

ABSTRACT

Title of Dissertation: AEROSOL-CLOUD-CLIMATE
INTERACTIONS DUE TO CARBONACEOUS
AEROSOLS

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Aerosols can affect the net radiation budget and global climate of the Earth either “directly” – through their radiative properties, or “indirectly” – through their cloud-forming abilities by acting as Cloud Condensation Nuclei (CCN). The interactions between aerosols and clouds are the most significant sources of uncertainty in the overall radiative forcing from due to a lack of understanding related to the droplet formation mechanism of aerosols. These uncertainties are majorly associated with the carbonaceous aerosols present in the atmosphere, notably due to their compositional diversity, vastly variable physicochemical properties, and unique water uptake characteristics. In this dissertation, new lab-based measurement techniques and computational methods have been developed to resolve the CCN activity and water uptake behavior of pure and mixed carbonaceous aerosol particles.

The first part of this dissertation accomplishes two goals: 1. The development and application of a new CCN measurement method, and 2. The formulation of a new computational framework for CCN activity analysis of aerosols. The results in this dissertation demonstrate the significance

of size-resolved morphology and dissolution properties of aerosol particles in improving their CCN activity analysis under varying ambient conditions. Furthermore, these results suggest that in the future, more comprehensive CCN analysis frameworks can be developed by explicitly treating other physical and chemical properties of the aerosols to further improve their CCN activity analysis.

The second part of this dissertation focuses on large-scale analysis. The CCN analysis framework is implemented into a climate model to quantify the water uptake behavior of carbonaceous aerosols, and then study the subsequent variabilities associated with the physical and radiative properties of ambient aerosols and clouds. Statistical techniques are also developed in this work for chemical characterization of ambient aerosols. The characterization results show large regional compositional variations in ambient aerosol populations. These results also suggest that the knowledge of chemical species is necessary to quantify the water uptake properties of the aerosol population.

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by

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Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
2022

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Dedication

To my grandparents, in loving memory

Acknowledgements

I want to say thank you to my mom for her unconditional love and for always keeping me grounded, and my dad for teaching me the value of resilience and hard work. To my sister, for always being there for me despite being several time zones apart. To my girlfriend, for being immensely patient and strong with me even while I had my blinders on, swamped with my work. To my friends, who kept me sane during these past 4 years. To my collaborators, who gave me the opportunity and platform to take on exciting projects.

I want to give a very special thanks my research advisor, Dr. Akua Asa-Awuku for her constant encouragement throughout the past 4 years of my graduate tenure. It is because of her support, I have had numerous opportunities to travel, present, network and grow overall as a researcher. Thank you for being an amazing mentor and making this work possible, and most of all, thank you for having trust in my abilities.

Last but not the least, I want to thank my coffee machine for not once letting me down and always being ready with a hot cup of java whenever I needed one!

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List of Symbols and Abbreviations

AAC	Aerodynamic Aerosol Classifier
ACCI	Aerosol-Cloud-Climate Interactions
AIE	Aerosol Indirect Effect
ALS	asymmetric least squares
AOD	Aerosol Optical Depth
ARS	Automated Raman Spectrometer
a_w	water activity
B	mechanical mobility
BC	black carbon
C	aqueous solubility
CAM	Community Atmosphere Model
C_c	Cunningham's slip correction factor
CN	condensation nuclei
CCN	cloud condensation nuclei
CCNC	CCN counter
CDNUMC	cloud droplet number concentration
CESM	Community Earth System Model
CFSTGC	Continuous Flow Streamwise Thermal Gradient CCN chamber
CPC	Condensation Particle Counter
CWT	continuous wavelet transform
D_{ae}	aerodynamic diameter
Db	Daubechies' type wavelet

D_{dry}	dry particle diameter
DMA	Differential Mobility Analyzer
D_{mo}	electrical mobility diameter
D_{p50}	critical dry diameter/activation diameter
D_{ve}	volume equivalent diameter
D_w	diameter of the water molecule
D_{wet}	droplet diameter
EDX	Energy Dispersive X-ray
EELS	Electron energy loss spectroscopy
ϵ	volume fraction
F	drag force
FHH	Frenkel-Halsey-Hill isotherm
FHH-AT	FHH Adsorption Theory
γ	water activity coefficient
GCM	Global Climate Model
G_f	hygroscopic growth factor
H-TDMA	Hygroscopicity Tandem Differential Mobility Analyzer
HAM	Hybrid Activity Model
IPTA	isophthalic acid
κ	single hygroscopicity parameter
KT	Köhler Theory
λ	AAC transmission efficiency
LWP	lifting wavelet transform

M	molecular weight
MAM	Modal Aerosol Model
μ	AAC transfer function width factor
ν	Van't Hoff factor
O:C	oxygen-to-carbon ratio
OPC	Optical Particle Counter
POA	primary organic aerosols
POM	primary organic matter
PTA	phthalic acid
PyCAT	Python-based CCN Analysis Toolkit
Q	instrument flowrate
R_a	size-resolved activation ratio
REBS	Resource Effective Bioidentification System
RH	relative humidity
ρ	mass density
S_c	critical/activation supersaturation
SMCA	Scanning Mobility CCN Analysis
SMPS	Scanning Mobility Particle Sizer
SNR	signal-to-noise ratio
SOA	secondary organic aerosols
τ	AAC particle relaxation time
θ	surface coverage term in the FHH isotherm
TPTA	terephthalic acid

TEM	Transmission Electron Microscopy
v	flow velocity
V	volume
VSA	Vapor Sorption Analysis
X_w	mole fraction of water
χ	dynamic shape factor
ω	AAC rotational speed
Ω	AAC transfer function
ZSR	Zdanovskii-Stokes-Robinson approximation

Chapter 1: Introduction

1.1 Background

The air around us contains solid or liquid particles that are known as aerosols. Most atmospheric aerosols are microscopic in size; ranging from several nanometers to a few microns (Speight, 2017). However, aerosols are still capable of significantly affecting human health, environment and even the climate (Seinfeld and Pandis, 1998). One significant way in which certain atmospheric aerosols affect the climate is by facilitating condensation of water vapor atop their surface to form droplets, and clouds (Köhler, 1936). Aerosols that form cloud droplets are referred to as Cloud Condensation Nuclei (CCN). And the tendency of the particles to take up water in supersaturated ambient conditions resulting in spontaneous droplet formation CCN activation is defined as their CCN activity. Clouds that are subsequently formed interact with solar and terrestrial radiations to alter the Earth's radiative budget thereby leading to either warming or cooling of the climate (Wallace and Hobbs, 2006; Rap et al., 2013). Although it is reported that clouds have an overall cooling effect on the atmosphere, the magnitude of the overall cloud radiative forcing has large uncertainty associated with it. Climate models have shown that uncertainties in the estimates of CCN activity subsequently translate to their cloud response (e.g., but not limited to Ghan et al., 1997, 2011; Nenes et al., 2001). Therefore, accurate estimation of CCN activity of aerosols is important for correctly predicting cloud growth and their impact on the climate.

Aerosols can affect clouds in either of the 2 ways (Figure 1) – by a change in the cloud lifetime and cloud radiative forcing (first indirect effect of aerosols) (Twomey, 1977), or by a change in the precipitation efficiency and cloud liquid water content (second indirect effect of aerosols) (Albrecht, 1989). Both effects are described as the “Aerosol Indirect Effect” (AIE). Aerosols and CCN in the atmosphere are multicomponent mixtures of organic and inorganic substances and have vastly variable chemical compositions, and therefore variable physicochemical properties (e.g., but not limited to Asa-Awuku et al., 2010; Bhattu & Tripathi, 2015; W. Liu et al., 2005). Furthermore, quantification of the effect of aerosols on the climate due to variations in their number concentration, chemical constituency, size, solubility, shape, and mass is a challenging task (Kulmala et al., 1998; Kanakidou et al., 2005). These properties play a significant role in determining their “CCN activity”. Previous studies have shown that the prediction of CCN activity of an aerosol species is highly sensitive to errors in their physical and chemical measurements (Zhang et al., 2017).

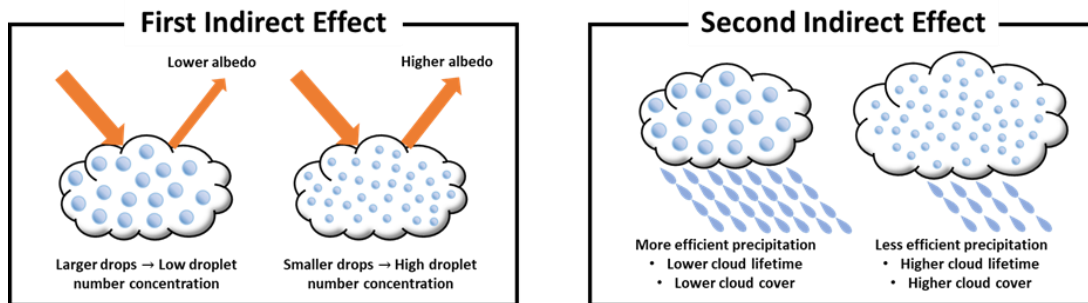


Figure 1. Schematics showing the aerosol indirect effect. The changes in the cloud radiative properties (first indirect effect) and precipitation (second indirect effect) are shown.

Recent and continuing studies show improvements in our understanding of CCN activity and the factors that affect droplet growth (e.g., but not limited to McFiggans et al., 2006; Petters & Kreidenweis, 2007; Thalman et al., 2017). One such example is the

application of computational and data-driven approaches for performing chemical analysis of ambient aerosols to identify their chemical compositions (Kyriakides et al., 2011). In addition to this, there are advancements in the representation of CCN activity in models under prescribed atmospheric conditions (Nenes et al., 2001; Morales and Nenes, 2010; Shipway, 2015). Governing dynamical and physical equations for evolving atmospheric conditions, coupled with CCN activation schemes can estimate droplet growth and cloud responses across a wide range of aerosol populations using Global Climate Models (Liu et al., 2012, 2016). However, despite such progress, models are still prone to systematic misrepresentations of CCN activity and its effects.

The uncertainties in radiative forcing and cloud responses are observed to be more pronounced in model responses for species with low hygroscopic yet wettable characteristics, such as carbonaceous (organic) aerosols (Xu et al., 2014; Vu et al., 2019). Carbonaceous aerosols have been well studied for their strong climate forcing resulting from their radiative effects (Talley et al., 2013). They innately possess low hygroscopicity, but act as CCN due to their interactions with more hygroscopic and soluble organic and inorganic species (Taylor et al., 2017; Dalirian et al., 2018). These interactions result in aging of carbonaceous aerosols which manifest as changes in their mixing state and are highly unpredictable. Furthermore, carbonaceous aerosols have high compositional variability and a high atmospheric burden (e.g., but not limited to Barati et al., 2019; Bhattu & Tripathi, 2015; Xu et al., 2014). The combined atmospheric mass burden of primary and secondary organic aerosols can vary anywhere between 20% and 90% of the total atmospheric aerosol mass, depending on the ambient conditions (Zhang et al., 2007). Also, organic, and carbonaceous aerosol

particles are generally either non-spherical or fractal-like (Wu and Colbeck, 1996; Schnitzler et al., 2014). Studies related to climate modeling also show that the uncertainties in CCN activity of carbonaceous aerosols directly relate their cloud response (Pringle et al., 2009; Spracklen et al., 2011; Karydis et al., 2012). As a result, this dissertation aims to improve current analytical measurement and analysis to better understand and estimate the CCN activity and cloud response from carbonaceous aerosols.

As stated previously, there are large uncertainties associated with the cloud radiative forcing. The Intergovernmental Panel for Climate Change has shown that the aerosol-cloud-climate interactions (ACCI) related to organic and carbonaceous aerosols are one of the largest source of uncertainty in the Earth's radiative forcing (Figure 2). Reducing these uncertainties requires improving our current understanding of the CCN activity and cloud forming abilities of aerosols. Even though field observations, controlled laboratory measurements and large-scale climate modeling extensively study carbonaceous ACCI, there have been few attempts to implement findings from controlled measurements for improving large-scale climate predictions. The following sections provide a brief overview of measurement and computational procedures adopted for controlled CCN experiments of carbonaceous aerosols relevant to this research. Furthermore, the details regarding parameterization of water uptake for carbonaceous aerosols and its implementation within a large-scale climate model are also provided. Next, a newly developed computational methodology is introduced for chemical characterization of atmospheric aerosols using their real-time Raman

spectral measurements. Lastly, this chapter concludes by providing an outline of the subsequent chapters of the dissertation.

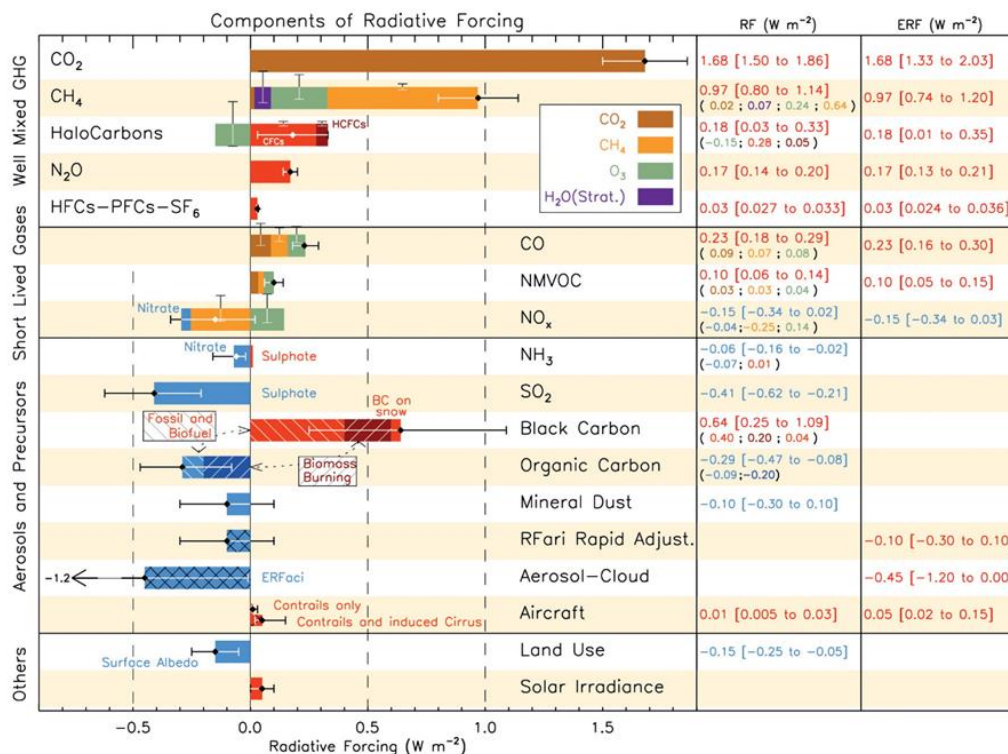


Figure 2. Contributions of forcing agents during the industrial era between 2011 and 1750 as presented in the IPCC 2022 Technical Summary. Colored bars represent the estimates for positive (heating; red) and negative (cooling; blue) radiative forcing in terms corresponding to the forcing precursors highlighted along the y-axis. Error bars represent the forcing uncertainty associated with each forcing term. Aerosol-cloud interactions contribute the greatest forcing uncertainty and climate sensitivity uncertainties; the mean uncertainty ranging between -1.2 to 0 W/m² with a mean around -0.45 W/m².

1.2 Controlled Experiments for CCN Activity Analysis and Global Climate Modeling

CCN activity of aerosols is linked with their cloud forming ability and therefore to their indirect effect on the climate. The CCN activity of aerosols is innately dependent on several physicochemical properties – particle size, chemical composition, mixing state, surface activity, aqueous solubility – to name a few (Petters and Kreidenweis,

2013; Padró et al., 2012; Lee et al., 2011; Petters and Kreidenweis, 2008; Kulmala et al., 1998). All aerosol properties can be measured experimentally or determined empirically to describe the CCN activity of any aerosol species. CCN activity is strongly dependent on dry particle size (Dusek et al., 2006). Most of the widely implemented CCN measurement procedures are based on the use of particle sizers, otherwise known as classifier instruments. Traditionally, a Differential Mobility Analyzer (DMA) is the most used aerosol classifier for CCN experiments.

In this dissertation, the CCN activity and droplet growth experiments in supersaturated conditions were measured using the Droplet Measurement Technologies Continuous Flow Stream-wise Thermal Gradient CCN Counter (CCNC) based on the design of (Roberts and Nenes, 2005). The CCNC is coupled with an aerosol classifier to size-select aerosol particles in the scanning mode to obtain the number size distributions of the aerosol population (Rose et al., 2008; Moore et al., 2010). The size-selected aerosol particles passing through the CCNC are then subjected to supersaturated relative humidity in the range of 0.2% - 1.8% to generate number concentrations resolved with respect to time at a resolution of 1 second. The CCNC consists of a cylindrical flow chamber and the aerosol sample streams passes through it. The flow chamber creates a supersaturated environment for aerosols by creating a temperature gradient across its ceramic-lined inner walls. Particle-free sheath air keeps the aerosol particles along the centerline of the column where the CCNC column retains supersaturated conditions, and the particles can take up water and form droplets.

Particles of a given size activate and form droplets when the instrument supersaturation in the CCNC exceeds their critical supersaturation. For the experiments

performed in the scanning mode, the instrument supersaturation is held constant while the DMA (or any other classifier instrument) generates a number distribution across the size spectrum. The number size distributions obtained from the CPC and CCNC for the aerosol species are then combined to get the size for which the particles will activate at the instrument supersaturation. The particle size thus obtained is called the critical dry diameter of the particles. The schematic of a typical DMA-CCN setup is shown in Figure 3.

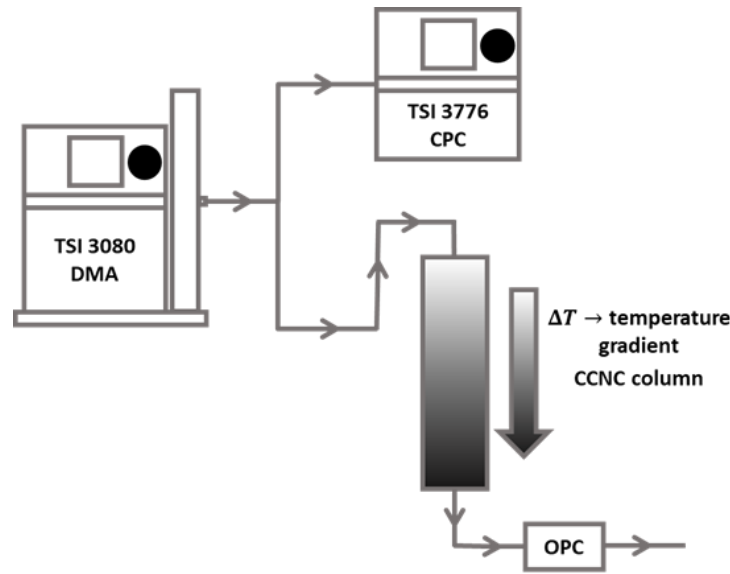


Figure 3. DMA-CCN experimentation setup for measuring the size-resolved number concentration of aerosols.

From the aforementioned experimental procedure (based on a DMA), the critical dry diameter is an electrical mobility diameter of the particles since the DMA classifies aerosols based on their electrical mobility. The DMA charges the particles moving through it electrostatically and balances drag force with the electrostatic force to characterize the electrical mobility diameter of the particles. The DMA is coupled with a Condensation Particle Counter (CPC) and a CCNC to measure aerosol number concentrations, and hence, estimate their CCN activity with respect to electrical

mobility diameters. The DMA is ideally supposed to apply a unit charge on the particles before classifying them. However, it is generally observed that the particles may carry more than one unit charge on them depending on the charging efficiency of the neutralizer. As a result, larger particles carrying a higher charge may have the same electrical mobility diameter as the smaller particles carrying one unit charge. This phenomenon associated with the DMA instrument is commonly known as multiple charging and can potentially lead to inaccuracies in the particle sizing and consequently in the CCN activity measurements (Fuchs and Daisley, 1965). In this dissertation, a new experimental setup without particle charging artifacts was proposed and tested with an Aerodynamic Aerosol Classifier (Cambustion™ AAC) for particle sizing (Gohil and Asa-Awuku, 2022). The AAC classifies particles by their relaxation time, which depend on the mass and the mechanical mobility of the particles (Tavakoli and Olfert, 2013). The particles passing through the AAC are then classified based on their aerodynamic diameters. A schematic of the AAC column is provided in Figure 4.

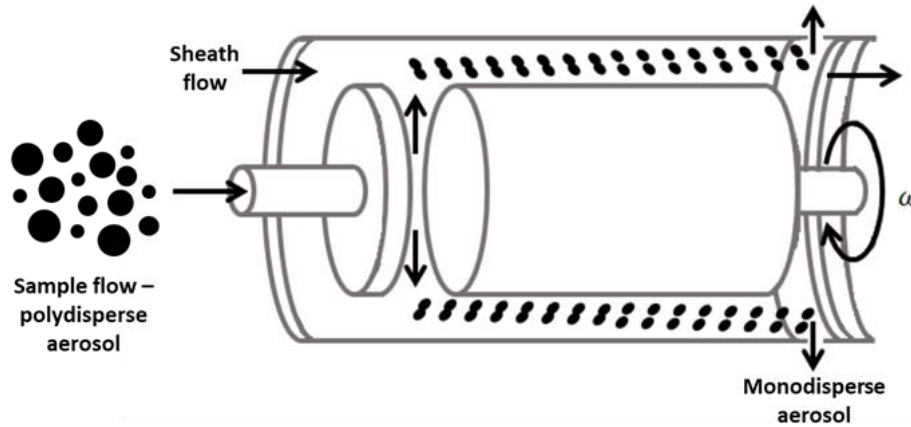


Figure 4. Schematic of the Aerodynamic Aerosol Classifier (AAC) instrument representing how the polydisperse aerosols classified to generate monodisperse population.

Unlike in the DMA, the drag force on the particles passing through the AAC is balanced by the centrifugal force due to the rotating AAC column. Since the AAC does not require particle charging for classifying aerosols, it eliminates any possible uncertainties in measurements due to multiple charging. The AAC can also be coupled with the DMA and be used for size-resolved shape factor and particle effective density measurements of the aerosols. These measurements can be highly useful for morphological corrections of aerosol particles, thereby helping with further reducing uncertainties in the CCN activity analysis (Tavakoli et al., 2014; Tavakoli and Olfert, 2014). Moreover, the AAC sizing resolution increases with the increasing aerodynamic diameter of the particles. A schematic of the AAC-CCN setup is shown in Figure 5. The details of the AAC-based experimental setups, uncertainty analysis, and the implementation for CCN and shape factor measurements are provided in chapter 2.

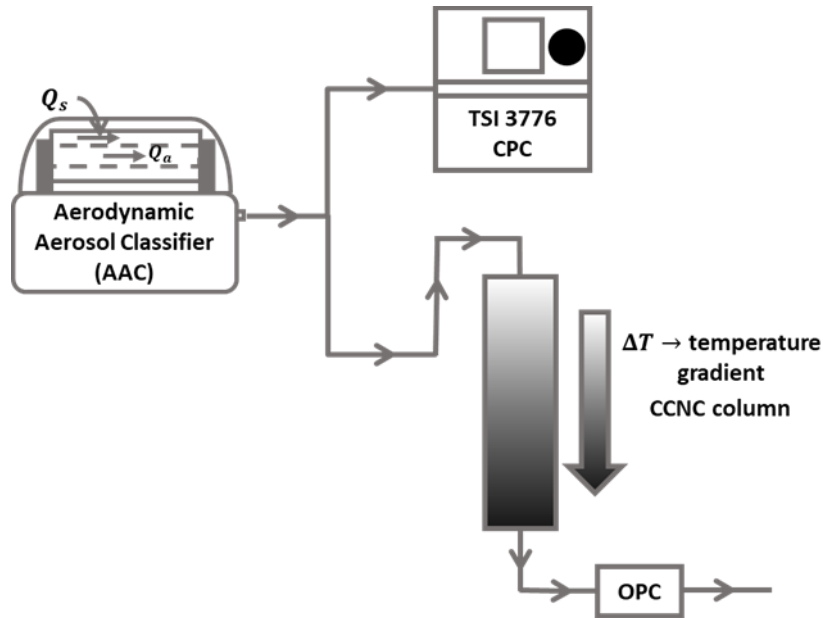


Figure 5. AAC-CCN experimentation setup for measuring the size-resolved number concentration of aerosols.

The CCN activity of any aerosol species can be expressed using a single hygroscopicity parameter (κ). (Petters and Kreidenweis, 2007) provided a simple, yet highly useful method based on the traditional Köhler theory to compute κ of any aerosol by combining their dry particle size (D_{dry}) with the supersaturated water vapor (S) amount at which the particles of the given size activate and form droplets. κ is not a physical quantity but rather an indicator of the affinity of a given type of particle towards water. And theoretically, κ based on the traditional Köhler theory expresses the chemical composition of the aerosols and is a function of the molar volume. κ is usually in the range of ~ 0 (highly water insoluble species like mineral dust and black carbon) to 1.4 (highly soluble compounds like sodium chloride). Furthermore, κ is widely used in climate models to represent the CCN activity of different atmospherically relevant aerosol species.

In the Köhler theory framework, all aerosols are assumed to be instantaneously and infinitely soluble in water. The complete water solubility assumption for any solute in Köhler theory is approximated using Raoult's law. This assumption reasonably applies for many inorganic and organic aerosols with high water solubility and has been validated experimentally (e.g., but not limited to Asa-Awuku et al., 2008; Chan et al., 2005; Gohil et al., 2022; Padró et al., 2010; Peng et al., 2021; Petters & Kreidenweis, 2007; Razafindrambinina et al., 2022; Xu et al., 2014). It is important to note that κ is strongly governed by the aqueous solubility of the aerosol particles (Petters and Kreidenweis, 2008; Sullivan et al., 2009) but does not require the aerosol particles to be soluble in water.

The distinction between aqueous solubility and κ is especially relevant in the case of carbonaceous and organic species. Several of these species are classified as sparingly water soluble (e.g., but not limited to succinic acid, various primary organic aerosols) for which solubility is explicitly treated for hygroscopicity parameterization using Köhler theory. Moreover, there are other species that are effectively water-insoluble (e.g., black carbon) but possess wettable characteristics and are CCN active (Dalirian et al., 2018; Dusek, Reischl, et al., 2006; Laaksonen et al., 2020). For such cases, more complex models (such as the Frenkel-Halsey-Hill Adsorption Theory; FHH-AT) have been used for CCN activity analysis (Sorjamaa and Laaksonen, 2007). Models like FHH-AT assume aerosol particles to be completely water insoluble and describe droplet growth via water monolayer adsorption on to particle surface.

In this dissertation, a new computational framework was developed that combines the effects of adsorption-driven water uptake with solubility partitioning of the solute (Gohil et al., 2022; Riipinen et al., 2015; Sorjamaa & Laaksonen, 2007). The FHH isotherm was used to describe water adsorption. A dynamic variability in the particle size was incorporated into the FHH isotherm through fractional dissolution of solute as the droplet continued to grow. Additionally, the effect of dissolved fraction of solute on the droplet growth was accounted for through the Raoult's law. The details of the formulation and application of this hybrid CCN activity framework are provided in chapter 3 and 4. Furthermore, a single hygroscopicity parameter has also been derived using the hybrid CCN activity model; details of the hygroscopicity parameterization are provided in chapter 3.

As it has been established so far, hygroscopicity of any given aerosol can be determined theoretically or using experimental measurements. Hygroscopicity of an aerosol is important for quantifying its affinity towards water; the single hygroscopicity parameter of different aerosol types are also used to represent their water uptake behavior within climate models (Liu et al., 2012, 2016a). Hygroscopicity parameters within climate models are generally prescribed for different aerosol species based on the literature (Liu and Wang, 2010). The hygroscopicity parameters of different aerosol types affect the CCN activity and droplet nucleation in the models. CCN activation can then affect the atmospheric burden of different chemical species and the cloud droplets which strongly control the physical and radiative properties of the clouds. Studies have shown that the primary and secondary aerosol burdens, cloud droplet number concentration in the atmosphere have a strong sensitivity towards hygroscopicity (Morales and Nenes 2014). Therefore, it is important to either prescribe or physically parameterize aerosol hygroscopicity with high certainty to improve cloud representation in climate models.

In this dissertation, a mathematical formulation of the single hygroscopicity parameter was derived from the hybrid CCN activity model and implemented within the Community Atmosphere Model 6.0 (NCAR-CAM6). Specifically, the single hygroscopicity parameter for organic and carbonaceous aerosols were computed based on the hybrid CCN model. As the default configuration, CAM6 takes the hygroscopicity parameters for different aerosol types through the Modal Aerosol Model (MAM4). In this work, the hygroscopicity parameter was explicitly calculated for organic species based on the mixing state and constituency of the modal aerosol

population. In particular, the hygroscopicity parameter used applies the HAM model developed in chapter 3 and thus provides a new approach to understand aerosol-cloud-climate interactions on a global scale.

1.3 Real-time Chemical Characterization of Atmospheric Aerosols

Recent and continuing studies show improvements in our understanding of CCN activity and the factors that affect droplet growth (McFiggans et al., 2006; Asa-Awuku and Nenes, 2007; Asa-Awuku et al., 2009a; Thalman et al., 2017). One such example is the application of computational and data-driven approaches for performing chemical analysis of ambient aerosols to identify their chemical compositions (e.g., but not limited to Carey et al., 2015; J. Liu et al., 2017). It has been shown that aerosol identification-related problems can be solved by utilizing measured chemical signatures (mass spectrometry, FTIR, X-ray diffraction, Raman spectrometry) (e.g., but not limited to Doughty & Hill, 2017; Stefaniak et al., 2009; Toprak & Schnaiter, 2013) of aerosol particles with the application of methods related to statistics, big data analysis, signal processing and machine learning (e.g., but not limited to Carey et al., 2015; Christopoulos et al., 2018; Kwiatkowski et al., 2010). This research combined the ideas related to these concepts to develop a tool for performing chemical analysis of ambient aerosols.

Chemical analysis of aerosol particles is required to determine their composition and mixing state. Over the past decades, researchers have demonstrated several inference-based (e.g., but not limited to Cubison et al., 2008; Gunthe et al., 2009) and measurement-based (e.g., but not limited to but not limited to Asa-Awuku et al., 2011; Ervens et al., 2007) approaches for discerning bulk aerosol chemical composition.

However, over the past few years, it has been argued that the use of size-resolved aerosol compositions for studying CCN activation results in more accurate estimates (e.g., but not limited to Cubison et al., 2008; Gunthe et al., 2009; Medina et al., 2007). Single-particle aerosol measurement techniques provide a means to obtain size-resolved aerosol composition and henceforth are being rigorously explored. Single-particle measurement techniques include mass spectrometry, fluorescence spectrometry, FTIR, Raman spectrometry, and electron-beam excited x-ray diffraction. Raman spectrometry (Raman, from hereon) has been shown to be a highly efficient technique employed for characterization of compounds (Blaha et al., 1978; Jacobson, 2001; Sadezky et al., 2005). There are 2 main reasons for that: 1. Raman spectra are the signatures of the chemical bonds present in the chemical compounds and are therefore unique for the compounds they correspond to; and 2. Raman spectra can be detected for particles of the order of nanometers. Hence, compositional data retrieved for aerosols using Raman measurements can be highly valuable for understanding their droplet forming abilities.

In this dissertation, chemical characterization of aerosols was done using their real-time Raman spectral measurements. A Resource Effective Bioidentification System (REBS)-based Automated Aerosol Raman Spectrometer (ARS) was used for measuring the Raman spectra of the ambient aerosols (schematic shown in Figure 6). An added benefit of ARS over a traditional Raman spectrometer is a significantly reduced stabilization time for the sample and high temporal resolution of spectral collection (about 15 minutes) (Doughty and Hill, 2017).

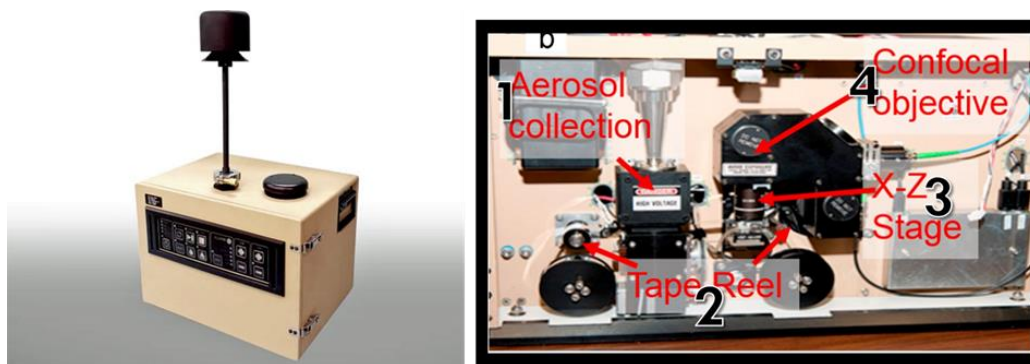


Figure 6. Schematic of a REBS-based Automated Aerosol Raman Spectrometer.

1.4 Overview of the Dissertation

The subsequent chapters of this dissertation describe in detail the experimental and computational work performed in this research. The main rationale for this research was to use findings from controlled laboratory experiments for deriving cloud and climate responses using a large-scale climate model. Chapter 2 discusses the development of a novel CCN experimental setup using an AAC instrument. The findings of this work provide three major conclusions – a. the CCN activity of low hygroscopicity organic and carbonaceous species are well-quantified with the new AAC-CCN experimental setup, b. using the AAC-CCN setup produces very good agreement with published single-hygroscopicity parameters, particularly in the case of sucrose, and c. dynamic shape factor measurements are necessary for CCN activity prediction and can be provided using an AAC-DMA coupling.

Chapters 3 and 4 describe the conception, formulation, and application of the hybrid CCN model as well as the hygroscopicity parameterization. The entirety of these chapters focuses on the CCN activity analysis of organics that were used as proxies for atmospherically relevant primary and secondary organic matter. As previously

established, the water uptake properties of ambient aerosols need to be well understood to quantify and explain aerosol-cloud-climate interactions with high certainty. The findings from chapter 3 describe that explicit solubility considerations within an otherwise purely adsorption based CCN activity model can improve the droplet growth predictions for aerosols possessing a wide range of aqueous solubility. Chapter 4 applies the hybrid CCN model for the analysis of soot-like species. Through chapters 3 and 4, it was established that a hybrid solubility-adsorption CCN framework can be successfully predict droplet growth associated with pure and mixed species with a variety of physical, chemical and morphological properties.

Chapter 5 utilizes the concepts developed in the preceding two chapters to modify the hygroscopicity treatment of aerosol species in the Community Atmosphere Model. The main feature of this work was the modification of the hygroscopicity of three aerosol modes considered within CAM – Black Carbon (BC), Primary Organic Matter (POM) and Secondary Organic Aerosol (SOA). Improvements were observed upon comparisons between observations and simulated aerosol and cloud responses from CAM. The work in chapter 6 was based on the development of a classification algorithm to identify different chemical species in the atmosphere. This work involved collection of Raman spectra of ambient aerosols in real-time over at White Sands (New Mexico) and comparison of the measured spectra with reference databases. The findings of this work revealed the presence of numerous organic and inorganic species with possibly varying mixing states on a particle-basis. Finally, chapter 7 outlines final remarks, future work, as well as the broader implications and overall conclusion of this dissertation research.

Chapter 2: Cloud Condensation Nuclei (CCN) Activity Analysis of Aerosols Using the Aerodynamic Aerosol Classifier (AAC)

Access published article at:

Gohil, K., & Asa-Awuku, A. A. (2022). Cloud condensation nuclei (CCN) activity analysis of low-hygroscopicity aerosols using the aerodynamic aerosol classifier (AAC). Atmospheric Measurement Techniques, 15(4), 1007-1019, <https://doi.org/10.5194/amt-15-1007-2022>

2.1 Abstract

The Aerodynamic Aerosol Classifier (AAC) is a novel instrument that size-selects aerosol particles based on their mechanical mobility. So far, the application of an AAC for Cloud Condensation Nuclei (CCN) activity analysis of aerosols has yet to be explored. Traditionally, a Differential Mobility Analyzer (DMA) is used for aerosol classification in a CCN experimental setup. A DMA classifies particles based on their electrical mobility. Substituting the DMA with an AAC can eliminate multiple charging artefacts as classification using an AAC does not require particle charging. In this work, an AAC-based CCN experimental setup was developed and applied for CCN activity analysis of aerosols. Computational methods were also developed to quantify the uncertainties associated with aerosol particle sizing. To do so, the AAC transfer function analysis was conducted to calculate the measurement uncertainties of the aerodynamic diameter from the resolution of the AAC. The analyses framework has been packaged into a Python-based CCN Analysis Tool (PyCAT 1.0) open-source code, which is available on GitHub for public use. Results show that the AAC size-selects robustly (AAC resolution is 10.1, diffusion losses are minimal and particle transmission is high) at larger aerodynamic diameters ($\geq \sim 85\text{nm}$). The size-resolved

activation ratio is ideally sigmoidal since no charge corrections are required. Moreover, the uncertainties in the critical particle aerodynamic diameter at a given supersaturation can propagate through droplet activation and the subsequent uncertainties with respect to the single-hygroscopicity parameter (κ) are reported. For a known aerosol such as sucrose, the κ derived from the critical dry aerodynamic diameter can be up to ~50% different from the theoretical κ . In this work, additional measurements were conducted in order to obtain dynamic shape factor information and convert the sucrose aerodynamic to volume equivalent diameter. The volume equivalent diameter applied to κ - Köhler theory improves the agreement between measured and theoretical κ . Given the limitations of the coupled AAC-CCN experimental setup, this setup is best used for low hygroscopicity aerosol ($\kappa \leq 0.2$) CCN measurements. This work demonstrates the application of the AAC for CCN applications, especially related to correcting morphological irregularities on the particle scale.

2.2 Background

Cloud Condensation Nuclei (CCN) activity is defined as the ability of an aerosol particle to facilitate the condensation of water vapor on its surface; the condensation occurs in supersaturated ambient conditions resulting in the formation of droplets. The use of size-resolved aerosol number concentrations obtained with the help of counting instruments is a reliable method for determining the CCN activity of aerosols (e.g., but not limited to Barati et al., 2019; Moore et al., 2010; Petters et al., 2007; Rose et al., 2008; Zieger et al., 2017). Currently, the most common method for studying CCN

activation uses a CCN counter (CCNC) and couples it with an aerosol classifier. CCN activity measurements have consistently improved over the past few years since the development and commercialization of the Continuous-Flow Streamwise Thermal Gradient CCN Chamber (CFSTGC) developed by the Droplet Measurement Technologies (DMT) (Roberts and Nenes, 2005; Rose et al., 2008; Lathem and Nenes, 2011) and it is widely used. However, there are several commercially available options to size-select ultrafine particles.

An aerosol classifier size-selects and generates a monodisperse aerosol from a polydisperse aerosol population. The most widely used aerosol classifier for CCN measurements is the Differential Mobility Analyzer (DMA) (Knutson and Whitby, 1975; Rader and McMurry, 1986; Wang and Flagan, 1990). The DMA classifies the aerosol particles based on their electrical mobility; a charge distribution is applied on the particles which then pass through an external electrostatic field that is generated by varying the voltage difference across the DMA column. Many CCN studies use the DMA in “scanning mode” for which stepwise voltage is applied across the aerosol flow to generate monodisperse particles between ~10-500nm. The size-selected particles are then counted by a Condensation Particle Counter (CPC) and a parallel CCNC to obtain the number size distributions for the total aerosol particles (Condensation Nuclei, CN) and activated droplets (CCN) respectively, at a constant instrument supersaturation. The aerosol CN and CCN number size distributions are then combined to calculate the size-resolved activation ratio $\left(\frac{\text{CCN}}{\text{CN}}\right)$ of the aerosol at the given instrument supersaturation.

A major limitation of this method is associated with the working mechanism of the DMA. The DMA uses a neutralizer (e.g., Kr-85, soft X-ray, or Po-210) to distribute electric charge to classify the polydisperse particles. The particles may receive multiple unit charges depending on the charging efficiency of the neutralizer. As a result, the particles carrying a unit charge possess the same electrical mobility as larger particles carrying a higher integral charge. Therefore, the perceived monodisperse aerosols likely contain a mixture of different-sized particles. This issue is known and can lead to discrepancies in the size-resolved activation ratio $\left(\frac{CCN}{CN}\right)$ (Moore et al. (2010)). Hence, charge correction algorithms (Fuchs, 1963; Wiedensohler, 1988) are commonly applied to resolve particle multiple charging issues and data correction is applied in CCN software. Multiple charging errors can still affect the reliability and efficacy of CCN activation data.

The multiple charging issues in electrical mobility-based classifiers have led to the development of instruments that use particle mechanical mobility. Classifiers can measure the relaxation time in pressurized flow or free-molecular (vacuum) regimes (e.g., but not limited to Chein & Lundgren, 1993; Conner, 1966; Flagan, 2004; Keskinen et al., 1992; Marple et al., 1991). Recently, the working principle and instrumentation details for an Aerodynamic Aerosol Classifier (AAC) were described (Tavakoli and Olfert, 2013; Tavakoli et al., 2014). The AAC does not require particle charging for size-selection and does not produce multiple charging artifacts (Yao et al., 2020). The AAC classifies particles with respect to their relaxation time and reports their corresponding aerodynamic diameter.

The AAC has been used with different instruments. Johnson et al., (2018) used the AAC in tandem with the Scanning Mobility Particle Sizer (SMPS) to characterize the transfer function of the AAC. The AAC can classify particles as large as 6 μm (Johnson et al., 2018). Furthermore, the AAC in tandem with a DMA can determine the aerosol dynamic shape factor (Tavakoli and Olfert, 2014; Barati et al., 2019; Yao et al., 2020; Tran et al., 2020) and particle effective density (Tavakoli and Olfert, 2014; Peng et al., 2021b). Sang-Nourpour & Olfert, (2019) and Tran et al., (2020) discuss methods for Optical Particle Counter (OPC) calibration using an AAC.

In short, the AAC is increasing in popularity (e.g., but not limited to Johnson et al., 2020, 2021; B. Su et al., 2021). However, the scientific knowledge of coupling an AAC with a CCNC is limited. One previous study (Barati et al., 2019) published results for the CCN analysis of low-hygroscopicity aerosols but did not investigate the uncertainties in AAC-CCN size-resolved measurements and CCN activity predictions. To our knowledge, the validation of AAC-CCNC coupling on CCN measurement and prediction has not been studied before, and hence the AAC-CCNC coupled system is currently not well understood. This work explains the AAC-CCNC coupling for CCN activity measurements and uncertainties associated with size-selection, number size distributions and CCN activity estimates employing the AAC transfer function.

In addition to a standardized experimental protocol for an AAC-CCNC setup, a computational tool also needs to be developed for CCN analysis. Currently, the Scanning Mobility CCN Analysis (SMCA) (Moore et al., 2010) package is widely used to calculate the CCN activity of aerosols using their electrical mobility-classified

number size distribution data. The processed size-distribution data from the SMCA can be analyzed using the Köhler theory (Köhler, 1936; Seinfeld and Pandis, 1998). SMCA has been shown to efficiently perform functions that include inversion of time series measurements to obtain size-resolved data (Wang and Flagan, 1990), and multiple charge correction using the algorithm given by Wiedensohler, (1988). SMCA works well for a variety of organic and inorganic aerosols to estimate their CCN activity (e.g Barati et al., 2019; Dawson et al., 2020; Fofie et al., 2018; Giordano et al., 2015; Moore et al., 2010; Padró et al., 2012; C. Peng et al., 2021; Vu et al., 2019). So far, there is no computational analysis tool for data processing or CCN analysis using their aerodynamic measurements based on AAC-CCNC setup.

In this work, the AAC was coupled with the CCNC instrument, ascribing to the aforementioned advantages and novelty of the AAC, for CCN activity analysis. The experimental setup and CCN analysis tool were developed and tested. The analysis tool was developed in Python (PyCAT 1.0, described in Section 2.3.3) and is available on GitHub for public use. In the following sections, the discussion begins with the description of the experimental setup to size select and count particles. The following section describes the theory and mathematical formulations used in CCN analysis of aerosols. After that, the uncertainty estimation is discussed associated with aerodynamic size selection and the propagated error into the CCN activity analysis, and the impact on the subsequently derived single-hygroscopicity parameter (κ) values.

2.3 Data and Methodology

2.3.1 Instrument and Setup

A CambustionTM Aerodynamic Aerosol Classifier (AAC) size-selected polydisperse aerosol. Briefly described here, the AAC contains 2 concentric cylindrical columns for particle selection. The schematic of a typical AAC is shown in Figure 4. The particles are introduced into the AAC from inside the inner cylinder and the aerosol flow is then passed into the space between the 2 cylinders. The particles move with axial and radial velocities because of the rotation of the cylinders. The rotational speed steps across a range of values when the AAC is operated in "scanning mode". Each of the rotational speeds correspond to a relaxation time and aerodynamic diameter. At different speeds, the particles can hit the inner surface of the outer cylinder depending on their size. The outer cylinder has an opening through which the particles of an optimum size corresponding to a specific rotational speed can pass through. Particles larger than the threshold optimum size hit the cylindrical surface before the opening, and the ones smaller than the threshold, exit the classifier along with the exhaust flow. The working principle of the AAC has been described previously in extensive detail (Tavakoli and Olfert, 2013; Tavakoli et al., 2014; Johnson et al., 2018).

Figure 7 shows the experimental setup used in this study. The classified aerosol was split into 2 streams - the first stream was passed through a Condensation Particle Counter (CPC, TSI 3776) to obtain total aerosol particle counts (condensation nuclei, CN), and the second stream was passed through a DMT Continuous-Flow Streamwise Thermal-Gradient CCN Chamber (CFSTGC, or simply CCNC; Roberts & Nenes,

2005) to obtain activated aerosol particle counts (cloud condensation nuclei, CCN). The CCNC consists of a cylindrical chamber that has internally wetted walls to maintain an approximately constant supersaturation along the CCNC column. A series of experiments were performed with sucrose at different instrument supersaturations (between 0.2% and 0.6%). Sucrose is a highly water-soluble, moderately hygroscopic oligomer that is an atmospherically relevant aerosol from biogenic sources (Dawson et al., 2020). The CCN properties of sucrose have been well-studied and characterized (e.g., but not limited to Dawson et al., 2020; Petters & Kreidenweis, 2007; J. Wang et al., 2017; Xu et al., 2014). Sucrose was selected as an appropriate choice of aerosol to benchmark the AAC-CCNC experimental setup.

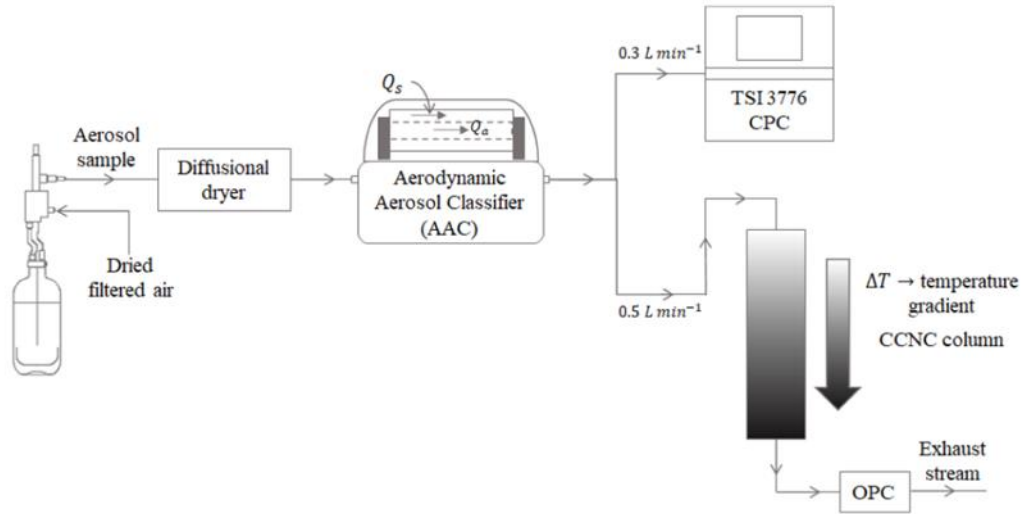


Figure 7. AAC–CCNC experimentation setup for measuring the size-resolved number concentration of aerosols.

The polydisperse aerosol population was generated from an aqueous solution using a Collision atomizer. The aerosol was passed through a series of 2 diffusion driers (for drying to <10% RH) and then introduced into the AAC to generate monodisperse

aerosol. The atomization typically produces dry particles in the submicron size range. A total sample flow rate of 0.8 L min^{-1} was split between 0.3 and 0.5 L min^{-1} for the CN and CCN measurements, respectively. Additionally, a sheath flow rate of 8 L min^{-1} was applied to maintain a sheath-to-sample flow ratio of 10:1. Furthermore, the AAC was maintained at a temperature and pressure of 21.5° C and 1 atm , respectively. The CCNC instrument supersaturations were calibrated using ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ (Rose et al., 2008). The details of CCNC calibration performed using DMA-based size-resolved $(\text{NH}_4)_2\text{SO}_4$ measurements from 0.2 to 0.6% supersaturation are provided in the appendix section 2A.1.

The AAC was operated in the "step-scanning mode". In step-scanning mode, there is a transit time and stabilization (delay) time when the AAC advances from one rotational speed setpoint to another. Each rotational speed is related with a corresponding size bin, and here the AAC was run between successive size bins for 14.5 seconds (transit time of 9.5 seconds and delay time of 5 seconds). Increasing the stabilization interval improves the repeatability of the particle counts and reduces uncertainties due to particle diffusion at lower sizes. The measured CCN to CN activation ratio $\left(\frac{\text{CCN}}{\text{CN}}\right)$ was calculated for each size-selected aerodynamic diameter. A sigmoidal fit was applied to the size-resolved activation ratio. The critical dry diameter is defined at the 50% activation efficiency at a constant instrument supersaturation and was reported every 30 minutes and repeated 5 times for the AAC-CCN experimental setup.

2.3.2 CCN Activation Theory

The critical dry diameter and instrument supersaturation can be used in Köhler theory (Köhler, 1936; Seinfeld and Pandis, 1998) to estimate the size-independent single-hygroscopicity parameter (κ) of the aerosol species. κ of an aerosol species is calculated as follows (Petters and Kreidenweis, 2007),

$$\kappa = \frac{4A^3}{27D_{p_{50}}^3 \ln^2(S)}; \text{ where } A = \frac{4M_w \rho_s}{RT \rho_w} \quad (2.1)$$

In the above equation, $D_{p_{50}}$ is the critical dry diameter of the aerosol species at supersaturation S . Physically, $D_{p_{50}}$ is a threshold size for activation; particles larger than this threshold are assumed to fully activate and convert into droplets and those smaller than the threshold remain unactivated. M_w , σ_w and ρ_w correspond to the molar mass, surface tension and density of water, respectively. R is the universal gas constant, and T is the average temperature inside the CCNC column. Under the Köhler theory framework, the κ of an aerosol species can be related to the molar mass (M_s), density (ρ_s), and Van't Hoff factor (v_s) of the solute (Sullivan et al., 2009; Mikhailov et al., 2013),

$$\kappa = \frac{v_s \rho_s M_w}{\rho_w M_s} \quad (2.2)$$

Eq. (2.2) assumes complete aqueous solubility of the aerosol species. Past studies have found sucrose κ from CCN measurements (obtained from Eq. 2.1) in the range of 0.06-0.1 (e.g., but not limited to Dawson et al., 2020; Ruehl et al., 2016; J. Wang et al., 2017; Z. Wang et al., 2015; Xu et al., 2014). Furthermore, the theoretical κ of sucrose

(obtained from Eq. 2.2) is 0.084 and implies that the previously reported κ estimates of sucrose are in good agreement with the theoretical κ of sucrose. Therefore, the theoretical κ (from Eq. 2.2) can also be used to validate the sucrose κ derived from the AAC-CCNC setup.

2.3.3 Python-based CCN Analysis Toolkit (PyCAT 1.0)

Each step-scanning mode timeseries using the AAC-CCNC setup measures 90 CN datapoints and 1400 CCN datapoints. Therefore, a computationally efficient method is required to synchronize and analyze the AAC and CCNC datasets. A computer code (Python-based CCN Analysis Toolkit, PyCAT) was developed to analyze both SMPS and AAC size-resolved CCN data for CCN activity analysis. The code is written in Python3.7 and uses the most recent version of the built-in libraries. It can perform timeseries data synchronization and analysis, CCN activity analysis (section 2.2) and uncertainty analysis (section 3). In addition, the code provides aerosol sizing properties at the point of activation and Köhler theory analysis based on user inputs. Additionally, the code is flexible and allows the user to organize and visualize the post analysis data. An opensource code has been completely packaged with the necessary capabilities and is available on GitHub for public use. Here the application of PyCAT has been demonstrated for the first time. PyCAT has been used for CCN activity analysis and to quantify the uncertainties associated with aerodynamic measurements and how they manifest in the CCN activity.

2.4 Uncertainty Analysis of Measurements

The uncertainty analysis for particle size-selection using the AAC in step-scanning mode has been described in detail previously (Johnson et al., 2018; Yao et al., 2020). In this section, the derivation of AAC uncertainty has been briefly described and fully describe the effects of size-selection for CCN activity and single-parameter hygroscopicity uncertainty analysis.

Aerosol particles moving with an axial speed v through the AAC column experience drag force. The drag force on a particle of an assumed spherical shape can be expressed as,

$$F_{drag} = \frac{v}{B_{spherical}} \quad (2.3)$$

where $B_{spherical}$ is defined as the mechanical mobility of the spherical particle (Tavakoli et al., 2014; Johnson et al., 2018; Yao et al., 2020). For a given set of AAC operating conditions, $B_{spherical}$ can be determined as (Tavakoli et al., 2014; Yao et al., 2020),

$$B_{spherical} = \frac{C_c(d_{spherical})}{3\mu\pi d_{spherical}} \quad (2.4)$$

where μ is the dynamic viscosity of the surrounding gas, $d_{spherical}$ is the particle diameter under the assumptions of sphericity, and $C_c(d_{spherical})$ is the Cunningham's slip correction factor of the particle with the diameter $d_{spherical}$ (described in appendix section 2A.2).

