iterations of the bootstrapping analysis < 0.015 µg m$^{-3}$ in the time series.
Although the solution at $f_{\text{Peak}} = -0.75$ is robust, a range of $f_{\text{Peak}} = -1.5$ to 0 provide physically reasonable solutions. The degree to which the composition and F44 are dependent on the solution can be seen in Figure 3.18 and Figure 3.19. Analyses were also performed on a data matrix calculated by adding together the mass spectra of the species of interest (i.e. nitrate, sulphate, organic and MSA) in nitrate equivalent mass with a corresponding error matrix calculated from the individual errors added in quadrature. However, results from the initial runs were similar enough to those calculated from the first method that only the first method was pursued.

a) Marine Biogenic Factor

b) Continental Factor

c) Organic Factor

d) Ship Emissions Factor

Figure 3.18 - Changes in fractional composition of the factors with varying $f_{\text{Peak}}$. 
Figure 3.19 - Changes in F44 with varying \( f_{\text{Peak}} \).

3.7. Acknowledgements

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3.8. Contributions

Rachel Chang is the author of the majority of the manuscript, made the AMS measurements, performed the PMF runs, and analysed the resulting data. Caroline Leck and Michael Tjernström were the principal investigators of the cruise and offered critical comments. The DMS data were provided by Martin Graus, Markus Müller and Armin Hansel and Section 3.2.3 was written by Martin. $^{210}$Pb and $^{222}$Rn data were provided by Jussi Paatero, who wrote Sections 3.2.4 and 3.2.5. Linda Orr ran the PSCF analysis and wrote Section 3.2.7, Andreas Stohl and John Burkhart ran FLEXPART and Andreas wrote Section 3.2.8, Katherine Hayden helped set up the AMS, whose use was provided by Shao-Meng Li and Richard Leaitch. Jonathan Abbatt provided useful feedback throughout the analysis and suggested different approaches.

Additional data used for the mass comparisons in Section 3.5 were provided by Douglas Orsini (DMPS); Caroline Leck and Qiuju Gao (BCI), Qiuju provided the text in the first two paragraphs of Section 3.5.2; and Risto Hillamo and Kimmo Teinilä (PM$_1$), who provided the text in Section 3.5.3.

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Chapter 4

The hygroscopicity parameter ($\kappa$) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation


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4.1. Introduction

Atmospheric aerosols can affect climate directly by scattering and absorbing incoming solar radiation, or indirectly by acting as cloud condensation nuclei (CCN), which form clouds and in turn can reflect light (Twomey 1977). The efficiency of particles as CCN also affects both aerosol particle and cloud droplet lifetimes (Albrecht 1989). It is well recognised that these effects represent one of the largest uncertainties in assessing the changes in radiative forcing from pre-industrial times to the present (Solomon et al. 2007). As such, understanding the hygroscopic properties of aerosols and the processes that govern cloud droplet activation are important.

Köhler theory has been used to predict the CCN-activity of inorganic compounds for many years (Köhler 1936). In the last decade, the focus has turned to the prediction of the CCN-activity of organic compounds in atmospheric particles. Laboratory studies have shown that the CCN-activity of organic, inorganic, or mixed aerosol systems can be predicted if the composition of the particles is well-characterised and their properties are known (Raymond and Pandis 2002; Raymond and Pandis 2003; Bilde and Svenningsson 2004; Broekhuizen et al. 2004a; Abbatt et al. 2005). However, ambient aerosols are composed of numerous organic compounds that are difficult to identify and quantify (Saxena and Hildemann 1996; Jacobson et al. 2000), therefore complicating the prediction of the CCN-activity of those ambient particles. The organic fraction comprises a significant fraction of the aerosol at many locations in the Northern Hemisphere (Zhang et al. 2007), highlighting the need to study organic aerosol hygroscopicity. In this study, we conduct an aerosol-CCN closure study of ambient aerosols at a continental site, in which we compare CCN concentrations measured using a CCN counter with those predicted using modified Köhler theory aiming to better describe the hygroscopicity of the organic components of the particles.

Two strategies are used in this paper to simplify the experimental approach to studying this aerosol property. These approaches reflect recent major developments in the aerosol field. First, field observations of the organic aerosol made by an aerosol mass
spectrometer (AMS) are characterised by the degree of oxygenation. One method of doing this is by using the molar ratio of atomic oxygen to atomic carbon (O/C) as measured by the AMS to represent the aerosol's degree of oxygenation (Aiken et al. 2008). Another method is to use factor analysis techniques such as the recently more popular positive matrix factorization (PMF) (Lanz et al. 2007; Ulbrich et al. 2009) to separate the oxygenated and unoxygogenated components. Here, aerosol mass spectra, which contain signals from hundreds if not thousands of organic molecules, are described as a linear combination of a few characteristic factors relating to emission sources, atmospheric processing, etc. This approach characterises the overall organic composition in terms of a sufficiently small number of factors that might match the number of organic aerosol species specified in climate and air quality models, such as the hydrophilic and hydrophobic organic fractions used in some global models (Cooke and Wilson 1996; Lohmann et al. 1999; Chung and Seinfeld 2002). A combination of AMS measurements (Zhang et al. 2007) and the subsequent application of PMF (Lanz et al. 2007; Ulbrich et al. 2009) is now a common approach used in the organic aerosol community.

The second simplifying advance of which we take advantage is to describe the organic hygroscopicity using the κ-Köhler method (Petters and Kreidenweis 2007; Petters and Kreidenweis 2008). Specifically, this expression of the Köhler model groups the properties of each compound present in the aerosol particle that affects its hygroscopicity into a single variable, κ. Thus, knowledge of the individual chemical properties (e.g. molecular solubility, molecular weight), which are largely unknown in ambient aerosol, is obviated. And so, as described in detail below, the specific goal of this work is to determine the hygroscopic properties (expressed as the κ parameter) of the oxygenated organic component of the aerosol, under the assumption that the oxygenated component drives the hygroscopicity for the entire organic fraction of the aerosol.

An extensive review of early aerosol-CCN closure studies that had limited information about the organic component of the aerosol can be found in Broekhuizen et al. (2006). However, with the recent widespread use of the AMS and following the initial study of Broekhuizen et al. (2006), a few closure studies have since been conducted in which the
aerosol chemical composition is highly time resolved and the organic fraction quantified. These studies from the field achieved closure by determining the hygroscopicity of either the entire aerosol by assuming an average chemical composition in continental China (Rose et al. 2008), or the entire organic component by assuming that the hygroscopicity in the organic component was constant at rural locations (Chang et al. 2007; Medina et al. 2007; Stroud et al. 2007), in the Amazon (Roberts et al. 2002; Gunthe et al. 2009), at cloud level (Wang et al. 2008), as well as sites that are removed from major source areas (Ervens et al. 2010). A general conclusion is that the organic fraction is hygroscopic. This contrasts with urban closure studies indicating insoluble organics (Lance et al. 2009), especially at small sizes (e.g. Broekhuizen et al. 2006; Cubison et al. 2008; Quinn et al. 2008), although this can also be true for remote locations (Ervens et al. 2007). Here we conduct a study of the hygroscopicity of the organic component at supersaturated conditions, focusing on the oxygenated component under the assumption that the unoxygenated component is non-hygroscopic. Similar results have been published for subsaturated conditions (McFiggans et al. 2005; Raatikainen et al. 2010) and more recently for laboratory and ambient measurements (Jimenez et al. 2009), although laboratory experiments have shown that organic aerosol hygroscopicity under subsaturated conditions can be lower than under supersaturated conditions (Prenni et al. 2007; Petters et al. 2009b; Wex et al. 2009). This study builds on the results from previous closure studies conducted in our group at urban and rural sites (Broekhuizen et al. 2006; Chang et al. 2007).

4.2. Experimental Method

The Egbert 2007 study took place between 14 May and 15 June 2007, at Environment Canada's Centre for Atmospheric Research and Experiment (CARE). This rural site, situated at Egbert, Ontario, Canada (44.23 N, 79.78 W, 251 m above sea level), approximately 70 km north of Toronto, is surrounded by farmland, and experiences minimal influence from local sources. The actual sampling location is 125 m from the main CARE building and the nearest road, 75 m away, is used by only a few vehicles per hour. The site is often impacted by polluted urban outflow from the populated and
industrialised regions of Southwestern Ontario and mid-western United States, as well as cleaner continental air from the north (Rupakheti et al. 2005).

The overall goal of Egbert 2007 was to improve our understanding of the sources and hygroscopicity of organic aerosols. To this end, recent publications from this campaign have shown that the oxidation state of the aerosol correlates with the photochemical age of the air (Vlasenko et al. 2009), significant secondary organic aerosol (SOA) mass can be formed from monoterpane oxidation (Slowik et al. 2010a), oxygenated organic aerosols from anthropogenically-influenced air could have primary and secondary sources, while biogenically-influenced air only had secondary sources (Chan et al. 2009), and aerosols from anthropogenically-influenced air showed a delay in cloud droplet activation compared to biogenically-influenced air (Shantz et al. 2010). The present study focuses on the hygroscopicity of the organic component of the aerosol by performing an aerosol-CCN closure experiment alongside measurements of the organic component of the gas and particulate phases, so as to best define the source of air sampled at CARE. A wide variety of instruments were deployed during the study, but only those of direct relevance to this analysis are described here.

4.2.1. Scanning Mobility Particle Sizer

A scanning mobility particle sizer (SMPS, TSI 3071, 3081, 3010) measured aerosol size distributions between 10 nm and 420 nm in diameter every 15 min with a sample to sheath flow ratio of 1:6, where the sheath flow was dried with silica gel. All instruments sampled from the roof of the building, with intakes \(\approx 5.5\) m above ground. The main inlet was a PVC pipe (0.2 m inner diameter), lined with aluminium tape to decrease electrostatic deposition, where the residence time was \(\approx 1\) min. The SMPS sampled from the central axis of the main inlet in stainless steel tubing with a residence time of the secondary lines of \(\approx 1\) s.
4.2.2. CCN counter

The CCN concentration was measured at a constant supersaturation using a parallel-plate continuous flow thermal gradient diffusion chamber that was previously used in a closure study at the same site (Chang et al. 2007). This instrument, built at the University of Toronto, is a more portable and automated version of the design described by Pradeep Kumar et al. (2003). It consists of two parallel aluminium plates held at different temperatures, which results in a supersaturation forming at the centre of the chamber (Saxena et al. 1970). A sheath flow (1.8 L min\(^{-1}\)) keeps the sample aerosol flow (0.2 L min\(^{-1}\)) at the centre of the chamber such that particles that are CCN-active at that supersaturation activate and are counted by an aerodynamic particle sizer (APS, TSI 3320) as they exit the chamber. The cooler bottom plate was maintained at room temperature while the warmer upper plate was actively heated with a resistive heating pad (Omega) to the temperature required for the desired supersaturation as calculated and controlled by a Labview (National Instruments) program from the temperature of the cooler bottom plate. Like the chamber described by Pradeep Kumar et al. (2003), this instrument has a movable injector that allows the residence time to vary from 9 to 21 s. The residence time of the chamber was adjusted to optimise the CCN concentration, which, for most of this study, occurred at 19 s. This time is a balance between giving the droplets sufficient time to grow to sizes large enough to be counted by the APS and preventing the aerosols from growing so large that they are lost to gravitational settling. The optimal residence time can also depend on the aerosol chemical composition. This effect was not explored systematically during this study, although (Shantz et al. 2010) discuss the kinetics of activation during the Egbert 2007 study.

The CCN counter was calibrated four times throughout the study using monodisperse ammonium sulphate particles to determine the activation diameter (i.e. the size at which 50% of the aerosols activate). Based on these calibrations and water activity coefficients from (Clegg et al. 1996), the effective supersaturation in the chamber was determined to be 0.42±0.04%. This instrument also sampled from the main inlet with a residence time in its secondary line of <6 s. The uncertainties in the CCN counter are estimated to be ±20%, principally based on the uncertainties in the APS counter and sample flow rate.
4.2.3. Proton-transfer-reaction mass spectrometer

Volatile organic compounds (VOCs) were measured using a proton-transfer-reaction mass spectrometer (PTR-MS, Ionicon Analytik). The details of this method and its application to ambient air sampling have been described elsewhere (de Gouw and Warneke 2007). A description of the instrument performance during this particular study can be found in Vlasenko et al. (2009). In brief, ambient air was sampled at 4.4 L min$^{-1}$ through a 7.5 m long PFA tube with 0.48 cm inner diameter whose inlet was 2 m from the main aerosol inlet. The PTR-MS sampled 0.2 L min$^{-1}$ from the main flow through a heated 0.2 cm outer diameter silcosteel line. Protonated VOC species were recorded in scanning mode from $m/z$ 21 to 160 on a 140 s time interval. The system was calibrated by standard addition using commercial custom-made gas mixtures (Apel-Riemer Inc. and Scott Specialty Gases). In addition, background measurements were made by installing a charcoal cartridge (Supelco) upstream of the PTR-MS inlet line.

4.2.4. Aerosol mass spectrometers

A time-of-flight aerosol mass spectrometer (C-ToF AMS, Aerodyne) measured the aerosol chemical composition that was non-refractory at 870 K and 10$^{-7}$ torr. The operation of the AMS has been described elsewhere (Jayne et al. 2000; Jimenez et al. 2003; Drewnick et al. 2005) and the specific operation of this instrument for this study is described by (Slowik et al. 2010a). This AMS sampled off a separate stainless steel and copper inlet ≈3 m from the main inlet with a residence time of ≈15 s. In this analysis, the bulk aerosol mass spectrum was used instead of the mass size distribution data because the PMF analysis, described below, was performed on the bulk data and is thus more representative of the entire aerosol. In addition, the signal was quite low at sizes < 100 nm diameter, which is the typical activation diameter, resulting in a low signal to noise. Using the bulk mass spectra assumes that the aerosol is internally mixed. This is not unreasonable since the mass distributions were mostly unimodal and there were no
significant local sources at the sampling site, although uncertainties from this assumption will be addressed in Section 4.4.4.

