HYGROSCOPIC GROWTH AND CLOUD CONDENSATION NUCLEI ACTIVITY OF FRESH AND CHEMICALLY-AGED BIOMASS-PYROLYZED ORGANIC AEROSOL

BY

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THESIS

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ABSTRACT

Biomass burning is one of the prominent contributors of organic aerosols and cloud condensation nuclei (CCN) in the atmosphere. Aerosol-cloud interactions contribute to uncertainties in estimates of climate forcing, not only because of the complexities in their initial size and chemical composition, but also because of transformations (aging) they undergo in the atmosphere upon exposure to reactive species (e.g., NH$_3$ and O$_3$). This study presents results of bench-scale experiments on biomass pyrolysis organic carbon (OC) particles to determine its hygroscopic growth at sub-saturated relative humidities (RH) as well as CCN activity and droplet sizes at super-saturated humidity. This thesis investigates changes in these properties upon controlled, atmospherically-relevant exposures of NH$_3$, O$_3$ and RH. Measurements of hygroscopic growth and CCN activity are analyzed using $\kappa$-Köhler theory to calculate representative hygroscopicity parameters, $\kappa_{GF}$ and $\kappa_{CCN}$, respectively (c.f. Petters and Kreidenweis 2007). Discrepancies as large as factors of three between $\kappa_{GF}$ and $\kappa_{CCN}$ suggest that approximating the surface tension of solution droplets to that of pure water, as assumed in $\kappa$-Köhler theory, overestimates the CCN activity of these complex organic particles. A possible evidence of the presence of surfactants is the formation of more than one hygroscopic activation modes in size-resolved CCN activation curves. While no change in $\kappa_{GF}$ is observed after a 9 day-equivalent of atmospheric NH$_3$-aging, a 72% increase in $\kappa_{CCN}$ of OC particles suggests the presence of organic acidic groups in sufficient amount to influence the overall hygroscopic behavior of the particles. Chemical aging with O$_3$ has no measurable impact on the $\kappa_{GF}$ and $\kappa_{CCN}$ of OC particles. My results suggest the possibility that oxidation of gas-phase volatile organic compounds in the aerosol by O$_3$ causes them to condense as films on pre-existing particles. An evidence of such film formation is the reduced diameters of droplets exiting a cloud chamber, wherein the CCN have been exposed to a controlled supersaturation ratio for a fixed amount of time. We find that the possible participation of water taken up during aging at controlled relative humidity conditions does not affect hygroscopicity of OC particles. The results in this thesis are consistent with previously published results of effects of chemical aging with NH$_3$ and O$_3$ on the hygroscopicity of organic particles. Moreover, while previous studies have investigated organic particles of controlled initial composition, the results presented here apply to biomass pyrolysis OC particles. This thesis aids in understanding the important chemical aging mechanisms that
organic particles emitted from pyrolysis of biomass could undergo, leading to their possibly increased hygroscopicity in the atmosphere.
Who has wisdom to count the clouds?
Job 38:37a
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Often times, when I think of humanity’s existence in this vast universe, I analogize that humans are naught but particles of infinitesimal size, suspended in a gigantic gaseous medium of knowledge and virtues. There is negligible uptake of these gaseous species by us in our initial, nascent stages. Over time, however, we undergo an aging process that not only helps us grow, but also transforms us. Aging includes two mechanisms: (a) interaction with other differently or similarly aged particles and (b) depending on our affinity for them, our uptake of some of the gaseous species in our surrounding medium. Chapters 1 through 4 of this thesis present an evidence of the latter i.e., my uptake of knowledge in the last 2 years. But first, I emphasize the former mechanism by thanking other particles that have significantly transformed me.

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1. INTRODUCTION

1.1 Background

Aerosols are defined as suspended solid or liquid particles suspended in a gaseous medium. Sources of aerosols in the atmosphere could be natural as well as anthropogenic. Aerosols have been found to affect the Earth’s climate both directly and indirectly. Direct effects of aerosol particles are absorption and scattering of radiation by these particles, which affects the radiative budget of the Earth (McCormick and Ludwig 1967). Aerosol optical depth is a commonly used measure of absorption and scattering of radiation by aerosols. An enhancement in this property indicates a reduced transmission of radiation to the Earth’s surface due to presence of aerosols in the atmosphere. An indirect effect is the ability of aerosols to act as cloud condensation nuclei (CCN), which may lead to an increase in number of cloud droplets. This in turn increases the cloud albedo, or the reflectance of incoming radiation by clouds, causing global cooling (Twomey 1974). This effect has been termed the ‘first indirect effect’ of aerosols. Moreover, due to increase in number of CCN and limited liquid water in the atmosphere, the formed droplets are not able to rain out, causing suppressed precipitation and increased cloud lifetime and thus prolonged reflectance of radiation by clouds (Albrecht 1989). This effect has been termed the ‘second indirect effect’. The change in radiative equilibrium of the Earth due to the effect of aerosols (also known as “radiative forcing”) is expressed in watts per square meter. The global mean radiative forcing estimate due to direct effects of aerosols is -0.95 to +0.05 Wm\(^{-2}\) while that including indirect effects is -1.9 to -0.1 Wm\(^{-2}\) (Myhre et al. 2013). However, due to complexity of the various aerosols and the magnitude of their direct and indirect effects, the confidence level of these estimated forcing values of aerosols are ranked “medium” by the fifth assessment report (AR5) of the Intergovernmental Panel on Climate Change (ranks used are low, medium, high and very high). The ranking is a qualitative judgment based on the confidence in and evidence for different estimates climate effects such as that of greenhouse gases (“very high”) and stratospheric ozone (“high”). This type of ranking aids in identifying the gaps in which research efforts are needed to gain a more accurate overall picture of climate effects. For a more accurate estimation of the net effect of aerosols on the climate, detailed information is needed about the
sources and sinks of these aerosols as well as their physical and chemical properties and processes during their lifetime in the atmosphere.

This thesis describes research that contributes to the understanding of aerosol direct and indirect effects on climate. The rest of this chapter presents: (i) a review of atmospheric aerosols and their properties relevant to this research, (ii) a review of previously published literature to develop a strong base of the current knowledge in this area, (iii) the uninvestigated questions in this area, which form the motivation for the research presented in this thesis and the objectives of this thesis. Chapter 2 of this thesis describes the overall research approach as well as the experimental methods and data analysis procedures used in this research. Chapter 3 describes (i) the results from performance evaluation tests to instill a level of confidence in my experimental setup and (ii) a discussion of the measurements done and results obtained in this research. Finally, Chapter 4 provides a summary of the thesis as well as concluding remarks as to how the results presented in this thesis are important in addressing the uninvestigated questions that motivated this research.

1.2 Atmospheric aerosol

1.2.1 Atmospheric aerosol sizes

Of the various physical properties, particle size is an important physical parameter that governs the behavior of aerosols in the atmosphere. It is a common practice to classify particles based on their size. One of the earliest representation of size distribution of particles was proposed by Junge (1963) using a power law fit. Transforming the number-distribution to volume-based plot, Whitby (1978) showed three distinct peaks. These peaks were named nucleation, accumulation and coarse modes. The nucleation mode particles are mainly formed by gas-to-particle conversion of gases due to photochemical reactions. Due to ability of particles in the 10-100 nm size range to penetrate human lung tissue, these particles are of emphasized interest and thus often binned separately as Aitken nuclei mode, or “ultrafine” mode (John 2011). The accumulation mode is often sub-divided into “condensation” and “droplet” modes. Particles in the condensation mode are formed by condensation of inorganic gases into nuclei followed by coagulation. Because the rate of this growth is size-limited, condensation mode particles do not grow larger than 0.2 µm. Aqueous-phase reactions cause the formation of the droplet mode
particles (John et al. 1990). A number-based size distribution of atmospheric particles is shown in Fig. 1.1.

![Number-based size distribution of atmospheric aerosols](image1.png)

**Fig. 1.1**: Number-based size distribution of atmospheric aerosols (Watson 2002)

An illustration of the processes that these particles undergo in the atmosphere is shown in Fig. 1.2.

