Atmospheric Nucleation Potential Model for

Chemically Diverse Systems

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Dedication:

To chill lofi study beats on Spotify,

you were always there for me through thick and thin.

Acknowledgments

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Abstract

Atmospheric aerosol particles play an important role in Earth's weather and climate. Aerosol particles influence Earth's weather patterns and radiation balance by acting as "seed particles" or cloud condensation nuclei (CCN) for cloud droplet formation. A significant fraction of CCN originate from gas phase compounds reacting to form aerosol particles in the atmosphere, in a process known as nucleation. These particles are stable at approximately 1 nm in diameter as at this size, the particle has a higher probability of continuing to grow and coagulate with other particles, than it does to evaporate back to the gas-phase. Sulfuric acid is major contributor to the nucleation process in the lower troposphere and has been shown to readily react with ammonia, amines, oxidized organics, and numerous other compounds to form stable particles. While having accurate nucleation rates at a high spatial and temporal scale would greatly reduce uncertainty in global climate models, there is currently only sparse measurements of atmospheric nucleation rates. This is partially due to instrumentation limitations, as well as the use of only very simplified nucleation reactions in global climate models. For this thesis, I have developed a new nucleation model that can accurately predict particle nucleation rates by estimating the concentration of precursor gases. This model could be used in conjunction with a new measurement technique that is much more portable and complements measurements taken from mass spectrometers. Additionally, this thesis explores the formation of molecular clusters with increasingly complex mixtures of atmospherically relevant compounds, including methanesulfonic acid.

Nucleation experiments were conducted using a glass flow reactor that was continuously purged with nitrogen, water vapor, and sulfuric acid vapor. The conditions of the reactor are kept clean with continuous flow of nitrogen, water vapor and sulfuric acid vapor. These flow reactors have been used previously to measure and characterize the first steps of nucleation using chemical ionization mass spectrometers, and condensation particle counters. This work includes the use of a custom-built chemical ionization inlet with an atmospheric pressure interface time-of-flight mass spectrometer, known as the Pittsburgh Cluster CIMS (PCC) to measure gas-phase as well as small molecular clusters. Additionally, another custom-built chemical ionization mass spectrometer, known as the Minnesota Cluster CIMS (MCC) was also used for measurements of gas phase and molecular clusters. Both the MCC and the PCC use soft ionization techniques with nitrate, acetate, or hydronium to charge molecular clusters as well as gas-phase compounds. This chemical ionization technique is used to minimize the cluster fragmentation during the ionization process. In addition to the mass spectrometers, a versatile water CPC (vwCPC) was used to measure particles that are greater than 1nm in size. These measurements give a greater insight as to what is happening at size ranges that are too large for the mass spectrometer to measure. Combined, the Cluster CIMS, the vwCPC, and the sulfuric acid flow reactor allowed for the in-depth study of sulfuric acid nucleation in a pristine environment.

Modeling sulfuric acid nucleation was another important aspect of this thesis. The nucleation potential model (NPM) was built as a part of this thesis with the goal of capturing the process of sulfuric acid nucleation. NPM is a simplified acid-base model, that assumes sulfuric acid react with amines in a 1:1 ratio within the molecular cluster. NPM has the benefits of still modeling sulfuric acid nucleation reactions close to what computational chemistry models predict, but without the computational intensity that is required for these models. Results for the NPM showed that the model can capture sulfuric acid nucleation and can estimate the concentration of stabilizing molecules in each sample. In addition, NPM could also capture the enhancement effects of mixtures of stabilizing molecules, which has previously been too computationally intensive to model.

Sulfuric acid-amine nucleation has been studied intensively over the past few decades. It has been shown that sulfuric acid readily reacts with many atmospherically relevant amines, amides, oxidized organics, ions, and water. However, nucleation events have only been measured in scattered locations across the world as they can be difficult to measure due to the instrumentation required. Because of the difficulty in measuring sulfuric acid nucleation rates, there are very few measurements and limited understanding of nucleation events in the open ocean. Dimethyl sulfide is a highly prevalent molecule in the marine atmosphere and is largely emitted from phytoplankton. Dimethyl sulfide oxides to form sulfuric acid as well as methanesulfonic acid. Methanesulfonic acid has recently been shown to also have the potential to react with amines to form particles. However, it is unclear how methanesulfonic acid impacts sulfuric acid-amine nucleation. This thesis explored the sulfuric acid-methanesulfonic acid-amine nucleation pathways by looking at the first steps of particle formation with a cluster CIMS. In addition, particle concentrations were measured using a vwCPC to determine MSA's effect on nucleation rates for SA-amine nucleation. Results showed that MSA is involved with the first steps of nucleation, and likely is impacting particle nucleation rates in a marine atmosphere. In addition, MSA is enhancing particle formation for some amines with sulfuric acid, while suppressing particle formation for others. The addition of MSA to global climate models is likely necessary in a marine atmosphere to accurately capture particle formation rates in those regions.

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Abbreviations

CCN	Cloud Condensation Nuclei	
VOC	Volatile Organic Compound	
CIMS	Chemical Ionization Mass Spectrometer	
tci	Chemical Ionization Time	
SA	Sulfuric Acid	
vwCPC	versatile water condensation particle counter	
SMPS	Scanning Mobility Particle Sizer	
MSA	Methanesulfonic Acid	
DMS	Dimethyl Sulfide	
NPM	Nucleation Potential Model	
MCC	Minnesota Cluster CIMS	
[Beff]	Effective Base Concentration	
[B]	Base Concentration	
N1	Monomer	
N2	Dimer	
N3	Trimer	
N4	Tetramer	
[A ₁] ₀	Initial Sulfuric Acid Concentration	

RH	Relative Humidity
Т	Temperature
PCC	Pittsburgh Cluster CIMS
NH3	Ammonia
MA	Methylamine
DMA	Dimethylamine
TMA	Trimethylamine
J _{1nm}	Nucleation Rate
Afuchs	Fuch's Surface Area
CS	Condensation Sink
SO ₂	Sulfur Dioxide
OxA	Oxalic Acid
MaA	Malonic Acid
FA	Formic Acid

Chapter 1: Introduction

1.1 Aerosol particles in the atmosphere

Atmospheric aerosol particles have a significant impact on Earth's weather and climate. Aerosol particles ranging from nanometer size up to microns in size can influence Earth's climate by scattering incoming solar radiation. The scattering effect influences Earth's energy balance and can either heat or cool the planet. Aerosol particles indirectly influence Earth's weather patterns and radiation balance by acting as "seed particles" or cloud condensation nuclei (CCN) for cloud droplet formation. Once the aerosol particle reaches a specific size (~100 nm in diameter), water will condense onto the particle to form a cloud droplet. Understanding the rates at which aerosol particles are emitted into the atmosphere is critical for accurate weather and climate predictions.

Aerosol particles are introduced into the atmosphere through the direct emission of pre-formed particles (primary formation) or by chemical reactions of gas-phase compounds in the atmosphere (secondary formation or nucleation). Some examples of primary formation mechanisms include crashing ocean waves, burning forests, and combusting coal and fossil fuels. Gaseous emissions for secondary formation typically originate from animal husbandry, phytoplankton, and fossil fuel combustion. Recent studies have shown that over half of global CCN originate from nucleation (Gordon et al., 2017). Many nucleated particles form from sulfuric acid nucleation (Kuang et al., 2008; Riipinen et al., 2007; Sihto et al., 2006). However, most global climate models have not been able to accurately predict particle formation rates in the atmosphere due to both lack of measurements of nucleation precursor molecules, as well as the complexity of nucleation reactions. Inaccuracies in estimated particle formation rates lead to considerable uncertainty in the global climate model's predictions of aerosol and clouds' radiative effects on Earth's atmosphere (Gordon et al., 2017; Merikanto et al., 2009).

The high uncertainty in global climate models is partially due to the complexity of the chemical reactions that occur to form aerosol particles. Global models can make predictions anywhere from a few months to several decades into the future. Because of their large spatial and temporal scales, many of these global climate models are computationally intensive; thus, many global climate models only estimate sulfuric acid binary or ternary nucleation with water and ammonia (Semeniuk & Dastoor, 2018). However, experimental observations have shown sulfuric acid nucleates with a much more diverse set of compounds. Many of these compounds, like dimethylamine, react to form particles at much faster rates than ammonia (Glasoe et al., 2015; Jen et al., 2014; Kurtén et al., 2008). Additionally, emissions inventories have minimal data sets with insufficient spatial and temporal measurements of nucleating compounds. While some emissions inventories have emission factors for sulfur dioxide, ammonia, and volatile organic compounds (VOC), many do not have sufficient measurements of other essential nucleation precursors, such as amines (Hoesly et al., 2018; Y. H. Lee et al., 2013; Semeniuk & Dastoor, 2018; Spracklen et al., 2008a). These discrepancies between predicted particle nucleation rates from global climate models and measured particle nucleation rates has indicated that there is still significant uncertainty in global climate models.

1.2 Instrumentation for quantifying sulfuric acid nucleation

There are numerous methods to measure and quantify aerosol particles in the atmosphere. For example, Chemical Ionization Mass Spectrometers (CIMS) measure gas-phase compounds and small molecular clusters (Hanson & Eisele, 2002a; Jen et al., 2014; J. Zhao et al., 2010). The basic principle of the CIMS is that gas-phase compounds, such as sulfuric acid, will react with the reagent ion, including nitrate and acetate, which will subsequently charge the sulfuric acid

molecule. The charged sulfuric acid molecule then can be mass filtered in the mass spectrometer. Equation 1 describes an example ionization process of Acetate (A_c) ionizing sulfuric acid (SA).

$$A_c^- + SA \rightarrow SA^- + A_c$$

The ionization of gas molecules typically depends on the relative gas-phase pKa's of the molecule and reagent ion. For this reason, different reagent ions can be used to measure a wider or narrower range of compounds.

While CIMS instruments provide useful information about the composition of small molecular clusters and concentrations of gas-phase compounds, they also have significant uncertainties. First, molecules and clusters travel differently through the inlet of the CIMS based on fluid dynamics and the electric field. The electric field of the inlet is optimized by changing the chemical ionization time (t_{ci}) to allow a diverse set of compounds through the flow reactor. Additionally, the mass transmission efficiency of various-sized compounds can be determined to account for higher losses of compounds through the CIMS based on their size (Heinritzi et al., 2016; Jen, Zhao, et al., 2016; Junninen et al., 2010). Moreover, while these changes can help mitigate uncertainties of measurement with the CIMS, the overall uncertainty of the instrument is still estimated to be approximately a factor of two (Glasoe et al., 2015).

Another class of instruments used to measure freshly formed particles is the versatile water condensation particle counter (vwCPC) (Hering et al., 2005, 2017). A vwCPC takes advantage of water's high diffusivity compared to air's thermal diffusivity to create a supersaturation region that can activate and grow aerosol particles as small as 1 nm in diameter (Hering et al., 2017). These vwCPC are calibrated to determine their d_{50} cut-point, the size of the aerosol particle at which the vwCPC can measure half of the particles. For example, a vwCPC with a d_{50} cut-point of

3 nm can count 50% of the 3 nm particles in that sample. vwCPCs are robust, easy-to-use instruments that can provide real-time measurements of particle concentrations. Since a vwCPC cannot determine the size of the particles it is counting, a mobility analyzer is required to size select particles. Combining these two instruments is referred to as a scanning mobility particle sizer (SMPS) and determines particle size distributions. However, due to the small size of nucleated particles, there are significant losses within the differential mobility analyzer due to diffusion of the particles, as well as inefficient charging. These losses within the SMPS lead to compounding errors when determining the concentration of 1 nm particles using a differential mobility analyzer combined with a wCPC.

1.3 Chemical formation pathways for sulfuric acid nucleated particles

Sulfuric acid has been extensively shown to drive particle nucleation rates in the lower troposphere. Sulfuric acid typically forms in the atmosphere as an oxidation product of either sulfur dioxide or dimethyl sulfide (Sihto et al., 2006). While sulfuric acid concentration has been shown to correlate with atmospheric nucleation rates, compounds such as ammonia and amines are required for nucleation to occur in the lower troposphere (Coffman & Hegg, 1995; Hanson & Eisele, 2002a; Kirkby et al., 2011; Kurtén et al., 2008). Some of these compounds include amines/ammonia (Kirkby et al., 2011), diamines (Jen, Bachman, et al., 2016), oxidized organics (Ehn et al., 2014; Riccobono et al., 2014), and ions (Eisele et al., 2006; Kirkby et al., 2011). While numerous compounds have been shown to react with sulfuric acid to form particles, much is still not understood about the chemical reaction mechanisms for particle formation in the atmosphere.

There has been extensive work to determine the chemical reactions occurring with sulfuric acid and amines to form particles. Recent studies have found that methanesulfonic acid (MSA, CH₄O₃S) also contributes to particle nucleation and growth in the atmosphere (Eisele & Tanner, 1993; Saltzman et al., 1983). MSA is primarily found in coastal and oceanic regions(Saltzman et al., 1983) as it is an oxidation product of dimethyl sulfide (Hatakeyama et al., 1982; Hatakeyama & Akimoto, 1983). Recent computational studies have shown that methanesulfonic acid, another oxidation product of dimethyl sulfide (DMS), also contributes to particle nucleation and atmospheric growth (Elm, 2021, 2022). However, there is still limited information on how methanesulfonic acid influences the chemical reaction pathways of sulfuric acid-amine nucleation. However, these results are typically limited to clusters only containing two acid molecules and are simulated with no water present. While cluster formation energies are essential in understanding the chemical reactions between methanesulfonic acid, sulfuric acid, and amines/ammonia. Additionally, there have only been limited studies on other organic acids, such as formic acid, oxalic acid, and malonic acid, and how they impact sulfuric acid nucleation rates, despite their atmospheric relevance (Kawamura & Kaplan, 1987; Liang et al., 2021; Narukawa et al., 1999; Rozaini, 2012).

1.3 Modeling sulfuric acid nucleation in the atmosphere

Atmospheric nucleation occurs in diverse locations worldwide, including highly remote locations like the Hyytiälä Forest in Finland and highly urban locations like Beijing, China (Cai et al., 2021; Sihto et al., 2006). Through both experimental and computational studies, it has been found that these small molecular clusters are considered stable once they reach approximately 1 nm in size (M. Chen et al., 2012; Jen et al., 2015). After this, the particles grow through different mechanisms, such as condensation of gaseous vapors onto the particle or coagulation with other particles. Figure 1.1 outlines the nucleation process as defined in this thesis.



Figure 1.1: Schematic for aerosol particle nucleation.