AMS mass concentration measurements are complicated by uncertainties in collection efficiency due to the possibility of particle bounce at the vaporiser surface that can vary with chemical composition. In general, this does not affect the analysis below, which only uses the fractional composition and assumes an internally mixed aerosol. If the aerosol were not internally mixed, then the collection efficiency could be important, and potential effects will be considered in Section 4.4.4 by considering relative uncertainties in the organic to inorganic ratios.

The PMF receptor modelling technique uses multivariate statistical methods to represent an input data matrix as a linear combination of a set of factor profiles (mass spectra, for AMS data) and their time-dependent intensities (Paatero and Tapper 1994; Paatero 1997). Application of PMF to AMS datasets have previously been discussed (Lanz et al. 2007; Ulbrich et al. 2009; Allan et al. 2010; Slowik et al. 2010b), as has the PMF analysis for the present study (Slowik et al. 2010a). In the present study, four factors were resolved for the organic component: a hydrocarbon-like organic aerosol (HOA) component correlating with tracers for primary anthropogenic emissions (e.g. NOx and benzene); a biomass burning organic aerosol (BBOA) component; and two oxygenated organic aerosol components (OOA-1, OOA-2), where OOA-1 is more oxygenated than OOA-2. OOA-1 correlates with tracers for long-range transport (e.g. particulate sulphate), while OOA-2 correlates with VOCs measured by the PTR-MS at m/z 71 (ion C4H6OH+), which is thought to arise from products of photochemistry (e.g. methacrolein and methyl vinyl ketone). Further detailed discussion about the PMF solutions can be found in (Slowik et al. 2010a), which also discusses that although the OOA-1 and OOA-2 factor mass spectra are similar to those of low-volatility OOA (LV-OOA) and semivolatile OOA (SV-OOA), respectively (Jimenez et al. 2009), tracer correlations suggest that the Egbert time series are not necessarily driven by volatility. As such, we continue to use the more general OOA-1/OOA-2 terminology, which allows the paper to remain consistent with the other publications from this study. However, after each mention of these factors we put in
brackets the new terminology that is being used in the community, e.g. OOA-1 (LV-OOA). The important point for the current analysis is the differentiation between the oxygenated (OOA and BBOA) and unoxygenated (HOA) components of the organic aerosol.

A high-resolution time-of-flight AMS (HR-ToF AMS, Aerodyne) was also deployed at the site. The mass resolution of the HR-ToF AMS, (3000–5000), allows for fragments of nominally the same $m/z$ to be quantified separately, and hence the total molar ratio of oxygen to carbon (O/C) can be determined. The application, accuracy, precision and limitations of the HR-ToF AMS in quantifying total C and O have been discussed previously (Aiken et al. 2007; Aiken et al. 2008). Although the absolute accuracy of determining O/C for ambient aerosols using an AMS is not well established, it can be used as a tracer for atmospheric oxidation. High resolution data analysis for this study was completed using a custom algorithm, which incorporated a peak fitting procedure, typical AMS correction factors and a correction for the O/C as suggested by (Aiken et al. 2008) to account for discrepancies between AMS derived O/C and that derived from laboratory standards. While the subsequent calculations and results are from the C-ToF AMS, they will be compared with O/C results from the HR-ToF AMS in Section 4.4.2.

### 4.3. Methodology for determining $\kappa$

#### 4.3.1. Determining the hygroscopicity of the organic component

Data were averaged into 15 min intervals. Using the chemical composition measured by the C-ToF AMS, the activation diameter for a dry particle at the supersaturation of the CCN chamber (0.42%) was calculated using $\kappa$-Köhler theory (Petters and Kreidenweis 2007; Petters and Kreidenweis 2008), which simplifies the Köhler equation to

$$S = \frac{D^3 - D_0^3}{D^3 - D_i^3(1 - \kappa)} \exp\left(\frac{4\sigma M_w}{\rho_w RTD}\right), \quad \text{Equation 4.1}$$
where $D$ and $D_i$ are the droplet wet diameter and initial dry diameter, respectively, $\sigma$ is the droplet surface tension (assumed to be that of water, 0.072 N m$^{-2}$), $M_w$ is the molecular weight of water, $\rho_w$ is the density of water, $R$ is the universal gas constant, $T$ is the temperature, and $\kappa$ is a single parameter that combines all the compound-specific variables (e.g. molecular weight, density, van't Hoff factor) of the aerosol.

In this equation, the overall $\kappa$ of the aerosol is calculated as the volume-weighted average of the $\kappa$ of the components, which assumes that the total volume of the water content can be calculated by adding the water contents of the individual components (Petters and Kreidenweis 2007), i.e.

$$\kappa_{tot} = \sum_i \varepsilon_i \kappa_i,$$

Equation 4.2

$\varepsilon_i$ and $\kappa_i$ are the volume fraction and $\kappa$ of the $i^{th}$ components of the aerosol. For a soluble compound, $\kappa_i$ can theoretically be expressed as:

$$\kappa_i = \frac{i \rho_i M_w}{\rho_w M_i},$$

Equation 4.3

where $i$, $\rho_i$, and $M_i$ are the van't Hoff factor, density and molecular weight, respectively, of the compound. In practise, however, $\kappa$ for a well-characterised compound such as ammonium sulphate can be inferred by using water activity data (e.g. Clegg et al. 1996) to calculate a Köhler curve, and then recreating this curve using Equation 1.1 and adjusting $\kappa$ until it has the same critical supersaturation as that calculated from the water activity data. In this way, $\kappa$ for ammonium sulphate and ammonium nitrate at 0.42% were determined to be 0.59 and 0.72, respectively (Clegg et al. 1996; Clegg et al. 1998; Wexler and Clegg 2002).

The inorganics measured by the AMS, ammonium, nitrate and sulphate, were grouped together and assumed to behave as ammonium sulphate, with a $\kappa$ of 0.59 and density of 1770 kg m$^{-3}$ (Windholz 1983) so that Equation 3.1 can be written as
\[ \kappa = \varepsilon_{\text{inorg}} \cdot \kappa_{\text{inorg}} + \varepsilon_{\text{org}} \cdot \kappa_{\text{org}}, \]  

**Equation 4.4**

where \( \text{inorg} \) and \( \text{org} \) represent the inorganic and organic components measured by the AMS, respectively. The errors associated with this assumption are not large (Section 4.4.4) since the aerosol was not acidic during the study and the \( \kappa \) and density of ammonium nitrate are 0.72 and 1730 kg m\(^{-3}\) (Windholz 1983), respectively, which are close to the values for ammonium sulphate. The sensitivity of our results to the presence of black carbon is discussed in Section 4.4.4 and the contribution of mineral dust to the aerosol submicron fraction is considered negligible at this site.

There are numerous approaches in representing \( \kappa_{\text{org}} \). However, in this analysis we will focus on two methods, both of which are based on the degree of oxygenation of the organic component as determined from AMS measurements. We generally assume that a more oxygenated organic aerosol is more polar and therefore more soluble and hygroscopic than a less oxygenated organic aerosol. In contrast, the more hydrocarbon-like component of the aerosol is non-polar and therefore less hygroscopic. We justify these assumptions in depth in Section 4.3.3. Under these assumptions, there is the expectation that the aerosol's hygroscopicity will increase with the degree of oxygenation, although this relationship would intrinsically arise from factors such as molecular weight or solubility, that would affect hygroscopicity and be related to the oxygenation of the organic components.

The first approach to representing \( \kappa \) uses the factors from the PMF analysis grouped into two components: a non-hygroscopic, un oxygenated component consisting of the HOA factor, whose \( \kappa \) (\( \kappa_{\text{unox}} \)) is approximated by 0, and a hygroscopic component, consisting of the oxygenated factors OOA-1 (LV-OOA), OOA-2 (SV-OOA) and BBOA with a \( \kappa \) of \( \kappa_{\text{ox}} \) such that \( \kappa_{\text{org}} \) in Equation 4.4 can be expressed as:

\[ \kappa_{\text{org}} = \varepsilon_{\text{ox}} \cdot \kappa_{\text{ox}} + \varepsilon_{\text{unox}} \cdot \kappa_{\text{unox}} = \varepsilon_{\text{ox}} \cdot \kappa_{\text{ox}}, \]  

**Equation 4.5**
where the density for the organic component used to calculate the volume fractions in both Equation 4.4 and Equation 4.5 are 1500 kg m$^{-3}$ (Kostenidou et al. 2007) for the oxygenated organic components, thought to be similar to SOA, and 900 kg m$^{-3}$ (Cylinder Lube 2008) for the unoxygenated organic component, thought to be composed of lubricating oil-like compounds (Zhang et al. 2005b). Note that $\varepsilon_{ox}$ in Equation 4.5 refers to the volume fraction of the oxygenated component in relation to the organic component only. Since $\kappa_{ox}$ is the only parameter that is not measured, it can be varied until the ratio of predicted to measured CCN number concentrations ($R_{CCN}$) is internally consistent (as described in Section 4.3.2). The oxygenated factors were grouped together because our model was not sensitive enough and/or our measurements were not accurate enough to elucidate separate hygroscopicities for each factor.

The second approach assumes a direct relationship between the organic aerosol's degree of oxygenation and its hygroscopicity. The simplest relationship is a linear one, so that

$$\kappa_{org} = a \cdot (O / C),$$

Equation 4.6

where \(O / C\), the mole ratio of atomic oxygen to atomic carbon, is a measurement of the organic aerosol's degree of oxygenation and can be estimated from the fraction of the total organic signal occurring at \(m/z 44\) measured by the C-ToF AMS using the equation in Figure 4b of Aiken et al. (2008). In Equation 4.6, \(a\) is the sensitivity of \(\kappa_{org}\) on O/C and is unknown, allowing it to be varied until \(R_{CCN}\) is again internally consistent. We stress that this postulated relationship between the organic aerosol's O/C and hygroscopicity may not be linear and more complicated relationships between the two quantities will exist that may be more accurate, but for the purposes of this study, we start with the simplest functionality.

Using either approach, \(\kappa\) for the entire aerosol can be calculated from Equation 4.4 combined with either Equation 4.5 or Equation 4.6. The initial particle size ($D_i$) in Equation 1.1 was increased until the critical supersaturation was equal to the supersaturation of the CCN counter (0.42%) to determine the critical diameter. The
aerosol size distribution, as measured by the SMPS, was then integrated for all dry particle sizes greater than the activation diameter to arrive at the predicted CCN concentration. $\kappa_{\text{org}}$ was then iteratively varied (either by changing $\kappa_{\text{ox}}$ in Equation 4.5 or $a$ in Equation 4.6), changing the activation diameter and thus predicted CCN concentration, until $R_{\text{CCN}}$ was internally consistent, as will be described in the next section.

4.3.2. Statistical methods

The relative contribution of the organic component to the hygroscopicity of the ambient aerosol at Egbert depends on the magnitude of the inorganic fraction (Chang et al. 2007), with the organic fraction contributing less to a particle's overall hygroscopicity in inorganic-rich particles. In addition, since the hygroscopicity of inorganic particles has been studied extensively, it is expected that the predicted CCN concentrations during periods in which the aerosol is mostly inorganic would be more accurate. A plot of $R_{\text{CCN}}$, the ratio of CCN concentrations predicted using the $\kappa$-Köhler model to concentrations measured with the CCN counter, for the entire study is plotted as a function of aerosol inorganic fraction in Figure 4.1a (consider all data points in the figure). Figure 4.1a shows that $R_{\text{CCN}}$ is dependent on composition when the entire organic component is assumed to be non-hygroscopic (i.e. $\kappa_{\text{org}}=0$), with the organic-rich data points, the lower 50th percentile of the entire population in Figure 4.1a, being underpredicted ($R_{\text{CCN}}=0.871\pm0.007$) compared to the inorganic-rich data points, the upper 50th percentile of the entire population in Figure 4.1a, which averaged to $1.17\pm0.01$. Note that the average $R_{\text{CCN}}$ over all chemical compositions is $0.974\pm0.006$. As the distributions were log-normal, the values given are the geometric mean and the uncertainties are the standard error, calculated based on the geometric standard deviation, although these values do not vary greatly from the linear statistics ($R_{\text{CCN}}=0.902\pm0.007$ and $R_{\text{CCN}}=1.15\pm0.01$ for the organic-rich and inorganic-rich halves of the population, respectively).
Figure 4.1 – \( R_{CCN} \) as a Function of Inorganic Fraction
Ratio of predicted to measured CCN concentrations plotted against aerosol inorganic fraction. Panel (a) shows the case in which all of the organic component is assumed to be non-hygroscopic (\( \kappa_{org}=0 \)) while (b) shows the case in which \( \kappa_{ox}=0.22 \). Panel (c) assumes a constant \( \kappa \) of 0.30 for the entire aerosol. Red and green points refer to data from the Anthropogenic and Biogenic periods, respectively (see Figure 4.4), while the remainder of the study is represented by black points.