![Production, interaction and deposition of atmospheric aerosols](image2.png)

**Fig. 1.2**: Production, interaction and deposition of atmospheric aerosols (Jacob 1999)
Polydisperse populations of particles are often summarized and reported using one or two key parameters of the log-normal size distribution such as the diameter representing the central tendency of the distribution and the standard deviation or the ‘width’ of the bell curve. Diameters used for describing central tendency are mean, median, mode diameters. In this study, the median diameter is used.

1.2.2 Atmospheric aerosol sources

Fig. 1.3 shows a representation of the fluxes of natural and anthropogenic aerosols for the year of 2000, as estimated by Andreae and Rosenfeld (2008).

A majority of atmospheric aerosol mass arises from natural sources such as inorganic sea salt. Sea salt particles are produced at the ocean surface (Blanchard and Woodcock 1957). Natural mineral dust is emitted due to mobilization of soil particles in deserts by wind (Tegen 2003). These naturally occurring aerosol particles are in the coarse (> 2.5 µm) size range, which explains their high mass fraction in the atmosphere. However, for the purpose of discussing aerosol-cloud interactions, the sea salt and mineral dust aerosol masses are not significant because the fraction of these masses that serve as CCN is low (1% for sea salt particles; Andreae and Rosenfeld 2008). Anthropogenic activities such as fossil fuel combustion are the biggest source of precursors of sulfate aerosols although there are also primary contributors of sulfate aerosols such as volcanic eruptions (Andreae and Rosenfeld 2008). Sulfate aerosols formed in the atmosphere from anthropogenic emissions of SO$_2$ are considered to be one of the most prominent contributors to the total aerosol indirect effect on climate (Myhre et al. 2013).
Research efforts in the last few decades have identified that organic aerosols can also serve as CCN in the atmosphere (Roberts et al. 2003; Camponogara, Silva-Dias, and Carrió 2014). Primary organic carbon (OC) aerosols are emitted directly as particles into the atmosphere while secondary organic aerosols (SOA) form when volatile organic compounds (VOCs) in the atmosphere undergo oxidation and lose their volatility, undergoing gas-to-particle conversion.

A technology-based emission inventory review by Bond et al. (2004) showed that almost 90% of primary OC is estimated to come from biomass burning (BB), which includes open vegetation fires (forests and agricultural waste) and domestic biofuel use (Fig. 1.4). Nearly 40% of the world’s population uses BB as a heat source for household purposes, mainly cooking and heating (IEA 2013). The estimated radiative forcing of the Earth’s climate due to OC emission is -0.29 Wm^{-2}, of which -0.2 Wm^{-2} is only due to OC emitted from BB. Moreover, the uncertainty in this estimate is large (-63 to +72%) (Myhre et al. 2013). It is thus important to understand whether or not the OC particles emitted from BB are able to serve as CCN in the atmosphere, both at their initial properties during emission as well as their modified properties after they have undergone physical and chemical transformations in the atmosphere.

The ability of particles to form droplets in the atmosphere and serve as CCN depends on several factors such as their affinity for water (“hygroscopicity”) and their diameter. In the next
two sections, the dependence of droplet formation and ability to serve as CCN on particle hygroscopicity and diameter is presented.

1.3 Hygroscopic growth of particles

An understanding of the concept of relative humidity (RH) is required before studying hygroscopicity of particles. An indication of the hygroscopicity of particles is their ability to take up water from the environment around them. The amount of water uptake depends on the water content in the environment. At a given absolute temperature ($T$), RH is the ratio of the partial pressure of water vapor in air, $e$, to the saturation vapor pressure, $e_s(T)$, at that temperature. The thermodynamic property, $e_s(T)$, is a function of temperature and is given by the Magnus-Tetens equation:

$$e_s(T) = 6.112 \exp \left[ \frac{17.62(T-273)}{(T-273)+243.12} \right]$$ \[1.1\]

The environment is saturated when RH is 1 (or 100%). RH values below and above 100% describe a subsaturated and supersaturated environment, respectively.

The growth of particles by water uptake at subsaturated RH is typically reported as the size growth factor, $GF_{RH}$, as a function of RH:

$$GF_{RH} = \frac{D_{RH}}{D_{dry}}$$ \[1.2\]

where $D_{RH}$ is the diameter of particle at a given RH and $D_{dry}$ is the dry diameter of the particle.

The behavior of $(\text{NH}_4)_2\text{SO}_4$ and NaCl particles, two well-characterized inorganic compounds, at subsaturated RH is shown in Fig. 1.5. There is no growth in size of both particles at RH less than 75%. The $GF_{RH}$ for $(\text{NH}_4)_2\text{SO}_4$ increases abruptly at 80% RH (75% for NaCl). This critical RH is called the deliquescence RH and indicates the value at which the solid solute dissolves into the aqueous phase. For RH higher than deliquescence RH, there is continued growth in the size of the wet particle due to uptake of water vapor. However, with decreasing RH, crystallization of the particle does not occur at the deliquescence RH. Instead, a metastable equilibrium is established till the RH drops below the efflorescence RH (Tang 1979). At efflorescence RH, the droplet is supersaturated with respect to the solute. A further drop in RH causes it to nucleate into a crystal. This thermodynamic property allows these particles to exist as metastable droplets at subsaturated conditions in the atmosphere (Rood et al. 1989).
An atmospheric implication of the hygroscopic growth of particles at subsaturated RH is the perturbed radiative transfer in near-cloud regions. RH can be as high as 85% to 90% up to 4 km horizontal distance from clouds and as high as 96% within 100 m of the cloud (Twomey, Coakley, and Tahmk 2009). Besides near-cloud regions, high subsaturated RH conditions also develop during the summer in tropical regions due to evaporation of surface water. The water vapor pressure is lower at higher latitudes than in tropical regions. However, low temperatures cause the saturation vapor pressure to be low (Eq. [1.1]) and this leads to high subsaturated RH. Due to increased particle diameter upon water uptake, the aerosol optical depth in such high subsaturated RH regions can be enhanced by up to 25% (Chand et al. 2012). Moreover, upon water uptake, the chemical composition of the particles may also be affected (Abbatt, Lee, and Thornton 2012). It is thus of interest to investigate the hygroscopic growth of particles at subsaturated RH.

1.4 CCN activity of particles

CCN are the subset of atmospheric aerosol particles that are able to “activate” into cloud droplets when the environment around them is supersaturated with humidity. A supersaturated environment is expressed as percentage of water vapor above the saturation point, or supersaturation (SS):
The phenomenon of activation of CCN into droplets is governed by principles of thermodynamics discussed below. Theoretically, homogenous nucleation of water vapor and formation of cloud droplets is possible if the environment is sufficiently supersaturated with respect to liquid water content. The nucleation of droplets from water vapor is a thermodynamic process given by the following relation:

\[
\Delta E = 4\pi R^2 \sigma - \frac{4}{3}\pi R^3 n k T \ln \left( \frac{e}{e_s(T)} \right)
\]

where, \( R \) is the radius of droplet that is in equilibrium with surrounding water vapor pressure; \( \sigma \) is the interfacial energy between vapor and liquid; \( n \) is the number density of water molecules; \( k \) is the Boltzmann constant. Here, the first term on the right-hand side of the equation accounts for surface tension of the droplet, while the second term accounts for change in the Gibbs free energy of the system due to condensation of vapor from the surroundings of the droplet.