Numerous methods have been developed to model sulfuric acid nucleation in the atmosphere. Power-law nucleation models parameterize experimental data to extrapolate nucleation rates in the atmosphere (Glasoe et al., 2015; Kirkby et al., 2011; Yao et al., 2018). These models are fitted using nucleation rates measured in a laboratory with changing parameters. These parameters include temperature, relative humidity, and concentrations of nucleation precursor vapors. These models have been shown to predict nucleation rates in diverse locations such as Beijing and The Amazon Rainforest (Dunne et al., 2016; Yao et al., 2018; B. Zhao et al., 2020). However, power-law models rely heavily on massive experimental data sets that must continue to grow to examine different conditions. Nucleation precursor compounds that need to be accounted for in power law models are constantly being discovered. Additionally, these models depend on two or three nucleation precursor compounds, which is significantly lower than in the atmosphere. Consequently, power-law nucleation rates struggle to accurately predict nucleation rates in areas where unknown compounds react with sulfuric acid to form particles.

Another type of nucleation model uses computational chemistry techniques to rigorously solve for the formation energies of small molecular clusters. Computational models compute Gibb's formation free energies of various molecular clusters that contain sulfuric acid and other stabilizing compounds (Elm, 2019; McGrath et al., 2012; Myllys et al., 2018; Ortega et al., 2012). Minimizing the Gibbs free energy of reactions allows the model to find the most probable pathway for clusters to form. Results from the computational chemistry models can then be used in an Atmospheric Cluster Dynamics Code (ACDC) model, which contains the cluster balance equations, to determine particle nucleation rates. While this model is the most rigorous, it is also exceptionally computationally intensive, especially for complex mixtures of nucleating compounds. Additionally, many computational chemistry models ignore effects due to relative humidity, an important driver of atmospheric nucleation.

Kinetic reaction models describe sulfuric acid nucleation using elementary reaction equations to describe the nucleation process (M. Chen et al., 2012; Jen et al., 2014; Kürten et al., 2018). These kinetic models treat sulfuric acid nucleation as a series of acid-base chemical reactions that form molecular clusters. Laboratory experiments using a CIMS to measure gas phase reactant concentrations and molecular cluster concentrations to estimate cluster evaporation rates. While kinetic models have been able to model sulfuric acid nucleation in a controlled laboratory setting, they require many experiments to determine evaporation rates for each cluster composition and, thus, reactant mixture. Additionally, current instrumentation technology is too complex to determine evaporation rates of nucleation precursors, such as those found in the atmosphere.

Each of these models described above provides beneficial information on how sulfuric acid nucleates to form particles. Power-law nucleation models are simple and have been effectively applied to diverse locations to predict particle nucleation rates. Computational chemistry models rigorously determine cluster composition and give the best insight as to what exact steps the molecules take to react to form particles. Kinetic models use experimental measurements to build a kinetic model framework for particle formation. However, each of the described models is either experimentally or computationally intensive and cannot accurately model sulfuric acid nucleation in diverse environments where hundreds of different compounds could react with sulfuric acid to form particles.

1.4 Research Objectives

The goal of this dissertation is to address two distinct knowledge gaps (1) Develop and test a simplified nucleation model that can estimate the concentrations of nucleation precursors and a mixture's influence on enhancing sulfuric acid nucleation rates and (2) Examine kinetic pathways of sulfuric acid, methanesulfonic acid, and amines to describe sulfuric acid nucleation in a marine environment.

In Chapter 2, the Nucleation Potential Model (NPM) is designed and tested to determine its ability to estimate the concentration of nucleation precursor vapors. NPM uses simplified reaction kinetics to describe sulfuric acid nucleation as a series of acid-base reactions. The NPM is based on the previously described kinetic and computational chemistry models showing that sulfuric acid reacts with many nucleation precursor compounds in a 1:1 ratio. The results from this chapter show that the NPM can estimate nucleation precursor concentrations of individual amines and of mixtures of up to four unique amine compounds using a parameterized value called the Effective Base Concentration ($[B_{eff}]$). A steady-state version of NPM was also constructed to apply the model to atmospheric data worldwide. These results show that NPM can be applied to atmospheric data sets to estimate nucleation precursor concentrations.

Chapter 3 explores the reaction kinetics of sulfuric acid, methanesulfonic acid, and ammonia/amines. The Minnesota Cluster CIMS (MCC) instrument is used to determine concentrations of small molecular clusters. Results from the MCC show MSA is participating in nucleation's first steps through forming the SA dimer, MSA heterodimer, and MSA dimer. However, results show that some base compounds react more readily with MSA than others. Additionally, particle measurements were taken to determine the concentrations of particles formed with various mixtures of compounds injected into the flow reactor. The main results showed that MSA is enhancing particle formation rates of sulfuric acid methylamine nucleation but is suppressing particle formation rates of sulfuric acid trimethylamine nucleation. This work shows that future modeling efforts will need to account for MSA, especially in marine environments, when making predictions for particle formation rates.

Chapter 4 further tests NPM to include significantly more complicated mixtures of gaseous compounds to see their impact on sulfuric acid nucleation. NPM is first used to validate the results from Chapter 3, including MSA as a stabilizing compound to the NPM. NPM shows that it can capture both MSA's suppression and enhancement effects on SA-amine nucleation. A mixture of amine compounds was also tested with mixtures of MSA and organic acids, including formic acid, malonic acid, and oxalic acid. These mixtures showed that while MSA has been previously shown to influence the nucleation rates of SA-amine systems, the predicted [B_{eff}] value can largely be attributed to the concentrations of strong bases like dimethylamine and trimethylamine. These results also show that NPM can correctly quantify [B_{eff}] of room air. Additionally, a correction factor was developed for the model to account for changes in [B_{eff}] based on relative humidity.

Appendices A, B, and C contain the supporting information for chapters 2, 3, and 4.

Chapter 2: A Sulfuric Acid Nucleation Potential Model for the Atmosphere^a

2.1 Abstract

Observations over the last decade have demonstrated that the atmosphere contains potentially hundreds of compounds that can react with sulfuric acid to nucleate stable aerosol particles. Consequently, modeling atmospheric nucleation requires detailed knowledge of nucleation reaction kinetics and spatially and temporally resolved measurements of numerous precursor compounds. This study introduces the Nucleation Potential Model (NPM), a novel nucleation model that dramatically simplifies the diverse reactions between sulfuric acid and any combination of precursor gases. NPM predicts 1-nm nucleation rates from only two measurable gas concentrations, regardless of whether all precursor gases are known. NPM describes sulfuric acid nucleating with a parameterized base compound at an effective base concentration, [B_{eff}]. [B_{eff}] captures the ability of a compound or mixture to form stable clusters with sulfuric acid and is estimated from measured 1-nm particle concentrations. NPM is applied to experimental and field observations of sulfuric acid nucleation to demonstrate how [Beff] varies for different stabilizing compounds, mixtures, and sampling locations. Analysis of previous field observations shows distinct differences in [Beff] between locations that follow the emission sources and stabilizing compound concentrations for that region. Overall, NPM allows researchers to easily model

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nucleation across diverse environments and estimate the concentration of non-sulfuric acid precursors using a condensation particle counter.

2.2 Introduction

Atmospheric aerosol particles play an important role in cloud formation and Earth's radiation balance. Global climate models estimate that around 50% of cloud condensation nuclei (CCN) are produced by nucleation (Gordon et al., 2017; Merikanto et al., 2009; Spracklen et al., 2008a; F. Yu & Luo, 2009), whereby gas-phase compounds react and form a stable particle approximately 1-nm in diameter (M. Chen et al., 2012; Jen et al., 2015). As a result, nucleation influences cloud properties and lifetimes, which subsequently impact Earth's radiation balance (Spracklen et al., 2006, 2008a). Therefore, accurate modeling of nucleation rates in the atmosphere is necessary to predict atmospheric aerosol concentrations used in global weather and climate models.

Aerosol nucleation in the troposphere is primarily driven by sulfuric acid (Kuang et al., 2008; Kulmala et al., 2004; S.-H. Lee et al., 2019a; Sihto et al., 2006; Sipilä et al., 2010; Weber et al., 1996, 1997a) which reacts with a large variety of compounds, to form particles (Almeida et al., 2013; Coffman & Hegg, 1995; Glasoe et al., 2015; Jen et al., 2014; Kirkby et al., 2011; Kürten, Bianchi, et al., 2016; Weber et al., 1998). Laboratory studies have demonstrated that sulfuric acid nucleates with various compounds at rates spanning over seven orders of magnitude (Elm et al., 2016; Glasoe et al., 2015; Jen, Bachman, et al., 2016; Jen et al., 2014; Kürten et al., 2014). The ever-expanding list of compounds includes ammonia (Coffman & Hegg, 1995; Hanson & Eisele, 2002a; Kirkby et al., 2011), amines (Glasoe et al., 2015; Jen et al., 2014; Kurtén et al., 2008), diamines (Elm et al., 2016, 2017; Jen, Bachman, et al., 2016), alcohol amines (Xie et al., 2017), organic acids (Zhang et al., 2004; J. Zhao et al., 2009), oxidized organics (Ehn et al., 2014; Riccobono et al., 2012, 2014; J. Zhao et al., 2013), water (Kulmala et al., 1998; Merikanto et al., 2014; Nerikanto et al., 2014; Nerikanto et al., 2014; J. Zhao et al., 2013), water (Kulmala et al., 1998; Merikanto et al., 2014).

2007), and ions (Eisele et al., 2006; Kirkby et al., 2011). Additionally, sulfuric acid has been shown to nucleate with multiple compounds synergistically, such as dimethylamine/ammonia (Glasoe et al., 2015; H. Yu et al., 2012) and oxidized organics/ammonia (Lehtipalo et al., 2018).

Currently, three classes of nucleation models are used to estimate atmospheric nucleation rates, but no existing model is capable of capturing the true complexity of atmospheric nucleation reactions. First, power-law nucleation models estimate nucleation rates from empirically derived power-law functions fitted from measured nucleation rates with concentrations of sulfuric acid with various precursor gases (Glasoe et al., 2015; Kirkby et al., 2011; Yao et al., 2018). These power-law models have been used to predict nucleation rates in areas such as Asian megacities, the Amazon Rainforest, and globally (Dunne et al., 2016; Yao et al., 2018; B. Zhao et al., 2020). The fitted coefficient and exponentials on the precursor concentration may be indicative of key rate-limiting steps (Sihto et al., 2006) or may have no physical meaning (Kupiainen-Määttä et al., 2014). Furthermore, The power-law models are typically only dependent on two to three nucleation precursor concentrations, and thus cannot accurately predict nucleation rates in areas where numerous and unknown compounds are nucleating with sulfuric acid (B. Zhao et al., 2020). Computational chemistry nucleation models compute formation free energies of clusters containing sulfuric acid and stabilizing compounds in order to numerically solve the cluster balance equations (Elm, 2019; McGrath et al., 2012; Myllys et al., 2018; Olenius et al., 2013; Ortega et al., 2012; F. Yu et al., 2018). While computational chemistry models can rigorously show the formation pathways of sulfuric acid clusters, the method becomes too computationally expensive when determining formation pathways for a mixture of nucleating compounds. Finally, acid-base nucleation models are based on experimentally observed nucleation kinetics that have demonstrated particles form via the sequential addition of acid and base molecules (M. Chen et al.,

2012; Jen et al., 2014; Kürten et al., 2018). These experiments use a chemical ionization mass spectrometer (CIMS) to measure gas and cluster concentrations to estimate cluster evaporation rates. Though acid-base models can experimentally determine the reaction kinetics of sulfuric acid clusters, finding evaporation rates for numerous cluster types is experimentally arduous due to its dependence on nucleation precursor composition and concentration. While each model type provides unique and beneficial information about how sulfuric acid nucleates, they fail to predict particle nucleation rates in complex mixtures, such as the atmosphere, and require high spatial and temporal speciated precursor measurements to accurately predict global nucleation rates.

Currently, most global climate models only account for sulfuric acid binary or ternary nucleation with water or water and ammonia (Semeniuk & Dastoor, 2018). Only a few models incorporate power-law nucleation models (Dunne et al., 2016; Gordon et al., 2017; B. Zhao et al., 2020). However, experimental observations indicate that even low concentrations of other stabilizing compounds can enhance sulfuric acid nucleation rates beyond those predicted from models (Li et al., 2020; Wang et al., 2018). Moreover, many emission inventories used in global climate models only contain emission factors for sulfur dioxide and ammonia (Dunne et al., 2016; Y. H. Lee et al., 2013; Semeniuk & Dastoor, 2018; Spracklen et al., 2008a) with some including volatile organic compounds (Hoesly et al., 2018). Furthermore, only sparse measurements, both in time and space, exist of the numerous precursor compounds in the atmosphere. Combined, these factors contribute to significant model error in predicting aerosol number concentrations in regions with no dominant nucleation pathway (Dunne et al., 2016; Kerminen et al., 2018; Ranjithkumar et al., 2021).

This study presents a generalized, semi-empirical model for sulfuric acid nucleation, known as the Nucleation Potential Model (NPM), that simplifies the numerous and often unknown nucleation reactions into a single reaction pathway. Specifically, NPM reflects how sulfuric acid reacts with an effective base compound and predicts 1-nm nucleation rates from sulfuric acid and a parameterized base concentration ($[B_{eff}]$). $[B_{eff}]$ captures the combined concentrations of compounds and their ability to stabilize sulfuric acid clusters. This parameterized concentration is estimated from measured 1-nm particle concentrations formed from controlled reactions between sulfuric acid and a complex mixture. This study demonstrates the dependencies of $[B_{eff}]$ from a variety of stabilizing gas mixtures and how $[B_{eff}]$ varies across diverse regions of the world.

The full impact of using the Nucleation Potential Model is two-fold: (1) The effective nucleation precursor concentration needed to predict 1-nm nucleation rates can be measured with a portable and cost-effective condensation particle counter (CPC), instead of a mass spectrometer. The increased development and deployment of 1-nm CPCs (Hering et al., 2017; Kuang, 2018; Lehtipalo et al., 2022) will enable researchers to measure [B_{eff}] at high spatial and temporal resolution which is currently challenging to achieve with mass spectrometers. Furthermore, the combined observations from NPM with a CPC and mass spectrometry will also provide a detailed understanding on which compounds nucleate and the rate at which they nucleate. In addition, (2) the NPM is currently the only model that can represent nucleation of arbitrarily complex mixtures of compounds found in the atmosphere.