In order to assess this systematically, the data points were sorted based on the magnitude of their inorganic fraction and the mean \( R_{CCN} \) of the upper and lower 50\(^{th}\) percentiles were then compared. \( \kappa_{org} \) for the entire data set was varied until the means of the two halves were no longer significantly different (two-tailed t-test, unequal variances, significance level of <0.05). Since aerosols with a high inorganic fraction are less sensitive to changes in the hygroscopicity of the aerosol's organic component (see
Broekhuizen et al. 2004a; Chang et al. 2007), the mean of the more inorganic half of the population was used as a reference.

This method of internal comparison was chosen because both measured and predicted CCN concentrations are precise but not necessarily fully accurate due to experimental uncertainties, such as different line losses to the SMPS and CCN counter, errors in the sizing of the SMPS and counting errors in both systems, as well as uncertainties in model assumptions, such as mixing state, particle sphericity, density, etc. As such, the criterion for the best value of $\kappa_{ox}$ is a consistent $R_{CCN}$, whether over- or underpredicted, regardless of composition. However, this method is susceptible to any systematic errors that may selectively affect either the inorganic or organic components measured by the AMS. These uncertainties are considered in Section 4.4.4.

4.3.3. Degree of Oxygenation and Hygroscopicity: Assumptions and Approach

It should be noted that our goal in this work is to extend previous studies by working from an assumption that has been used in the past, i.e. that some part of the organic aerosol component leads to CCN-activity and another does not. Whereas past aerosol-CCN closure studies have only assumed that a constant fraction of the organic aerosol component is soluble and that the remainder is insoluble (Broekhuizen et al. 2006; Chang et al. 2007; Medina et al. 2007; Stroud et al. 2007), in this paper we suggest that the oxygenated factors from the PMF analysis represent the soluble organic component while the unoxygenated factor represents the insoluble organic component. Or, using the concept of hygroscopicity, we postulate that the oxygenated factors contribute to the hygroscopicity of the aerosol, and that the unoxygenated factor does not, whether due to its solubility, as suggested by (Petters et al. 2009b), or its intrinsic hygroscopicity.

Although extraction of the $\kappa$ of both the oxygenated and unoxygenated components from an unconstrained fit of the data to a model would be the ideal approach, the uncertainties in our measurements were too large to evaluate the difference between sets of $\kappa$
parameters. In part, this is because of the relatively narrow range of oxygenation observable at one field site during one campaign. And so, we constrained our model by assuming that the unoxygenated (HOA) component of the organic aerosol contributed minimally to the aerosol hygroscopicity. This is not unreasonable because HOA is thought to be hydrocarbon-like (Zhang et al. 2005b) and aliphatic in nature, and in general, these types of compounds have not been found to be CCN-active in laboratory experiments (e.g. Raymond and Pandis 2002; Pradeep Kumar et al. 2003). In addition, ambient measurements of particles at locations in which HOA is high, especially at the smaller sizes, have shown that the organic component does not appear to contribute to the CCN-activity (Broekhuizen et al. 2006; Cubison et al. 2008; Quinn et al. 2008). Based on these literature results, we feel that the assumption that the unoxygenated component is non-hygroscopic is reasonable.

In contrast to the HOA factor, the OOA factors, which make up most of the oxygenated component of the organic aerosol, are thought to be characteristic of highly processed organic aerosols (Zhang et al. 2005b) formed from secondary processes (Zhang et al. 2007). Again, laboratory experiments of compounds that are formed from these types of processes such as glutamic, glutaric, pinonic and norpinic acids have found that these aerosols are moderately CCN-active (Raymond and Pandis 2002) and smog chamber studies of gaseous organic precursors with ozone or OH have also found that the organic aerosols formed are moderately CCN-active (e.g. Duplissy et al. 2008). In addition, this assumption is supported by laboratory studies that have found that oleic acid particles that have undergone ozonolysis become somewhat CCN-active (Broekhuizen et al. 2004b; Shilling et al. 2007) and chamber studies that show that ageing organic aerosols can also increase their CCN-activity to varying amounts (Petters et al. 2006; Duplissy et al. 2008; Wex et al. 2009). We do note that there is also some evidence that the hygroscopicity of SOA under supersaturated conditions in chamber studies do not vary with ageing (Prenni et al. 2007; Juranyi et al. 2009).

These findings lend credence to treating the oxygenated component of the organic aerosol as CCN-active and that it is reasonable to assume that this factor dominates the overall
organic aerosol hygroscopicity. Thus, the main objective of this work was to attempt to constrain the hygroscopicity of the oxygenated organic component of ambient aerosols.

The hygroscopicity of the BBOA component has uncertainty associated with it. Originally, we viewed the full BBOA factor to be similar to the biomass burning marker levoglucosan (see Lanz et al. 2007), which is quite hygroscopic (Petters and Kreidenweis 2007) and was therefore grouped with OOA in the oxygenated component. However, more recent work has suggested that there are other components that make up the BBOA fraction (Petters et al. 2009a) that are not as hygroscopic, which is why its solubility is considered in Section 4.4.4.

Table 4.1 – O/C calculated for the PMF factors of the organic aerosol component.

<table>
<thead>
<tr>
<th>Factor</th>
<th>m/z 44 / Total Organic</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>OOA-1 (LV-OOA)</td>
<td>0.19</td>
<td>0.81</td>
</tr>
<tr>
<td>OOA-2 (SV-OOA)</td>
<td>0.10</td>
<td>0.46</td>
</tr>
<tr>
<td>BBOA</td>
<td>0.025</td>
<td>0.17</td>
</tr>
<tr>
<td>HOA</td>
<td>8×10^{-8}</td>
<td>&lt;0.08</td>
</tr>
</tbody>
</table>

The reasoning behind the postulated relationship between $\kappa_{\text{org}}$ and O/C is similar to that above. Since PMF finds factors by reconstructing the organic mass spectrum as linear combinations of these factors, the O/C of the organic component (since it is based on the signal at m/z 44) can also be calculated as a linear combination of the O/C of our factors, with the O/C of the unoxygenated component approaching zero and the O/C of the most oxygenated component at 0.81 (see Table 4.1). Organic aerosols with mixed compositions will lie between these two values. Mathematically, both Equation 4.5 and Equation 4.6 can be considered for an organic component that is composed entirely of the oxygenated factors, resulting in a $\kappa_{\text{org}}$ of $\kappa_{\text{ox}}$ or $a \cdot (\text{O/C of the oxygenated component})$, while a completely unoxygenated organic aerosol would have $\kappa_{\text{org}}=0$ using either equation (since the O/C of the unoxygenated (HOA) component approaches 0). In reality, these two methods are not exactly the same (see Figure 4.2) since the factor method uses the volume-weighted average while the O/C method uses mass-weighted averages, which
result in a slightly different shape to the curves. However, for the most part, these two methods essentially represent the same relationship between the degree of oxygenation of the aerosol and its hygroscopicity.

Figure 4.2 - $\kappa_{\text{org}}$ using Equation 4.5 (red dotted line) and Equation 4.6 (black line). $\kappa_{\text{ox}} = 0.22$ and $\alpha = 0.29$ as described in Section 4.4.

Results from laboratory studies are inconclusive about the relationship between organic oxygenation and hygroscopicity under supersaturated conditions. Un oxygenated organic aerosols that are non-hyg roscopic such as oleic acid, stearic acid and bis-2-ethylhexyl sebacate, can be heterogeneously oxidised such that they become moderately hygroscopic (Broekhuizen et al. 2004b; Petters et al. 2006; Shilling et al. 2007; George et al. 2009). A smog chamber study by (Wex et al. 2009) also showed that the hygroscopicity of SOA increased in the absence of an OH scavenger, which the authors suggested was due to increased oxidation in the organic aerosol. Finally, (Duplissy et al. 2008) also showed that the hygroscopicity increased slightly throughout the photoxidation of $\alpha$-pinene. However, there have also been several studies of SOA in smog chambers that have not observed any dependence of hygroscopicity on degree of oxygenation, whether by varying precursor concentrations that should result in varying oxygenation in the final aerosol (Juranyi et al. 2009), or by monitoring the hygroscopicity throughout a reaction (Prenni et al. 2007). As such, the dependence of hygroscopicity on the degree of oxygenation from laboratory studies is unclear. However, the applicability of these lab
experiments to ambient conditions has not been fully confirmed, given that chamber-generated SOA tend to be less oxygenated than the OOA-1 (LV-OOA) component found in highly processed ambient aerosols (Ng et al. 2010). Although the focus of this work is on supersaturated conditions, and it is unclear whether such \( \kappa \) parameters are fully the same as those derived from subsaturated conditions, we do note that \( \kappa \) for organic aerosols measured under subsaturated conditions have recently been reported to scale with the O/C of the aerosol (Jimenez et al. 2009).

4.4. Results and Discussion

4.4.1. Results from the Entire Study

4.4.1.1. Calculations using oxygenated and unoxygenated factors

Using the method described in Section 4.3.2 and Equation 4.5, \( \kappa_{\text{ox}} \) for the entire study was found to be 0.22±0.04. Figure 4.1b shows that increasing the hygroscopicity of the organic component reduces the difference between the mean \( R_{\text{CCN}} \) of the organic-rich data points and the inorganic-rich data points (geometric mean \( R_{\text{CCN}} \) are 1.19±0.02 and 1.18±0.01, respectively), compared to the completely non-hygroscopic case (Figure 4.1a). It is difficult to reconcile the overprediction from this calculation of almost 20% to that calculated from a linear regression of the predicted and measured CCN concentrations, which resulted in a slope of 1.03 (see Figure 4.3). While the slope from the linear regression is comparable to other field studies (Broekhuizen et al. 2006; Chang et al. 2007; Medina et al. 2007; Wang et al. 2008) which have found similar values, it is calculated in a different way and puts more emphasis on the data points at high concentrations. In an attempt to lessen this effect, a linear regression of the logarithm of the concentrations was also attempted, although this resulted in a similar slope of 1.02. Finally, if the data points are weighted by their estimated error (±20% for measured CCN concentrations) and the intercept forced through zero, then the slope can be increased to 1.10 (1.05 if the intercept is not forced through zero), which halves the discrepancy with the value obtained from \( R_{\text{CCN}} \). Nevertheless, this difference is within the uncertainties of our CCN counter.
4.4.2. Calculations using O/C

Using the O/C to calculate $\kappa_{\text{org}}$ from Equation 4.6, and varying $a$ in the method described in Section 4.3.2 resulted in the relationship

$$\kappa_{\text{org}} = (0.29 \pm 0.05) \cdot (O/C), \quad (0.3 < O/C < 0.6),$$

Equation 4.7

where the uncertainties are values for which the means of the two halves of the population are not significantly different (two-tailed t-test, unequal variances, significance level of $p<0.05$) and the range of O/C observed during this study and used to derive this relationship was 0.3 to 0.6. As mentioned previously, the O/C was estimated from the fraction of the organic signal at $m/z$ 44, directly from the C-ToF AMS mass spectra, which, on average, is 6% higher than that calculated from the HR-ToF AMS. The grey trace in the top panel of Figure 4.4 shows the time series for $\kappa_{\text{org}}$ calculated using the PMF factors, assuming $\kappa_{\text{ox}} = 0.22$ and $\kappa_{\text{unox}} = 0$, while the black and red traces are from
Equation 4.7, using O/C estimated from the C-ToF and HR-ToF AMSs, respectively. We see that all three estimates of $\kappa_{\text{org}}$ yield similar results. This is not unexpected since both the PMF and O/C approaches incorporate the degree of oxygenation of the organic component calculated using different analyses. In essence, this shows that the O/C of the entire aerosol can be reasonably expressed as a linear combination of the O/C of the PMF factors.

![Figure 4.4 - Time series during Egbert 2007. Time series in local time of $\kappa_{\text{org}}$ calculated from PMF factors and O/C (top panel, see text for more detail), toluene/benzene (black trace in middle panel), PMF factors (middle panel, note that these are cumulative), and aerosol chemical measurements measured by the AMS and CCN concentrations (bottom panel).](image)

The attraction of this method is that $\kappa_{\text{org}}$ is calculated from the degree of oxygenation of the organic component of the aerosol as deduced from aerosol mass spectra and does not depend on PMF, which involves a stage of statistical analysis. However, it is unclear whether this approach can be generalised to other aerosol types and locations because the
range in the O/C for this study was quite limited (0.3 to 0.6). As such, analysis of ambient aerosols with a wider range of oxygenation should be tested to determine whether this simple relationship between hygroscopicity and aerosol oxygenation is widely applicable.

As a general caveat, the slope in Equation 4.7 may only be representative of the conditions in this study, which examine the bulk ambient, non-refractory organic aerosols measured specifically by the AMS. Also, it does not account for organonitrate or organosulphate components that may be present. Not only do these compounds contribute to an underestimation of the actual O/C (Farmer et al. 2010), but they are also oxygenated and likely hygroscopic, without contributing to the O/C itself, further underestimating the organic component's hygroscopicity. It is important to note that a relationship between O/C and $\kappa_{\text{org}}$ would not necessarily indicate that the former controls the latter. Rather, it would suggest that O/C correlates to molecular properties that affect an organic particle's hygroscopicity, such as molecular weight and solubility. Nonetheless, we feel that this relationship may provide useful insight since O/C can be derived directly from mass spectral data.