The particle drag force is balanced by the particle centrifugal force in the AAC for size-selection (Tavakoli and Olfert, 2013). The particle centrifugal force is defined as follows,

$$F_{centrifugal} = m\omega^2 r \quad (2.5)$$

where m , ω and r are the mass, rotational speed, and radial position of the particle, respectively. The aerosol particle relaxation time, $\tau = mB_{spherical}$. Using this definition, the force balance expression τ is expressed as,

$$\tau = \frac{v}{\omega^2 r} \quad (2.6)$$

The maximum particle relaxation time (τ^*) is calculated as follows (Tavakoli et al., 2014),

$$\tau^* = \frac{Q_{sh} + Q_{exh}}{\pi\omega^2(r_1 + r_2)^2 L} \quad (2.7)$$

where r_1 , r_2 and L denote the classifier inner radius, outer radius, and length respectively. Q_{sh} and Q_{exh} are the inlet sheath flow and outlet exhaust flow, respectively. In this study, Q_{sh} and Q_{exh} were fixed by the CPC sample flowrate. ω is the only variable parameter in Eq. (2.7) and defines the setpoint for size-selection and determines the τ^* corresponding to particles of desired aerodynamic diameter.

The particle relaxation time can also be expressed in terms of the particle aerodynamic diameter as follows (Johnson et al., 2018),

$$\tau = \frac{C_c(d_{ae})\rho_0 d_{ae}^2}{18\mu} \quad (2.8)$$

where ρ_0 is the reference density of 1000 kg/m³ and $C_c(d_{ae})$ is the Cunningham slip correction factor of the particle with aerodynamic diameter d_{ae} . The aerodynamic diameter of a particle is defined for a spherical particle with a density of 1000 kg/m³. A non-dimensional relaxation time, $\tilde{\tau} = \frac{\tau}{\tau^*}$ is calculated by dividing Eq. (2.8) with Eq. (2.7).

Previous studies have developed models to calculate the probability of selecting a particle passing through the AAC, otherwise known as the AAC transfer function (TF) (Johnson et al., 2018; Tavakoli and Olfert, 2013). Tavakoli & Olfert, (2013) developed the AAC transfer function following the methodology from Knutson & Whitby, (1975). In this work, the non-diffusing particle streamline TF theory is used to describe particle classification (Tavakoli and Olfert, 2013). The AAC TF is denoted by, and for ideal non-diffusion conditions, it is defined as follows (Martinsson et al., 2001; Tavakoli and Olfert, 2013; Johnson et al., 2018),

$$\Omega_{ND}(\tilde{\tau}; \beta; \delta) = \frac{1}{2\beta(1-\delta)} \cdot [|\tilde{\tau} - (1 + \beta)| + |\tilde{\tau} - (1 - \beta)| - |\tilde{\tau} - (1 + \beta\delta)| - |\tilde{\tau} - (1 + \beta\delta)|] \quad (2.9)$$

where $\beta = \frac{Q_s + Q_a}{Q_{sh} + Q_{exh}}$ and $\delta = \frac{Q_s - Q_a}{Q_s + Q_a}$, such that Q_a is the inlet aerosol flow, and Q_s is the outlet sample flow. The AAC was operated under balanced flow conditions ($Q_s = Q_a$) and ($Q_{sh} = Q_{exh}$), and thus β and δ were reduced to $\frac{Q_s}{Q_{sh}}$ and 0, respectively. Under the balanced flow assumption, Eq. (2.9) can be simplified to (Johnson et al., 2018),

$$\Omega_{ND,B}(\tilde{\tau};) = \frac{1}{2\beta} \cdot [|\tilde{\tau} - (1 + \beta)| + |\tilde{\tau} - (1 - \beta)| - 2 \cdot |\tilde{\tau} - 1|] \quad (2.10)$$

The non-ideal particle behavior was accounted for by incorporating a transmission efficiency (λ_Ω) and transfer function width factor (μ_Ω) in the TF (described in appendix section 2A.2). The resulting TF for non-ideal, non-diffusing, balanced flow conditions is expressed as (Johnson et al., 2018),

$$\Omega_{ND,B,NI}(\tilde{\tau}; \beta; \lambda_\Omega; \mu_\Omega) = \frac{\lambda_\Omega \cdot \mu_\Omega^2}{2\beta} \cdot \left[\left| \tilde{\tau} - \left(1 + \frac{\beta}{\mu_\Omega}\right) \right| + \left| \tilde{\tau} - \left(1 - \frac{\beta}{\mu_\Omega}\right) \right| - 2 \cdot |\tilde{\tau} - 1| \right] \quad (2.11)$$

Figure 8 compares the theoretical TFs for ideal (Eq. 10) and non-ideal (Eq. 2.11) particle behaviors under the balanced flow, non-diffusion AAC framework. The two transfer functions are shown for a particle aerodynamic diameter of 150 nm ($\tau = 147.7$ ns, Eq. 2.8).

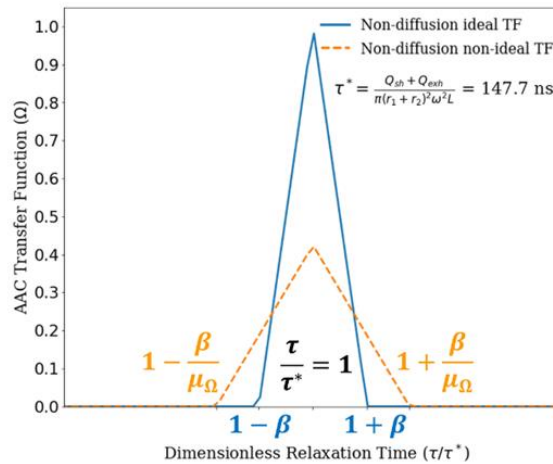


Figure 8. The ideal (blue) and nonideal (NI) (orange) AAC trans-fer functions based on the particle streamline non-diffusion (ND) model as developed by Tavakoli and Olfert (2013). The transfer functions are shown relative to 150 nm aerodynamic diameter as the set point. This corresponds to a relaxation time set point of 147.7 ns. It can be observed that the NI transfer function maximum is significantly reduced compared to the ideal transfer function, which is attributed to a reduced transmission efficiency for the NI transfer function. Additionally, the transfer function broadening is higher for the NI transfer function, which is quantified using the transfer function width factor. Overall, the NI transfer function provides an improved basis for particle size selection using the AAC.

The AAC resolution can be determined from the TF broadening relative to the setpoint at $\tau = \tau^*$ (or $\tilde{\tau} = 1$). The AAC resolution can be correlated with the uncertainty associated with the relaxation time or aerodynamic diameter. Particles classified by the AAC only contain a narrow range of aerodynamic diameters. The AAC resolution is expressed as $\frac{1}{R_\tau} = \frac{\Delta\tau}{\tau} = \frac{Q_s}{Q_{sh}}$ and assumes the flows to be balanced, laminar and constant (Yao et al., 2020). The AAC resolution can also be expressed in the coordinates of the aerodynamic diameter as $\frac{1}{R_{ae}} = \frac{\Delta d_{ae}}{d_{ae}}$ which forms the basis to determine the uncertainties associated with the aerodynamic diameters. Using Eq. (2.11), the uncertainty in relaxation time is (Yao et al., 2020),

$$\left[\frac{\Delta\tau}{\tau}\right]^2 = \left[\frac{\delta Q_{sh}}{Q_{sh}}\right]^2 + 4 \left[\frac{\delta\omega}{\omega}\right]^2 + 4 \left[\frac{\delta r}{r}\right]^2 + \left[\frac{\delta L}{L}\right]^2 \quad (2.12)$$

which can further be used to derive the uncertainty associated with the corresponding aerodynamic diameter as follows,

$$\frac{\Delta d_{ae}}{d_{ae}} = \frac{\Delta\tau}{\tau} \cdot \left[\frac{d_{ae} + \alpha_c \cdot \lambda + \beta_c \cdot \lambda \cdot e\left(-\gamma_c \cdot \frac{d_{ae}}{\lambda}\right)}{2d_{ae} + \alpha_c \cdot \lambda + \beta_c \cdot \lambda \cdot e\left(-\gamma_c \cdot \frac{d_{ae}}{\lambda}\right) \cdot \left(1 - \gamma_c \cdot \frac{d_{ae}}{\lambda}\right)} \right] \quad (2.13)$$

where $\alpha_c = 2.33$, $\beta_c = 0.966$ and $\gamma_c = 0.4985$ are the Cunningham slip correction factor coefficients taken from (Kim et al., 2005), and λ is the mean free path of the particles. The aerodynamic diameter can be converted to the volume equivalent diameter, which is a more accurate representation of the particle morphology and size. The volume equivalent diameter is expressed using the dynamic shape factor and aerosol density as follows,

$$d_{ve} = d_{ae} \sqrt{\frac{\chi \rho_0 C_c(d_{ae})}{\rho_p C_c(d_{ve})}} \quad (2.14)$$

where ρ_p is the particle density, $C_c(d_{ve})$ is the Cunningham's slip correction factor for the particle with the volume equivalent diameter, d_{ve} , and χ is the size-dependent dynamic shape factor. The uncertainties in the volume equivalent diameter are quantified using the uncertainties in measured aerodynamic diameter and dynamic shape factor as follows,

$$\left[\frac{\Delta d_{ve}}{d_{ve}}\right]^2 = \left[\frac{\delta d_{ae}}{d_{ae}}\right]^2 + \frac{1}{4} \left[\frac{1}{\chi \rho_0} \frac{\Delta C_c(d_{ae})}{C_c(d_{ae})}\right]^2 + \frac{1}{4} \left[\frac{1}{\rho_p} \frac{\Delta C_c(d_{ve})}{C_c(d_{ve})}\right]^2 + \frac{1}{4} \left[\frac{\Delta \chi}{\chi}\right]^2 \quad (2.15)$$

The uncertainty given by Eq. (2.15) has a direct implication to the aerosol κ . For a given supersaturation, the uncertainty in κ is dependent on the uncertainty in the volume equivalent diameter, and is expressed as,

$$\frac{\Delta \kappa}{\kappa} = 3 \cdot \frac{\Delta D_{p_{50}}}{D_{p_{50}}} \quad (2.16)$$

Eq. (2.16) implies that the relative uncertainty in κ is theoretically 3 times more than that of the critical dry diameter. In Eq. (2.16), the $D_{p_{50}}$ can either be the critical dry electrical mobility, aerodynamic or volume equivalent diameter. In this work, the uncertainties in Eq. (2.16) are evaluated with respect to volume equivalent diameters derived from the measured electrical mobility and aerodynamic diameters. Another important point to note here, is that since the activation diameter varies with supersaturation, the uncertainty at every activation diameter will also be different. This

implies that for each measured activation diameter, the uncertainty in aerosol κ will vary, and will thus depend on the uncertainty in critical dry diameter.

2.5 Results for Laboratory Aerosols

The AAC-CCNC measurements of sucrose were reported at varying CCNC instrument supersaturations (0.2 to 0.6%). The aerosol particles classified with the AAC were counted using a CPC and CCNC. An example dataset of CN and CCN number size distributions measured at 0.39% supersaturation is shown in Figure 9(a). The CN and CCN particle counts are plotted against the aerodynamic diameters. Error bars in the y-axis denote the relative uncertainties in the CN and CCN number concentrations. The errors in CN and CCN concentrations are calculated from counting uncertainties of the CPC and CCNC, and uncertainties in the instrument flow rate of CPC and CCNC. Details of uncertainty estimation for the CN and CCN counts are provided in Moore et al., (2010) and are briefly described in appendix section 2A.4. The observed relative uncertainties in the CN and CCN concentrations were $< 1\%$ for every aerodynamic diameter, which indicates that counts are repeatable. Figure 9(b) shows the size-resolved activation ratio $\left(R_a = \frac{CCN(S; D_p)}{CN(D_p)}\right)$ for 0.39% supersaturation (S), where $CCN(S; D_p)$ is the CCN measurement at the constant S and D_p divided by CN measurements at constant D_p , $CN(D_p)$. A brief description of the sigmoidal fitting and its mathematical representation is provided in the appendix section 2A.3. The sigmoidal fit applied to the R_a is also shown in Figure 9(b). Error bars on the y-axis in Figure 9(b) show the uncertainties in R_a . The R_a uncertainties were calculated by

propagating the uncertainties in CN and CCN number concentrations. Details of the estimation of y-axis uncertainties of R_a in Figure 9(b) are also provided in the appendix section 2A.4.

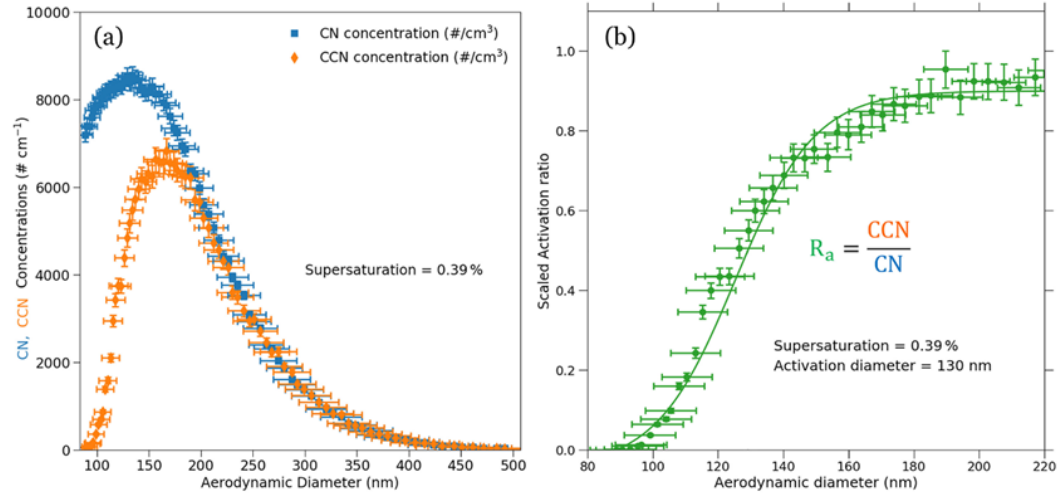


Figure 9. The CN and CCN number size distributions (a) and the corresponding size-resolved activation ratio (b) for sucrose are shown. The measurements were performed at a supersaturation of 0.39%. The activation aerodynamic diameter was found to be about 130 nm from the activation ratio obtained using the size-resolved measurements. The dry aerodynamic activation diameter corresponds to the 50% activation efficiency, which corresponds to an activation ratio of 0.47. Furthermore, the uncertainties in the aerodynamic diameters, CN and CCN number concentrations, and size-resolved activation ratio are also denoted on the plot using their respective error bars.

In both Figure 9(a) and 9(b), the error bars along the x-axis show uncertainties in aerodynamic diameters estimated using the AAC TF. The x-axis uncertainties in Figure 9(a) and 9(b) decreased with increasing aerodynamic diameters. The decrease in the x-axis uncertainties can be explained using Figure 10(a) which shows the AAC TF for non-ideal particle behavior. For non-ideal AAC TF, the increase in the AAC resolution can be attributed to a monotonic increase in the transmission efficiency (λ_Ω) and transfer function width factor (μ_Ω) with respect to the aerodynamic diameter (Figure

10(b)). Figure 10(a) shows that the AAC TF broadening decreases with an increase in aerodynamic diameter for a fixed sheath flow rate. This is likely due to a reduced classifier flow effect with increasing aerodynamic diameter (Johnson et al. (2018)). As a result, the AAC resolution increases with increasing aerodynamic diameter. An increased resolution results in a decrease in the x-axis uncertainty with increasing particle sizes. In other words, the diffusion losses decrease with an increase in the mobility mass and aerodynamic diameter, in turn decreasing Ra uncertainties associated with AAC particle size-selection and counting. From our AAC-CCNC measurements at 8 L min⁻¹, the minimum AAC resolution was 10.1 to prevent excess transfer function broadening and improve the accuracy of the size-resolved measurements. Figure 10(a) is a direct result of Eq. (2.13) and suggests that reducing the error in size measurement reduces the magnitude of error propagation for single-hygroscopicity parameter (κ).

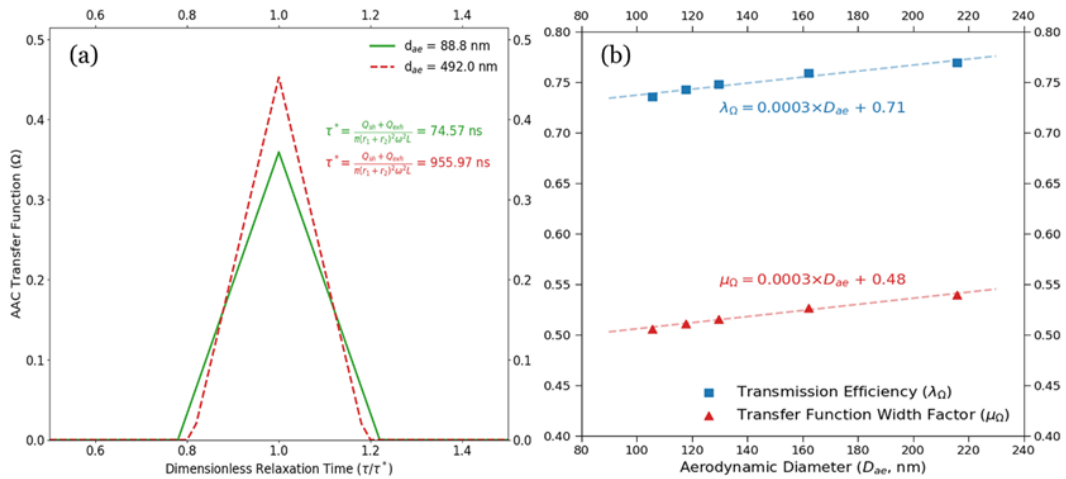


Figure 10. (a) ND–B–NI transfer functions for low-flow measurement conditions from the AAC-based setup are shown. The transfer functions are plotted with respect to dimensionless relaxation time. The lower and upper aerodynamic diameter limits for the measurements are 90 and 392.3 nm, respectively. The corresponding relaxation

times are highlighted for the aerodynamic diameter set points. The resolution increases, and hence the measurement uncertainties, decrease with an increase in the particle aerodynamic diameter. (b) The size-dependent transmission efficiency (λ_Ω , blue) and transfer function width factor (μ_Ω , red) are shown above. The marked points on the plot correspond to λ_Ω and μ_Ω computed at the dry activation diameters at the set instrument supersaturations used in this study (between 0.2% and 0.5%). As a general trend, both the transfer function parameters increase with the increase in aerodynamic diameter. This results in an increase in the AAC transfer function resolution and a decrease in the size-related uncertainty with an increase in aerodynamic diameter (that is, the particle relaxation time). The plot also shows that the transfer function width factor is slightly more sensitive to the increase in the aerodynamic diameter, which can be followed by comparing the slopes of the linear fits of the transmission efficiency and width factor relative to the aerodynamic diameter.

The critical dry aerodynamic diameter at 0.39% supersaturation was approximately 130nm. The AAC-CCNC sigmoidal fitting is similar to that applied by SMCA (Moore et al. (2010)). However, the sigmoid applied to the AAC-CCNC measurements does not require the correction of multiple charging artefacts. The critical dry aerodynamic diameter (130nm) and S (0.39%) were then combined using the Köhler theory framework (Section 2.2) to estimate the single-hygroscopicity parameter (κ) of sucrose. At 0.39% the κ was found to be 0.041 (Eq. 2.1). This had a $\sim 51\%$ difference with respect to the theoretical κ (0.084) of sucrose. Like Figure 9(b), Figure 11 shows the size-resolved activation ratios estimated from the measured number size distributions at 5 different supersaturations (0.23%, 0.31%, 0.39%, 0.48%, and 0.57%). The uncertainties associated with the aerodynamic diameters and their corresponding activation ratios are also shown on the plot. In addition to this, the critical dry aerodynamic diameters obtained from the size-resolved activation ratios at respective supersaturations are provided. For every set of size-resolved activation data, the y-axis uncertainties increase, while the x-axis uncertainties decrease with increasing aerodynamic diameters (Table 2.1). κ was calculated for each supersaturation using Eq.

(2.1), and the propagated uncertainty from the critical dry volume equivalent diameter was calculated using Eq. (2.16). The κ and associated uncertainties were averaged for 5 sets of measurements at every instrument supersaturation. Accounting for changing instrument supersaturations, the mean κ for the set of 5 aerodynamic measurements was 0.036 ± 0.008 (slightly < 0.041 , the mean κ at 0.39% supersaturation). The 0.036 κ value was less than previously reported sucrose κ values from electrical mobility CCN measurements (in the range of 0.06-0.1) (Xu et al., 2014; Ruehl et al., 2016; Dawson et al., 2020), as well as the theoretical sucrose κ (0.084). This relatively large differences between κ values are attributed to the use of the aerodynamic diameter in Eq. (2.1).

Aerodynamic diameters are generally overpredicted as they are based on a spherical particle with a density (ρ_0) = 1000 kg/m³, and is likely true in the case of sucrose as its bulk density = 1586 kg/m³, which is significantly larger than ρ_0 . In such a case, a more reliable measure of particle size is required to improve the accuracy of the AAC-CCN hygroscopicity estimates. The measured aerodynamic diameters were converted into volume equivalent diameters by accounting for the particle dynamic shape factor and true particle density (Tavakoli and Olfert, 2014). Size-resolved shape factor measurements of sucrose are described in detail in the appendix section 2A.5. Dynamic shape factor (χ) = 1 corresponds to spherical particles, and $\chi > 1$ marks a deviation of particle shape from sphericity. For sucrose particles with aerodynamic diameters between ~ 100 nm and 250nm, the size-resolved dynamic shape factor was approximately 1 and was observed to be only as high as ~ 1.1 for particles with $d_{ae} = 100$ nm. Table 2.1 provides a summary of critical dry aerodynamic diameters and their

volume equivalent counterparts found in this study for CCN measurements at different supersaturations.

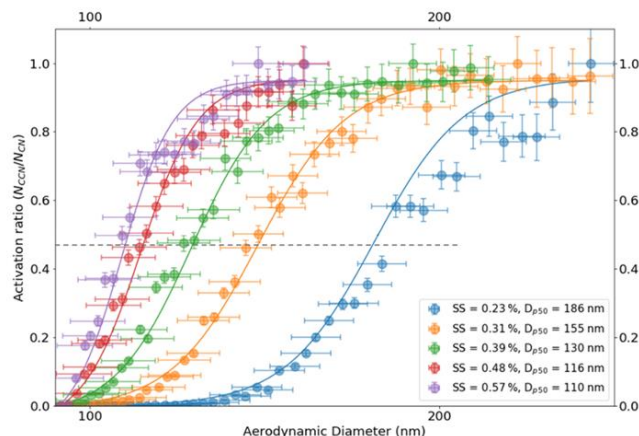


Figure 11. Size-resolved activation ratios are shown over a range of instrument supersaturations as presented on the plot. Their corresponding dry activation aerodynamic diameters are also depicted on the plots. The dotted line passing through the 50% activation efficiency (activation ratio of about 0.47) point on the plot intersects the activation ratio plots at their respective dry activation diameters. The dry activation diameter systematically decreases with increasing ambient supersaturation. Moreover, the volume equivalent diameters corresponding to their aerodynamic diameters are not shown here.

The κ computed using Köhler theory from 5 different dry aerodynamic activation diameters and their respective volume equivalent diameters are summarized in Table 2.1. Physically, the volume equivalent diameter represents a spherical particle with the same mass as that of a non-spherical aerodynamic particle. However, the volume equivalent diameter accounts for the aerosol density as well as the deviation of the aerosol particles' shape from sphericity and improves the accuracy of hygroscopicity estimates. The mean κ of sucrose computed from critical dry volume equivalent diameters was estimated to be 0.09 ± 0.006 . The critical dry volume equivalent diameters combined with their respective critical supersaturations provided estimates

of sucrose κ that are in a better agreement with the theoretical and previously reported hygroscopicity values.

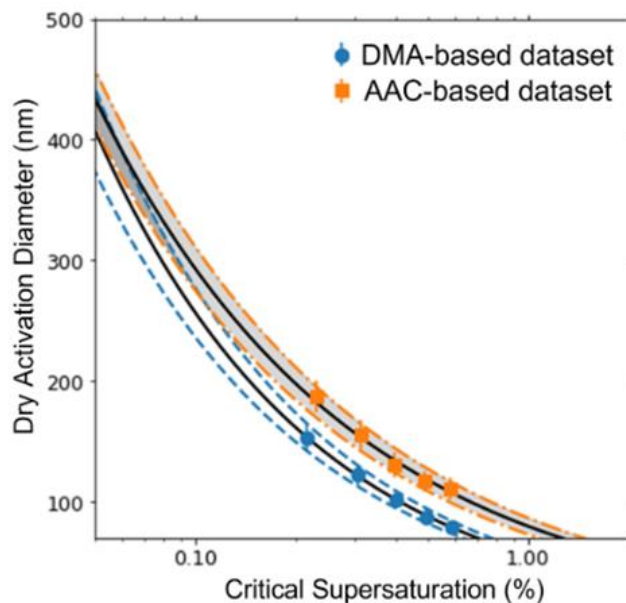


Figure 12. The variation in uncertainty of size-resolved measurements using a DMA and AAC are compared in this plot. The orange dot-dashed lines denote the range of uncertainty in measurements in an AAC, and the blue dashed lines denote the range of uncertainty in measurements in a DMA. The black solid lines are the best fits for the size-resolved measurements for sucrose obtained using the Köhler theory.

Table 1. The table provides the analysis summary of the set of measurements performed for sucrose with the help of the AAC–CCNC setup. At low supersaturations, sucrose has large dry activation diameters for which the measurement uncertainties are slightly lower. Furthermore, the CCN activity predictions in terms of κ using the Köhler theory are also accurate. With an increase in the supersaturation the dry activation diameter reduces, and correspondingly the variations in κ continue to rise, being as high as about 35% at 0.58% instrument supersaturation. The conversion of dry aerodynamic activation diameters of sucrose to their corresponding volume equivalent diameters was done with the help of the dynamic shape factor. The shape factor measurements and analysis were performed following the procedure described in Tavakoli & Olfert, (2014).

Instrument supersaturation (S)	D_{p50} (nm)	Uncertainty D_{p50}	κ^a	Relative difference – measured κ vs. $\kappa_{\text{theoretical}}^b$	Dynamic shape factor (χ)	Volume equivalent diameter $D_{v,p50}$ (nm) ^c	$\kappa_{\text{corrected}}^d$	Relative difference $\kappa_{\text{corrected}}$ vs. $\kappa_{\text{theoretical}}$
0.23 %	186	±7 %	0.04 ± 0.0083	52.4 %	1.019	140	0.093	10.7 %
0.31 %	155	±7.3 %	0.038 ± 0.0082	54.8 %	1.023	116	0.087	3.6 %
0.39 %	130	±7.6 %	0.041 ± 0.0092	51.2 %	1.044	95	0.099	17.8 %
0.48 %	116	±7.8 %	0.04 ± 0.0091	52.4 %	1.037	86	0.088	4.76 %
0.57 %	110	±8 %	0.032 ± 0.0074	61.9 %	1.052	80	0.081	3.6 %

^a κ determined using the dry aerodynamic activation diameter in the Köhler theory framework. ^b Theoretical κ of sucrose determined from ideal Köhler theory = 0.084. ^c Volume equivalent diameter including the dynamic shape factor with the dry aerodynamic activation diameter. ^d κ determined using the volume equivalent activation diameter in the Köhler theory framework.

2.6 Summary, Recommendations and Implications

This study presents the AAC-CCNC experimental setup. The presented methodology can be applied for CCN activity analysis of different aerosol species. Aerosol size-selection with the AAC does not require charging of particles; thus, the AAC-CCNC coupling generates truer monodisperse aerosols, ideally sigmoidal activation data, and improves the accuracy of size-resolved measurements. For AAC-derived critical dry aerodynamic diameters, the sizing uncertainty is larger at low particle sizes and reduces with an increase in particle size (Table 1). Thus, larger critical dry aerodynamic diameters are preferred with the AAC-CCNC setup and so the AAC-CCNC setup more applicable for CCN measurements of low-hygroscopicity aerosols. It should be noted that this phenomenon is reversed for electrical mobility measurements. In the DMA, this can be attributed to increased diffusion losses due to a drop in transmission efficiency for the particles larger than 100nm. A similar observation can be made based on the findings in Figure 10 of Johnson et al., (2018). To reiterate, the uncertainties in the electrical mobility diameter increase for larger particle sizes (Figure 12). Table S6.1 provides the measure of uncertainties in aerodynamic and mobility diameters of sucrose at the same supersaturations.

An optimum range of aerodynamic diameters for CCN measurements can be suggested based on the findings of this work. There are fewer particles larger than $0.5\mu\text{m}$ generated via Collison atomization. Therefore, atomization produces extremely low number concentrations for particles larger than $0.5\mu\text{m}$, which can significantly reduce the counting statistics. This suggests that $\sim 0.5\mu\text{m}$ was a suitable upper limit of aerodynamic diameters for laboratory AAC-CCNC measurements. The lower size limit can be defined using the AAC resolution, the TF broadening and hence the flow rates used in the experiments. The sample and sheath flow rates were set to 0.8 L min^{-1} and 8 L min^{-1} , respectively. Additionally, AAC TF equations (section 3), indicate a lower size limit of $\sim 85\text{nm}$. The minimum measurement resolution to obtain good counting statistics corresponding to any aerodynamic diameter 85nm was 10.1. Based on the TF analysis in this paper and the previously described CCN activity measurements (Rose et al., 2008; Moore et al., 2010), it can be inferred that AAC is useful for particle classification and size-resolved measurements for relatively larger particles in the submicron regime. Furthermore, 85nm is a reasonable lower limit for CCN measurements of low-hygroscopicity aerosols. Low-hygroscopicity aerosols (predominantly organics with $\kappa \leq 0.2$; Petters & Kreidenweis, 2007; Vu et al., 2019; J. Wang et al., 2019; Xu et al., 2014) do not activate readily at smaller particle sizes and atmospherically relevant supersaturations ($<1\%$). The laboratory number size distribution measurements for such aerosols are reliable at low to mid-range supersaturations with the AAC-CCNC setup.

The uncertainty analysis in this work shows that size-resolved aerodynamic measurements are precise. However, the accuracy of the aerosol hygroscopicity

estimates from aerodynamic measurements is low; this is seen from the lack of agreement between aerodynamic diameter-derived κ and previously reported well-accepted κ values of sucrose. The aerodynamic diameter can be converted to a volume equivalent diameter if an additional aerosol classifier is used in series with the AAC (Yao et al., 2020). The size-resolved dynamic shape factor (χ) was measured using the DMA-AAC setup to convert the aerodynamic diameters to their respective volume equivalent diameters. The volume equivalent diameter of the particles was estimated by incorporating χ and known aerosol density (Eq. 2.14). The aerosol hygroscopicity estimates using volume equivalent diameters in the analysis showed good agreement with previously reported sucrose hygroscopicity values in literature.

Overall, the AAC-CCNC coupling offers a promising tool for obtaining size-resolved CCN activity measurements for challenging low-hygroscopicity organic aerosols. Using the AAC-CCNC setup, the measurements and activation properties are obtained in terms of aerodynamic diameter. However, the sole use of aerodynamic diameters should be avoided in the context of CCN activity. CCN activity depends on particle size and chemistry; aerodynamic diameters assume a constant density of 1000kg/m^3 , therefore neglecting the densities of different chemical species. The use of aerodynamic diameters for CCN analysis has significant consequences for the representation of aerosols and for the estimation of hygroscopicity (κ). Future work should add the dynamic shape factor and particle density in aerodynamic diameter-derived CCN activity analysis. The additionally known parameters improve agreement between the measured and theoretical κ values. It should also be noted that the uncertainty calculations presented in this manuscript solely focus on the uncertainties

from changing sizing instrumentation used before the CCN counter. That is, if one uses the same CCN counter, the uncertainty in the supersaturation (from changes in the ΔT , flow rate, and ΔP) are constant. One can add additional calculations of error in supersaturations by referring to Roberts & Nenes, (2005) and Rose et al., (2008). If the user intends to perform CCN measurements using the AAC and DMA, they should run the CCN measurements at the same time.

Appendix 2A

Summary: This appendix contains the CCNC supersaturation calibration data, calculation of necessary AAC measurement parameters, methods for uncertainty analysis of number concentration data, description of the dynamic shape factor measurement method, and DMA-based CCN measurement data and associated uncertainties.

2A.1 CCN counter (CCNC) calibration

Dry particles are subjected to supersaturated conditions when passing through the CCNC column. The CCNC supersaturation is set by applying an axial temperature gradient for specified flow and pressure gradient within the CCNC column. Theoretically, the temperature gradient stays constant if the CCNC parameters are maintained constant. However, in practice there are fluctuations in the CCNC parameters which can cause deviations in the instrument supersaturation from the set supersaturation. These deviations in CCNC supersaturations were resolved by calibrating the CCNC. Calibration was performed by following the procedure described by Rose et al. (2008).

Table 2A.1 $(\text{NH}_4)_2\text{SO}_4$ CCN Counter (CCNC) calibration data

Supersaturation Setting (%)	Calibrated Supersaturation (%)	Critical Dry Diameter (nm)
0.2	0.215	75.6 ± 2
0.3	0.308	61.7 ± 0.6
0.4	0.402	52.3 ± 0.6
0.5	0.493	45.5 ± 1
0.6	0.586	41.2 ± 0.4
0.8	0.771	34.7 ± 0.7
1.0	0.957	29.6 ± 0.6

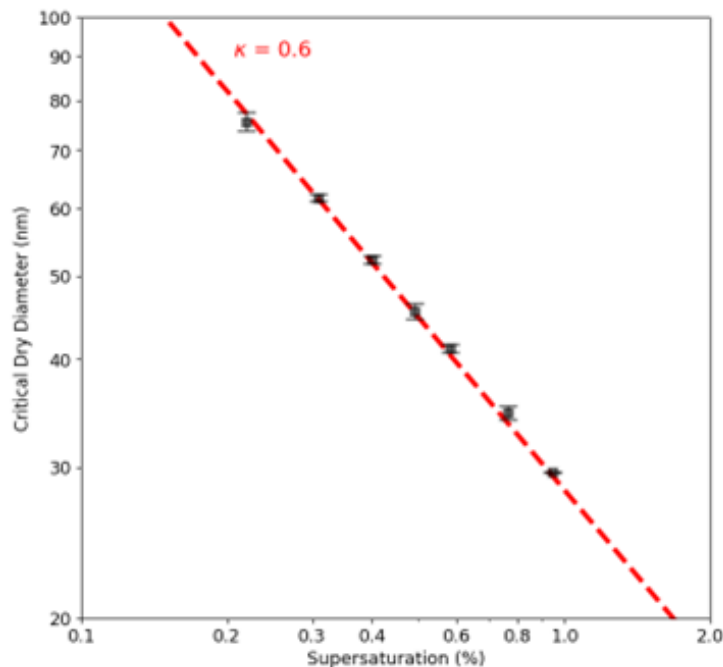


Figure 2A.1. CCN counter (CCNC) calibration using $(\text{NH}_4)_2\text{SO}_4$ CCN measurements from DMA-based setup. The critical dry electrical mobility diameters are plotted against their respective instrument supersaturations and are overlayed against the $\kappa = 0.6$ line that corresponds to pure ammonium sulfate (Petters and Kreidenweis (2007)).

2A.2 Estimation of AAC measurement parameters

2A.2.1 Cunningham's Slip Correction Factor

Particles experience a drag force when they move along a fluid of given viscosity. Stokes' law provides a solution for estimating the viscous drag in laminar flow regimes where the Reynold's number $\ll 1$ (Crowder et al., 2002). An underlying assumption in the estimation of this viscous drag is that there is no slip at the particle surface when particles move through the fluid. However, this assumption starts to break down when the particle size becomes several times larger than the mean free path. In such cases, the drag force needs to be corrected for the slip to maintain a constant flow velocity.

Cunningham derived a correction factor for the drag force, which is commonly expressed as a function of particle size (d) and is as follows,

$$C_c(d) = 1 + \frac{\lambda}{d} \cdot \left(\alpha_{C_c} + \beta_{C_c} \cdot \exp\left(-\gamma_{C_c} \cdot \frac{d}{\lambda}\right) \right) \quad (2A.1)$$

where $\alpha_{C_c} = 2.33$, $\beta_{C_c} = 0.966$ and $\gamma_{C_c} = 0.4985$ (Kim et al. (2005)). λ in Eq. (2A.1) is the mean free path of the surrounding gas particles which is estimated as follows (Eq. (2A.2)),

$$\lambda = \lambda_0 \cdot \left(\frac{T}{T_0}\right)^2 \cdot \left(\frac{P_0}{P}\right) \cdot \left(\frac{T_0+S}{T+S}\right) \quad (2A.2)$$

where λ_0 is the air mean free path at the reference conditions of 67.3 nm , T is the air temperature in the classifier in K , T_0 is the reference temperature of 296.15 K , P is the air pressure in the classifier in Pa , P_0 is the reference pressure of 101325 Pa and S is the Sutherland constant for air of 110.4 K .

2A.2.2 Cunningham's Slip Correction Factor

The AAC transfer function includes non-ideal particle behavior using the transmission efficiency (λ_Ω) and transfer function width factor (μ_Ω). The λ_Ω of the AAC is empirically determined using Eq. (2A.3) (Johnson et al. (2018)),

$$\lambda_\Omega = \lambda_D \cdot \lambda_e \quad (2A.3)$$

where λ_e is the entrance/exit transmission efficiency of the classifier, and λ_D is the diffusional transmission efficiency. λ_e for the AAC has been typically observed as 0.8. λ_D is given as,

$$\lambda_D = \begin{cases} 0.819e^{-11.5\delta_{dep}} + 0.0975e^{-70.1\delta_{dep}} + 0.0325e^{-179\delta_{dep}} & \text{if } \delta_{dep} \geq 0.007 \\ 1 - 5.5\delta_{dep}^{2/3} + 3.77\delta_{dep} + 0.814\delta_{dep}^{4/3} & \text{if } \delta_{dep} < 0.007 \end{cases} \quad (2A.4)$$

where δ_{dep} in Eq. (2A.4) is a size-dependent deposition parameter and is given as,

$$\delta_{dep}(d) = \frac{L_{eff} \cdot D(d)}{Q_a}, \text{ such that } L_{eff} \text{ is the effective deposition length of the AAC and}$$

has a value of 46m, $D(d)$ is the size-dependent diffusion coefficient of the particles,

and Q_a is the aerosol flow rate.

2A.3 Sigmoidal fitting for size-resolved activation ratio

The critical dry diameter ($D_{p,50}$) for an aerosol at a given supersaturation is determined with the help of the size-resolved activation ratio (denoted by $\frac{N_{CCN}}{N_{CN}}$). The $\frac{N_{CCN}}{N_{CN}}$ for a single-component aerosol population is known to fit a sigmoidal function with one plateau. The half-maximum point of the sigmoidal fit then corresponds to the $D_{p,50}$ of the aerosol at the given supersaturation. A 4-parameter sigmoidal function was applied to the $\frac{N_{CCN}}{N_{CN}}$ v/s D_p measurements of sucrose at different supersaturations to calculate their respective $D_{p,50}$. The sigmoidal function used fit the data is shown as Eq. (2A.5).

$$\frac{N_{CCN}}{N_{CN}} = \frac{A_1 - A_2}{1 + e^{(D_p - D_{p,50})/dx}} - A_2 \quad (2A.5)$$

A_1 and A_2 are the minimum and maximum of the sigmoid respectively, dx is the slope of the sigmoid. The sigmoid fit was scaled over a range of 0.0 to 1.0, i.e., A_1 and A_2 were set to 0 and 1, respectively.

2A.4 Uncertainty estimation for size-resolved counting and activation measurements

If N generally denotes the particle counts from a CPC or CCNC, and Q_a denotes the aerosol flow rate, the relative uncertainty in the measured particle concentration (ϵ_C) is determined from the relative counting uncertainty (ϵ_N) and the relative flow rate uncertainty (ϵ_{Q_a}) as follows (Moore et al. (2010)),

$$\epsilon_C^2 = \epsilon_N^2 + \epsilon_{Q_a}^2 \quad (2A.6)$$

Particles are assumed to be randomly distributed throughout the sample. Poisson statistics can be used to estimate ϵ_N as $\frac{\sigma_N}{N} \approx N^{-1/2}$. For the CCN counter (CFSTGC), the ϵ_{Q_a} is generally $\sim 4\%$. For the TSI CPC 3776, ϵ_{Q_a} is about 2% . The uncertainties in the particle concentrations can be used to propagate the uncertainties in the size-resolved activation ratio ($R_a = \frac{C_{CCN}}{C_{CN}}$). The uncertainties in size-resolved activation ratio (ϵ_{R_a}) can be denoted as,

$$\epsilon_{R_a}^2 = \epsilon_{CCNN}^2 + \epsilon_{CCN}^2 = \epsilon_{NCCN}^2 + \epsilon_{N_{CN}}^2 + \epsilon_{Q_{CCN}}^2 + \epsilon_{Q_{CN}}^2 \quad (2A.7)$$

$$\epsilon_{R_a}^2 = N_{CCN}^{-1/2} + N_{CN}^{-1/2} + \epsilon_{Q_{CCN}}^2 + \epsilon_{Q_{CN}}^2 \quad (2A.8)$$

Eq. (2A.7) can be simplified to Eq. (2A.8). Under standard experimental conditions, for most atmospherically relevant CN concentrations, ϵ_{CCN} is 7% or less, while ϵ_{CCNN} is less than 17% . The subsequent ϵ_{R_a} is less than 18% (Moore et al. (2010)).

2A.5 Shape factor measurements

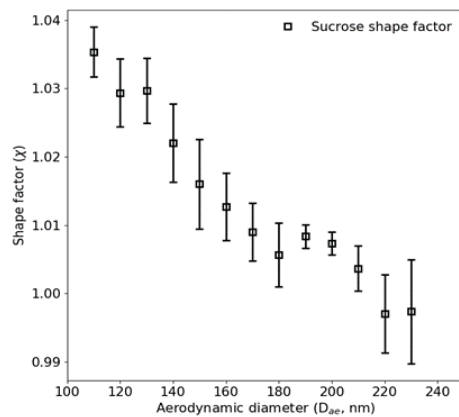


Figure 2A.2. Sucrose dynamic shape factor data for sucrose, collected using an AAC-DMA setup (Tavakoli and Olfert (2014)). The size-resolved shape factor is plotted against the aerodynamic diameter measurements of sucrose. Shape factor relates aerosol density with the particle size and was used to derive volume equivalent diameters corresponding to the respective aerodynamic diameters (details in sections 3 and 4 of main text). The above figure shows that the shape factor of sucrose is close to 1 over a range of sizes, which implies that sucrose particles are mostly spherical.

2A.6 DMA-CCNC measurements

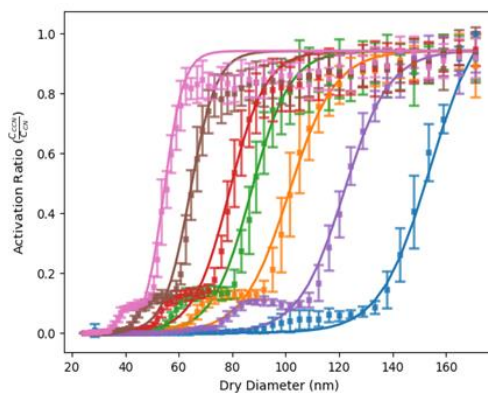


Figure 2A.3. Size-resolved activation data of sucrose determined using CCN measurements using the DMA-based setup. The activation ratios are shown with respect to electrical mobility diameter of the particles.

Table A2.2. Sucrose DMA-based CCN Activation Data. Uncertainties in Critical Dry Diameters Using Electrical Mobility Measurements from a DMA-based Setup

Instrument	Supersaturation (%)	Critical Dry Diameter (nm)	Uncertainties in Critical Dry Diameters (%)
	0.215	153.3	± 7.42
	0.308	122.3	± 7.11
	0.402	99.1	± 6.91
	0.493	87.2	± 6.75
	0.586	78.2	± 6.67
	0.771	64.5	± 6.23
	0.957	55.3	± 6.41

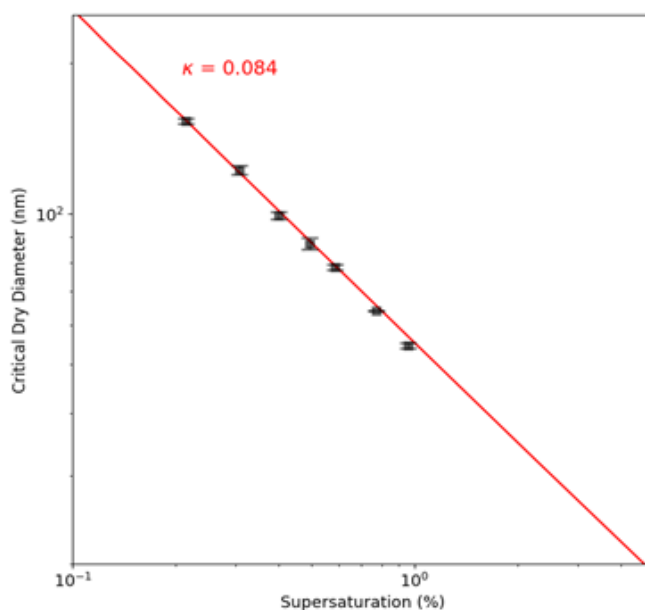


Figure 2A.4. CCN measurements of sucrose from DMA-based setup. The activation measurements overlaid with $\kappa = 0.084$ line which corresponds to pure (ideal) sucrose.

Chapter 3: Droplet Growth Analysis and Hygroscopicity Parameterization using an Adsorption-Solubility Partitioning Hybrid Model

Access published article at:

Gohil, K., Mao, C.-N., Rastogi, D., Peng, C., Tang, M., and Asa-Awuku, A.: Hybrid water adsorption and solubility partitioning for aerosol hygroscopicity and droplet growth, Atmos. Chem. Phys., 22, 12769–12787, <https://doi.org/10.5194/acp-22-12769-2022>, 2022.

3.1 Abstract

In this work, the Cloud Condensation Nuclei (CCN) activity and subsaturated droplet growth of phthalic acid (PTA), isophthalic acid, (IPTA) and terephthalic acid (TPTA) was studied. Kohler Theory can be effectively applied for hygroscopicity analysis of PTA due to its higher aqueous solubility compared to IPTA and TPTA. As with other hygroscopicity studies of partially water-soluble and effectively water insoluble species, the supersaturated and subsaturated hygroscopicity derived from (KT) principles do not agree. To address the disparities in the sub- and supersaturated droplet growth, a new analytical framework called the Hybrid Activity Model (HAM) was developed. HAM incorporates the aqueous solubility of a solute within an adsorption-based activation framework. Frenkel-Halsey-Hill (FHH)-Adsorption Theory (FHH-AT) was combined with the aqueous solubility of the compound to develop HAM. Analysis from HAM was validated using laboratory measurements of pure PTA, IPTA, TPTA and PTA-IPTA internal mixtures. Furthermore, the results generated using HAM were tested against traditional KT and FHH-AT to compare their water uptake predictive capabilities. A single-hygroscopicity parameter was also developed based on the HAM framework. Results show that the HAM based

hygroscopicity parameter based can successfully simulate the water uptake behavior of the pure and internally mixed samples. Results indicate that the HAM framework may be applied to aerosols of varying chemical structures and aqueous solubility. This is the first time the adsorption-based droplet growth is combined with solubility partitioning to formulate a hybrid droplet growth framework. Chapters 4 and 5 demonstrate the application of this hybrid framework for CCN activity analysis of soot proxies and cloud response estimation, respectively.

3.2 Background

Aerosols can affect the global radiative balance and climate by either absorption and scattering of radiation (direct effect of aerosols), or by acting as Cloud Condensation Nuclei (CCN) resulting in cloud formation (indirect effect of aerosols). While the direct effect is well-studied and understood, the indirect effect is still the most significant source of uncertainties in climate forcing. This is primarily attributed to the poor understanding of the CCN activity and hygroscopic properties of organic aerosols (Talley et al., 2013). Organic aerosols are ubiquitous in the atmosphere. They contribute significantly to the atmospheric aerosol mass burden and account for 20-90% of total tropospheric fine aerosol mass (Kanakidou et al., 2005). Furthermore, organic aerosols can mix with other organic and inorganic species in the atmosphere to modify their the CCN activity and hygroscopic properties (e.g., but not limited to Baustian et al., 2012; Fofie et al., 2018; Padró et al., 2012; Sánchez Gácita et al., 2017; Schill et al., 2015; H. Su et al., 2010; Vu et al., 2019). Consequently, the CCN activity

of organic aerosols needs to be well-characterized to reduce uncertainties in the climate forcing due to indirect effect of aerosols.

Much of the CCN related research focuses on highly water-soluble and sparingly water-soluble compounds (e.g., but not limited to Asa-Awuku et al., 2010; Jing et al., 2018; Samy et al., 2010; Taylor et al., 2017). For such compounds, Köhler Theory (KT) is traditionally applied to study their CCN activity and predict their hygroscopic properties. KT explains droplet growth by combining the water activity described using Raoult's law (solute effect) with the Kelvin effect (curvature effect) (Köhler, 1936). KT is applied under the assumptions of infinite and spontaneous water solubility of the solute and an infinitely dilute water droplet solution (Asa-Awuku et al., 2010; Huff Hartz et al., 2006; Barati et al., 2019; Dawson et al., 2020). That is, if the aerosol instantaneously disassociates in water, traditional KT aptly explains the droplet growth driven by molar volume and droplet surface tension (Köhler, 1936; Sullivan et al., 2009; Giordano et al., 2015). These assumptions work well for many aerosols that are highly soluble ($> 10^{-1} \text{ m}^3 \text{ solute } m^{-3} \text{ water}$; Petters and Kreidenweis 2007) that form thermodynamically ideal solutions in water. Moreover, the water uptake characteristics of such highly water-soluble compounds can be predicted with a single KT hygroscopicity parameter (κ) (Petters and Kreidenweis, 2007). The κ parameter derived in this way is defined as the “intrinsic κ ” of the aerosol.

However, there is an abundance of partially and effectively water insoluble organic compounds in the atmosphere. The CCN activity of such limited water solubility compounds has been predicted by incorporating the compound solubility in traditional

KT (Huff Hartz et al., 2006; Petters and Kreidenweis, 2008; Riipinen et al., 2015) prescribed a “solubility partitioning” framework using the traditional KT for CCN analysis of pure and internally mixed aerosols in a large range of aqueous solubility. Furthermore, a modified κ parameter accounting for the water solubility of the aerosols can also be derived based on this solubility-modified KT framework (Petters and Kreidenweis, 2008; Sullivan et al., 2009; Nakao, 2017). This modified hygroscopicity varies over the course of droplet growth and is dependent on the droplet size. Despite the modifications to traditional KT, differences have been observed between the experimental κ with either the intrinsic or solubility modified κ of the aerosol. Specifically, aerosols with solubility $< 5 \times 10^{-4} \text{ m}^3 \text{ m}^{-3}$ are “effectively insoluble” (Petters and Kreidenweis, 2008) and do not agree with the water uptake predictions using either traditional or solubility-modified KT.

Droplet growth can be explained for the effectively insoluble organic compounds using a water adsorption framework. CCN activity from adsorption can be modeled by combining the water activity from an adsorption isotherm with the Kelvin effect (e.g., but not limited to Goodman et al., 2001; Hatch et al., 2012; Henson, 2007; Kumar et al., 2011a, 2011b; Kumar, Nenes, et al., 2009; Kumar, Sokolik, et al., 2009; Malek et al., 2022; Rahman & Al-Abadleh, 2018; Tang et al., 2016). One such mathematical formulation accounts for adsorption using the Frenkel-Halsey-Hill (FHH) isotherm (Sorjamaa and Laaksonen, 2007). The FHH isotherm consists of 2 empirical parameters denoted as A_{FHH} and B_{FHH} . A_{FHH} explains the interaction of the first adsorbed water layer and the particle surface, while B_{FHH} explains the interaction between subsequently adsorbed water layers and the particle. The FHH isotherm combined with

the Kelvin effect provides the FHH-Adsorption Theory (FHH-AT) for CCN activity analysis. Parameters specific to a given aerosol species can be experimentally determined by fitting FHH-AT through their CCN activity measurements. Studies have so far explored the application of the FHH-AT for CCN analysis of several water-insoluble compounds (e.g., but not limited to (Dalirian et al., 2018; Hatch et al., 2014, 2019; Kumar et al., 2009b, 2011a, b, 2009a; Laaksonen et al., 2020a, 2016)). FHH-AT consists of 2 empirical parameters as opposed to a single κ parameter in traditional or modified KT. Additionally, an important assumption in FHH-AT and other similar adsorption models is that the aerosols are treated as completely water insoluble. Only recently, FHH-AT has been shown to work for insoluble particles with water-soluble and molecular level functionalized surfaces (Mao et al., 2022). Thus, there now exists a transitional regime from a soluble to water-insoluble models to correctly describe droplet growth.

This work probes several aspects of water uptake to develop a comprehensive model to describe droplet formation of effectively water insoluble to partially soluble organics. Specifically, a new CCN activity model is developed by combining the components of the solubility modified KT with the FHH isotherm. In this work, the newly developed model will be referred to as the Hybrid Activity Model (HAM). Within the HAM framework, the aerosol particles are treated as completely water insoluble at the start of the droplet growth process. The particle continues to fractionally dissolve into the aqueous phase as droplet growth progresses. While the dissolved fraction of the aerosol contributes to droplet growth via Raoult's law, the undissolved fraction contributes to droplet growth via adsorption of water on the

surface. Furthermore, this work discusses the development of a single κ parameter based on HAM that includes the effect of aqueous solubility on droplet growth for a compound that would be otherwise treated as effectively water insoluble.