2.3 Methodology

2.3.1 Model Description

The Nucleation Potential Model (NPM) generalizes the formation of 1-nm particles from sulfuric acid nucleation as a series of second-order reactions. Reaction 1 shows the reaction pathway for the NPM, where *n* represents the number of sulfuric acid (SA) and base (B) molecules in a cluster. N_n denotes the cluster size with N_1 as the monomer (i.e., one sulfuric acid molecule with that same number of base or other attached compounds) up to N_4 as the tetramer. The reaction pathway is based on the most energetically probable pathway for sulfuric acid and base clusters to form, with less probable pathways excluded to reduce model calculation time and complexity (Olenius et al., 2017). The final step in Reaction 1 is the formation of the tetramer, N_4 . At the tetramer size, the particles are approximately 1-nm in diameter or 1.3-nm in mobility diameter (M. Chen et al., 2012; Jen et al., 2015; Larriba et al., 2011). Coagulation losses are estimated from the collision rate constant between clusters. Any cluster formed through N₈ in size is accounted for in the total concentration of particles. Coagulation loss to larger particles (i.e., growth to sizes larger than N₈) is not included in this model when no pre-existing particles are present. Coagulation to pre-existing particles is included as a separate loss term when analyzing ambient observations. Cluster balance equations (i.e., rates laws) for Reaction 1 are provided in the supplementary information (SI, Equation S1).

$$A_{1} + B_{eff} \xrightarrow{k} A_{1} \cdot B_{eff}$$

$$N_{n} = A_{n} \cdot B_{n}$$

$$N_{1} + N_{1} \xrightarrow{k} N_{2}$$

$$N_{1} + N_{2} \xrightarrow{k} N_{3}$$
Reaction 1
$$N_{2} + N_{2} \xrightarrow{k} N_{4}$$

$$N_{1} + N_{3} \xrightarrow{k} N_{4}$$

The forward reaction constant is assumed to be equal for all clusters at $k = 4.2 \text{ x } 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and is the collision rate constant calculated using parameters estimated from density functional theory and bulk properties (Ortega et al., 2012). The effective base concentration ([B_{eff}]) represents the stabilization effects that a compound or mixture of compounds has on the formation rate of sulfuric acid clusters. [B_{eff}] also depends on the nucleation precursors' concentrations, composition, temperature, and humidity. A compound that effectively stabilizes sulfuric acid clusters has a higher value for $[B_{eff}]$ than a weaker stabilizing compound. $[B_{eff}]$ is numerically solved from the cluster balance equations (Equation S1) with inputs of the initial concentration of sulfuric acid monomer ($[A_1]_o$), the final concentration of nucleated 1-nm particles (i.e., $[N_4]$), and nucleation reaction time ($t_{nucl.}$).

2.3.2 Experimental Setup

[B_{eff}] was determined for nucleating systems consisting of sulfuric acid and various combinations of atmospherically relevant bases reacting in an extremely clean and repeatable flow reactor at 300 K and 20% relative humidity (RH). [B_{eff}] is likely influenced by temperature and RH. Lowering temperature would stabilize sulfuric acid clusters, leading to an increase in [B_{eff}] (Dunne et al., 2016; Hanson & Eisele, 2002a; Vehkamäki et al., 2002). The effects of RH are not clear and would depend on the concentration and composition of the other nucleation precursor vapors in the system (Ball et al., 1999; Henschel et al., 2014; Merikanto et al., 2007; Olenius et al., 2017). Future experiments will examine NPM over a wider range of temperature and RH to determine the impact this has on [B_{eff}]. The flow reactor system used for these measurements was constantly purged with a mixture of sulfuric acid, nitrogen, and water (Ball et al., 1999; Fomete et al., 2021; Jen et al., 2014). This creates extremely clean and repeatable conditions in the reactor. Baseline measurements are taken daily to verify the flow reactor's cleanliness and repeatability in concentration, temperature, and RH. The method for these baseline measurements is described in Fomete et al., 2021. [A1]o and base concentrations ([B]) were measured with a custom-built, transverse atmospheric pressure acetate/hydronium chemical ionization inlet coupled to a long time-of-flight mass spectrometer (Pittsburgh Cluster CIMS, PCC) (Fomete et al., 2021). The bases included dilute concentrations of ammonia (NH₃), methylamine (MA, CH₃NH₂), dimethylamine

(DMA, (CH₃)₂NH), and trimethylamine (TMA, C₃H₉N) that are injected into the flow reactor by flowing nitrogen over a custom-made permeation tube (Fomete et al., 2021; Zollner et al., 2012). The t_{nucl} was determined to be 2 s from the modeled centerline velocity of the reactor (Hanson et al., 2017; Panta et al., 2012). The concentrations of N₄ and larger particles were measured with a 1-nm versatile water-based Condensation Particle Counter (vwCPC, TSI 3789) (Hering et al., 2017). The flow tube was optimized to minimize the concentration of particles >1-nm by lowering the sulfuric acid monomer concentration ($[A_1]_o$). This was done to prevent the vwCPC from saturating and minimize particle coagulation with particles larger than N₈. See Figure A.1 for more details on 1-nm particle optimization experiments.

2.4 Results and Discussion

2.4.1 Experimental Model Validation

Figure 2.1 shows [B_{eff}] for the single component injections of NH₃, MA, DMA, and TMA in the sulfuric acid reactor. These atmospherically relevant compounds have previously been shown to nucleate with sulfuric acid at different rates (Glasoe et al., 2015; Jen, Bachman, et al., 2016; Jen et al., 2014; Kurtén et al., 2008). [A₁]_o, was measured daily and ranged between $9x10^7$ cm⁻³ to $3x10^8$ cm⁻³. Daily measurements of [A₁]_o were then used as the initial concentration of sulfuric acid in the NPM. The average value for [A₁]_o ([A₁]_{o,avg}=1x10⁸ cm⁻³) will be used for simplicity. While [A₁]_o is higher than those typically measured in the atmosphere, any range of [A₁]_o can be modeled as this parameter is an input to the NPM. Each base compound was injected at various measured [B], ranging from 0.5 to 32 pptv. The base concentrations examined in this study fall within the range observed in the atmosphere (Cai et al., 2021; Hanson et al., 2011; Kürten, Bergen, et al., 2016). Note, the error bars in Figure 2.1 represent how the standard deviation in particle concentration measurements effects [B_{eff}].
From Figure 2.1, [Beff] for NH₃ remains unchanged at approximately 10-15 pptv across the entire [NH₃] range. This constant [B_{eff}] trend suggests that NH₃ does not significantly stabilize sulfuric acid clusters and enhance nucleation rates under the experimental conditions in the flow tube. This is expected due to the relatively short nucleation time when compared to previous flow reactor studies (Glasoe et al., 2015; Jen, Bachman, et al., 2016). In contrast, [Beff] increases up to ~40 pptv with increasing [MA], demonstrating that this compound enhances sulfuric acid nucleation more than NH₃. The [B_{eff}] curves for DMA and TMA exhibit higher slopes than MA and NH₃, indicating that DMA and TMA substantially enhance sulfuric acid nucleation rates at low [B]. Furthermore, at [B] = 10 pptv, $[B_{eff}]$ for DMA and TMA are two to three times higher than MA and four to six times higher than NH₃. This indicates that DMA and TMA have a much stronger interaction with sulfuric acid clusters than MA and NH₃. Note, the plateau in [B_{eff}] occurs when a significant concentration of >1-nm particles at high [B] increases the coagulation rate beyond what is predicted by the NPM (up to N_8). The relative strength of these compounds in enhancing nucleation is consistent with previously published results indicating that the NPM is correctly capturing the nucleation potency of NH₃, MA, DMA, and TMA (Glasoe et al., 2015; Jen et al., 2014; Kürten et al., 2018).



Figure 2.1: Comparison of effective base concentration from NPM ($[B_{eff}]$) with measured base concentration ([B]) for single component injections of ammonia (blue squares), methylamine (red circles), dimethylamine (black triangles), and trimethylamine (green pentagons). The average sulfuric acid concentration was 1×10^8 cm⁻³, and the reaction time was 2 s.

NPM was also used to determine [B_{eff}] for more complex mixtures of nucleation precursors. Figure shows [B_{eff}] from simultaneous injections of NH₃ at 73 pptv and varying [DMA] into the sulfuric acid flow reactor. NH₃ and DMA mixture injections have higher values for [B_{eff}], up to 120 pptv, which are especially prominent at higher concentrations of DMA. At [B] = 20 pptv, [B_{eff}] for the mixture of NH₃ and DMA is significantly higher than linear addition of the [B_{eff}] from individual DMA and NH₃, ~110 pptv compared to ~80 pptv, respectively. This suggests that DMA and NH₃ react synergistically with sulfuric acid to form particles. The synergist effect is due to ammonia's ability to stabilize sulfuric acid clusters long enough for DMA to collide and react with the sulfuric acid-ammonia clusters (DePalma et al., 2012; Glasoe et al., 2015; Myllys et al., 2019).



Figure 2.2: Comparison of $[B_{eff}]$ and measured dimethylamine (DMA) concentration for multi-component injections. Mixture experiments for DMA (black triangles), DMA with 73 pptv NH₃ (blue diamonds), DMA with 7 pptv MA, 40 pptv NH₃ and 2 pptv TMA (green squares), and DMA with 3 pptv MA and 15 pptv NH₃ (orange

circles). The average sulfuric acid concentration was 1×10^8 cm⁻³ and a reaction time of 2 s.

Figure 2.2 also shows mixtures containing combinations of NH₃, MA, and TMA with varying amounts of DMA. Again, an increase in [DMA] leads to an increase in [B_{eff}], and all mixture curves display an enhancement to nucleation compared to pure sulfuric acid-DMA nucleation. There is no significant distinction in the trends of [B_{eff}] between the 3 and 4 component mixture curves. This could be due to the higher base concentrations in these systems compared to the sulfuric acid concentration which results in particles being formed at the sulfuric acid collision limit. Addition of more bases could also help grow particles, causing higher coagulation losses not captured in the coagulation loss term in NPM. As discussed further in the SI, NPM only accounts for coagulation with particles up to of N₈ in size, indicating that NPM may not be capturing coagulation effects in the system saturated with base. Additionally, [B_{eff}] is ~ 60 pptv at 10 pptv of DMA in the DMA and NH₃ curve in Figure 2.2, while [B_{eff}] is ~100 pptv at 10 pptv of DMA for the 3 and 4 component mixture curves in Figure 2.2. These observations imply that NH₃ and

DMA are reacting synergistically with sulfuric acid, while MA and TMA are individually reacting with sulfuric acid to contribute the additional 40 pptv to $[B_{eff}]$. However, a computational chemistry model is required to draw further conclusions on how these molecules are reacting in a complex mixture. Regardless, observations from Figure 2.2 indicate that NPM determines to what extent a complex mixture of compounds will enhance sulfuric acid nucleation solely using measurements from the vwCPC.

The measured uncertainty in [Beff] observed for the mixture experiments in Figure 2.2 is higher than the single-component results (Figure 2.1). The error bars were estimated from the standard deviation in the concentration of particles for each experiment. Fluctuations in particle concentrations capture the small variation in injected base concentrations, as well as disruption to the flow profiles. Additionally, the mixture experiments were measured over multiple days while many of the single component measurements were taken in 1-2 days. There are likely small dayto-day changes in the mixing within the dilution system which would increase the uncertainty across a longer time frame of measurements. The overall uncertainty in $[B_{eff}]$ is also primarily influenced by the uncertainty in the particle size distribution, and to a lesser extent the particle concentration measurements, measured concentrations of gas-phase compounds, the flow dynamics within the flow reactor, temperature, and humidity. The estimated systematic uncertainty in PCC measurement of [A₁]_o and [B] are approximately a factor a two and would not impact the trends observed in Figures 1 and 2 (Erupe et al., 2010; Simon et al., 2016; J. Zhao et al., 2010). Currently, daily baseline measurements were taken following the procedure in Fomete et al. (2021) to ensure consistent and stable concentrations of both gas-phase and particle-phase compounds within the flow reactor. Furthermore, the measured particle concentrations are not corrected for detection efficiency as it is not known for electrically neutral sulfuric acid-amine 1-nm particles.

The detection efficiency of clusters composed of sulfuric acid and amines/ammonia is normally assumed to be similar, and thus accounting for this will not impact the reported $[B_{eff}]$. In future studies, electrically neutral size distributions will be measured to constrain the coagulation rates in NPM.

2.4.2 Estimation of [Beff] in Various Regions of the World

The NPM was also used to determine how the effective concentration of stabilizing compounds vary around the world. Nucleation rates of 1-nm particles $(J_{1nm}, which equals the$ formation rate of N_4) and sulfuric acid concentrations were obtained from previous field campaigns including in Hyytiälä Forest, Finland (Sihto et al., 2006); Mexico City, Mexico (Iida et al., 2008); Atlanta, Georgia (McMurry & Eisele, 2005); Boulder, Colorado (Eisele et al., 2006); and Beijing, China (Cai et al., 2021). The equations of the NPM (Equation S1) were solved at steady state to determine $[B_{eff}]$ from the observed J_{1nm} , and coagulation rates of each cluster to pre-existing particles were calculated from the Fuch's surface area for Atlanta, Boulder, Mexico City, and Hyytiälä (Kuang et al., 2010). Figure 2.3 shows how [B_{eff}] varies based on measured [A₁]. Each location exhibits clear differences in the range of [B_{eff}] regardless of measured sulfuric acid concentration. For example, Beijing shows the highest [Beff] of any location with an average value of 2 pptv, indicating high concentrations of potent stabilizing compounds (e.g., DMA). The [B_{eff}] for Beijing are consistent with the measured [Beff] of single-component injection of [DMA]~2-5 pptv (Figure 2.1) which is similar to the measured [DMA]=2-3 pptv concentration at Beijing (Cai et al., 2021). In addition, the [Beff] observed in Beijing contrasts with the other locations. Specifically, Hyytiälä Forest, where [Beff]~0.02 pptv, is lower than even sulfuric acid-ammonia shown in Figure 2.1. Mexico City and Atlanta are moderately polluted cities and exhibit [Beff] of 0.8 and 0.1 pptv respectively. These values are less than Beijing but higher than Boulder and Hyytiälä Forest,

suggesting that Mexico City and Atlanta contain moderate amounts and types of nucleating precursors.

The values of $[B_{eff}]$ for all the sites except Beijing are lower than observed in the laboratory (Figure 2.1 and Figure 2.2). This could be due to uncertainties in calculating J_{1nm} from >3 nm particle size distributions in Hyytiälä, Mexico City, Atlanta, and Boulder whereas J_{1nm} was measured directly during the Beijing campaign. Beijing also exhibited the highest nucleation rates and condensation sink rates, while also having the lowest concentration of sulfuric acid. This means [B_{eff}] would need to increase to account for the higher nucleation rates with all other variables held constant. In addition, the lowest amine concentration examined in laboratory experiments for Figure 2.1 and Figure 2.2 was 1-2 pptv which may be higher than what occurred during the campaigns in Hyytiälä, Mexico City, Atlanta, and Boulder. Another reason the field [B_{eff}] are lower than observed in the laboratory is that other compounds exist in the atmosphere that help supress sulfuric acid nucleation. Further laboratory experiments are needed to better understand which and how specific compounds interfere with sulfuric acid nucleation.