Formation of droplets is thermodynamically favorable when \( \Delta E \) is negative. Since the surface tension term on the right-hand side of Eq. [1.4] is always positive, the only way to achieve a negative \( \Delta E \) is if the ratio \( e/e_s(T) \) is sufficiently large. At subsaturated RH, the ratio \( e/e_s(T) \) is less than 1 and thus the second term on the right-hand side is negative, making \( \Delta E \) positive (Eq. [1.4]). Hence formation of droplets is not thermodynamically favored at subsaturated RH. At supersaturated RH, however, \( \Delta E \) increases with \( R \) and reaches a maximum \( [d(\Delta E)/dR = 0] \) at a critical radius \( (R^*) \). At this point, the droplet is at thermodynamic equilibrium. Upon a further increase in droplet radius, \( \Delta E \) is reduced. The supersaturated RH corresponding to this maximum is given by Lord Kelvin’s equation:

\[
\frac{e}{e_s(T)} = \exp \left( \frac{2\sigma}{nkTR^*} \right)
\]

[1.5]

Thus, the equilibrium vapor pressure over a curved surface is much larger than that over a flat surface of a liquid. Eq. [1.5] indicates that this effect, known as the Kelvin effect, becomes less pronounced as droplet diameter increases.

Fig. 1.6 shows the RH with respect to a plane surface of water, at which a pure water droplet is at unstable thermodynamic equilibrium at 298 K. Homogeneous nucleation of water into a droplet of 0.01 \( \mu \)m radius requires an environmental RH of about 111 % (or 11% \( SS \); Eq. [1.3]).
Cloud droplet formation from homogenous nucleation requires as large as 4 to 7% SS (Madonna et al. 1961; Wilson 1897). Such a large SS is never actually achieved in the atmosphere and thus droplets cannot form homogenously.

Fig. 1.6: The relative humidity at which pure water droplets are in unstable equilibrium at 298 K

Droplets are formed in the atmosphere due to heterogeneous nucleation, or condensation of water vapor on aerosol particles when the water-soluble content in particles dissolve and form a salt solution. This phenomenon is explained by the concept of Raoult’s law, which states that the saturation vapor pressure over a surface of a salt solution is smaller compared to that over a surface of pure water. This reduction is expressed mathematically:

\[
\frac{e_s'}{e_s(T)} = f \quad [1.6]
\]

\[
f = \left[1 + \frac{imM_w}{M_s\left(\frac{4}{3}\pi R^3 \rho' - m\right)}\right]^{-1} \quad [1.7]
\]

where, \(e_s'\) is the saturation vapor pressure over a salt solution having a mole fraction \(f\) of water; \(i\) is the number of ions the solute dissociates into upon dissolution; \(m\) is the mass of solute; \(M_w\) is the molecular mass of pure water; \(M_s\) is the mass of solute; \(\rho'\) is the density of the solution.

Combining Eq. [1.5], [1.6] and [1.7], the vapor pressure over a salt solution \((e')\) is:
Eq. [1.8], when plotted as a function of droplet radius, produces a curve known as a Köhler curve (Köhler 1936), which describes the supersaturation adjacent to a solution droplet surface as a function of droplet radius. Köhler theory is illustrated in Fig. 1.7 and explained below.

![Köhler curves for inorganic salts at 15 °C. Solid lines are for (NH₄)₂SO₄; Dashes lines are for NaCl](image)

Assume that a solution particle of mass $10^{-19}$ kg NaCl is placed in an ambient RH of 100.5% ($SS = 0.5\%$). Köhler theory predicts that the particle will take up water until the radius of the solution droplet is $R_e$. At this point, the droplet is in a state of stable thermodynamic equilibrium. This means that at the constant ambient $SS$ of 0.5%, a positive or negative perturbation in the radius of the particle will cause water to evaporate from the droplet or condense to the droplet, respectively, bringing the droplet radius back to $R_e$. Now, if the ambient $SS$ increases, the droplet will take up water such that its radius follows the Köhler curve. In other words, the droplet will always be in thermodynamic equilibrium with its surrounding. At the peak in its Köhler curve, however, the droplet is in unstable equilibrium because a positive perturbation in its radius will cause the droplet to surpass this peak and “activate” into a cloud droplet. This peak in the Köhler curve of a solution droplet is called its critical supersaturation ($S_C$). Droplets of different
chemical composition have different Köhler curves and thus a different $S_C$. The significance of chemical composition of droplets in their activation behavior is discussed below.

Assume that two solution particles, both of mass $10^{-19}$ kg, one $(\text{NH}_4)_2\text{SO}_4$ and the other NaCl, are placed in ambient RH of 100.85% ($SS = 0.85\%$). Condensation of vapor occurs on both particles as they grow till radius $R_e$. At this point, condensation of vapor on the $(\text{NH}_4)_2\text{SO}_4$ is no longer thermodynamically favorable, because its critical supersaturation ($S_C,(\text{NH}_4)_2\text{SO}_4$) is larger than the ambient $SS$ of 0.85%. Thus, the $(\text{NH}_4)_2\text{SO}_4$ droplet is in stable equilibrium at radius $R_e$. However, the supersaturation adjacent to the NaCl droplet is still less than ambient supersaturation at $S_C,\text{NaCl}$. Hence the activated NaCl droplet will continue to grow larger if sufficient vapor is available.

A common measure of CCN activity of a particle population is the particle diameter, $D_{50}^{SS}$, at which 50% of the particles activate into cloud droplets at a given $SS$. A decrease in $D_{50}^{SS}$ for a single size distribution indicates an increase in CCN activity due to higher soluble content of the particles.

1.5 Hygroscopicity and the $\kappa$-Köhler theory

As established earlier, both hygroscopic growth and CCN activity of particles depend on their hygroscopicity, or the amount and nature of soluble matter in the particles. Hygroscopicity has been parameterized using the $\kappa$-Köhler theory (Petters and Kreidenweis 2007): for a particle of dry diameter $D_{dry}$, the hygroscopicity parameter, $\kappa$, relates its wet diameter, $D_{wet}$, to its water activity, $a_w$

$$
\frac{1}{a_w} = 1 + \kappa \left[ \frac{D_{dry}^3}{D_{wet}^3 - D_{dry}^3} \right]
$$

[1.9]

Reported values of $\kappa$ range from strongly hydrophobic ($\kappa = 0$ for completely insoluble particles) to strongly hygroscopic ($\kappa = 0.6$ for $(\text{NH}_4)_2\text{SO}_4$). Moreover, $\kappa$ can be calculated from measurements of either $GF_{RH}$ or $D_{50}^{SS}$ (denoted as $\kappa_{GF}$ and $\kappa_{CCN}$, respectively), as will be discussed in detail in Section 2.7.2. Compiling previously published measurements of hygroscopic growth and CCN activity, Petters and Kreidenweis (2007) calculated $\kappa_{GF}$ and $\kappa_{CCN}$ for 25 organic and inorganic compounds. The agreement between $\kappa_{GF}$ and $\kappa_{CCN}$ was within 15% for inorganic and within 30% for organic substances. These discrepancies were attributed to experimental
uncertainties. Measured $\kappa_{CCN}$ of more than 30% higher than measured $\kappa_{GF}$, indicates the possible presence of surfactant and sparingly soluble matter (Dusek et al. 2003; Petters and Kreidenweis 2007; Li, Williams, and Rood 1998). As described earlier, Köhler theory predicts the CCN activity of a particle based on the equilibrium between the surface tension and solute presence, quantified by the Kelvin and Raoult terms, respectively. Thus, the possible presence of surfactants and sparingly soluble matter will affect the Kelvin and Raoult terms, thereby affecting the overall CCN activity of the particle.

1.6 Aging of aerosols

By now it has been established that BB is a prominent source of OC aerosols globally. While freshly emitted organic aerosol particles are hydrophobic and thus serve as CCN only at very high SS, these particles can become hygroscopic within 24 h of emission (Stier et al. 2006). Particles in a BB plume are rapidly transformed by several processes, collectively termed ‘aging’. Aging includes physical processes (i.e., coagulation and condensation) as well as chemical processes (i.e., surface-based chemical interaction with reactive species). It is important to identify the chemical aging pathways that render these initially hydrophobic particles more hygroscopic and more able to serve as CCN, or “CCN-active.” Identifying aging mechanisms also aids in estimating the atmospheric lifetime of the aerosols (Slade and Knopf 2013).