Similar to the method described by Shinozuka et al. (2009), it is possible to directly infer $\kappa$ for the organic component of the aerosol. The activation diameter is first determined by finding the diameter above which the aerosol size distribution would equal the measured CCN concentrations. Using the activation diameter and the supersaturation of the chamber, $\kappa$ for the entire aerosol can be determined and $\kappa_{\text{org}}$ calculated from Equation 4.4. These values are plotted against the O/C in black in Figure 4.5. In this figure, the grey lines are the uncertainties in $\kappa_{\text{org}}$ calculated based on the ±20% uncertainty in the measured CCN concentration and the blue line is the relationship postulated in this analysis. Further, following the method described by Shinozuka et al. (2009), these values were binned by O/C in increments of 0.025, as shown by the red points in Figure 4.5, although only $\kappa_{\text{org}}< 5$ were considered in this analysis. These results do not change significantly if the geometric mean for each bin is used instead of the presented arithmetic mean. The uncertainties in these binned data were determined by adding in quadrature the standard error to the error calculated from error propagation of the
uncertainties in the inferred $\kappa_{\text{org}}$. The uncertainties in the O/C have not been included in the figure to maintain clarity, however, they are approximately ±0.1 as determined from Aiken et al. (2008).

![Inferred $\kappa_{\text{org}}$ inferred from size distributions as a function of O/C. Grey lines are the uncertainties in the inferred $\kappa_{\text{org}}$. Red points are data binned by 0.025. The uncertainties in the O/C for the binned data points are ±0.1. See text for more detail.](image)

The binned $\kappa_{\text{org}}$ have high uncertainties associated with them. To derive an empirical relationship, we note that the unweighted least-squares-fit indeed indicates a positive correlation between $\kappa_{\text{org}}$ and O/C ($\kappa_{\text{org}} = (0.9±0.5) \cdot (\text{O/C}) - (0.3±0.2)$, $0.3 < \text{O/C} < 0.6$), although the uncertainties in the fit parameters are very high. It is for this reason that we chose to constrain our data by assuming that the un oxy genated component of the aerosol is completely non-hygroscopic, thus focusing our analysis on extracting only one parameter, (i.e. either the $\kappa_{\text{ox}}$ or the slope of the $\kappa_{\text{org}}$ vs. O/C linear relationship). If the empirical relationship in Figure 4.5 between $\kappa_{\text{org}}$ and O/C is valid, then it suggests that inclusion of a negative intercept may be more appropriate in Equation 4.6. However, we do not feel comfortable making that conclusion based on our data alone, given the high uncertainties.
These results appear to be similar to those published by Jimenez et al. (2009), despite the fact that their measurements were made at subsaturated conditions and numerous studies have found that hygroscopicity of chamber-generated SOA at subsaturated regimes appears to be more dependent on the organic aerosol's degree of oxygenation than at supersaturated regimes (e.g. Prenni et al. 2007; Juranyi et al. 2009; Petters et al. 2009b). However, as stated above, we do not feel that our data sufficiently constrain the $\kappa_{\text{org}}$ vs. O/C relationship.

4.4.3. Results from Select Time Periods Using Oxygenated and Unoxygenated Factors

Because local sources were not prominent at the sampling site, it was possible to characterise regional air masses during which the organic aerosol composition was assumed to be more uniform. From this analysis, we can assess the degree to which the organic components have the same hygroscopicity regardless of source by seeing how consistent these results are with the results from Section 4.4.1 for the entire study. The study was broken down into four air regimes based on aerosol chemical composition, the characteristics of the organic component (based on the PMF factors), local wind direction and wind speed, the photochemical age of the air from the ratio of toluene to benzene (Roberts et al. 1984; de Gouw et al. 2005), and back trajectories. The four air regimes are described below and illustrated in Figure 4.4 with typical back trajectories calculated using HYSPLIT (Draxler and Rolph 2003; Rolph 2003) shown in Figure 4.6. All dates and times are local, eastern daylight savings time.
1. For this study, periods of high anthropogenic influence were characterised by both high sulphate and organic aerosol mass loading. The toluene/benzene was often high, suggesting a shorter photochemical age, and back trajectories show that the air masses originated from populated regions to the south (thick red trace in Figure 4.6). These periods are referred to as “Anthropogenic”, while recognizing that aerosol precursors will not be exclusively anthropogenic.

2. Two of the Anthropogenic periods were preceded by times when the local winds were from the southeast (not shown) and the aerosol was mostly organic (specifically high HOA and OOA-1 (LV-OOA) and very low OOA-2 (SV-OOA), as opposed to the
Anthropogenic period which had more OOA-2 (SV-OOA)) with very little sulphate. The back trajectories tended to be from the northwest to northeast, suggesting that these air masses did not originate from highly populated or polluted regions (dashed purple trace in Figure 4.6) However, because the toluene/benzene was notably high (suggesting that the photochemical age was short), it would appear that the aerosols during these times were from clean continental air but were influenced by quite fresh, local anthropogenic emission (e.g. a highway 10 km to the east). These periods are referred to as “Pre-Anthropogenic”.

3. Continental air, characterised by low sulphate loadings, low toluene/benzene (suggesting enhanced photochemical processing) and higher organic mass fractions, was associated with trajectories from the mostly forested north (thin green trace in Figure 4.6). The earlier episode (19–21 May) was colder and expectedly less influenced by biogenic emissions whereas the episode near the end of the study (8–13 June) was characterised by warmer temperatures and high organic mass loadings mostly from biogenic sources (Slowik et al. 2010a). These periods are referred to as “Biogenic” for this analysis. Measurements during the second biogenic period were interrupted by a failure in the CCN counter, as well as a period (11 June, 18:15–12 June, 18:30) during which the air was elevated in SO₂ and particulate sulphate concentrations. The majority of the sulphur in the latter case is suspected to have originated from smelters in the Sudbury region based on the back trajectories (not shown); such an observation at Egbert is not uncommon (Rupakheti et al. 2005).

4. At the end of the study, after the final Biogenic period, the winds shifted from the north to the east and the air was characterised by a high toluene/benzene as well as a higher HOA fraction (compared to the Biogenic period). Back trajectories show the air originating from the east (dotted blue trace in Figure 4.6), suggesting that it is different from the Biogenic period. This period will be referred to as “Easterly Flow”.

The composition of the aerosol during the Anthropogenic periods was dominated by the inorganic fraction, and similar to the arguments made in Section 4.3.2, is expected to be less sensitive to changes in the hygroscopicity of the organic component (Chang et al. 2007). An analysis similar to that described in Section 4.3.2 was used to evaluate κ_{ox}, but
in this case, the mean $R_{CCN}$ of the Anthropogenic periods was used as a reference and compared to the mean $R_{CCN}$ of the other time periods to determine their $\kappa_{ox}$. This is illustrated in Figure 4.1, which shows that $R_{CCN}$ for the Anthropogenic periods (in red) is mostly inorganic (and makes up the majority of the points that are highly inorganic) and is less sensitive to an increase in $\kappa_{ox}$ compared to the Biogenic periods (in green). Table 4.2 shows $\kappa_{ox}$ found for the different air regimes and the uncertainties denote when the mean $R_{CCN}$ of the time periods became significantly different from that of the Anthropogenic periods.

Table 4.2 – $\kappa_{ox}$ for select air regimes.

<table>
<thead>
<tr>
<th>Air Regime</th>
<th>$\kappa_{ox}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogenic</td>
<td>0.25±0.06</td>
</tr>
<tr>
<td>Easterly Flow</td>
<td>0.29±0.03</td>
</tr>
<tr>
<td>Pre-Anthropogenic</td>
<td>0.07±0.03</td>
</tr>
</tbody>
</table>

For the Biogenic and Easterly Flow periods, $\kappa_{ox}$ are similar, suggesting that the hygroscopicity of the organic component can be characterised in the same manner. They are also similar to the value of 0.22 that was found from the analysis for the entire study period in Section 4.4.1.1. However, the Pre-Anthropogenic periods had a lower $\kappa_{ox}$ than the rest of the study, suggesting that during this time, the oxygenated components are not contributing significantly to the hygroscopicity of the aerosol. At this point we can only suggest reasons why this behaviour was observed. In particular, noting that the HOA component of the aerosol is high and that the air mass may have experienced recent traffic emissions, it is possible that the HOA plays a role in suppressing CCN-activity, perhaps through an effect on the mass accommodation coefficient for water uptake, similar to the observations by (Shantz et al. 2010). However, this is only speculation and we have no firm evidence that this is the case during this air regime.

For all these cases, we stress that the extracted $\kappa$ values have been derived using the Anthropogenic case as a reference, under an assumption that the organics do not strongly affect the hygroscopicity for such inorganic-rich particles.
Figure 4.7 shows plots of predicted to measured CCN concentrations for the different air regimes assuming $\kappa_{ox}=0$ (black points) and $\kappa_{ox}=0.22$ (red points). As expected, we see that during the Anthropogenic time (Figure 4.7a), the predicted CCN concentrations do not change significantly compared to the Biogenic and Easterly Flow times (Figure 4.7c and d), as well as the Pre-Anthropogenic time, which is even overpredicted (Figure 4.7b) when $\kappa_{ox}=0.22$.

![Figure 4.7](image_url)

Figure 4.7 – Comparison of predicted and measured CCN concentrations for different time periods. $\kappa_{ox}=0$ (black) and 0.22 (red) for periods shown in see Figure 4.4. The lines are 1:1 lines.

### 4.4.4. Uncertainties

Table 4.3 shows the sensitivity of our results to different uncertainties, calculated by changing each parameter and adjusting $\kappa_{org}$, as described in Section 4.3.2, and reporting the difference. Systematic uncertainties in the chamber supersaturation ($\pm 0.04\%$ supersaturation, Case 1) and SMPS diameter sizing ($\pm 5\%$, Case 2) are quantified for both
calculation methods in Table 4.3. However, because the statistical method used to evaluate $\kappa_{ox}$ and $a$ compares the mean ratio of predicted to measured CCN concentrations, our results are not sensitive to systematic uncertainties in the total concentrations of either the SMPS or the CCN counter.

Other uncertainties pertain to the aerosol chemical composition and attempts to quantify uncertainties in the density of the unoxygenated and oxygenated components (Cases 3 and 4, respectively), both of which affect the calculation of the volume fraction in Equation 4.4 but appear to have minimal effect on $\kappa$. If the BBOA component is considered non-hygroscopic (Case 5), the results for $\kappa_{ox}$ are 0.04 higher. The uncertainties in determining the oxygenated and unoxygenated components can be large. Case 6 considers the case in which the mass fraction of the total organic that is oxygenated is increased by 0.1 (and the corresponding unoxygenated mass fraction decreases by 0.1) while Case 7 considers the effects if the opposite occurred. Similarly, Case 8 considers the effects of a 20% uncertainty in the O/C.
Table 4.3 – Sensitivity analysis for potential uncertainties in the two calculation methods. See text for description of each case.

<table>
<thead>
<tr>
<th>Case</th>
<th>Description</th>
<th>Uncertainty in $\kappa_{ox}$</th>
<th>Uncertainty in $a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.04% uncertainty in supersaturation</td>
<td>±0.06</td>
<td>±0.07</td>
</tr>
<tr>
<td>2</td>
<td>5% uncertainty in SMPS size</td>
<td>±0.04</td>
<td>±0.06</td>
</tr>
<tr>
<td>3</td>
<td>10% uncertainty in density of unoxygenated component</td>
<td>±0.01</td>
<td>±0.01</td>
</tr>
<tr>
<td>4</td>
<td>10% uncertainty in density of oxygenated component</td>
<td>&lt;0.01</td>
<td>±0.01</td>
</tr>
<tr>
<td>5</td>
<td>BBOA as insoluble</td>
<td>+0.04</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>0.1 increase in mass fraction of oxygenated fraction</td>
<td>+0.07</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>0.1 decrease in mass fraction of oxygenated fraction</td>
<td>-0.05</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>20% uncertainty in O/C</td>
<td>–</td>
<td>±0.06</td>
</tr>
<tr>
<td>9</td>
<td>EC/OM ratio = 0.2</td>
<td>+0.05</td>
<td>+0.05</td>
</tr>
<tr>
<td>10</td>
<td>Ammonium nitrate separate</td>
<td>&lt;0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>11</td>
<td>Composition of small particles</td>
<td>+0.08</td>
<td>+0.11</td>
</tr>
<tr>
<td>12</td>
<td>50% increase in organic mass</td>
<td>+0.04</td>
<td>+0.05</td>
</tr>
<tr>
<td>13</td>
<td>50% increase in inorganic mass</td>
<td>-0.06</td>
<td>-0.09</td>
</tr>
<tr>
<td>14</td>
<td>10% decrease in surface tension</td>
<td>-0.08</td>
<td>-0.12</td>
</tr>
<tr>
<td>15</td>
<td>20% decrease in surface tension</td>
<td>-0.16</td>
<td>-0.22</td>
</tr>
</tbody>
</table>

Results from (Chan et al. 2009) for Egbert 2007 found that the ratio of elemental carbon to organic matter (EC/OM) for the study was 0.2 except for the final Biogenic periods, during which it decreased to 0.15. Case 9 considers the normal case in which the ratio is 0.2 and the extra EC mass is assumed to be non-hygroscopic with a density of 1800 kg m$^{-3}$.

As mentioned in Section 4.3.1, the inorganics were grouped together in this analysis and assumed to behave as ammonium sulphate. Case 10 considers the change in $\kappa_{ox}$ and $a$.
if ammonium nitrate is calculated separately. The difference is not great, which is not surprising since its density and $\kappa$ are similar to that of ammonium sulphate.