Differences in temperature and relative humidity also play a role in $[B_{eff}]$. However, these differences may not be significant. A lower temperature should increase $[B_{eff}]$ but Hyytiälä Forest (~0 °C) is lower than observed for Boulder (~22 °C). Boulder air quality is more impacted by agriculture (Flocke et al., 2020) and should contain more basic compounds which likely explains the higher $[B_{eff}]$ compared to Hyytiälä Forest (Sipilä et al., 2015). This implies that the precursor compound concentration/composition plays a more significant role in $[B_{eff}]$ than temperature. However, more experiments are needed to determine how $[B_{eff}]$ is impacted by temperature and RH as this information is critical to predicting how $[B_{eff}]$ varies around the world. Overall, these observations demonstrate that $[B_{eff}]$ reflects the composition and concentration of stabilizing compounds detected in the atmosphere and can be used to model sulfuric acid nucleation rates in diverse areas.



Figure 2.3: Comparison of the effective base concentration ($[B_{eff}]$) at various measured sulfuric acid concentrations ($[A_1]$) across five locations: green diamonds Beijing, China; red triangles Mexico City, Mexico; black squares Atlanta, Georgia; blue circles Boulder, Colorado; and pink stars Hyytiälä Forest, Finland.

Figure 2.4 compares $[B_{eff}]$ to the weighted amine concentration ([DMA] + 0.2[TMA]) measured in Beijing (Cai et al., 2021). In Figure 2.4, $[B_{eff}]$ and the weighted amine concentration are positively correlated with a slope of 0.76 indicating that $[B_{eff}]$ is sensitive to the amine concentration over a wide range of sulfuric acid concentrations. Furthermore, the data were divided into October, November, and December (2018) to explore how the seasons may affect precursor concentrations and nucleation rates. For October, more variation in $[B_{eff}]$ is observed when compared to the weighted amine concentration. This variation could be due to weather and temperature changes that enhance or reduce sulfuric acid nucleation rates. Additionally, other compounds likely exist in Beijing that nucleate with sulfuric acid which were not reported. November and December are significantly colder in Beijing, which would correlate with higher fuel (e.g., coal) burning and greater emissions of sulfuric acid and amines.



Figure 2.4: Comparison of effective base concentration from NPM ($[B_{eff}]$) with the weighted amine concentration measured in Beijing, China in 2018. October measurements are green squares, November orange triangles, and December blue circles.

2.5 Conclusion

The Nucleation Potential Model (NPM) is presented that simplifies predicting sulfuric acid nucleation rates in the complex atmosphere with two precursor concentrations: sulfuric acid and an effective base concentration ([B_{eff}]). The effective base concentration captures the amounts and types of stabilizing compounds that enhance sulfuric acid nucleation rates. NPM was applied to systems containing up to four atmospherically relevant bases reacting with sulfuric acid in a flow reactor. [B_{eff}] was determined from measured 1-nm particle concentrations, and its value depends heavily on the presence of strong stabilizing compounds, such as DMA and TMA, and their concentrations. [B_{eff}] values also reflect synergistic effects between multiple compounds like DMA and ammonia. Finally, NPM was also used to calculate [B_{eff}] in various locations worldwide. Results show how the potency of the complex mixtures varies between polluted and unpolluted environments, and these observations did not require every potential stabilizing compound

nucleating with sulfuric acid to be measured. $[B_{eff}]$ can be determined from measured 1-nm particle concentrations produced from controlled reactions between a specified sulfuric acid concentration and a complex mixture. NPM complements current speciated measurements, such as those from a CIMS, by providing additional insights into the potency of combined atmospheric compounds at enhancing sulfuric acid nucleation. Future field measurements will involve reacting atmospheric gases with a specific sulfuric acid concentration for a known amount of time to produce 1-nm particles to estimate $[B_{eff}]$. This will minimize possible interference with other particle formation mechanisms such as ion-induced or biogenic nucleation. NPM and further measurement of $[B_{eff}]$ in diverse locations and seasons will help improve aerosol number concentrations predictions, reduce error in global climate models, and expand understanding of the anthropogenic contribution to Earth's radiative balance. **Appendix A: Supplementary information for Chapter 2**

1. Cluster Balance Equations for Nucleation Potential Model

Full cluster balances are given in Equation S1 for the Nucleation Potential Model (NPM). Cluster balances contain formation and loss terms for the various cluster types. Clusters are formed by collisions and lost via coagulation with larger clusters and diffusion to the walls of the flow reactor. Forward rate constants are assumed to be equal with the $k = 4.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ based on an ideal solution where partial volumes of each component are independent from the liquid composition (Ortega et al., 2012). The forward rate constant is assumed equal across all clusters due to the minimal changes in the rate constant from the smallest cluster to the largest cluster. Cluster size, mass, and dipole moment all impact k, sometimes in opposing ways, and these parameters have not been measured for the vast majority of freshly formed clusters. Furthermore, any inaccuracies in the reaction constant will likely be captured by [Beff]. In other words, if the reaction constant is higher than the used value, this will likely lead to an increase in [B_{eff}]. The wall loss rate constant, k_d, is calculated from the diffusion constant of each cluster and a diameter of the reactor (5 cm). k_d ranges from 0.05 s⁻¹ to 0.045 s⁻¹ for monomer to tetramer, respectively (Froyd & Lovejoy, 2003). The final concentration of particles is the combined concentration of tetramers ($[N_4]$) and larger particles ($[N_{>4}]$).

For the steady-state case of the model, which was applied to atmospheric data, cluster balances through [N₄] are set equal to zero and the equation for N_{>4} is removed (M. Chen et al., 2012; Kerminen et al., 2018; Kuang et al., 2008). This is because nucleation reactions in the field are calculated at the peak sulfuric acid concentration, which occurs when the J_{1nm} has plateaued at large reaction times (i.e. steady state) (M. Chen et al., 2012; Kerminen et al., 2018). J_{1nm} is calculated from the formation rate of [N₄]. Additionally, wall loss rates are removed from the model, while coagulation loss rates to pre-existing particles are added. The coagulation loss rate

was calculated from the Fuch's surface area (A_{fuchs}) of measured particle size distributions (Kuang et al., 2010) during the various field campaigns. The condensation sink (CS) is calculated from $CS = \frac{1}{4} \bar{c} \cdot A_{fuchs}$ where \bar{c} is the mean thermal speed. A_{fuchs} is estimated for each J_{1nm} value from the campaign by binning of A_{fuchs} measurements based on the peak sulfuric acid concentrations for each field-campaign (Cai et al., 2021; Eisele et al., 2006; Iida et al., 2008; McMurry & Eisele, 2005; Sihto et al., 2006).

$$\begin{aligned} \frac{d[A_1]}{dt} &= -k[A_1][B_{eff}] - k_d[A_1] \\ \frac{d[B_{eff}]}{dt} &= -k[A_1][B_{eff}] - k_d[B_{eff}] \\ \frac{d[A_1 \cdot B_{eff}]}{dt} &= k[A_1][B_{eff}] - k[N_1](2[N_1] + [N_2] + [N_3] + [N_4]) - k_d[N_1] \\ [N_1] &= [A_1 \cdot B_{eff}] \\ \frac{d[N_2]}{dt} &= k[N_1]^2 - k[N_2]([N_1] + 2[N_2] + [N_3] + [N_4]) - k_d[N_2] \\ \frac{d[N_3]}{dt} &= k[N_1][N_2] - k[N_3]([N_1] + [N_2] + 2[N_3] + [N_4]) - k_d[N_3] \\ \frac{d[N_4]}{dt} &= k_1[N_2]^2 + k_1[N_1][N_3] - k_1[N_4]([N_1] + [N_2] + [N_3] + 2[N_4]) - k_d[N_4] \\ \frac{d[N_{24}]}{dt} &= k_1[N_1][N_4] + k_1[N_2][N_3] + k_1[N_2][N_4] + k_1[N_3]^2 + k_1[N_3][N_4] + k_1[N_4]^2 - k_d[N_4] \end{aligned}$$

Equation S1

2. Methodology to Evaluate the Nucleation Potential Model

As seen in Figure A.1, the left-hand bars at a high concentration of sulfuric acid ($[A_1]_0 = 5x10^9 \text{ cm}^{-3}$) show a high concentration of particles of $2x10^5 \text{ cm}^{-3}$ at the 1-nm 50% cut-point (d_{50}), ($T_{\text{conditioner}} = 1 \text{ °C}$, $T_{\text{initiator}} = 99 \text{ °C}$), with almost half of these particles also present when the cutpoint was changed to 2 nm ($T_{\text{conditioner}} = 2 \text{ °C}$, $T_{\text{initiator}} = 90 \text{ °C}$). This indicates that there is a significant concentration of particles larger than 2 nm at high $[A_1]_0$ which would lead to inaccuracies in coagulation rates up to N₈ within NPM. The right-hand set of bars at lower $[A_1]_0$ shows a significantly lower particle concentration of 8×10^3 cm⁻³ at d₅₀=1 nm and 30 cm⁻³ at d₅₀=2 nm. Low concentrations of 2-nm particles suggests that most formed particles are less than 2 nm in diameter. This inferred size distribution is compatible with the nucleation model, which explicitly accounts for the formation and loss rates for particles up to N₈ (larger than 1 nm). This method of varying d₅₀ cut-point to determine the size of the particles was used instead of a Scanning Mobility Particle Sizers (SMPS) due to the large uncertainty associated with charging particles in the 1-nm size range (Jen et al., 2015; Jiang et al., 2011). Future work will explore sizeresolved measurements in greater detail to further increase the accuracy of NPM in estimating coagulation loss rates.



Figure A.1: Comparison of particle concentrations at 1-nm and 2-nm d_{50} cut-points for the vwCPC at $[A_1]_0 = 5x10^9$ (cm⁻³) and at $[A_1]_0 = 4x10^8$ (cm⁻³).

Chapter 3: Role of Methanesulfonic Acid in Sulfuric Acid-Amine and Ammonia New Particle Formation^b

3.1 Abstract

Aerosol nucleation accounts for over half of all seed particles for cloud droplet formation. In the atmosphere, sulfuric acid (SA) nucleates with ammonia, amines, oxidized organics, and many more compounds to form particles. Studies have also shown that methanesulfonic acid (MSA) nucleates independently with amines and ammonia. MSA and SA are produced simultaneously via dimethyl sulfide oxidation in the marine atmosphere. However, limited knowledge exists on how MSA and SA nucleate together in the presence of various atmospherically relevant base compounds, which is critical to predicting marine nucleation rates accurately. This work provides experimental evidence that SA and MSA react to form particles with amines and that the SA-MSA-base nucleation has different reaction pathways than SA-base nucleation. Specifically, the formation of the SA-MSA heterodimer creates more energetically favorable pathways for SA-MSA-methylamine nucleation and an enhancement of nucleation rates. However, SAtrimethylamine nucleation is suppressed by MSA, likely due to the steric hindrance of the MSA and trimethylamine. These results display the importance of including nucleation reactions between SA, MSA, and various amines to predict particle nucleation rates in the marine atmosphere.

3.2 Introduction

Particle nucleation in the atmosphere may impact cloud formation and the Earth's radiation balance (Spracklen et al., 2006, 2008a). Atmospheric nucleation occurs when gas-phase

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compounds react to form a stable cluster. Sulfuric acid (SA, H₂SO₄), an oxidation product of sulfur dioxide (SO₂) and dimethyl sulfide (DMS, C_2H_6S), has been shown to nucleate in the atmosphere, and its concentration in the atmosphere typically correlates with particle nucleation rates (M. Chen et al., 2012; Kuang et al., 2008; Kulmala et al., 2004; S.-H. Lee et al., 2019a; Sihto et al., 2006; Sipilä et al., 2010; Weber et al., 1996). While sulfuric acid is an important molecule for atmospheric nucleation, sulfuric acid concentration alone cannot explain observed particle nucleation rates (M. Chen et al., 2012; Vehkamäki et al., 2002). Various compounds can react with sulfuric acid to form particles, including ammonia (Coffman & Hegg, 1995; Hanson & Eisele, 2002a; Kirkby et al., 2011) and amines (Glasoe et al., 2015; Jen et al., 2014; Kurtén et al., 2008). These basic compounds are found in the atmosphere and are emitted through biomass burning, animal husbandry, and chemical and industrial plants (Ge et al., 2011). For sulfuric acid-amine systems, extensive work has been conducted to determine the acid-base reaction steps for forming these particles (M. Chen et al., 2012; Jen et al., 2014; Kürten et al., 2018; Myllys et al., 2018; Ortega et al., 2012). In addition, sulfuric acid–base nucleation has been observed in ambient air, and its rates are quantified in the atmosphere worldwide (Cai et al., 2021; Eisele et al., 2006; Iida et al., 2008; McMurry et al., 2005; Sihto et al., 2006). As sulfuric acid nucleation is an integral part of weather and climate; recent studies have incorporated sulfuric acid-ammonia and amine nucleation into global climate models to improve predictions of atmospheric aerosol number concentrations (Dunne et al., 2016; Gordon et al., 2017; B. Zhao et al., 2020).

In addition to sulfuric acid, recent studies have found that methanesulfonic acid (MSA, CH₄O₃S) also contributes to particle nucleation and growth in the atmosphere (Eisele & Tanner, 1993; Saltzman et al., 1983). MSA is primarily found in coastal and oceanic regions(Saltzman et al., 1983) as it is an oxidation product of DMS, a marine emission (Hatakeyama et al., 1982;

Hatakeyama & Akimoto, 1983). Amines and ammonia are also emitted in a marine environment, mainly from phytoplankton (Cree et al., 2018; M. Johnson et al., 2007; Sauer et al., 2021). Previous field measurements indicate that MSA exists at around 10–100% of SA concentration, (Berresheim et al., 2002a; Eisele & Tanner, 1993) with laboratory measurements showing MSA can nucleate with amines like dimethylamine (DMA, (CH₃)₂NH) (Dawson et al., 2012). Despite MSA's importance in atmospheric nucleation and its prevalence in the marine environment, no global climate models currently account for MSA nucleation.

While SA, MSA, amines, and ammonia coexist in a marine atmosphere, limited information exists on how these compounds nucleate together to form particles. Chen et al. (H. Chen et al., 2016) have demonstrated that MSA-amine reactions can form particles at parts per billion level concentrations of reactants, higher than measured in the atmosphere (H. Chen et al., 2016). In addition, Elm's computational chemistry results previously showed that the inclusion of MSA to the SA-base system creates a strong interaction between MSA, SA, and ammonia/amines that could potentially enhance the nucleation rates compared to the SA-base systems (Elm, 2021, 2022). However, this study was limited to clusters containing up to two acid molecules, any number of base molecules, and no water. While these cluster binding energies suggest that MSA could influence sulfuric acid nucleation rates, experimental observations are required to uncover the dominant stepwise reactions between MSA, SA, and amines/ammonia.

The experimental study presented here examines the nucleation reactions in the SA-MSAamine/ammonia systems. Mass spectrometer measurements of freshly nucleated clusters show that MSA is involved in the first steps of nucleation. Particle concentration measurements also show that MSA could enhance or suppress sulfuric acid–base particle formation rates depending on the base compound. Results demonstrate that the role of MSA in MSA-SA-base in new particle formation, i.e., nucleation and growth, is dependent on the ratio of SA and MSA concentrations and the interaction of MSA with the various basic compounds. Including MSA when modeling atmospheric new particle formation, especially in marine environments, is needed to accurately predict particle concentrations in the atmosphere.