The development and application of HAM is explained using the experimental droplet growth measurements of 3 low water solubility structural isomers of benzene di-carboxylic acid – Phthalic acid (PTA), Isophthalic acid (IPTA) and Terephthalic acid (TPTA). PTA, IPTA and TPTA are among some of the significant benzene polycarboxylic acids detected in the atmosphere (Fu et al., 2009; Haque et al., 2019; Kanellopoulos et al., 2021; Kunwar et al., 2019; H. Liu et al., 2019; Meng et al., 2018; Singh et al., 2017; Yassine et al., 2020). PTA and its isomers are known to be tracers of benzantracene, naphthalene-1 and methylnaphthalene-1, prominent emissions from combustion (Kleindienst et al., 2012a; Al-Naiema et al., 2020a; He et al., 2018). PTA is also a byproduct of pre-ozonation of fulvic acid, another significant marker of biomass burning emissions (Zhong et al., 2017a, b). IPTA and TPTA are also predominantly produced from biomass burning and emissions of automobile exhausts (Kawamura and Kaplan, 1987; Mkoma and Kawamura, 2013; Balla et al., 2018; Al-Naiema and Stone, 2017).

The hygroscopic properties of PTA, IPTA and TPTA have been studied in the past (e.g., but not limited to Huff Hartz et al., 2006; Petters & Kreidenweis, 2007; W. Wang et al., 2021). However, a comprehensive comparison and discussion of the effects of structural isomers on the droplet growth of benzene-dicarboxylic acids does not exist. Vapor sorption measurements of bulk PTA indicate hygroscopic growth at high

ambient relative humidity (> 90% RH) (Wang et al., 2021). (Hämeri et al., 2002) used Tandem Differential Mobility Analyzer (TDMA) technology and observed that PTA aerosol did not grow in subsaturated conditions. Other studies show PTA internal mixtures with inorganics can deliquesce under subsaturated conditions (Jing et al., 2016, 2018). Furthermore, Huff Hartz et al., (2006) showed that PTA could activate as CCN at 1% supersaturation. The activation was consistent with KT that assumed complete dissolution with no solubility considerations. Petters & Kreidenweis, (2007) report the $\kappa = 0.059$ and 0.051 for PTA under sub- and supersaturated conditions, respectively. To our knowledge only one other paper has measured droplet growth of IPTA. Huff Hartz et al., (2006) found that IPTA behaves as an insoluble compound and does not obey traditional KT. Few studies have measured hygroscopic properties of TPTA, but not in context of CCN (Diniz et al., 2017; Zhao et al., 2021). To our knowledge, the adsorption models have not been applied for the CCN analysis of PTA, IPTA or TPTA.

Overall, HAM is used in this paper to extensively study the hygroscopic properties of PTA, IPTA and TPTA that are not yet cogently known. In addition to the aforementioned pure compounds, the internal mixtures of PTA and IPTA are also studied. The compounds and their mixtures considered in this work are useful and help us understand the efficacy of different CCN models to describe the droplet growth associated with different organic CCN with varying aqueous solubilities. The experimental CCN measurements provide an efficient means to validate the application of the newly developed HAM. In the following sections, the experimental setup is described that was used in this study to obtain droplet growth data for PTA, IPTA and

TPTA and PTA-IPTA internal mixtures. Then, the theory and formulation of HAM is described based on KT and FHH-AT, and how it was implemented for droplet growth analysis of aerosols. This is followed by the derivation of the single κ parameter using the HAM framework, and then the discussion of results and conclusions of this study.

3.3 Experimental Section

3.3.1 Compounds and Aerosol Generation

Phthalic acid (PTA, 1,2 – benzenedicarboxylic acid, >99.5%, Sigma-Aldrich®) and terephthalic acid (TPTA, 1,4 – benzenedicarboxylic acid, 98%, Sigma-Aldrich®) and Isophthalic acid (IPTA, 1,3 – benzenedicarboxylic acid, >99%, Fisher Scientific®) were used as representative compounds for the aromatic acid aerosols (AAAs, hereafter, shown in Figure 13). The physical properties of PTA, IPTA and TPTA are summarized in Table 1. Aqueous solutions of PTA, IPTA and TPTA were formed by mixing 30 mg of acid in 500 ml of ultrapure water (Milli-Q or Millipore®, 18.2M Ω cm⁻¹). Additionally, 3 internally mixed solutions of PTA and IPTA were also prepared by mixing 30 mg of dry acid mixture in 500 ml ultrapure water. The internally mixed solutions were prepared for 3 different mass fractions of PTA and IPTA (5:1, 1:1 and 1:5 wt/wt). To facilitate the dissolution of solute in aqueous solution, all the solutions were sonicated for 2 hours in a warm water bath maintained at ~ 40 °C to create a uniform suspension. The solution was subsequently cooled and maintained at 20 °C. Polydisperse aerosols were generated using a Collison Nebulizer (TSI Atomizer 3076). The wet aerosol particles were then passed through a series of 2 silica gel diffusion

dryers (TSI 3062) to remove moisture (to RH < 10%). The dry particles were then classified for supersaturated and subsaturated measurements.

Table 2. Physical and chemical properties of AAA compounds

Compounds	Molecular weight (M_s , g mol ⁻¹)	Density (ρ_s , g cm ⁻³)	Solubility (C , m ³ m ⁻³)
Phthalic acid	166.14	1.59	3.77×10^{-3}
Isophthalic acid	166.14	1.53	7.84×10^{-5}
Terephthalic acid	166.13	1.52	1.12×10^{-5}

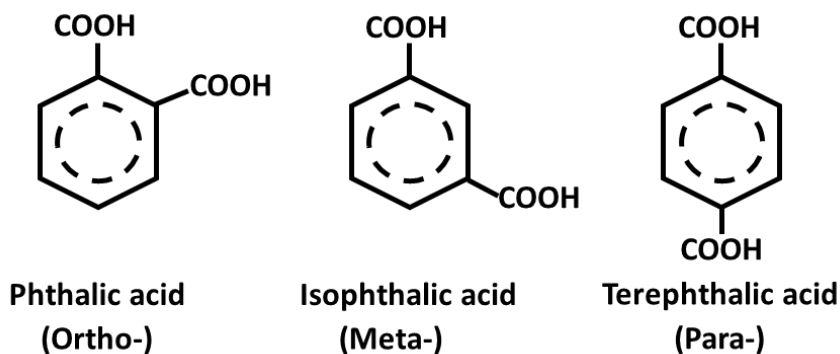


Figure 13. Molecular structures of the aromatic acid aerosols used in this work.

3.3.2 CCNC Experiments for Supersaturated Measurements and Data Analysis

A continuous flow stream-wise thermal gradient Cloud Condensation Nuclei Counter (CCNC, Droplet Measurement Technologies (DMT) (Roberts & Nenes, 2005 - CCN 100) was used for the droplet activation measurements (e.g., but not limited to (Engelhart et al., 2008a; Moore et al., 2010; Tang et al., 2016; Barati et al., 2019; Vu et al., 2019)) of AAAs in supersaturated conditions. Briefly described here, polydisperse aerosol was generated and dried as described in Sect. 2.1. The electrical

mobility aerosol size from 8 nm to 352 nm was measured with an electrostatic classifier (TSI 3936, DMA 3081, and CPC 3776) every 2.25 minutes. The size-selected aerosols exiting the DMA were then split into 2 streams. A Condensation Particle Counter (CPC, TSI 3776) samples the first stream at 0.3 L min^{-1} to measure total dry particle concentration (C_{CN}), and the CCNC samples the second stream at 0.5 L min^{-1} and constant supersaturation to measure activated particle (droplet) counts (C_{CCN}). A sheath flow rate of 8 L min^{-1} was applied to maintain a sheath-to-sample ratio of 10:1 across the experimental setup. The measurements were repeated 10 times for each supersaturation. Furthermore, the measurements were performed over supersaturations ranging between 0.6% and 1.6%. CCNC supersaturations were calibrated using ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, AS) aerosol (Sigma-Aldrich®, >99.9%). AS data used for CCN calibration is provided in the appendix (Section 3A.1).

PyCAT 1.0 (Gohil and Asa-Awuku, 2022) was employed for data processing, analysis, and visualization of the CCN measurements. CCN size-resolved activation curves were generated at a fixed supersaturation (S) as $\left(\frac{C_{CCN}}{C_{CN}}\right)$ across a range of dry particle diameters (D_{dry}). The volume equivalent diameters were used to represent particle sizes that were obtained by combining size-resolved particle dynamic shape factor (χ) with measured electrical mobility diameters (see appendix Figure 3A.3). Multiple charging errors were removed from the size-resolved activation ratio following a combination of charge correction algorithms from Gunn (1956) and Wiedensohler (1988). Following this, a Boltzmann sigmoidal fit expressed as,

$$y = \frac{A_1 - A_2}{1 + e^{\frac{x - x_0}{dx}}} - A_2 \quad (3.1)$$

was applied to the size-resolved activation ratio curve. In Eq. (3.1), y is the dependent variable $\frac{C_{CCN}}{C_{CN}}$, A_1 and A_2 are the minimum and maximum of the sigmoid respectively, dx is the slope of the sigmoid, x_0 is the inflection point of the sigmoid (generally the midpoint of the sigmoid), and x is the independent variable (D_{dry}). The sigmoid fit is typically scaled over a range of 0.0 to 1.0, and so x_0 corresponds to the critical dry diameter ($D_{dry,c}$) at the instrument supersaturation and is physically defined as the size at which 50% of all particles are activated.

3.3.3 H-TDMA Experiments for Subsaturated Measurements

A Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) measured droplet growth of AAAs in the subsaturated regime. The H-TDMA setup has been previously explained in detail (Rader and McMurry, 1986; Cruz and Pandis, 1997) and only a brief description is provided here. Dried polydisperse aerosol were first charged with a Kr-85 bipolar aerosol neutralizer (TSI 3081). Monodisperse charged particles with a dry diameter (D_{dry}) were size selected using a Differential Mobility Analyzer (DMA 1). The sample and the sheath flow rates were maintained at 0.3 L min^{-1} and 3.0 L min^{-1} respectively (i.e., sheath-to-sample flow ratio = 10:1). The size-selected particles from DMA 1 were then exposed to $95 \pm 0.46\%$ RH using a nafion humidification membrane (PermaPure M.H series). The humidified aerosol stream was then passed through the second DMA (DMA 2) that was equilibrated to a constant RH. DMA 2 was coupled with a Condensation Particle Counter (CPC, TSI 3756) and operated in Scanning Mobility Particle Sizer (SMPS) mode. The median wet diameter (D_{wet}) of the size-resolved number concentration of the humidified aerosol stream from

DMA 2 was reported. D_{wet} was used as the approximate final size to which the particles of size D_{dry} would grow under $95 \pm 0.46\%$ RH conditions. The hygroscopic growth factors (G_f) were obtained by taking the ratio of D_{wet} with respective D_{dry} ,

$$G_f = \frac{D_{wet}}{D_{dry}} \quad (3.2)$$

The RH of H-TDMA setup was calibrated using ammonium sulfate (see Figure 3A.1; Taylor et al. 2011). $((\text{NH}_4)_2\text{SO}_4, \text{AS})$ aerosol (Sigma-Aldrich®, > 99.9% purity). Calibration data is found in the appendix section 3A.1.

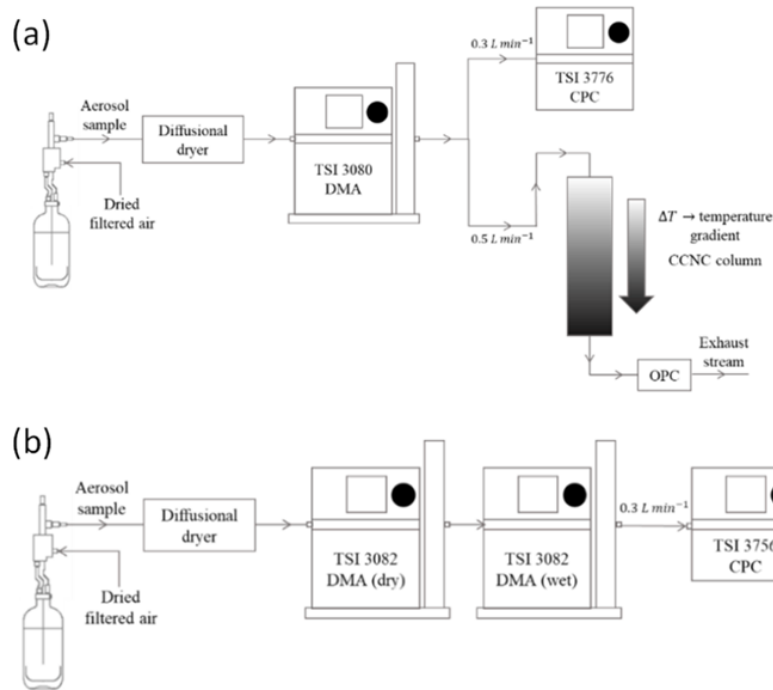


Figure 14. (a) Schematic of a typical CCN measurement setup under supersaturated conditions. The DMA and the CPC collectively operate as an SMPS to obtain a distribution of dry particles. The CCNC is connected in parallel and provides the distribution of activated particles. (b) Schematic of a typical H-TDMA setup for subsaturated droplet growth measurements. The dry DMA (DMA 1) selects dry particles of a specified size. The classified particles are then humidified and passed through the wet DMA (DMA 2) and the CPC operating as an SMPS to generate the droplet distribution.

3.3.4 VSA Experiments for Subsaturated Measurements

A vapor sorption analyzer (VSA, TA Instruments New Castle, DE, USA) setup was used for the hygroscopicity measurements of bulk samples in the subsaturated regime. Mass change in AAAs as a function of RH (5-95%) was measured at 25 °C. The instrument setup for the VSA has been described in detail in literature (Gu et al., 2017), and thus, experimental procedure is briefly explained here. During each experiment, bulk samples were first dried at <1% RH, then the RH was incremented up to 90% with a 10% step and followed by a 5% step from 90 to 95%. A high-precision balance was used in the VSA to measure the sample mass at different RHs with a stated sensitivity of < 0.1 µg. For every RH, a $\leq 0.1\%$ change in the sample mass was considered as the standard for stabilization. The initial dry mass of AAA samples used in this measurement was typically around 1.0 mg. For each sample, a minimum of 3 experiments were performed. At every RH, the sample mass (m) was normalized with respect to the initial mass of the dry sample (m_0). Subsequently, the mass-based growth factor was calculated as $\frac{m}{m_0}$.

3.4 Water Uptake and Hygroscopic Theory and Analysis

3.4.1 Köhler Theory (KT)

The equilibrium supersaturation (S) can be estimated over a droplet as a function of its size (D_p) as,

$$S = a_{w,KT} \cdot \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D_p}\right) \quad (3.3)$$

where a_w is the water activity term, $\sigma_{s/a}$ is the droplet surface tension at the interface, M_w and ρ_w are respectively the molecular weight and density of water, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature. The water activity is mathematically expressed as $a_{w,KT} = \gamma_w x_w$, where γ_w and x_w are the activity coefficient and mole fraction of water in the droplet, respectively. In traditional Kohler Theory (KT), the water activity is approximated as $a_{w,KT} = x_w$ (Raoult's law), which assumes infinite dilution and complete dissolution of the solute. Furthermore, $\sigma_{s/a}$ is approximated as the surface tension of a pure water droplet. The exponential quantity is the Kelvin term that describes the curvature effect. The solute effect and curvature effect are competing effects that describe droplet growth – the solute effect accounts for the water vapor pressure drop over the droplet due to the aerosol particle, and the curvature effect accounts for the water vapor rise over the droplet due to surface tension reduction.

3.4.2 Frenkel-Halsey-Hill (FHH) Adsorption Theory (FHH-AT)

Traditional KT, with or without the explicit treatment of aerosol solubility, can be effectively applied for highly soluble species. However, for partially or completely insoluble species Raoult's law is substituted with adsorption isotherms to model water uptake behavior. One such isotherm is the Frenkel-Halsey-Hill (FHH) adsorption isotherm. The original FHH adsorption isotherm is a physically based framework that

defines water activity through multilayer water adsorption as a function of relative surface coverage (θ , or the number of adsorbed water monomolecular layers). The surface coverage can be mathematically formulated similar to that in the Brunauer-Emmett-Teller multilayer adsorption model (Henson, 2007), which relates the θ to the Gibbs' free energy change associated with the adsorption. For CCN activity and droplet growth applications, the FHH isotherm is typically expressed as follows (Sorjamaa and Laaksonen, 2007),

$$a_{w,FHH} = \exp(-A_{FHH}\theta^{-B_{FHH}}) \quad (3.4)$$

where A_{FHH} and B_{FHH} are FHH fit parameters that describe the intermolecular interactions responsible for the adsorption of water on particle surfaces. A_{FHH} describes the interactions between the particle surface and first adsorbed water monolayer. B_{FHH} describes the interactions between successively adsorbed monolayers. A_{FHH} and B_{FHH} regulate the amount of water adsorbed on the particle surface and the radial distance up to which attractive forces can contribute to adsorption of water, respectively. θ in Eq. (3.4) is expressed as $\frac{D_p - D_{dry}}{2 \cdot D_w}$ where D_p and D_{dry} have been previously defined, and D_w is the size of the water molecule. The mathematical representation for the FHH-AT is analogous to traditional KT, and combines the FHH isotherm with the Kelvin term (Sorjamaa and Laaksonen, 2007; Kumar et al., 2009b) such that,

$$S = a_{w,FHH} \cdot \exp\left(\frac{4\sigma_w M_w}{RT \rho_w D_p}\right) \quad (3.5)$$

The FHH parameters can be empirically determined for any aerosol species from their droplet growth measurements (Kumar et al. 2009a). For measurements in supersaturated environments, A_{FHH} and B_{FHH} are determined from least square minimization of the experimental data with the maxima of the FHH-AT equilibrium curves (Kumar et al., 2011a, 2011b; Kumar et al., 2009a, 2009b). A higher value of A_{FHH} implies a higher water adsorption, and a smaller value of B_{FHH} implies stronger attractive forces over larger distances. It has been observed that B_{FHH} has a larger influence on the shape of the adsorption isotherm, and hence strongly drives CCN activation using FHH-AT (Kumar et al., 2009b; Hatch et al., 2019).

3.4.3 Hybrid Activity Model (HAM)

The assumptions of complete aqueous solubility or insolubility associated with KT and FHH-AT, respectively, represent two extreme possibilities of CCN activation and droplet growth. In this work, the two water activities were combined to develop a generalized “hybrid” water activity term. The droplet growth model thus obtained is called the Hybrid Activity Model, or HAM. Previous studies have discussed several other mathematical models built upon the traditional Köhler theory under different conditions. One such example is that of the solubility-partitioned Köhler theory (Petters et al., 2009; Riipinen et al., 2015) which explicitly includes the activity coefficient (γ_w) of the aerosol compounds to estimate the water activity. $\gamma_w \simeq 1$ in the traditional Köhler theory only under the assumption of the infinite dilution of the aqueous phase of the droplet, which holds true for several highly soluble aerosol species. For limited

water solubility compounds, γ_w is calculated by treating the aqueous solubility of the compound. However, even then the contribution of the undissolved fraction of the solute to the droplet growth is not treated. Another example of modified Köhler model is the ‘core-shell’ model Kumar et al. (2011b) that combines the FHH isotherm and Raoult’s law in a single framework to evaluate the contribution of the insoluble and soluble component of the mixture, respectively, on droplet growth. In the core-shell model, partial water solubility is not considered for any of the mixture components. HAM builds up on the concepts delineated by Kumar et al. (2011b) and Riipinen et al. (2015) and considers all particles as a ‘core-shell’ morphology, while also treating all the components as partially water-soluble. The general mathematical representation of HAM is as follows,

$$S = a_{w,HAM} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w D_p}\right) \quad (3.6)$$

where $a_{w,HAM} = a_{w,KT} \cdot a_{w,FHH}$, and the definitions of $a_{w,KT}$ and $a_{w,FHH}$ are provided in subsections 3.1 and 3.2, respectively.

HAM sandwiches different phases of droplet growth for any given particle in three stages. In stage 1, HAM assumes that a particle suspended in humidified ambient conditions does not dissolve at the start of the activation process (time, $t \rightarrow 0$). That is, droplet growth at $t \rightarrow 0$ occurs entirely due to the adsorption of a water monolayer on the particle surface and can be explained using the FHH isotherm. In stage 1,

$$a_{w,HAM,1} = a_{w,FHH} = \exp(-A_{FHH}\theta^{-B_{FHH}}) \quad (3.6a)$$

The FHH parameters (A_{FHH} , B_{FHH}) for any given species are determined by fitting the FHH-AT to the experimental data and can be subsequently used in the HAM framework.

Stage 2 begins as the droplet continues to grow and more water accumulates in the aqueous phase. In this stage, the particle starts dissolving and enters the aqueous phase. The fraction of particle mass that dissolves or enters the aqueous phase depends on the solubility of the compound. Moreover, the dissolved fraction of the particle can be estimated at each step of droplet growth using the solubility partitioning concept introduced by Riipinen et al. (2015). Briefly described here – a droplet comprises of a bulk dry (undissolved) phase and an aqueous (dissolved) phase. The bulk phase can be composed of one or more internally mixed species with varying water solubility. This causes the composition and core size of the bulk phase to vary dynamically during droplet growth. The amount of water in the aqueous phase increases as the droplet grows, thereby increasing the concentration of the compounds in the aqueous phase. There is a competition for dissolution between the compounds in the bulk phase which is dependent on their solubilities. Considering a dry particle consisting of n species with limited solubility, the undissolved mass fraction of a species i (χ_i) during droplet growth is expressed as (Riipinen et al. 2015),

$$\chi_i = 1 - \frac{\gamma_i \chi_i Y_{i,dry} c_{i,pure} m_w}{m_{i,dry} \sum_i \chi_i Y_{i,dry}} \quad (3.6a-1)$$

where γ_i is the activity coefficient, c_i ($g \text{ } g\text{H}_2\text{O}^{-1}$) is the solubility of the pure species, m_w is the mass of water in the droplet, $m_{i,dry}$ is the initial mass of the pure species in

the dry particle, and $Y_{i,dry}$ is the initial mole fraction of the pure species in the dry particle. Eq. (3.6a-1) implies that the dissolved mass fraction of the species i in the aqueous phase is given as $1 - \chi_i$. A set of n coupled equations are simultaneously solved to obtain χ_i for all n species in the mixture. χ_i is then used to calculate the mole fraction of species i dissolved in the aqueous phase (x_i) at any point during droplet growth. Subsequently, the KT water activity can be given as $a_{w,KT} = x_w = \frac{n_s}{n_s + n_w}$, where n_s and n_w are respectively the number of moles of solute and water in the aqueous phase. In stage 2, the contribution of the dissolved fraction of the compound in the aqueous phase (through Raoult's law) can be combined with the undissolved fraction in the solid phase (through the FHH isotherm) to generate the overall water activity term,

$$a_{w,HAM,2} = a_{w,KT} \cdot a_{w,FHH} = x_w \cdot \exp(-A_{FHH}\theta^{-B_{FHH}}) \quad (3.6b)$$

Eq. (3.6b) highlights the main difference between the models presented by Kumar et al. (2009a) and Riipinen et al. (2015).

Stage 3 begins when the droplet is large enough to accommodate enough water in the aqueous phase and dissolve the particle mass entirely. This point onward, the droplet growth can be explained using traditional KT. In stage 3,

$$a_{w,HAM,3} = a_{w,KT} = x_w \quad (3.6c)$$

Eq. (3.6a), (3.6b) and (3.6c) were combined to describe the water activity through the three stages of droplet growth in the HAM framework. Thus, HAM can effectively estimate the droplet growth across a wide range of aqueous solubilities. The HAM

combines 2 extremes represented by fully soluble and fully insoluble behavior in a single framework. Moreover, the HAM concept can also be applied to improve upon the single hygroscopicity parameterization (κ).

3.5 Hygroscopicity Parameterization – Single-Hygroscopicity Parameter (κ)

Commonly, the CCN activity and water uptake tendencies of any given compound is expressed using a single hygroscopicity parameter (κ). A theoretical κ is derived using a simple parameterization of the solute water activity term in the droplet growth model. Additionally, critical dry particle sizes can be combined with their supersaturations to experimentally determine κ . In the following subsections, the κ parameter derived from different models are explained.

3.5.1 KT Hygroscopicity

A single hygroscopicity parameter (κ) has been developed using the KT framework. κ can be defined through its effect on the water activity in the droplet as follows,

$$a_w^{-1} = 1 + \kappa \frac{V_s}{V_w} \quad (3.7)$$

where V_s is the dry particulate (solute) volume, and V_w is the volume of water in the droplet. κ obtained from Eq. (3.7) is a parameterized quantity determined from the water activity based on the Raoult's law. Using κ -based parameterization of a_w , Eq. (3.3) can be modified for any D_{dry} as,

$$S = \left(\frac{D_p^3 - D_{dry}^3}{D_p^3 - (1-\kappa) \cdot D_{dry}^3} \right) \cdot \exp \left(\frac{4\sigma_w M_w}{RT \rho_w D_p} \right) \quad (3.8)$$

For a given D_{dry} , the droplet size increases as the supersaturation above the droplet surface increases. Supersaturation increases until the point of activation, which is characterized using the critical wet droplet size ($D_{p,c}$). The supersaturation at the point of activation along with the corresponding D_{dry} and $D_{p,c}$ depend on the κ of the compound. κ of any compound in an aqueous phase is difficult to measure, but it can be theoretically approximated using the Raoult's law ($\kappa_{intrinsic}$). The $\kappa_{intrinsic}$ of any species (denoted using a subscript i) can be expressed as follows,

$$\kappa_{intrinsic,i} = \frac{\nu \rho_i M_w}{\rho_w M_i} \quad (3.9)$$

where ν is the Van't Hoff factor of the compound and is related to its aqueous dissociation, M_i and M_w are the molecular weights of the solute i and water, and ρ_i and ρ_w are the density of the solute i and water, respectively. $\kappa_{intrinsic,i}$ defined in Eq. (3.9) here is dependent only on solute composition and solvent (water) properties and is independent of size. $\kappa_{intrinsic}$ of a mixture can be computed using a volume average mixing rule with the Zdanovskii-Stokes-Robinson (ZSR) approximation as follows (Petters and Kreidenweis, 2007),

$$\kappa_{intrinsic} = \sum_i \epsilon_i \kappa_{intrinsic,i} \quad (3.10)$$

where ϵ_i is the volume fraction of i^{th} component in the dry particle and $\kappa_{intrinsic,i}$ is the intrinsic hygroscopicity parameter of the i^{th} component. ϵ_i in an internal mixture

of n components are estimated as $\epsilon_i = \frac{m_i/\rho_i}{\sum_i^n m_i/\rho_i}$, where m_i is the mass of the pure component i in the mixture. κ in Eq. (3.10) assumes complete aqueous solubility of the compound or mixture. Moreover, κ for a mixture in Eq. (3.10) can be applied to mixtures of soluble and insoluble compounds, where the κ of the insoluble species are considered to be 0. The hygroscopicity parameterization requires explicit treatment of aqueous solubility for compounds that are inherently insoluble or sparingly soluble but possess water uptake tendencies (Petters and Kreidenweis 2008; Sullivan et al. 2009). In such cases, κ is mathematically expressed by modifying $\kappa_{intrinsic,i}$ of the mixture components ($\kappa_{solubility}$) as follows,

$$\kappa_{solubility} = \sum_i \epsilon_i \kappa_{intrinsic,i} H(x_i) \quad (3.11a)$$

$$x_i = \left(\frac{D_p^3}{D_{dry}^3} - 1 \right) \frac{C_i}{\epsilon_i} \quad (3.11b)$$

$$H(x_i) = \begin{cases} x_i, & x_i < 1 \\ 1, & x_i > 1 \end{cases} \quad (3.11c)$$

where C_i is the water solubility of the i^{th} component of the dry particle (expressed as solute volume per volume of water), x_i is the fraction of i^{th} component dissolved in water, and $H(x_i)$ is the distribution function of the fraction of the i^{th} component dissolved in water. Eq. (3.11) (a)-(c) determines κ as a function of D_p . For unknown species with limited water solubility, some range of D_p corresponds to a volume of water which might not be sufficient to dissolve the volume of dry particle. Therefore, experimental droplet growth data is required to determine particle hygroscopicity.

κ can also be determined if the supersaturation (S) and the critical dry diameter ($D_{dry,c}$) measured at S are experimentally known. The experimental κ derived using KT is denoted as κ_{KT} and expressed as follows,

$$\kappa_{KT} = \frac{4 \left(\frac{A \sigma_w M_w}{RT \rho_w} \right)^3}{27 D_{dry,c}^3 \log^2(S)} \quad (3.12)$$

Eq. (3.12) also incorporates the same set of assumptions as Eq. (3.7-11) – dilute solution, and infinite and complete solubility of the compound.

3.5.2 FHH-AT Hygroscopicity

For the FHH-AT, a similar κ parameterization as KT can be developed by combining the water activity with the FHH isotherm using Eq. (3.7) (Mao et al., 2022),

$$a_{w,FHH} = \left(1 + \kappa_{FHH} \cdot \frac{V_s}{V_w} \right)^{-1} = \exp(-A_{FHH} \theta^{-B_{FHH}}) \quad (3.13)$$

which can be expanded to derive the FHH single hygroscopicity parameter (κ_{FHH}). The κ_{FHH} thus determined depends on the experimental data. The measured S and the corresponding $D_{dry,c}$ can be used to compute the $D_{p,c}$ using Eq. (3.5) and subsequently used to estimate κ_{FHH} as follows,

$$\kappa_{FHH} = \frac{6 \theta D_w}{D_{dry,c}} \cdot \left[\frac{1}{\exp(-A_{FHH} \theta^{-B_{FHH}})} \right]^{-1} \Rightarrow f(D_{dry,c}, D_{p,c}) \quad (3.14)$$

The hygroscopicity obtained using the FHH framework explains water uptake and droplet growth through adsorption. At the point of activation, the FHH hygroscopicity

explicitly depends on the dry particle size and the corresponding critical wet diameter.

That is, $\theta \rightarrow \theta_c = \frac{D_{p,c} - D_{dry,c}}{2D_w}$ at the point of activation. κ_{FHH} in Eq. (3.14) can be further simplified ($\kappa_{FHH,S}$) such that at the point of activation,

$$\kappa_{FHH,S} = \frac{6\theta_c D_w}{D_{dry,c}} (A_{FHH} \theta_c^{-B_{FHH}+1}) \quad (3.15)$$

Eq. (3.15) can be constrained using the critical surface coverage. At the point of activation, the critical surface coverage is determined as follows,

$$\left. \frac{dS}{dp} \right|_c = 0 \Rightarrow 1 - \frac{2\theta_c D_w}{D_{dry,c}} - \left(\frac{2AD_w}{A_{FHH} B_{FHH} D_{dry}^2} \right)^{0.5} \cdot \theta_c^{\frac{B_{FHH}+1}{2}} = 0 \quad (3.16)$$

θ_c from Eq. (3.16) is substituted in Eq. (3.15) such that $\kappa_{FHH,S} \equiv f(D_{dry,c})$, which essentially represents the theoretical κ_{FHH} . It is important to note that $\kappa_{FHH,S}$ is particle size-dependent as opposed to $\kappa_{intrinsic}$ (Eq. (3.9)), which is not.

3.5.3 HAM Hygroscopicity

Similar to KT or FHH-AT, a single hygroscopicity parameter was developed from the HAM framework (κ_{HAM}) using Eq. (3.7),

$$a_{w,HAM} = \left(1 + \kappa_{HAM} \cdot \frac{V_s}{V_w} \right)^{-1} = x_w \cdot \exp(-A_{FHH} \theta^{-B_{FHH}}) \quad (3.17)$$

The inclusion of the Raoult term (x_w) is the main difference between Eq. (3.13) and (3.17). κ_{HAM} is also dependent on the experimental information (S , or $D_{p,c}$ along with

the corresponding $D_{dry,c}$) and so Eq. (3.17) can be accordingly rearranged to obtain HAM single hygroscopicity parameter as follows,

$$\kappa_{HAM} = \frac{6\theta D_w}{D_{dry,c}} \left(\frac{1}{x_w \cdot \exp(-A_{FHH} \theta^{-B_{FHH}})} - 1 \right) \Rightarrow f(D_{dry,c}, D_{p,c}) \quad (3.18)$$

κ_{HAM} explains water uptake and droplet growth by combining the effects of aqueous solubility and water adsorption. At the point of activation, the HAM hygroscopicity depends on the dry particle size and the corresponding critical wet diameter. That is, $\theta \rightarrow \theta_c$ at the point of activation where $D_{p,c}$ can be computed using the generic Eq. (3.6) with the help of measured $D_{dry,c}$ vs. S . In Eq. (3.6), x_w is calculated using solubility partitioning as explained in section 3.3. Eq. (3.18) is the representation of experimental hygroscopicity of the particle based on the HAM framework. Eq. (3.18) can be further simplified ($\kappa_{HAM,s}$) for the point of activation,

$$\kappa_{HAM,s} = \frac{6\theta_c D_w}{D_{dry,c}} \left(1 - x_w (1 - A_{FHH} \theta_c^{-B_{FHH}}) \right) \quad (3.19)$$

Eq. (3.19) is the theoretical hygroscopicity based on the HAM framework which is constrained using the surface coverage. The constraint at the point of activation is estimated from the Eq. (3.6) as given by the following expression,

$$\left. \frac{dS}{dD_p} \right|_c = 0 \Rightarrow \frac{d}{dD_p} \left(a_{w,HAM} \exp \left(\frac{4\sigma_s/a M_w}{RT \rho_w D_p} \right) \right) = 0 \quad (3.20)$$

Eq. (3.20) provides θ_c at the point of activation to substitute in Eq. (3.19) and hence $\kappa_{HAM,s} \equiv f(D_{dry,c})$. A_{FHH} and B_{FHH} are the empirically determined parameters from FHH-AT specific to the compound. Like κ_{FHH} and $\kappa_{FHH,s}$, κ_{HAM} and $\kappa_{HAM,s}$ are also

size-dependent. However, the size-dependence in κ_{HAM} is variable and is controlled by the aqueous solubility of the compound. An extended derivation of κ_{HAM} is provided in the appendix section 3A.2.

3.6 Results

3.6.1 Köhler theory application for pure and internally mixed AAAs

The critical dry diameters ($D_{dry,c}$) at supersaturations (S) in the range of 0.6% – 1.6% were calculated using PyCAT 1.0. At any given supersaturation, the $D_{dry,c}$ for each sample was calculated from the size-resolved activation ratio. The CCN measurements for pure AAAs over a range of supersaturations are shown in Figure 3A.2 (appendix section 3A.3). The activation diameters determined for every sample at applied supersaturations were corrected using their dynamic shape factor. The experimental setup for shape factor measurements and the shape factor dataset for AAAs and PTA-IPTA internal mixtures are shown in appendix Sections 3A.1 and 3A.2, respectively. The size-resolved shape factors were then used to transform the measured electrical mobility diameters to their respective volume equivalent diameters (Tavakoli and Olfert, 2014; Yao et al., 2020; Gohil and Asa-Awuku, 2022). The volume equivalent diameters and their corresponding supersaturations were then used to estimate the experimental hygroscopicity based on traditional KT (κ_{KT}), for all the AAA samples.

The activation properties of pure AAAs (PTA, IPTA and TPTA) along with their predicted $\kappa_{intrinsic}$ and κ_{KT} are summarized in Table 2. The S versus their corresponding $D_{dry,c}$ for the samples are plotted in Figure 15(a). The experimental data is represented using individual markers. The solid and dashed lines represent the KT fits using the theoretical $\kappa_{intrinsic}$. The R^2 scores are provided in Table 3. PTA is observed to have the best agreement with the KT prediction ($R^2 \approx 0.99$). IPTA and TPTA show poor agreement with traditional KT. The lack of agreement between measurements and traditional KT predictions for IPTA and TPTA can be attributed to their significantly low aqueous solubility compared to PTA (by an order of magnitude $\sim 10^2$). In addition to the predicted and measured AAA data, $(\text{NH}_4)_2\text{SO}_4$ is also shown in Figure 15 (a).

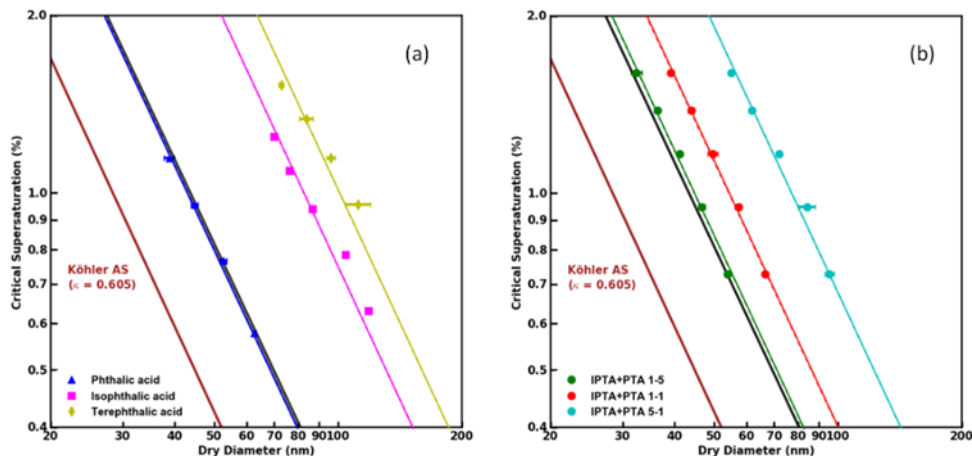


Figure 15. (a) S vs. $D_{dry,c}$ data obtained from supersaturated CCN measurements of pure phthalic acid (PTA), isophthalic acid (IPTA) and terephthalic acid (TPTA). (b) S vs. $D_{dry,c}$ data obtained from supersaturated CCN measurements of internal mixtures of PTA and IPTA. The mixtures studied shown in this plot are 5:1, 1:1 and 1:5 by mass of PTA. The solid brown line in both subplots corresponds to ammonium sulfate and was used for CCNC calibration. The solid black lines were generated using the ideal Köhler theory (KT) for the respective samples, and the dashed colored lines are the KT fits obtained using the measured CCN data of each sample.

For compounds that are considered “sparingly soluble” or “effectively insoluble” (Petters and Kreidenweis 2008; Figure 3), an explicit treatment of the compound solubility can typically improve the agreement between predicted and measured activation properties. Based on this convention, PTA would also be considered “sparingly soluble”. However, our results suggest that an explicit treatment of PTA solubility is not required. Moreover, $\kappa_{intrinsic}$ is a good representation of PTA hygroscopicity. Figure 15(b) shows the traditional and solubility-limited KT fits for internal mixtures of PTA and IPTA using their $\kappa_{intrinsic}$. The traditional KT predicts the CCN activity of the mixture containing excess PTA (5:1 mass ratio). This suggests that the mixture dominated by PTA must have an aqueous solubility closer to pure PTA and a $\kappa_{intrinsic} \approx \kappa_{KT}$ that can be obtained using the ZSR approximation. The agreement between traditional KT fits and experimental data reduces as the mass fraction of IPTA increases in the mixture.

The application of solubility limited (modified) KT showed poor agreement with the pure AAAs and PTA-IPTA internal mixtures (appendix Figure 3A.4). Modified KT overpredicted the critical supersaturation for any given dry particle size for all 6 samples. Thus, the underprediction of AAAs CCN activity is attributed to significantly low water solubility (in the range of $10^{-5} - 10^{-3}$ vol/vol water). Furthermore, a significant droplet growth is required to facilitate $\kappa_{solubility} = \kappa_{intrinsic}$ when solubility dependence is included in the hygroscopicity analysis (appendix Figure 3A.5). The AAA solubilities are 3 or more orders of magnitude smaller compared to highly soluble species such as ammonium sulfate (0.42 vol/vol water) or sucrose (1.26 vol/vol water). Quantitatively, the AAA droplets should grow to about 6.5, 23 and 45

times the dry particle size of PTA, IPTA and TPTA, respectively, when $\kappa_{solubility} = \kappa_{intrinsic}$. The required droplet growth is significantly large compared to compounds like ammonium sulfate or sucrose for which the droplet growth is 1.2 and 1.5 times the initial particle size, respectively, when $\kappa_{solubility} = \kappa_{intrinsic}$ (appendix Figure 3A.6). All of this implies that the hygroscopicity and CCN activity of AAAs and PTA-IPTA internal mixtures is more likely a consequence of water adsorption, and not aqueous solubility.

Table 3. Intrinsic and experimental hygroscopicity parameter, and FHH empirical parameters used for FHH-AT and HAM analysis.

Sample	Experimental hygroscopicity			
	Intrinsic hygroscopicity $\left(\kappa_{int} = \frac{\nu M_s \rho_w}{M_w \rho_s}\right)^a$	$\left(\kappa_{exp} = \frac{4 \left(\frac{4\sigma_w M_w}{RT\rho_w}\right)^3}{27D_{dry}^3 \log^2(S_c)}\right)^b$	A_{FHH}^c	B_{FHH}^c
Phthalic acid	0.172	0.169 ± 0.007	0.41	0.76
Isophthalic acid	0.168	0.023 ± 0.0027	0.39	0.87
Terephthalic acid	0.165	0.013 ± 0.0018	0.16	0.84
5:1 Pth-to-IPth	0.171	0.159 ± 0.007	0.28	0.69
1:1 Pth-to-IPth	0.169	0.085 ± 0.003	0.21	0.65
1:5 Pth-to-IPth	0.168	0.029 ± 0.0024	0.11	0.61

^a $M_w = 18 \text{ g mol}^{-1}$, $\rho_w = 1 \text{ g cm}^{-3}$, $\nu = 1$

^b $\sigma_w = 0.072 \text{ J m}^{-2}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, measured D_{dry} v/s S_c

D_{dry} = Dry diameter

S_c = Measured critical supersaturation

^c Empirically determined FHH parameters from measured D_{dry} v/s S_c data for the given samples

3.6.2 FHH-AT application for pure and internally mixed AAAs

FHH Adsorption Theory (FHH-AT) was applied for the analysis of pure and internally mixed AAAs. Figure 16 shows the measured S vs. $D_{dry,c}$ data for pure AAAs and PTA-IPTA internal mixtures. The dashed lines represent FHH-AT fits for their respective

CCN activity datasets. It should be noted that agreement for the FHH-AT can be obtained for every set of CCN measurements since the FHH parameters are determined by applying power law fitting to the datasets. The empirically determined FHH parameters (A_{FHH} , B_{FHH}) for pure compounds and internal mixtures are summarized in Table 2.

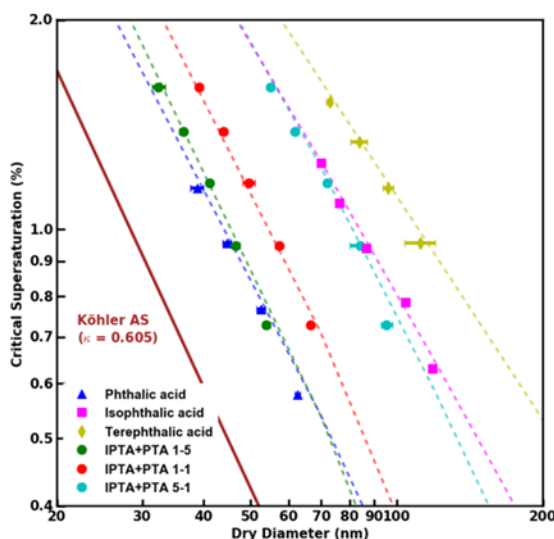


Figure 16. S vs. $D_{dry,c}$ data obtained from supersaturated CCN measurements of pure and internally mixed AAA samples. FHH-AT fits applied to the experimental data are shown as dashed lines.

The values of A_{FHH} and B_{FHH} can be used to qualitatively compare the water uptake properties of the pure and internally mixed species (Kumar et al., 2009b; Hatch et al., 2019). A_{FHH} dictates the attractive forces between the particle surface and the first adsorbed monolayer of water. A larger A_{FHH} implies a tendency to adsorb a higher amount of water on the particle surface. For the pure compounds, A_{FHH} decreases in the order of PTA > IPTA > TPTA (Table 2). This suggests a declining tendency to adsorb water. Additionally, A_{FHH} for the pure PTA, IPTA and TPTA decrease like their

aqueous solubilities (Table 1). For internal mixtures, A_{FHH} decreases with a decreasing PTA mass fraction (5:1 > 1:1 > 1:5). This also suggests a declining tendency to adsorb water with a decrease in PTA concentration.

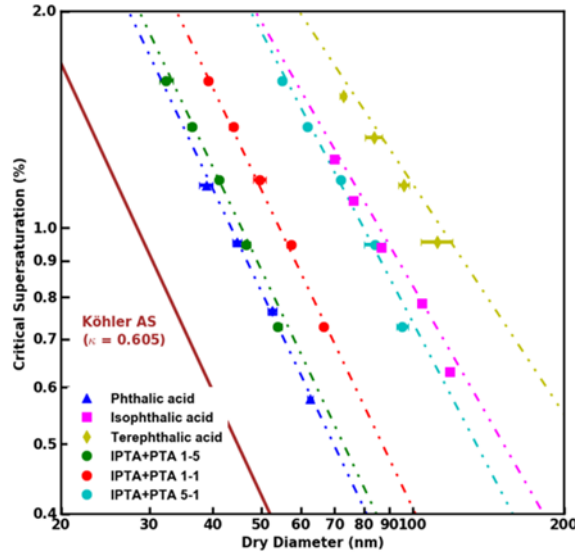


Figure 17. S vs. $D_{dry,c}$ data obtained from supersaturated CCN measurements of pure and internally mixed AAA samples. HAM fits applied to the experimental data are shown as dot-dashed lines.

B_{FHH} controls the attractive forces between the particle surface and subsequently adsorbed monolayers of water. Smaller the value of B_{FHH} , stronger the attractive forces over a larger radial distance from the particle surface. For the pure compounds, B_{FHH} varies in the order of IPTA > TPTA > PTA (Table 2). This suggests that the attractive force across the adsorbed monolayers is lowest in case of the droplets formed on IPTA particles. For internal mixtures, B_{FHH} follows a similar trend as A_{FHH} and decreases with a decreasing PTA mass fraction (5:1 > 1:1 > 1:5). This suggests that the attractive force across the adsorbed monolayers become stronger with a decrease in PTA concentration.

It can be inferred that A_{FHH} follows the trends of solubility and is most likely controlled by functional groups and B_{FHH} drives overall droplet growth across different compositions and molar volumes. The results here are consistent with Mao et al. (2022), that showed that the A_{FHH} values correlated with functionalized surfaces of aerosol with the same core (polystyrene latex; PSL). This suggests that the A_{FHH} values may play a more important role with compounds of similar molar volume and highlight the importance of functionalized groups and isomeric structures in determining overall droplet growth.

3.6.3 Hybrid Activity Model (HAM) application for pure and internally mixed AAAs

One of the major factors affecting droplet growth studied in this work is the aqueous solubility of the compound. AAAs and their mixtures used in this work possess approximately equal molar mass and densities, and hence equal molar volumes. Nonetheless, they differ in terms of their water uptake. Analysis shows that the differences in their water uptake behavior could arise due to the significant variation between their aqueous solubilities. Results in the previous subsection show that either KT or an adsorption theory (FHH-AT) can be applied for the CCN analysis of moderate and low aqueous solubility species, respectively. Alternatively, the Hybrid Activity Model (HAM) that sandwiches the FHH isotherm with the Raoult's law through solubility partitioning may agree well with the experimental data.

Figure 17 shows the S vs. $D_{dry,c}$ measurements for AAAs and PTA-IPTA internal mixtures plotted along with their HAM fits. The dot-dashed lines represent the HAM

fits for the respective CCN dataset. The calculation of the water activity term for all the samples studied in this work was done following the method described in section 3.3. It was observed that KT, FHH-AT and HAM provided similar fits for samples with aqueous solubility of the order of $10^{-3} \text{ m}^3 \text{ m}^{-3}$. Thus, similar fits for KT, FHH-AT and HAM were observed for the samples with higher PTA mass percentage (pure PTA and 5:1 PTA-IPTA mixture). The comparison of the goodness of fit between KT, FHH-AT and HAM can be made using the R^2 scores provided in Table 3. For pure PTA and 5:1 PTA-IPTA samples, all three models provided a goodness of fit. As the aqueous solubility of the sample was decreased (1:1 and 1:5 PTA-IPTA mixtures, pure IPTA and pure TPTA, in that order), HAM still provided an improved CCN activity prediction for the samples (R^2 scores of 0.92, 0.97, 0.94, 0.91, respectively; Table 3). FHH-AT and HAM provided similar and improved R^2 scores along the decline in the aqueous solubility of the species, whereas the R^2 scores corresponding to KT fits were found to decline with decreasing aqueous solubility of the samples. Moreover, the R^2 scores for HAM fittings were observed to be uniformly > 0.9 and generally higher than those obtained for FHH-AT.

3.6.4 Hygroscopicity parameterization for supersaturated conditions

The S vs. $D_{dry,c}$ of the AAA samples were transformed into a single hygroscopicity parameter (κ) based on KT, FHH-AT and HAM (Section 3.4). Figure 18 shows a closure plot between theoretical and experimental κ estimated for PTA, IPTA, TPTA and PTA-IPTA internal mixtures from KT, FHH-AT and HAM. The closure analysis

provides a better understanding of the applicability of different CCN models. The shaded portion of the graph denotes a 95% prediction interval across a 1-1 line (dashed, black).

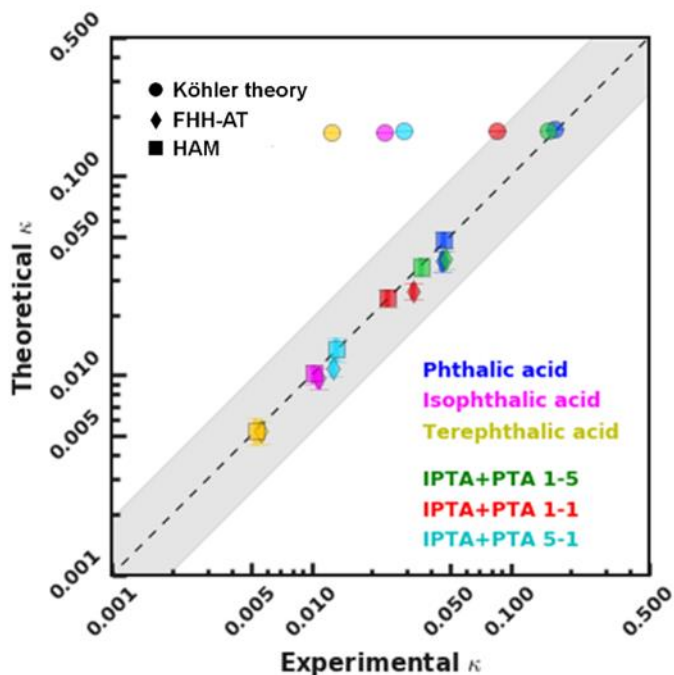


Figure 18. Closure plot representing the experimental and theoretical single hygroscopicity parameters obtained using KT, FHH-At and HAM CCN analysis frameworks. The goodness of fit was calculated for each compound and internal mixture.

The theoretical κ for KT has been represented using size-independent $\kappa_{intrinsic} = 0.172$ calculated using Eq. (3.4) and Eq. (3.5), respectively. κ_{KT} computed using S vs. $D_{dry,c}$ measurements are plotted for each compound. For KT (solid circles), the agreement between κ_{KT} and $\kappa_{intrinsic}$ decreases with a decreasing aqueous solubility of the solute. Specifically, the experimental κ lies within 95% confidence of the theoretical κ of pure PTA, 5:1 PTA-IPTA internal mixture, and 1:1 PTA-IPTA internal

mixture. TPTA is the sample with the lowest aqueous solubility and hence the lowest agreement between κ_{KT} and $\kappa_{intrinsic}$.

The theoretical adsorption-based parameterization ($\kappa_{FHH,S}$) and κ_{FHH} computed from the experimental data using the FHH-AT framework are shown using solid diamond markers in Figure 18. The $\kappa_{FHH,S}$ and κ_{FHH} were estimated using Eq. (3.15) and (3.14), respectively. It was found that κ_{FHH} had a generally good agreement with their respective $\kappa_{FHH,S}$ (R^2 in the range of 0.91 to 0.99). The lowest agreement between FHH-AT κ was observed for PTA and the 5:1 PTA-IPTA internal mixture, as both they likely have the highest aqueous solubilities among the studied samples. Moreover, the κ_{FHH} and $\kappa_{FHH,S}$ values of IPTA and TPTA are highly consistent with each other.

The theoretical and experimental κ_{HAM} were computed using Eq. (3.19) and (3.18), respectively. The datapoints for κ_{HAM} and $\kappa_{HAM,S}$ are denoted using solid squares in Figure 18. The most important feature of the HAM-based κ framework is that it explicitly accounts for the compound solubility within the hygroscopicity parameterization. Accounting for the contribution from the solid organic phase and dissolved aqueous phase to the overall hygroscopicity of the solute generates the best agreement between the κ_{HAM} and $\kappa_{HAM,S}$ values. Consequently, the R^2 scores observed between κ_{HAM} and $\kappa_{HAM,S}$ of the 6 AAA samples are > 0.97 . It is also important to note that κ values for AAA samples obtained from FHH-AT and HAM frameworks are smaller than those obtained using KT.

3.6.4 Hygroscopicity parameterization for supersaturated conditions

All the measurements shown in Figures 19 were performed at a 95% RH. Figure 19 (a-c) show the droplet sizes (D_{wet}) with respect to their initial dry sizes (D_{dry}) for pure PTA, IPTA and TPTA. Figure 19 (d-f) show the D_{wet} with respect to the D_{dry} for PTA-IPTA internal mixtures. The D_{wet} predictions based on the KT-Raoult term, FHH isotherm and hybrid water activity were derived from the parameters in Table 2. The Raoult's model estimates (black dashed lines) for the pure and internally mixed samples were generated using their average hygroscopic growth factor (G_f ; Fig. 19, Eq. (3.7)). The supersaturated average κ of 0.17 for the AAA samples was used to obtain the theoretical D_{wet} and G_f at given dry sizes. The R^2 scores for the KT-Raoult model are summarized in Table 3. The KT-Raoult model agreed well for pure PTA and 5:1 PTA-IPTA mixture.