The greatest uncertainty in the chemical composition of the aerosol arises from the degree to which the composition of the particles < 100 nm (i.e. the activation diameters typical of this study) is similar to the composition of the bulk aerosol. To this end, three cases are considered. Case 11 considers the changes in $\kappa_{ox}$ and $a$ if the chemical composition is calculated from the size distribution data of the C-ToF AMS for vacuum aerodynamic diameters 80–250 nm, as an indication of the composition of the smaller particles, while Case 12 and 13 consider the more general cases of the organic and inorganic components of the aerosol being 50% greater at smaller sizes compared to the bulk aerosol, respectively. In general, the composition of the smaller particles would be expected to be more organic (Zhang et al. 2005a), suggesting that the values derived from the bulk analysis may be biased low. These last two cases also allow us to evaluate the uncertainties in the event that the AMS preferentially under- or over-measured either the inorganic or organic component of the aerosol.

In general, uncertainties associated with the chemical composition are individually similar to the uncertainty determined statistically for $\kappa_{ox}$ and $a$, although the cumulative effects of multiple cases occurring at once are not quantified. The uncertainties are relatively low for each individual case because the composition of the aerosol is, for the majority of the study, > 25% inorganic and < 25% unoxygenated organic in mass, making the CCN-activity fairly insensitive to changes in the chemical composition (i.e. upper right section of Figure 5 in Chang et al. (2007)). However, it is possible that uncertainties in multiple factors combine to reduce the overall apparent uncertainty.

Finally, Cases 14 and 15 show the sensitivity of the results to a decrease in the surface tension of the droplet by 10% and 20%, respectively, which have the greatest effect on the predicted values. Reductions in the droplet surface tension result in the greatest uncertainty since they affect the exponential term in Equation 1.1. However, the $\kappa$-Köhler model usually uses the surface tension of water and $\kappa$ is varied to account for aerosol
properties (Petters and Kreidenweis 2007). As such, the uncertainties in Cases 14 and 15 are presented to gain general understanding in the sensitivity of our results.

4.4.5. Comparison with literature values

A class of compounds that could be representative of the oxygenated component of the aerosol would be SOA. These typically have a van't Hoff factor of one, a molecular weight that can be approximated by 150 g mol⁻¹ (e.g. small diacids with molecular weights of 104 g mol⁻¹ for malonic acid to 132 g mol⁻¹ for glutaric acid and monoterpene oxidation products such as norpinic acid, 172 g mol⁻¹, and pinic acid, 214 g mol⁻¹) and a density of 1500 kg m⁻³ (1400–1600 kg m⁻³ for glutaric and malonic acids, respectively (Weast et al. 1983) and 1500 kg m⁻³ for oxidation products of monoterpenes, (Kostenidou et al. 2007)). For this theoretical compound, \( \kappa \) is calculated to be 0.18 from Equation 4.3. This is consistent with the 0.22 calculated for \( \kappa_{\text{ox}} \), suggesting that its hygroscopicity could be explained by these reasonable assumptions in physical properties.

Studies of SOA formed in smog chambers with monoterpene VOC precursors have measured the \( \kappa \) of the entire aerosol to be in the range of 0.04–0.14 (Prenni et al. 2007; Duplissy et al. 2008; Engelhart et al. 2008; Wex et al. 2009) as compared to 0.22 for the oxygenated factors measured in this study. However, chamber-generated aerosols are typically less oxidised than the OOA components of ambient aerosols (in particular, the OOA-1 (LV-OOA) component (Ng et al. 2010)), suggesting that they may not be completely representative of the oxygenated component of ambient aerosols. This could in part be due to higher precursor concentrations, perhaps arising from increased particle-phase partitioning of the more volatile, less oxygenated and hygroscopic components that can arise at high mass loadings frequently used in chamber experiments (Duplissy et al. 2008; Kostenidou et al. 2009; Shilling et al. 2009). The difference could also arise from the limited number of SOA precursors being used in the chamber experiments. Finally, it may not be entirely valid to compare the \( \kappa \) for OOA factors for aerosol measured in the field to that of lab aerosol, since the latter may have different molecular weights and solubilities, and may not be a fully oxygenated aerosol, i.e. it may have some saturated
hydrocarbon functional groups that lower its hygroscopicity. As such, it is not surprising that the ambient data are slightly more hygroscopic than the results from the chamber studies.

For example, and to be more specific, in an OH oxidation study performed by (Duplissy et al. 2008), Κ for the entire aerosol was found to be 0.12 for initial precursor concentrations of 10 ppb for α-pinene and 3.8 ppbv NOx. The fraction of the organic signal at m/z 44 was approximately 0.12 (O/C ≈ 0.54), which would result in a Κ of 0.16, calculated using Equation 4.7. Similarly, in an ozonolysis study of α-pinene by George and Abbatt (2010), the ratio of m/z 44 to total organic ranged from 0.046 to 0.063 (O/C = 0.26 to 0.32), corresponding to a calculated range of Κ for the entire aerosol from 0.08 to 0.09, which is comparable to the measured values of 0.098 to 0.12. In both cases, the resulting Κ for the entire aerosol is consistently lower than the 0.22 found for the OOA components in this study, where the m/z 44 to total organic fraction was 0.10 to 0.19.

Other studies that have attempted to quantify Κorg in the field found that using a value of 0.1 can adequately describe the CCN-activity of the aerosol at cloud-level (Wang et al. 2008) and in the Amazon rainforest (Gunthe et al. 2009). This is comparable to the campaign-wide average for this study of 0.15 for Κorgs, calculated using both Equation 4.4 and Equation 4.7. However, if a constant Κorg of 0.15 is used in our analysis, the organic-rich particles tend to be slightly overpredicted (RCCN=1.21±0.01) compared to the inorganic-rich particles (RCCN=1.10±0.01).

Others have simplified aerosol hygroscopicity even further by using a single Κ for the whole aerosol over an entire study. This would yield an average Κ of 0.3, which is consistent with the 0.3 value that was found in continental China (Rose et al. 2008). However, if this constant Κ is applied to all the data, the CCN numbers are significantly overpredicted when the aerosol is dominated by the organic-rich fraction (RCCN=1.31±0.01) compared to times when the aerosol is mostly inorganic (RCCN=1.10±0.01) (Figure 4.1c). This indicates that more chemical information is needed in order to accurately predict the CCN-activity of ambient aerosols, as opposed to the
simplest approach of assuming that the chemical composition is constant and that one value for \( \kappa \) can be applied to all aerosol types.

### 4.5. Conclusions

In this analysis we use the degree of oxygenation of the organic fraction of continental aerosol to determine its overall hygroscopicity. Two methods are used to determine the degree of oxygenation, factors elucidated from PMF analysis and from the values of O/C, both of which yield a similar result in terms of the overall \( \kappa_{\text{org}} \). Analysis of the entire study found that a \( \kappa_{\text{ox}} \) of 0.22±0.04 is suitable if we assume that the unoxygenated HOA component is non-hygroscopic. This overall value is similar to those for two of the three specific time periods for the study. It is important to point out the one air regime when this relationship does not hold, referred to as the Pre-Anthropogenic period, which we believe was characterised by aged continental aerosol mixed with fresh traffic emissions. At this point, we can speculate that this may have been due to a surface coating or oligomerization process that inhibited water uptake, but clearly the mechanism for this suppression is not well-understood. Additional studies to test the generality of the relationships with the hygroscopicity of the oxygenated organic components as presented in the paper are needed. For example, if fresh traffic emissions are again observed to suppress the apparent hygroscopicity then the possibility of a kinetic inhibition from the presence of high levels of unprocessed HOA components may prove to be a viable mechanism.

By assuming that the hygroscopicity of the organic component scales linearly with the O/C, we find that \( \kappa_{\text{org}}=(0.29\pm0.05) \cdot (\text{O/C}) \) for the full study (0.3<\text{O/C} < 0.6), although the degree of oxygenation of the aerosol in this study was limited in range and further studies in locations with aerosols of different degrees of oxygenation are needed to determine if this relationship is widely applicable.

With the widespread use of the AMS and subsequent PMF analysis to characterise ambient aerosol composition, these results are especially relevant in light of the
limitations inherent to climate models that can only incorporate a limited number of aerosol components. Specifically, these models frequently only incorporate a hydrophobic and a hydrophilic organic aerosol species, similar in nature to the HOA and OOA AMS factors. By associating specific $\kappa$ to these two aerosol types, as derived from analyses of the type presented in this paper, an empirically-based hygroscopicity constant for the climate model organic aerosol component can be determined.

### 4.6. Acknowledgements

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### 4.7. Contributions

Rachel Chang is the author of the manuscript, made the CCN measurements and interpreted all the data. Jay Slowik provided the C-ToF AMS and AMS PMF data and Nicole Shantz contributed to the discussion and overall interpretation. Alexander Vlasenko and Steven Sjostedt provided the PTR-MS data and John Liggio provided the HR-ToF AMS O/C data. The overall study was designed by Richard Leaitch and Jonathan Abbatt.
4.8. References


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Chapter 5

The Hygroscopicity of Organic Aerosol in a Forested Region: A Comparison with Urban and Rural Sites
5.1. Introduction

The ability of particles to activate into cloud droplets can be predicted using Köhler theory (Köhler 1936), and in the past, this theory has been applied successfully to inorganic particles. In the last 10-15 years, the focus has turned to understanding the effect that organic compounds have on aerosol hygroscopicity. This is in part because of the wide-spread use of the aerosol mass spectrometer (AMS) manufactured by Aerodyne, which is able to quantify the organic component of sub-micron aerosol at high time resolution and has shown that up to 70% of the aerosol mass at continental sites in the northern hemisphere is organic in nature (Zhang et al. 2007).

Early studies of ambient cloud condensation nuclei (CCN) in remote environments either did not include an organic fraction (Liu et al. 1996; VanReken et al. 2003), or assumed that the organic fraction was insoluble (Cantrell et al. 2001; Roberts et al. 2002; Medina et al. 2007). Similarly, in polluted environments, the organic component was successfully represented by an insoluble organic (Broekhuizen et al. 2006; Cubison et al. 2008). These latter studies justified this assumption because of the high primary emissions from traffic that are normally insoluble (Zhang et al. 2005) and not CCN-active.

More recent studies have incorporated a soluble organic component in the aerosol, either by assuming a constant soluble organic fraction (Chang et al. 2007; Stroud et al. 2007; Gunthe et al. 2009), or by allowing the CCN-activity of the organic component to vary based on measurements (Chang et al. 2010; Padro et al. 2010). Nonetheless, the question of whether the effect of a hygroscopic organic component can be observed in ambient aerosol still remains. The conditions under which the hygroscopicity of an organic aerosol can be important are: 1) the inorganic component is sufficiently small that it does not dominate CCN-activation; and 2) the organic component has to be hygroscopic, otherwise it could be simply treated as being non-hygroscopic.
This study examines the effect of a hygroscopic organic aerosol on the predicted CCN concentration at a forested site in British Columbia. It is the latest in a series of CCN studies that look at the importance of a soluble and hygroscopic ambient organic aerosol component and the findings from this study will be compared to earlier studies measured at urban and rural sites. Of all the studies completed in our lab, the CCN-activity of the organic component of the aerosol during this study affected the aerosol's overall CCN-activity the most, demonstrating that there are locations in which the hygroscopicity of the organic component is so large, that it cannot just be ignored.

5.2. Sampling Equipment

5.2.1. Description of Location

The Whistler 2008 study took place between 16 May and 17 June 2008 at Whistler, British Columbia (50.1°N, 122.9°W). The sampling site was at the Children's Learning Centre, which was situated at 1019 m asl, near the Olympic Station. This location was chosen because of its potential for high biogenic organic aerosol mass since it is in the Pacific coniferous forest ecozone, which stretches along the west coast of BC (Marshall 1999). Coniferous trees have greater terpene emissions (Guenther et al. 1994) and therefore have higher secondary organic aerosol yields compared to vegetation that emits isoprene (Griffin et al. 1999; Kroll et al. 2006). Since the sampling site was away from the main village, local sources of anthropogenic emissions were expected to be minimal and the aerosol was expected to be from either long range transport or organic from biogenic sources.

5.2.2. Scanning Mobility Particle Sizer

A scanning mobility particle sizer (SMPS, 3080, 3081, 3010, TSI Inc.) measured the size distribution of particles with diameters between 10 and 500 nm. The SMPS works by forcing a known charge distribution on the aerosol population and then selecting a specific size based on the particle’s mobility diameter. These size-selected particles are then counted by a condensation particle counter. The diameter range is scanned in order
to determine the entire size distribution. The sample flow of the system was $1 \text{ L min}^{-1}$ and the sheath flow was $5 \text{ L min}^{-1}$.

5.2.3. **CCN Counter**

Cloud condensation nuclei were counted using a continuous flow thermal gradient diffusion chamber. The chamber consists of two parallel plates maintained at different temperatures and continuously wetted. The steady-state linear temperature and water partial pressure gradients result in a maximum supersaturation between the two plates. A particle-free sheath flow ($2 \text{ L min}^{-1}$) keeps the sample flow ($0.2 \text{ L min}^{-1}$) at the centre of the chamber such that CCN-active aerosol can be exposed to the maximum supersaturation and activate into droplets. As the activated droplets exit the chamber, they are optically counted by an aerodynamic particle sizer (APS, 3320, TSI Inc.). The development of this instrument is described in detail by Chang (2006).

The CCN counter was held at a constant supersaturation of $0.34\pm0.03\%$ throughout the study and was calibrated using near-monodisperse ammonium sulphate particles. By measuring the activation diameter (i.e. where 50% of the aerosol activates), and using water activity coefficients by Clegg et al. (1996), the supersaturation of the chamber was determined.