3.3 Methods

Nucleation experiments were conducted using a clean and repeatable glass flow reactor as described in (Fomete et al., 2021) with pertinent details repeated here. The flow rate and temperature of the reactor are held constant at 4 LPM and 298–300 K (based on small fluctuations in room temperature), respectively, while relative humidity (RH) is 20%. There are three main injection flows into the flow reactor: nitrogen entrained with sulfuric acid, dry nitrogen, and humidified nitrogen. Sulfuric acid vapor is generated by passing nitrogen over a liquid sulfuric acid reservoir and injected at the top of the reactor. Sulfuric acid concentration is controlled by specifying the flow rate through the reservoir with concentrations ranging from 10^7 to 10^9 cm⁻³. Humidified nitrogen and dry nitrogen streams are also injected into the top of the reactor to control the RH in the flow reactor and provide a dilution stream for sulfuric acid. The reactor has been continuously purged for ~ 2 years with gaseous sulfuric acid, nitrogen, and water to remove potential contaminant compounds and ensure repeatable reaction conditions (Ball et al., 1999; Fomete et al., 2021; Jen et al., 2014). Baseline measurements of the sulfuric acid dimer (i.e., a cluster containing two sulfuric acid molecules and any water molecules that evaporate upon measurement) and particle concentrations as a function of sulfuric acid concentration are taken daily to ensure consistent measurements across all experiments (Fomete et al., 2021). MSA was injected into the flow reactor at 80-120 sccm, and its concentration was varied from 10⁷ to 10^{10} cm⁻³ by adjusting the flow rate of N₂ over the liquid MSA reservoir. Gaseous ammonia (NH₃,

Wards Science 40 wt % in H₂O), methylamine (MA, CH₃NH₂, Sigma-Aldrich 40 wt % in H₂O), dimethylamine (DMA, (CH3)₂NH, Acros Organics 40 wt % in H₂O), and trimethylamine (TMA, C₃H₉N, Sigma-Aldrich 45 wt % in H₂O) were generated and injected into the flow reactor using custom-built permeation tubes and a double dilution system (Fomete et al., 2021; Freshour et al., 2014). No unexpected or unusually high safety hazards were encountered.

For the nucleation experiments, MSA was injected into the flow reactor, allowing SA and MSA to mix for \sim 8 s. Amines/ammonia were injected into the flow reactor and allowed to nucleate with MSA and SA for \sim 2 s prior to measurement. This nucleation time is based on the centerline velocity from the flow parameters and distance to the measurement point.

Concentrations of MSA, SA, and the base compounds, as well as freshly formed molecular clusters, are measured using an atmospheric pressure chemical ionization quadrupole mass spectrometer known as the Minnesota Cluster CIMS (MCC) (Jen et al., 2014; Jen, Zhao, et al., 2016; Titcombe, 2012; J. Zhao et al., 2010). Acetate and nitrate were used as reagent ions to ionize acidic molecular clusters. Nitrate was used for dimer cluster observations and most particle observations. Acetate ionization was used to measure SA and MSA concentrations during the particle observations for MA and TMA when varying [MSA]. The reaction rate constant was 2×10^{-9} cm³ s⁻¹ for nitrate and 4.6×10^{-9} cm³ s⁻¹ for acetate (Fomete, Johnson, Myllys, Neefjes, et al., 2022a; Viggiano et al., 1982, 1997). Additionally, it is assumed that MSA is ionized by nitrate and acetate at the same rate as SA, as no previous measurements have been conducted on its ionization rate constant. Hydronium ions (and its larger clusters) were used to ionize the basic gases. Ion signals are converted to concentrations using the method described in (Fomete, Johnson, Myllys, Neefjes, et al., 2022a) a chemical ionization time of 0.02 s. Mass-dependent transmission efficiency values for the MCC were used to account for differences in the detection due to ion

mass (Jen, Zhao, et al., 2016). The systematic uncertainty of the MCC has been estimated to be a factor of two (Glasoe et al., 2015). However, this uncertainty would affect all measurements equally and thus would have little impact on the overall trends in the data.

Particle concentrations were measured with a 1 nm versatile water condensation particle counter (vwCPC, TSI 3789) (Hering et al., 2017). The conditioner on the vwCPC was set to 1 °C, and the initiator was set to 99 °C. The nucleation time of 2 s was chosen to ensure that freshly formed particles did not grow beyond ~1 nm in diameter during the short nucleation time. Longer nucleation times would result in higher coagulation losses, which would obscure the reaction formation pathways. In comparison, shorter nucleation times would mean particles are smaller than 1 nm and would not get measured by the vwCPC. Figure B.1 shows the difference in particle counts of the vwCPC at a 1 nm setting vs the 2 nm setting (conditioner set to 2 °C and the initiator set to 90 °C) while injecting 7 pptv of TMA and [MSA] = 4×10^9 cm⁻³ into the sulfuric acid flow reactor. Particle concentrations decreased by over 97% when changing the vwCPC temperatures from the 1 nm to the 2 nm setting. The decrease in particle concentration indicates that almost all of the particles formed are 1–2 nm.

3.4 Results and Discussion

3.4.1 Dimer Cluster Observations

Dimer concentrations measured by the MCC using nitrate ionization include the SA dimer ([SA·SA]), MSA dimer ([MSA·MSA]), and heterodimer ([SA·MSA]). Dimer clusters likely had water and base molecules attached that evaporated upon measurement (Kupiainen-Määttä et al., 2013). Throughout the discussion of monomers and dimers, the convention used is a monomer or dimer refers to the number of acid molecules in the cluster rather than the total number of molecules. An increase in acid dimer concentrations is a useful indicator of particle formation, and

likely, the acid dimers contained a base molecule that evaporated when the cluster was ionized. Figure 3.1 shows measured dimer concentrations in the sulfuric acid flow reactor upon adding MSA, DMA, TMA, MA, and NH₃ at RH = 20%. Each panel illustrates how dimer concentrations change when [SA] is roughly equal to and greater than $[MSA] = 2 \times 10^8 \text{ cm}^{-3}$ and the base concentration is constant. Uncertainty bars for SA and SA-MSA with no base addition represent the standard deviation in the background [SA·SA], [MSA·SA], and [MSA·MSA]. This standard deviation was calculated over the four experimental days for each base compound. [MSA·SA] during the SA background measurements is 11, 18, and 34% of the total dimer concentration with decreasing [SA]. While the fraction of [MSA·SA] does increase at low [SA]/[MSA], the [MSA·SA] = 6×10^5 cm⁻³ is low when compared to the SA-MSA injections. The [MSA·SA] during the SA background measurements is likely due to trace amounts of contamination of MSA ($\sim 8 \times 10^7 \text{ cm}^{-3}$) carried over from previous experiments. The addition of MSA to a pure SA (and water) system does not significantly impact [SA·SA], with the [SA·SA] concentration increasing by approximately 2×10^5 cm⁻³ (1.3%) for high [SA]/[MSA], 6×10^4 cm⁻ ³ (1.1%) for medium [SA]/[MSA], and 1×10^3 cm⁻³ (0.2%) for low [SA]/[MSA]. This negligible increase in [SA·SA] concentrations indicates that there are little to no molecular interactions occurring between acid molecules when no base is present in the reactor. The SA·SA dimer without a base is likely forming via ion-induced clustering (IIC) as the binding free energy of the uncharged cluster is weak at -5.5 kcal/mol (Jen, Zhao, et al., 2016). IIC occurs within the inlet of the MCC and is where ions that have been electrically charged by the reagent ion (e.g., nitrate) continue to react and form clusters with other neutral molecules within the flow reactor (Fomete et al., 2021). Similarly, MSA·SA and MSA·MSA may also form via IIC in the SA and MSA injection conditions. IIC likely influences all of the dimers as SA·SA, MSA·SA, and MSA·MSA

have similar computed binding free energies of -5.5, -5.1, and -5.4 kcal/mol, respectively. Note that all referenced binding free energies are provided by Elm (Elm, 2021, 2022) and summarized in Table B.1. [MSA·MSA] remains low and unchanged for all of the base molecules, implying that either the MSA·MSA base or MSA·base clusters are unstable at 298–300 K. In addition, (Elm, 2021) has shown that the computed MSA·base free energies range from -3.4 to -8.7 kcal/mol. In contrast, SA·base free energies are generally stronger, ranging from -5.6 to -12.6 kcal/mol (Elm, 2021). Interestingly, the [MSA·MSA] and [MSA·SA] are lower than [SA·SA] when [SA]/[MSA] ~ 1 , even though the free energies of the uncharged clusters are similar. Note that when [SA] is approximately equal to [MSA], a cluster has an equal probability of colliding with either a SA or MSA molecule. It may be possible that MSA does not ion-induce a cluster with MSA or SA as effectively as negatively charged SA with SA. However, MSA could still be participating in IIC, which would explain the higher ratios of the MSA·MSA and MSA·SA clusters when [SA]/[MSA] ~ 1 . Regardless, the trends show that MSA appears to have little impact on the formation of the dimers when no base is present.



Figure 3.1 Comparison of the total concentrations of sulfuric acid (SA) and methanesulfonic acid (MSA) dimers with various base compounds. Each panel represents an increasing ratio of [SA]/[MSA], with [MSA] = 2×10^8 . Solid orange represents [SA·SA], green with forward slash lines is [MSA·SA], and purple with back slash lines is [MSA·MSA]. SA bar shows the background concentrations of dimers when no MSA or base is injected into the flow reactor. SA-MSA bar is the system without a base. The remaining bars correspond to the SA+MSA+ base systems. The uncertainty bars represent the variations in concentrations of dimers across each set of experiments.

Figure 3.1 also shows the [SA·SA], [MSA·MSA], and [MSA·SA] when injecting amines and ammonia. Likely, many of the dimers formed in Figure 3.1 contained a base molecule before ionization, as pure acid dimers are unstable at 298–300 K. Dimer concentrations generally increase compared to the SA and SA-MSA measurements when a base compound is present, indicating the base compounds are reacting to form acid dimers. In the case of NH₃ addition, the total dimer concentration increased by 4% at high [SA]/[MSA] but decreased by 13% at low [SA]/[MSA]. The slight decrease in dimer concentration is within the uncertainty at low [SA]/[MSA] where there is greater fluctuation in [SA] due to small changes in flow rate for sulfuric acid. Additionally, due to the relatively weak binding interactions between SA and NH₃, there is likely minimal dimer formation at lower [SA]/[MSA], which is evident by the low [SA·SA] of 1×10^6 cm⁻³. The dimer diversity is especially noticeable when the [SA]/[MSA] ~ 1 in the top panel. MSA·SA and MSA·MSA become a more significant fraction of the total dimer concentration, especially with the addition of either DMA or MA. The increase in MSA-containing dimers indicates that the amine is reacting with MSA and SA to enhance the formation of MSA·SA and MSA·MSA. As previously mentioned, MSA·SA and MSA·MSA quickly evaporate at 298–300 K. Thus, the amine molecule likely attaches to SA and MSA prior to reacting with another SA or MSA to form a stable dimer.

The [SA·SA] displayed in Figure 3.1 is slightly higher ([SA·SA] = 1.9×10^7 cm⁻³ for SA, and $[SA \cdot SA] = 2.3 \times 10^7 \text{ cm}^{-3}$ for SA-MSA-NH₃) between SA and SA-MSA-NH₃ systems, showing that SA-MSA-NH₃ nucleation forms weakly bonded clusters, similar to SA-NH₃ nucleation (Glasoe et al., 2015; Loukonen et al., 2010; Zollner et al., 2012). The [MSA·SA] and [MSA·MSA] also do not vary between the SA-MSA and SA-MSA-ammonia systems, indicating that ammonia does not help form stable MSA clusters. Also, increasing the [SA]/[MSA] ratio does not alter the dimer concentrations compared to the no ammonia addition case. This result signifies ammonia does not preferentially prefer to react with SA or MSA and agrees with computed binding free energies, where SA·SA·NH₃ is -19.4 kcal/mol and MSA·SA·NH₃ is -18.3 kcal/mol (Elm, 2022). The binding free energies for SA·SA·NH₃·NH₃ and MSA·SA·NH₃·NH₃ are -27.0 and -23.6 kcal/mol, respectively (Elm, 2022). The more strongly bonded SA·SA·NH₃·NH₃ cluster indicates that ammonia shows some preference to form SA dimer and could explain the slightly higher [SA·SA] compared to SA and SA-MSA systems.

For MA = 15 pptv in Figure 3.1 at [SA]/[MSA] ~ 1, the [MSA·SA] and [SA·SA] are approximately equal. The similar [MSA·SA] and [SA·SA] in this regime then suggest the stability of the MSA·SA·MA and SA·SA·MA clusters are roughly equal, or the stability of the monomers (SA·MA and MSA·MA) are similar. The binding free energies of SA·SA·MA is –24.4 and –24.2 kcal/mol for MSA·SA·MA (Elm, 2021, 2022). In contrast, the free energies of the monomers are not similar as SA·MA is more strongly bonded at –7.2 kcal/mol when compared to MSA·MA at –3.9 kcal/mol (Elm, 2021, 2022). These free energies suggest that [MSA·SA] and [SA·SA] are equal when [SA] ~ [MSA] because MA first reacts with SA before adding either SA or MSA. In addition, MSA·SA·MA and SA·SA·MA·MA have similar binding free energies of –33.8 and –36.6 kcal/mol respectively, which are both stable. As the [SA]/[MSA] ratio increases, [SA·SA] also increases. This trend is expected since a cluster is more likely to collide with SA in this high SA regime, and MA has previously been shown to help form relatively stable sulfuric acid clusters (Elm, 2017; Glasoe et al., 2015; Jen et al., 2014).

For DMA = 16 pptv in Figure 3.1, the [SA·SA] and [MSA·SA] increase by over 50% compared to the no DMA system. The higher [SA·SA] is not surprising, given DMA's well-established high stability effects on sulfuric acid clusters (Jen et al., 2014). For [SA]/[MSA] ~ 1, the [SA·SA] = 3.0×10^6 cm⁻³ and [MSA·SA] = 4.6×10^6 cm⁻³, which suggests similar stabilities of MSA·SA·DMA and SA·SA·DMA clusters. The similar stabilities of these two clusters are also confirmed by (Elm, 2022) computed binding free energies, where SA·SA·DMA and MSA·SA·DMA are roughly equal at -29.4 and -28.2 kcal/mol, respectively (Elm, 2022). Furthermore, the fraction of [MSA·SA] out of the total dimer concentration decreases with increasing [SA]/[MSA], even though the total dimer concentration is increasing. The [SA·SA] also increases by an order of magnitude with higher [SA]/[MSA]. These combined observations

suggest that the SA·DMA cluster is more stable than MSA·DMA, which is confirmed by previously computed binding free energies of -11.5 and -7.1 kcal/mol (Elm, 2021, 2022). Thus, DMA will preferentially form dimers faster with SA than MSA.