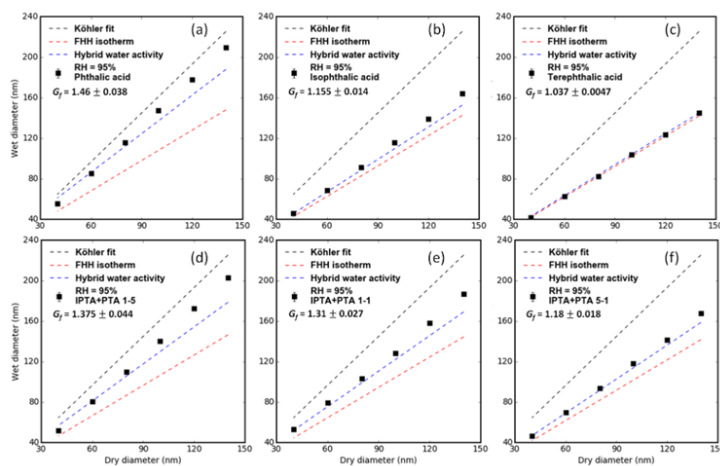


Figure 19. Subsaturated measurements for pure AAA samples obtained using the H-TDMA setup are shown. Panels(a), (b) and (c) show the D_{wet} vs. D_{dry} data along with model fits for pure PTA, IPTA and TPTA. Panels (d), (e) and (f) show the D_{wet} vs. D_{dry} data along with model fits for PTA–IPTA internal mixtures. The KT–Raoult term, FHH isotherm and hybrid water activity fits are shown in black, red and blue, respectively, overlaid with the experimental data. The hygroscopic growth factors (G_f) for all AAA samples are shown in their legends.

The red dashed lines in Figure 19 show the D_{wet} estimated using the FHH isotherm (Eq. (3.4)). The empirical FHH parameters used here were determined by fitting the FHH-AT to the supersaturated CCNC measurements (Section 4.2; Table 2). FHH noticeably underpredicts the hygroscopic behavior of the AAAs except for IPTA and TPTA in the subsaturated regime (R^2 estimates in Table 3). This implies that the insoluble behavior of IPTA and TPTA can be represented with high certainty in subsaturated as well as the supersaturated regime, using the FHH theory. Moreover, the KT and FHH models (that agreed for soluble compounds, PTA and 5:1 PTA-IPTA mixture) have different droplet growth predictions in the subsaturated regime.

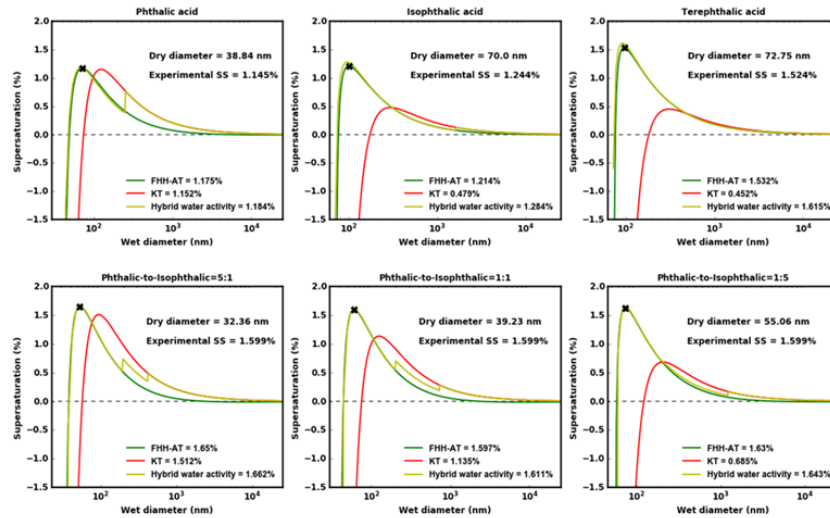


Figure 20. Equilibrium droplet growth curves for PTA, IPTA, TPTA and PTA–IPTA internal mixtures are shown here. The figure header shows the solute for which the respective equilibrium curves are plotted. KT, FHH-AT and HAM lines are shown in red (solid), green (solid) and yellow (solid), respectively. An exemplarily measured activation point for the respective solute is denoted using a solid red cross. The $D_{dry,c}$ and corresponding S used to generate these equilibrium curves are provided in Fig. 15.

The blue dashed lines in Figure 19 show the D_{wet} estimated using the comprehensive hybrid water activity expressions described in Section 3.3 (Eq. (3.6)). Again, the hybrid water activity requires the empirical FHH parameters obtained by fitting FHH-AT to the supersaturated CCNC measurements (Table 2) and the aqueous solubility of the compound to account for the dissolved fraction of solute (Table 1). The hybrid water activity replicated the subsaturated water uptake of all 6 of the AAAs with high certainty (R^2 estimates in Table 3). This is due to the explicit consideration of both compound solubility and water adsorption to describe the droplet growth process. Notably, the hybrid water activity is similar to either the KT-Raoult or the FHH isotherm depending on the compound solubility. For sparingly soluble samples (e.g., pure PTA), the KT-Raoult and hybrid water activity generated similar fits (R^2 of 0.938 and 0.948, respectively). For effectively insoluble samples (e.g., pure TPTA), the FHH isotherm and the hybrid water activity generated similar fits (R^2 of 0.998 and 0.999, respectively) for subsaturated measurements.

The sub- and supersaturated analyses are consistent with the equilibrium curves for the pure and internally mixed AAA samples. Figure 20 shows droplet growth predicted using KT, FHH-AT and HAM corresponding to one of the experimentally determined $D_{dry,c}$. The predicted critical supersaturations (S_c) are also shown in the plots. KT predicted S_c values deviate significantly ($> 10\%$) from the experimental S_c , as the aqueous solubility of the solute decreases. This is because KT for the structural isomers assumes similar droplet growth ($\kappa_{intrinsic}$ is ~ 0.17). However, FHH-AT and HAM require higher supersaturations and are less CCN active and therefore the points of activation are shifted upwards and to the left. At a given relative humidity (RH) $<$

100%, the KT-derived D_{wet} is found to be larger than those predicted using either FHH-AT or HAM. This is consistent with the models and experimental data at 95% RH shown in Figure 19. KT-based D_{wet} was found to be close to the experimental D_{wet} for pure PTA and 5:1 PTA-IPTA mixture, whereas D_{wet} from FHH-AT and HAM were found close to the experimental D_{wet} for the remaining solutes. After critical activation, there may be a jump from a water adsorption-driven droplet growth to one driven by complete dissolution of the solute (vertical jump in green line from blue to red). This is prominently seen in PTA but not in as evident in TPTA. Furthermore, multiple transitions are observed in internal mixtures.

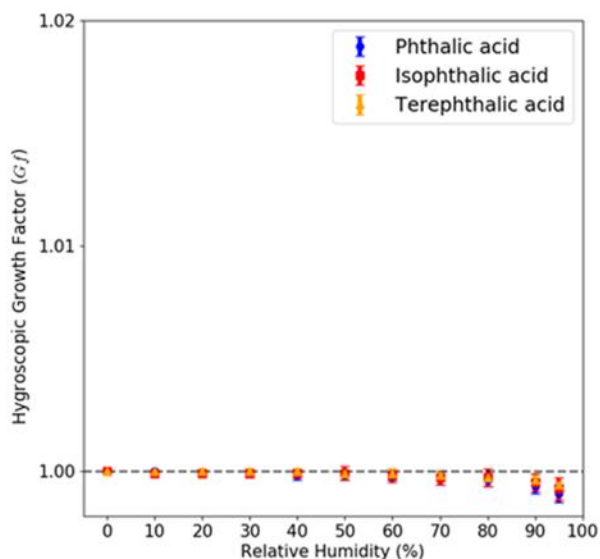


Figure 21. Subsaturated measurements for pure AAA samples obtained using the VSA setup are shown. The mass hygroscopic growth factor is shown with respect to the relative humidity (RH). The measurements show that neither of PTA, IPTA or TPTA show any mass-based growth as the RH is increased from 5 % to 95 %.

VSA measured the water uptake of the three AAA compounds in the subsaturated regime. None of AAAs showed significant water uptake (with mass growth factors smaller than <1%) even at high RH (95%) (Figure 21). It should be noted that the VSA

measurement uses materials in the range of μm to mm . Thus, the observed κ_{HAM} in Eq. (19) decreases with increasing diameter and eventually approaches zero. The results across different particle measurement platforms are consistent with the hygroscopicity parameterization that is particle size-dependent.

Table 4. Goodness of fit (R^2) scores for model fits applied to supersaturated and subsaturated measurements of pure and internally mixed samples.

Sample	Supersaturated R^2			Subsaturated R^2		
	KT	FHH-AT	HAM	KT	FHH-AT	HAM
Phthalic acid	0.99	0.87	0.99	0.938	0.459	0.948
Isophthalic acid	—	0.94	0.96	—	0.894	0.975
Terephthalic acid	—	0.9	0.91	—	0.998	0.999
5:1 PTA-to-IPTA	0.71	0.91	0.91	0.869	0.549	0.933
1:1 PTA-to-IPTA	—	0.89	0.92	0.604	0.667	0.957
1:5 PTA-to-IPTA	—	0.94	0.97	0.007	0.894	0.987

It should be noted that in this work, the particle shape morphology (dynamic shape factor) was explicitly accounted for, and the electrical mobility diameters consequently corrected to their respective volume equivalent diameters as described in Gohil and Asa-Awuku (2022). Shape factors were measured and computed for all samples studied (appendix Figure 3A.3). Over the mobility diameters of interest (from 50nm to 150nm), the dynamic shape factor values were found to range from 1.00 to 1.08 and were therefore within 10% of 1.00. This suggests that the AAA samples studied in this work are composed mainly of spherical particles. The application of the dynamic shape factor of aerosols composed of fractals/agglomerates such as black carbon to the transition from soluble to sparingly soluble activation must be considered in future work.

3.7 Summary and Implications

This paper presents the droplet growth analysis of AAAs using a new Hybrid Activity Model (HAM). HAM estimates the thermodynamics of the droplet growth by combining the aqueous solubility of the compound in an adsorption activation framework. HAM accounts for the contributions from undissolved as well as the dissolved fractions of the particle mass to predict droplet growth. Thus, HAM is able to predict critical properties (e.g., $D_{wet,c}$, S_c , G_f) for droplet growth in both the supersaturated and subsaturated regimes.

HAM also predicts the droplet growth of internal mixtures. The three PTA-IPTA internal mixtures (5:1, 1:1, and 1:5 with respect to PTA) show a clear transition from sparingly water soluble to effectively water insoluble mixtures (Petters and Kreidenweis, 2008). For a mixture containing two or more components, the water activity based on Raoult's law is computed using solubility partitioning (Riipinen et al., 2015). Moreover, a solubility limit of $\sim 8 \times 10^{-4}$ vol/vol water (corresponding to a 3:1 internal mixture with respect to PTA) was determined using solubility partitioning. Below this limit, the discrepancies in CCN activity will likely be $> 10\%$ for traditional KT. It is therefore reasonable to assume that the effect of adsorption on droplet growth would be more dominant in determining the growth of the pure and internally mixed AAAs as their solubilities are decreased below $\sim 8 \times 10^{-4}$ vol/vol water. Current literature considers the two paradigms separately and HAM provides a continuum to bridge and combine both mechanisms.

To do so, HAM requires three compound-specific parameters (C_i , A_{FHH} and B_{FHH}) and the use of the full HAM in cloud microphysical models may extend the computational burden to account for the aerosol chemistry. Therefore, a single hygroscopicity parameter was also developed and exhibited an improved hygroscopicity parameterization for all solutes studied in this work. Raoult's law was generally overpredicts the hygroscopicity of effectively insoluble solutes. And the FHH isotherm generally underpredicts the hygroscopicity of sparingly soluble solutes. Combining the two droplet growth mechanisms in HAM provided a more robust approximation of the water uptake behavior in both subsaturated and supersaturated environments. Consequently, the experimental and simplified (theoretical) hygroscopicity estimates based on HAM (κ_{HAM} and $\kappa_{HAM,s}$) showed the best agreement and highest goodness of fits when it was applied to the experimental data.

Overall, HAM is a promising new droplet growth model that can be potentially used for the analysis of any type of atmospheric compound. HAM is effective because it combines the characteristic features of the traditional KT with solubility partitioning and FHH-AT. Additionally, HAM differs from previous analytical frameworks that are based on compound solubility in that for any species using HAM, the particles are treated as completely undissolved at the start of the activation process. This is vital because other solubility limiting approaches begin with instantaneous dissolution and add the element of reduced solubility along the course of droplet growth. Indeed, the approach is congruous to the concept of earlier works that explored the impact of slow dissolution (e.g., Asa-Awuku & Nenes, 2007; Shulman et al., 1996) and aligns with more current findings that describe the droplet growth of viscous, amorphous, or glassy

aerosols (e.g., Altaf et al., 2018; Mikhailov et al., 2009; C. Peng et al., 2022; Tandon et al., 2019; Zobrist et al., 2008).

In HAM, the contribution of the theorized undissolved fraction facilitates a surface until the particle fully dissolves, after which further droplet growth is controlled solely by the entire particle mass present in the aqueous phase. The HAM concept may have even more utility at lower temperatures and higher altitudes. In general, the solubility of compounds in water will likely decrease at lower temperatures; thus, the role of surface adsorption on the undissolved fraction will be important to droplet growth. Additionally, solute viscosity of atmospheric compounds has been shown to have more significant effects on droplet growth at lower temperatures in the subsaturated regime (Kasparoglu et al., 2021). Rather than considering complex morphological parameters (diffusivity, viscosity, rheology), HAM simplifies the concept by considering the presence (or lack thereof) of a surface. In addition to the factors considered in this work, surface tension can potentially play a role in both the water activity term and also in the solute partition and should therefore be treated explicitly in the droplet growth process. Incorporation of surface tension in the analysis was beyond the scope of this work, and well-designed experiments will be required to observe whether surface tension has any contribution on the water uptake of the AAAs studied in paper. Furthermore, surface effects of a given species can be parameterized within the HAM framework and subsequently into the hygroscopicity to understand such effects for partially insoluble to effectively insoluble systems.

The next step is to evaluate the application of HAM for the CCN analysis of aerosol mixtures for a wider range in aerosol species and compositions. The shift from volume to surface based absorption principles maybe more appropriate for significantly water-insoluble compounds. Specifically, the application of HAM can be examined for the hygroscopic growth and water uptake on black carbon agglomerates. Furthermore, HAM developed in this work may improve our predictions of a wide variety of atmospherically relevant aerosols. For example, many atmospheric organic aerosols may vary significantly from each other in terms of their chemical structures and aqueous solubilities (Petters and Kreidenweis, 2008; Sullivan et al., 2009). Therefore, HAM may potentially improve the representation of hygroscopicity of organic aerosols in large-scale Global Climate Models (GCMs), hence reducing the uncertainties in the climate forcing due to the aerosol indirect effect.

Appendix 3A

Summary: This appendix contains the CCNC supersaturation calibration data, CCN measurements for pure and internally mixed AAA samples, description of shape factor measurement setup along with the shape factor data and conversion to volume equivalent sizes for pure and internally mixed AAAs, and application of solubility-limited Köhler theory to pure and internally mixed AAA data.

3A.1 CCN counter (CCNC) calibration

CCNC calibration was performed using the $(\text{NH}_4)_2\text{SO}_4$ aerosol. Dry $(\text{NH}_4)_2\text{SO}_4$ were subjected to supersaturated conditions when passing through the CCNC column. The set supersaturation inside the CCNC column depends on the axial temperature gradient for specified flow and pressure gradient. Ideally, the temperature gradient inside the CCNC column is assumed to stay constant. That is, if the CCNC parameters are maintained constant, then the temperature gradient and hence the supersaturation across the CCNC column must stay constant. However, in practice there are fluctuations in the CCNC parameters and so there are deviations in the “true” instrument supersaturation relative to the set supersaturation displayed on the CCNC software interface. These deviations can be resolved by calibrating the CCNC supersaturation using a compound like $(\text{NH}_4)_2\text{SO}_4$. $(\text{NH}_4)_2\text{SO}_4$ is one of most well-understood and well-characterized aerosol compounds that is widely used for CCNC calibration. Calibration was performed by following the procedure described by Rose et al. (2008).

Table 3A1. Sample CCN Counter (CCNC) calibration data using $(\text{NH}_4)_2\text{SO}_4$

Supersaturation Setting (%)	Calibrated Supersaturation (%)	Critical Dry Diameter (nm)
0.2	0.215	75.6 ± 2
0.4	0.402	52.3 ± 0.6
0.6	0.586	41.2 ± 0.4
0.8	0.771	34.7 ± 0.7
1.0	0.957	29.6 ± 0.6
1.2	1.125	26.1 ± 0.9
1.4	1.357	23.1 ± 1.1
1.6	1.546	$21.2 \pm 1.$

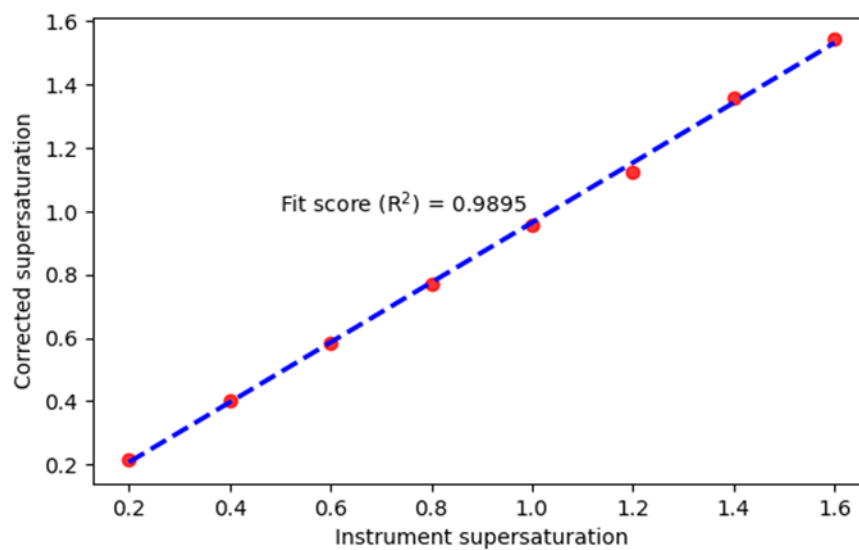


Figure 3A.1. CCNC calibration curve generated using the ammonium sulfate activation data provided in Table 3A.1. This curve was used to calibrate the CCNC supersaturations at which AAA data was collected.

3A.2 Hybrid Activity Model single hygroscopicity parameterization (κ_{HAM})

Hybrid Activity Model (HAM) is mathematically expressed as,

$$S = a_{w,HAM} \cdot \exp\left(\frac{A}{D_p}\right) \quad (3A.1)$$

where S is supersaturation, $a_{w,HAM}$ is the water activity derived by combining features from FHH adsorption theory and Kohler theory, D_p is the intermediate diameter of the droplet, and A is a constant which is given as,

$$A = \frac{4M_w\sigma_w}{RT\rho_w} \quad (3A.2)$$

Where M_w is the molecular weight of water, R is the gas constant, T is the temperature and ρ_w is the density of water. σ_w is the surface tension of the droplet and is assumed to be the same as that of pure water.

The development of $a_{w,HAM}$ has been described in detail in the main literature (Section 3.3) explaining that $a_{w,HAM} = X_w \cdot \exp(-A_{FHH}\theta^{-B_{FHH}})$. $a_{w,HAM}$ is equated with the parameterization defined in terms of the single hygroscopicity parameter (κ) which is expressed as,

$$a_{w,HAM} = X_w \cdot \exp(-A_{FHH} \cdot \theta^{-B_{FHH}}) = \left[1 + \kappa \cdot \frac{v_s}{v_w}\right]^{-1} \quad (3A.3)$$

Rearranging Eq. (3A.3) provides the expression for κ_{HAM} as,

$$\kappa_{HAM} = \frac{6\theta D_w}{D_d} \left(\frac{1}{X_w \cdot \exp(-A_{FHH}\theta^{-B_{FHH}})} - 1 \right) \quad (3A.4)$$

Eq. (3A.4) is the function of the measured D_d and D_p derived corresponding to the point of activation. Eq. (3A.4) can be further simplified using Eq. (3A.3). The exponential on the right-hand side of Eq. (3A.4) can be simplified using the Taylor's series expansion for an exponential function such that,

$$\exp(-A_{FHH}\theta^{-B_{FHH}}) = 1 + (-A_{FHH}\theta^{-B_{FHH}}) + (-A_{FHH}\theta^{-B_{FHH}})^2 + \dots \quad (3A.5)$$

Since $-A_{FHH}\theta^{-B_{FHH}} \ll 1$, (3A.5) can be restated as,

$$\exp(-A_{FHH}\theta^{-B_{FHH}}) \approx 1 + (-A_{FHH}\theta^{-B_{FHH}}) \quad (3A.6)$$

The X_w term on the right-hand side of Eq. (3A.3) is expressed depending on the ongoing phase of the droplet formation/growth. The phases of droplet formation/growth are described in detail in the main literature (Section 3.3). The left-hand side of Eq. (3A.3) can be simplified under the assumption that $v_w \gg v_s$,

$$\left[1 + \kappa \cdot \frac{v_s}{v_w}\right]^{-1} \approx 1 - \kappa \cdot \frac{v_s}{v_w} \quad (3A.7)$$

Combining Eq. (3A.6) and Eq. (3A.7) provides a simplified theoretical expression for κ_{HAM} ,

$$\kappa_{HAM,s} = \frac{6\theta_c D_w}{D_{dry}} \cdot \left(1 - X_w(1 - A_{FHH} \cdot \theta_c^{-B_{FHH}})\right) \quad (3A.8)$$

Eq. (3A.8) contains critical θ defined as the point of activation such that $\theta = \theta_c$. θ_c is determined by taking the first derivative of Eq. (3A.1) and equating it to 0 for the point of activation such that,

$$\frac{dS}{dD_p} = \frac{d}{dD_p} \left(X_w \cdot \exp \left(-A_{FHH} \cdot \left[\frac{D_p - D_d}{2 \cdot D_w} \right]^{-B_{FHH}} \right) \cdot \exp \left(\frac{A}{D} \right) \right) = 0 \quad (3A.9)$$

$$1 - \frac{2\theta_c D_w}{D_d} = \left(\frac{2AD_w}{A_{FHH} B_{FHH} D_d^2} \right)^{1/2} \theta_c^{\frac{B_{FHH}+1}{2}} \quad (3A.10)$$

Solving Eq. (3A.9) and (3A.10) under different conditions prescribed by X_w (depending on the phase of droplet growth) will yield the appropriate θ_c to then subsequently parameterize κ_{HAM} .

3A.3 CCN data for pure and internally mixed aromatic acid samples

Figure 3A.2 shows exemplary size-resolved activation ratios derived using the CCN measurements of the pure and internally mixed AAA samples. The activation ratio data are shown with respect to the electrical mobility diameter of the particles which were converted to their respective volume equivalent diameters using their shape factor measurements (shown in Section 3A.4).

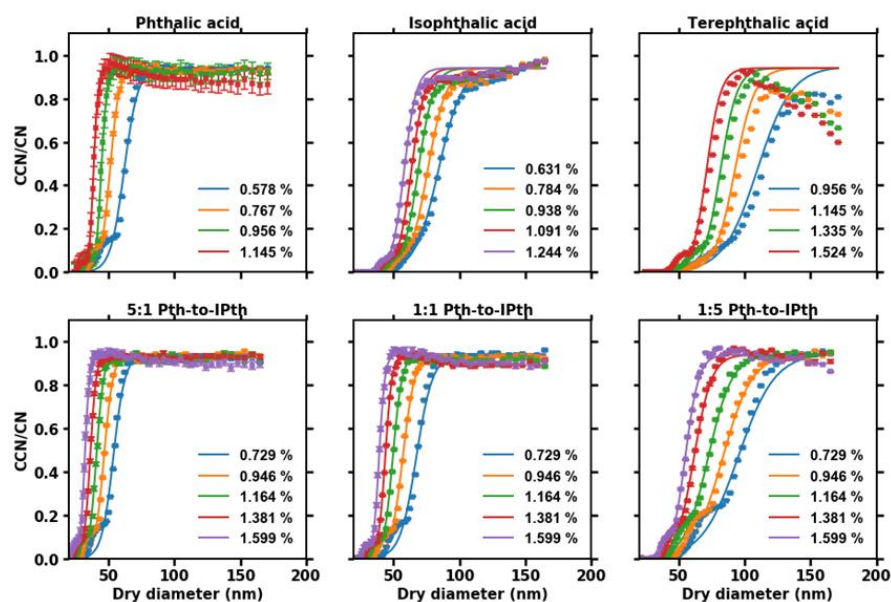


Figure 3A.2. Size-resolved activation ratio of pure and internally mixed AAA samples from a typical DMA-based CCN setup. The size-resolved activation ratios are overlayed with their corresponding sigmoidal fits which were used to determine the critical diameters ($D_{dry,c}$) at the respective supersaturations provided in the legend.

3A.4 Shape factor experiments

3A.4.1 Experimental Setup

Shape factor measurements were conducted using a setup based on the Aerodynamic Aerosol Classifier (AAC) instrument. The experimental setup has been explained in detail in the literature (ref). Briefly explained here – the AAC is used to size-select particles of a specific aerodynamic diameter from the incoming polydisperse population. The size-selected aerosols are then passed through a Scanning Mobility Particle Sizer (SMPS) setup to generate a distribution with respect to electrical mobility diameter. The geometric mean of the number distribution is considered as the mobility size measurement corresponding to the aerodynamic diameter. The mobility diameter and aerodynamic diameter are then used to estimate the volume equivalent diameter and dynamic shape factor using a set of coupled equations (Section 3.3, Tavakoli and Olfert (2014)).

3A.4.2 Measured data for aromatic acid aerosols (AAAs)

The exemplary shape factor data of pure AAA samples are shown with respect to the aerodynamic diameter of the particles (Fig. 3A.3). The aerodynamic diameters chosen here ranged from ~100 to 200 nm. This range of aerodynamic diameters corresponds to the electrical mobility diameters ranging from ~50 to 120 nm. This is similar to the range in which the measure critical dry diameters ($D_{dry,c}$) of pure and internally mixed samples were observed.

The following system of equations are solved to simultaneously obtain the size-resolved shape and volume equivalent diameter using the measured electrical mobility and aerodynamic diameters,

$$\frac{C_c(D_{ve})}{\chi D_{ve}} = \frac{C_c(D_{mo})}{D_{mo}} \quad (3A.11)$$

$$D_{ve} = D_{ae} \sqrt{\frac{\chi \rho_0 C_c(D_{ae})}{\rho_p C_c(D_{ve})}} \quad (3A.12)$$

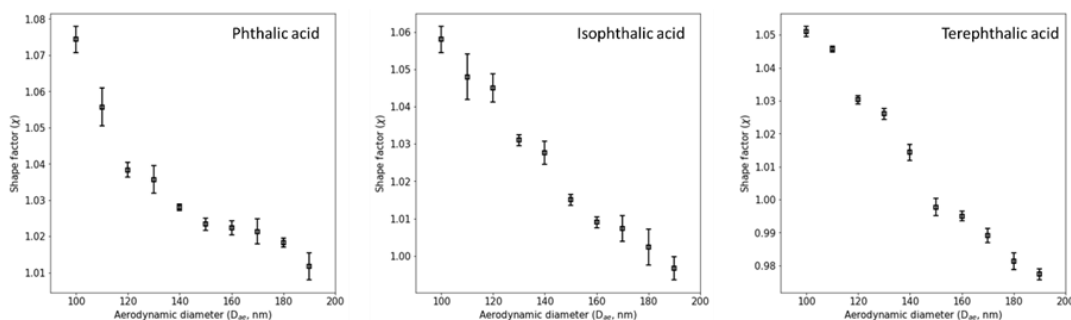


Figure 3A.3. Dynamic shape factor measurements for pure phthalic acid (PTA), isophthalic acid (IPTA) and terephthalic acid (TPTA). The shape factor data is plotted against the aerodynamic diameter of the particles and can be converted their respective mobility diameters or volume equivalent diameter using Eq. (3A.11) or (3A.12), respectively. Since most of the shape factor values lie in close range to 1 ($\sim 5\%$ of 1; or close to 1.05), it can be assumed that AAA particles studied in this work are spherical in shape.

3A.5 Solubility-limited Köhler theory application to pure and internally mixed aromatic acids

Köhler theory traditionally accounts for the intrinsic hygroscopicity of the compounds that depends only on the solute and solvent (water) properties (Section 3.1; Section 4.1 for results). For compounds that are not completely water soluble, traditional Köhler theory can be modified by explicitly accounting for the aqueous solubility of the compound.

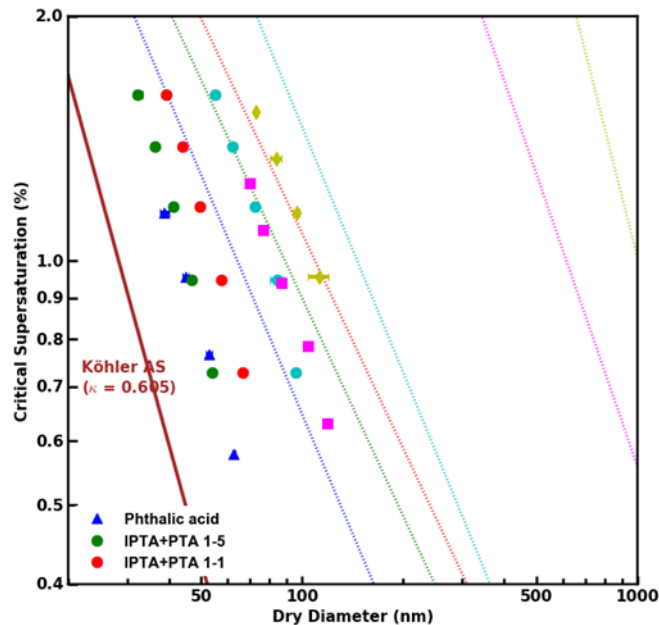


Figure 3A.4. CCN measurements of pure and internally mixed AAA samples from a typical DMA-based CCN setup. The activation measurements are overlayed with solubility limited Köhler theory fits line which were derived using the apparent hygroscopicity parameter ($\kappa_{apparent}$) of the pure and internally mixed samples.

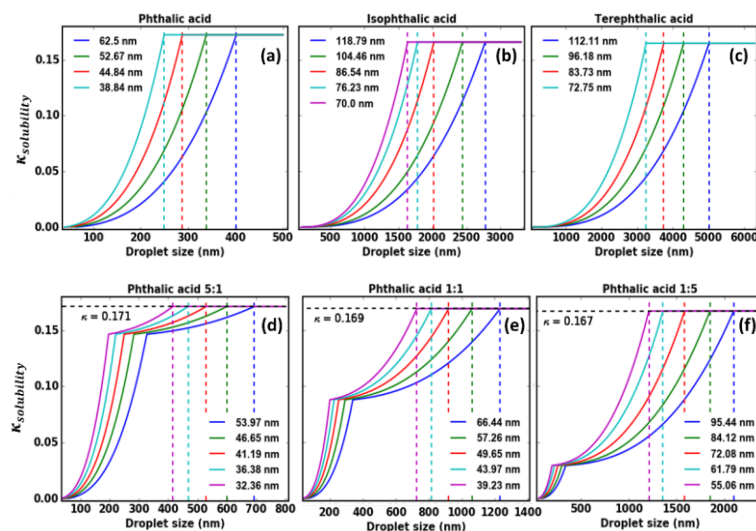


Figure 3A.5. $\kappa_{apparent}$ plotted against droplet size for pure and internally mixed AAA samples. $\kappa_{apparent}$ was determined using Eq. (3.11) described in detail in Section 3.5.1.

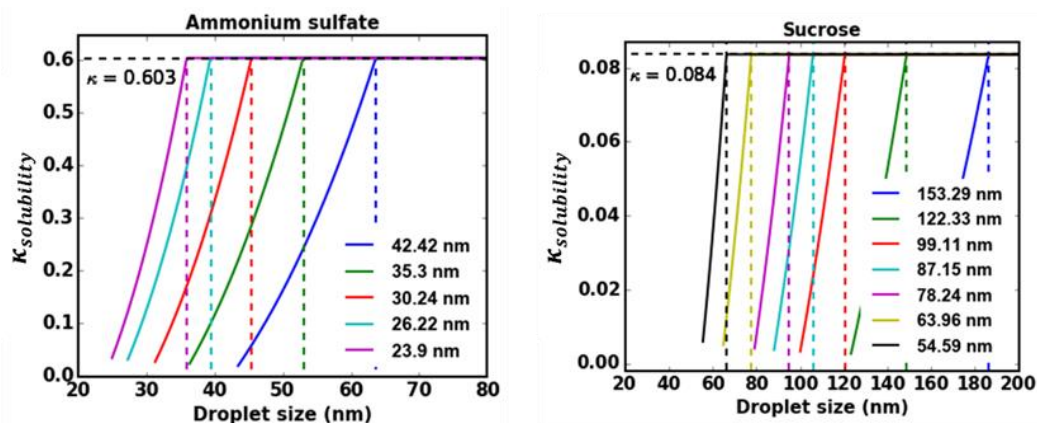


Figure 3A.6. $\kappa_{apparent}$ plotted against droplet size for high solubility compound – ammonium sulfate (AS) and sucrose, respectively. $\kappa_{apparent}$ was determined using Eq. (3.11) described in detail in Section 3.5.1. It can be observed that the droplet sizes that needs to be attained at $\kappa_{apparent}$ for highly soluble compounds is significantly lower than those for AAAs (described in detail in Section 3.5.1). This is an important consideration for the assumption that AS and sucrose almost instantly dissolve in water, hence making traditional KT applicable for analysis.

Chapter 4: Solubility Considerations for Cloud Condensation Nuclei (CCN) Activity Analysis of Pure and Mixed Black Carbon Species

Submitted work under review:

Gohil, K., Barrett, R., Rastogi, D., Mao, C.-N., and Asa-Awuku, A.: Solubility Considerations for Cloud Condensation Nuclei (CCN) Activity Analysis of Pure and Mixed Black Carbon Species, Environ. Sci. Technol.

4.1 Abstract

Black Carbon (BC) is an aerosol that is released into the atmosphere due to the incomplete burning of biomass and can affect the climate directly or indirectly. BC commonly mixes with other primary or secondary aerosols to undergo aging, thereby changing its radiative properties and cloud condensation nuclei (CCN) activity. The composition of aged BC species in the atmosphere is difficult to measure with high confidence and so their associated CCN activity can be uncertain. In this work, the CCN activity analysis of BC is performed using laboratory measurements of proxy aged BC species. Vulcan® XC72R Carbon Black was used as the representative of BC, and 3 structural isomers of benzenedicarboxylic acid – phthalic acid (PTA), isophthalic acid (IPTA) and terephthalic acid (TPTA) – were mixed with BC to generate 3 different proxies of aged BC species. Most studies related to CCN activity analysis BC aerosol use the traditional Köhler Theory or an adsorption theory (such as the Frenkel-Halsey-Hill Adsorption Theory). PTA, IPTA and TPTA fall in the sparingly water-soluble range and therefore do not fully obey either of the aforementioned theories. Consequently, a novel hybrid activity model (HAM) was used for the CCN activity analysis of the BC mixtures studied in this work. HAM combines the features of adsorption theory via the adsorption isotherm with the features of Köhler Theory by

incorporating solubility partitioning. The results in this work show that HAM improves the representation of CCN activity of pure and mixed BC aerosol species with high certainty; evident from a generally better goodness of fit, $R^2 > 0.9$. This work implies that the hygroscopicity parameterization based on HAM captures the size-dependent variability in the CCN activity of the pure and aged BC species. In short, the hybrid water uptake method has been applied for the CCN analysis of the soot proxies for the first time and provides an overall improved water uptake estimations.

4.2 Background

Black carbon (BC) aerosol is significant due to its effect on the atmosphere and climate. This is a result of the observed effects of BC on air quality, climate change, and human welfare. BC is produced from incomplete biomass combustion and is one of the main biomass burning tracers in the atmosphere alongside other primary and secondary organic aerosols (POAs and SOAs). BC is the second most important contributor to the warming of the climate after carbon dioxide (Bond et al., 2013; IPCC, 2007). However, BC aerosols may also significantly indirectly affect the climate via interactions with clouds. The aerosol-indirect effect of pure and coated BC aerosols must be well understood to better understand their climate forcing.

Carbonaceous aerosols, and BC aerosol particularly, have complex molecular level interactions with water (e.g., but not limited to (Laaksonen et al., 2020a; Weingartner et al., 1997; Zhang et al., 2008)). BC particles in the atmosphere exist as agglomerates or nodules and conglomerates with other species; BC are rarely observed in pure form are known to age downwind of emission sources (Canagaratna et al., 2015). Aging can

substantially alter the morphology of the BC particles, and the aged particles, can range in size from a few nm to several μm , and may contain co-condensed phases (Zhang et al., 2016; Peng et al., 2016). Aged BC can internally or externally mix with other aerosols present in the atmosphere (Bond et al., 2013). The pure and mixed, or aged BC are known to act as Cloud Condensation Nuclei (CCN) under supersaturated ambient conditions and can therefore affect the climate “indirectly” through altering cloud properties (e.g., but not limited to Dusek et al., 2006; Maskey et al., 2017; Stratmann et al., 2010; R. Zhang et al., 2008). BC aerosol is considered water insoluble; however, it is wettable and known to take up water and display hygroscopic behavior leading to cloud droplet formation. CCN activation is traditionally described using Köhler theory and works well for highly water-soluble solutes. However due to the strong water insoluble nature of BC, traditional Köhler theory should not be applied to study BC CCN activity and droplet growth.

For insoluble aerosols such as BC, CCN activity and water uptake is aptly described via the effect of water vapor adsorption on the particle surface (Dalirian et al., 2018; Laaksonen et al., 2016, 2020). Adsorption activation theory combines adsorption isotherms and curvature effects to describe insoluble aerosol droplet growth. Frenkel-Halsey-Hill adsorption theory (FHH-AT) is formulated by combining the FHH isotherm with the Kelvin effect (Sorjamaa and Laaksonen, 2007) and is the most widely used CCN activity theory for the droplet growth of insoluble wettable aerosols (e.g., but not limited to Hatch et al., 2012, 2014, 2019; Kumar et al., 2011b, 2011a; Kumar et al., 2009a; Kumar et al., 2009b; Dalirian et al., 2018; Mao et al., 2022). Additionally, the FHH isotherm has been combined with the Köhler Theory for the CCN activity

analysis of insoluble particles coated with soluble species assuming a “core-shell” morphology. Kumar et al., (2011a, 2011b) also described CCN activation of mineral dust species containing a soluble salt fraction using the combination of the classical Köhler and FHH adsorption theories. Other studies have developed frameworks to theoretically describe CCN activity of insoluble aerosols, such as BC and coated BC aerosols, using multilayer adsorption models accounting for the curvature and contact angle of the droplets forming on aerosol particles (Laaksonen et al., 2020).

A systematic theoretical and experimental examination of the changes in the CCN activity of BC particles, as they are mixed with low solubility organic aerosols, is absent from current literature. So far, the CCN activity studies of BC particles under supersaturated or subsaturated conditions predominantly focus on BC mixed with readily water-soluble species. One such compound is NaCl (observed as a component of sea salt); Dusek et al., (2006) performed chamber CCN measurements and showed a significant enhancement in the CCN activity of BC particles on mixing with 5% NaCl. Zhang et al., (2008) observed that BC particles aged with sulfuric acid showed up to ~10-fold and ~2-fold enhancement in their scattering and adsorption properties, after undergoing hygroscopic growth at 80% relative humidity. Dalirian et al., (2018) performed CCN analysis of BC particles coated with various water soluble and insoluble organic compounds using the core-shell CCN model. Other studies include CCN analysis of ambient BC aged with high hygroscopicity sea salt aerosols (Furutani et al., 2008).

This work studies the water uptake and droplet formation of particles composed of effectively water-insoluble organics mixed with BC using controlled laboratory

measurements. Vulcan® was chosen as the representative of BC aerosol; it is a synthetic BC substance that possess high electrical conductivity and is widely used for electrocatalytic applications (M.J. Lázaro et al., 2011). Three low water solubility structural isomers of benzene di-carboxylic acid – Phthalic acid (PTA), Isophthalic acid (IPTA) and Terephthalic acid (TPTA) – were used as the proxies for low water solubility organic aerosols and mixed with BC. PTA, IPTA and TPTA are prominent benzene polycarboxylic acids detected in the atmosphere (Fu et al., 2009; Singh et al., 2017b; Meng et al., 2018; Haque et al., 2019; Kunwar et al., 2019; Liu et al., 2019; Yassine et al., 2020; Kanellopoulos et al., 2021). PTA, IPTA and TPTA are produced from biomass burning and emissions of automobile exhaust (Mkoma and Kawamura, 2013; Balla et al., 2018; Al-Naiema and Stone, 2017; Zhong et al., 2017a, b). PTA and its isomers are known tracers of benzantracene, naphthalene-1 and methylnaphthalene-1 (Kleindienst et al., 2012b; He et al., 2018; Al-Naiema et al., 2020b) and are likely co-emitted with soot. Therefore, the mixtures of aromatic acids with BC can be considered proxies for aged soot.

Recently a hybrid activity model (HAM) was developed to model the water-uptake and hygroscopicity of effectively water-insoluble aerosol (Gohil et al., 2022). HAM combines solubility partitioning with the FHH adsorption isotherm to describe the droplet growth. HAM was observed to work well for PTA, IPTA and TPTA; the goodness of fit (R^2) metrics for subsaturated and supersaturated measurements were found to be in the range of 0.9 – 0.99 for all the studied aerosol (Gohil et al., 2022). HAM suggests that the hygroscopicity is size dependent and pure and mixed aerosols are initially treated as completely insoluble at the start of droplet growth. Depending

on their aqueous solubility, the particles then continue to fractionally dissolve into the aqueous phase as droplet growth progresses. While the dissolved fraction of the aerosol contributes to droplet growth via Raoult's law, the undissolved fraction contributes to droplet growth via adsorption of water on the surface. HAM was found to be effective with sparingly soluble organic aerosol – however, its utility with relevant atmospherically mixed insoluble species (BC, mineral dust, nanopolymers etc.) has yet to be tested.

In this manuscript, HAM is applied and used to describe the variability in the water uptake behavior of BC particles mixed with low solubility water solubility compounds (PTA, IPTA and TPTA). Additionally, Transmission Electron Microscopy (TEM) captures images of mixed aerosol to identify particle morphology that may affect water uptake behavior. The compounds and their mixtures considered in this work are useful because they could represent atmospheric organic aerosol composition. The CCN activity measurements of pure and mixed BC particles also provide an efficient means to further validate the application of the newly developed HAM. In the following sections, we first describe the experimental setup to obtain experimental CCN activation data for pure and mixed BC. We then briefly describe FHH-AT and HAM models and compare predictions to data and discuss the results in the context of aged soot particles, droplet growth, and cloud formation.

4.3 Experimental Section

4.3.1 Chemicals and Sample Preparation – Pure BC and Internal Mixtures with Aromatic Acid Aerosols (AAAs)

Vulcan® (Cabot Vulcan® XC72R Carbon Black) was used as the representative of black carbon (BC). Phthalic acid (PTA, 1,2 – benzenedicarboxylic acid, >99.5%, Sigma-Aldrich®) and terephthalic acid (TPTA, 1,4 – benzenedicarboxylic acid, 98%, Sigma-Aldrich®) and Isophthalic acid (IPTA, 1,3 – benzenedicarboxylic acid, >99%, Fisher Scientific®) were aromatic acid aerosols (AAAs) used in this study. The physical properties of BC and AAAs are summarized in Table 1. AAA compounds were mixed with BC in a 1:1 mass ratio. The water uptake behavior of the 3 AAA compounds in this study have been previously described in detail in (Gohil et al., 2022). The mass-to-volume concentration of the pure BC solution was 72 mg BC in 200 ml ultrapure water (Milli-Q or Millipore®, $18.2\text{M}\Omega\text{ cm}^{-1}$). The mass-to-volume concentration of BC-to-AAA internal mixtures was also 72 mg (36 mg BC was mixed with 36 mg of AAA) in 200 ml ultrapure water (Milli-Q or Millipore®, $18.2\text{M}\Omega\text{ cm}^{-1}$). Furthermore, the acidity of the pure AAA aerosol and 1:1 BC-to-AAA aerosol was quantified with their pH. The pH of PTA, IPTA and TPTA was found to be 5.24, 5.43 and 5.94, respectively. Low acidity suggests that the AAA samples are not strong organic solvents. BC readily dissolves in strong acid solutions; therefore, the weak organic acid solutions here have minimal dissolution of BC in AAA. Before preparing all the pure and internally mixed BC aerosol, dry Vulcan® was first heated at 450 °C for 6 hours. The pure and internally mixed aqueous suspensions of BC were then sonicated in a 30 °C water bath for 9 hours. The BC aerosol was constantly sonicated

in a 20 °C water bath during all aerosol measurement; including the CCN, shape factor and TEM grid experiments as described in detail below.

Table 5. Physical and chemical properties of BC and AAA compounds used throughout the chapter.

Compounds	Molecular weight ($M_s, \text{g mol}^{-1}$)	Density ($\rho_s,$ g cm^{-3})	Solubility ($C,$ $\text{m}^3 \text{m}^{-3}$)
Black Carbon (Vulcan® XC72R)	12	~1.8	$< 10^{-5}$
Phthalic acid	166.14	1.59	3.77×10^{-3}
Isophthalic acid	166.14	1.53	7.84×10^{-5}
Terephthalic acid	166.13	1.52	1.12×10^{-5}

4.3.2 CCN Measurements

A continuous flow stream-wise thermal gradient Cloud Condensation Nuclei Counter (CCNC, Droplet Measurement Technologies (DMT) (Roberts & Nenes, 2005 - CCN 100) measured CCN of pure and internally mixed BC aerosol. The DMT CCNC is a widely used instrument for droplet growth measurements in supersaturated conditions (e.g., but not limited to Engelhart et al., 2008; Moore et al., 2010; Barati et al., 2019; Vu et al., 2019) and only a brief description of experimental setup is provided here. Polydisperse aerosol was generated and dried from aqueous suspensions as described in Sect. 2.1. An electrostatic classifier (TSI 3936, DMA 3081) size selected monodisperse aerosol corresponding to a fixed electrical mobility diameter. The size-selected aerosols exiting the DMA were then split into 2 streams. One stream entered a condensation Particle Counter (CPC, TSI 3776) at 0.3 L min^{-1} to measure total dry particle concentration (C_{CN}), and a second stream entered the CCNC at 0.5 L min^{-1} and

constant supersaturation to measure activated particle (droplet) counts (C_{CCN}). A sheath flow rate of 8 L min^{-1} was applied across the experimental setup to maintain a sheath-to-sample ratio of 10:1. The experiments were performed over a range of varying supersaturations from 0.2%-1.6%, with 0.1% step size. Each supersaturation was held constant for 15 minutes for every sample and particle size to provide sufficient time for the CCNC column temperature gradient, and hence the supersaturation to stabilize. This process of stepping through each particle size for a range of supersaturations is hence forth referred to as a “step-mode” process. Furthermore, CCNC supersaturations ranging between 0.2% and 1.6% were calibrated using ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, AS) aerosol (Sigma-Aldrich®, >99.9%) prior to performing measurements for pure and mixed BC samples. AS data used for CCN calibration is provided in the appendix (Section 4A.1).

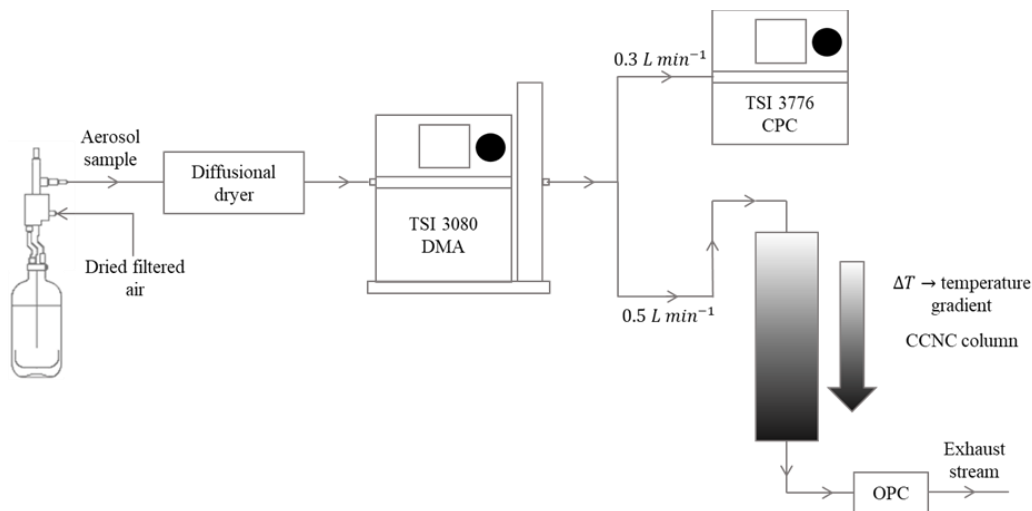


Figure 22. Schematic of a CCN measurement experimental setup. The DMA and the CPC are operated in the stepping mode to obtain number concentrations at selected electrical mobility diameter. The CCNC is connected in parallel and measures the number concentration of activated particles at the selected dry particle electrical mobility diameter.

4.3.3 Effective Density Estimation and Shape Factor Measurements

Dynamic shape factor and effective particle density are measured with an Aerodynamic Aerosol Classifier (AAC, Cambustion Ltd.), TSI DMA 3080 and TSI CPC 3776 connected in series. The AAC and DMA measure the aerodynamic and electrical mobility diameters of the particles, respectively. The application of the experimental setup has been examined in the literature (e.g., Tavakoli et al., 2014; Tavakoli and Olfert, 2014; Yao et al., 2020; Gohil and Asa-Awuku, 2022). A brief description of the experimental setup is provided in this paper. Polydisperse aerosol was generated from aqueous suspensions as described above. The AAC selected monodisperse aerosol corresponding to an aerodynamic diameter (D_{ae}). The sample and the sheath flow rates were maintained at 0.3 L min^{-1} and 3.0 L min^{-1} respectively (i.e., sheath-to-sample flow ratio = 10:1). The monodisperse aerosol was then passed through the DMA and the CPC in series operating in the Scanning Mobility Particle Sizer (SMPS) mode to generate a number size distribution with respect to the electrical mobility diameter. The median diameter of the distribution was considered as the approximate electrical mobility diameter (D_{mo}) corresponding to the initially set D_{ae} . The size-resolved effective density and dynamic shape factor of the pure BC and mixed BC-AAA aerosols were calculated using coupled aerodynamic and electrical mobility measurements. Henceforth, the measured mobility diameters to their respective volume equivalent diameters using the effective density (ρ_{eff}) and dynamic shape factor (χ) for the subsequent CCN analysis of the pure and mixed samples.

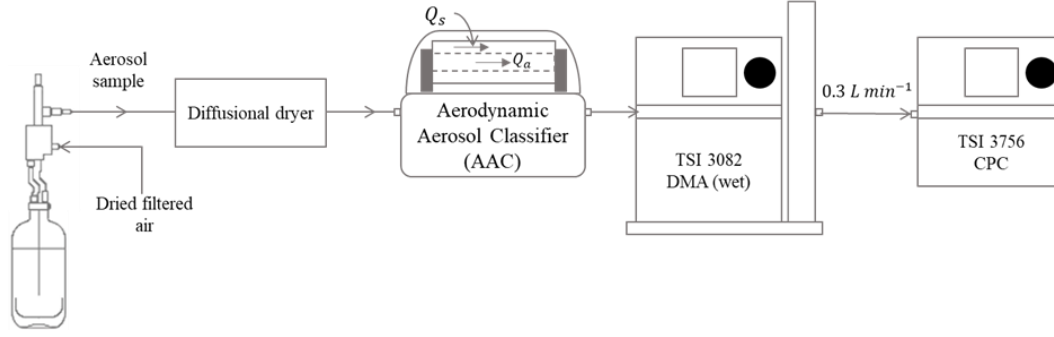


Figure 23. Schematic of the shape factor and effective density experimental setup. The AAC selects dry aerosol with aerodynamic diameter (D_{ae}). The DMA and the CPC collectively operate as an SMPS and measure a number size distribution of AAC-selected dry particles with electrical mobility diameters (D_{mo}). The geometric mean of the number size distribution of the particles was selected as the electrical mobility diameter measurement corresponding to the initially set aerodynamic diameter.

4.3.4 CCN Activity Analysis – PyCAT

Python-based CCN Analysis Tool – PyCAT (Gohil and Asa-Awuku, 2022) was used to process, analyze, and visualize the calibration and BC data. PyCAT was developed for CCN analysis using scanning data collected using the DMA or AAC size selection experimental setup. In this study, a new module has been added to PyCAT to perform CCN analysis of step-mode data. The new module of PyCAT is capable of processing and analyzing data collected with respect to fixed electrical mobility diameter and varying CCNC supersaturations. Consequently, the activation ratio ($\frac{C_{CCN}}{C_{CN}}$) of a given sample for a fixed dry diameter (D_{dry}) are resolved by supersaturations (S). Following this, a sigmoidal function can be fit to the activation ratio as,

$$y = \frac{(A_1 - A_2)}{1 + \exp\left(\frac{x - x_0}{dx}\right)} + A_2 \quad (4.1)$$

In Eq. (4.1), y is the dependent variable $\frac{C_{CCN}}{C_{CN}}$, A_1 and A_2 are the minimum and maximum of the sigmoid respectively, dx is the slope of the sigmoid, x_0 is the inflection point of the sigmoid (generally the midpoint of the sigmoid), and x is the independent variable (S). x_0 corresponds to the critical supersaturation (S_c) at the fixed dry diameter and is physically defined as the size at which 50% of all particles are activated. It is important to note that size-resolved χ and ρ_{eff} were used to convert electrical mobility sized to volume equivalent diameters. The volume equivalent diameters of the particles are implemented as their dry diameter (D_{dry}).

4.3.5 Transmission Electron Microscopy (TEM)

Pure and mixed BC nano-sized particles were collected and analyzed with Transmission Electron Microscopy. The JEOL 2100 (TEM; LaB6 filament) was used in this work (Niemi et al., 2006; Rastogi and Asa-Awuku, 2022). Specifically, aerosols pass through a neutralizer and the charged particles (Kr-85, TSI 3077A) were then deposited for 4 hours onto an electrically grounded lacey carbon-coated copper TEM grid (TED PELLA). For EDX and EELS analysis the particles were deposited on a Silicon Nitride (SiN) grid. The deposited particles were then imaged at an accelerating voltage of 200 kV and a magnification range of 50-150 k. To minimize sample damage, the exposure time was kept limited to 90 sec.