5.2.4. **Aerosol Mass Spectrometer**

A high-resolution time-of-flight (HR-ToF) aerosol mass spectrometer (AMS, Aerodyne Research Inc.) measured the non-refractory submicron chemical composition at $870 \text{ K}$ and $1.33 \times 10^{-5} \text{ Pa}$ (i.e. sulphate, nitrate, ammonium and organics). The AMS consists of a vacuum chamber with an 870 K oven which vapourises the aerosol, then ionises the gas plume using electron impact, and detects the resulting ions using a time-of-flight mass spectrometer. The data used in this study are the bulk aerosol composition from mass spectrum mode measured with a mass resolution of approximately 3000 (V-mode) for greater sensitivity. More detail about the operation of the AMS in general can be found
in the literature (Jayne et al. 2000; Jimenez et al. 2003) as well as for the high-resolution instrument (DeCarlo et al. 2006).

Positive matrix factorisation (PMF) was preformed on the organic mass spectrum in order to learn more about the character and processing of the organic aerosol fraction. This has been done successfully in the past on AMS data from urban areas (Ulbrich et al. 2009; Allan et al. 2010; Slowik et al. 2010b), as well as more rural settings (Lanz et al. 2007; Slowik et al. 2010a). PMF is a multivariate receptor modelling technique that is used for factor analysis (Paatero and Tapper 1994; Paatero 1997). It attempts to recreate an input matrix $X$ as a product of scores ($G$) and loadings ($F$) such that

$$X = GF + E,$$  \hspace{1cm} \text{Equation 5.1}$$

where $E$ is the residual matrix. In the case of AMS data, $X$ is the organic mass spectra, with the rows representing the mass spectrum at each time (each column is filled with the signal at a mass-to-charge ratio ($m/z$)); $F$ is the mass spectrum of the resulting factors; and $G$ is the corresponding time series for these factors. The PMF program varies the matrices $F$ and $G$ such that the residual matrix $E$ is minimised. In this study, a combined data set was used that included the organic mass spectrum of the AMS at the Children's Learning Centre with that measured by a unit resolution compact time-of-flight AMS at the peak of the mountain (2182 m). This was done to help separate the factors more easily, although it assumes that the factor mass spectra observed at the two sites are identical. This is a reasonable assumption since the two sites were often influenced by similar air masses.

The number of factors in the final solution is subjective and in theory, many factors (>> 10) could be included to account for all the variation in the observed mass spectrum. However, once that many factors are included, instrumental artefacts become more important in explaining the variance in the data set and additional information about the ambient aerosol may not be gained. In this study, a three-factor solution was found to best represent the ambient aerosol with a hydrocarbon-like organic aerosol (HOA) factor.
and two oxygenated organic aerosol factors, OOA-1 and OOA-2, where OOA-1 is more oxygenated, and likely less volatile, than OOA-2. These factors are typical of what has been observed in ambient sites around the world (summarised by Zhang et al. 2007), with the HOA component representing primary emissions from vehicles and the OOA components representing organic aerosol mass originating from secondary processes.

5.3. CCN Calculations

The method for predicting CCN concentration is identical to the method described in the previous chapter. The aerosol chemical composition, as measured by the AMS, was used to predict an activation diameter using the $\kappa$-Köhler equation (Petters and Kreidenweis 2007; Petters and Kreidenweis 2008) based on the supersaturation of the CCN counter:

$$ S = \frac{D^3 - D_i^3}{D^3 - D_i^3(1-\kappa)} \exp \left( \frac{4\sigma M_w}{\rho_w RTD} \right), $$

Equation 5.2

where $\kappa$ is the hygroscopicity parameter, $D$ and $D_i$ are the droplet wet diameter and initial dry diameter, respectively, $\sigma$ is the surface tension of water (0.072 N/m$^2$), $M_w$ is the molecular weight of water, $\rho_w$ is the density of water, $R$ the universal gas constant and $T$ the temperature. In order to determine the activation diameter, $D_i$ is increased until the maximum in the Köhler curve (i.e. the critical supersaturation) reaches that of the chamber. All particles larger than the activation diameter are assumed to activate and so the predicted CCN concentration can be determined from the size distribution. (This introduces an assumption that the aerosol is internally mixed. However, since the activation diameter was constant at ~ 100 nm throughout the study (Figure 5.3), this is a reasonable assumption.) The predicted CCN concentration can then be compared to the measured concentration to determine the degree of closure and $\kappa$ of the aerosol adjusted until good agreement is obtained.

The advantage of this expression of the Köhler equation is that it groups all the properties of the hygroscopic components, such as molecular weight and solute non-idealities, into
the single empirical hygroscopicity term $\kappa$ in Equation 1.1. For an aerosol with multiple components, the total $\kappa$ can be calculated as the volume weighted average of the $\kappa$ of individual components:

$$\kappa_{\text{tot}} = \sum_i \varepsilon_i \kappa_i,$$

*Equation 5.3*

where $\varepsilon_i$ is the volume fraction of the $i^{th}$ component. A list of $\kappa$ for individual compounds can be found in Petters and Kreidenweis (2007), however, the $\kappa$ of ambient organic aerosol is not well known, and the objective of this study is to reduce the uncertainty in its value.

In this study, the aerosol composition has been simplified into three components: an inorganic component (inorg), with the properties of ammonium sulphate; an oxygenated organic component (ox), consisting of the two OOA components and is assumed to be hygroscopic; and an unoxygenated organic component (unox), consisting of the HOA component and is assumed to be non-hygroscopic. The oxygenated organic component is expected to be more processed and therefore more polar, soluble and hygroscopic, as confirmed by chamber studies of secondary organic aerosol (Prenni et al. 2007; Duplissy et al. 2008; Engelhart et al. 2008; Wex et al. 2009). In contrast, the HOA factor, which comprises the unoxygenated component, is thought to be similar to lubricating oils (Zhang et al. 2005) which are aliphatic and unlikely to be soluble or hygroscopic. As such, it is assumed to not contribute to an aerosol's CCN-activity. It is possible that the unoxygenated organic component was deliquesced (still had liquid water associated with the particle), in which case it would potentially be hygroscopic (Huff Hartz et al. 2006). It is also possible that the HOA component identified by PMF was the hydrocarbon components of biogenically formed oxygenated organic aerosol, in which case they would originate from a hygroscopic component and should therefore be treated as being hygroscopic. Although both of these possibilities would cause the unoxygenated organic component to contribute to the overall aerosol’s hygroscopicity, they will not be explored here and will be followed-up in future studies.
In this way Equation 3.1 can be simplified to:

$$\kappa_{\text{tot}} = \varepsilon_{\text{inorg}} \kappa_{\text{inorg}} + \varepsilon_{\text{ox}} \kappa_{\text{ox}} + \varepsilon_{\text{unox}} \kappa_{\text{unox}} = \varepsilon_{\text{inorg}} \kappa_{\text{inorg}} + \varepsilon_{\text{ox}} \kappa_{\text{ox}}$$  \hspace{1cm} \textit{Equation 5.4}

since the unoxygenated organic component is assumed to be non-hygroscopic (i.e. $\kappa_{\text{unox}} = 0$). A summary of the chemical properties of the different components can be found in the following table.

**Table 5.1 - Components used in the $\kappa$-Köhler model and their densities and $\kappa$.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Species</th>
<th>Density (kg m$^{-3}$)</th>
<th>Solubility (m$^3$ m$^{-3}$)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic (inorg)</td>
<td>SO$_4$, NO$_3$, NH$_4$</td>
<td>1770$^1$</td>
<td>0.43$^3$</td>
<td>0.60$^5$</td>
</tr>
<tr>
<td>Oxygenated Organic (ox)</td>
<td>OOA-1, OOA-2</td>
<td>1500$^2$</td>
<td>0.011$^4$</td>
<td>Variable</td>
</tr>
<tr>
<td>Unoxygenated Organic (unox)</td>
<td>HOA</td>
<td>900$^3$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

1 value for ammonium sulphate (Windholz 1983)  
2 density of lab-generated secondary organic aerosol (Kostenidou et al. 2007)  
3 density of lubricating oil (Cylinder Lube 2008)  
4 values for ammonium sulphate and adipic acid (Windholz 1983)  
5 calculated at 0.34% supersaturation using data from Clegg et al. (1996)

Since $\kappa_{\text{ox}}$ is the only unknown variable, it is adjusted until the predicted concentration agrees with the measured concentration, the criteria for which will be discussed in Section 5.4.2.

A second method for calculating $\kappa_{\text{org}}$ is to assume that it varies with the degree of oxygenation (ratio of atomic oxygen to atomic carbon, O/C) of the organic component. As discussed at length in the previous chapter, this assumption relies on the supposition that an increase in the O/C will result in an increase in the organic component's polarity and therefore hygroscopicity. The most simple relationship between $\kappa_{\text{org}}$ and O/C is assumed here, with

$$\kappa_{\text{org}} = a \times (O / C) .$$  \hspace{1cm} \textit{Equation 5.5}

In this approach, $a$ is varied until the predicted CCN concentrations agree with those measured.
In reality, the solubility of the components should be considered in Equation 3.1 (Petters and Kreidenweis 2008), especially the oxygenated organic component since it can be sparingly soluble. However, decreasing the solubility of the oxygenated organic component down to 0.011 m$^3$ m$^{-3}$ (the solubility of adipic acid (Windholz 1983)) did not affect the results, suggesting that all of the oxygenated organic component dissolved during activation at this solubility, assuming that there are no kinetic effects. Of course, it is possible that some organic components have a solubility below this value but we ignore that possibility here.

Studies that predate κ-Köhler theory often describe the organic component as soluble or insoluble and do not refer to the hygroscopicity. As such, in order to compare findings from older studies, in this chapter both soluble and hygroscopic will refer to aerosol components that are CCN-active, and insoluble and non-hygroscopic will refer to aerosol components that are CCN-inactive. This is not always true, e.g. when the molecular weight of a soluble compound is high, however, this will facilitate comparisons between studies.

5.4. Results

5.4.1. General Results

The time series of the aerosol size distribution (dN/dlogD), as measured by the SMPS, is shown in the top panel of Figure 5.1. The study was marked by several nucleation and growth events, although the aerosol particles rarely grew larger than 60 nm diameter and were not detected by the AMS. The exception is the last event, starting on 13 June, which, based on the chemical composition, was composed mostly of organic compounds (bottom panel, Figure 5.1).
Figure 5.1 - Time series for the entire Whistler study. The data are: non-refractory aerosol composition from AMS (bottom panel); O/C, as calculated from Aiken et al. (2008) (black dots on lower panel); PMF apportionment of organic component, stacked (middle panel); and aerosol size distributions (top panel). The shaded green area are the Biogenic times and the shaded red area are the Inorganic times.

The bottom panel of Figure 5.1 shows the non-refractory submicron aerosol chemical composition measured by the AMS. The organic component (green trace) dominated the aerosol mass for most of the study, with 90% of the study having an organic mass fraction > 0.5, demonstrating the organic-rich nature of this air. The O/C is shown in the bottom panel (black dots, right axis) and was inferred from the fraction of the organic signal at m/z 44 (F44) using the relationship:

\[ \text{O/C} = F_{44} \times 3.82 + 0.0794, \quad \text{(Aiken et al. 2008)} \]

Equation 5.6

with the average O/C for the entire campaign being 0.69 ± 0.01, where the uncertainty is from the uncertainty given by Aiken et al. (2008) for Equation 5.6.
The apportionment of the organic component as determined by PMF is seen in the middle panel of Figure 5.1. The organic aerosol mass is mostly composed of the oxygenated components (OOA-1 and OOA-2) with very little unoxygenated component (HOA), consistent with this as a forested site with minimal local anthropogenic emissions. The exception can be seen in the intermittent spikes of HOA which coincided with spikes in the organic mass. These were caused by trucks passing the sampling site on their way to and from the Peak-to-Peak chair lift construction site further up the mountain, in preparation for the 2010 Winter Olympics.

In order to determine the acidity of the aerosol, the measured particulate ammonium mass concentration is shown in black in Figure 5.2 along with the ammonium required to neutralise the particulate sulphate (light grey) and nitrate (dark grey) mass concentrations measured. In general, the measured and predicted ammonium concentrations are in agreement, suggesting that the aerosol was neutralised. The peaks in the ammonium mass spectrum have known interferences from water at $m/z$ 17 and 18. This can affect the ammonium mass concentrations, especially at low aerosol loadings such as this. As such, the slight discrepancies between the measured and predicted ammonium are not necessarily indicative of an acidic aerosol. This is supported by the presence of particulate nitrate, which if it were assumed to be inorganic (and not present in the form of organonitrate), would indicate a neutralised aerosol.
Figure 5.2 - Comparing predicted and measured NH$_4^+$
NH$_4^+$ measured by the AMS (black) and calculated if SO$_4^{2-}$ was neutralised (light grey) and NO$_3^-$ was neutralised (dark grey). The latter two traces are stacked.

Figure 5.3 shows the concentration of particles greater than 50 nm (dotted line) and 100 nm (black), as measured by the SMPS, as well as the CCN concentration (light grey). It is interesting to note that the CCN concentration follows the concentration of particles > 100 nm for almost the entire study, which corresponds to a $\kappa_{\text{tot}}$ for the entire aerosol of 0.12 at a supersaturation of 0.34%. This suggests that there was very little variability in the chemical composition throughout the study, which makes it more difficult to determine $\kappa_{\text{org}}$ for the entire study.
Figure 5.3 - Concentration of particles > 50 nm and 100 nm as well as CCN concentration.