At TMA = 13 pptv in Figure 3.1, the total dimer concentration is similar to the DMA-MSA-SA system at each ratio of [SA]/[MSA]. The [MSA·SA] is lower with TMA than DMA across the studied [SA]/[MSA] regimes. TMA likely reacts with MSA-containing clusters to a lesser extent compared to DMA. This result agrees with binding free energies where MSA·SA·DMA is -28.2 kcal/mol and MSA·SA·TMA is -24.9 kcal/mol. SA·TMA is also more strongly bonded (-12.6 kcal/mol) than MSA·TMA (-8.7 kcal/mol) (Elm, 2022). Additionally, there is a significant decrease in the binding free energy of MSA·SA·TMA·TMA (-31.9 kcal/mol) when compared to SA·SA·TMA·TMA (-41.5 kcal/mol). This decrease in the free energy for MSA·SA·TMA·TMA indicates that at larger cluster sizes, TMA is much more likely to react with SA, which matches the high fraction of [SA·SA] for TMA in Figure 3.1. Therefore, the main pathway for dimer formation for the TMA-MSA-SA system is TMA reacting with SA.

Comparison of the observed dimer concentrations of the TMA-SA-MSA and MA-SA-MSA systems leads to disagreement with computed free energies. Specifically, MSA·SA·TMA has similar binding free energies as MSA·SA·MA (-24.9 and -24.2 kcal/mol, respectively). Furthermore, TMA has stronger binding free energies with MSA than MA (-8.7 and -3.9 kcal/mol, respectively). Despite the overall stronger energies of TMA with MSA and SA, the [MSA·SA] in the TMA system is roughly half of the [MSA·SA] in the MA system when [SA]/[MSA] ~ 1. The unexpectedly lower [MSA·SA] with TMA suggests that steric hindrance is preventing the formation of MSA·TMA or MSA·SA·TMA, which are not captured in the computed binding free energies. In addition, the total dimer concentration of TMA is the highest of all bases at high

[SA]/[MSA], while DMA has the highest total dimer concentration when $[SA]/[MSA] \sim 1$. TMA's more significant reduction in total dimer concentration at $[SA]/[MSA] \sim 1$ could also suggest possible steric hindrance effects between TMA and MSA. This possibility is further explored below in the particle measurements.

Figure 3.2 summarizes the reaction pathways for the SA-MSA-base system. The likely formation pathway for these amines/ammonia starts with the reaction of SA and base. For DMA and MA, the monomer adds either a SA molecule or an MSA molecule at similar rates. From Figure 3.2B, the first step is still the addition of a TMA molecule to SA; however, for TMA, the more energetically favorable next step is the addition of SA instead of MSA. This reaction pathway is consistent with the cluster observations from Figure 3.1 that show a significant increase in the [SA·SA] when TMA is present in the flow reactor. Figure 3.2C shows how ammonia has relatively weak interactions with both acid molecules and likely only slightly prefers reacting with SA.



Figure 3.2 Summary of Reaction Pathways. Each symbol represents a molecule of sulfuric acid (red circle), methanesulfonic acid (yellow circle), and base (blue square). The arrow's width indicates the likelihood of that pathway for the reaction to occur when $[SA] \sim [MSA]$. Panel A shows the formation pathways for DMA and MA. Panel B for shows formation pathways for TMA, and Panel C shows the pathways for NH₃.

The combined observations demonstrate that MA and DMA can form stable clusters with MSA. Ammonia is likely too weak of a stabilizing base to cluster with MSA. TMA showed an appreciable increase in [MSA·SA] compared to no TMA, but [SA·SA] still dominates the total dimer concentration. Thus, TMA likely reacts primarily with SA. This result is possibly due to TMA's greater steric hindrance that does not allow TMA to react as readily with MSA beyond the monomer.

Clusters larger than the dimer were observed in the MSA-SA-base systems. Small amounts of SA timer and tetramer were observed for the amines/ammonia. However, there were likely other trimers that included amines and MSA that were not being measured due to cluster fragmentation inside the MCC or during the atmospheric ionization with nitrate. Future work should explore cluster ionization to better understand how to measure larger molecular clusters.

3.4.2 Particle Observations

Since clusters are larger than the dimer fragment in the MCC, particle measurements were taken with the vwCPC for the SA-MSA-base systems to better understand nucleated particles' formation rates. Figure 3.3 shows the particle concentrations from SA-MSA, SA-base, and SA-MSA-base nucleating systems. For the particle observations, the ratios of [SA]/[MSA] were generally lower than for the dimer cluster measurements (Figure 3.1) to avoid the saturation limit of the vwCPC (1×10^5 cm⁻³). For all [SA]/[MSA], particle concentrations increase or decrease by approximately 20–30% when injecting MSA, with the largest difference being 202–253 cm⁻³ when injecting MSA. These changes in particle concentrations are not significantly different when comparing SA and SA-MSA systems. The insignificant change in particle concentrations when injecting MSA agrees with the dimer observations of Figure 3.1, where SA-MSA does not form an appreciable number of dimers and thus does not form particles. In addition, at high [SA]/[MSA],

the observed particle concentrations between the SA-MSA-base systems are similar. However, particle concentrations exhibit significant differences at a lower ratio of [SA]/[MSA], specifically for MA and TMA. At low [SA]/[MSA], clusters are more likely to collide with MSA instead of SA, and thus this regime focuses on the influences of MSA on new particle formation. For MA, there is an increase in particle concentrations in the SA-MSA system when compared to SA, while for TMA, there is a decrease in particle concentrations with SA-MSA. MA and TMA will be explored further below to determine MSA's overall impact on their reaction pathways.



Figure 3.3 Comparison of total particle counts after 2 s nucleation time with various bases. Solid colors indicate SA-base nucleation, and solid colors with slashed lines indicate SA-MSA-base nucleation, where $MSA = 2.5 \times 10^8 \text{ cm}^{-3}$. Black bars show background particle counts, red is ammonia at 236 pptv, green is DMA at 13 pptv, dark blue is MA at 15 pptv, and light blue is TMA at 14 pptv. Error bars provide the standard deviation in particle concentrations across each set of experiments.

Following experiments where [SA] and [MSA] are changed, [TMA] was also varied to quantify the suppression of new particle formation at high [MSA]. Figure 3.4A shows the particle concentration results from the SA-MSA-TMA system. MSA and TMA concentrations were varied here, and $[SA] = 5 \times 10^7$ cm⁻³. Each curve represents a different ratio of [SA]/[MSA] from 0.55 to 0.04 for TMA. In Figure 3.4A, at high [TMA] = 15 pptv, the particle concentrations drop by approximately 50% when [MSA] concentration increases by an order of magnitude. Furthermore, Figure B. 2 shows that this decrease in particle counts was due to MSA suppressing SA-TMA nucleation and not coagulation. The observed decrease in particle concentration is likely due to the steric hindrance in the SA-MSA-TMA system, where MSA binds up available TMA (as MSA·TMA), preventing further reaction with MSA or SA. This result also agrees with the dimer cluster observations (Figure 3.1) that showed significantly less [MSA·SA] for TMA than other strong stabilizing amines like DMA. While computational results show strong binding free energies for SA-MSA-TMA clusters, steric hindrance that lowers the collision accommodation coefficient (i.e., sticking coefficient) is not captured by these ab initio calculations. MSA suppressing SA-TMA nucleation is a significant result, as there has been limited information in previous literature about compounds capable of suppressing SA nucleation.



Figure 3.4 (A) SA-MSA-TMA nucleation and (B) SA-MSA-MA nucleation, where $[SA] = 5 \times 10^7 \text{ cm}^{-3}$, with a nucleation time of 2 s. Black squares are $[MSA] \sim 1 \times 10^8 \text{ cm}^{-3}$, green triangles are $[MSA] \sim 2 \times 10^8 \text{ cm}^{-3}$, and blue triangles are $[MSA] \sim 1 \times 10^9 \text{ cm}^{-3}$.

Figure 3.4B shows the particle concentration results for the SA-MSA-MA system. MSA and MA concentrations were varied with $[SA] = 5 \times 10^7$ cm⁻³. Each curve represents a different ratio of [SA]/[MSA] from 0.55 to 0.07 for MA. Figure 3.4B shows the opposite phenomena to Figure 3.4A, where increasing [MSA] by an order of magnitude leads to an increase in the particle concentrations up to a factor of three. The increase in particle concentrations signifies that MA can nucleate with MSA and SA. MA likely nucleates with both acids because MA is a significantly smaller molecule than TMA and less likely to be sterically hindered when colliding and reacting with MSA. MSA reacting with MA to form particles is also in agreement with computational chemistry results that showed equal stabilities of the SA·SA·MA cluster and the MSA·SA·MA cluster.

Particle concentrations for the SA-MSA-MA system are still lower than SA-MSA-TMA until [SA]/[MSA] < 0.55. This difference between base systems is due to the first step in monomer cluster formation, which is likely the new particle formation rate-limiting step. Though MA can add to MSA and SA, these clusters (SA·MA and MSA·MA) are still more weakly bonded than those with TMA (specifically SA·TMA). Thus, while MA enhances particle formation rates for the SA-MSA system, TMA remains a potent nucleating compound with SA and still plays an important role in atmospheric marine nucleation.

3.4 Conclusion

Methanesulfonic acid (MSA) impacts the initial steps of cluster formation in the SA-MSAbase system. Specifically, adding MSA to the SA-base system allows more pathways for dimer cluster formation, as indicated by the formation of the MSA dimer and the SA-MSA heterodimer. The fraction of [SA·SA], [MSA·MSA], and [SA·MSA] formed out of the total dimer concentration also indicates which base compounds are reacting more readily with MSA than others. Methylamine and dimethylamine react with SA and MSA to form relatively equal ratios of [MSA·SA] and [SA·SA], indicating that MSA is readily reacting with MA and DMA. However, [MSA·SA] in the case of TMA is significantly lower than the [SA·SA], indicating that TMA is preferentially nucleating with SA. There are only minor increases to dimer concentrations for ammonia, indicating that any interactions between ammonia and MSA are likely negligible compared to SA and ammonia.

Particle measurements showed that while MSA enhances sulfuric acid nucleation in the case of MA, it may suppress nucleation in the case of SA-TMA. Introducing MA into the SA-MSA system saw an increase in particle concentrations at higher concentrations of MSA, whereas TMA saw a decrease in particle concentrations at high MSA concentrations. However, in the atmosphere, MSA concentration typically never surpasses that of SA, so while the laboratory results show suppression in the case of TMA, the ratios of acids may not be atmospherically relevant.

Overall, results indicate that MSA is an important contributor to atmospheric nucleation and can increase particle formation rates for SA-base nucleation. Including MSA in models will be especially important as anthropogenic emissions of SO₂ decrease, thus decreasing the [SA]/[MSA] ratio. These conclusions indicate that nucleation models that account for MSA-SA-base nucleation are required to better predict particle number concentrations in atmosphere, especially in the marine environment.

Appendix B: Supplementary Information for Chapter 3

Section 1: vwCPC cut point experiments

Figure B.1 compares the particle concentrations measured by the vwCPC (TSI3789) (Hering et al., 2017) at a 1-nm and a 2-nm cut points when 7 pptv of trimethylamine (TMA) is injected into the flow reactor ($[SA] = 6x10^7$ cm⁻³ and $[MSA] = 2x10^9$ cm⁻³). These results show that at a 2.4 s nucleation time, over 97% of the particles formed are 1 nm (assuming sharp cut points). Thus, a significant fraction of the particles formed during the nucleation experiments is freshly nucleated particles that have experienced little to no growth or coagulation.



Figure B.1 Comparison of particle concentrations at the 1-nm cut point vs. 2-nm cut point on the vwCPC. The black bar shows particle concentrations at the 1-nm cut point and the red bar at the 2-nm cut point. [TMA]=7 pptv and [SA]= $6x107 \text{ cm}^{-3}$ and [MSA] = $2x109 \text{ cm}^{-3}$

Figure B.2 provides evidence that SA-MSA-TMA particle concentration decrease with increasing [TMA] is not due to larger particles due to coagulation. This figure compares the particle concentrations from the vwCPC at a 1-nm cut point and a 2-nm cut point when 52 pptv of trimethylamine (TMA) is injected into the flow reactor ([SA] = 5×10^7 cm⁻³ and [MSA] = 9×10^8 cm⁻

³). These results show that particle counts drop over 90% in the SA-TMA system at the larger cutpoint. In addition, 98% of the particles observed in the SA-MSA-TMA system are \sim 1 nm. Due to the significant drop in particle concentrations between cut-points, coagulation does not drive the decrease in particle concentrations when injecting MSA.



Figure B. 2 Compares particle concentration at the 1-nm cut point vs. the 2-nm cut point on the vwCPC. The black bar shows particle concentrations at the 1 nm cut point and the red bar at the 2 nm cut point. The first set of bars shows SA+TMA, and the second set is SA-MSA-TMA. [TMA] is 52 pptv, [SA] is $5x10^7$ cm⁻³ and [MSA] is $9x10^8$ cm⁻³.

Section 2: Computational Chemistry Results

Compiled binding free energies of uncharged clusters containing MSA, SA, and DMA from Elm and are given in Table B. 1 (Elm, 2021, 2022).

Clusters	Binding Free Energies (kcal/mol)
SA·SA	-5.5
MSA·SA	-5.1
MSA·MSA	-5.4
SA·MA	-7.2
MSA·MA	-3.9
SA·DMA	-11.5
MSA·DMA	-7.1
SA·TMA	-12.6
MSA·TMA	-8.7
SA·SA·NH ₃	-19.4
MSA·SA·NH ₃	-18.3
SA·SA·NH ₃ ·NH ₃	-27.0
MSA·SA·NH ₃ ·NH ₃	-23.6
SA·SA·MA	-24.4
MSA·SA·MA	-24.2
SA·SA·MA·MA	-36.6
MSA·SA·MA·MA	-33.8
SA·SA·DMA	-29.4
MSA·SA·DMA	-28.2
MSA·SA·TMA	-24.9
SA·SA·TMA·TMA	-41.5
MSA·SA·TMA·TMA	-31.9

 Table B. 1 Binding free energies from Elm of clusters pertinent to this study.(Elm, 2021, 2022).
Chapter 4: Sulfuric Acid Nucleation Potential Model Applied to Complex Reacting Systems in the Atmosphere

4.1 Abstract

Atmospheric aerosol particles can impact Earth's radiation balance and act as the seed for cloud droplet formation. Over half of all the cloud seed particles are formed through nucleation, which is when gas-phase compounds react to form particles. Reactions of sulfuric acid with a wide variety of atmospheric compounds have been previously shown to drive nucleation in the lower troposphere. However, global climate models poorly predict particle nucleation rates since current nucleation models are currently unable to describe particle nucleation rates of complex nucleation reactions. The nucleation potential model (NPM) was recently developed to model sulfuric acid nucleation of complex mixtures of compounds. This work expands on the NPM, which has previously been shown to accurately estimate the concentration of nucleation precursor compounds using particle concentrations measured with a 1 nm condensation particle counter. This work further applies the NPM to show that the model can accurately capture both enhancement and suppression effects of atmospherically relevant compounds such as methanesulfonic acid. NPM is shown to capture sulfuric acid nucleation rates with a complex mixture of organic and inorganic acids, ambient air, and across a range of atmospherically relevant relative humidities. An expression for calculating nucleation rates was also derived from the NPM for aerosol modelers to estimate nucleation rates using the NPM accurately. NPM provides a simple and effective way to estimate how various compounds in a complex mixture enhance sulfuric acid nucleation rates using a condensation particle counter.