Chemical aging of organic aerosols by reactive gases can affect their solubility and surface active properties, which affects their CCN activity (Petters et al. 2006). NH$_3$ and O$_3$ are observed throughout the lower atmosphere in trace amounts, with exact values varying spatially and temporally. Ambient levels of NH$_3$ have been observed to be as low as 0.5 ppb$_v$ in rural locations (Lewin, De Pena, and Shimshock 1986) and as high as 8 ppb$_v$ in regions with high BB activity (Trebs et al. 2005). Surface O$_3$ levels of 10 to 30 ppb$_v$ have been measured in the United States (Fiore 2003) and concentrations as high as 40-60 ppb$_v$ have been measured in regions with high BB activity (Bela et al. 2015). As discussed earlier, water uptake from atmospheric humidity may also participate in the chemical reactions of organic aerosol particles.

1.7 Hygroscopicity of fresh and aged organic aerosols

As discussed in the previous section, freshly emitted organic aerosols are rapidly transformed in the atmosphere due to aging. Chemically reactive species such as NH$_3$ and O$_3$ are present in
varying concentrations spatially and temporally and it is thus important to investigate the change in hygroscopicity of organic aerosols upon chemical aging with these species. I presently review studies that have reported changes in hygroscopicity of organic particles due to chemical aging with NH$_3$ and O$_3$. Trebs et al. (2005) showed that NH$_4^+$ ions in ambient aerosol particles neutralize the acidic groups in ambient organic aerosols. Hygroscopicity of laboratory-generated surrogates of atmospheric organic aerosols increases through this mechanism (Dinar, Anttila, and Rudich 2008; Wu et al. 2011). Dinar et al. (2008) observed that the hygroscopic growth of sparingly soluble organic particles was unaffected by exposure to 1 ppm$_v$ NH$_3$ at RH below 94%. Above that point, the particles deliquesced and growth factor became a function of increasing NH$_3$ exposure. In the supersaturated regime, the $D_{50}^{0.64}$% of the particles decreased by 55% after exposure to NH$_3$. Slade et al. (2015) showed that oxidation by O$_3$ had no impact on the CCN activity of single, binary and ternary mixtures of BB surrogate compounds in the laboratory.

Oxidative species like O$_3$ also react with the volatile organic compounds (VOCs) in the aerosol and reduce their vapor pressure, causing them to condense as films on pre-existing particles (Lambe et al. 2015). An effect of such organic films is that depending on the hydrocarbon chain length and number of hydrophobic and hydrophilic groups in these films, they can impede mass transfer of water vapor and thus inhibit the rate of droplet growth at supersaturated RH (Feingold and Chuang 2002). This change in growth rate may be important in the wet removal of ambient aerosols because the droplets exhibiting slower growth are prone to cause broadening of the droplet size distribution in the atmosphere (Feingold and Chuang 2002) and increased atmospheric lifetimes of the droplets (Ruehl, Chuang, and Nenes 2007).

Studies have also investigated properties of aerosols emitted from BB, instead of surrogates (for e.g., Petters et al. 2009, Dusek et al. 2011). These studies analyzed emissions from burning different species of biomass and found $\kappa$ ranging from 0.06 to 0.2 for emissions from burning of wood or branches with leaves. They found that measured $\kappa_{GF}$ and $\kappa_{CCN}$ for a given BB aerosol population differed within the aforementioned 30% uncertainty that could be ascribed to measurement error. Moreover, Petters et al. (2009) also found that the size-resolved CCN activation curves of different BB emissions differ in shape owing to chemical and morphological heterogeneity of the particles. These studies investigated BB emissions without isolating the stages of combustion. However, in a BB event, vaporized volatile compounds can either condense to form OC particles (Evans and Milne 1987) or burn in a diffusion flame to form BC
particles. Emissions from an isolated stage of a BB event have not been investigated to determine the possible differences in hygroscopic properties of OC and BC aerosols emitted from BB. This should be studied to understand how sensitive the hygroscopicity of emitted particles is to the stage of BB during emission.

1.8 Research motivation and objectives

One of the major challenges in estimating climate forcing by aerosols is the insufficient knowledge of the cloud-interactions of aerosols in the atmosphere. As described earlier, there are estimates of the amount of aerosols, both of natural and anthropogenic origin, emitted into the atmosphere. However, there is a need to understand the hygroscopic properties of these aerosols at the time of their emission, as well as how these properties transform under the influence of various physical and chemical processes in the atmosphere.

BB is the most important contributor to organic aerosols in the atmosphere. Laboratory investigations of single-component and controlled mixtures of surrogates of BB aerosols have helped identify prominent mechanisms that could transform their hygroscopicity in the atmosphere. However, relatively fewer studies have investigated the initial hygroscopic properties of BB aerosols under controlled laboratory conditions as well as transformations of these properties under simulated atmospheric processing. Moreover, while it is known that the composition of aerosols from BB depends on the conditions during the burn, no study has investigated the hygroscopicity of particles emitted from an isolated stage of burning such as pyrolysis, which generates much of the atmospheric primary OC. The motivation for this thesis is to increase the understanding of the hygroscopicity of particles emitted from controlled laboratory pyrolysis of biomass and how these properties evolve upon simulated atmospheric chemical processing.

Studies reviewed earlier in this chapter have measured the hygroscopicity of either chemically-aged BB surrogate aerosols or freshly emitted BB aerosols. The objective of this study is to combine these two approaches by studying aerosols generated by biomass pyrolysis and then simulating atmospheric chemical aging of these aerosols to characterize the hygroscopic growth and CCN activity of particles before and after chemical aging.

This thesis describes bench-scale measurements of the hygroscopicity of biomass pyrolysis OC particles, both initially as well as after controlled chemical aging. Because the chemical
composition of these particles is unknown, measurements of hygroscopicity are done at both, sub- and supersaturated RH. The relationship between properties measured at both these RH conditions is quantified to best infer the chemical composition of every aerosol. Size distribution of droplets after activation in the cloud chamber are also investigated in order to detect the possible effect of condensed films on the growth of droplets at supersaturated RH.

Properties of both initially generated and aged aerosols govern their interactions with clouds and their wet removal. It is beyond the scope of this thesis to evaluate direct or indirect radiative climate forcing based on the obtained results. Nonetheless, results of this study are important in understanding the hygroscopic properties of these aerosols and in identifying the chemical mechanisms that can be significant in altering these properties. A better understanding of these initial and eventual hygroscopic properties of organic aerosols can aid in better representation of aerosol properties in climate models so that these models can then achieve less uncertain estimates of climate forcing by aerosols.
2. METHODS

2.1 Overall research approach

I measured the hygroscopic growth and CCN activity of OC aerosol generated in biomass pyrolysis. For the remainder of this paper, the term “OC” will refer to this pyrolytically generated aerosol. A schematic describing the research approach used in this study is shown in Fig. 2.1. All aerosol flow rates described herein are standardized to 1 atm and 273 K.

![Fig. 2.1: Overview of research approach (dashed borders indicate activities that were only implemented in some tests)](image)

2.2 Generation and sampling of aerosol

Ammonium sulfate (AS; ACS Certified, Fisher Scientific A702) and 100, 207 nm polystyrene latex (PSL; Thermo Scientific Inc. 3200A) aerosols were generated using a constant output atomizer (TSI 3076) using deionized water to produce reference aerosols for calibration. Aerosol was dried (<1% RH) using a custom-built silica gel diffusion dryer. AS is a common inorganic salt, the hygroscopic properties of which have been well-characterized. Hence AS was used for calibrating instruments that measure the hygroscopic properties of aerosols. PSL spheres were used for evaluating the particle sizing instrumentation.