4.4 Theory and Analysis

4.4.1 Effective Density and Shape Factor Calculations

4.4.1.1 Effective Density

The effective density of a particle can be calculated by dividing the mass by the volume of a spherical particle that has a diameter equal to the mobility diameter of the particle. The effective density (ρ_{eff}) is mathematically expressed as follows:

$$\rho_{eff} = \frac{m}{\left(\frac{\pi}{6}\right)D_{mo}^3} = \frac{6C}{\pi} D_{mo}^{(D_{fm}-3)} \quad (4.2)$$

where m is the particle mass, D_{mo} is the particle mobility diameter, C is a constant, and D_{fm} is the fractal dimension of the given species, also known as the mass-mobility exponent. C and D_{fm} are empirical coefficients that are used relate the mass and mobility diameter of the particle through a power law relationship given as,

$$m = C D_{mo}^{D_{fm}} \quad (4.3)$$

The mass m in Eq. (4.3) is directly related to the particle relaxation time and mobility, which can be measured with the AAC-DMA setup. Therefore, m can be obtained by solving the following system of equations using the measured data,

$$\tau = \frac{C_c(D_{ae})\rho_0 D_{ae}^2}{18\mu} \quad (4.4a)$$

$$B = \frac{C_c(D_{mo})}{3\pi\mu D_{mo}} \quad (4.4b)$$

$$\tau = Bm \quad (4.4c)$$

where C_c represents the size-dependent Cunningham's slip correction factor, ρ_0 is the reference density (1000 kg m^{-3}), D_{ae} is the aerodynamic diameter of the particle, μ is the viscosity of the carrier gas in the instrumentation, τ is the particle relaxation time, and B is the particle mobility

Solving the system expressed as Eq. (4.4) for a measured size distribution provides the mass distribution of the aerosol. Fitting the Eq. (4.3) to the mass vs. mobility diameter distribution generates empirical parameters, which can then be used in Eq. (4.2) to obtain the distribution of the particle effective density. The effective density is important because it explicitly accounts for the void fraction and therefore accounts for irregularities present in the particle shape and morphology (Tavakoli and Olfert, 2014). BC and BC-like species may be fractal, and so their effective density can be especially useful to observe the deviation from their bulk density.

4.4.1.2 Dynamic Shape Factor

The dynamic shape factor (χ) of a particle quantifies its non-sphericity. The effect of non-sphericity of the particle is represented using the drag force. χ is expressed as follows,

$$\chi = \frac{F_D}{F_{D,ve}} \quad (4.5)$$

where F_D is the drag force on the non-spherical particle, and $F_{D,ve}$ is the drag force on an equivalent spherical particle with the density equal to that of the original particle. The spherical particle is referred to as a volume equivalent sphere, and the

corresponding size is the volume equivalent diameter (D_{ve}). Size-resolved χ and the respective D_{ve} of any given species can be determined using the measured electrical mobility and aerodynamic diameters by solving the following pair of non-linear equations,

$$\frac{C_c(D_{ve})}{\chi D_{ve}} = \frac{C_c(D_{mo})}{D_{mo}} \quad (4.6a)$$

$$D_{ve} = D_{ae} \sqrt{\frac{\chi \rho_0 C_c(D_{ae})}{\rho_p C_c(D_{ve})}} \quad (4.6b)$$

ρ_p is density of the density of particle inclusive of voids and is therefore equivalent to the size-resolved ρ_{eff} of the particles. The known measured relative distributions of electrical mobility and aerodynamic diameters are used to solve the coupled system represented by Eq. (4.6) and obtain the distributions for the volume equivalent diameter and dynamic shape factor.

4.4.2 Frenkel-Halsey-Hill Adsorption Theory (FHH-AT)

The FHH-AT model describes droplet formation and growth via the adsorption of water on particle surface. FHH-AT combines the FHH isotherm with the curvature effect (Kelvin term) to determine the water vapor over the droplet surface (supersaturation) during water uptake (Sorjamaa and Laaksonen, 2007). The FHH isotherm defines the water activity through adsorption of aqueous multilayers as a function of surface coverage (the number of adsorbed aqueous monolayers on the particle surface; θ). The FHH isotherm is mathematically expressed as follows,

$$a_{w,FHH} = \exp(-A_{FHH}\theta^{-B_{FHH}}) \quad (4.7)$$

The 2 empirical parameters (A_{FHH} , B_{FHH}) account for the surface and bulk contributions to droplet growth. A_{FHH} parameterizes the interactions between particle surface and the first adsorbed aqueous monolayer. B_{FHH} parameterizes the interactions between particle surface and the subsequently adsorbed aqueous monolayers. A_{FHH} and B_{FHH} respectively describe the amount of adsorbed water on particle surface as well as the radial distance away from the particle up to which the attractive forces can cause the adsorption. In Eq. (4.7), $\theta = \frac{D_p - D_{core}}{2D_w}$, where D_p is the droplet diameter, D_{core} is the diameter of the insoluble core, and D_w is the diameter of a water molecule and has a value of 0.275 nm. Combining Eq. (4.7) with the curvature effect (Kelvin term), the FHH-AT can be expressed as,

$$S = a_{w,FHH} \exp\left(\frac{4\sigma_w M_w}{RT \rho_w D_p}\right) \quad (4.8)$$

where σ_w , M_w and ρ_w are the surface tension, molecular weight, and density of water, respectively. R is the ideal gas constant and T is the temperature. It is important to note that the 2 empirical parameters are species dependent and can be determined by applying least square minimization on the maxima of FHH-AT equilibrium curve fitted to the experimental CCN activity measurements.

The FHH-AT has previously been modified to incorporate different physical properties of aerosol particles. One such modification is based on the inclusion of the contact angle of the adsorbed aqueous layers on the particle surface (Laaksonen et al., 2016, 2020). Another modification expands the FHH-AT framework by including the

aerosol solubility (Gohil et al., 2022), resulting in the development of a hybrid activity model (HAM).

4.4.3 Hybrid Activity Model (HAM)

The hybrid activity model (HAM) incorporates solubility partitioning (Riipinen et al., 2015) with FHH-AT. The solubility partitioning transforms the ideal Raoult's law such that it includes the solubility of the compound (or, compounds) in the aerosol composition. With this approach, the effect of solid, undissolved core on droplet activation and water uptake can be included towards water uptake along with the contribution from dissolved particle within the aqueous phase. Moreover, the FHH empirical parameters (A_{FHH} , B_{FHH}) for each sample are the same computed by fitting the FHH-AT to the CCN activation data. The mathematical formulation of HAM is as follows,

$$S = a_{w,HAM} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w D_p}\right) \quad (4.9)$$

where $a_{w,HAM} = a_{w,Raoult} \cdot a_{w,FHH}$. $a_{w,Raoult}$ is the Raoult's law term which is defined as $\gamma_w X_w$, where γ_w is the activity coefficient and X_w is the mole fraction of water in the aqueous phase of the droplet. Considering the droplet to be infinitely dilute, $\gamma_w \approx 1$ and $a_{w,Raoult}$ can then be approximated as $X_w = \frac{n_w}{n_w + n_s}$, where n_w are the number of moles of water and n_s are the total number of moles of the solute(s) in the aqueous phase of the droplet.

Physically, the HAM water activity describes the droplet growth and water uptake process in 3 stages. Stage 1 is the start of the water uptake by adsorption on the particle surface followed by minute droplet growth. Since there is an infinitesimal amount of solute dissolved in the aqueous phase in stage 1, $X_w \approx 1$ and therefore $a_{w,HAM} \approx a_{w,FHH}$. In stage 2, a finite amount of solute continues to dissolve into the aqueous phase. Therefore, $a_{w,HAM} = X_w \cdot a_{w,FHH}$ in stage 2. X_w and $a_{w,FHH}$ vary continuously during the droplet growth in stage 2 and are estimated using the bulk solubilities of each compound with the instantaneous droplet diameter and solute mass dissolved (Gohil et al., 2022; Riipinen et al., 2015). Stage 3 begins when the entire mass of the initial solute particle has dissolved into the aqueous phase with no undissolved solute left. In stage 3, the $a_{w,HAM} = X_w$ (Raoult's law). Additional details and description of the formulation of HAM is provided in (Gohil et al., 2022).

4.4.4 Hygroscopicity Parameterization from FHH-AT and HAM

The single hygroscopicity parameter is denoted by κ and is mathematically formulated by relating it to the water activity of the CCN activity model. The general formulation for κ was provided by (Petters and Kreidenweis, 2007) and is expressed as follows,

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \quad (4.10)$$

where a_w is the water activity term, V_s is the volume of the dry particle, and V_w is the volume of water in the aqueous phase. The κ parameter derived from a CCN model can

be parameterized by substituting the a_w in Eq. (4.10). Following this procedure, the experimental and theoretical single hygroscopicity parameters for FHH-AT and HAM have been previously developed. The details of the hygroscopicity parameterizations based on FHH-AT and HAM (κ_{FHH} and κ_{HAM} , respectively) have been provided by Mao et al., (2022) and Gohil et al., (2022), respectively.

4.5 Results

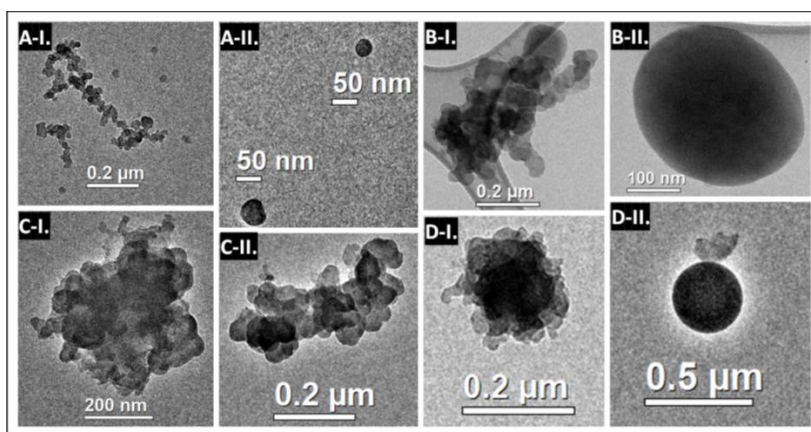


Figure 24. TEM images of different sized particles of pure BC (A-I, AII) and BC mixed with Phthalic (B-I, B-II), Isophthalic (C-I, C-II) and Terephthalic (D-I, D-II) acid, respectively.

The particles generated from BC and BC mixtures in this study have a range of non-uniform sizes and shapes (Figure 24). TEM images show that small BC particles can be spherical however can agglomerate to form larger sized particles. BC mixtures with aromatic acids can modify the shape of these particles. Thus size-resolved effective density and dynamic shape factor of pure and mixed BC particles must be calculated prior to CCN analysis.

4.5.1 Particle Shape and Effective Density for Pure and Mixed BC

The dry electrical mobility diameters (D_{mo}) of the pure and mixed BC samples were converted to their corresponding volume equivalent diameters (D_{ve}) using in-situ measurements. The size-resolved effective density and shape factor of the particles was computed following the method described in Section 3.1.1 and 3.1.2, respectively. The effective density and shape factor of the samples are shown in Figure 25 (a) and (b). Fig. 25(c) shows the D_{ve} of the pure and mixed BC particles plotted against the corresponding D_{mo} . The black dashed line in Fig. 25(a) signifies the mean bulk density of the pure BC (Vulcan® XC72R) particles. The effective density of the particles increases towards the theoretical bulk density with an increasing D_{mo} . The significantly low effective density with respect to the bulk density of pure BC at low D_{mo} (towards the left end of Fig. 25a) suggests that smaller particles could be existing in the form of agglomerates. Moreover, the agglomeration of pure and mixed BC particles likely decreased with an increase in the D_{mo} which can be understood from the increase in the size-resolved effective density.

The likely reduction in fractal-like structures is also evident from the decrease in the size-resolved shape factor of the particles with an increasing D_{mo} . For pure BC, the lowest value of shape factor was measured to be ~ 1.2 for a $D_{mo} = 260\text{nm}$. Among the mixed BC particles, BC-PTA particles were measured to be most spherical, with a maximum shape factor of ~ 1.15 for $D_{mo} \approx 40\text{nm}$, and minimum shape factor of ~ 1.0 for $D_{mo} > 135\text{nm}$. BC-TPTA particles were measured to be the non-spherical out of the 3 types of BC mixtures with a maximum shape factor of 1.21 for $D_{mo} = 45\text{nm}$, and minimum shape factor of 1.06 even at $D_{mo} > 220\text{nm}$. The size-resolved shape

factor of BC-IPTA particles were found in the intermediate range between the shape factor of BC-PTA and BC-TPTA particles. In Eq. 4.6(a), it is observed that the Cunningham's slip correction factors for the D_{mo} and D_{ve} have small variabilities related to the respective variables. Therefore, an approximate linear relationship can be assumed between the D_{ve} and D_{mo} . The straight lines fitted to the D_{ve} vs. D_{mo} for the pure and mixed BC samples are also shown in Fig. 25(c). These straight-line fits were used to determine the D_{ve} for the CCN analysis with respect to every D_{mo} at which the CCN measurements were performed.

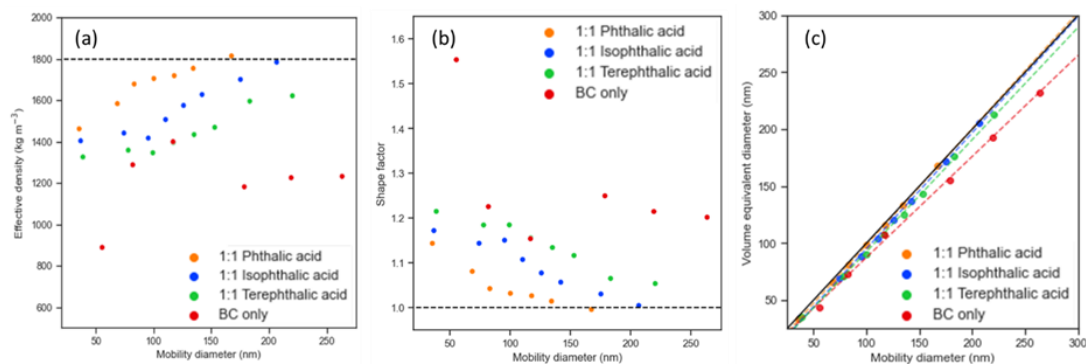


Figure 25. Size-resolved effective density (a), size-resolved dynamic shape factor (b) and size-resolved volume equivalent diameter (c) with respect to electrical mobility diameter are shown. The measurements were performed with respect to electrical mobility diameters in range of 50nm and 250nm. The estimated volume equivalent diameter vs. electrical mobility diameter for pure and mixed BC samples were used to generate linear fits.

4.5.2 CCN Activity of Pure and Internally Mixed BC

CCN measurements of pure and mixed BC particles were performed following the procedure described in Section 2.2. The CCN activity data of pure and mixed BC are summarized in detail in the appendix (Section 4A.2). For each sample, number concentrations were measured with respect to varying supersaturations in the CCNC

while the dry particle diameters were held fixed. Figure 4A.1 shows the activation data versus supersaturation data for pure and mixed BC samples. The sigmoidal functions fitted to the activation ratio is also shown. The critical supersaturations for each sample determined from the sigmoidal fits are summarized alongside the corresponding dry diameter. It is important to note that the sigmoidal fits for mixed BC samples corresponding to each dry particle diameter consisted of a single plateau. The single plateau is indicative of a homogenous particle (Vu et al., 2019) and implies that BC-AAA mixtures can be treated as internal mixtures for subsequent CCN analysis. The assumption of internally mixed aerosol mixtures is also supported by Energy Dispersive X-ray (EDX) analysis results (Figure 26). Fig. 26 shows mixtures of BC with Phthalic, isophthalic, and terephthalic acid species and the elemental mapping for Carbon and Oxygen. Images show the homogeneous distribution of aromatic species throughout the mixed particle.

The primary CCN analysis was done using the FHH-AT. The FHH-AT fits and CCN data of pure BC and mixed BC-AAA species were compared with the pure AAA samples (Figure 27). Fig. 27 shows the D_{ve} of the dry particles with respect to critical supersaturations. The empirically determined FHH parameters for pure and mixed BC samples, with the FHH parameters of the pure AAA samples that were determined in Gohil et al., (2022) are summarized in Table 2. Mixed BC aerosol are less active than their pure aromatic acid CCN activity. Moreover, the CCN activity of the mixtures decrease in the same order as that of the corresponding pure AAAs. It is interesting to note that the slope of the FHH-AT fits of mixed samples diverged away from the FHH-AT fits of the corresponding AAA with an increasing D_{ve} .

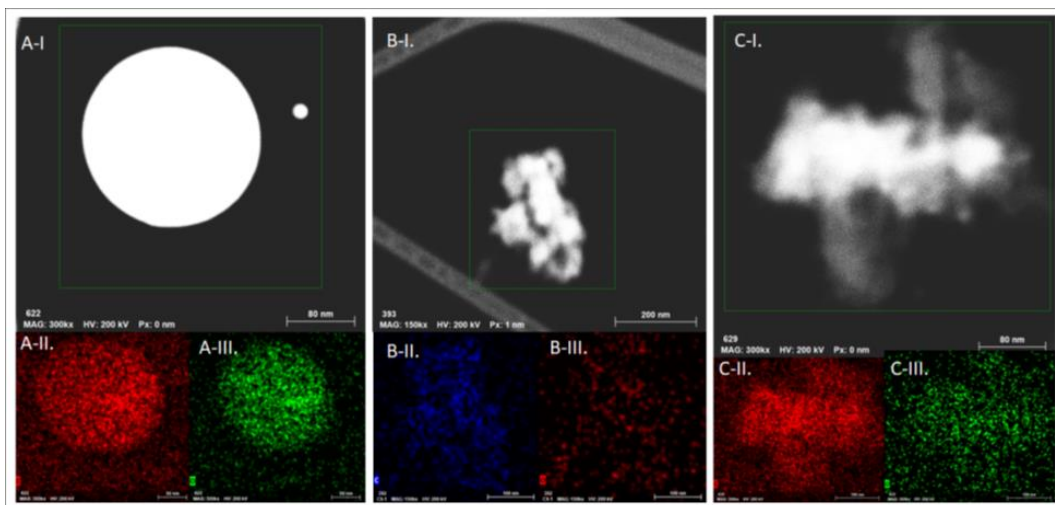


Figure 26. Images show dark field images of BC mixtures with Phthalic (A-I), Isophthalic (B-I) and Terephthalic acid (C-I). Images II and III for each mixture are EDXs images showing relative distribution of carbon and oxygen respectively for each mixture.

The changing slope of S_c vs. D_{dry} of the BC mixtures with respect to their corresponding pure AAA can be used to understand the relative importance of the mixture components on the overall CCN activity of the mixture in consideration. The FHH-AT fits at relatively smaller particle sizes for each mixture converge towards the FHH-AT fits of the corresponding pure AAA. This implies that the CCN activity of the given BC mixture is predominantly affected by the AAA present in the mixture. In other words, the particle morphology and composition of a given BC mixture is predominantly affected by the corresponding AAA at smaller D_{ve} . Conversely, the FHH-AT fits of a given BC mixture noticeably diverges away from the FHH-AT fit of the corresponding pure AAA. This implies that the morphology and composition, and hence the CCN activity of the mixture particles is affected by BC at larger D_{ve} .

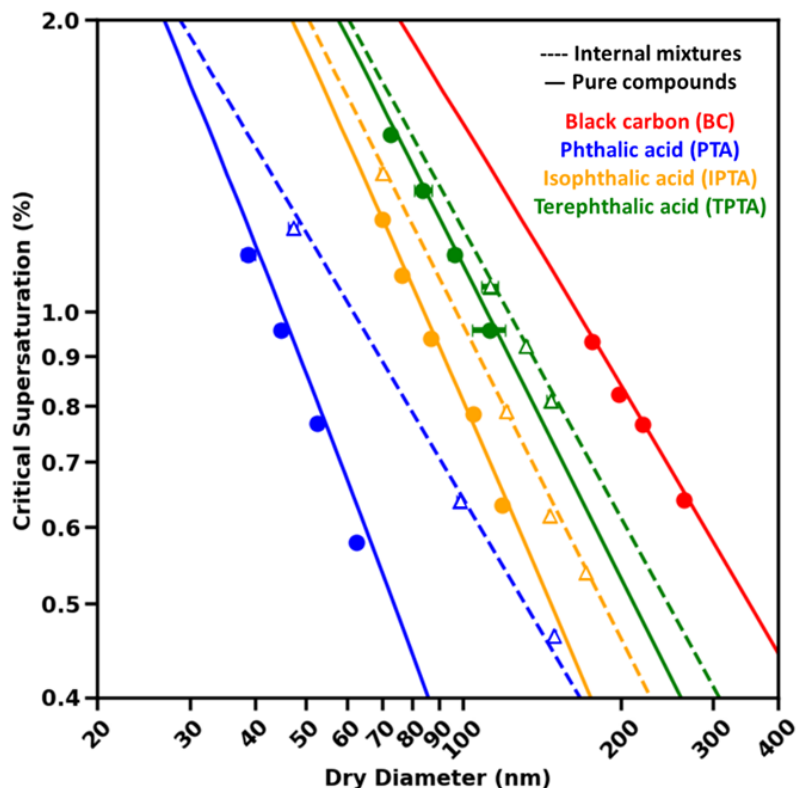


Figure 27. D_{dry} vs. S_c pairs derived from CCN measurements of pure (solid circles) and mixed BC (open triangles) aerosol is shown. The CCN measurements of the pure AAA samples (from Gohil et al. 2022) are also plotted. The FHH-AT fits are depicted using solid and dashed lines for pure and mixed samples, respectively. The particle dry diameter refers to the calculated volume equivalent diameters.

Table 6. FHH empirical parameters and R^2 scores for pure and mixed aerosol.

Sample	A_{FHH}^c	B_{FHH}^c	R_{FHH}^2	R_{HAM}^2
Black Carbon (Vulcan® XC72R)	7.54	2.26	0.957	0.899
Phthalic acid (PTA)	0.41	0.76	0.892	0.986
Isophthalic acid (IPTA)	0.39	0.87	0.936	0.967
Terephthalic acid (TPTA)	0.16	0.84	0.944	0.989
1:1 PTA-to-BC	1.37	1.11	0.875	0.991
1:1 IPTA-to-BC	0.23	0.87	0.908	0.954
1:1 TPTA-to-BC	0.27	1.04	0.934	0.943

Along with FHH-AT, the application of HAM was also studied for the pure and mixed BC aerosol (Figure 28). 2 sets of analysis were performed using HAM with different assumptions for the aqueous solubility of BC. For the CCN activity analysis with HAM, the aqueous solubility of BC was assumed to be 10^{-6} g/g water. Similar to FHH-AT, HAM fittings for pure and mixed BC aerosol were also compared to those for pure AAAs. Generally, the FHH-AT and HAM generate similar CCN activity predictions for pure and mixed BC aerosol under either of the BC aqueous solubility assumption. The R^2 goodness of fit scores (summarized in Table 3) for mixed aerosol all marginally increase for HAM; this is likely due to the explicit treatment of the AAA mixed with BC. However, there are subtle differences between the CCN activity predictions of FHH-AT and HAM for pure BC ($R^2_{FHH} = 0.957$ vs. $R^2_{HAM} = 0.899$). These differences could be the consequences of the explicit treatment of aqueous solubility of BC and AAA in the HAM framework. FHH-AT fundamentally assumes the particles to be completely water insoluble and therefore the CCN activity predictions based on FHH-AT are independent of the considerations related to the water solubility of the compounds. On the other hand, HAM-based CCN activity predictions can vary depending on the treatment of water solubility. Pure BC is assumed to have a non-zero aqueous solubility which results in a non-zero contribution from solubility partitioning in HAM and thus a slight underprediction of CCN activity as compared to FHH-AT.

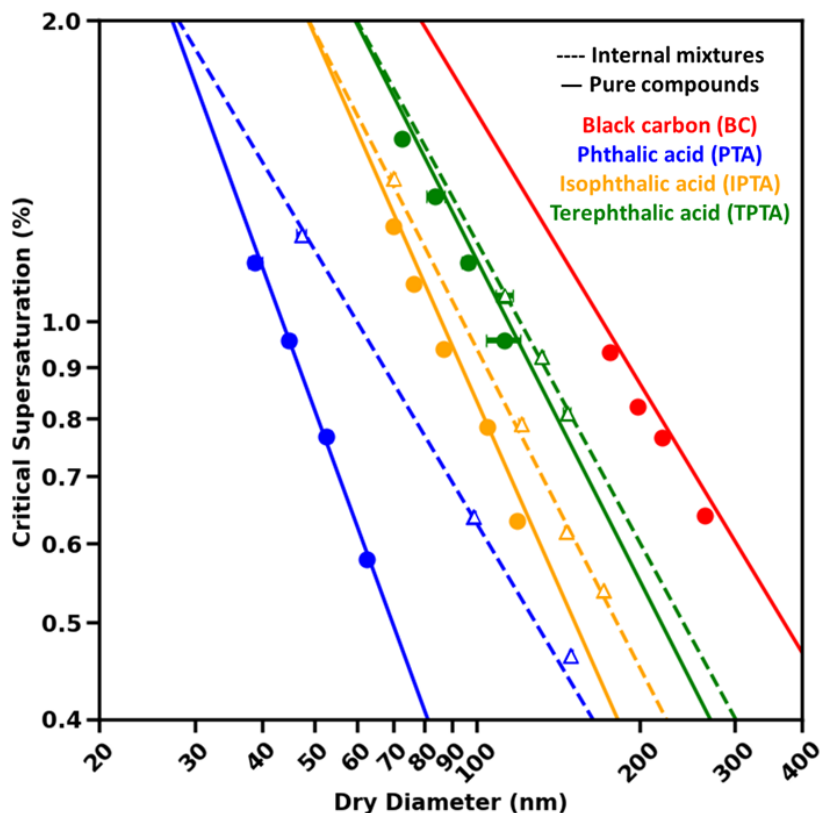


Figure 28. D_{dry} vs. S_c pairs derived using the CCN measurements are shown as in Fig. 27. HAM fits for pure and mixed BC are depicted as solid and dashed lines, respectively. The HAM fits for pure AAA are also shown as solid lines using the same colors as their corresponding mixture with BC. The HAM fits for all 7 sets of D_{dry} – S_c pairs used the FHH empirical parameters determined by fitting FHH-AT across the measured data (Table 2); the same set of empirical parameters that were used to fit FHH-AT fitting in Fig. 27. The R^2 correlation values are also presented in Table 3. A slight underprediction in the CCN activity of pure BC was observed with HAM compared to FHH-AT (R^2 of 0.899 and 0.957, respectively). This underprediction can likely be a result of the explicit treatment of BC solubility (10^{-6} g/g water) in HAM.

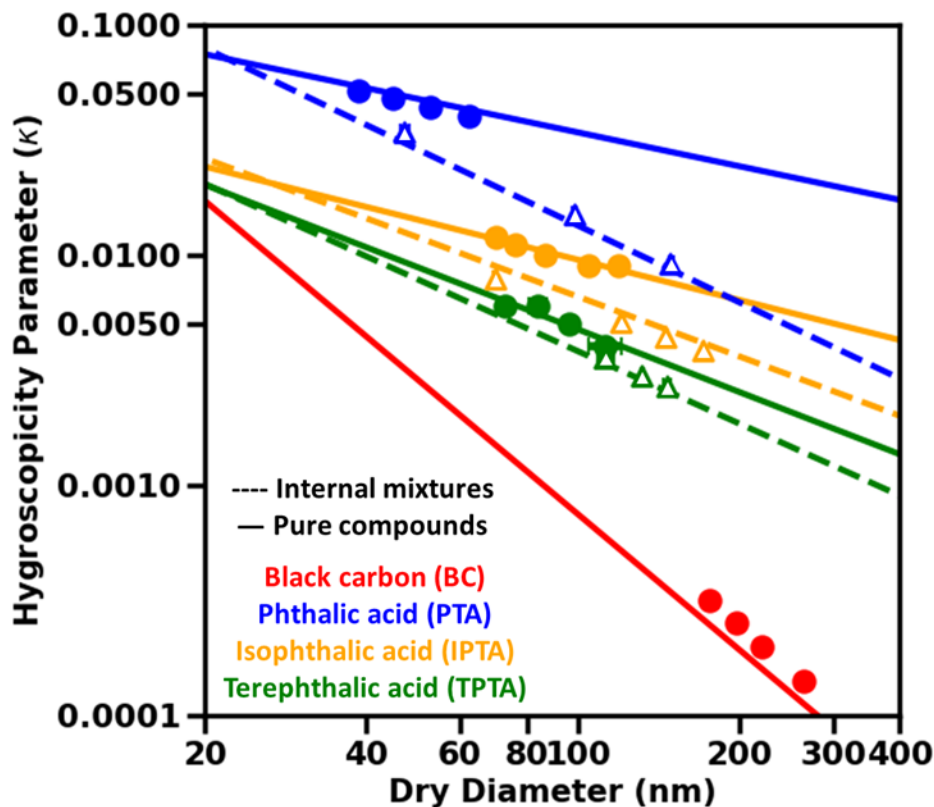


Figure 29. Hygroscopicity parameterization from HAM (κ_{HAM}) is shown for pure (closed circles) and mixed BC with pure AAAs (open triangles). The individual points correspond to κ_{HAM} parameterized using experimental data, and the fitted curves correspond to the D_{dry} -dependent theoretical (or, simplified) κ_{HAM} as described in detail in Gohil et al. (2022). Notable size-dependent trends in the hygroscopicity are observed for all studied aerosols. Furthermore, the size-dependent decrease in the hygroscopicity of BC-PTA is much more prominent than that in the hygroscopicity of BC-IPTA and BC-TPTA as compared to their pure AAA counterparts.

The hygroscopicity of the pure and mixed BC aerosol was also parameterized from HAM (κ_{HAM}) and compared to the κ_{HAM} of pure AAAs (Figure 29). It was noted that κ_{HAM} of mixed BC aerosol declined sharply compared to κ_{HAM} of the corresponding pure AAA. This sharp decline in the hygroscopicity of the mixture can be attributed to an increased influence of BC on the overall water uptake behavior of the BC mixtures. Moreover, κ_{HAM} of BC mixtures are especially low compared to the κ_{HAM} of the

corresponding pure AAA at larger D_{dry} . These disparities in the κ_{HAM} at larger sizes between BC mixtures and their corresponding AAAs further suggests a strong influence of BC on the overall CCN activity of the larger sized mixture particles. As with the S_c vs D_{dry} data, subtle underestimations can be observed in the size-resolved BC κ_{HAM} . This slight underprediction is also associated with the explicit implementation of BC solubility (10^{-6} g/g water) in the κ_{HAM} parameterization.

4.6 Summary and Implications

This work presents the analysis of the water uptake of pure black carbon (BC) and BC mixed with low-water solubility organic compounds. Because BC is known to show changes in mixing state across size distributions, CCN measurements were performed for constant size particles selected in stepping mode. However, at a constant particle size, TEM and CCN analysis suggested that the mixtures presented here had components of carbon and oxidized species uniformly distributed throughout the particles. Therefore, BC mixtures in this work were treated as internal mixtures implying that BC with other carbonaceous aerosol has the propensity to form homogenous internal mixtures.

The dynamic shape factor and effective density were also estimated for pure and mixed BC aerosol with respect to electrical mobility diameters. For all aerosol, the effective density was found to increase, and the shape factor was found to decrease with respect to size. It was inferred that these size-resolved trends were a consequence of the agglomeration of BC particles. It is to be noted that the TEM of BC mixtures also show that larger particles are more spherical than the smaller ones. However, TEM

of the pure BC particles suggest that smaller particles are more compact and spherical compared to particles with larger volume equivalent diameters that exist as agglomerated fractal-like structures. Further examination of changes in particle shape and density is needed to understand the possible causes for large deviations from sphericity at smaller sizes for pure BC particles. It should be noted that the volume equivalent diameter values derived using the shape factor and effective density data are similar to their corresponding electrical mobility diameter. Nonetheless, the volume equivalent diameters are a better representation of particle sizes as compared to the electrical mobility diameters (Gohil and Asa-Awuku, 2022). The utility of volume equivalent diameters is especially high for CCN analysis of aerosol using droplet growth models that show strong particle size dependence. Furthermore, hygroscopicity parameterizations based on FHH-AT or HAM also have explicit dependence on particle sizes. Therefore, volume equivalent diameters instead of the corresponding electrical or aerodynamic mobility diameters can result in hygroscopicity parameterization with a high confidence.

The CCN activity analysis of the pure and internally mixed (or, homogenous) BC was performed using the FHH-AT and HAM frameworks. FHH-AT is a widely known CCN activity model that describes water uptake through adsorption of water on particle surface. HAM is a recently developed framework that combines the FHH isotherm with the dissolved fraction of the particle accounting for the solubility limit of the compound. An explicit treatment of the solubility becomes significant for compounds that are sparingly soluble or effectively insoluble in water, and therefore HAM is particularly useful for the CCN analysis of such compounds. The utility of HAM is

notable through its application to the experimental CCN data of pure and mixed BC aerosol. The CCN activity for internal mixtures predicted using HAM is comparable to that predicted using FHH-AT (Table 2, R^2 scores for BC internal mixtures). The CCN activity prediction of pure BC using HAM is only marginally different from that predicted using FHH-AT on account for a finite water solubility consideration for BC in HAM (Table 2, R^2 scores for pure BC). Since there is no significant difference between FHH-AT and HAM predictions, HAM should be generally used for CCN analysis since HAM explicitly accounts for the effect of the bulk aqueous solubility on the overall water uptake behavior of any given chemical species.

The utility of HAM for the CCN analysis of low-water solubility species such as BC can also be understood using their single hygroscopicity parameter (κ_{HAM}). The experimental hygroscopicity of the pure and mixed BC species based on the HAM framework show high agreement with the theoretical estimates. The very good agreement between theoretical and experimental hygroscopicity suggests that explicit treatment of aqueous solubility for CCN activity analysis is important. Furthermore, HAM suggests a size-dependence associated with the hygroscopicity; κ_{HAM} decreases with an increase in the particle sizes. It is important to note that the size-dependent decline in the κ_{HAM} of the BC mixtures is more significant than the decline in the κ_{HAM} of their corresponding pure aromatic acids. The comparison between the aforementioned size-dependent trends is evident from the theoretical κ_{HAM} fits in Fig. 29. Additionally, the size-dependent experimental hygroscopicity of pure BC is slightly higher than the simplified hygroscopicity. This is likely analogous to the

underprediction in the HAM-based CCN activity estimates of pure BC when compared to the experimental measurements.

HAM was first developed for the CCN activity analysis and hygroscopicity parameterization of the atmospherically relevant aerosols that possess low water solubility. Previously, HAM had been applied on the controlled laboratory measurements of specific organic compounds with aqueous solubility varying over a range of 2-3 orders of magnitude. This work expands upon the applicability of HAM for the BC species observed in the atmosphere using agglomerated pure and mixed BC particles as a proxy. From here on, HAM can potentially be used for CCN activity analysis and hygroscopicity parameterization of other inorganic and organic species. This is valuable because HAM may be used for representing the hygroscopicity of organic and inorganic aerosol modes in Global Climate Models (GCMs), henceforth potentially improving the forcing due to aerosol indirect effect.

Appendix 4A

Summary: This supporting document contains the CCNC supersaturation calibration data, the description of effective density and shape factor calculations and conversion to volume equivalent sizes, and CCN measurements for pure and internally mixed BC-AAA samples.

4A.1 CCN counter (CCNC) calibration

(NH₄)₂SO₄ aerosol was passed through the CCNC column to calibrate the supersaturation. The set supersaturation inside the CCNC column depends on the axial temperature gradient for specified flow and pressure gradient. Calibration was performed by following the procedure described by Rose et al. (2008). Table 4A.1 provides a summary of the set and calibrated supersaturation datapoints that were used in this study for the CCN measurements of pure and mixed BC species.

Table 4A.1. Sample CCN Counter (CCNC) calibration data using (NH₄)₂SO₄

Supersaturation Setting (%)	Calibrated Supersaturation (%)	Critical Dry Diameter (nm)
0.2	0.210	76.4 ± 1.2
0.4	0.407	49.4 ± 0.86
0.6	0.578	39.2 ± 1.14
0.8	0.783	32.1 ± 0.88
1.0	0.94	28.5 ± 0.61
1.2	1.094	25.8 ± 0.85
1.4	1.334	22.6 ± 0.53

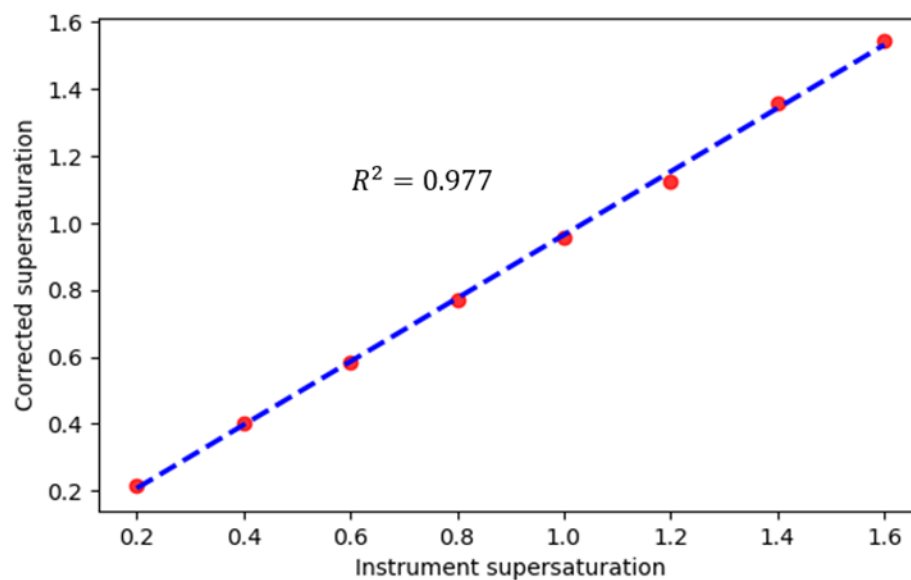


Figure 4A.1. CCNC calibration curve from the activation data provided in Table S1. This curve was used to calibrate the CCNC supersaturations at which AAA data was collected.

4A.2 CCN Measurement Data for Pure and Mixed BC species

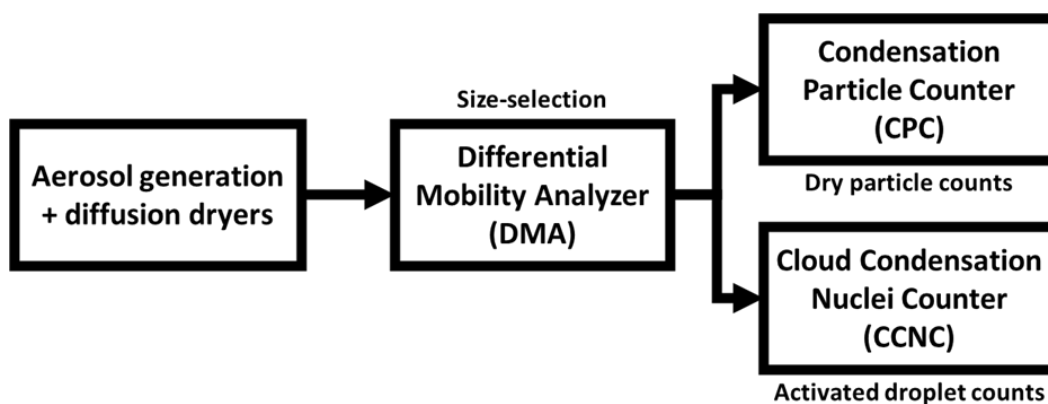


Figure 4A.2. Schematic of the step-sizing apparatus used to collect number concentration measurements of pure and mixed BC samples.

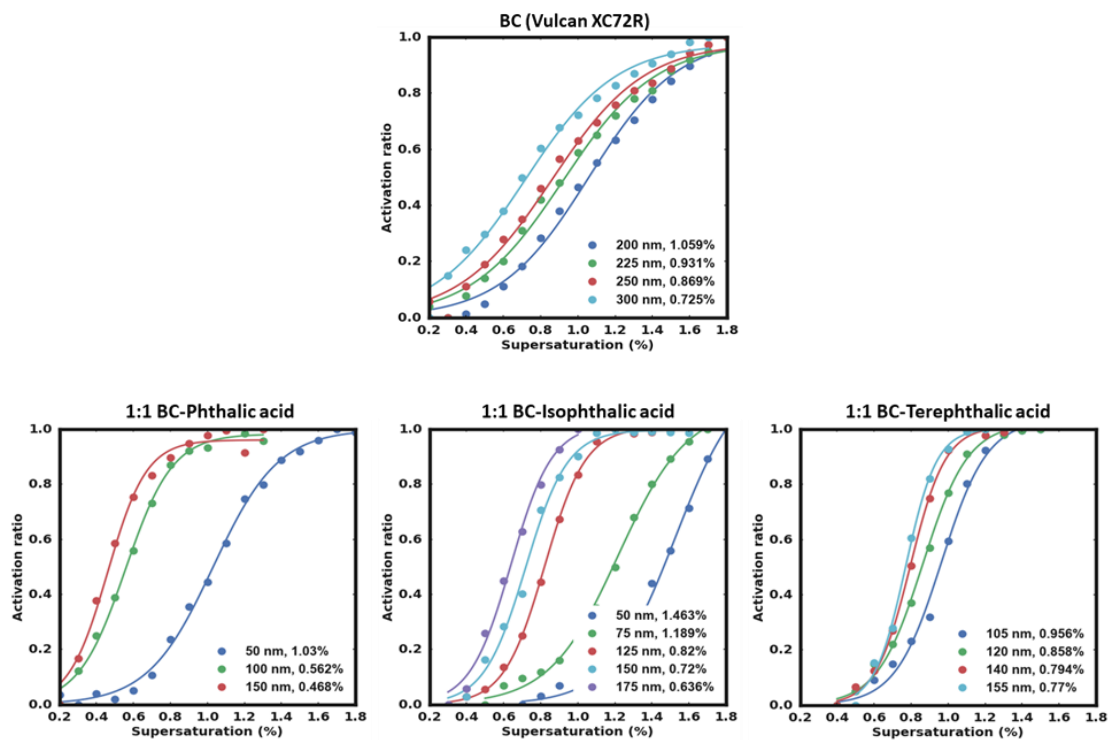


Figure 4A.3. Activation ratio and the corresponding sigmoidal fits for the pure and mixed BC samples. The measurements were performed with respect to the varying CCNC supersaturations for fixed electrical mobility diameters using the setup depicted in Fig. 4A.2.

Chapter 5: Application of a Size-Dependent Hygroscopicity Framework for Simulating Aerosol Water Uptake in a Large-scale Climate Model

5.1 Abstract

The indirect effect of aerosols on clouds, including that due to organic aerosols, is a significant source of uncertainties in climate modeling. One of the uncertainties in understanding aerosol-cloud interaction is systematic misrepresentation of the water uptake behavior (hygroscopicity) of mineral dust and carbonaceous aerosols – including primary organic matter (POM), secondary organic aerosols (SOAs), black carbon (BC). The hygroscopicity (denoted by κ) of aerosol species in large-scale models, such as the Community Atmosphere Model (CAM), are prescribed based on traditional Köhler droplet activation theory. Traditional Köhler theory (KT) assumes aerosols to be infinitely soluble in water and KT-based κ -values can be overestimated for partially water soluble and insoluble organic aerosols. These uncertainties can then translate to predicted aerosol-cloud interactions. In this work, we implemented a new hygroscopicity parameterization that accounts for partially soluble and water-insoluble aerosol, the Hybrid Activity Model (HAM) within CAM6. The HAM κ accounts for a wide range of low aqueous solubility organic aerosols by combining adsorption-based water uptake with water solubility as parameterized using the oxygen-to-carbon (O:C) ratio of the species. We investigate the changes in CCN and droplet properties from HAM-based hygroscopicity parameterization using sensitivity tests as well as the full 3D climate simulation. We also describe and analyze the resulting impacts on clouds

and climate. Furthermore, the fully developed HAM κ is further simplified to a power law function of particle size. Significant increase in atmospheric aerosol burdens and decrease in the CCN concentrations were observed after implementing the HAM κ in CAM6. Seasonal mean droplet sizes, cloud fraction and aerosol optical depth using HAM κ had better agreement with the observed seasonal means (within $\pm\sigma$). This work is the first to provide a computationally efficient treatment of size-dependent varied organic aerosol chemistry for cloud droplet formation. The results suggest that accounting for complex aerosol chemistry for hygroscopicity parameterization can improve estimates of physical and radiative properties of aerosols and clouds. An extensive hygroscopicity treatment of atmospherically relevant aerosols may now be considered in other global and regional climate models. This work shows that the hybrid hygroscopicity parameter developed in Chapter 3 can be implemented within a global climate model to modify the computation of cloud responses and the overall aerosol indirect forcing.

5.2 Background

Aerosol indirect effect (AIE) has been identified as the most significant source of uncertainty in the overall cloud forcing (IPCC 2007). Aerosols can act as Cloud Condensation Nuclei (CCN) resulting in cloud droplet formation, which can affect both the radiative properties of clouds (Twomey, 1977), as well as cloud lifetime and precipitation (Albrecht, 1989). Several studies show various strategies to reduce the uncertainty in AIE, therefore improving the estimates pertaining to the cloud radiative forcing within climate models. These strategies include modification of the CCN

activation schemes, inclusion of complex mechanisms for water uptake and droplet formation, and modification of aerosol properties (e.g., Abdul-Razzak & Ghan, 2000; Fountoukis, 2005; Morales Betancourt & Nenes, 2014; Rothenberg & Wang, 2016; Topping et al., 2013). The water uptake behavior of any species is quantified by the hygroscopicity of the given type of aerosol. The hygroscopicity parameter (denoted by κ) of an aerosol population determines droplet formation (Petters and Kreidenweis, 2007) by controlling the available CCN concentration, thereby affecting the resulting AIE. Therefore, it is important to understand the physicochemical properties that can vary aerosol κ to explain the uncertainties their water uptake behavior and subsequently in their AIE.

Previous studies have shown that predictions of AIE, cloud properties and radiative forcing can have a strong dependence on the aerosol hygroscopicity (denoted by κ). These sensitivity studies show that modifying κ in the large-scale Global Climate Models (GCMs) can result in the variations of several variables. Liu & Wang, (2010) performed CAM5 sensitivity runs by modifying the κ of organic aerosols and found that the uncertainty in the κ may cause an uncertainty in the aerosol indirect radiative forcing by a factor of 0.33. Betancourt et al., (2014) performed adjoint sensitivity analysis using CAM5 and found that a unit uncertainty in κ can cause uncertainties in the droplet concentration by a factor of 2 to 4. Other similar sensitivity studies include the use of chemical transport models for analyzing the effect of aerosol κ on the aerosol indirect effect (Karydis et al., 2011, 2012; Latimer and Martin, 2019). Aerosol κ has also been shown to cause variability in the aerosol atmospheric burdens (Liu et al., 2016). Rothenberg & Wang, (2016) showed that there can be up to a two-fold change

in the estimated ambient supersaturation from a unit change in κ depending on the CCN activation parameterization scheme. Recent studies have also demonstrated the κ dependence on relative humidity, thereby suggesting κ parameterization in climate models (Valenzuela et al., 2018; Zhao et al., 2022). Burrows et al., (2022) introduced a new aerosol mode (marine organic aerosol) with a $\kappa = 0.1$ in the Energy Exascale Earth System Model and found significant increments in the seasonal and annual cloud radiative forcing. In general, an improvement in the representation of κ is crucial for improving the estimations of AIE and radiative forcing.

The uncertainty in the κ of ambient aerosols, the CCN activity, and therefore the AIE is strongly linked to the presence of organic species in the atmosphere (Betancourt et al., 2014; Karydis et al., 2012; Liu & Wang, 2010). The uncertainties in the water uptake and therefore the indirect forcing due to organic aerosols are attributed to several reasons. First, there is a large compositional variability in the organic aerosols mass burden; organic aerosols can make up anywhere between 20%-90% for a given regional aerosol burden (Zhang et al., 2007). These compositional variances can significantly vary the overall κ of ambient particles. Organic aerosols also consist of compounds that are directly emitted into the atmosphere (primary organic matter; POM) and their oxidation products (secondary organic aerosol; SOA). The different organic aerosol sources can also result in notably different physical and chemical properties (Carrico et al., 2008; Petters et al., 2009). Consequently, more comprehensive, and detailed hygroscopicity parameterizations of organic aerosols are necessary to reduce the uncertainties in AIE.

Currently, the AIE estimations from GCMs use prescribed κ values for organic and inorganic aerosol types (Liu et al., 2016). These prescribed κ values for different aerosol types are based on the droplet growth measurements under sub- and supersaturated conditions for different types of atmospherically relevant aerosols (e.g., Burrows et al., 2022; Liu & Wang, 2010). For certain aerosols, these prescribed values can also be derived from their molar volume which is based on the Raoult's law in Köhler Theory. The hygroscopicity parameterization using Raoult's law is size-independent and provides a constant κ for the associated aerosol species across the entire particle distribution. Whereas κ of the particles containing water-soluble inorganic species can be quantified with high certainty, significant variability in the κ of the organic species can be observed with respect to their chemical compositions and mixing states. Moreover, organic and inorganic species interact with each other in the atmosphere which also results in significant modifications in the aerosol κ (e.g., Asa-Awuku et al., 2009; Bond et al., 2013; Dalirian et al., 2018; Fofie et al., 2018; Malek et al., 2022; Padró et al., 2012; Rastak et al., 2017). Generally, κ of highly hygroscopic species can take up values ≥ 1 , whereas effectively non-hygroscopic species have a κ of ~ 0 . It has been found that the κ of organic aerosols can vary from 0 (Kanakidou et al., 2005), e.g., black carbon and other primary organic compounds from biomass burning, to highly hygroscopic, e.g., amino acids and oligomers (Marsh et al., 2017; Dawson et al., 2020). Additionally, the CCN activity and κ of aerosols, can depend on various physicochemical properties (e.g., Kucinski et al., 2021; Laaksonen et al., 2016, 2020; P. Liu et al., 2018a; Malek et al., 2022; Mao et al., 2021; Petters & Kreidenweis, 2007, 2008; Schill et al., 2015; Sullivan et al., 2009) that may not be described by

Raoult's law. Therefore, more comprehensive CCN frameworks are required to parameterize their κ .

It has been found that explicit treatment of aqueous solubility can be made for improving the κ parameterization of organic compounds. Petters & Kreidenweis, (2008) showed that the use of bulk solubility can generate a more accurate κ of pure as well as mixed aerosol particles. The same concept has been implemented by other studies to understand the CCN activity and water uptake of several low water-solubility species like mineral dust (Sullivan et al., 2009). This solubility-inclusive parameterization accounts for the effect of variability in droplet size on κ . Mao et al., (2022) recently showed that adsorption-based CCN models (such as the Frenkel-Halsey-Hill Adsorption Theory; FHH-AT) can also be potentially used for parameterizing aerosol κ . They employed the methodology from Petters & Kreidenweis, (2007) using the water activity of FHH-AT to derive κ for effectively water-insoluble organic and polymeric species. Furthermore, Gohil et al., (2022) parameterized the aerosol κ using a hybrid CCN activity framework (called the hybrid activity model; HAM). HAM combines the adsorption isotherm from the FHH-AT with solubility partitioning to describe droplet growth and parameterize κ . It is worth noting that the κ parameterizations based on FHH-AT and HAM depend on particle size. κ parameterization by Gohil et al., (2022) explicitly accounted for the aqueous solubility of the species with particle size.

In this work, the HAM-based hygroscopicity parameterization was implemented in a GCM to study the AIE. The main idea of this work is to understand the size and

solubility dependence of the hygroscopicity parameterization in the HAM that can contribute to the variability in AIE estimations in a GCM. The NCAR Community Atmospheric Model (CAM) was used to examine the uncertainties in global simulated CCN concentration, droplet number concentration, and AIE arising from the uncertainty in the current representation of organic aerosol κ . In its current state, the CCN activation parameterization in CAM computes droplet growth by incorporating prescribed κ for all aerosol types. The aerosol κ is important in an activation parameterization because it directly relates to the water activity of the CCN model (Petters and Kreidenweis, 2007) and controls the subsequent droplet growth. In this work, the aerosol κ for different aerosol types were calculated using the size- and solubility-dependent HAM hygroscopicity parameterization. The particle size and mixing ratio information from the Modal Aerosol Model (MAM) was also used in the κ calculations for different aerosol types in the individual aerosol modes. Furthermore, to reduce the computational burden, a simplified form of the HAM hygroscopicity parameterization was implemented in CAM.

5.3 Model Description

5.3.1 NCAR Community Atmosphere Model (CAM)

The NCAR Community Atmosphere Model (CAM, version 6.3) performed all simulations in this work. CAM6.3 (hereafter CAM6) is the atmospheric component of the Community Earth System Model (CESM2.2). The Modal Aerosol Model (MAM) predicts the mixing state of different aerosol types in the aerosol modes and the number concentration of each aerosol mode. MAM4 is the current four-mode model used in

CAM6 (Liu et al., 2016). The prediction for the mass and number mixing ratios of cloud liquid and cloud ice, the diagnoses of the mass and number mixing ratios of rain and snow, and the treatment of the conversions among the cloud hydrometeors is done with the two-moment stratiform cloud microphysics scheme (Morrison and Gettelman, 2008; Gettelman and Morrison, 2015). CCN activation and droplet formation for the multi-modal lognormal aerosol size distribution in MAM4 is derived using the Abdul-Razzak & Ghan, (2000) CCN activation scheme.

Other major components included in the CAM6 runs – 1. A deep convection scheme (Zhang & McFarlane, 1995), 2. A unified turbulence scheme, Cloud Layers Unified By Binormals (CLUBB; Bogenschütz et al., 2010; Bogenschütz & Krueger, 2013; Golaz et al., 2002), that also incorporates warm cloud macrophysics and shallow convection, 3. A radiation scheme to treat aerosol and cloud radiative effects (Iacono et al., 2008), and 4. A cold cloud macrophysics scheme (Gettelman et al., 2010).