5.4.2. Results from Aerosol-CCN Closure

Typical closure plots are shown in Figure 5.4 and Figure 5.5 using Equation 5.4 to calculate $\kappa_{\text{org}}$ with $\kappa_{\text{ox}}$ of 0 and 0.22, respectively. A value of 0.22 was chosen based on the results from the Egbert 2007 study described in the previous chapter. In these plots, the data points are coloured by their inorganic fraction, with the red and orange points representing times when the aerosol was primarily organic, and the blue and violet points represent times when the aerosol was primarily inorganic. Comparing the organic-rich data points in Figure 5.4 and Figure 5.5 shows that they selectively move upwards while the more inorganic-rich data points do not change significantly. It is interesting to note that including a hygroscopic oxygenated organic component increases the slope by approximately 0.2 (27%), although the correlation coefficient only increases slightly.
Figure 5.4 - Predicted CCN concentrations assuming the kappa of the oxygenated component is 0. Data points are coloured by their inorganic mass fraction.

Figure 5.5 - Predicted CCN concentrations assuming that the kappa of the oxygenated component is 0.22. Data points are coloured by their inorganic fraction.

Whether closure was achieved can be difficult interpret. If all the instruments perfectly sampled the same aerosol population and there were no measurement errors, then closure would be achieved if the slope of these closure graphs was one. However, practically speaking, all three instruments measured on different sampling lines with different inlet flows and the measurement uncertainty in the CCN counter alone is on the order of 20% due to uncertainties in the counter and flow rates. In the previous chapter, a method was described in which the ratio of predicted to measured CCN concentrations (R_{CCN}) was plotted against the inorganic mass fraction of the aerosol for the entire study (e.g. Figure 5.6) and the organic-rich half of the population was compared to the inorganic-rich half.
Figure 5.6 - $R_{CCN}$ as a Function of Inorganic Fraction for the Entire Study

Ratio of predicted to measured CCN concentration as a function of inorganic mass fraction for a non-hygrosopic oxygenated organic component.

This method depends on the inorganic-rich half of the data points (i.e. the right half) to act as a reference by remaining relatively constant as the hygroscopicity of the organic component changes. In locations with inorganic mass fractions $> 0.5$, the $\kappa_{\text{tot}}$ of this part of the population will not change significantly because the inorganic component drives activation (see, for example, Broekhuizen et al. 2004; Chang et al. 2007). However, during this study, because the median inorganic mass fraction is 0.36, the inorganic-rich half of the population was deemed too sensitive to changes in $\kappa_{\text{ox}}$ to reliably act as a reference.

Instead, the approach used here was to split the data into two time periods: Biogenic times, identified by Schwartz et al. (2010), in which the aerosol is thought to originate primarily from secondary products of regional biogenic emissions; and Inorganic times, when the aerosol had a relatively higher inorganic contribution. These times are highlighted in Figure 5.1 as the green and red shaded regions, respectively, and were chosen such that they had a similar number of data points (217 and 263, respectively). The ratio of predicted to measured CCN concentrations ($R_{CCN}$) is shown in Figure 5.7 for a $\kappa_{\text{ox}}$ of 0 and 0.22 for the two time periods.
Figure 5.7 - $R_{\text{CCN}}$ as a Function of Inorganic mass for Different Times

(a) $\kappa_{\text{ox}} = 0$ and (b) $\kappa_{\text{ox}} = 0.22$ for the Inorganic (black squares) and Biogenic (light triangles) times.

The objective was to vary $\kappa_{\text{org}}$ by adjusting $\kappa_{\text{ox}}$ until the geometric means of the two populations were equal. The results are summarised in Figure 5.8, which shows that the means overlap at $\kappa_{\text{ox}} \geq 0.35$, although if the error bars, which represent the 95% confidence level, are considered, $\kappa_{\text{ox}} \geq 0.15$ for this study. A similar analysis was performed using Equation 5.5 to calculate $\kappa_{\text{org}}$ from the O/C. These results are shown in Figure 5.9, which show that a slope $a \geq 0.2$ is needed for the means of the two populations to be considered equal. The results from both of these methods are consistent with the findings from Egbert 2007, which found $\kappa_{\text{ox}} = 0.22 \pm 0.04$ and $a = 0.29 \pm 0.05$. 
5.5. Discussion

The problem with using the analysis method just described for this study is that the inorganic mass fraction is still too low even during the Inorganic times. As a result, the
CCN concentrations predicted with the Köhler model for the Inorganic times continued to increase, making it unsuitable to be used as a reference population. This is illustrated in Figure 5.10, which shows the chemical composition of the aerosol during the study simplified into inorganic, oxygenated (hygroscopic) organic and unoxygenated (non-hygroscopic) organic components on a ternary diagram. In this figure, the location on the graph represents the chemical composition of the aerosol, with the aerosol in the lower right corner representing aerosol that are mostly inorganic, with a hygroscopicity of 0.61, the upper vertex representing aerosol that are mostly oxygenated organic, with a hygroscopicity parameter of 0.22 and the aerosol in the lower left vertex representing aerosol that are mostly unoxygenated, non-hygroscopic, organic ($\kappa = 0$).

The colour in the background represents the activation diameter of a particle with that composition at a supersaturation of 0.34%. During Whistler 2008, the majority of the aerosol had an inorganic mass fraction < 0.5 and an unoxygenated, non-hygroscopic, organic mass fraction that was < 0.25. This resulted in a predicted CCN concentration that is inherently sensitive to changes in the $\kappa_{\text{org}}$ as the hygroscopicity of the oxygenated component is increased.
This can be visualised by projecting all the data points onto the bottom axis in the direction of the black arrow in Figure 5.10. This would represent the case in which the entire organic component is non-hygroscopic (i.e. $\kappa_{\text{org}} = \kappa_{\text{ox}} = 0$), e.g. Figure 5.7a. In the case of a particle that is 50% inorganic, when $\kappa_{\text{ox}} = 0$ (near the head of the arrow), it would have an activation diameter of 84 nm. However, increasing the $\kappa_{\text{ox}}$ to 0.22 (e.g. Figure 5.7b) would decrease the activation diameter down to 69 - 72 nm (towards the tail of the arrow). This explains why the mean $R_{\text{CCN}}$ for the Inorganic times increases so much with an increase in $\kappa_{\text{ox}}$, making it difficult for the mean $R_{\text{CCN}}$ of the Biogenic times to increase enough to match that of the Inorganic times.

In contrast, during the Egbert 2007 study described in the previous chapter, almost 50% of the particles had an inorganic mass fraction > 0.5. This resulted in $R_{\text{CCN}}$ of the inorganic-rich data points to be much less sensitive to changes in $\kappa_{\text{ox}}$ ($R_{\text{CCN}} = 1.17$ and
1.18 for \( \kappa_{\text{ox}} \) of 0 and 0.22, respectively), making this method more appropriate for the aerosol chemical composition observed during the Egbert 2007 campaign.

The results from this study can be put into the context of the four other aerosol-CCN closure studies that have been conducted in or in collaboration with our lab and are listed in Table 5.2. The two earlier studies used three-component K\( \ddot{\text{o}} \)hler models consisting of soluble inorganics and soluble and insoluble organics. In addition, factor analysis was only performed after the CCN analysis for the Toronto Intensive Field Campaign of 2003, and the original study only tested a case in which 10% of the organic fraction was assumed to be water soluble. The results from the ASCOS study (described in Chapter 3), are taken from the results of Martin et al. (2011), and the organic component was assumed to be completely hygroscopic, based on its mass spectrum.

Table 5.2 - Aerosol-CCN closure studies and the assumptions used in their calculations relevant to this discussion.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Location</th>
<th>Köhler Model</th>
<th>Hygroscopic Component</th>
<th>( \kappa_{\text{ox}} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toronto 2003</td>
<td>Urban</td>
<td>3-component</td>
<td>10% of organic</td>
<td>-</td>
<td>(Broekhuizen et al. 2006)</td>
</tr>
<tr>
<td>Egbert 2005</td>
<td>Rural</td>
<td>3-component</td>
<td>OOA</td>
<td>-</td>
<td>(Chang et al. 2007)</td>
</tr>
<tr>
<td>Egbert 2007</td>
<td>Rural</td>
<td>( \kappa )</td>
<td>OOA + BBOA</td>
<td>0.22</td>
<td>(Chang et al. 2010)</td>
</tr>
<tr>
<td>Whistler 2008</td>
<td>Forested</td>
<td>( \kappa )</td>
<td>OOA</td>
<td>0.22</td>
<td>This Study</td>
</tr>
<tr>
<td>ASCOS</td>
<td>Arctic</td>
<td>( \kappa )</td>
<td>Organic</td>
<td>0.2</td>
<td>(Martin et al. 2011)</td>
</tr>
</tbody>
</table>

The results from these campaigns are summarised in Figure 5.11, with Figure 5.11a showing the increase in slope of the fitted line for predicted CCN in a typical closure plot (e.g. Figure 5.4) for the case in which the oxygenated organic components (OOA and BBOA where applicable) are considered to be hygroscopic or soluble compared to the case in which the organic component is assumed to be completely non-hygroscopic (i.e. \( \kappa_{\text{org}} = \kappa_{\text{ox}} = 0 \)). For the Toronto 2003 study, the data are from the assumption that 10% of the organic is water soluble. This value can be interpreted as the importance that \( \kappa_{\text{ox}} \) be included in the calculation of the aerosol hygroscopicity.
Figure 5.11 - Summary over four campaigns
a) slope of fit to CCN predicted to CCN measured when assuming that the organic is completely non-hygroscopic (lighter triangles) and that the oxygenated, OOA, component is hygroscopic (black squares) and b) aerosol composition used in Köhler calculation. See Table 5.2 for details of each campaign.

Figure 5.11b shows the average chemical composition used in the Köhler calculation for each campaign. Of the five studies, Whistler 2008 had the greatest hygroscopic organic fraction (0.51), which resulted in the greatest increase in slope when the oxygenated OOA component was assumed to be hygroscopic. The two Egbert studies and ASCOS were relatively insensitive to changes in the hygroscopicity of the oxygenated organic components because their oxygenated organic mass fractions were $\leq 40\%$ and their inorganic component was large, causing the effects of a hygroscopic oxygenated organic component to be less pronounced.

Despite the fact that the predicted CCN concentrations during the Toronto 2003 study were also very sensitive to the presence of a soluble / hygroscopic organic component (10% increase in slope with a 10% soluble organic component), the organic component was assumed to be from local traffic emissions and therefore insoluble and not CCN-
active. As such, of these four studies, the results from the Whistler 2008 study most clearly demonstrate the effects of an ambient organic aerosol that is hygroscopic.

This can be generalised in Figure 5.12, which shows, in the coloured background, the percent change in the activation diameter if the oxygenated organic component were assumed to be non-hygroscopic ($\kappa_{ox} = 0$) compared to if it were assumed to be hygroscopic ($\kappa_{ox} = 0.22$). This can be viewed as the sensitivity of the activation diameter to the inclusion of a hygroscopic organic component, with the bluer the colour, the greater the importance. As expected, aerosol with a small inorganic fraction and a high oxygenated organic fraction are the most sensitive to the inclusion of a hygroscopic oxygenated organic component (green to purple). The letters represent the composition of the five studies conducted in our lab as well as the ASCOS campaign described in Chapter 3 and the numbers represent the aerosol composition at locations in the continental northern hemisphere, as compiled by Zhang et al. (2007). A complete listing of the locations and their change in activation diameter can be found in the Appendix in Section 5.7.
From this figure, we can see that although most locations are insensitive to the presence of a hygroscopic organic component (<10% change in the activation diameter), there are locations where the change is more prominent. Whistler (D), Mexico City (5) and off the coast of New England (15, 16) are all places where the activation diameter would decrease by 15-18% if the hygroscopicity of the oxygenated organic component were included, while Hyytiala (36, 37), Taunus (20), Vancouver, (10), Chebogue Point (33), Jungfraujoch (34), Edinburgh (11) and Egbert (C) show more moderate decreases of 10-15%.
Interestingly, the CCN-activity at all types of locations, i.e. remote / rural (Whistler, Hyytiala, Chebogue Point and Jungfraujoch), downwind of urban centres (Taunus and off the coast of New England) and urban centres (Mexico City, Edinburgh, and Vancouver), as classified by Zhang et al. (2007), are dependent on the hygroscopicity of the oxygenated organic component. This shows that finding a hygroscopic parameter for the oxygenated organic component is relevant to aerosol at a wide range of locations and is not only limited to remote and/or forested regions. As governments regulate sulphur emissions, these findings will become even more important.

5.6. Atmospheric Implications

This study confirms that the hygroscopicity of the ambient oxygenated organic component is \( \geq 0.15 \) at Whistler, which is consistent with what was found in the previous chapter and is greater than results from lab studies on secondary organic aerosol (\( \kappa_{\text{ox}} = 0.04 - 0.14 \), (Prenni et al. 2007; Duplissy et al. 2008; Engelhart et al. 2008; Wex et al. 2009)), where the organic aerosol is not as oxygenated as ambient air. It also shows that the assumed expression \( \kappa_{\text{org}} = a \times (O/C) \) has a slope \( a \) of \( \geq 0.2 \), consistent with our findings in the previous chapter, as well as with hygroscopic growth measurements at RH<100\% (Jimenez et al. 2009). More importantly, it shows that the hygroscopicity of the organic component can have a significant effect on the total aerosol hygroscopicity and that we cannot simply assume that the organic component is non-hygroscopic. This is true for urban, downwind of urban as well as remote locations, implying that the hygroscopicity of the organic aerosol component is relevant in a wide variety of environments.
5.7. Appendix

Table 5.3 - Location of sites in Figure 5.12 and the percent change in activation diameter when assuming the OOA component has a $\kappa$ of 0.22.