OC aerosol was generated by pyrolysis of oak wood biomass. Pyrolysis was controlled inside a reactor (Chen and Bond 2010) and is briefly described here for clarity. Oxygen-deficient conditions were created by passing gaseous N₂ (99.95% purity by mass) at 12.4 ± 0.1 slpm into the bottom of the reactor, with a residence time of 3.7 s at standard conditions. The temperature at the bottom of the reactor was maintained at 300 °C using a 650 W proportional-integral-
derivative (PID) controlled heater (Watlow VC403A06A). The mass of biomass used in a single batch test was 0.32 ± 0.01 g, measured using an analytical balance (Mettler-Toledo AB204-S). OC aerosol was drawn from top of the reactor at 2.03 ± 0.02 slpm and was diluted immediately in an annular sampling probe by mixing with clean air at 25.88 ± 0.21 slpm. Sampling of the high-concentration OC was done for 30 s and was directed to a 208 L stainless steel mixing chamber. Clean air for dilution was generated by passing compressed air through a high efficiency particulate air filter, a silica gel column and an ammonia adsorbent (AmmoSorb™, Imtek Environmental) column. A fan inside the chamber induced mixing of aerosol. Prior to OC injection, the chamber was purged with clean air to remove any residual particles and gases from the previous test. Particle concentration inside the chamber was measured less than 5 cm⁻³ with a condensation particle counter (CPC, TSI 3010) before each test.

### 2.3 Aging of aerosol

The atmospheric lifetime of primary organic aerosols typically considered in models is 4.3 to 11.1 days (Kanakidou et al. 2005). It is, however, challenging to chemically age organic aerosols over such time periods in laboratory studies. Assuming that the reaction between a gas-phase chemical and aerosol particles follows pseudo-first order kinetics (Rudich, Donahue, and Mentel 2007), an atmospheric equivalent aging with trace levels of a reactant over several days can be achieved by exposing aerosol particles to a high concentration of reactant for a short period of time. This equivalence is used in several experimental studies (e.g., Engelhart et al. 2008, Lambe et al. 2015).

Two concentrations of NH₃ were used in this study: 10 and 875 ppmᵥ. The duration of aging of OC between injection into chamber and drawing out for measurements was 10 min. A 10 min long aging with 10 ppmᵥ NH₃ is equivalent to 9 days of atmospheric aging at an 8 ppbᵥ ambient NH₃ level. A higher NH₃ concentration of 875 ppmᵥ was also used as an upper bound aging condition to observe whether changes in hygroscopicity occurred after aging OC for 10 min at this very high concentration. In tests with 10 ppmᵥ NH₃ aging, a pulse of NH₃ was injected into the mixing chamber immediately after it was filled with OC aerosol. For achieving 875 ppmᵥ NH₃ in the mixing chamber, reagent grade 3000 ppmᵥ NH₃ in N₂ was diluted to 875 ppmᵥ with clean air and the mixing chamber was flushed with this mixture for a minimum of 30 min to achieve steady-state concentration.
O₃ at 0.1 and 0.3 ppmᵥ were used in this study. The duration of aging of OC at both concentrations was 5 min. These conditions are equivalent to atmospheric aging of 15 min and 45 min at an ambient O₃ level of 35 ppbᵥ. However, the O₃ concentration inside the mixing chamber was maintained during a CCN activity test (120 min), causing a total equivalent atmospheric aging of 6 hours and 18 hours for aging concentrations of 0.1 and 0.3 ppmᵥ respectively. As will be discussed later, all CCN activity tests were done by measuring particles of successively greater diameters. Hence, particles drawn out of the chamber first experienced a shorter duration of O₃ aging. The direction of size-scanning was reversed and the test was duplicated to ensure that this did not have an effect on the results. O₃ was generated by passing 0.45 slpm clean air through a variable output O₃ generator (Jelight 610) and diluted with clean air to achieve steady-state O₃ concentration in mixing chamber prior to OC injection.

All experimental test conditions are summarized in Table 2.1. Unique aging IDs are assigned to each set of aging conditions because different combinations of aging conditions are used in different experiments.

<table>
<thead>
<tr>
<th>Aging ID</th>
<th>GF_RH Measured?</th>
<th>Aging conditions</th>
<th>Chemical</th>
<th>ppmᵥ of chemical</th>
<th>RH in during aging (%)</th>
<th>Duration of aging (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>Yes</td>
<td></td>
<td></td>
<td>N/A</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>Fresh-RH0</td>
<td>Yes</td>
<td></td>
<td></td>
<td>N/A</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>Fresh-RH70</td>
<td>No</td>
<td></td>
<td></td>
<td>N/A</td>
<td>70</td>
<td>N/A</td>
</tr>
<tr>
<td>Fresh-RH85</td>
<td>No</td>
<td></td>
<td></td>
<td>N/A</td>
<td>85</td>
<td>N/A</td>
</tr>
<tr>
<td>NH3-10-RH0</td>
<td>Yes</td>
<td>NH₃</td>
<td>10</td>
<td>0</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>NH3-10-RH70</td>
<td>No</td>
<td>NH₃</td>
<td>10</td>
<td>70</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>NH3-10-RH85</td>
<td>No</td>
<td>NH₃</td>
<td>10</td>
<td>85</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>NH3-875-RH0</td>
<td>Yes</td>
<td>NH₃</td>
<td>875</td>
<td>0</td>
<td></td>
<td>10</td>
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<tr>
<td>NH3-875-RH70</td>
<td>No</td>
<td>NH₃</td>
<td>875</td>
<td>70</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>NH3-875-RH85</td>
<td>No</td>
<td>NH₃</td>
<td>875</td>
<td>85</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>O3-0.1-RH0</td>
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<td>O₃</td>
<td>0.1</td>
<td>0</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>O3-0.1-RH70</td>
<td>No</td>
<td>O₃</td>
<td>0.1</td>
<td>70</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>O3-0.1-RH85</td>
<td>No</td>
<td>O₃</td>
<td>0.1</td>
<td>85</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>O3-0.3-RH0</td>
<td>Yes</td>
<td>O₃</td>
<td>0.3</td>
<td>0</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>O3-0.3-RH70</td>
<td>No</td>
<td>O₃</td>
<td>0.3</td>
<td>70</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>O3-0.3-RH85</td>
<td>No</td>
<td>O₃</td>
<td>0.3</td>
<td>85</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

AS = ammonium sulfate; N/A = not applicable; except AS, OC was the seed aerosol in all tests except AS
With the exception of AS, the seed aerosol for all tests is OC. Moreover, as shown in Table 2.1, hygroscopic growth measurements were only done for tests in which RH during aging inside the mixing chamber was less than 1%. For simplicity, I refer to all RH values less than 1% as 0% in this thesis. For every concentration of reactant (NH3 and O3), RH was controlled at 0, 70 and 85% in the mixing chamber during aging to investigate whether aerosol water would participate in the chemical aging process.

2.4 Instrumentation

This section describes the principles and operation conditions of various instruments used in this study.

2.4.1 Humidification during aging of OC

During aging of OC particles, controlled RH inside the mixing chamber was achieved by a custom annular humidifier that controls water vapor diffusion through a GoreTex™ membrane (Winter 2002). A schematic of the humidification system is shown in Fig. 2.2.
RH was measured using a capacitance-based RH sensor (Vaisala, HMP 330). Periodic calibration of the RH sensors was done in the 43% to 97% RH range using saturated solution cells of K₂CO₃ and K₂SO₄. Due to PID-based control of RH, the instantaneous RH of clean air entering the mixing chamber fluctuated within ±5% of the control value. However, these fluctuations were damped inside the mixing chamber and the measured steady-state RH inside the chamber was within ±2% of control value.

2.4.2 Differential mobility analyzer (DMA)

The DMA used in this study was custom-built was previously used by Brem et al. (2012). The operation principle of a DMA is based on the electric mobility of a charged particle in an electric field. The electric mobility of a single-charged particle, \( Z_{p,i} \), is given as

\[
Z_{p,i} = \frac{ieC_C}{3\pi \mu D_p}
\]  

where, \( e = \) elementary unit of charge in Coulomb; \( C_C \) is the Cunningham correction factor to account for non-continuum effects experienced by an aerosol particle in a medium as its size approaches the mean free path of the gas constituting the medium; \( \mu \) is the dynamic viscosity of the medium gas in Poise and \( D_p \) is the aerodynamic diameter of the particle in cm.

Before entering a DMA, particles are given a Fuchs equilibrium charge distribution (Fuchs 1963) by passing them through a bipolar diffusion charger consisting of four radioactive \(^{210}\)Po sources, 500 \( \mu \)Ci each, (Amstat Corp., Staticmaster 2U500) equidistantly placed in the walls of a stainless steel housing.