5.3.2 Prescribed Hygroscopicity of Aerosols through Modal Aerosol Model (MAM) in CAM6

MAM4 is the aerosol model that is coupled with CAM6. The initial versions of MAM included the seven-mode aerosol model (MAM7) and the three-mode aerosol model (MAM3) (Liu et al., 2012). MAM7 is known to be highly effective at representing different aerosol types segregated among the Aitken, accumulation, and coarse modes, but at the expense of computational efficiency. On the other hand, MAM3 is computationally efficient but significantly underestimates surface black carbon concentrations over Asia and higher latitude regions. MAM4 is an upgraded

version that includes a separate primary carbon mode, in addition to the Aitken, accumulation and coarse modes, to explicitly treat the microphysical aging of black carbon. A brief description of the individual modes in MAM4 are provided in Table 1.

Table 7. Interstitial and cloud-borne aerosol types of each aerosol mode in MAM4 (mmr: mass mixing ratio)

Aitken mode	Accumulation mode	Coarse mode	Primary carbon mode
Number mixing ratio	Number mixing ratio	Number mixing ratio	Number mixing ratio
Sulfate mmr	Sulfate mmr	Sulfate mmr	Fresh primary organic mmr
Ammonium mmr	Ammonium mmr	Ammonium mmr	Fresh BC mmr
Seasalt mmr	Seasalt mmr	Seasalt mmr	
Secondary organic mmr	Secondary organic mmr	Dust mmr	
	Aged primary organic mmr		
	Aged BC mmr		
	Dust mass mixing ratio		

The four modes in MAM4 include six different aerosol types; their names and alias as denoted in CAM6 are as follows – sulfate (SO₄), sea salt (SEASALT), black carbon (BC), soil/mineral dust (DUST), primary organic matter (POM) and secondary organic aerosol (SOA). The hygroscopicity parameter (κ) for all these species in CAM6 is prescribed through MAM4. The κ values of 0.507 and 1.16 are prescribed for SO₄ and SEASALT, respectively, indicating their highly hygroscopic nature (Liu et al., 2016). The κ value of ~ 0 is prescribed for both POM and BC aerosol types to denote the effectively non-hygroscopic nature of the organic matter generated from biomass and fossil fuel combustion. For SOA, the κ values are prescribed to be in the range of

0.06 – 0.30 (e.g., Asa-Awuku et al., 2008; Carrico et al., 2008; Gunthe et al., 2009; Prenni et al., 2007). The prescribed κ for all the aerosol types within each mode are constant values across the full particle size distribution. Using these values, the volume mean hygroscopicity of each aerosol mode is then calculated based on the individual species present in that mode. The volume mean hygroscopicity parameters of the modal aerosol population are then used in the CCN activation parameterization. This suggests that the certainty in the CCN activation and droplet nucleation will directly depend on the hygroscopicity of the aerosol modes and therefore on those of the individual aerosol types. Moreover, since POM and SOA aerosol types represent numerous compounds, a constant κ applied over the particle size distribution of the carbonaceous aerosols may not be the best representation of the overall water uptake behavior.

5.3.3 Hygroscopicity Parameterization for Droplet Nucleation

In this work, a simplified representation of κ is developed using the Hybrid Activity Model (HAM) framework to implement in droplet nucleation, for organics (POM, SOA, BC) and Dust. Such that κ for the organic and dust species are no longer prescribed and are instead computed prior to droplet nucleation. Additionally, the κ of the aerosol mode is computed as the volume mean of the κ of the individual aerosol types and the HAM-derived κ as explained by Gohil et al., (2022) is simplified to a power law functions. The following text briefly described the development of the size dependent κ to be implemented for carbonaceous aerosols.

The theoretical HAM-based κ as a function of dry particle size is expressed as follows,

$$\kappa = \frac{6\theta D_w}{D_{dry}} (1 - X_w(1 - A_{FHH}\theta^{-B_{FHH}})) \quad (5.1)$$

where D_{dry} is the diameter equivalent to the size of the dry particle of a given aerosol type in the aerosol mode, A_{FHH} and B_{FHH} are empirical FHH parameters that depend on the aerosol type, X_w is the mole fraction of water computed by incorporating solubility partitioning in the Raoult's law (Riipinen et al., 2015), D_w is the size of one water molecule, and θ is referred to as the surface coverage corresponding to the dry size (D_{dry}) and is theoretically estimated using HAM (Gohil et al., 2022). In Eq. (5.1), D_{dry} is the only independent variable while all the other quantities are the properties of a specific aerosol composition. The A_{FHH} and B_{FHH} of the BC and dust aerosols were obtained from literature and are summarized in Table 2. The A_{FHH} and B_{FHH} values of POM and SOA were obtained from least square minimization using their experimental data.

It is important to note that Gohil et al. 2022 showed HAM to work for known aerosol composition. However, when the carbonaceous aerosol composition is unknown the O:C ratio can be used as a proxy for water-solubility (Nakao, 2017) as follows,

$$\log(C) = 20 \left[\left(\frac{O}{C} \right)^{0.402} - 1 \right] \quad (5.2)$$

where C is the aqueous solubility, and $\left(\frac{O}{C}\right)$ is the O:C ratio of the species. The O:C ratio of the pure and mixed particles has been applied to parameterize the theoretical aqueous solubility and subsequent hygroscopicity of CCN (e.g., Kuwata et al., 2013; Nakao, 2017; Razafindrambinina et al., 2022). This work uses the published O:C ratios (Table 2) of known aerosol species to obtain average aqueous solubility of POM and SOA aerosol species in CAM6. Table 2 provides O:C ratios and the references from for different POM and SOA considered in this work. For BC and DUST aerosol species with exceptionally low water solubility, a value of 10^{-5} vol/vol water is used in the κ parameterization from Eq. (5.1).

Table 8. Previous studies for hygroscopicity values from experiments and observations

Organic aerosol species	A_{FHH}	B_{FHH}	Average O:C	References
Primary organic matter (POM)	1.61 ^a	2.45 ^a	0.2 ^b	#Aiken et al., (2008); #Lambe et al., (2011)
Secondary organic aerosol (SOA)	2.2 ^a	0.87 ^a	0.45 ^b	\$Asa-Awuku et al., (2009); #Canagaratna et al., (2015); #Cappa & Wilson, (2011); \$Engelhart et al., (2008); \$Huff Hartz et al., (2005); #Mahrt et al., (2021); \$Prenni et al., (2007)
Black carbon (BC)	7.54 ^b	2.26 ^b	—	&Gohil et al. (submitted)
Mineral dust	1.5 ^b	2.25 ^b	—	&Kumar et al., (2009 a, b)

^a Calculated using cited experimental CCN data

^b Acquired from literature

References O:C data

\$ References for CCN Activity information, specifically activation supersaturation-critical diameter ($S - D_c$) pairs

& References A_{FHH} and B_{FHH} data

Aerosols are treated as internally mixed in CAM6 – the overall hygroscopicity of aerosol species were calculated as molar averaged hygroscopicity parameters of the individual aerosol modes. The HAM hygroscopicity parameterization is a complex function of dry particle size (Eq. 5.1); thus, for computational efficiency, the hygroscopicity function was transformed into a power law expression using the species-dependent parameters for the aforementioned carbonaceous aerosol modes. Different set of parameters and properties were incorporated in Eq. (5.1) for different aerosol types to generate their size-resolved κ distributions. Subsequently, a generalized power law fit was applied to the size-dependent κ_i for each aerosol species that can be expressed as follows,

$$\kappa_i = C_i D_{dry}^{-a_i} \quad (5.3)$$

where D_{dry} is the dry particle size, and C_i and a_i are power law coefficients for the aerosol species i . The power law was also determined to be a function of dry particle size containing 2 power law parameters (Eq. 5.3). Table 3 provides the power law coefficients for the organic (POM, SOA and BC) and Dust aerosol species to use in CAM6.

Table 9. Power law coefficients for POM, SOA, DUST and BC

Organic aerosol species	C_i	a_i
Primary organic matter (POM)	1050	2.76
Secondary organic aerosol (SOA)	1261.7	2.55
Black carbon (BC)	5.84	1.94
Mineral dust	3.67	1.18

5.4 Global Climate Model Configuration and Experiments

Three set of simulations were performed using CAM6. The first was a control run (denoted as “CTRL”) that was performed to benchmark the default setup of CAM6. In CTRL run, the hygroscopicity for all aerosol types were prescribed through MAM4. The second set was referred to as the “KT” run for which the hygroscopicity values were no longer prescribed and were calculated based on the Raoult’s law water activity in Köhler theory. The density and molecular weights of the required aerosol types were obtained through MAM4 (Liu et al., 2016). The overall hygroscopicity of the individual modes were determined as the volume average of the hygroscopicity of individual aerosol types comprising the respective modes. The third set of experiments was called “HAM” in which the hygroscopicity of each aerosol types were estimated from HAM using the method described in Section 2.3. In addition to the density and molecular mass of the aerosol types, the mode diameter and mixing ratio were also acquired from MAM4. The mixing ratio of individual aerosol types were used to determine the equivalent volume and hence size of a given aerosol type present in the mode. This equivalent size was then used in the corresponding power law expression for quantifying the hygroscopicity of the aerosol type. The volume average of the hygroscopicity of each aerosol type in each mode was then treated as the hygroscopicity of that mode.

All the experiments were run with a horizontal resolution of $0.9^{\circ} \times 1.25^{\circ}$ (conventionally denoted as 1°), using specified dynamics configurations (also known as nudging). Under the specified dynamics configurations, the model meteorology is

strictly constrained using external meteorological analysis (Ma et al., 2015; Tilmes et al., 2015). For all the experiments, the NASA Modern-Era Retrospective analysis for Research and Applications version 2.0 (MERRA2.0) 1° data from the year 2018 was used to drive the model. The aerosol and greenhouse gas emissions were set to the present-day (year 2000) conditions for all experiments. Employing the nudging technique facilitated a direct comparison of model simulations with observational data since simulation of aerosol burdens for specified hygroscopicity parameterizations was based on realistic climatic conditions. The nudged simulations were performed between July 01, 2017, and June 30, 2019. The simulation results for the year 2018 from all three experiments were used for the analysis of the annual mean variables. The results between March 01, 2018, and February 28, 2019 were used to study the seasonal mean variables. The analyses from all three CAM6 experiments were compared to three distinct observational/reanalysis datasets.

5.4.1 Cloud Fraction and Cloud Droplet Radius - Moderate Resolution Imaging Spectroradiometer (MODIS)

MODIS (Terra/Aqua) was data for direct global observations of the daily cloud fraction and cloud droplet radius. The global distribution of the MODIS (Terra/Aqua) gridded daily product at a horizontal resolution of 0.1° was available for the year 2018.

5.4.2 Aerosol Optical Depth – AErosol RObotic NETwork (AERONET)

The quality-assured (Level 2.0) Aerosol Optical Depth (AOD) data from 1,348 locations were used for the analysis. The daily-averaged AOD product was available for the year 2018.

5.4.3 Modern-Era Retrospective analysis for Research and Applications version 2.0 (MERRA2.0)

MERRA2.0 is the NASA atmospheric reanalysis dataset from the satellite era (between 1980 and present). The MERRA2.0 data assimilation system uses the Goddard Earth Observing System Model version 5 (GEOS-5). The MERRA2.0 data with a spatial resolution $0.625^\circ \times 0.5^\circ$ (Gelaro et al., 2017) for the year 2018 was used to compare the model simulations in all experiments. Moreover, 5-year average of MERRA2.0 climatological data about the year 2018 was used.

5.5 Results and Discussion

In this section, the results from the CAM6 simulations are presented. The following subsections describe the simulated aerosol and cloud properties that have significant implication towards the understanding of the AIE. For instance, the indirect radiative forcing due to carbonaceous aerosols including different POM and SOA can range between -2.4 to -4.4 W m^{-2} (e.g., Kanakidou et al., 2005; Lohmann et al., 2000). The simulated results for these aerosol and cloud properties were compared against

observations and reanalysis datasets to validate the CAM6 simulations for each of the experiments.

5.5.1 Atmospheric Aerosol Burdens

The organic (POM+SOA), BC and DUST burdens simulated using three different configurations of CAM6 are shown in Figure 30. The vertically integrated annual mean global organic, BC and DUST burden from the three CAM6 simulations (CTRL, KT, and HAM), are compared to the organic burden from MERRA2.0 reanalysis. Fig. 30 (a), (d) and (g) show the organic burden simulated by the CTRL, KT and HAM experiments, respectively. Fig. 30 (j) shows the 5-year average of organic burden about the year 2018 from the MERRA reanalysis. Similarly, Fig. 30 (b), (e) and (h) show the BC burden simulated by the CTRL, KT and HAM experiment, respectively. The BC burden from the MERRA reanalysis shown in Fig. 30 (k). The dust burden simulated from CTRL, KT and HAM are presented in Fig. 30 (c), (f) and (i), respectively. The MERRA reanalysis for dust burden in Fig. 30 (l).

The major difference between the simulated and reanalysis mean burden for all organic and BC aerosol types was observed over polar regions (below -60°S and above 60°N). Moreover, the simulated global annual mean burdens (Fig. 30 a, b, and c) are generally underestimated with respect to the reanalysis data (Fig. 30 j, k, and l) even though the agreement between the simulations and reanalysis is better over tropics and mid-latitudes. The agreement between the KT-simulated burdens with respect to the reanalysis data is lower than the burdens simulated from CTRL or HAM

configurations. For example, the maximum global mean organic burden in the KT case was found to be 27.63 mg/m². This global mean increased to 31.86 mg/m² and 36.51 mg/m² for CTRL and HAM, respectively. It was found that HAM estimated the global mean organic burden most closely to the reanalysis data (46.18 mg/m²).

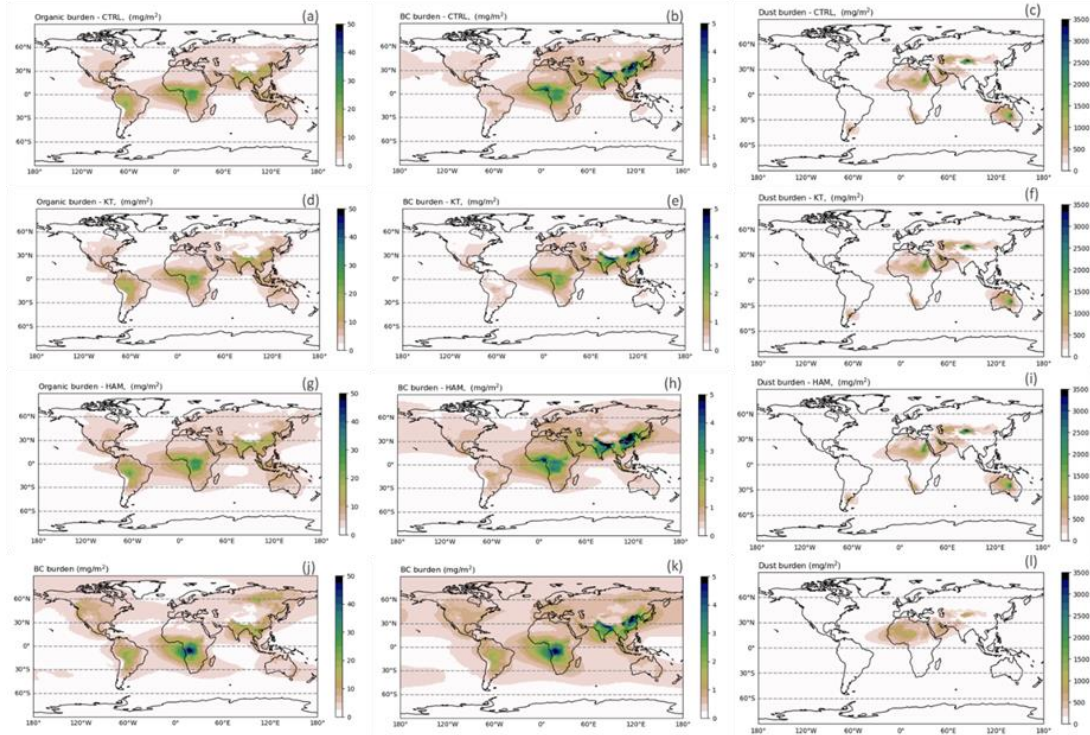


Figure 30. Annual global mean of vertically integrated burdens (mg m⁻²) of organic (left panels), BC (middle panels) and DUST (right panels) modes. First row (a, b, c) shows the simulations from the CTRL run. Second row (d, e, f) shows the simulations from the KT run. Third row (g, h, i) shows the simulations from HAM run. Fourth row (j, k, l) shows the MERRA2.0 reanalysis burden.

Similarly for BC, the simulated global mean burden from KT configuration (maximum of 4.84 mg/m²) has the lowest agreement with the reanalysis global mean burden (maximum of 5.95 mg/m²). On the other hand, the global mean burden from HAM configurations (maximum of 6.33 mg/m²) was overestimated compared to the reanalysis global mean burden as well as had the highest agreement. The lower overall

agreement between the KT-simulated burdens compared to the reanalysis burdens is due to the underestimated burdens in the KT configuration. The KT-simulated burdens were underestimated to the generally higher κ of the aerosol types. The increased κ would likely result in a greater CCN concentration. Consequently, there would be an increase in the droplet count and precipitation amount, ultimately leading to higher wet removal and decreased atmospheric burden.

For DUST, the simulated burden is larger than the reanalysis. Compared to the reanalysis DUST burden maximum of 1197.63 mg/m², the maximum global mean DUST burdens were found to be 3493.7 mg/m², 3500.2 mg/m² and 3622.6 mg/m² from the CTRL, KT and HAM simulations, respectively. It is important to note that all three κ configurations result in a higher DUST burden compared to the reanalysis burdens in southern tropics over Australia. The general overestimation of the DUST burden could be attributed to a lower prescribed (for CTRL) or parameterized (for KT or HAM) DUST κ than the real value.

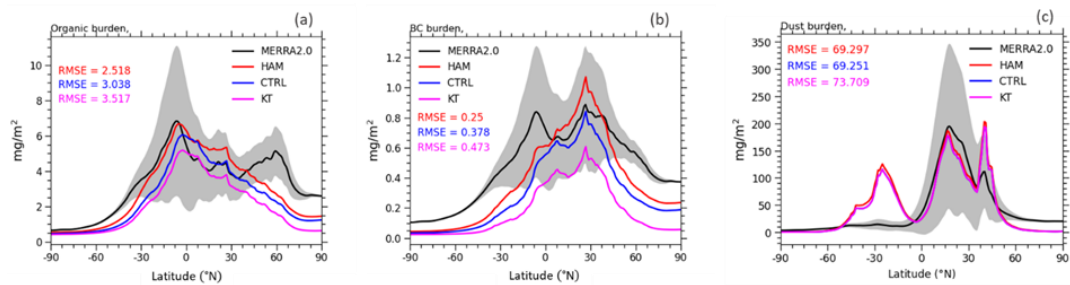


Figure 31. Annual zonal mean profiles for the organic (a), BC (b) and DUST (c) aerosol modes. The simulated aerosol burdens are color coded along with their RMSE with respect to the reanalysis data (shown in black). The gray shaded region denotes one standard deviation about the reanalysis data.

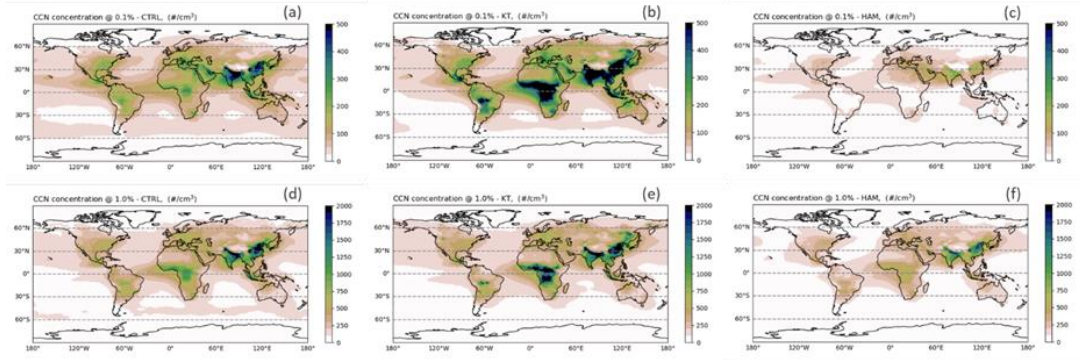


Figure 32. Annual global mean of the cloud condensation nuclei (CCN) concentrations at 0.1% supersaturation (a, b, c) and 1.0% supersaturation (d, e, f) between ~850hPa and ~920hPa. The simulated CCN concentrations from the CTRL run (left panels), KT run (middle panels) and HAM run (right panels) are shown.

The deviation between the simulated and reanalysis burdens becomes more evident by looking at the zonal means (Figure 31). The simulated organic, BC and DUST burden zonal means are plotted against their respective reanalysis zonal means in Fig. 31 (a), (b) and (c), respectively. The root-mean-squared error (RMSE) of the simulated vs. reanalysis means are also shown on the graphs for the respective aerosol type. Also, the gray shaded region represents the first standard deviation about the zonal mean reanalysis burdens. HAM-based simulated zonal mean burdens show notably better agreement with the reanalysis organic and BC that is also suggested by their lower RMSE with the reanalysis burdens. Also, the organic and BC burdens from HAM simulations lie within one standard deviation of the reanalysis burdens over the tropics. For DUST, burdens from all three simulations agree well with the reanalysis budget over northern tropics and midlatitudes. However, there is a significant overestimation in the DUST budget from all three simulations over the southern tropics and midlatitudes. This overestimation results in a generally large RMSE for the DUST budget zonal means ($\text{RMSE} \approx 70 \text{ mg/m}^2$). For all three simulations, the organic, BC

and DUST budget is consistently underestimated with respect to the reanalysis over the polar latitudes. HAM framework was specifically developed to study droplet formation in warm-cloud conditions, which could be the reason for the high bias with respect to the reanalysis over polar latitudes.

5.5.2 Cloud Condensation Nuclei (CCN) Concentrations

Significant variability was observed in the CCN number concentrations among the three κ configurations with respect to each other. The global annual mean CCN number concentrations between 950hPa and 820hPa levels for ambient supersaturated conditions of 0.1% and 1.0% were analyzed (shown in Figure 32). Fig. 32 (a), (b) and (c) show the CCN concentrations generated from CTRL, KT and HAM simulations at 0.1% supersaturation. It was found that KT estimated significantly larger CCN concentration than CTRL or HAM. A maximum global annual vertical mean concentrations of 807.81 cm^{-3} and 295.37 cm^{-3} were obtained from CTRL and HAM simulations, respectively compared to 1471.42 cm^{-3} from KT. A similar trend was observed for the CCN concentrations at 1.0% supersaturation. Fig. 32 (d), (e) and (f) show the CCN concentrations at 1.0% from CTRL, KT and HAM simulations, respectively. An overall increase in the CCN concentrations was observed between 0.1% and 1.0% supersaturations. Furthermore, the CCN concentrations from KT simulations were considerably larger than those obtained from the CTRL and HAM simulations (maximum CCN concentrations of 2934.87 cm^{-3} , 3540.92 cm^{-3} and 2032.54 cm^{-3} from CTRL, KT and HAM simulations, respectively). The higher CCN

concentrations in the KT case is due to the generally large, parameterized value of κ for all aerosol types. On the other hand, κ parameterized from the HAM framework is generally lower than the Raoult's law counterpart due to the size-dependence and explicit solubility considerations (Gohil et al. 2022).

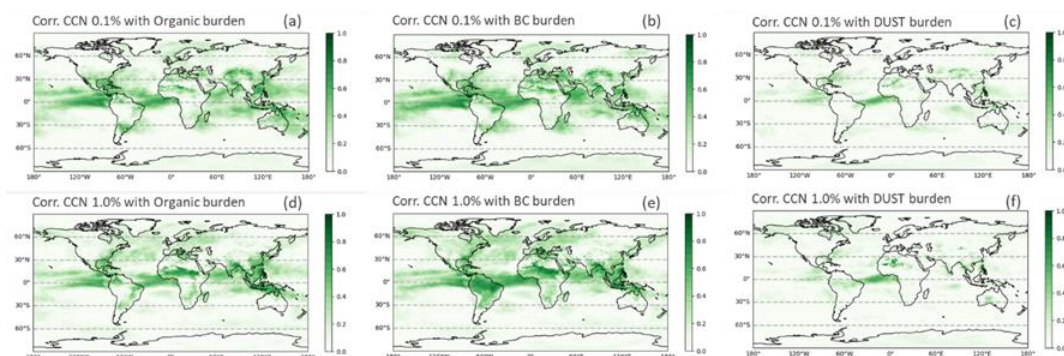


Figure 33. Correlation of the relative change in the CCN concentrations at 0.1% (top row) and 1.0% (bottom row) with the relative changes in organic (a, d), BC (b, e) and DUST (c, f) aerosol modes. The correlation between CCN concentration changes and aerosol burden changes between HAM and CTRL cases are plotted.

Lowest CCN concentration estimates were also generally observed for the HAM simulations at other ambient supersaturation conditions (not shown here). A correlation analysis was performed to understand the decline in the HAM-generated CCN concentrations. The correlation of the change in the global annual mean CCN concentrations at 0.1% and 1.0% supersaturations with respect to the changes in the different global annual mean aerosol burdens are shown in Figure 33. The correlations between were calculated between the relative changes in the CCN concentrations and aerosol burdens derived from CTRL and HAM simulations. The change in the CCN concentrations at 0.1% supersaturation has a strong correlation with the change in the organic burden between CTRL and HAM simulations (Fig. 33a). That is, the relative

decrease in the organic burden strongly affects the relative change in the CCN concentration at 0.1% between CTRL and HAM. Similar trends are observed corresponding to the relative decrease in the BC burden correlation with the CCN concentration (Fig. 33b). The highest correlation coefficient was found to be ≥ 0.95 for both organic and BC burdens, and strong correlations are spread uniformly across tropics and midlatitudes. The average correlation coefficients between 45°S and 45°N corresponding to changes in organic and BC burdens were 0.51 and 0.58, respectively. The correlation between relative decrease in the CCN concentration at 0.1% vs. DUST burden is generally low. These low correlations could be resulting from comparable DUST burdens simulated in CTRL and HAM configurations (shown in Fig. 33c). Whereas higher correlations in the case of organic and BC burdens is due to a reduced κ parameter of the aerosols, i.e., small changes in organic and BC burdens generate notable changes in the CCN concentration.

5.5.3 Droplet Number Concentration and Liquid Water Path

The available CCN concentrations govern the cloud droplet number concentration (CDNUMC) and the liquid water path (LWP), which directly relate to the cloud radiative and physical properties. Figure 34 (a), (b) and (c) illustrate the global annual means of the vertically integrated CDNUMC simulated from CTRL, KT and HAM experiments, respectively. Similar to the CCN concentrations, KT simulated the highest CDNUMC (maximum of $251.31 \times 10^9 \text{ m}^{-2}$) whereas the HAM simulated the lowest CDNUMC (maximum of $145.46 \times 10^9 \text{ m}^{-2}$). The distinction between them is

more apparent from relative differences of the control experiments with respect to the KT and HAM experiments. Fig. 34 (d) and (e) show the relative difference between global annual mean vertically integrated CDNUMC from CTRL experiment with respect to the simulated values from KT and HAM experiments, respectively. The overestimation in the CDNUMC from KT compared to that from CTRL was about 12%. Whereas the underestimation in the CDNUMC from HAM compared to CTRL was about 36%. Furthermore, while the overestimation in KT from CTRL was distributed uniformly across the domain, the underestimation in HAM was more significant around the equator in the tropics. It is also important to note that the CDNUMC in all three cases was analyzed for the regions where the cloud fraction was ≥ 0 , as well as the fractional occurrence of liquid was ≥ 0.05 . The CDNUMC was found to be more than two orders of magnitude smaller than the average where these conditions were not met and were considered effectively 0.

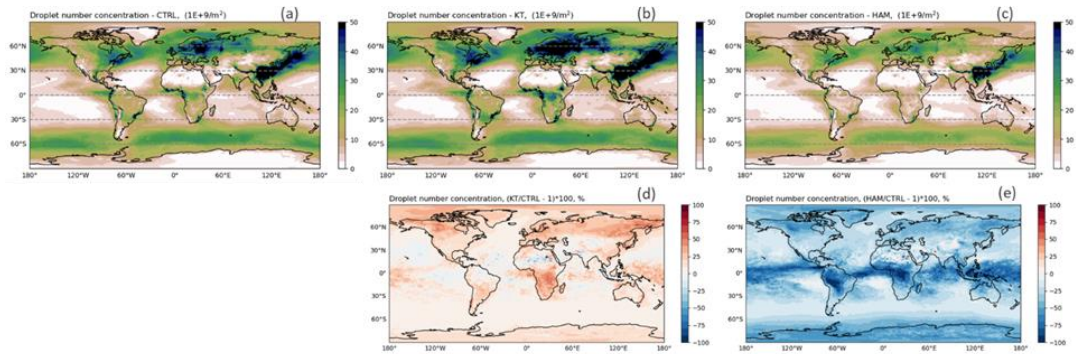


Figure 34. Annual global mean of the vertically integrated cloud droplet number concentration (CDNUMC) from CTRL (a), KT (b) and HAM (c) simulations. The relative changes in the CDNUMC between KT and CTRL simulations (d) and those between HAM and CTRL simulations (e) are also shown.

Figure 35 (a) and (b) demonstrate the sensitivity of CDNUMC on CCN concentrations at 0.1% and 1.0% supersaturations, respectively. The variability in the CDNUMC and CCN counts between the CTRL and HAM cases were considered to compute the adjoint sensitivity $\left(\frac{\partial \text{CDNMC}}{\partial \text{CCN}}\right)$ between CDNUMC and CCN concentrations. The CCN concentrations within the vertical levels of 950hPa and 820hPa were considered. Except for the regions with no cloud fraction, low liquid fraction (≤ 0.05) or low droplet count ($\leq 10^{-7} \text{ m}^{-2}$), CDNUMC was found to be sensitive to CCN concentrations at 0.1% and 1.0%. CDNUMC has an overall greater sensitivity to the CCN concentration at 1.0%; a larger with aerosol population relatively with low hygroscopicity particles is CCN active at higher supersaturation. This implies that the CDNUMC has a strong sensitivity towards the low hygroscopicity aerosol.

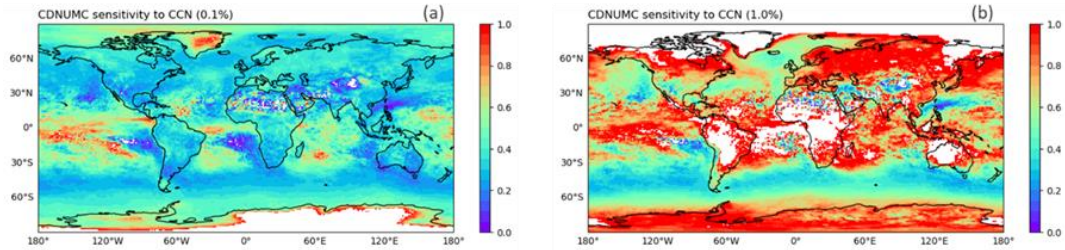


Figure 35. CDNUMC sensitivity to CCN concentrations at 0.1% supersaturation (a) and 1.0% supersaturation (b). The sensitivities were computed between the values from CTRL and HAM simulations. The regions with no cloud cover or liquid water fraction ≤ 0.05 are masked and shown in white.

The variability in CDNUMC can change physical and radiative properties of clouds. One such properties is the liquid water path (LWP). Figure 36 (a), (b) and (c) illustrate the global annual means of the vertically integrated LWP simulated from CTRL, KT and HAM experiments, respectively. Like CDNUMC, similar results for LWP were also observed. The global annual mean LWP from CTRL and KT had a

similar distribution – the maximum values were 67.63 g m^{-2} (CTRL) and 69.28 g m^{-2} (KT), respectively. The LWP from KT was slightly overestimated with respect to the LWP from CTRL (Fig. 36d), also implied by the average relative difference of 2.6%. The LWP from HAM was notably underestimated compared to that obtained for the CTRL case (Fig. 36e) – maximum of 59.38 g m^{-2} for HAM. The average relative difference between the global annual mean LWP from HAM and CTRL was -13.05% . Like CDNUMC, the analysis for LWP in all three cases was also done for the regions where the cloud fraction was ≥ 0 . and fractional occurrence of liquid was ≥ 0.05 .

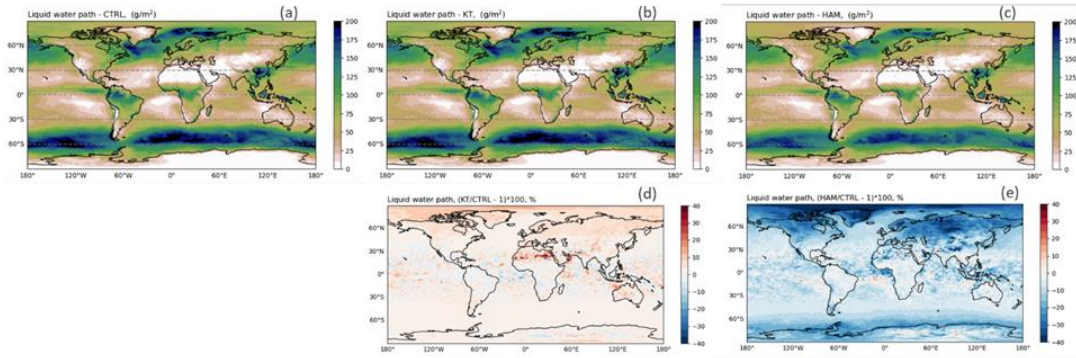


Figure 36. Same as Fig. 34 but for the annual global mean of the vertically integrated liquid water path (LWP)

CDNUMC is also related to the cloud droplet radius. The effective droplet radius decreases when there is an increase in the droplet number concentration. Figure 37 (a), (b) and (c) show the vertically integrated global annual mean effective droplet radius generated from CTRL, KT and HAM simulations, respectively. The regions with liquid water fraction ≤ 0.05 are shown in white in all three plots. Variations between the droplet radius estimation in KT or HAM with respect to CTRL are evident on looking

at their relative differences. Fig. 37 (d) and (e) respectively illustrate the relative difference in the KT- and HAM-derived droplet radius distribution with the CTRL-derived droplet radius distribution. Fig. 37 (d) suggests that droplet radius distribution from CTRL and KT are similar; a uniform underestimation can be observed in the droplet radius simulation from KT by an average of -3.03% . Meanwhile, Fig. 37 (e) shows that droplet radius distribution from the HAM simulations is overestimated with respect to the droplet radius from the CTRL simulations by an average of 8.84% . An important point to note is that the regions of high bias CDNUMC in HAM (Fig. 34e) overlap with the regions of droplet radius overestimation in HAM (Fig. 37e). In essence, an average of $\sim 36\%$ variability in CDNUMC is associated with $\sim 9\%$ variability in droplet radius.

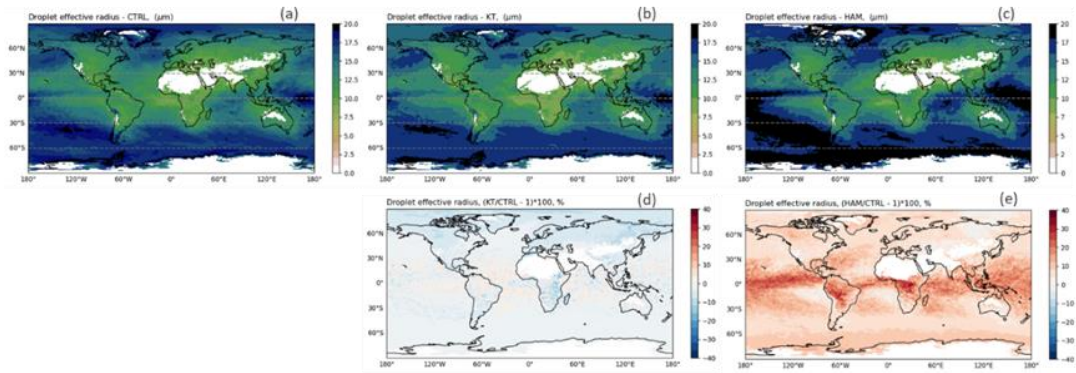


Figure 37. Same as Fig. 34 but for the annual global mean of the vertically integrated droplet effective radius

Figure 38 illustrates the sensitivity of the LWP and droplet radius to the CDNUMC ($\frac{\partial \text{LWP}}{\partial \text{CDNUMC}}$; Fig. 38a and 38b, respectively). The correlation between the change in the LWP and droplet radius to the change in CDNUMC is also shown in Fig. 38 (c) and (d), respectively. For LWP, a low sensitivity ($\leq \sim 0.2$) to CDNUMC was observed in

the tropics, and a relatively high sensitivity ($\geq \sim 0.4$) to CDNUMC was observed in the northern polar regions. For droplet radius, a low sensitivity ($\leq \sim 0.2$) to CDNUMC was observed over the poles, and a relatively high sensitivity ($\geq \sim 0.4$) to CDNUMC was observed in the tropics. Variability in LWP is correlated to the change in CDNUMC – this is because LWP and droplet radius depend on the amount of water present in the clouds (which is quantified CDNUMC). Droplet radius moderate to low sensitivity to CDNUMC. Moreover, droplet radius and CDNUMC are negatively correlated to each other. As CDNUMC increases, average effective droplet radius increases and vice versa. CDNUMC decreases between HAM and CTRL cases while droplet radius simultaneously increases thereby resulting in a notable negative correlation between the two variables.

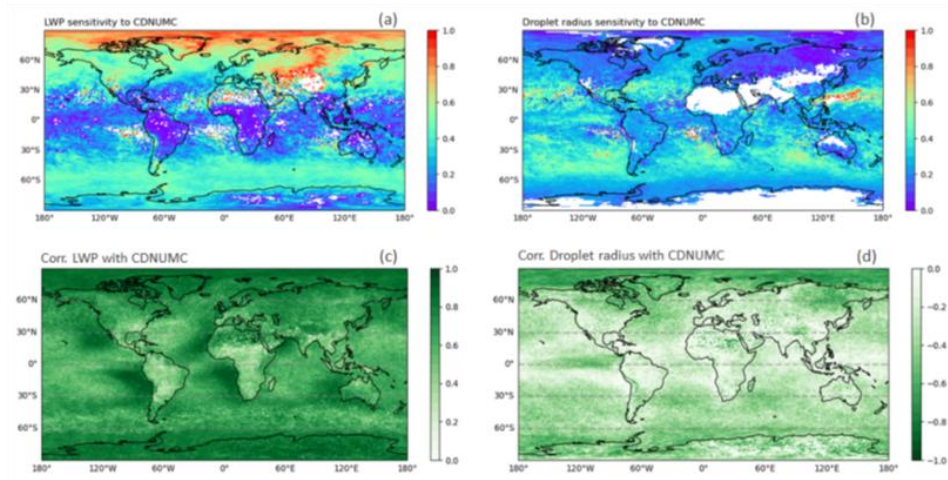


Figure 38. Sensitivity of the LWP and droplet radius with respect to CDNUMC (a, b). Correlation of the change in LWP and droplet radius with respect to CDNUMC (c, d). On average, the LWP and droplet radius have a moderate sensitivity towards CDNUMC. However, the variability in both LWP and droplet radius have a strong correlation with the variability in CDNUMC. It is to be noted that that droplet radius has a negative correlation with CDNUMC. The sensitivities and correlations were computed between the values from CTRL and HAM simulations. The regions with no cloud cover or liquid water fraction ≤ 0.05 are masked and shown in white.

The droplet radius simulated with the HAM configuration of CAM were also found to be in better agreement with the observational data as compared to the other two cases. The zonal mean droplet effective radius (μm) from CAM simulations and MODIS observations (Terra/Aqua) are shown in Figure 39. Each panel of Fig. 39 shows the seasonal averages during the year 2018-19 for the droplet radius. The gray shaded region denotes the first standard deviation across the observational data. For all seasons, the droplet radius distribution simulated with the HAM case has the lowest RMSE score as compared to the other two cases. Furthermore, the droplet radius from all three simulations lies within one standard deviation from the observations across the tropics and midlatitudes. The improved agreement between the simulated and observed droplet radius can be attributed to the modified aerosol κ in HAM. This is because κ dictates the CCN activity and hence droplet formation and growth associated with any aerosol species. It is important to note that during the four seasons, all three model configurations result in underpredicted droplet radius at the Intertropical Convergence Zone (ITCZ.)

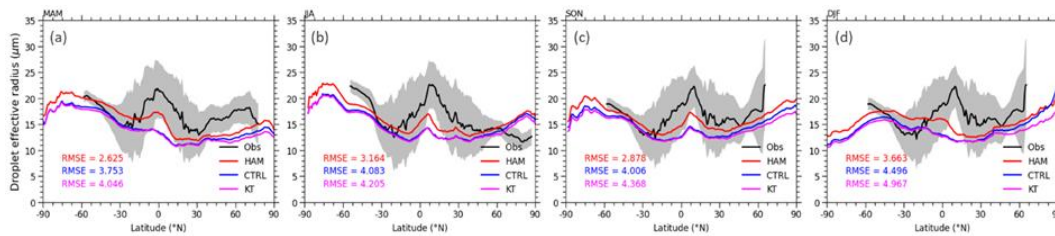


Figure 39. Zonal mean profiles for the droplet effective radius, by season. The simulated aerosol burdens are color coded along with their RMSE with respect to the observational data from MODIS (shown in black). The gray shaded region denotes one standard deviation about the observational data.

The effect of altering the aerosol hygroscopicity was also analyzed on the cloud fraction. The annual global mean of total cloud fraction showed little variability across the three simulated cases of CAM (not shown here). The maxima of the three total cloud fractions were found to be 0.987, 0.996 and 0.971 for CTRL, KT and HAM cases, respectively. Additionally, the average of the annual global mean total cloud fraction was 0.726 ± 0.012 . For a better comparison of the simulated cloud fraction, the zonal mean of the simulated values was plotted against the zonal means of the observed global total cloud fraction from MODIS. Figure 40 shows the seasonal averages during the year 2018-19 for the cloud fraction. Like Fig. 39, the mean of the observations is shown in black with the gray regions representing one standard deviations across the mean values. For all three simulations, the cloud fraction agrees well with the observations between approximately 60°S and 60°N. Within this same region and for all four seasons, cloud fraction predictions from the HAM configuration produced the highest agreement with the observations (RMSE provided for each case). However, all three cases consistently overpredict the cloud fraction in the polar regions which increases the overall RMSE of the simulated cloud fraction.

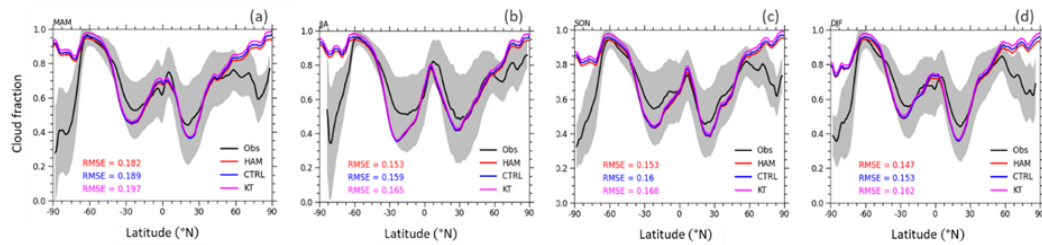


Figure 40. Same as Fig. 39, but for the annual global mean cloud fraction. Cloud fraction observational data was also acquired from MODIS.

The effect on the shortwave cloud forcing (SWCF) was also analyzed. The annual global SWCF from the three configurations of CAM are presented in Figure 41 (a, b, c), along with the relative differences of SWCF from KT and HAM with respect to CTRL-based SWCF (Fig. 41 d, e). The annual global SWCF distribution from the three simulations are similar; maximum of 184.36 W m^{-2} , 190 W m^{-2} and 171.95 W m^{-2} , and average of 39.3 W m^{-2} , 40.8 W m^{-2} and 36.25 W m^{-2} for CTRL, KT and HAM, respectively. The average relative differences of 4.37% and -9.85% imply that the HAM-based SWCF profile on average has larger disparities than the KT-based SWCF profile with respect to CTRL. Furthermore, the relative change in the SWCF simulated using HAM vs. CTRL experiments of CAM is correlated with the relative change in cloud fraction simulated in the same two CAM experiments (Figure 42). The mean correlation coefficient between the changes in SWCF and cloud fraction was 0.348 with a maximum value of 0.83. The moderate to high correlation coefficients suggest that even minute changes in the cloud fraction can have notable changes in their overall radiative forcing. Additionally, the cloud fraction and hence the SWCF are associated with the droplet concentration (or, the available water content of the cloud). Therefore, any variability in the SWCF computation is likely associated with the water uptake behavior (dictated by the κ) of the aerosol particles.

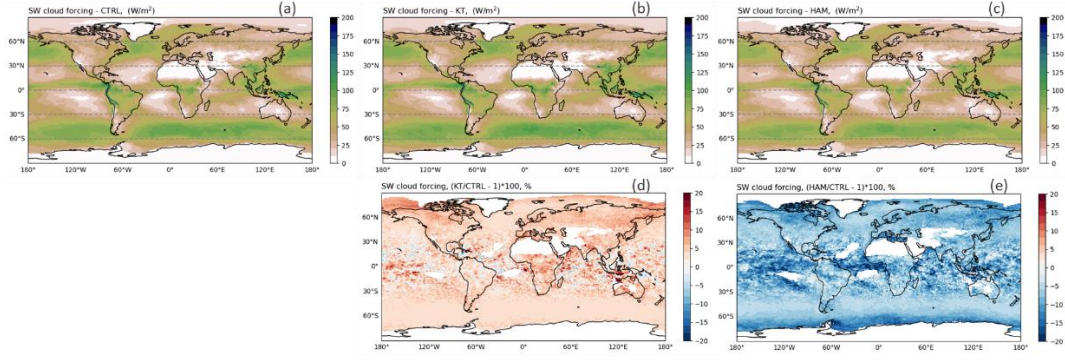


Figure 41. Same as Fig. 34 but for the annual global mean shortwave cloud forcing (SWCF).

5.5.4 Aerosol Optical Depth

Aerosol optical depth (AOD) is an important measure of the aerosol direct effect. AOD is an indicator of the amount of the solar radiations unable to reach the surface because of absorption or scattering from the atmospheric aerosol burden. Figure 43 shows the zonal means of the AOD observations (AERONET) compared against the zonal means of the AOD simulated using CTRL, KT and HAM configurations for the four seasons for the year 2018-19. For all seasons, the HAM-based AOD simulations agree better with the observational data than the AOD from other CAM simulations; explained using the higher RMSE scores for HAM AOD. Generally, the RMSE scores are lowest for JJA and SON (Fig. 43 b, c) with predicted AOD within one standard deviation of the observations. The RMSE scores for MAM and DJF (Fig. 43 a, d) are greater than ~ 0.05 for all three simulations implying larger uncertainties in the predicted AOD.

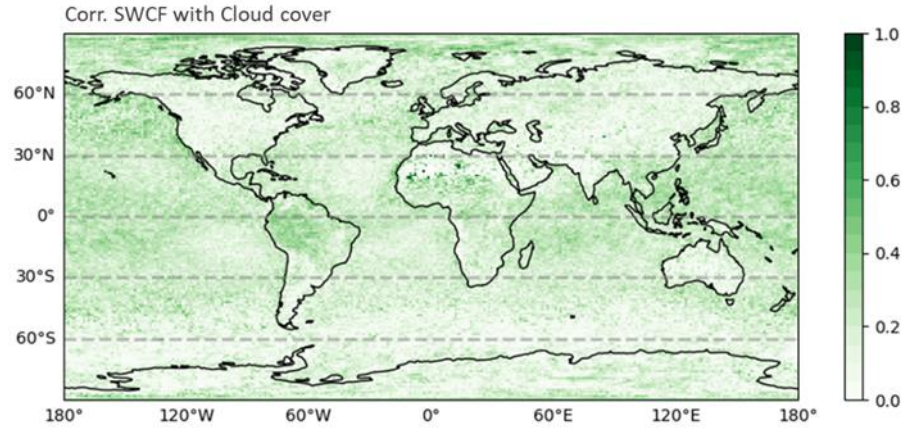


Figure 42. Correlation of the change in SWCF with respect to cloud fraction (or, cloud cover). The correlation was computed between the values from CTRL and HAM simulations.

For MAM, the uncertainties are due to underpredictions in the AOD over the tropics, whereas for DJF, the uncertainties are due to notable overpredictions over the tropics. The underpredictions for the MAM season could mostly be due to the underrepresentation of the increased anthropogenic emissions in the simulations. The overpredictions in the DJF season could likely be due to natural events (such as, dust aerosols over desert areas). This could be due to fewer observations over locations of such natural aerosols where the burden, and henceforth the AOD may be overestimated by the model. Figure 44 displays all locations (red crosses) where the HAM-based simulated $AOD \geq 2.5 \times$ (AERONET observational AOD data). The locations on the map are overlaid with the HAM-based simulated DUST burden. It can be observed that several of these locations (Australia, Northern Africa and Southern Africa) overlap with regions of large DUST burdens simulated by CAM using the HAM configuration.

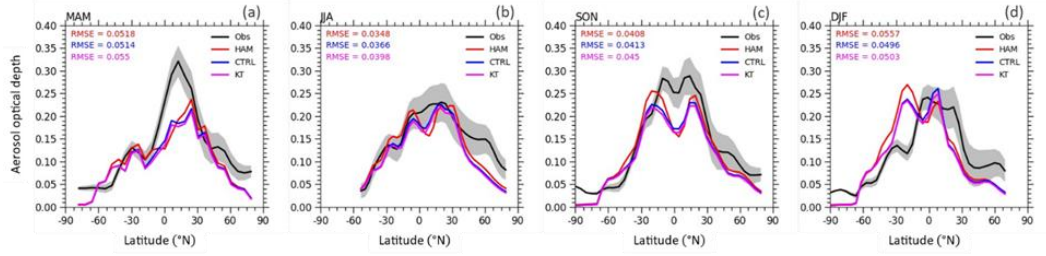


Figure 43. Same as Fig. 39, but for the annual global mean aerosol optical depth (AOD). AOD observational data was acquired from AERONET.

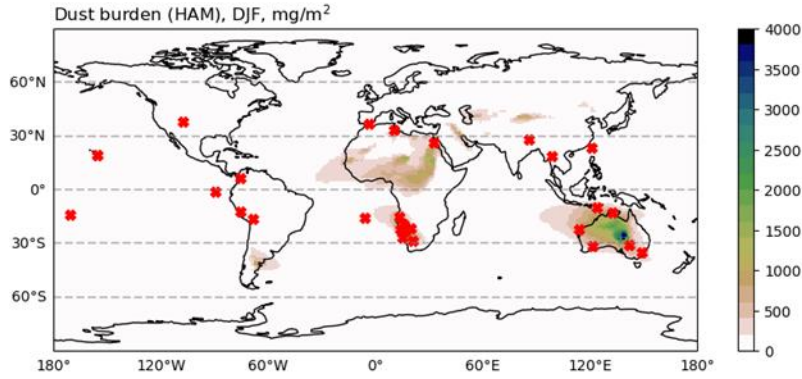


Figure 44. A map of the AERONET sites (marked as red crosses) where the AOD simulation from HAM were $\geq 2.5 \times$ (AERONET AOD observational data). The AERONET sites are overlaid with the simulated burden of the DUST mode obtained from the HAM case. Several of the AERONET sites coincide with large, simulated DUST burdens from HAM.

Fundamentally, the AOD is dependent on the atmospheric aerosol burden. Thus, it is important to understand which aerosol can significantly affect the AOD. Figure 45 shows the sensitivity of the global annual mean AOD over organics, BC, DUST burdens. Fig. 45 shows the sensitivity of AOD over the aerosol burdens (units of $\text{m}^2 \text{mg}^{-1}$) for the simulations from HAM and CTRL configurations of CAM. According to the adjoint sensitivity analysis, AOD is most sensitive to the organic burden ($\frac{\partial \text{AOD}}{\partial \text{BURDEN}_X}$ where $X \equiv \text{Organic, BC, DUST}$; Fig. 45a) and least sensitive to the BC burden (Fig. 45b). The average global sensitivity of the AOD to the organic, BC

and DUST burdens 1.41, 1.13, and 1.32 units, respectively. The regions where the relative difference between the respective aerosol burden simulated from HAM and CTRL is $\leq 5\%$ are shown in white.

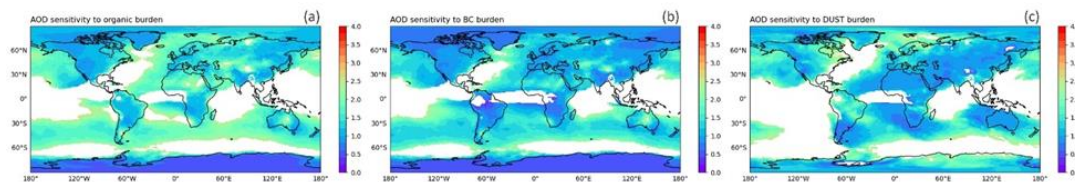


Figure 45. AOD sensitivity to aerosol burdens are shown (a) AOD sensitivity to organic burden, (b) AOD sensitivity to BC burden, and (c) AOD sensitivity to DUST burden. The sensitivities were computed between the values from CTRL and HAM simulations. The regions with no cloud cover or liquid water fraction ≤ 0.05 are masked and shown in white.

5.6 Summary and Implications

The aerosol indirect effects estimation has large uncertainties and the hygroscopicity parameterization is known to be an important factor of these uncertainties. The hygroscopicity parameters (κ) for all aerosol modes are prescribed within climate models such as NCAR CAM, and not calculated. κ of various aerosol types in CAM are prescribed from the ideal Köhler theory (KT). κ of organic aerosols are prescribed based on experimental findings in the literature. Variation in the aerosol and cloud properties can be observed if κ of all aerosol types are explicitly calculated from their molar properties using Raoult's law. Additionally, a physically based size-dependent hygroscopicity parameterization (such as that based on the Hybrid Activity Model; HAM) that can also be used in CAM to determine aerosol κ . More importantly, a simplified hygroscopicity parameterization based on HAM can be implemented in

CAM to estimate aerosol κ . The simplified hygroscopicity parameterization helps in retaining the computational efficiency of the model, while also capturing all the important features of the full hygroscopicity parameter derived from HAM.