4.2 Introduction

Atmospheric aerosol particles impact Earth's climate and act as seed particles for cloud formation (Spracklen et al., 2006, 2008b). One significant source of aerosol particles in the atmosphere is nucleation, which describes the reactions of gaseous compounds to form stable particles (Kulmala et al., 2013). Recent works have shown that new particle formation accounts for over half of all seed particles in the atmosphere (Gordon et al., 2017). Atmospheric nucleation involves chemical reactions of numerous gas-phase compounds in the atmosphere, one of the most prevalent being sulfuric acid (Kuang et al., 2008; S.-H. Lee et al., 2019b; Sipilä et al., 2010; Spracklen et al., 2006; Weber et al., 1997b). Atmospheric sulfuric acid is formed by oxidizing sulfur dioxide and dimethyl sulfide (Hatakeyama et al., 1982; Hatakeyama & Akimoto, 1983; Takahashi et al., 1975). Once in the atmosphere, sulfuric acid chemically reacts with numerous precursor compounds such as ammonia (Hanson & Eisele, 2002b), amines (Glasoe et al., 2015; Jen et al., 2014), oxidized organics (Riccobono et al., 2012), alkanolamines (Fomete, Johnson, Myllys, & Jen, 2022), and ions (Eisele et al., 2006; Kirkby et al., 2011, 2016) to nucleate stable particles (about 1 nm in diameter). In addition, methanesulfonic acid has been shown to nucleate with and without sulfuric acid to participate in sulfuric acid nucleation in terrestrial and marine environments (H. Chen & Finlayson-Pitts, 2017; Elm, 2022; J. S. Johnson & Jen, 2023; Saltzman et al., 1983). There are many other atmospherically relevant organic acids, such as formic acid, oxalic acid, and malonic acid, that may impact sulfuric acid nucleation rates but have not been extensively studied (Kawamura & Kaplan, 1987; Liang et al., 2021; Narukawa et al., 1999; Rozaini, 2012). Recent research has yielded conflicting results regarding the impact of RH on sulfuric acidbase nucleation systems. Some studies suggest that higher RH may increase nucleation rates (Ball et al., 1999), while others suggest that higher RH may decrease nucleation rates depending on the

conditions (Merikanto et al., 2007; Olenius et al., 2017). Recent computational work has also shown that the effect of RH on nucleation rates is dependent on sulfuric acid concentration as well as base concentration and composition (Henschel et al., 2014, 2016; Olenius et al., 2017). While sulfuric acid has been shown to react with various compounds in the atmosphere, current nucleation models cannot accurately predict particle nucleation rates at a high spatial and temporal resolution.

Currently, several model types are used to predict atmospheric nucleation rates. Power law nucleation models use experimental data to find trends in nucleation rates based on the concentration of precursor gases, temperature, and relative humidity (Glasoe et al., 2015; Kirkby et al., 2011; Yao et al., 2018). Power law nucleation models are inexpensive computationally and require large amounts of experimental data with a chemical ionization mass spectrometer (CIMS). Some climate models use power-law nucleation models, but these typically have significant associated uncertainties due to limited measurements of nucleation precursor concentrations (e.g., dimethylamine) (Dunne et al., 2016; Gordon et al., 2017; B. Zhao et al., 2020). Computational chemistry models have also been used to determine the formation pathways of nucleated clusters. Computational chemistry models rigorously solve for the formation energies of molecular clusters, which can then be minimized to find the most likely pathway for particle formation (Elm, 2022; McGrath et al., 2012; Myllys et al., 2018; Olenius et al., 2013; Ortega et al., 2012; F. Yu et al., 2018). However, computational chemistry models describe sulfuric acid nucleation with only 2-3 unique molecules, and they typically ignore RH effects due to computational constraints. Reaction kinetic models rely on a series of elementary acid-base reactions to describe the formation of nucleated particles (Chen et al., 2012; Jen et al., 2014; Kürten et al., 2018). However, determining the cluster evaporation rates is experimentally intensive and becomes exceedingly difficult for

reaction systems with more than 2-3 unique compounds. Thus, the experimental and computational complexity of the current nucleation models makes them challenging to implement in global climate models.

The Nucleation Potential Model (NPM) was recently developed to reduce the computational and experimental intensity required to predict sulfuric acid atmospheric nucleation rates. NPM is a semi-empirical model that simplifies the complex and often unknown nucleation reactions into a single acid-base reaction pathway for forming a 1 nm particle (J. S. Johnson & Jen, 2022). The main output of the model is the effective base concentration ([B_{eff}]) which can describe the concentration and potency of the nucleation precursors in a sample. The main inputs to NPM are the nucleation time estimated based on fluid dynamic calculations, the initial sulfuric acid concentration measured with a chemical ionization mass spectrometer, and the concentration of particles formed from nucleation reactions measured with a condensation particle counter. Johnson & Jen, 2022 showed that NPM describes the potency of amines/ammonia and complex mixtures of amines and ammonia.

This study builds upon the previously published results from the NPM (J. S. Johnson & Jen, 2022) to show that NPM can be further applied to complex nucleation environments, including sulfuric acid, amines, ammonia, methanesulfonic acid, formic acid, oxalic acid, and malonic acid at various relative humidities. These results show that even in chemically diverse nucleation systems, NPM can still accurately predict $[B_{eff}]$ and the dependency of $[B_{eff}]$ on the mixture composition. Additionally, $[B_{eff}]$ was estimated for Pittsburgh, PA, room air samples to show that NPM can be applied to measure $[B_{eff}]$ in the atmosphere. Finally, an analytical expression for nucleation rate (J_{1nm}) was developed to predict atmospheric nucleation based on measured $[B_{eff}]$ and sulfuric acid concentration.

4.3 Materials and Methods

Evaluation of the Nucleation Potential Model (NPM) with a variety of atmosphericallyrelevant gases was conducted using a glass flow reactor continuously purged with sulfuric acid (SA, H₂SO₄), nitrogen, and water vapor (Ball et al., 1999; Fomete et al., 2021; Jen et al., 2014; J. S. Johnson & Jen, 2022). The temperature of the flow reactor was held at room temperature, which experienced small day-to-day fluctuations from 298 to 300 K. Relative humidity (RH) is controlled in the flow reactor between a range of 10 to 60% by adjusting the flow of humidified nitrogen. Baseline measurements of the flow reactor are taken daily to ensure repeatable sulfuric acid concentration ([SA]), particle concentration, temperature, and RH (Fomete et al., 2021). Baseline [SA] = $7.5 \times 10^7 \pm 1.3 \times 10^7 \text{ cm}^{-3}$ when SA flow rate is held constant, and indicates that the flow reactor was repeatable across multiple days of measurements.

The concentrations of particles were measured with a 1 nm versatile water-based condensation particle counter (vwCPC, TSI 3789) (Hering et al., 2017). The nucleation reaction time was optimized to minimize particle concentrations >2nm, as described in Johnson & Jen (2022). Concentrations of gas compounds, such as sulfuric acid and amines, are measured with a custom built, atmospheric pressure Cluster Chemical Ionization Mass Spectrometer (Minnesota Cluster CIMS, MCC) (Jen et al., 2014; Jen, Zhao, et al., 2016; Titcombe, 2012; J. Zhao et al., 2010). Mass-dependent transmission efficiency values for the MCC were gathered from Jen et al. (2014). Acetate reagent ions (CH₃COO⁻, H₂O·CH₃COO⁻, or (H₂O)₂·CH₃COO⁻) were used to measure the concentration of sulfuric acid and other organic acids such as methanesulfonic acid (MSA, CH₄O₃S), oxalic acid (OxA, C₂H₂O₄), malonic acid (MaA, C₃H₄O₄) and formic acid (FA, CH₂O₂). The ionization rate constant of acetate with the various acids was assumed to be that of sulfuric acid-acetate ($k_{acetate} = 3.6x10^{-9} \text{ cm}^{-3}\text{s}^{-1}$) (Fomete et al., 2022). Additionally, hydronium ions

 $(H_2O \cdot H_3O^+, (H_2O)_2 \cdot H_3O^+, \text{ or } (H_2O)_3 \cdot H_3O^+)$ was used to measured base concentrations of ammonia (NH₃), methylamine (MA, CH₃NH₂), dimethylamine (DMA, (CH₃)₂NH), and trimethylamine (TMA, C₃H₉N) with a reaction constant of k_{hydronium} = 2x10⁻⁹ cm⁻³s⁻¹.

For the experiments outlined in this work, gaseous organic acids, including MSA, OxA, MaA, and FA, were injected into the flow reactor and mixed with the sulfuric acid for ~8 s prior to amines/ammonia injection. MSA was injected into the flow reactor by flowing dry nitrogen over a liquid reservoir of MSA. OxA, MaA, and FA mixtures were also injected by flowing dry nitrogen over a liquid reservoir of OxA, MaA, and FA. OxA and MaA were super-saturated in the mixture due to their low vapor pressures. Following the injection of organic acids, gaseous amines are injected into the flow reactor and allowed to react for 3.4 s with the acids in the flow reactor. This nucleation time and mixing times are estimated using an ANSYS model of the flow reactor, which estimates the centerline velocity of the laminar flow within the reactor. Amines and ammonia vapors were generated using custom-built permeation tubes serially diluted through a double dilution system (Fomete et al., 2021; Zollner et al., 2012). In addition to injecting laboratorygenerated mixtures, particle-free room air was introduced into the sulfuric acid flow reactor. Particles in compressed air, which likely contained numerous organic compounds, were removed with a HEPA filter. Removing pre-existing particles reduces the background levels of particles not formed through nucleation pathways.

NPM uses a generalized chemical reaction pathway to model sulfuric acid nucleation as a series of second-order elementary reactions (J. S. Johnson & Jen, 2022). Reaction 1 shows the reaction pathways for the NPM, where *n* represents the number of SA and base (B) molecules in the cluster. The reaction pathways represent the most energetically favorable pathway for forming sulfuric acid and base clusters, with approximately a 1:1 ratio of acid to base. Other, less

energetically favorable pathways are excluded from the model. Reaction S1 shows the full cluster balance equations for NPM. Coagulation losses are estimated using the collision rate constant between clusters up to size N₈. The forward rate constant is assumed equal for each cluster ($k = 5.4 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$) and is based on the unit density of the cluster (Ortega et al., 2012). This reaction constant was chosen to keep the *k* generalizable when describing complex mixtures' diverse and sometimes unknown nucleation reactions.

$$A_{1} + B_{eff} \xrightarrow{k} A_{1} \cdot B_{eff}$$

$$N_{n} = A_{n} \cdot B_{n}$$

$$N_{1} + N_{1} \xrightarrow{k} N_{2}$$

$$N_{1} + N_{2} \xrightarrow{k} N_{3}$$

$$N_{2} + N_{2} \xrightarrow{k} N_{4}$$

$$N_{1} + N_{3} \xrightarrow{k} N_{4}$$
Reaction 1

4.4 Results

4.4.1 Quantifying the effect of methanesulfonic acid on [Beff]

Figure 4.1a shows measured [B_{eff}] for MA injections into the flow reactor with varying [MSA] at T = 298-300K and RH = 20%. Higher [MSA] leads to a factor of 2-3 increase in [B_{eff}], which is consistent with previous studies showing SA-MSA-MA and MSA-MA nucleation as favorable reaction pathways (Elm, 2022; J. S. Johnson & Jen, 2023). Each curve reaches a point of saturation where increasing [MA] does not lead to an appreciable increase in [B_{eff}]. The saturation point occurs when the base reacts with most of the initial SA. With the addition of [MSA], [B_{eff}] reaches a saturation point at higher concentrations of [MA] due to more acid availability for MA reactions. At low [MA], [B_{eff}] curves for each [MSA] converges because [MA] preferentially reacts with SA before reacting with MSA (Elm, 2021, 2022).



Figure 4.1 (a) Comparison of $[B_{eff}]$ values for SA-MA and SA-MSA-MA reactions. Black squares show previously published data for SA-MA nucleation (J. S. Johnson & Jen, 2022). Blue triangles at [SA]/[MSA] = 0.69, red triangles at [SA]/[MSA] = 0.34, and green triangles at [SA]/[MSA] = 0.08. (b) Comparison of $[B_{eff}]$ for SA-TMA and SA-MSA-TMA reactions. Black squares show previously published data for SA-TMA nucleation (J. S. Johnson & Jen, 2022). Blue triangles at [SA]/[MSA] = 0.76, purple triangles at [SA]/[MSA] = 0.52, red triangles at [SA]/[MSA] = 0.21, and green triangles at [SA]/[MSA] = 0.07. Error bars show the standard deviation of the particle concentrations during each measurement. Initial [SA] is $7.5 \times 10^7 \pm 1.3 \times 10^7$ cm⁻³.

Figure 4.1b shows measured [B_{eff}] for TMA injections into the flow reactor with varying [MSA] at T = 298-300K and RH = 20%. Unlike MA, higher [MSA] leads to a factor of 2-3 decrease in [B_{eff}]. Furthermore, for TMA, the saturation [B_{eff}] is lower at [SA]/[MSA] = 0.07, decreasing from approximately 70 pptv to 30pptv when compared to the no MSA case. These combined observations indicate that reactions of TMA and MSA are suppressing sulfuric acid nucleation. Johnson & Jen (2023) showed that MSA is binding with TMA, but the molecular clusters cannot continue to react and grow due to steric hindrance. Like MA, [B_{eff}] values converge at low [TMA], likely due to the high availability of SA that readily nucleates with TMA. Figure 1 also illustrates that high [MSA] leads to higher [B_{eff}] values for MA than TMA. High [B_{eff}] for MA indicates that if localized [MSA] is significantly higher than [SA] in the atmosphere, MA reacting with MSA and SA could be a significant driver of particle nucleation. However, current

evidence indicates that [MSA] is typically lower than [SA] (Berresheim et al., 2002b; Eisele & Tanner, 1993), and it is unclear how significant MSA-base pathways are in the atmosphere.