The charged particles then enter the DMA (Fig. 2.3), which is in form of two concentric stainless steel cylinders of radii \( R_1 \) and \( R_2 \) \( (R_1 < R_2) \). A sample flow, carrying charged particles, enters the DMA along with a particle-free sheath air at the top. The combined sample-and-sheath streams experience a laminar flow through the annular configuration. The central rod is a negative electrode, the voltage, \( V \), on which is controlled. This causes an electric field, \( E \), in the annular region, given as a function of radial distance, \( r \), from the rod:

\[
E = \frac{V}{r \ln \left( \frac{R_2}{R_1} \right)}
\]
As a positively charged particle migrates through the DMA, it experiences a horizontal force towards the central rod, the magnitude of which depends on the voltage of the rod and its electric mobility. Only particles having mobilities within a focused range are able to exit the DMA through the slit at the bottom and these particles are thus “size-selected”. Particles with mobilities larger and smaller than this range are precipitated on the rod before reaching the slit and discharged with the excess sheath flow, respectively. The characteristic mobility, $Z$, of particles that reach and exit through the aerosol outlet port depends on the flow rates of aerosol and sheath air ($Q_a$ and $Q_s$, respectively; in cm$^3$/s) through the DMA as well as the central rod voltage. Mathematically,

$$ Z = \frac{(Q_s + Q_a) \ln \left( \frac{R_2}{R_1} \right)}{4\pi VL} $$  \[2.3\]

is the mean mobility of the size-selected aerosol exiting the DMA. In the DMA used in this study, $L = 44.44$ cm; $R_1 = 0.937$ cm; $R_2 = 1.958$ cm. Excess air was recirculated by using a diaphragm pump (3025, Thomas Inc.) and measured using a mass flow meter (Alicat Scientific). The volumetric flows of polydisperse aerosol inlet and size-selected aerosol outlet should equal each other for accurate classification of aerosol.
2.4.3 Condensation particle counter (CPC)

The CPC and CCN counter have a similar working concept: condensation of a vapor is used to grow small aerosol particles into a larger size that can be optically detected using an optical particle counter (OPC). In a CPC, shown in Fig. 2.4: Schematic of a CPC (graphic adapted from TSI 3010 manual), the aerosol stream is first saturated with n-butanol vapor in the saturator block. The sample is then cooled in a condenser column, creating a supersaturation such that the n-butanol condenses onto all particles, irrespective of size or chemical composition. The alcohol droplets are then passed through a thin laser beam, where due to their size, they scatter the radiation which is detected by a photo-detector.

2.4.4 Scanning mobility particle sizing (SMPS)

The SMPS system is used for measuring the size distribution of a stream of aerosol particles. An SMPS is an assembly of a CPC and a DMA (Model 3071A, TSI) coupled together. For a controlled central rod voltage $V$ in the DMA, particles of a corresponding electric mobility $Z$ exit the DMA and enter a CPC where the particle count is measured. The DMA voltage is increased exponentially and for each voltage, a particle count is measured. The dimensions of the DMA used in this SMPS are identical to the one described earlier.
2.4.5 CCN counter

The CCN counter used in this study employs a continuous flow streamwise thermal gradient chamber (CFSTGC), schematized in Fig. 2.5. The CFSTGC has been thoroughly characterized (Roberts and Nenes 2005; Lance et al. 2006) and is commercially sold by Droplet Measurement Technologies (DMT CCN-100).

Fig. 2.5: A schematic of (left) the CCN counter adapted from Lance et al. [2006] and (right) the CFSTGC (not to scale)

The sheath flow is HEPA-filtered, heated and humidified in a humidifier column before it is introduced in the cloud chamber. A positive temperature gradient is controlled in the flow direction, shown in Fig. 2.5, by means of thermo-electric coolers (TEC). The temperature is higher at point B than at point A. Heat and water vapor diffuse radially, but because water vapor diffuses faster than heat. Due to this, the temperature-independent specific humidity values at points B and C are same, but the temperature at point C is lower than at point B. Thus, a supersaturation is experienced by the water vapor at point C. If this supersaturation is larger than the $S_c$ of the particles, the particles activate into droplets. An optical particle counter (OPC) at the exit of the CFSTGC counts and sizes the activated droplets from 0.5 to 10 $\mu$m with a resolution of 0.5 $\mu$m.

2.5 Hygroscopic growth measurement

A controlled RH humidified-tandem differential mobility analyzer (H-TDMA) setup (Rader and McMurry 1986), shown in Fig. 2.6, was used for measuring the hygroscopic growth of aerosols at subsaturated humidity conditions.
Dry aerosol from the chamber was first passed through a $^{210}$Po charger (Amstat Corp. 2U500) to achieve equilibrium charge distribution and a constant voltage was used to select an electric mobility diameter of 100 nm with a DMA. Size-selected dry aerosol was humidified to controlled RH with a smaller replica of the humidifier described in Fig. 2.2. The humidified size distribution was then measured using an SMPS system. The DMA and the EC were both operated with a 10:1 sheath-to-sample flow ratio with total flow being $10.13 \pm 0.08$ slpm. Four capacitance-based RH sensors (Sensirion SHT-75) were installed in different locations in the setup, shown in Fig. 2.6, to ensure that the sampled aerosol experienced consistent RH through the setup. These sensors were coupled with band gap-based dry-bulb temperature sensors.

### 2.6 CCN activity measurement

The experimental setup used for measuring CCN activity in this study is shown in Fig. 2.7. Particles were selected based on their electric mobility diameter by a DMA. Mobility diameters between 50 and 180 nm were typically scanned in increasing order with increments of 15 nm and sampled by three instruments: a CPC (TSI 3010), an SMPS and a continuous flow streamwise thermal gradient CCN counter (Roberts and Nenes 2005, Lance et al. 2006; DMT CCN-100).
This CCN counter is described here briefly for clarity. A sheath-to-sample flow ratio of 10:1 was used with total aerosol inlet flow of $0.56 \pm 0.004$ slpm. Pressure inside the cloud chamber was $985.7 \pm 8.4$ mbar. Sample aerosol was exposed to a constant supersaturation by applying a temperature gradient across a cloud chamber with wetted walls. An atmospherically relevant $SS$ of 0.3% was used in all CCN tests. Typical atmospheric values of $SS$ are as low as 0.01% to as high as 1% at cloud base (Andreae and Rosenfeld 2008). In this range, 0.3% is the midpoint in logarithmic space.

### 2.7 Data analysis

#### 2.7.1 SMPS data inversion for hygroscopic growth tests

It was discussed earlier that $GF_{RH}$ is the ratio of the particle diameter at a given elevated, controlled RH ($D_{RH}$) to the reference diameter at RH < 10% ($D_{dry}$). The raw SMPS data were inverted using TDMA$^{inv}$, the data inversion toolkit by Gysel et al. (2009). In this toolkit, raw SMPS data from scans done at RH < 10% ($GF_{RH} = 1$) were used to calculate corrections for sizing offsets and the width of the DMA’s transfer function. A piecewise linear function was then fit to the corrected SMPS data and the true mean $GF_{RH}$ values were retrieved.

#### 2.7.2 Calculation of $\kappa_{GF}$ and $\kappa_{CCN}$

The derivation of $\kappa_{GF}$ assumes that $\kappa$-Köhler theory is valid (Petters and Kreidenweis 2007). The water vapor saturation ratio, $S$, over an aqueous solution droplet of diameter, $D$, is given as
where, \(a_w\) = water activity; \(\sigma_w\) = surface tension of pure water (0.072 Nm\(^{-1}\)); \(M_w\) = molecular weight of water; \(\rho_w\) = density of water; \(R\) = universal gas constant; \(T\) = absolute temperature. The water activity, \(a_w\), is given in Eq. [2.6]. In this study, \(GF_{RH}\) values were measured between 10 and 92\% RH and \(\kappa_{GF}\) was calculated by iterative solution of Eq. [2.6] and [2.7]. \(\kappa\)-Köhler theory can also be used to derive \(\kappa_{CCN}\) using Eq. [2.8].

\[
a_w = \frac{D_{RH}^3 - D_{dry}^3}{D_{RH}^3 - D_{dry}^3 (1 - \kappa)} \quad [2.6]
\]

\[
GF_{RH} = \left[ 1 + \frac{a_w \kappa_{GF}}{1 - a_w} \right] \quad [2.7]
\]

\[
\kappa_{CCN} = \frac{4 A^3}{27 (D_{SS_{50}}^3 \ln^2 SS)} \quad [2.8]
\]

where, the constants in Eq. [2.5] were combined to give \(A = 2.1\) nm (at 298.15 K).