In this work, CAM simulations with κ estimations using KT and HAM were compared to the free-run CAM simulations. It was observed that the KT based modifications resulted significant increment in the CCN concentrations compared to the control (CTRL) case. These increments could be attributed to the generally increased κ for all aerosol types in the KT case, thereby overestimating their CCN activity. The generally higher organic κ in the KT case likely resulted in an increased wet removal of the aerosols, henceforth decreasing their atmospheric burdens. The KT case, however, did not have significant effects on the subsequent physical and radiative properties of the clouds. Since the meteorology forcing was maintained the same for the CTRL and KT cases, the atmospheric water vapor content and so the resulting droplet concentration and other properties have minor changes between CTRL and KT case simulations.

The CAM simulations with the implementation of HAM based κ show marked differences compared to the free-run CAM simulations. It has been demonstrated using CCN experiments that HAM based κ of moderately water soluble and effectively insoluble species can be smaller than their Raoult's law κ counterparts. These differences can be up to several orders of magnitude and arise due to explicit size-dependence and solubility treatment in HAM κ . Due to substantially reduced κ of aerosols, the CCN concentrations simulated in the HAM case showed significant

reduction compared to those simulated in the CTRL case. The reduction in the atmospheric CCN concentration translated to a decreased droplet concentration, liquid water path and other physical and radiative cloud properties. The reduced aerosol κ also reduced the aerosol scavenging or wet removal pathway and hence showed major increase in the atmospheric burdens of organic, black carbon and dust aerosols compared to the CTRL case. The physical and radiative properties of aerosols and clouds simulated in the HAM case showed highest agreement with the observational data. Since aerosol and cloud droplet number counts strongly dictate the direct and indirect effect of aerosols, it is implied that HAM-derived aerosol burdens and droplet concentration may be an improved representation of the state of the atmosphere. An important point is that certain aerosol and cloud properties (optical depth, cloud fraction, large-scale and convective precipitation) show minor variability across the three simulated cases. Their low variability may be due to averaging out over large climatological scales (seasonal or annual).

Overall, the implementation of HAM κ in a climate model was valuable for understanding the uncertainties associated with the aerosol and cloud properties. Previously, HAM had been applied on the controlled laboratory measurements of specific organic compounds with aqueous solubility varying over a range of 2-3 orders of magnitude. HAM has also been applied for the water uptake analysis of BC species observed in the atmosphere using agglomerated pure and mixed BC particles as proxies. This work expands upon the applicability of HAM for representing the aerosol κ in NCAR CAM. Since organic aerosols are the major sources of uncertainties in the indirect effect, using HAM for representing their hygroscopicity in Global Climate

Models can potentially reduce the forcing uncertainties due to aerosols and clouds. Moreover, modifying the aerosol κ for individual chemical species in the climate models can further improve upon the estimations presented in this work.

Currently, HAM incorporates the effects of only the water solubility of the aerosol particles on their cloud activity. Whereas in the atmosphere, the physicochemical nature of aerosol particles and therefore their cloud activity can drastically change due to chemical transformations – aging, gas phase reactions, phase separation – to name a few. Incorporating one or more such modes of chemical transformation in the describing the water uptake behavior of the aerosols can further improve the representation of their direct and indirect effects. In future, additional modifications of HAM or a similar framework could be developed to incorporate more complex characteristics of atmospheric aerosols.

Chapter 6: Chemical Characterization of Atmospheric Aerosol using their Measured Raman Spectra

6.1 Abstract

Single-particle aerosol measurement techniques provide a means to obtain size-resolved aerosol composition and henceforth are being rigorously explored. These measurement techniques include mass spectrometry, fluorescence spectrometry, FTIR, Raman spectrometry, and electron-beam excited x-ray diffraction. These are useful for retrieving information about the composition of minority species in the atmosphere, their mixing state, and the process they undergo over different scales. Raman spectrometry (Raman, from hereon) has been shown to be a highly efficient technique employed for characterization of chemical compounds. There are 2 main reasons for that: 1. Raman spectra are the signatures of the chemical bonds present in the chemical compounds and are therefore unique for the compounds they correspond to; and 2. Raman spectra can be detected for particles of the order of nanometers. In this work, a computational tool was developed using techniques related to machine learning, signal processing and statistics for Raman data collected for ambient aerosols using the Resource Effective Bioidentification System (REBS)-based Automated aerosol Raman Spectrometer (ARS). The developed algorithm has been designed to perform 3 major operations: 1. Spectral clean-up – this is required because generally the Raman spectra obtained using our ARS have a low signal-to-noise ratio, 2. Spectral peaks (feature) detection – peaks are the characteristic features of a Raman spectrum that play a major role in characterizing the sample through its spectrum, and 3. Identification of the

aerosol chemical species, using the Raman data from a reference database, using a “vector similarity” metric. This work demonstrates that simple statistical techniques can be employed for characterizing the atmospheric aerosols using their single particle Raman signatures. Basically, the chemical composition and mixing state of aerosols can be determined on particle scale with the help of their Raman signatures using statistical methods.

6.2 Background

Atmospheric aerosols can affect human health, weather, and global climate directly or indirectly (Brooks et al., 2010; Dominici et al., 2015). Several harmful cardiovascular and pulmonary diseases are known to be caused by prolonged exposure to soot and heavy metal emissions (von Klot et al., 2011; Shiraiwa et al., 2012). Fine and ultrafine particles can easily cross the nasal passage to enter the lungs. Several disease-causing bacteria and viruses can also become airborne and be treated as aerosols. Particulate Matter (PM) such as black carbon is known to cause scattering of solar radiation in the atmosphere (Petzold and Schönlinner, 2004; Seinfeld, 2008). This is generally observed in the case of coarse particles capable of causing tropospheric and stratospheric heating from the scattering of solar radiation. At lower altitudes within the troposphere, high aerosol density can significantly affect visibility. Thus, the tracking and identification of atmospheric aerosols can be highly valuable to study their effect on health and the environment.

The real-time identification and characterization of aerosols with accuracy is particularly challenging. The most common approach taken to perform these tasks is the analysis of the electromagnetic properties of observed aerosols. Different tools have been employed to quantify electromagnetic properties of materials comprising the atmospheric aerosols, primarily by observing their interactions with electromagnetic radiations. Techniques such as mass spectroscopy (Jayne et al., 2000), FTIR (Toprak and Schnaiter, 2013; Pan et al., 2007), magnetic resonance spectroscopy (Decesari et al., 2007; Cleveland et al., 2012) and X-ray diffraction (Stefaniak et al., 2009) relate with different properties of the aerosol materials which can be used for their identification. Despite being widely implemented for the characterization of materials, these processes often suffer from shortcomings. Mass spectroscopy is dictated by particle size and mass distribution. These properties are not unique to any chemical species, as well as accounting for the variations in particle size and mass distribution becomes increasingly difficult when analyzing a mixture of chemical compounds. Likewise, FTIR spectrometry suffers from the inability to directly generate spectra and requires preprocessing on the recorded interferograms to yield any useful information. FTIR spectrometry is also highly susceptible to inferences from instrumental noise. Furthermore, techniques such as magnetic resonance spectroscopy and X-ray diffraction are hard to automate and are also considerably expensive, while requiring large sample sizes to operate.

During the past few years, the application of Raman spectroscopy has significantly improved the characterization of materials (Ault et al., 2013). Raman spectroscopy is a non-destructive and versatile technique that can be run continuously to detect chemical

species. In addition to this, Raman is easy to automate and can be performed for single-particle measurements. Furthermore, Raman provides as a unique fingerprint for any chemical species as it is related to the vibrational and rotational frequencies of the chemical bonds in a chemical species (Turrell et al., 1989). The Resource Effective Bioidentification System (REBS)-based Automated aerosol Raman Spectrometer (ARS) is a portable device that has been used to record Raman spectra corresponding to ambient aerosols (Doughty and Hill, 2017; Ronningen et al., 2014). Figure 46 is a labeled representation of the ARS used in this work. The REBS-based ARS has multiple advantages that further improve the utility of Raman spectroscopy for analyzing atmospheric aerosols. Firstly, Raman spectra ideally require longer to record as compared to the previously mentioned techniques. This is directly correlated with the time between excitation and stabilization of the sample, and the significantly low probability of the occurrence of Raman scattering. The ARS is capable of recording Raman of a given sample within times that are of the order of a few minutes, and therefore significantly reducing the sampling time. A second important advantage of the ARS is that it is a simple instrument consisting of a single laser source, a means to collect aerosol samples, a spectrometer, and an imager. Additionally, the ARS has smaller dimensions compared to other forms of spectrometers which further its portability.

Despite the high applicability of Raman spectrometry attributed to the versatility and high useful information content of Raman spectra, it is significantly susceptible to noise. Raman spectra of laboratory samples are collected over a period of a few hours (Vehring et al., 1998; Andreae and Gelencsér, 2006). This is done to facilitate full

stabilization of the samples before recording the spectra so that the spectra is a good representation of the ‘true’ Raman signal of the samples. The main sources of noise in Raman spectroscopy are cosmic radiations and fluorescence (Sinanis et al., 2011; Bozlee et al., 2005; Craig et al., 2017). Cosmic radiations are observed as high-frequency spikes throughout the spectra, and fluorescence is observed as low-frequency unsteady baseline variations in the spectra. To effectively utilize the Raman spectra for the purposes of classification, these 2 components need to be eliminated or at least be greatly suppressed, from the collected sample spectra (Smulko et al., 2014; Murray and Dierker, 1986). Several preprocessing methods have been proposed in earlier studies for efficiently removing of both these ‘noisy’ components from Raman spectra (Hill and Rogalla, 1992; Kwiatkowski et al., 2010).

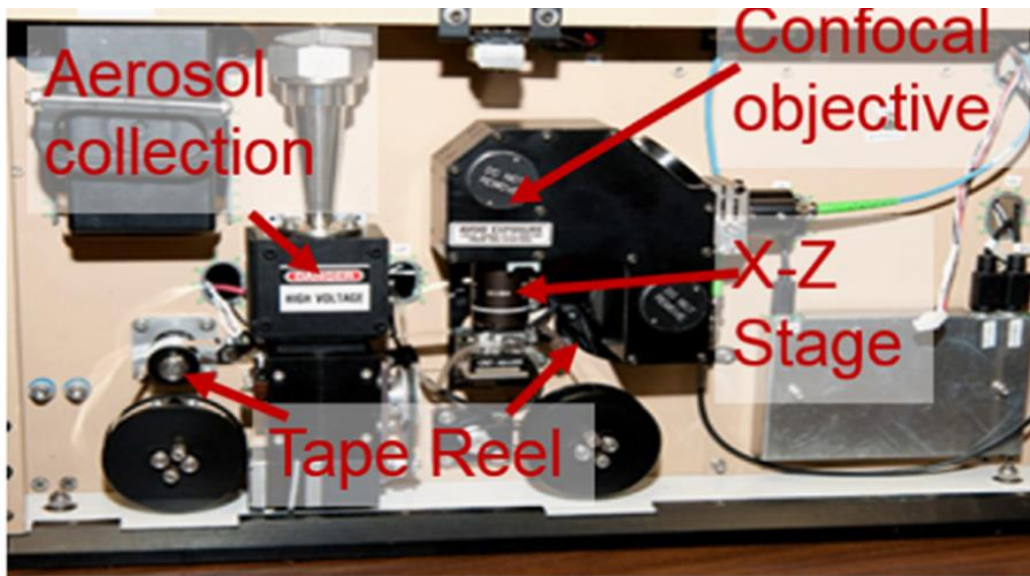


Figure 46. The side-view of the REBS-based ARS used to collect the Raman spectra of the aerosol samples in this work. The components of the device are labeled. This image has been directly taken from Doughty and Hill (2017).

The high-frequency spikes are removed from the spectra by passing them through smoothing/filtering algorithms. One of the most common algorithms for filtering out noise from the Raman spectra is the Savitzky-Golay filter (Člupek et al., 2007; Bromba and Ziegler, 1981). In this algorithm, the original Raman spectrum is smoothed by breaking it up into fragments and smoothing them in a small ‘window’ by fitting a polynomial function through them. The extent of smoothing can be altered by varying the window length. This feature of the Savitzky-Golay filter can be exploited for preserving and eliminating features of interest in the Raman spectra under consideration - a smaller window length is used to preserve shape and narrower peaks present in the spectra, and the wider window is used to preserve broader peaks/plateaus in the spectra. A major disadvantage of this approach is that there is no effective way to optimize the window length and the order of the fitting polynomial - a very high window length (of more than approximately 41) can easily lead to a significant distortion in the smaller features of the spectra. Achieving a tradeoff between eliminating the noise and retaining the necessary features in any given spectrum is a challenge with employing the Savitzky-Golay filter.

Another common approach that has been explored for denoising Raman spectra is the Discrete Wavelet Transform (DWT) (Ehrentreich and Sümmchen, 2001; Kaiser, 2010; Mallat, 1989). Several studies have demonstrated DWT to be a highly efficient denoising technique for Raman spectra. Use of certain specific types of wavelets, namely Daubechies, Symlet, and Coiflet wavelets have been shown to perform better than other alternatives like Haar and Biorthogonal wavelets (Ehrentreich and Sümmchen, 2001). Some recent studies provide an insight into a variation of DWT,

referred to as the Lifting Wavelet Transform (LWT) and has been shown to perform well in the case of Raman spectra with low Signal-to-Noise Ratio (SNR), with a minor drawback of being computationally expensive over DWT (Chen et al., 2011, 2018a, b). (Chen et al., 2014) discussed a technique for retrieving denoised Raman spectra with low SNR by implementing Wiener transform on them. The performance of Wiener transform was compared with the performances of some of the more commonly employed methods involving the Savitzky-Golay filter, the wavelet transform, the Finite Impulse Response (FIR) filter, and the Gaussian filter (Villaruel et al., 2011; Wang et al., 2006; Palacký et al., 2011). The Wiener transform was shown to perform better than its counterparts, which was quantified by computing the Root Mean Squared Error between the low-SNR and the high-SNR samples for the Raman spectrum under consideration. Other filtration methods involve the use of Principal Component Analysis (PCA) and factor analysis which have been shown to be useful with denoising low-SNR signals but are known to be computationally expensive at that.

Like that for the high-frequency spikes, several methods have been proposed for removing the low-frequency fluorescence component from Raman spectra. Baseline correction is performed to remove the fluorescence component from the spectra. Several methods such as polynomial fitting, Asymmetric Least Squares (ALS) fitting, cubic spline fitting and PCA (Eilers and Boelens, n.d.; Shao and Griffiths, 2007; Peng et al., 2010) have been used to determine the approximate baseline for Raman spectra. ALS was noted as the most commonly employed method for performing baseline correction on Raman spectra, along with several of its variations such as the Improved

Asymmetric Least Squares (IALS) (He et al., 2014) method and the adaptive iteratively reweighted Penalized Least Square (airPLS) (Zhang et al., 2010) method.

Spike and fluorescence removal help with obtaining the true Raman signal from the spectra under consideration. Removing unwanted components from the spectra reduces the likelihood of extracting incorrect peaks from the spectra. Peak/feature extraction is an essential step in a classification problem that greatly improves the efficiency of the algorithm by making it computationally less expensive. Several studies have discussed the application and performance of different peak finding algorithms on spectroscopy data. These methods include the use of Continuous Wavelet Transform (CWT) (Wee et al., 2008), Gaussian fitting (Shang and Lin, 2010), and Lorentzian fitting (Gunnink, 1977). The spectra for different kinds of materials have different types of characteristic peaks - peaks in solid samples fit well using a Gaussian profile whereas peaks in gaseous and liquid samples fit well using a Lorentzian profile. “findpeaksG3” (O’Haver 1995, O’Haver 2014) is a user-defined class for finding peaks in electromagnetic signals by fitting Gaussian functions throughout the signal. The class was originally written in MATLAB was translated into Python 3.6 to be used in this work. Furthermore, the utility of findpeaksG3 compared and tested against the updated “autofindpeaks” (O’Haver 2016).

A vast variety of classification methods currently exist to identify the composition of chemical species. Implementing classifiers to identify aerosols has become highly commonplace due to the continuous developments within the machine learning and deep learning communities. Sophisticated methods including the use of algorithms

such as K-nearest neighbors, Support Vector Machines (SVMs) (VAPNIK and N, 1995), decision trees, random forests (Ho, 1998), and neural networks (Maquelin et al., 2003) have been shown to perform with high accuracy in classification problems involving the use of Raman spectra (Liu et al., 2017). However, a disadvantage with the aforementioned and other similar data-driven techniques is that they are highly computationally expensive. Other approaches include the application of simpler vector-based algorithms (Kwiatkowski et al., 2010; Carey et al., 2015). These algorithms treat Raman spectra as vectors and classify unknown vectors based on their “similarity” with other known vectors in the database. The similarity between any 2 spectrometric vectors can be determined using a variety of metrics such as the absolute difference value search, the Euclidean distance, the cosine distance, and the correlation coefficient.

This study aims to develop an algorithm that facilitates a simple and computationally inexpensive way of classifying chemical species using real-time Raman spectra. The proposed algorithm includes 1. Preprocessing of Raman spectra that consists of spike removal from the spectra using Discrete Wavelet Transform (DWT) and fluorescence removal by performing baseline correction using Asymmetric Least Squares (ALS) fitting, and 2. Classification of measured Raman spectra using cosine similarity. The discussion pertinent to the databases used in this study along with the analysis and methodology is reported. Additionally, statistical techniques that were implemented for validating the algorithms is also presented. Lastly, conclusive remarks are provided with regards to the developed algorithms and their corresponding

results, along with the advantages and disadvantages of the classification approach developed in this work.

6.3 Data and Methodology

The algorithms were developed to classify data using the spectrometric data from the LR-Raman database of RRUFF. A total of 9,330 Raman spectra were used to construct the reference database and will be hereafter referred to as the “RRUFF database”. Within the RRUFF database, the spectroscopic data was distributed into a total of 1342 different mineral classes. The unclassified data was obtained using the Resource effective Bionidentification System-based automated Aerosol Raman Spectrometer (REBS-based ARS). The unclassified dataset was made from the ambient samples procured at Jornada. A total of about 199,000 samples were collected and analyzed by the ARS. These samples were observed to have a significantly lower intensity as compared to the samples in the RRUFF database. A threshold of 0.0065 A.U. was set up for the maximum Raman intensity to extract out data that would be used for classification. A total of 903 unclassified Raman spectra were selected in the measured dataset and will be hereafter referred to as the “Jornada dataset”.

Compared to the RRUFF database, the Jornada dataset contained spectra with a significantly lower signal-to-noise ratio, with their true Raman signal content heavily polluted by high-frequency noise and fluorescence. Two preprocessing algorithms were developed and tested on spectra from the RRUFF and Jornada databases. These algorithms were designed in such a way that they may be successfully implemented on

signals with any amount of noise and fluorescence. The preprocessing algorithms were called preprocessing α and preprocessing β .

Preprocessing α comprised of removal of high-frequency noisy spikes from the spectra using employing Discrete Wavelet Transform (DWT). Daubechies-type wavelets were employed for performing DWT on all the Raman spectra in both datasets. Daubechies wavelets have been shown to perform better than other kinds of wavelets when used for Raman spectroscopic data, which possess Gaussian and Lorentzian type features. DWT using the Daubechies-type wavelet 5 (db5) was implemented for all the spectra in the RRUFF database. Signal-to-Noise Ratio (SNR) was calculated for all the spectra before and after applying DWT on them. It was observed that for about 96% of the spectra in the RRUFF database, the SNR increased by more than 0.25. The spectra in the Jornada dataset were observed to have a significantly lower SNR compared to the spectra in the RRUFF database. Three different Daubechies-type wavelets were tested on the Jornada spectra - db4, db7, and db11. Of all the Daubechies-type wavelets, db4, db7 and db11 produced the most prominent improvement in the SNR of the spectra. An increment of 0.3 or above was noted for all the spectra in the Jornada spectra using the 3 Daubechies-type wavelets.

Preprocessing β involved removal of high-frequency noise followed by the removal of fluorescence from the spectra. The removal of noise was done by the implementation of DWT on the spectra in consideration, which was like preprocessing α . The removal of fluorescence was done by performing baseline correction on the spectra. For

correcting the baseline, Asymmetric Least Squares (ALS) fitting was done on the spectra. The baseline thus obtained was then subtracted from the spectra.

2 sets of classification algorithms were developed and tested on the Jornada spectra. Classification using all 6 algorithms was done in 2 steps - step 1 included a procedure that was termed “reconstruction”, and step 2 included a procedure that was termed “cropping”. Reconstruction of a given spectrum was done after detecting the peaks contained in it - the Raman intensity of all the detected peaks within the regions equivalent to their respective peak width were retained and appended to a 0-vector of the length same as that of the Raman spectrum at their respective Raman shift positions. Cropping was performed on the reconstructed spectra - all the peaks were “cropped” out and concatenated with each other to generate a “cropped” spectrum representative of the base spectrum.

6.3.1 Preprocessing α

For the first set of algorithms, the RRUFF and Jornada spectra were preprocessed using preprocessing α . The 3 algorithms were named α_1 , α_2 , and α_3 . For the first set of preprocessing algorithms, wavelet transformation was performed depending upon the algorithm being implemented. This was followed by feature (peak) detection, which was done by fitting Gaussian across the spectroscopic vectors. For the second set, the RRUFF and Jornada spectra were preprocessed using preprocessing β , and the algorithms were named β_1 , β_2 , and β_3 . For the second set of preprocessing algorithms, wavelet transformation followed by baseline correction was performed depending upon

the algorithm being implemented. Feature (peak) detection was done after that by fitting Gaussian across the vectors.

$\alpha 1$ – Raw spectra from the Jornada dataset were read into the code (Figure 47). The raw Jornada spectra were interpolated over the same Raman shift range as that of the RRUFF spectra. All Jornada spectra were retained in their original form (i.e., Jornada spectra do not undergo any preprocessing). First, for step 1, the spectra in the RRUFF database were preprocessed using preprocessing α were then passed into the “reconstruction” function. Then, the dot product (cosine similarity function, Eq. 6.1) of the one Jornada spectrum at a time was computed with “reconstructed” spectra in the RRUFF database.

$$\cos \theta = \left| \frac{\vec{P} \cdot \vec{Q}}{\|\vec{P}\| \|\vec{Q}\|} \right| \in [0,1] \quad (6.1)$$

where $\vec{P}$ and $\vec{Q}$ are the vectors P and Q, respectively representing 2 spectra, $\|\vec{P}\|$ and $\|\vec{Q}\|$ are the magnitudes of $\vec{P}$ and $\vec{Q}$, respectively, and θ is the angle between $\vec{P}$ and $\vec{Q}$ that quantifies the similarity between the vectors through the cosine metric.

A fixed threshold was set for this initial dot product to shortlist the RRUFF spectra as the true positive matches. The matches obtained as “true positives” from the RRUFF database were then shortlisted for step 2 involving cropping. The Jornada spectrum was “cropped” with the help of the features (peaks) of one shortlisted RRUFF spectrum at a time. The positions corresponding to the peak positions of the RRUFF spectrum were marked on the Jornada spectrum, and fragments as wide as the respective peaks of the same RRUFF spectrum were cropped out and appended together. In addition to this,

“cropping” was also performed on the RRUFF spectrum under consideration. These representative vectors for the Jornada and RRUFF spectra were used to compute the dot product. This dot product was computed to obtain matches for individual peaks between a given RRUFF spectrum and the Jornada spectrum which is being classified. If the dot product exceeded the threshold, the RRUFF spectrum was returned as a match.

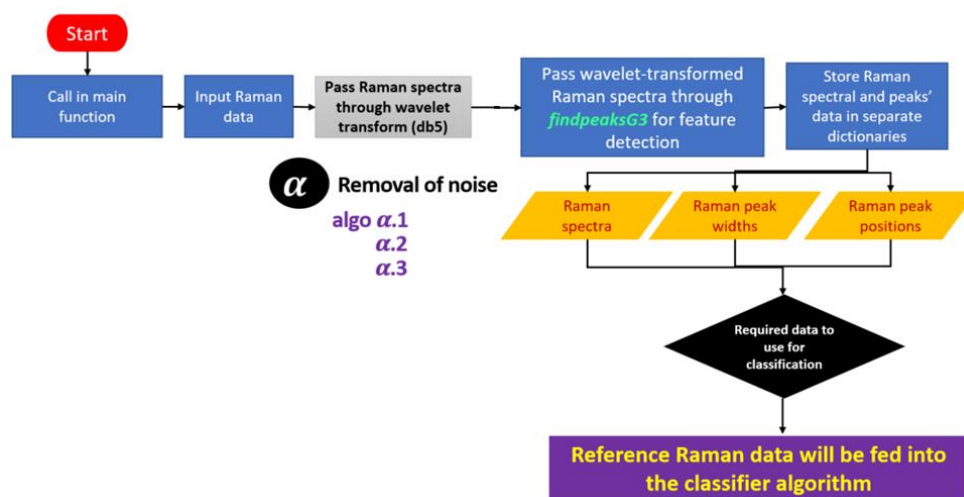


Figure 47. The flowchart depicting the steps taken when implementing preprocessing α before employing cosine similarity to find matches for the measured spectra. The flowchart includes steps taken for both measured and reference spectra.

$\alpha 2$ – Raw spectra from the Jornada database was read into the code. The raw Jornada spectra were interpolated over the same Raman shift range as that of the RRUFF spectra. Jornada spectra were picked up from the database one at a time, and wavelet transform was performed on them to remove the high-frequency noise interfering with the signal. No baseline correction was done on the spectral samples and hence, all the spectral samples in the Jornada database were retained in their original shape. RRUFF spectra were observed to possess a generally higher signal-to-noise ratio (SNR). For

maintaining all the reference spectra at a high SNR, they were run through the wavelet transformation routine using a Daubechies-type db5 wavelet. Baseline correction was not performed on the reference spectra and their wavelet transformed versions were used directly for feature detection using Gaussian fitting. After the features (peaks) were detected for all the reference spectra, that information was stored in a separate python dictionary labeled under the respective sample. All the spectra in the reference database were reconstructed using their respective peak(s) information – all detected peaks (i.e., their position, width and intensity) for a spectrum under consideration were retained and appended on to a 0-vector of the same length as that of the original sample, and this was repeated for every spectrum in the database. After this, classification of the samples in the measured dataset was done. The wavelet transformed version of one measured sample at a time from the dataset was passed into the classification function to evaluate the similarity metric with respect to every reconstructed spectrum in the reference database. Firstly, the measured sample underwent interpolation in order to rescale it to the same range as that of the reference spectra. Next, the interpolated measured spectrum was passed into a local function along with one reconstructed reference spectrum at a time to evaluate the “cosine similarity”. The reconstructed measured spectrum and the reconstructed reference spectrum were then used to compute the similarity metric. The value of the metric was compared against a set threshold – if the value exceeded the threshold, the matched spectrum was carried forward to the next step of comparison in which all its individual matching peaks were located in the measured spectrum. This was repeated for all the spectra in the reference database for any given measured spectrum. The matches obtained as “true positives”

from the RRUFF database were then shortlisted for step 2 involving cropping. The Jornada spectrum was “cropped” with the help of the features (peaks) of one shortlisted RRUFF spectrum at a time. The positions corresponding to the peak positions of the RRUFF spectrum were marked on the Jornada spectrum, and fragments as wide as the respective peaks of the same RRUFF spectrum were cropped out and appended together. In addition to this, “cropping” was also performed on the RRUFF spectrum under consideration. These representative vectors for the Jornada and RRUFF spectra were used to compute the dot product. This dot product was computed in order to obtain matches for individual peaks between a given RRUFF spectrum and the Jornada spectrum which is being classified. If the dot product exceeded the threshold, the RRUFF spectrum was returned as a match.

α_3 – Similar to that in algorithm 2, the measured spectra were treated with 3 different Daubechies wavelets (db4, db7, and db11) to remove the noise from the spectra. The wavelet transformed version of measured spectra (one at a time) were passed through Gaussian fitting for features (peaks) detection. It was observed that cleaning up the a given measured spectrum using 3 different wavelets to create 3 subcases occasionally facilitated in different sets of features (peaks) being detected for that measured spectrum.

After peak detection was performed for all 3 variants of wavelet transformed measured spectrum, 3 separate reconstructed forms of the measured spectrum were prepared. All the detected peaks in the sample were retained and appended at their

respective positions to a 0-vector of the size of the measured spectrum generating 3 separate reconstructed vectors. This was followed by the preprocessing and feature detection for the reference spectra in the RRUFF database. The preprocessing of the reference spectra involved removal of noise by performing DWT using the db5 Daubechies wavelet. Baseline correction was not performed on any of the reference spectra in this method. After noise removal was done on the spectra, “features detection” was performed on them by fitting Gaussians of appropriate dimensions to all the detectable sharpest characteristic peaks of every spectrum. Next, the reconstruction of the reference spectra was done with the help of the peaks which were detected for them. The dot product was then calculated for a given measured spectrum and compared to a set threshold, and all the reference spectra that yielded a dot product higher than the threshold were shortlisted for step 2 of comparison.

In step 2, the shortlisted vectors from the set of reconstructed reference spectra were used for computing the metric for the measured sample in consideration. Vectors were picked up one at a time from the set of reconstructed reference spectra data and “cropped” with the help of their peaks’ information. This was done by cropping out fragments of the length equivalent to the width of each peak from the vector, at locations corresponding to the corresponding peaks. These fragments were then concatenated with each other to create a new vector representative of the original, containing only the peaks from the original vector. Cropping was performed on the sample with the help of the peaks’ information on the reference spectrum it was being compared with. Fragments from the reconstructed measured spectrum were obtained at the locations corresponding to the peak positions of the reference spectrum, of length

equivalent to the width each peak. These fragments were then joined together to obtain a vector representative of the measured spectrum, which may or may not contain any of the peaks present in the measured spectrum. These two “cropped” vectors were then used to compute the dot product which was then compared to a set threshold to suggest a “match”.

6.3.2 Preprocessing β

The general implementation of β algorithms is described using the flow diagram in Figure 48, and the detailed description of the algorithms follow within the text.

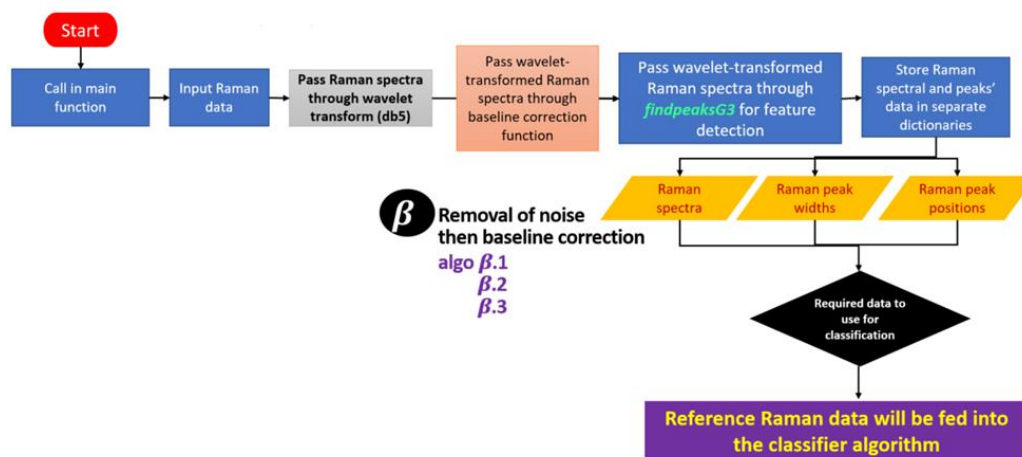


Figure 48. The flowchart depicting the steps taken when implementing preprocessing β before employing cosine similarity to find matches for the measured spectra. The flowchart includes steps taken for both measured and reference spectra. The difference between preprocessing α and preprocessing β is the inclusion of baseline correction in the latter.

β_1 – This algorithm was a modification of α_1 . Prior to performing feature detection, the preprocessing of the reference spectra involved a baseline correction step, followed by the wavelet transform. The baseline correction was done by Asymmetric Least

Square (ALS) fitting. This was done to remove the low-frequency fluorescence signal from the spectra, which would yield just the Raman signal present in each spectrum, with a uniform zero baseline everywhere else along each spectrum. The remainder of this algorithm remained same for every other step as $\alpha 1$.

$\beta 2$ – This algorithm was a modification of $\alpha 2$. Like that in $\beta 1$, the baseline correction was performed for all the spectra in the reference database after wavelet transform, prior to performing feature detection. However, baseline correction was not done for the measured spectra and the preprocessing involved only wavelet transform. The remaining steps were same as those for $\alpha 2$.

$\beta 3$ – This algorithm was a modification of $\alpha 3$. Baseline correction was performed on the wavelet transformed reference spectra prior to feature detection using Gaussian fitting. In addition to this, baseline correction was also performed on all 3 variants (derived using db4, db7 and db11) of the wavelet transformed measured spectrum before feature detection. Rest of the algorithm follows the methodology described under $\alpha 3$.

6.3.3 Cross-validation

A simple model evaluation algorithm was devised to assess if the performance of the classifiers. The distribution of the cosine similarity values for all the measured samples in the measured dataset is collected and plotted. This was done by empirically determining a probability distribution function to look at the distribution of the cosine similarity values for all the measured samples in the measured dataset (Gholamy and

Kreinovich, 2017). The probabilities corresponding to the values of the cosine similarity were estimated with the help of the number distribution of the cosine similarity values, i.e., the histogram of the cosine similarity values. The p-values of the cosine similarity values were distributed into a total of 20 bins to display the values between 0 and 1.0. If the probability values follow an exponential distribution, the values at the tail end of the curve become increasingly unique depending upon the steepness of the curve (Benjamini and Hochberg, 1995; Breheny et al., 2018). Intuitively, the greater the more unique the values are, the lesser the chance for them to be a consequence of “chance” and the greater the likelihood for them to be accurate.

6.4 Results

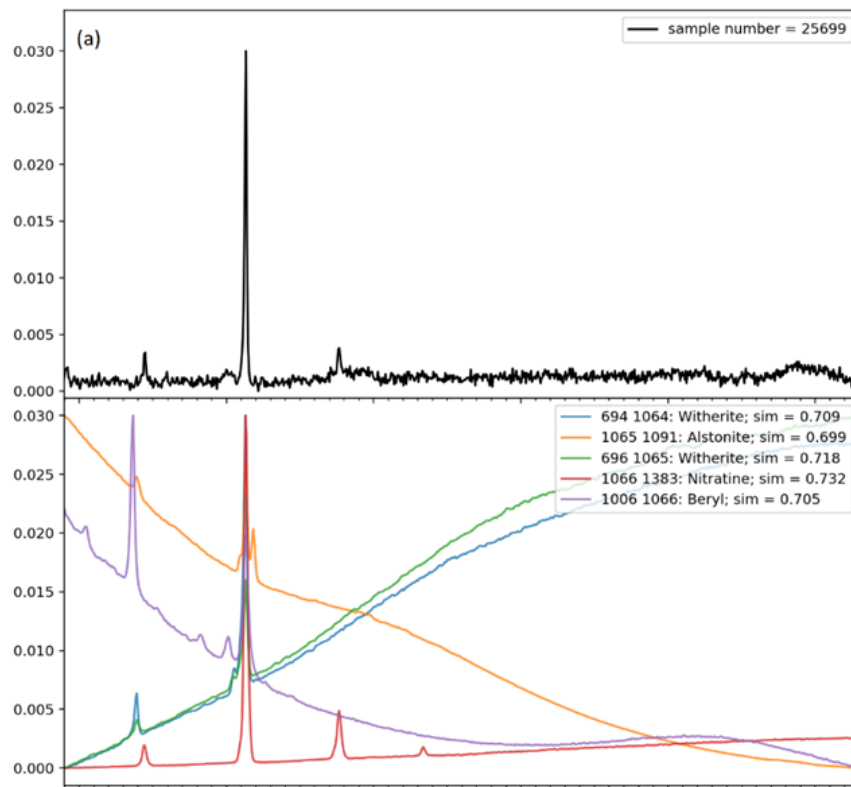
6.4.1 Preprocessing α – Results and Validation

The results pertaining to all six algorithms are presented in this section in sequential order as presented above. The results for the measured sample number 25699 in the parent database (of which the measured dataset is a subset) are discussed in this section. For all the algorithms and different preprocessing schemes used, the highest match is generally observed with “Nitratine” with several other mineral species following it with a decline in the match score. Depending upon the complexity of the classification algorithm, significant variations in the match scores were observed. A detailed description of the overall performance of the algorithms along with the advantages and disadvantages will follow. Towards the end of this section, an analysis of the methodology adopted for validating the results is provided at the end of the section.

$\alpha 1$ provided the simplest form of cosine similarity classifier among all the available alternatives (results for measured sample label 25699 in Figure 49 (a)). Its simplicity is a consequence of the lack of preprocessing done on the measured samples. This made the computation of the dot product in step 1 and 2 of algorithm $\alpha 1$ quicker and easier to evaluate. Cosine (vector) similarity cannot differentiate a peak from a noisy spike in any given vector. The cosine similarity between 2 given spectra was observed to be affected by the feature of cosine similarity. For the measured samples with relatively low noise, this algorithm produced match results which would look correct by glancing at them without doing any cross-validation. Contrarily, the match results for the samples with a significant amount of high frequency noise (usually $\text{SNR} < 1.0$) sometimes looked completely bogus, despite resulting in a high cosine similarity value. In addition to this, the preprocessing of the reference spectra did not include baseline correction prior to feature detection, which suggested the possibility of false peak detection in the samples. This was also speculated to have negatively affected the dot product, and hence the match, by giving non-zero product in the regions where there were no observable peaks.

Another notable disadvantage of $\alpha 1$ were the lack of spread of the dot product values for the matches (validation for the match results for measured sample label 25699 in Figure 49 (b)). A significant portion of the match values were observed to be above 0.9 and showed little, if any distinction from each other, making the choice of a good match from a poor one extremely hard without any cross-validation. This also led to difficulties in setting up a threshold value for shortlisting reference spectra, and hence accurately matching peaks between the measured and reference spectra. Results

of the validation algorithm produce a discrete frequency histogram of all the possible match values. The probability frequency of α lmatch values is best fit to a Poisson distribution. The intuitive validation approach described in the previous section has not been shown to be useful with a Poisson distribution in past research (Breheny et al., 2018). This means that the cosine similarity values obtained with the help of this algorithm may or may not be reliable.



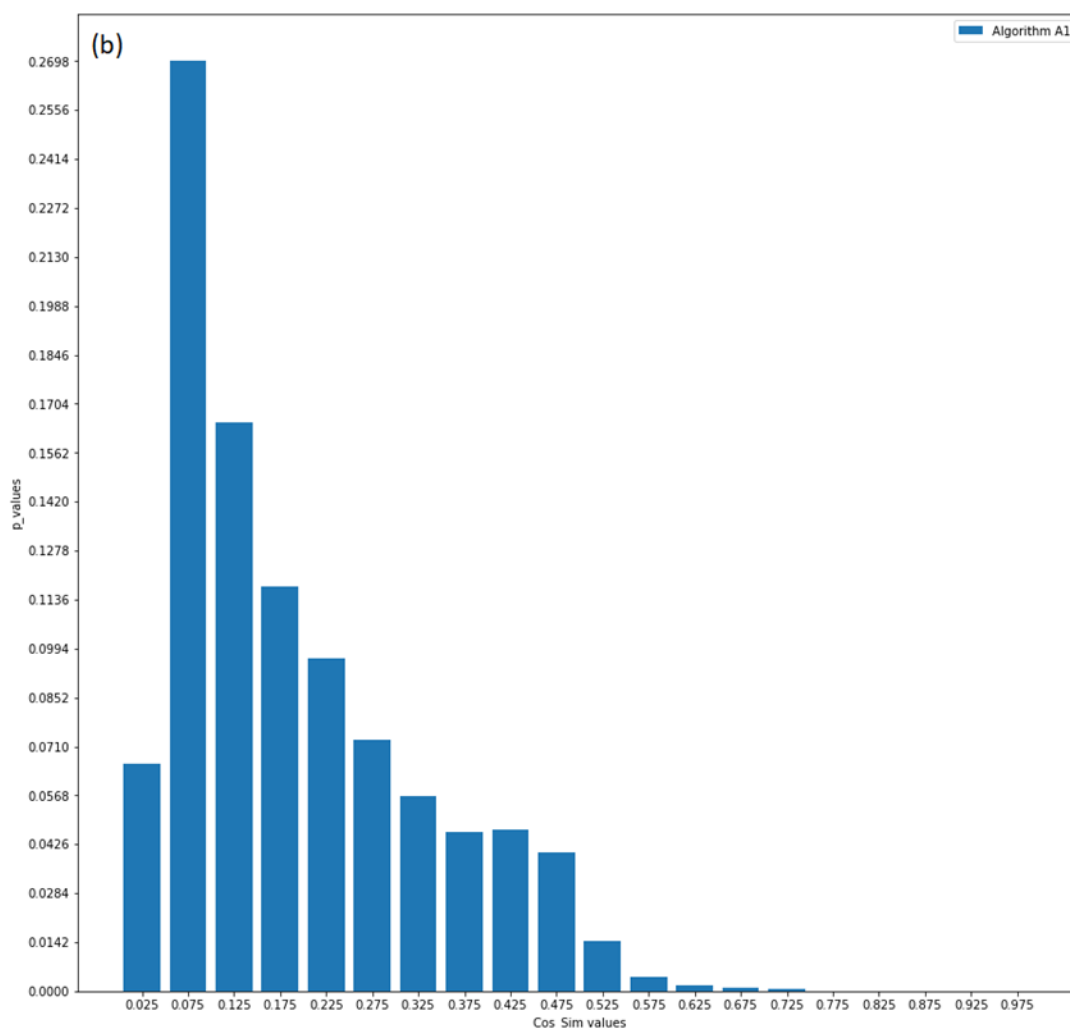
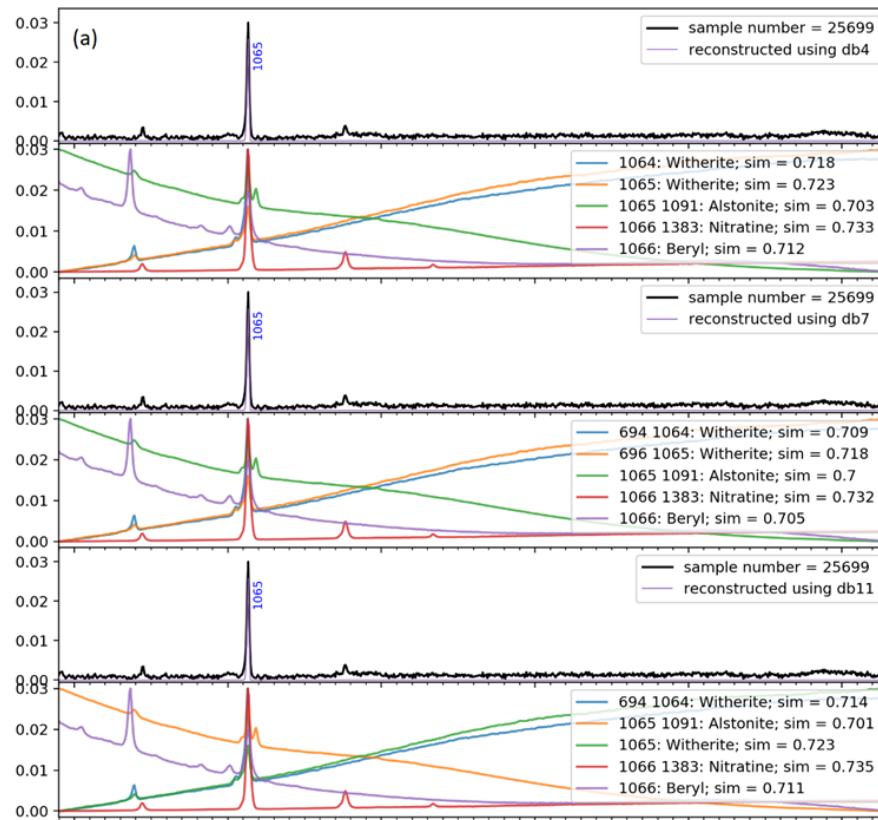


Figure 49. (a). The match results obtained by implementing algorithm $\alpha 1$ are presented. The top panel shows the unclassified measured spectrum, and the bottom panel shows the reference spectra obtained as the matches for the measured spectrum. The top 5 spectral matches and their corresponding cosine similarity values along with their respective mineral classes have been shown on the plot. (b). The validity of the match results has been shown in the plot. The distribution of the cosine similarity values seems to follow Poisson distribution which implies underlying systemic issues with the procedure.

α_2 was an improvement on α_1 in that the measured spectrum was first passed through a DWT treatment before the similarity metric was evaluated with any of the reference spectra. The top 5 matched spectra and their corresponding scores for the measured spectrum labeled 25699 are shown in the Figure 50 (a). As described in section 2.1, 3 different wavelets are implemented to perform wavelet transform of the measured spectrum, leading to the generation of 3 wavelet transformed spectra representative of the measured spectrum. Each of the 3 wavelet transformed spectra underwent a significant reduction in the high frequency noisy spikes. Therefore, as compared to α_1 , the dot products computed in step 1 of α_2 were observed to yield matches which were considered more reasonable on preliminary inspection based on observation. However, on passing the similarity values through the validation algorithm, it was observed that they also follow a Poisson distribution which implies a low reliability of this algorithm. A significant number of matches corresponding to high dot products were suspected to be a consequence of the fluorescence present in the wavelet transformed measured spectrum. Despite performing DWT, the non-zero baseline of the measured spectrum led it to have non-zero Raman intensity at almost every Raman shift. These regions of non-zero intensity were speculated to be resulting in high a similarity metric when their dot product was computed against the peak regions in any given reference spectrum.

A threshold was set to shortlist reference spectra for computing dot products in the second phase. As opposed to the resulting dot products after step 1 of α_1 , a much more uniform spread was observed in the distribution of the dot products resulting from step 1 of α_2 . The distribution of the match scores for all reference spectra corresponding to

the measured spectrum labeled 25699 is shown in Figure 50 (b). This helped with setting up a more robust threshold for shortlisting the reference spectra. Like the first phase of α_1 , the issue of “false positives” being thrown out as matches persisted in the first phase of α_2 . This issue was attributed to the presence of a non-zero baseline, but it was relatively less proliferated due to the removal of noise from the samples.



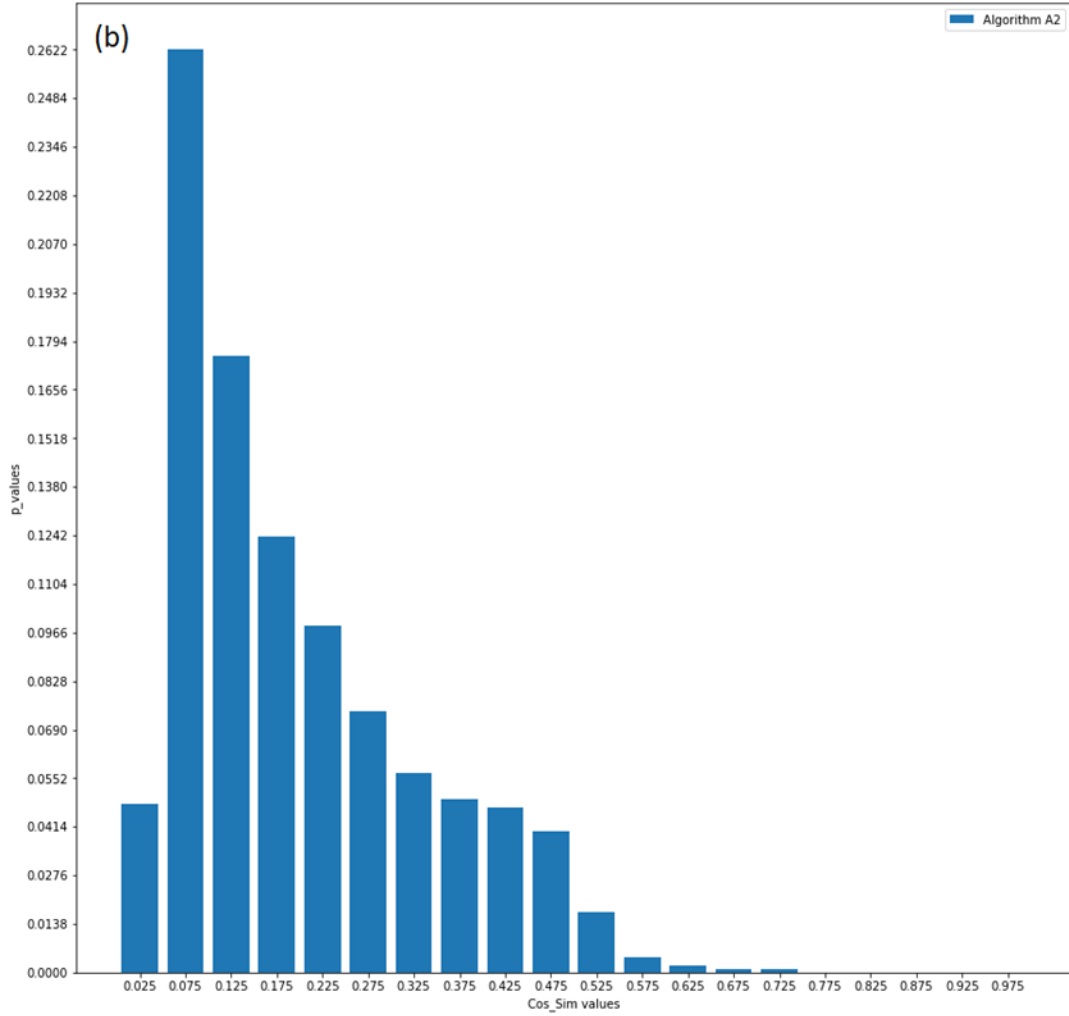
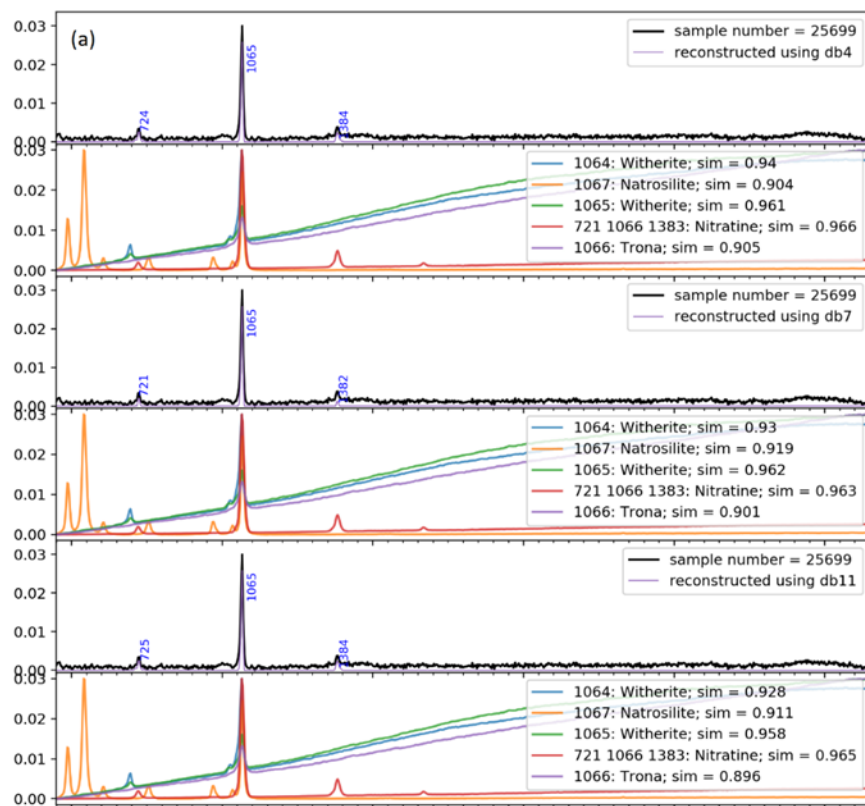


Figure 50. (a). The match results obtained by implementing algorithm $\alpha 2$ are presented. The 1st, 3rd and 5th panels of the plot show the unclassified measured spectrum along with their DWT versions derived using (i) db4, (ii) db7, and (iii) db11 wavelets respectively. The top 5 matched reference spectra obtained for all these cases are shown in the 2nd, 4th and 6th panel of the plot. (b). The result of the validation test for the matches obtained for (iii) is shown. The p-values obtained for the cosine similarity values show Poisson distribution which highlights an intrinsic problem in the method.

α_3 was an improvement on both algorithms α_1 and α_2 . In addition to performing wavelet transform on the measured spectra, “feature detection” was also done for them. Top 5 matched reference spectra with their cosine similarity scores corresponding to the measured spectrum labeled 25699 are shown in Figure 51 (a). Like α_2 , the wavelet transform was performed on the measured spectra using 3 different Daubechies’ type wavelets – db4, db7, db11. The effect of using 3 different wavelets was prominently observed after feature detection. Generally, all the prominent sharp features were not captured for any one of the wavelet-transformed measured spectra. However, feature detection for all 3 variants of the wavelet transformed measured spectrum was collectively able to determine all the prominent features for any given measured spectrum. After feature detection was performed on a measured spectrum, it was reconstructed using the detected peaks – all the peaks were individually cropped out of the original spectrum and appended at their respective positions to a 0-vector of the same length as that of the measured spectrum. In the first phase of this algorithm, the dot products were computed between the reconstructed measured spectrum and a reconstructed spectrum taken up from the reference database one at a time. A major advantage speculated in the implementation of this algorithm was that it completely nullified the influence of those regions on the dot product which did supposedly did not contain any sharp peaks. A disadvantage of this method was that baseline correction was not conducted on any of the measured or reference spectra, which could have potentially led to the detection of false peaks in some samples. This was similar to that for α_1 and α_2 and could have further reduced the reliability of the match metric value and the match itself. The matched spectra from RRUFF database were shortlisted and

their reconstructed forms were thrown in with the reconstructed measured spectrum for computing the dot products in step 2.