<table>
<thead>
<tr>
<th>#</th>
<th>Location</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
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<td>C</td>
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<td>D</td>
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<td>14.8</td>
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<td>E</td>
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<tr>
<td>3</td>
<td>Tokyo, Japan, Winter</td>
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<tr>
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<tr>
<td>36</td>
<td>Quest campaign, Finland</td>
<td>10.4</td>
</tr>
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<td>37</td>
<td>Hyytiala, Finland</td>
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5.8. Acknowledgements

Funding for this study was provided by the Canadian Foundation for Innovation through Clouds-Aerosol-Feedbacks for Climate Network, Environment Canada, University of Toronto and the Natural Sciences and Engineering Research Council, including a CGS D. The work for this study was done in collaboration with Richard Leaitch, Anne Marie MacDonald, Shao-Meng Li, Desiree Toom-Sauntry, Kathy Hayden, John Liggio, Dave Halpin and Armin Gaudenzi from Environment Canada and Jay Slowik, Nicole Shantz, Steven Sjostedt, Alexander Vlasenko and Ingrid George from University of Toronto.

5.9. Contributions

Rachel Chang is the author of the manuscript, made the CCN and SMPS measurements for the first half of the study and interpreted all the data. Jay Slowik provided the AMS and AMS PMF data, and along with Nicole Shantz, operated the CCN counter for the second half of the study. The study was designed by Richard Leaitch and Jonathan Abbatt and overall logistical support was provided by Anne Marie MacDonald and the other employees of Environment Canada.

5.10. References


Chapter 6

Conclusions and Future Research
6.1. Summary and Future Direction of Arctic Studies

The sources of particles in the Arctic summer time boundary layer are not well known, mostly because of the limited observations available. Long term observations have been made at a few stations in the far north (e.g. Alert and Eureka, Canada; Barrow, USA; Ny-Alesund, Spitsbergen), however, there are still many processes and feedback mechanisms involving aerosol that are not understood. The studies in this thesis contribute towards our understanding of the sources of Arctic particles in the summer.

The nucleation and growth of particles have been observed in the polar marine boundary layer in the past (Wiedensohler et al. 1996; Koponen et al. 2003; Lihavainen et al. 2003), however, no studies have been able to conclusively show that the sulphuric acid needed for nucleation originated from oceanic sources and not the free troposphere. The findings from Chapter 2 show that nucleation mode particles are found in the Canadian Arctic and that they occur when atmospheric and ocean surface DMS concentrations are high, suggesting that the source of sulphuric acid was oceanic. Model runs from an aerosol microphysics box model show that it is possible that the DMS could have initiated the nucleation if 1) \([\text{OH}] \geq 3 \times 10^5\) molecules cm\(^{-3}\), which is not unreasonable as average \([\text{OH}]\) in Antarctica were \(1.1 \times 10^5\) molecules cm\(^{-3}\) (Jefferson et al. 1998) and 2) the A factor is \(\leq 10^{-8}\) s\(^{-1}\). Although the empirical A factor is typically 1 - 4 orders of magnitude higher at continental sites (Sihto et al. 2006), it has not been characterised in the Arctic where the concentrations of volatile organic compounds that are possibly participating in the nucleation and growth process are lower, which would result in a lower A factor.

Measurements of gaseous SO\(_2\), H\(_2\)SO\(_4\) and OH mixing ratio would have constrained the model results more tightly and improved our understanding of nucleation in the Arctic marine boundary layer. Observations of nucleation events from a moving platform such as a ship allows for different potential source regions to be studied, but complicates the analysis because the particle growth areas may be limited in spatial extent. In the future, it would also be beneficial to conduct long term measurements of aerosol size distribution near a meteorological station in order to study the prevalence of these nucleation events.
In this way, it would be possible to estimate the contribution of marine nucleation to Arctic aerosol loading, and ultimately on climate.

In contrast, local sources of aerosol in the central Arctic Ocean have been hypothesised in the past but they have been difficult to measure. The focus of the Arctic aerosol modelling community has been on transport from lower latitude continental regions (Shindell et al. 2008) and none have considered local sources. However, the findings from Chapter 3 show that at least 33% of the non-refractory aerosol mass < 1 µm originates from marine biogenic sources, with an additional 31% of the mass whose source is currently unknown. This suggests that the models are missing an additional source of particles that is likely changing with warming temperatures. The models also do not include particulate organic matter, which contributed, on average, to 43% of the mass during August 2008. Although decreases in SO₂ emissions from tighter regulations will result in lower predicted aerosol mass in the Arctic, there will still be an organic fraction to the aerosol that will vary with climate as well as changes in land use in southern latitudes.

Assuming that the findings from Chapter 4 apply to Arctic aerosol, κ of the organic components and total aerosol in the Arctic can be calculated. Table 6.1 shows the κ for the three ambient factors as well as the total aerosol during ASCOS assuming that the density of the organic, MSA, sulphate and nitrate components are 1500, 1480, 1770 and 1730 kg m⁻³, respectively (Weast et al. 1983; Kostenidou et al. 2007). The κ of the inorganic components (MSA, sulphate and nitrate) is assumed to be 0.6 and the relationship developed in Chapter 4 (0.29 × O/C) is assumed for the organic component.

**Table 6.1 - κ of the organic component and total aerosol for the aerosol during ASCOS**

<table>
<thead>
<tr>
<th></th>
<th>F1: Marine Biogenic</th>
<th>F2: Continental</th>
<th>F3: Organic</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Component</td>
<td>0.12</td>
<td>0.31</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>Total Aerosol</td>
<td>0.52</td>
<td>0.49</td>
<td>0.25</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Based on these calculations, the overall Arctic aerosol is more hygroscopic than the average continental aerosol, which has a $\kappa$ of 0.3 (Chapter 4, Rose et al. 2008). This is because the organic component is more oxygenated over the central Arctic Ocean than over land, resulting in an organic component that is more hygroscopic.

The boundary layer aerosol mass in the central Arctic is quite low ($< 0.8 \, \mu g \, m^{-3}$) and the mass spectrum of the organic component did not vary enough to uniquely identify one that could be attributed to a local source from the ocean surface. Separate flux and gradient measurements were made on the total aerosol over a lead during ASCOS, and both concluded that the lead was a source of particles, although it only contributed a few percent to the overall aerosol variation. Nonetheless, it would be interesting to conduct gradient measurements over the lead and over the ice surfaces to measure chemical composition, similar to the work of Ceburnis et al. (2008), but with different methods of detecting chemical composition, either AMS or FTIR. A method of separating local sources from aerosol subsided from the free troposphere would also be beneficial. Further collaboration with meteorologists participating in ASCOS could reveal interesting findings about the influence of the free troposphere.

The pioneering work done by Bigg and Leck (2001) with TEM images showing sulphuric acid coatings on proposed biological particles are extremely intriguing. Unfortunately, it is labour intensive work that very few people are trained to do. If this could be expanded so that more samples could be examined and the counting statistics improved such that it could be compared with other measurements (e.g. atmospheric particle size and number), then this would go a long way to lending credence to their hypothesis that exopolymer secretions from oceanic biological organisms are emitted into the atmosphere through bubble bursting mechanisms.

Future studies would repeat these measurements for longer periods of the marine productive season to determine the variability and relevance of the composition and sources of the Arctic aerosol found here. Finally, these findings could also be incorporated into models to improve their predictions. Because the Arctic climate is
rapidly changing, it is vital that we learn to predict the sources of aerosol and their effects on climate.

6.2. Summary and Future Directions on Hygroscopicity Studies

The CCN-activity of the inorganic aerosol has been understood for a long time. However, research on the hygroscopicity of the organic component of ambient aerosol has only gained momentum in the last 10 years. Before the start of the research in this thesis, the organic component of ambient aerosol was either assumed to be completely insoluble, and the hygroscopicity irrelevant, or assumed to have a constant hygroscopicity regardless of composition. Chapter 4 represents the hygroscopicity of the organic component at Egbert, ON in two ways: 1) by separating the organic component into an oxygenated and unoxygenated component using PMF and then assuming that the unoxygenated component is non-hygroscopic ($\kappa = 0$) and fitting for $\kappa$ of the oxygenated component to be $0.22 \pm 0.04$ and 2) by assuming that the $\kappa$ of the organic component varies linearly with the O/C ratio, with a relationship of $\kappa_{\text{org}} = (0.29 \pm 0.05) \times (\text{O/C})$ for the conditions in our study. Using these methods and with these assumptions, the hygroscopicity of the entire aerosol could be predicted such that it was in agreement with measurements. This study is the first to characterise the hygroscopicity of the organic fraction based on its degree of oxygenation and further work should be done to confirm these findings, especially the linear assumption of hygroscopicity to O/C since the conditions during our study were limited.

Although the findings from Chapter 4 are interesting, it remained to be shown that the hygroscopicity of the organic component can actually affect the hygroscopicity of the overall aerosol in ambient air. The findings from Chapter 5 confirm our findings at Egbert, but more importantly, they show that there are locations where the findings from Chapter 4 are actually important. These are locations that have a high oxygenated organic fraction and include urban, downwind urban centres and remote locations. At first this might be surprising because in North America, urban aerosol is often sulphate-
rich from coal fired power plants. However, in countries where power is predominantly from nuclear power plants, such as Switzerland and France, the aerosol from urban areas can be dominated by the organic fraction. As sulphur emissions become regulated and coal power plants are phased out, the importance of the hygroscopicity of the organic component will increase and this work will become even more relevant. This is also true for pre-industrial conditions when the organic aerosol component was likely more important since sulphur emissions were not as high. For these cases, it is even more important that climate models consider the hygroscopicity of the organic component.

The uncertainties in the predicted and measured CCN concentrations in Chapter 4 and Chapter 5 are large, suggesting that these methods of determining $\kappa_{\text{org}}$ are limited by the instrumentation. Future studies should use size-selected aerosol to measure the $\kappa$ of the aerosol directly, as described by Rose et al. (2008) and Gunthe et al. (2009), and infer the $\kappa_{\text{org}}$ from parallel measurements of chemical composition. This would help reduce the variability encountered when sampling a polydisperse aerosol population that inherently increases the complexity of the analysis and the assumptions required to interpret the results. The studies presented here all assumed an internally-mixed aerosol over the entire aerosol population, meaning that not only is the particle composition assumed to be the same for all particles of a certain size, but also that the composition is the same at all sizes. This introduces uncertainties in the predicted CCN concentrations. For example, the composition of the smaller particles, especially those to which the CCN counter are sensitive (<100 nm), is often not captured by the AMS, or are under-represented in the bulk average since they are often different than the accumulation mode particles. One way to circumvent this would be to size select the particles that enter the CCN chamber and then pass the exit flow through a counterflow virtual impactor to capture only the activated fraction, and then measuring the composition of these aerosol, either by AMS, or by filter followed by an offline technique such as IC. The difficulty in this would be obtaining enough aerosol mass to get sufficient signal since there are many dilution factors involved with each instrument. The presence of an externally-mixed aerosol population would additionally complicate the calculation, however, this may be a limitation of our current instrumentation. Finally, the parameterisations of $\kappa_{\text{org}}$ described
in Chapter 4 should be confirmed under different ambient conditions that have different organic character.

There are many questions that still remain about CCN-activation. The effect that a surface organic can have on the kinetics of droplet activation are still unknown. Except for the study by Shantz et al. (2003), no other laboratory study has reproduced the delay in droplet growth observed in the field by Ruehl et al. (2008) and Shantz et al. (2010). This could be important in the actual formation of clouds since a slight delay could result in a much higher supersaturation in the cloud, resulting in a greater number of cloud droplets, i.e. a more reflective cloud, compared to a cloud with no delay (Shantz et al. 2010).

Another question that still remains outstanding is the effect that a surface active species can have on the surface tension. To date, there have been very few studies that have actually observed a surface tension decrease in droplet activation (Broekhuizen et al. 2004; Asa-Awuku et al. 2008), although some studies have inferred it (George et al. 2009) and many have tried to look for an effect (Li et al. 1998; Bilde and Svenningsson 2004; Sorjamaa et al. 2004; Abbatt et al. 2005; Prisle et al. 2010). It is unknown whether the surface active layer would have to completely cover the droplet in order to have an observable effect on the surface tension and how the time required for a surface active species to diffuse from the particle to the droplet surface, particularly if it is insoluble, compares to the time needed for a droplet to activate (and whether this is relevant). In addition, the reactive uptake \( \text{N}_2\text{O}_3 \) has been shown to decrease above the critical micelle concentration (McNeill et al. 2006) and it is unclear whether this would also apply for the uptake of water.

Finally, the real test of our understanding of cloud droplet activation would be to conduct an aerosol-CCN-droplet closure study at cloud level. The results at ground level are interesting, however, they are not necessarily relevant once inside cloud where physical processes could be even more important than aerosol microphysics. Although adiabatic parcel models are often used to simulate cloud conditions, actual measurements would be
invaluable. This might be best conducted on a mountain with sites above, in and below cloud to see how they compare and to observe the different regimes. Alternatively, if the instrumentation could be made small enough, they could be placed on a tether-balloon that would be raised and lowered in and out of clouds at a location with low-level clouds.

Incorporating these findings into a climate model would be the long term goal of this work. This could potentially be done by simplifying the cloud droplet activation behaviour of the aerosol into the three parameters described in Chapter 4: with inorganic, oxygenated organic and unoxygenated components, each with their own hygroscopicity parameter, or with an inorganic and organic component as well as a degree of oxygenation (O/C) that would describe the hygroscopicity of the organic component.

6.3. References