### 2.7.3 Droplet size distribution

The CCN counter, in addition to counting the number of particles that activate into droplets at a given supersaturation, also measures the diameters of activated droplets, \(D_{drop}\), downstream of the cloud chamber. The output from the CCN counter is in the form of frequency distribution of droplets numbers classified into 0.5 \(\mu\)m-wide “bins” between 0 and 10 \(\mu\)m. All CCN in this study were exposed to the same \(SS\) for the same time inside the cloud chamber. The factors that can affect \(D_{drop}\) downstream of the cloud chamber include sample pressure, \(SS\) in the cloud chamber, sample flow rate, critical \(SS\) of particles, CCN concentration and the water uptake rate of the activated CCN (Lathem and Nenes 2011). As described in Section 2.6, the first three factors were maintained constant during all CCN activity tests. I measured the size distribution of droplets that activated from CCN of 130.5 \(\pm\) 3.2 nm initial mobility diameter, a value that is well above the largest \(D_{50}^{0.3\%}\) measured in this study (= 108.5 nm). Thus, all particles of this size
were expected to activate and any differences in size distribution between two tests reflects the effect of water uptake rate, which in turn depends on chemical composition of the particles. Depletion of condensable water vapor does not affect $D_{\text{drop}}$ by more than 10% if the CCN concentration is less than 5000 cm$^{-3}$ (Lathem and Nenes 2011). In different tests, the absolute number concentration of the 130 nm size-selected particles entering the cloud chamber varied between 1000 and 2000 cm$^{-3}$. To aid comparison of frequency distribution of droplet diameters measured in different tests, the frequencies in each test were normalized to the total number of droplets across all bins.

2.7.4 Effects of surfactants on $\kappa$

The $\kappa$-Köhler theory approximates the effective surface tension of a solution droplet ($\sigma'$) as $\sigma_w$. While this assumption may hold for calculating $\kappa_{GF}$, it may result in an overestimation of $\kappa_{CCN}$ for an aerosol particle population such as BB aerosol, if $\sigma'$ is affecting its CCN activity (Dusek et al. 2011). This effect was accounted for in this study by setting $\kappa_{CCN}$ in Eq. [2.8] equal to the measured value of $\kappa_{GF}$. Iterative solution of Eq. [2.5] and [2.8] using the measured value of $D_{50}^{0.3\%}$ then returned a fitted value for $\sigma'$. 
3. RESULTS AND DISCUSSION

This chapter begins with the results of instrumentation performance (Section 3.1). This is followed by the results of hygroscopic growth and size-resolved CCN activity measurements of fresh and aged OC as well as a discussion of these results (Section 0). Section 3.3 presents the results of size distributions of activated droplets measured downstream of the cloud chamber and a discussion of these results. Finally, in Section 3.4, the effect of surfactant presence on the inferred values of $\kappa_{CCN}$ is briefly discussed by accounting for an effective surface tension of solution droplets (Section 2.7.4).

3.1 Instrumentation performance

3.1.1 SMPS

Accuracy of the SMPS was verified by always measuring mobility diameters within 2% of the certified diameters of PSL spheres, as shown in Fig. 3.1.

![Fig. 3.1: SMPS performance test results for certified (a) 100 nm and (b) 207 nm polystyrene latex aerosols](image-url)
3.1.2 RH sensing

Fig. 3.2 shows the measured agreement of the four capacitance-based RH sensors (SHT; described in Section 2.5) with a calibrated reference RH sensor (Vaisala; calibration procedure described in Section 2.4.1). The four sensors always measured RH within 1% value of the calibrated sensor in the RH range of interest in this study (55 to 95%).

![Diagram](image)

Fig. 3.2: Performance of four capacitance-based RH sensors (a) with respect to calibrated reference and (b) modulus of residuals
3.1.3 H-TDMA and CCN counter

Measured hygroscopic growth, CCN activity and activated droplet size distribution of AS are shown in Fig. 3.3. Calculated values of $\kappa_{GF}$ and $\kappa_{CCN}$ (as outlined in Section 2.7.2) are $\kappa_{GF} = 0.59$ and $\kappa_{CCN} = 0.61$. These values agree within 3% of each other and are also consistent with previously reported values for AS (Petters and Kreidenweis 2007). Moreover, diameters of droplets activated from initially dry AS particles at 0.3% SS are in the 3 to 4 $\mu$m range, which is consistent with previously reported measurements (Engelhart et al. 2008; Asa-Awuku et al. 2010).

![Hygroscopic growth of AS particles](image-a)

![Size-resolved CCN activity at 0.3% SS](image-b)

![Size distribution of activated droplets](image-c)

Fig. 3.3: Measurements of (a) hygroscopic growth, (b) size-resolved CCN activity and (c) activated droplet size distribution of ammonium sulfate (AS) particles
3.2 Hygroscopic growth and CCN activity of fresh and aged OC particles

Hygroscopic growth factors of fresh and chemically-aged OC particles are shown in Fig. 3.4. The dependence of $GF_{RH}$ on RH, as predicted by $\kappa$-Köhler theory, is consistent with measured values.

Size-resolved CCN activation curves of fresh and chemically-aged OC particles are shown in Fig. 3.5. The measured $\kappa_{GF} = 0.06$ and $\kappa_{CCN} = 0.12$ of fresh OC are within the range of $\kappa = 0.02$ to 0.15 measured by Dusek et al. (2011) and 0.05 to 0.20 measured by Petters et al. (2009) for particles emitted from burning of similar wood fuels. Moreover, as shown by comparing tests Fresh-RH0, Fresh-RH70 and Fresh-RH85 in Fig. 3.5, the $D_{50}^{0.3\%}$ (and thus $\kappa_{CCN}$) values for fresh OC aerosol particles are not affected by chemical participation of aerosol water during aging at either 70 or 85% RH.
In the different size-resolved CCN activation curves shown in Fig. 3.5, it is seen that while the fresh OC curves have a somewhat sigmoidal structure, the aged OC activation curves exhibit an increased fraction of activated sub- and super-$D_{50}^{0.3\%}$ mobility diameter particles (or, “activation modes”). These activation modes were also observed in the duplication tests shown in Fig. 3.6. The measured $D_{50}^{0.3\%}$ in each test was always within 8% of its corresponding duplication.
An activation mode in the 70 to 100 nm diameter range would be observed if surfactant solutions are present in the droplets. Even though the fraction of surfactant may be equal in the
70 and 100 nm particles, droplets formed by condensation of water on the 70 nm particle will be more concentrated with surfactant than the droplet formed on the 100 nm particle. This is a likely explanation for the enhanced activation of the sub-$D_{50}^{0.3\%}$ particles after aging with NH$_3$ and O$_3$. This reasoning is also consistent with the findings of Dusek et al. (2011). Some of the activation curves in Fig. 3.5 also exhibit another activation mode for particles larger than the $D_{50}^{0.3\%}$ (for instance, a second activation mode is observed for the 110 to 170 nm mobility diameter particles aged with 0.1 ppm$_v$ O$_3$ in dry conditions; test O3-0.1-RH0). It is difficult to explain the occurrence of these secondary activation modes observed after aging. As mentioned earlier, similar activation modes have been observed previously for BB particles in this diameter range by Petters et al. (2009). Based on their results, one possible explanation is that chemical aging induces heterogeneity in the aerosol. Chemical transformation mechanisms could be different for particles in different size bins, due to which particles in the 110 to 170 nm range of mobility diameters are more CCN active after aging. This explanation could be further supported if the $\kappa_{CCN}$ is measured only for particles of mobility diameter in this range and then compared to the overall $\kappa_{CCN}$ measured for the entire 50 to 170 nm range.