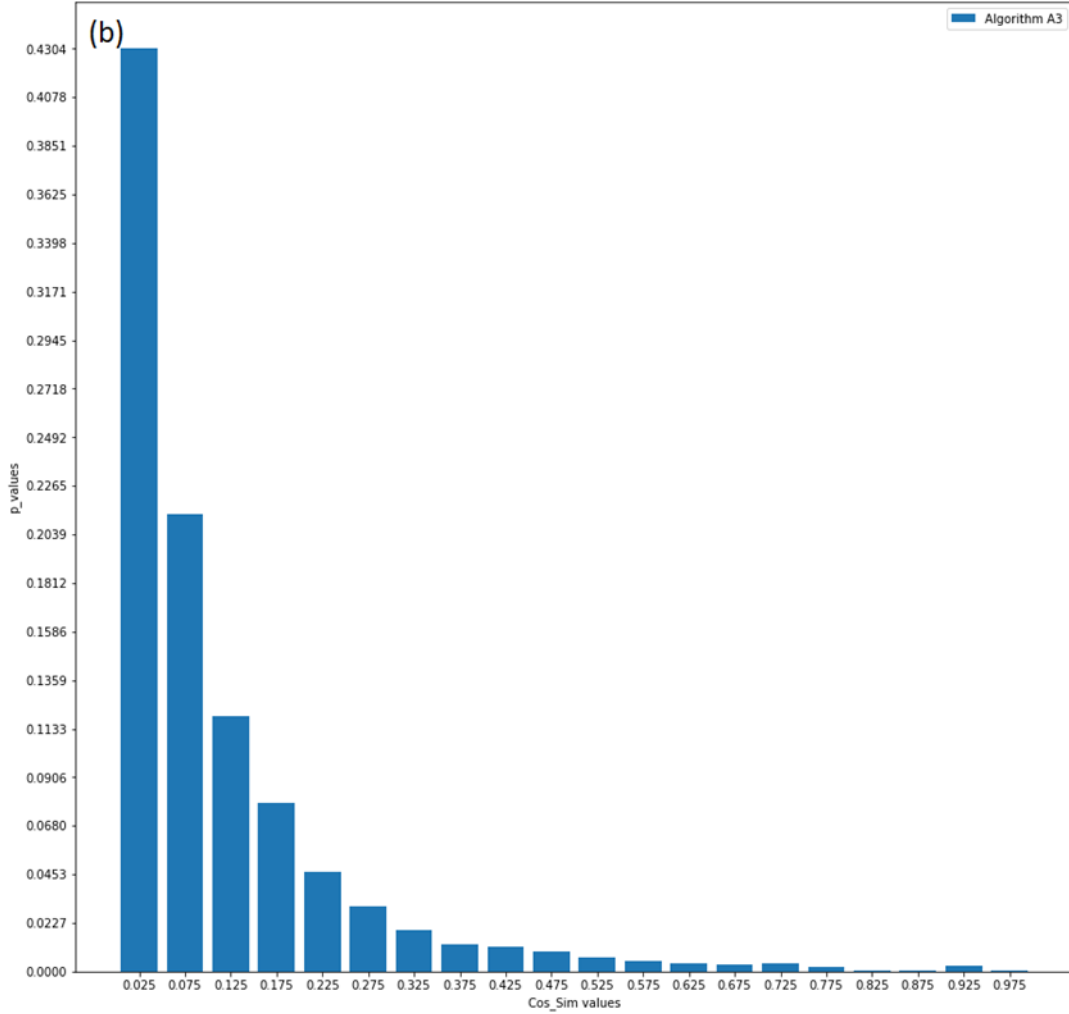


Figure 51. (a). The match results obtained by implementing algorithm $\alpha 3$ are presented. The 1st, 3rd and 5th panels of the plot show the unclassified measured spectrum along with their DWT versions derived using (i) db4, (ii) db7, and (iii) db11 wavelets respectively. The top 5 matched reference spectra obtained for all these cases are shown in the 2nd, 4th and 6th panel of the plot. (b). The result of the validation test for the matches obtained for (iii) is shown. The p-values obtained for the cosine similarity values show exponential distribution. All the p-values for cosine similarity values beyond the 0.675-mark account for less than 5% of the cosine similarity population, which implies the uniqueness of the similarity values in this range. This suggests improved reliability of the matches obtained using this algorithm.

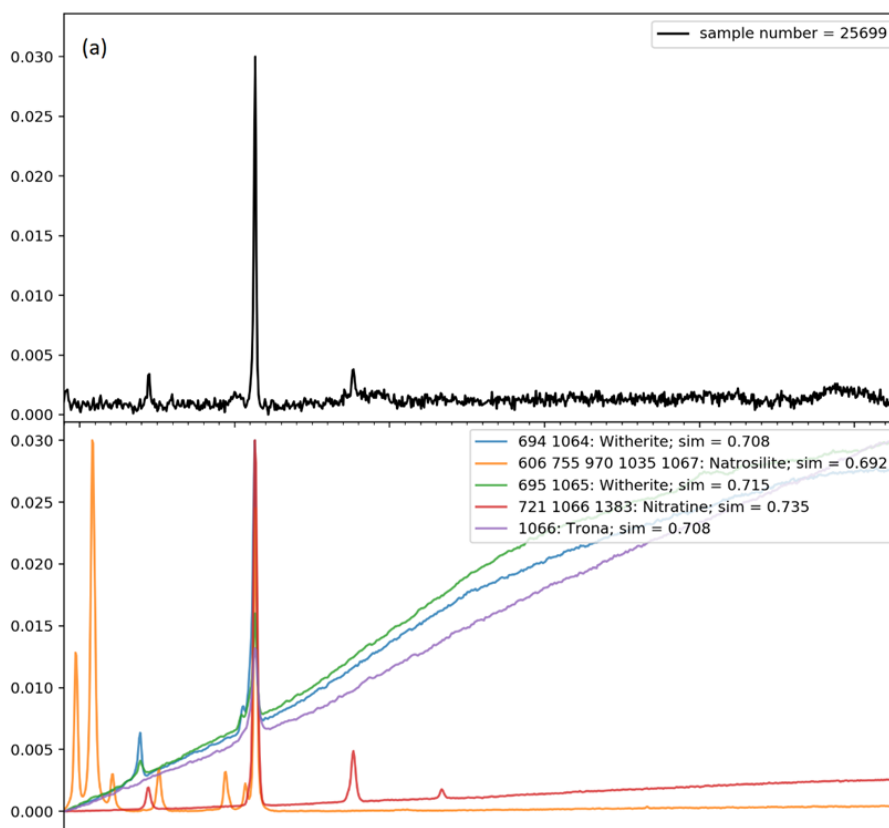
Like the previous algorithms, step 2 involved cropping the reconstructed measured spectrum and the reconstructed reference spectrum under consideration with the help of the peaks of the said reference spectrum. The 2 cropped spectra were dotted against each other to surmise the peaks that match between the spectra. The reconstruction of the measured spectrum with the help of its own peaks prior to computing dot products in either of the phases provided a significant advantage over the preceding algorithms – this nullification of the dot product to 0 where there was no match for any peak in the reference spectrum, with any of the peaks in the measured spectrum.

Unlike the 2 previous algorithms, the probabilities of the similarity values followed a declining exponential distribution. The distribution of the cosine similarity scores for all the reference RRUFF spectra corresponding to the measured spectrum 25699 is shown in Figure 51 (b). Towards the higher end of the similarity values, the probabilities were observed to become drastically low with their number distribution towards the tail end of the exponential. This confirmed the uniqueness of the higher cosine similarity match scores obtained by implementing algorithm $\alpha 3$.

6.4.2 Preprocessing β – Results and Validation

$\beta 1$ was designed as an improvement on $\alpha 1$ and included baseline correction on the reference spectra (top 5 matches for measured spectrum 25699 in Figure 52a). This was assumed to have improved feature detection for reference spectra by reducing the possibility of extracting false peaks in any of the spectra. The presence of high frequency noise remained as the prime reason behind numerous “false positives” being

extracted as matches. Additionally, the issue of ambiguous high metric values for matched spectra was still prevalent. The results of the validation test on the cosine similarity values obtained in this algorithm had the same trend as that observed in the $\alpha 1$. This implied that the implementation of baseline correction on $\alpha 1$ did not make any improvements on the reliability of the obtained match results.



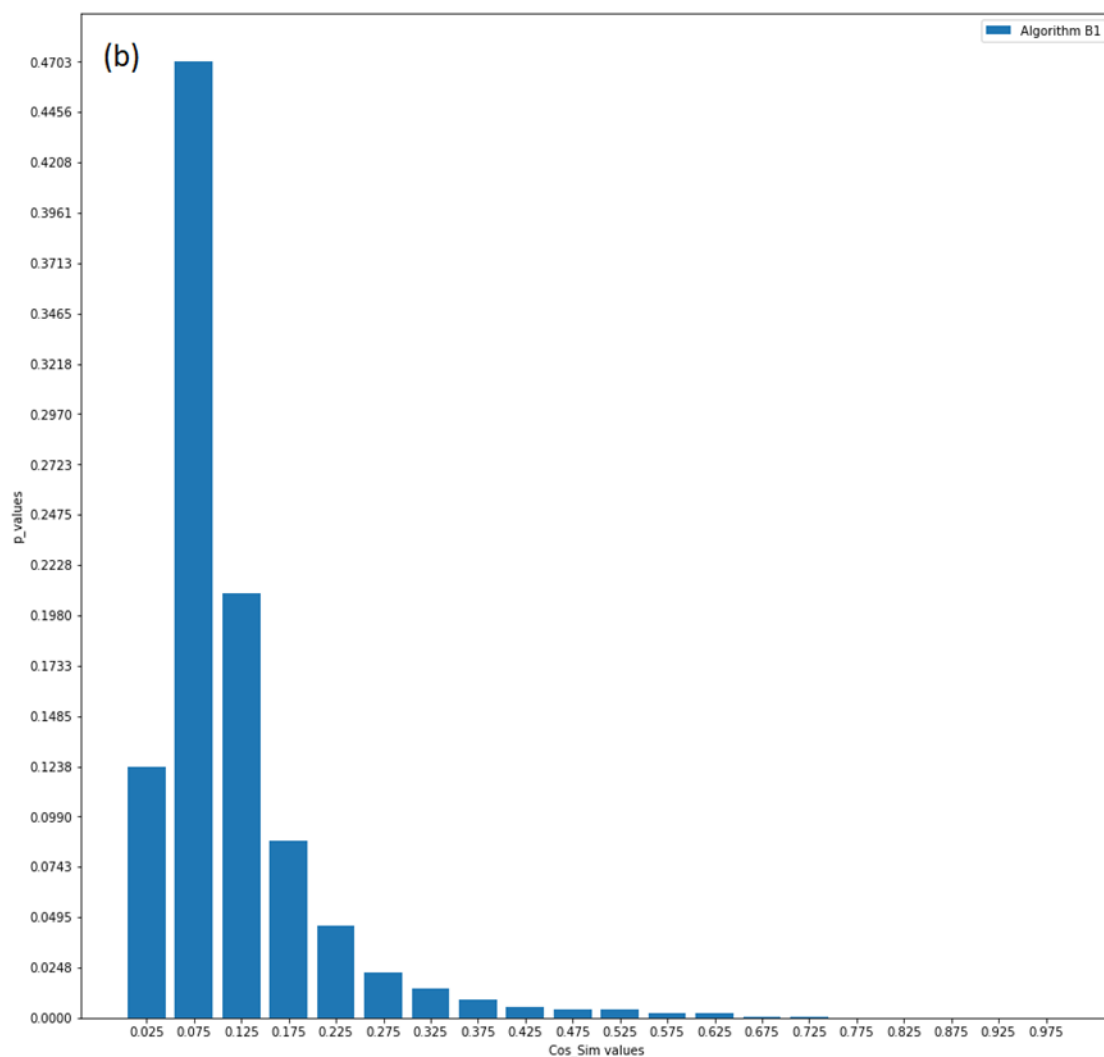
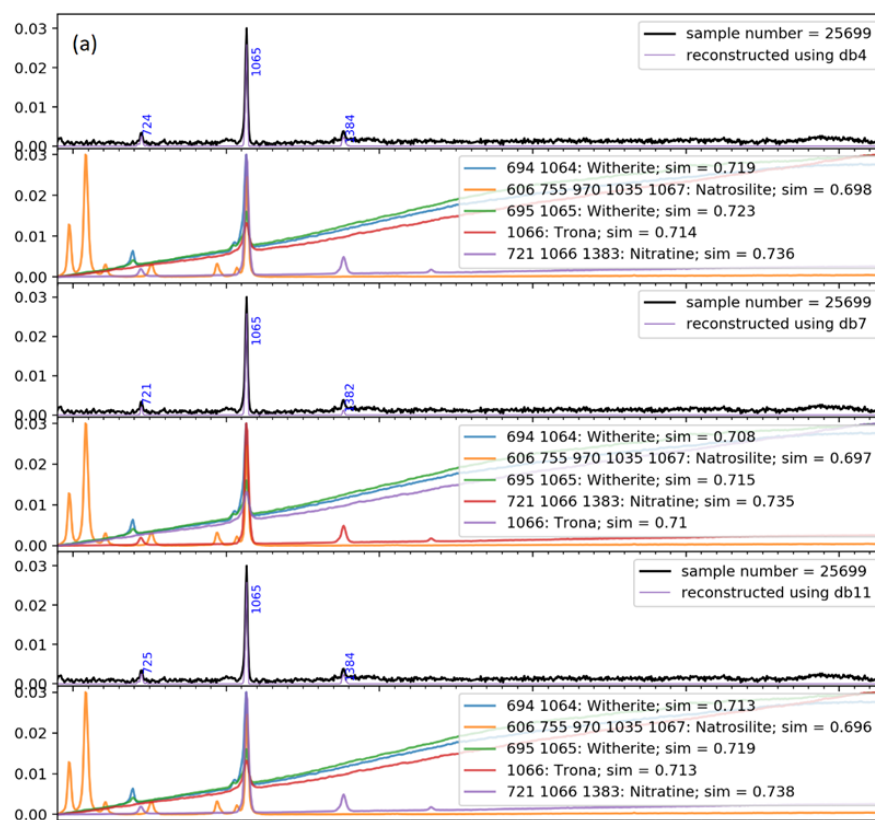


Figure 52. (a). The match results obtained by implementing algorithm $\beta 1$ are presented. The top panel shows the unclassified measured spectrum, and the bottom panel shows the reference spectra obtained as the matches for the measured spectrum. The top 5 spectral matches and their corresponding cosine similarity values along with their respective mineral classes have been shown on the plot. (b). The validity of the match results has been shown in the plot. The distribution of the cosine similarity values seems to follow Poisson distribution which implies underlying systemic issues with the procedure.

There was no observable difference in the matches which obtained in the second phase of the procedure (match scores distribution for algorithm $\beta 1$ in Figure 52b). Most of the highest match scores corresponded to the same reference spectra which resulted from implementing algorithm 1, with a reduced number of matched peaks in step 2 of the current algorithm compared to those observed in step 2 of $\alpha 1$.



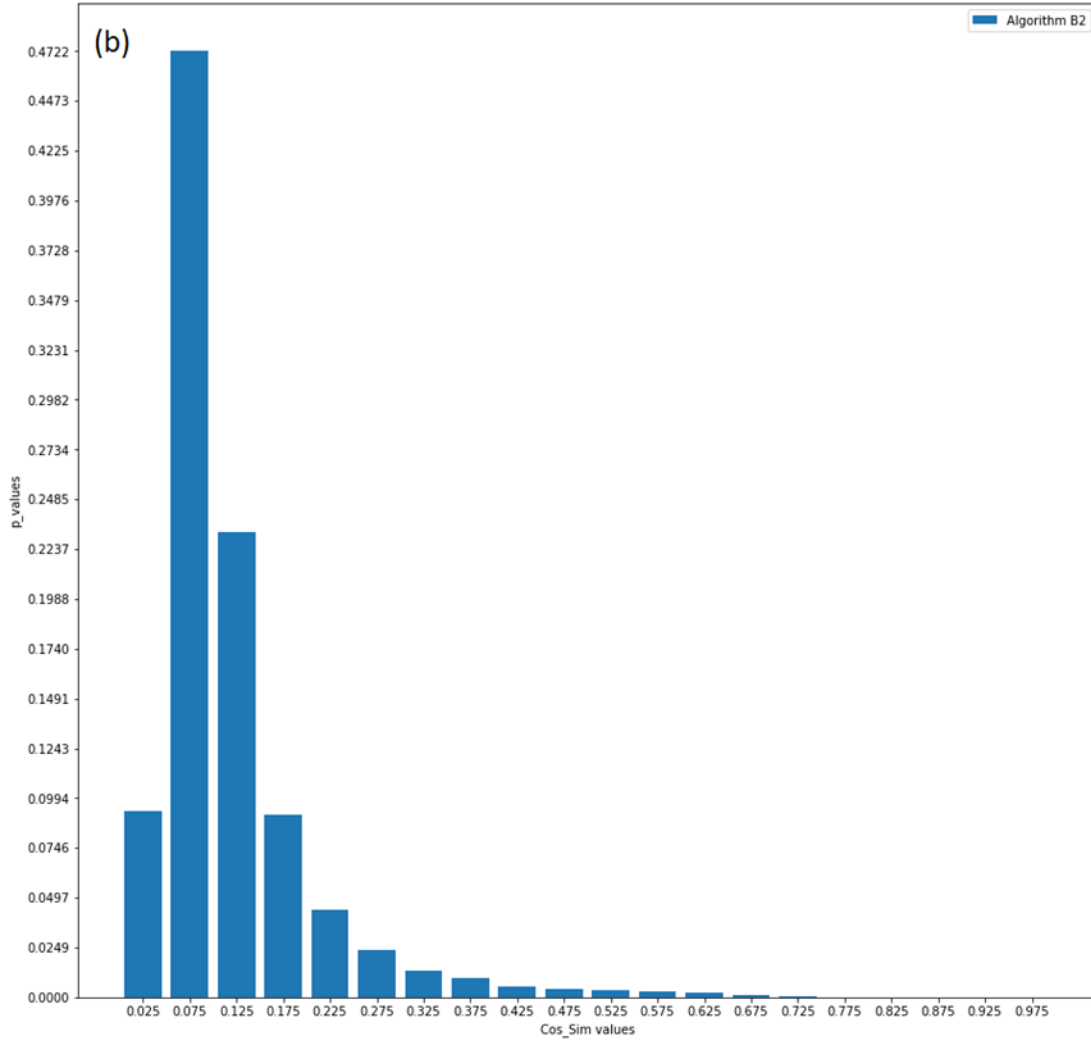


Figure 53. (a). The match results obtained by implementing algorithm $\beta 2$ are presented. The 1st, 3rd and 5th panels of the plot show the unclassified measured spectrum along with their DWT versions derived using (i) db4, (ii) db7, and (iii) db11 wavelets respectively. The top 5 matched reference spectra obtained for all these cases are shown in the 2nd, 4th and 6th panel of the plot. An important distinction between algorithm $\alpha 2$ and algorithm $\beta 2$ can be noted in terms of the performance of the preprocessing routines - the much smaller characteristic peaks can also be easily retrieved when implementing the latter. (b). The result of the validation test for the matches obtained for (iii) is shown. The p-values obtained for the cosine similarity values show Poisson distribution which highlights an intrinsic problem in the method.

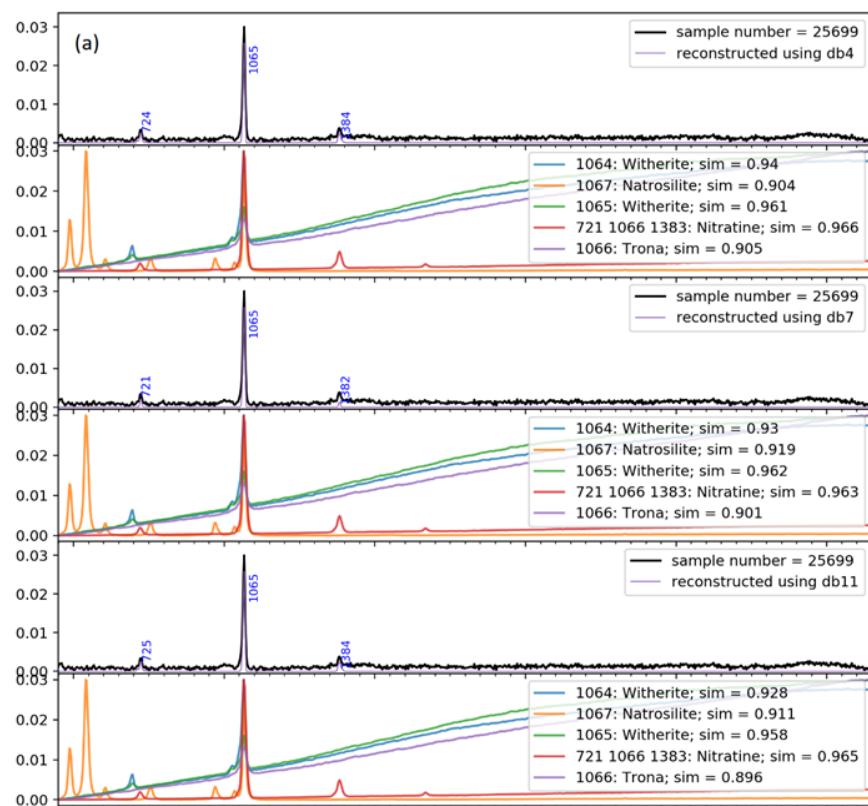
Similar to β_1 , β_2 improved the preprocessing of reference spectra by performing baseline correction on them in addition to wavelet transform prior to feature detection. Top 5 matches found using each Daubechies' wavelet for measured spectrum 25699 are shown in Figure 54 (a). This was assumed to have improved the feature detection for the reference spectra. No changes were made to the preprocessing methodology of the measured spectrum. As opposed to the matches obtained for α_2 , there was a noticeable improvement in the matches for β_2 . This was assumed because of the improvement in feature detection. However, there were still several instances where the matches appeared out of place which was attributed to the variable baseline in any given measured spectrum. The results of the validation test on the cosine similarity values obtained in this algorithm had the same trend as that observed in the α_2 . This implied that the implementation of baseline correction on α_1 did not make any significant improvements on the reliability of the obtained match results.

In step 2, there were issues like those observed for α_2 . The cropped-out regions from any measured spectrum still generally non-zero intensity and therefore resulted in non-zero contribution to the overall metric value when dotted with the peak regions of the reference spectrum being compared against (match score distribution shown in Figure 53b). At times, this seemed to be resulting in matches being found in the regions where peaks could be observed in the measured spectrum via preliminary inspection.

The β_3 algorithm was an improvement over all the previous algorithms and was analogous to α_3 (top 5 corresponding to each Daubechies' wavelet applied to measured spectrum 25699 shown in Figure 54a). In addition to the methodology adopted as α_3

the spectra from the reference database as well as the measured spectra underwent baseline correction before feature detection. This helped with reducing the chance of finding false peaks in both the reference spectra as well as the measured spectra. Both the spectra were reconstructed with the help of their respective peaks, which was postulated to minimize “false positives”. This was expected to be happening from the 0-ing out of the spectra everywhere except for the peaks’ regions, which would effectively squash the dot product to an appropriate value due to 0 contribution from the regions with 0 intensity. On performing the validation test on the cosine similarity values for this algorithm, a trend similar to α_3 was observed. Additionally, the number density of the higher cosine similarity values was further reduced as compared to that observed in the case of α_3 . This suggested that β_3 was a further improvement over α_3 .

The shortlisting of the matched spectra from the first phase was also expected to be increasingly accurate compared to that from the first phase of α_3 . It was assumed that extensive preprocessing of the reference and measured spectra was major contributing factor to that. Furthermore, the metric values were found to be very well spread over a wide range between 0 and 1 that suggested an improved reliability of the matching algorithm (match score distribution for measured spectrum 25699 shown in Figure 54b). In step 2, the matching of the individual peaks between the spectra being compared against one another also seemed to generate overall acceptable results. On some occasions, the results did not seem accurate in the second phase as all the peaks did not appear to come out as matches as were found through preliminary inspection.



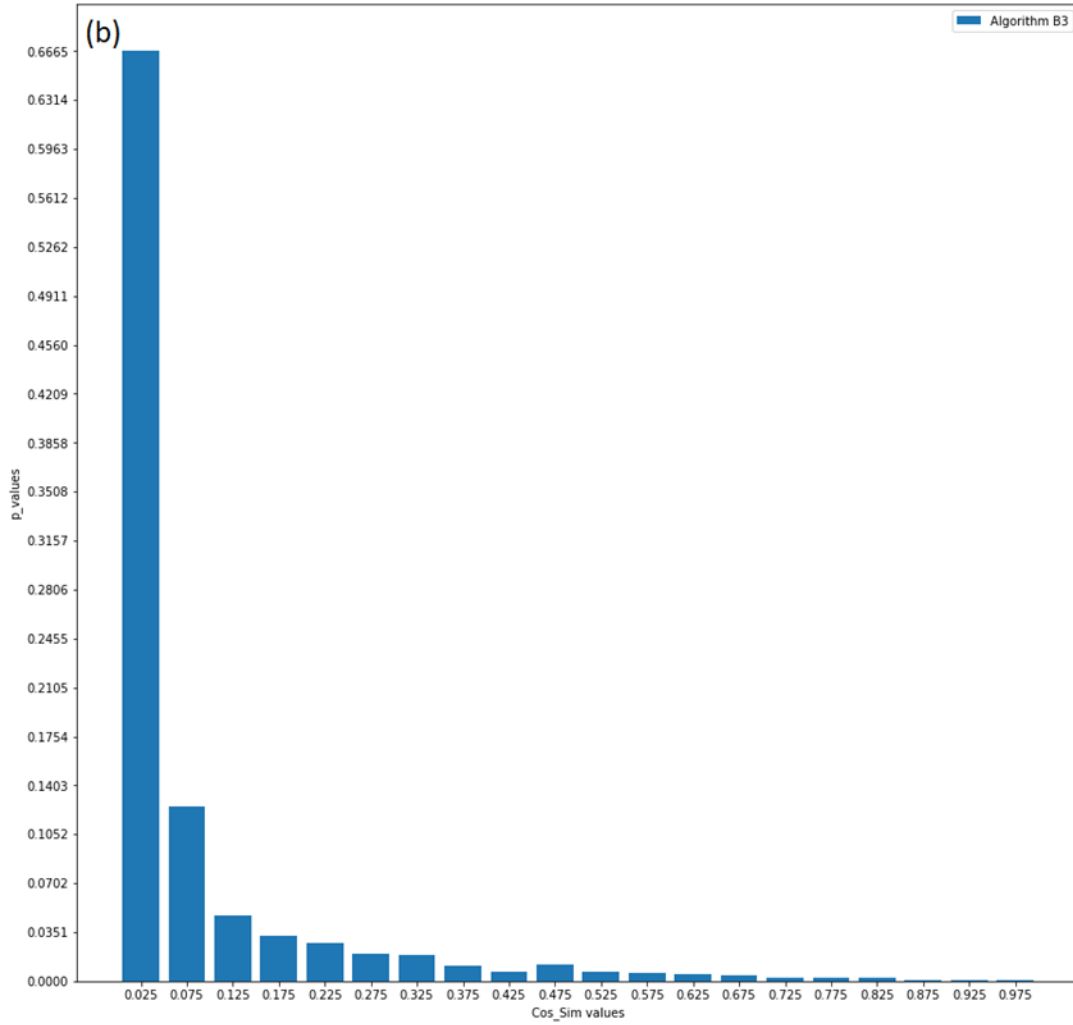


Figure 54. (a). The match results obtained by implementing algorithm $\beta 3$ are presented. The 1st, 3rd and 5th panels of the plot show the unclassified measured spectrum along with their DWT versions derived using (i) db4, (ii) db7, and (iii) db11 wavelets respectively. The top 5 matched reference spectra obtained for all these cases are shown in the 2nd, 4th and 6th panel of the plot. An important distinction between algorithm $\alpha 3$ and algorithm $\beta 3$ can be noted in terms of the performance of the preprocessing routines - the much smaller characteristic peaks can also be easily retrieved when implementing the latter. (b). The result of the validation test for the matches obtained for (iii) is shown. The p-values obtained for the cosine similarity values show exponential distribution. All the p-values for cosine similarity values beyond the 0.675-mark account for less than 5% of the cosine similarity population, which implies the uniqueness of the similarity values in this range. This suggests improved reliability of the matches obtained using this algorithm. In addition to this, the decline of the exponential is steeper than that obtained for algorithm $\alpha 3$ that suggests an improved reliability of the matches thus obtained.

6.5 Summary and Implications

The performances of the six classification algorithms developed in this work differ substantially. These performances were quantified with the help of a validation/model evaluation algorithm. Results show that the performance of α_1 , α_2 , β_1 , and β_2 produced fewer appropriate matches. On the contrary, the results obtained using α_3 and β_3 were generally reliable, with the latter delivering an overall superior quality of matches (p-values $\leq \alpha = 0.05$) for the measured spectra. It was observed that the matches for individual mineral species were obtained with a greater precision using β_3 , whereas the matches for mixture species or those corresponding to individual peaks in the spectra were found to be better using α_3 . This suggests that to obtain an overall reliable and accurate match for the measured Raman spectra in any new database, α_3 and β_3 can be used together to complement each other.

To perform feature (peak) detection in the measured and reference spectra, two different user-defined functions were tested – “findpeaksG3” and “autofindpeaks”. “autofindpeaks” is as an automated version of “findpeaksG3” that does not require user-defined inputs for the amplitude and slope thresholds for determining the peaks in any given signal, where “signal” in this context is the Raman spectrum/signal under consideration. The only distinction observed in terms of the precision with which they could detect all the significant features in any spectrum, with autofindpeaks having a more intricate algorithm as compared to findpeaksG3 and hence performing slightly better. However, findpeaksG3 was able to run faster on same spectra compared to autofindpeaks. For any given sample, autofindpeaks had about 4-6 seconds longer

runtime compared to findpeaksG3. This translated to about 12 hours of additional runtime for the entire measured and reference databases when using autofindpeaks, while algorithm $\beta 3$ was implemented. This time was observed to noticeably increase for other algorithms involving the use of peak detection methods on lesser preprocessed samples. In other words, autofindpeaks produced similar results as those of its counterpart at the expense of time required to perform the computations. Due to this reason, findpeaksG3 was preferred over autofindpeaks for carrying out feature detection.

Daubechies' wavelets were extensively explored for spectral samples in this study. DWT has been previously shown to work well with Raman spectra for removing noise from them. Daubechies' wavelets are one of the wavelet types that are known to work best with the Lorentzian and Gaussian type peaks present in the Raman spectra. In this work, a general algorithm for performing DWT for noise removal using Daubechies' wavelets was developed. The algorithm demonstrated the performance of 3 different wavelets, db4, db7 and db11, on the measured spectra, and the performance of db5 on the reference spectra. The choice of these empirically made. These wavelets worked well to remove a significant amount of noise from the spectra while preserving their shape so that the feature detection algorithm would also work efficiently for extracting most of their characteristic features.

Previous studies have shown the performance of wavelets for analyzing Raman spectra via DWT or CWT, but not on a dataset of such magnitude. A total of 9,330 reference spectra and about 900 measured spectra were used to analyze the

performance of Daubechies' wavelets for removing high frequency noise from them via DWT method. The 3 different Daubechies' wavelets – db4, db7 and db11 – occasionally produced distinct kinds of smoothed spectrum from each other, which was noticeable after performing feature detection on the spectra. Often some of the features were not detected in the one or more kinds of the smoothed spectra by the feature detection function despite the said features being observable through preliminary (visual) analysis. Despite this challenge, at least 3 of the wavelets produce a smooth spectrum for which all the significant features can be detected by the feature detection function.

Raman spectroscopy can be a time-intensive process. It can require long time intervals between the excitation and stabilization of the samples for which the spectra are being observed. These long intervals reduce corruption of the signal by noise, fluorescence, and cosmic radiations. On contrary to this, REBS-based ARS spends about 20 minutes to obtain one spectrum and hence there is an abundance of high frequency noise, fluorescence and cosmic radiations in the spectra detected by this device. To our knowledge, this is the first work to study the performance of wavelet algorithms for analyzing considerably large Raman spectra datasets with low signal-to-noise ratio. This work shows that one can effectively employ 3 different Daubechies' wavelets to remove noise. Furthermore, removal of noise is a necessary process that ought to be performed before comparing spectra in databases against each other. And additionally, baseline correction using ALS to remove fluorescence may also be performed, if required.

The results obtained using the proposed algorithms are consistent with previous literature. (Kwiatkowski et al. 2010) found a cosine similarity match metric of approximately 70% when attempting to obtain a match using the low-SNR Raman spectrum of an organic mixture. In this work, the six algorithms applied to classify the Raman spectra in the Jornada dataset using the Raman spectra in the RRUFF database yielded similar results. (Kwiatkowski et al. 2010) also compared the performance of other possible classification algorithms with that of cosine similarity and concluded that other vector-based classification algorithms can perform equally well or better depending on the algorithm. Other vector-based, trajectory-based and machine learning algorithms cited in this work provide even more reliable matches for unclassified Raman spectra (Carey et al., 2015; Liu et al., 2017; Park et al., 2017; Zhao et al., 2017; Stables et al., 2017; Kyriakides et al., 2011). Overall, we infer that efficient preprocessing strategies followed by sophisticated algorithms can significantly improve the aerosol chemical characterization using their Raman spectra.

Chapter 7: Conclusions

With increasing natural and anthropogenic emissions, we observe a vast compositional diversity in carbonaceous and dust-like substances in the atmosphere. The cloud effects of these aerosols continue to be the most significant source of uncertainty in the overall aerosol indirect radiative forcing. Consequently, a better understanding of the effect of different aerosol physicochemical properties on their water uptake behavior is critical. In this dissertation, we used experimental and computational methods to study the effects of particle morphology and aqueous solubility on the water uptake characteristics of changing chemical composition related to carbonaceous aerosols.

7.1 Summary and Implications

We began our study by proposing and testing a new methodology for cloud condensation nuclei (CCN) analysis of aerosols (chapter 2). This new methodology involves the use of the novel Aerodynamic Aerosol Classifier (AAC) instrument for improving the number concentration measurements and particle sizing. The AAC-based measurements were found to be comparable to that of the more traditional CCN measurement setup that employs a Differential Mobility Analyzer (DMA) instrument for the CCN analysis of aerosols. However, the AAC seemed to offer notable advantages in terms of the CCN analysis of large molecules (such as, sucrose), and also provided a method for morphological correction in particle sizes, and thus resulting in

the CCN activity analysis with reduced uncertainties. These advantages were especially evident from the hygroscopicity parameterization of the aerosols from the measurements using the AAC instrument.

Our work suggests that the use of the AAC instrument could be valuable in laboratory and field measurements, particularly for low hygroscopicity aerosols and particles with significantly irregular morphology (such as, black carbon). Furthermore, our results suggested that the explicit treatment of the particulate shape and density in the CCN analysis can significantly improve the water uptake predictions of aerosols.

In chapters 3 and 4, we extensively discuss the development and application of a new CCN analysis framework using laboratory measurements. The new CCN analysis framework was called the hybrid activity model (or, HAM) and was based on the explicit treatment of the dissolution properties of aerosols on the particulate level. The water uptake and hygroscopicity of aerosols are closely linked to their aqueous solubility (Köhler, 1936; Petters and Kreidenweis, 2007). Additionally, solubility-based hygroscopicity parameterizations and CCN analysis frameworks only account for the dissolved fraction of aerosol particles in their droplet growth (Petters and Kreidenweis, 2008; Sullivan et al., 2009). In this dissertation, we showed that a combined treatment of dissolved and undissolved solute fraction can enhance the water uptake predictions and hygroscopicity parameterization of pure, as well as mixed particles. Moreover, HAM agreed well with experimentally observed droplet growth under both supersaturated and subsaturated relative humidity conditions. Our results

suggest that using a comprehensive CCN analysis model can improve droplet growth estimates for aerosols with wide range of aqueous solubilities.

In this dissertation, we also derived the single hygroscopicity parameter using the HAM framework. We found two main advantages of the HAM-based single hygroscopicity parameter. First, the HAM hygroscopicity accounts for the contribution of the aqueous solubility as well as the particle size on the droplet growth and water uptake. And second, the single hygroscopicity parameter simplistically quantifies a comprehensive water uptake mechanism in the form of an empirical variable. Therefore, the HAM hygroscopicity parameter provides the flexibility to implement a complex water uptake mechanism within large-scale climate models to represent the water uptake behavior of aerosols.

Chapters 5 and 6 describes the computational work in this dissertation. Chapter 5 presented the implementation of the HAM single hygroscopicity parameter in the global climate model (the Community Atmosphere Model). We found that a simplified form of the HAM hygroscopicity was feasible to use within the climate model, without compromising the computational efficiency. Findings in this work suggest that the use of a comprehensive hygroscopicity approximation of particle water uptake can substantially improve the predictions of physical and radiative properties of the aerosols and clouds. Through sensitivity tests and correlation analysis it was confirmed that the representation of aerosol hygroscopicity can significantly alter the aerosol and cloud properties.

Chapter 6 demonstrates the applicability of statistical and data-driven techniques for chemical characterization of aerosol particles using their Raman spectrometric measurements. In past studies, machine learning and statistics have been rigorously implemented for characterizing the chemical composition of aerosols using their Raman signatures. However, these studies have been limited to laboratory measurements of up to a few tens of samples. This work shows the application of similar computational techniques to characterize ambient aerosol particles. Furthermore, this work is the first to present the use of the Raman spectra measured with a portable Automated Raman Spectrometer for the chemical characterization of atmospheric aerosols. Results from this work suggest that the chemical composition and mixing states of the aerosols can be determined using their single-particle spectrometric measurements. This work emphasizes that rigorous spectral de-noising strategies are generally necessary before meaningful inferences regarding chemical composition can be made for a given aerosol population. Additionally, this work describes the species that may be likely encountered in the atmosphere for whose hygroscopic properties would need to be understood.

7.2 Final Thoughts and Recommendations for Future Work

The primary goal of this dissertation is to contribute to reducing the uncertainties in the AIF due to carbonaceous species. The experimental and computational methods developed in this work show promising results towards improving the confidence with which the water uptake properties and CCN activity of aerosols are understood. As

such, this dissertation describes feasible methods which can be adopted to develop CCN activity models in the future. Similar to HAM, more intricate CCN activity models can be developed by explicitly incorporating other well-understood physicochemical properties of aerosols (viscosity, surface tension, etc.).

In future studies, advancements in instrumentation techniques can be integrated within CCN models to improve the droplet growth from aerosols in ambient conditions. For instance, incorporation of parameterized particle morphological descriptors (size-resolved dynamic shape factor, effective density, etc.) within the CCN activity frameworks can be explored. Morphological properties of the particles can be used to explicitly resolve surface and bulk contributions on the droplet growth, without relying on empirical parameters. Therefore, through explicit inclusion of these properties in CCN analysis, a more thorough understanding of water uptake behavior atmospheric aerosols can be achieved. Furthermore, implementation of such CCN activity frameworks within climate models can lead to better climate and air quality predictions.

In addition to the above, more advanced machine learning and deep learning methods may be developed in the future for the chemical and mixing state characterization of ambient aerosol particles. Advanced machine learning algorithms (such as, neural networks) have been shown to effectively classify chemical compositions with high precision. Combining the de-noising strategies developed in this dissertation may have the potential to effectively classify ambient aerosols when combined with neural network approach.

Finally, this dissertation provides recommendations for future research with the help of quantified key physicochemical properties of aerosol particles that directly relate to their CCN activity and water uptake behavior. Findings reported in this work can be potentially used to reduce the uncertainties in physical and radiative properties predicted by climate models. Lastly, results in this dissertation show that small-scale experimental methods can generate valuable data that can in turn be used within large-scale modeling frameworks to obtain meaningful inferences about the impact of aerosols on the climate. Overall, results presented in this work can be used to improve our understanding the climate and air quality.

Appendix A: Curriculum Vitae

Kanishk Gohil

4318 Rowalt Drive, Apt #301, College Park, MD 20740		+1 (240) 660-8527 kgohil@umd.edu linkedin.com/in/kanishk-gohil github.com/kgohil27
EDUCATION	University of Maryland, College Park (UMD), MD Ph.D. Chemical and Biomolecular Engineering (ChBE) May 2023 Advisor: Dr. Akua Asa-Awuku M.S. Atmospheric and Oceanic Science (AOSC) May 2018 Advisor: Dr. Menglin Susan Jin Indian Institute of Space Science and Technology (IIST), India M.Tech. Earth System Sciences (ESS) May 2016 Advisor: Dr. Govindan Kutty M. Birla Institute of Technology and Science-Pilani (BITS-Pilani), India B.E. (Hons.) Chemical Engineering (CHE) May 2014 Advisor: Dr. Saroj Sundar Baral	
SKILLS	Programming: Python, MATLAB, C/C++, FORTRAN, LATEX, NCAR Command Language (NCL) Software: MS Office, Powershell, Aerosol Instrument Manager (AIM) Design and Modeling: AutoCAD, COMSOL, Minitab, NCAR Weather Research and Forecasting (WRF), NCAR-WRF CHEM, NCAR-Community Atmosphere Model (CAM) Instruments: Condensation Particle Counter (CPC), Scanning Mobility Particle Sizer (SMPS), Differential Mobility Analyzer (DMA), Cloud Condensation Nuclei counter (CCNC), Aerodynamic Aerosol Classifier (AAC) Engineering: CCN Activity Measurements, Hygroscopic Growth Measurements, Raman Spectroscopy	
RESEARCH EXPERIENCE	ChBE Department, UMD Aug 2018 – Present Graduate Research Assistant - Currently modifying the description of the water uptake of organic aerosols in the Community Atmosphere Model (CAM, NCAR) to study their subsequent cloud response - Formulated a novel computational framework for Cloud Condensation Nuclei (CCN) activity analysis of atmospheric aerosols over wide ranges of aqueous solubility - Designed a new CCN experimental methodology based on the state-of-the-art AAC instrument - Developed a CCN analysis tool for atmospheric aerosols using laboratory measurements (<i>Python</i>) UCAR, Boulder, CO Jul 2022 - Aug 2022 Visitor Graduate Student - Developed the routine for parameterizing the hygroscopicity of organic and carbonaceous atmospheric aerosols through the Modal Aerosol Model (<i>FORTRAN90</i>)	

- Tested the application of the hygroscopicity parameterization over different Intensive Observation Periods (IOPs) for quantifying the sensitivity of different cloud properties and radiative forcing on aerosol hygroscopicity

Army Research Laboratory, Adelphi, MD

Aug 2018 - Dec 2019

Graduate Student Researcher

- Developed a Python-based classification algorithm for chemical characterization of atmospheric aerosols using their Raman spectral signatures (*Python*)

AOSC Department, UMD

Aug 2016 - May 2018

Graduate Research Assistant

- Demonstrated a new method for estimating urban heat fluxes within the Building Environment Parameterization (BEP) scheme of NCAR-Weather Research and Forecasting (WRF) model (*WRF; FORTRAN77, MATLAB*)

ESS Department, IIST

Jun 2015 - May 2016

Student Researcher

- Investigated the impact of a strong midlevel vortex towards the intensification of a tropical cyclone
- Performed a comparative study on 3 cases of tropical disturbances for the justification of the role of a midlevel vortex in the genesis and intensification of tropical storms over the Indian ocean (*WRF; FORTRAN77, NCL*)

CHE Department, BITS-Pilani

Jul 2012- May 2014

Undergraduate Researcher

- Performed test to optimize experimental conditions (temperature, solvent-to solute ratio and stirring time) for the separation of acetic acid and water using Liquid-Liquid Extraction (LLE) (*COMSOL*)
- Conducted mathematical analysis using Minitab for experimental parameters' optimization (*Minitab*)

TEACHING
EXPERIENCE

ChBE Department, UMD

Aug 2022 - Dec 2022

Co-instructor (CHBE472)

- Conducted lectures for a class of 15 students in the Control of Air Pollution course (CHBE472)
- Regularly assisted in graded homework and reading assignments and examinations alongside lead instructor

Environmental Aerosol Research Lab (EARL), UMD

Aug 2019 - Present

Student Mentor

- Provided hands-on instruction in instrumentation and analysis at EARL
- Volunteered with student on-boarding into EARL

ChBE Department, UMD

Aug 2019 - May 2020

Graduate Teaching Assistant

- Regularly graded homework and reading assignments, held office hours and sporadically delivered classroom lectures for a 50-student Air Pollution course (Fall 2019/20)
- Conducted weekly discussion sessions for ASPEN and graded projects for 90 students in the Process Design course (Spring 2019/20)

EMPLOYMENTS

Maryland Innovation Initiative (MII), Columbia, MD

Jul 2017 - May 2018

Weather Forecast Developer

- Developed an urban weather forecast delivery interface

National Aerospace Laboratories (NAL), India

Jul 2013 - Dec 2013

Undergraduate Intern

- Outlined the standard operating procedure for nanowire fabrication at the Material Sciences Division, NAL

- Fabricated cobalt nanowires following the Template Assisted Growth (TAG) technique to implement in silica-based storage devices

Bharat Heavy Electricals Limited (BHEL), India

May 2012- Jul 2012

Undergraduate Intern

- Outlined the standard operating procedure for Eddy Current Clutch fabrication and assembly (Tools and Gauge Manufacturing Division, BHEL)
- Drafted a 2-D and a 3-D floor plan on AutoCAD (Tools and Gauge Manufacturing Division, BHEL)

HONORS AND AWARDS

1. Sengers Ph.D. Candidacy Scholarship, Department of Chemical and Biomolecular Engineering (UMD, Fall 2022)
2. Sengers Ph.D. Travel Award, Department of Chemical and Biomolecular Engineering (UMD, Fall 2022)
3. American Association for Aerosol Research (AAAR) student travel grant (Fall 2022)
4. Future Faculty Fellowship and travel grant (UMD, Spring 2022)
5. Dean's Fellowship, Department of Atmospheric and Oceanic Science (UMD, Fall 2016)
6. Graduate Fellowship, Department of Space, Government of India (IIST, 2014)

MEMBERSHIPS

1. American Institute of Chemical Engineers (AIChE), student member
2. American Association of Aerosol Research (AAAR), student member
3. American Geophysical Union (AGU), student member

SERVICES

- | | |
|--|----------------|
| 1. AAAR Student Chapter at UMD, Vice-president | 2022 – present |
| 1. AAAR 40 th Annual Meeting, Student Assistant | Oct 2022 |

Appendix B: List of Publications and Presentations

Peer-reviewed Publications

1. **Gohil, Kanishk**, Barrett, Reese, Rastogi, Dewansh, Mao, Chun-Ning, and Asa-Awuku, Akua, "Cloud Condensation Nuclei (CCN) Activity of Black Carbon Mixed with Low Aqueous Solubility Organics.", *Environ. Sci. Technol.* (In review)
2. Razafindrambinina, Patricia N., Malek, Kotiba A., De, Anomitra, **Gohil, Kanishk**, Riemer, Nicole, and Asa-Awuku, Akua A., "Using Particle-Resolved Aerosol Model Simulations to Guide the Interpretations of Cloud Condensation Nuclei Experimental Data.", *Aerosol Science and Technology* (In review)
3. Mao, Chun-Ning, **Gohil, Kanishk**, and Asa-Awuku, Akua. "A Single Parameter Hygroscopicity Model for Functionalized and Insoluble Aerosol Surfaces." *Atmospheric Chemistry and Physics* 22.19 (2022): 13219-13228.
4. **Gohil, Kanishk**, Mao, Chun-Ning, Rastogi, Dewansh, Peng, Chao, Tang, Mingjin, and Asa-Awuku, Akua. "Hybrid Water Adsorption and Solubility Partitioning for Aerosol Hygroscopicity and Droplet Growth." *Atmospheric Chemistry and Physics* 22 (2022): 12769–12787.
5. **Gohil, Kanishk**, and Asa-Awuku, Akua A. "Cloud condensation nuclei (CCN) activity analysis of low-hygroscopicity aerosols using the aerodynamic aerosol classifier (AAC)." *Atmospheric Measurement Techniques* 15.4 (2022): 1007-1019.
6. Malek, Kotiba A., **Gohil, Kanishk**, Al-Abadleh, Hind A., and Asa-Awuku, Akua A. "Hygroscopicity of polycatechol and polyguaiacol secondary organic aerosol in sub- and supersaturated water vapor environments." *Environmental Science: Atmospheres* 2.1 (2022): 24-33.
7. **Gohil, Kanishk**, and Jin, Menglin S. "Validation and Improvement of the WRF Building Environment Parametrization (BEP) Urban Scheme." *Climate* 7.9 (2019): 109.
8. Kutty, Govindan, and **Gohil, Kanishk**. "The role of mid-level vortex in the intensification and weakening of tropical cyclones." *Journal of Earth System Science* 126.7 (2017): 1-12.

Forthcoming Publications

1. **Gohil, Kanishk**, Ferdousi, Nahin, and Asa-Awuku, Akua, "A Solution to New Mobility Particle Sizing Instrumentation and CCN Measurement using Scanning Mobility CCN Analysis (SMCA)" (In preparation)
2. Rastogi, Dewansh, **Gohil, Kanishk**, Peng, Chao, Tang, Mingjin, and Asa-Awuku, Akua A. "Hygroscopicity and Shape Factor Measurements of Uric Acid Aerosol Towards the Treatment of Medical Conditions" (In preparation)

3. Malek, Kotiba A., **Gohil, Kanishk**, Raymond, Timothy M., Dutcher, Dabrina D., Freedman, Miriam Arak, and Asa-Awuku, Akua A. "The Effect of Phase Separation on Cloud Condensation Nuclei (CCN) Activity of Ternary Mixtures containing Surface-active Species." (*In preparation*)

Conference Proceedings (Presentations[#], Posters[&], PRESENTER)

1. CHUN-NING MAO, **Kanishk Gohil**, and Akua Asa-Awuku, *Differences in Droplet Growth Model of Functionalized Insoluble Aerosol Surfaces*, ICACGP-IGAC Joint International Atmospheric Chemistry Conference, Manchester, UK, 2022 ([&])
2. **KANISHK GOHIL**, Chun-Ning Mao, Dewansh Rastogi, Chao Peng, Mingjin Tang, Akua Asa-Awuku, *Hybrid Water Activity - a Novel Framework for CCN Analysis of Sparingly Water-Soluble Organic Aerosols*, American Association of Aerosol Research (AAAR), Annual Conference, Rayleigh, NC, 2022 ([#])
3. **KANISHK GOHIL**, Reese Barrett, Dewansh Rastogi, Chun-Ning Mao, Akua Asa-Awuku, *Cloud Condensation Nuclei (CCN) Activity of Black Carbon Mixed with Low Aqueous Solubility Organics*, American Association of Aerosol Research (AAAR), Annual Conference, Rayleigh, NC, 2022 ([#])
4. **Kanishk Gohil**, NAHIN FERDOUSI, Akua Asa-Awuku, *A solution to new mobility particle sizing instrumentation and CCN measurement using Scanning Mobility CCN Analysis (SMCA))*, American Association of Aerosol Research (AAAR), Annual Conference, Rayleigh, NC, 2022 ([&])
5. KOTIBA A. MALEK, **Kanishk Gohil**, Hind Al-Abadleh, Akua Asa-Awuku, *Hygroscopicity of Polycatechol and Polyguaiacol Secondary Organic Aerosol in Sub- and Supersaturated Water Vapor Environments*, American Association of Aerosol Research (AAAR), Annual Conference, Rayleigh, NC, 2022 ([#])
6. DEWANSH RASTOGI, **Kanishk Gohil**, Kotiba A. Malek, Chao Peng, Mingjin Tang, Akua Asa-Awuku, *Phase, Morphology, and Water Uptake Measurements of Mixed Salt Nano-Nuclei Found in Kidney Stones*, American Association of Aerosol Research (AAAR), Annual Conference, Rayleigh, NC, 2022 ([#])
7. CHUN-NING MAO, **Kanishk Gohil**, Akua Asa-Awuku, *The Hygroscopicity of Functionalized Insoluble Aerosol Surfaces*, American Association of Aerosol Research (AAAR), Annual Conference, Rayleigh, NC, 2022 ([#])
8. **KANISHK GOHIL**, Chun-Ning Mao, Dewansh Rastogi, Chao Peng, Mingjin Tang, Akua Asa-Awuku, *Hybrid Water Activity – A Novel Framework for CCN Analysis of Sparingly Water-Soluble Organic Aerosols*, American Institute of Chemical Engineers (AIChE), Annual Meeting, Phoenix, AZ, 2022 ([#])

9. **KANISHK GOHIL**, Chun-Ning Mao, Dewansh Rastogi, Chao Peng, Mingjin Tang, Akua Asa-Awuku, *The Effect of Water Adsorption on Cloud Condensation Nuclei Activity and Hygroscopic Properties of Aromatic Acid Aerosols*, The American Chemical Society (ACS) Spring Meeting, San Diego, CA, 2022 ^(#)
10. **KANISHK GOHIL**, Akua Asa-Awuku, *The application of an Aerodynamic Aerosol Classifier (AAC) instrument for Cloud Condensation Nuclei (CCN) analysis of atmospheric aerosols*, The International Chemical Congress of Pacific Basin Societies (Pacifichem), Honolulu, HI, 2021 ^(&)
11. **KANISHK GOHIL**, Akua Asa-Awuku, *Cloud Condensation Nuclei (CCN) Activity Analysis of Low-Hygroscopicity Aerosols Using the Aerodynamic Aerosol Classifier (AAC)*, American Institute of Chemical Engineers (AIChE) Annual Meeting, Boston, MA, 2021 ^(#)
12. **KANISHK GOHIL**, Akua Asa-Awuku, *Cloud Condensation Nuclei (CCN) Activity Analysis of Low-Hygroscopicity Aerosols Using the Aerodynamic Aerosol Classifier (AAC)*, American Association of Aerosol Research (AAAR) Annual Conference, virtual, 2021 ^(#)
13. **KANISHK GOHIL**, Menglin Jin, *Validation and Improvement of WRF Building Environment Parametrization (BEP) Urban Physics Scheme*, The 4th Annual Clean Energy and Sustainability Extravaganza, University of Maryland, College Park, MD, 2018 ^(&)

Appendix C: Sources of Funding

I, Kanishk Gohil, would like to acknowledge the following awards below that have funded the research presented in this thesis:

1. National Science Foundation Grant, AGS-1723920
2. National Science Foundation Graduate Student Fellowships (CHEM-1708337 and CHEM-2003927)

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