Hygroscopic growth factors of OC aerosol particles aged with 10 ppm$_v$ NH$_3$ are unaffected when compared to those of fresh OC, as shown in Fig. 3.4. Values of $\kappa_{GF}$ are unaffected after aging with 10 and 875 ppm$_v$ NH$_3$ (tests NH3-10-RH0 and NH3-875-RH0 in Fig. 3.4). However, CCN activity is affected by NH$_3$. Compared to fresh, dry OC, values of $D_{50}^{0.3\%}$ are smaller by 18% and 22% after aging with 10 and 875 ppm$_v$ NH$_3$, respectively. The corresponding increase in $\kappa_{CCN}$ is 84% and 109%, respectively. For all values of RH controlled inside the mixing chamber, there is a consistent reduction in $D_{50}^{0.3\%}$ and increase in $\kappa_{CCN}$. I find that while NH$_3$ does not affect hygroscopic growth of OC particles, it increases their CCN activity. Water taken up in the mixing chamber does not participate further in this effect. The increase in $\kappa_{CCN}$ after NH$_3$ aging with unaffected $\kappa_{GF}$ suggests the presence of insoluble or sparingly soluble organic acidic groups in the OC particles. The highest RH at which $GF_{RH}$ is measured in this study is 92%. It is likely that these substances of limited water solubility do not dissolve into the taken up water even at 92% RH, thereby not contributing to $GF_{RH}$ of the particles. However, as RH approaches and surpasses 100% in the cloud chamber, these substances experience dissolution and thus increase the $\kappa_{CCN}$ (Dusek et al. 2003).
Hygroscopic growth of OC particles is unaffected by aging with 0.1 ppm O₃, as shown in Fig. 3.4 (test O3-0.1-RH0). The $D_{50}^{0.3\%}$ (and subsequently, $\kappa_{CCN}$) of dry OC is also unaffected by O₃ (tests O3-0.1-RH0 and O3-0.3-RH0 in Fig. 3.5d). For tests conducted at 70 and 85% RH in the mixing chamber during aging, water taken up also does not participate further in chemical aging (Fig. 3.5e and Fig. 3.5f). The two O₃ aging conditions used in this study can be converted to $1.7 \times 10^{16}$ and $5.1 \times 10^{16}$ molecule cm$^{-3}$ s using the Ideal gas law with $P = 1$ atm and $T = 273$ K. My results are consistent with the findings of Slade et al. (2015), who observed that 0 to $2 \times 10^{16}$ molecule cm$^{-3}$ of O₃ exposure did not affect the hygroscopicity of single, binary and ternary mixtures of BB surrogate aerosols.

A summary of all results presented and discussed so far in this section is graphed in Fig. 3.7.

![Graph showing inferred values describing hygroscopic growth and CCN activity](image)

**Fig. 3.7:** Summary of inferred values describing hygroscopic growth and CCN activity

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3.3 Droplet size distribution of fresh and aged OC particles

Fig. 3.8 shows the frequency distribution of diameters of droplets exiting the cloud chamber after activation of 130 nm particles at 0.3% SS. Owing to the normalization of data as described in Section 2.7.3, the area under each curve is unity.

I find an evidence of possibly retarded droplet growth of the O₃-aged particles as compared to the fresh OC particles (tests O3-0.1-RH0 and O3-0.3-RH0). A possible mechanism causing this retardation is the presence of condensed films on the O₃-aged particles is impeding droplet growth after activation of CCN inside the cloud chamber. Oxidation by O₃ could have devolatilized some of the gas-phase organics emitted during the biomass pyrolysis, causing them to condense as films on pre-exiting particles (Lambe et al. 2015). It is not clear why the droplet growth appears unaffected for particles aged with 0.1 ppmv O₃ in presence of humidity during
aging (test O3-0.1-RH85; results at 70% RH not shown). However, with a higher concentration of O₃ (0.3 ppm, O3-0.3-RH85), I find that retardation of droplet growth is consistent in presence of humidity during aging.

3.4 Effective surface tension of solution droplets

Fig. 3.7 showed that while the measured $\kappa_{GF}$ and $\kappa_{CCN}$ of the fresh and aged OC aerosol particles are within the previously reported ranges of $\kappa$ for biomass burning particles, discrepancies as large as factors of three occur between $\kappa_{CCN}$ and $\kappa_{GF}$ for each test. By setting $\kappa_{CCN}$ equal to $\kappa_{GF}$ in Eq. [2.8], the effective surface tension $\sigma'$ was calculated (see Section 2.7.4). The average $\sigma'$ calculated for all hygroscopic growth tests was $0.053 \pm 0.006$ Nm⁻¹. This is 25% lower than the surface tension of pure water I find that the approximation of surface tension of a solution droplet to that of pure water underestimates the CCN activity of organic aerosol emitted from biomass pyrolysis.
4. SUMMARY, CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

The hygroscopic growth and CCN activity of complex biomass pyrolysis OC aerosol was experimentally measured with and without controlled conditions of humidity and chemical aging by atmospherically relevant tracer species, NH$_3$ and O$_3$. The role of these aging conditions in the enhancement of hygroscopicity of organic aerosols was investigated. From measurements of hygroscopic growth at subsaturated RH and CCN activity at supersaturated RH, I measured the hygroscopicity parameters, $\kappa_{GF}$ and $\kappa_{CCN}$, respectively. I compared the $\kappa_{GF}$ and $\kappa_{CCN}$ of each aerosol population and analyzed the discrepancies to infer the presence of surfactants in these aerosol particles. My results suggest that approximating the surface tension of droplets to that of pure water, which is the basis of $\kappa$-Köhler theory, underestimates the CCN activity of biomass pyrolysis particles. An evidence of surfactant presence in OC particles is the enhanced CCN activation of particles in the 70 to 100 nm mobility diameter range.

Increase in $\kappa_{CCN}$ of NH$_3$-aged OC particles, while $\kappa_{GF}$ remains unaffected, suggests the presence of insoluble or sparingly soluble organic acidic groups in enough proportions to influence the overall hygroscopicity of the particles. My results suggest that in atmospheric conditions of humidity and gas-phase NH$_3$ levels, neutralization of acidic groups in organic particles by gas-phase NH$_3$ is a prominent pathway to an increased CCN activity of these particles. Whether or not this increase in hygroscopicity has significant atmospheric implications depends on several other factors such as mixing of aerosol particles with other hygroscopic or hydrophobic particles, updraft velocity of the parcel carrying these particles, availability of condensable water vapor and number of CCN competing for the water (Petters et al. 2006; Roberts et al. 2003). Reutter et al. (2009) modeled deep clouds formed above BB fires (pyro-convective clouds) using a cloud parcel model, and showed that the cloud droplet number concentration, $N_{CD}$, is sensitive to changes in $\kappa$ of aerosol particles, when $\kappa$ is lower than 0.2. For instance, an 81% increase in $\kappa$ (as measured in this study) of particles having initial $\kappa = 0.057$ can cause a 20% increase in $N_{CD}$.

I confirm the findings of Slade et al. (2015) that O$_3$-aging has no effect on the measured hygroscopicity of OC aerosol. However, my findings suggest the formation of organic films on particles after O$_3$ oxidation and condensation of organic gases in the aerosol. An evidence of this finding is the retarded growth of droplets after they activate in the cloud chamber. Even though
cloud chamber studies do not simulate limitations on the amount of condensable water available for droplets to grow, these limitations exist in the atmosphere (Roberts et al. 2003). As shown by Feingold and Chuang (2002) and Ruehl et al. (2007), in such conditions of competition, CCN coated with such growth-retarding organic films could grow slower compared to other uncoated CCN, leading to broadened size distributions and possibly prolonged lifetimes of droplets in the atmosphere.


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