Note that the data from Johnson & Jen (2022) have been updated in this study due to two revised rate constants. First, the acetate-sulfuric acid ionization rate constant, $k_{acetate}$, has been revised to match newly published results for $k_{acetate}$. Updating $k_{acetate}$ resulted in a lower measured [SA] and a higher [B_{eff}] than published in Johnson & Jen, 2022. Second, the forward reaction rate constant for the NPM ($k = 5.4 \times 10^{-10}$ cm³s⁻¹) was updated from the previously used value of 4.2×10^{-10} cm³s⁻¹ (J. S. Johnson & Jen, 2022) to act as a more generalized reaction constant to potentially reduce the uncertainty in k due to the molecular composition of the nucleating clusters. The increase in the reaction constant led to an overall decrease in [B_{eff}]. In addition, wall loss reactions was done since the vwCPC is measuring the centerline flow of the reactor, where wall losses are significantly lower than the reactor walls. In general, the changes made to NPM lead to a decrease in [B_{eff}] over those in Johnson and Jen (2022) but did not impact the overall trends.

The NPM is based on computational chemistry results that have shown that sulfuric acid nucleation will nucleate typically at a 1:1 ratio of acids to base. However, results from Figure 1 are capturing MSA's impact on particle nucleation in $[B_{eff}]$ rather than including MSA in the initial acid concentration, i.e. [SA]+[MSA]. Figure C.1 shows the impact of including [MSA] into the initial acid concentration. When MSA is included in the initial acid concentration there is a significantly lower $[B_{eff}]$ value for MSA injections compared to **Figure 4.1**. However, since MSA is enhancing nucleation rates for SA-MSA, $[B_{eff}]$ should be increasing as shown in **Figure 4.1**. For this reason, the initial acid concentration for the NPM is solely [SA], so that $[B_{eff}]$ is capturing the enhancement and suppression effects that both acids and bases have on sulfuric acid nucleation rates.

4.4.2 [Beff] of mixtures of sulfuric acid, amines, and organic acids

Figure 4.2 shows NPM's capability in capturing [B_{eff}] of complex mixtures of sulfuric acid, amines/ammonia, and organic acids. Figure 4.2 also includes previously published various mixture results of NH₃, MA, DMA, TMA for comparison (J. S. Johnson & Jen, 2022). [B_{eff}] for mixtures are compared by varying the concentrations of strong bases ([DMA]+[TMA]). Varying strong base concentrations were conducted as [B_{eff}] is particularly sensitive to the concentrations of strong bases, and [B_{eff}] was independent of [NH₃] and [MA]. As expected, increasing the concentration of the base mixture (NH₃, MA, DMA, and TMA) leads to an increase in [B_{eff}], with a plateau at higher concentrations. Specifically, [B_{eff}] are significantly higher than Figure 4.1 with the maximum values in Figure 4.2 reaching ~125 pptv at an injected base concentration of 20 pptv, while the TMA injections only reaching ~80 pptv at an injected base concentration of 20 pptv with no MSA. Additionally, [B_{eff}] ~ 60 pptv when [TMA] ~ 10 pptv in Figure 4.1, and [B_{eff}] is ~ 100 pptv when [DMA]+[TMA] ~20 pptv in Figure 4.2. This likely points to [B_{eff}] capturing the individual impacts of SA-DMA and SA-TMA nucleation.

To expand the mixtures to include other atmospherically relevant compounds, the addition of a mixture of organic acids (OA) were added to the sulfuric acid flow reactor. OA contained $[OxA] = 3.1x10^8 \text{ cm}^{-3}$, $[MaA] = 2.5x10^8 \text{ cm}^{-3}$, and $[FA] = 2.3x10^9 \text{ cm}^{-3}$. The SA-OA mixture did not form any particles and thus had a $[B_{eff}]$ of zero. In Figure 4.2, SA-OA-amine system does not show significantly different $[B_{eff}]$ compared to SA-amine. The lack of change in $[B_{eff}]$ with the addition of the OA mixture suggests that SA nucleation is still largely driven by the concentrations of strong bases such as DMA and TMA.

Finally, the base mixture, MSA ([SA]/[MSA] =0.64), and OA mixture ([OxA] = 2.9×10^8 cm⁻³, [MaA] = 1.4×10^8 cm⁻³, and [FA] = 1.2×10^9 cm⁻³) were injected representing a mixture of nine unique compounds when including water. [B_{eff}] is still only dependent on [DMA]+[TMA] and is minimally impacted by the addition of OA and MSA to the mixture. The complex mixture of nine nucleating compounds further illustrates that sulfuric acid nucleation is going to be largely driven by the concentration of strong bases such as TMA and DMA. Additionally, the [SA]/[MSA] is lower than what has been measured in the atmosphere previously, indicating that even at higher [SA]/[MSA] than what is atmospherically relevant, MSA is not significantly impacting [B_{eff}] of complex mixtures. These results for complex mixtures indicate that future field measurements of [B_{eff}] will likely be strongly correlated with the concentrations of strong bases, and be minimally influenced by other atmospherically relevant acids and bases.

Following complex mixture reactions, $[B_{eff}]$ of particle-free room air was quantified to test NPM's capabilities in capturing how the real atmosphere nucleates with sulfuric acid and if $[B_{eff}]$ can also be described by [DMA] and [TMA]. Figure 4.2 shows [Beff] of room air in the range of 18-23 pptv. The measured [DMA] and [TMA] in room air were approximately 1-2 pptv and 5-6 pptv, respectively. Room air $[B_{eff}]$ are like those observed the laboratory amine injections at equivalent [DMA] and [TMA]. While there are potentially hundreds of unique species in the atmospheric air sample, $[B_{eff}]$ is still largely describing the concentrations of strong nucleating compounds. Overall, results from complex mixture reactions show that organic acids are not influencing $[B_{eff}]$. And while MSA can influence $[B_{eff}]$ for specific amines as shown in Figure 4.1, MSA's impact on the base mixture is small when compared to the influence of the concentration of strong bases.



Figure 4.2 Comparison of $[B_{eff}]$ for complex mixture reactions. Black and orange squares show previously published data for SA-amine mix nucleation (J. S. Johnson & Jen, 2022). Green diamonds show base mix, red diamonds show base mix and MSA, blue diamonds show room air, light green diamonds show base mix with organic acids, light blue diamonds show base mix, MSA, and organic acids. Error bars show standard deviation of the particle concentrations during each measurement. Initial [SA] is $7.5 \times 10^7 \pm 1.3 \times 10^7$ cm⁻³.

4.4.3 The Effects of Relative Humidity on [Beff]

The impact of RH on $[B_{eff}]$ was measured to validate the NPM's performance with varying atmospherically relevant conditions. Figure 4.3 displays results of mixtures injected in the flow reactor, indicating a general decrease in $[B_{eff}]$ as RH increases. This trend holds true for all mixtures studied and may be attributed to water molecules impeding acid-base chemical reactions. Specifically, previous computational results have shown that NH₃ clusters are less stable at higher RH (Henschel et al., 2016; Olenius et al., 2017). Similar trends are presented in Figure C.2 for significantly higher concentrations of amines. While this work agrees with some previous results that increasing RH will lead to a decrease in particle formation, further detailed kinetic studies are needed to better understand how RH influences specific reaction mechanisms.





4.4.4 Applications of NPM to the atmosphere

To address the decreasing $[B_{eff}]$ with increasing higher RH observed in Figure 4.3, an extra parameter value (RH_{corr}) is included in Equation S2 of the NPM. Including RH_{corr} will allow for the NPM to accurately reflect the concentration of strong nucleation precursor vapors, rather than changes in measured (RH_{meas}). RH_{corr} was calculated using the $[B_{eff}]$ value at RH = 20% as the baseline condition. NPM was then iteratively solved until $[B_{eff}]$ at 10%, 30%, 40%, and 50% RH all matched $[B_{eff}]$ at 20% RH. This was repeated for several RH experiments and then the average correction factor was found for each RH. Equation 1 displays the correction factor values alongside their respective standard deviations, which shows the overall variability in RH_{corr} across the complete data set. RH_{meas} refers to the measured RH during the experiment, while RH_{corr} is the correction factor used in the NPM to correct for changes in RH. Figure C.3 demonstrates that [B_{eff}], once corrected using RH_{corr} , does not vary with RH. As a result, $[B_{eff}]$ can be compared between various systems (or regions of the atmosphere) with minimal influence of RH.

$$RH_{corr} = \begin{cases} 0, & RH_{meas} \leq 20\\ (0.0239 * (RH_{meas} - 20)) \pm 0.16, & 20 < RH_{meas} \leq 30\\ 0.221 \pm 0.15, & 30 < RH_{meas} \leq 40\\ 0.0340 * (RH_{meas} - 34) \pm 0.18, & 40 < RH_{meas} \leq 50 \end{cases}$$
 Equation 1

An analytical expression was derived from the NPM to estimate the nucleation rate of 1 nm particles (J_{1nm}) based on measured [B_{eff}] and ambient sulfuric acid concentrations. This expression was derived by assuming the nucleation process in the atmosphere is steady-state, and that molecular coagulation terms are relatively small compared to the condensation sink (CS). As explained in Johnson and Jen (2022), [B_{eff}] can be easily measured by reacting sampled air with a known concentration of sulfuric acid in flow reactor and measuring the resulting particle concentration using a 1 nm CPC. The J_{1nm} expression from NPM given in Equation 2 provides modelers a computationally simple method to estimate nucleation rates across the world if [B_{eff}] is known. Equation 2 shows the final derivation for J_{1nm,model}, where CS, the condensation sink to pre-existing particles, is the main loss term, [SA] is the ambient measurements of sulfuric acid, and [B_{eff}] is the measured effective base concentration.

$$N_{1} = \frac{-CS + \sqrt{CS^{2} + 8k^{2} [SA][B_{eff}]}}{4k}$$

$$N_{2} = \frac{kN_{1}^{2}}{kN_{1} + CS}$$
Equation 2
$$N_{3} = \frac{kN_{1}N_{2}}{kN_{1} + CS}$$

 $J_{1nm,model} = kN_1N_3$

Equation 2 was applied to nucleation data that was taken in Beijing, China (Cai et al., 2021). Previous NPM results determined $[B_{eff}]$ for the field data collected in Beijing, however these values have been updated in this work with the updated k-values as described previously. Figure C.4 shows the new calculated $[B_{eff}]$ for Beijing. Figure C.5 shows a comparison between the modeled nucleation rate (J_{1nm,model}) and the measured nucleation rate (J_{1nm, meas}). Figure C.5 shows good agreement between the measured and modeled nucleation rate with a slope of 0.55 and an R²=0.997. The agreement between nucleation rates indicates that the analytical solution is correctly capturing particle nucleation rates. While the analytical solution is capturing trends in J_{1nm}, atmospheric data that directly measured [B_{eff}] will be necessary to solidify this method of estimating particle nucleation rates.

4.5 Conclusions

The Nucleation Potential Model, NPM, has been applied to diverse set of atmospheric bases and acids. The resulting observed effective base concentration, $[B_{eff}]$, has been shown to primarily depend on the concentration strong base compounds, such as dimethyl and trimethylamine (DMA and TMA), even in the presence of high concentrations of organic acids. NPM and the subsequent [Beff] was also measured for room air in Pittsburgh, PA. The $[B_{eff}]$ of room air correlated with the combined concentration of DMA and TMA and agreed well with the values measured in laboratory-generated complex mixtures. In addition, varying RH during nucleation experiments revealed a correlation between increasing RH and decreasing $[B_{eff}]$. To account for changes in RH in the atmosphere, RH_{corr} was added to NPM. An analytical equation for J_{1nm} was also derived for NPM that uses measured $[B_{eff}]$ to estimate particle nucleation rates. The combined observations of this study demonstrate NPM ability to estimate concentrations and

potency of a diverse and complex set of nucleating compounds in enhancing sulfuric acid nucleation rates. Overall, NPM is a simple model for estimating nucleation rates around the world and provides a useful tool for measuring [Beff] at higher spatial and temporal resolution than is possible with current instrumentation. Appendix C: Supplementary Information for Chapter 4

Figure C.1 compares the NPM with and without adding [MSA] to the initial acid concentration. Black squares and black triangles represent when [MSA] is not added to [A₁], and green diamonds represent when $[A_1] = [SA]_i + [MSA]_i$. When acid concentrations are combined, the value of $[B_{eff}]$ is lower than in the case of SA-MA nucleation. Because $[B_{eff}]$ for SA-MSA-MA nucleation should be higher than SA-MA nucleation, the results indicate that NPM can better capture MSA's impact on SA nucleation in $[B_{eff}]$ rather than including [MSA] in the initial acid concentration.



Figure C.1: Comparison of the measured base concentration [B] and the Effective Base Concentration $[B_{eff}]$ for MA injections in the flow reactor. Black squares and blue triangles show $[B_{eff}]$ when the initial acid concentration is set equal to sulfuric acid concentration. Green diamonds show $[B_{eff}]$ when the initial acid concentration is the summation of sulfuric acid and methanesulfonic acid concentration. Uncertainty bars represent the standard deviation in particle concentrations across the experiment.

Equation S1 shows the cluster balance equations for the NPM, with the now included RH_{corr} parameter. Cluster balances include both the formation and loss terms for each cluster

type. Clusters are formed from collisions and lost via coagulation. Forward rate constants are assumed to be equal with $k = 5.4 \times 10^{-10} \text{ cm}^{-3} \text{s}^{-1}$ (Ortega et al., 2012).

$$\begin{split} \frac{d[A_1]}{dt} &= -k[A_1][B_{eff}] \\ \frac{d[B_{eff}]}{dt} &= -k[A_1][B_{eff}] - RH_{corr}[B_{eff}] \\ \frac{d[A_1 \cdot B_{eff}]}{dt} &= k[A_1][B_{eff}] - k[N_1](2[N_1) + [N_2] + [N_3] + [N_4]) \\ [N_1] &= [A_1 \cdot B_{eff}] \\ \frac{d[N_2]}{dt} &= k[N_1]^2 - k[N_2]([N_1) + 2[N_2] + [N_3] + [N_4]) \\ \frac{d[N_3]}{dt} &= k[N_1][N_2] - k[N_3]([N_1) + [N_2] + 2[N_3] + [N_4]) \\ \frac{d[N_4]}{dt} &= k_1[N_2]^2 + k_1[N_1][N_3] - k_1[N_4]((N_1) + [N_2] + [N_3] + 2[N_4]) \\ \frac{d[N_{24}]}{dt} &= k_1[N_1][N_4] + k_1[N_2][N_3] + k_1[N_2][N_4] + k_1[N_2][N_4] + k_1[N_3]^2 + k_1[N_3][N_4] + k_1[N_4]^2 \end{split}$$

Equation S1

Figure C.2 shows the $[B_{eff}]$ for amine/ammonia and organic acid mixtures at varying RH. Figure C.2 shows similar results to Figure 4.3, but with higher concentrations of amines injected into the flow reactor. Here, it is shown that the injections of the OA and MSA mixtures leads to either no change in $[B_{eff}]$ as is the case for just organic acids, or a decrease in $[B_{eff}]$ in the case of organic acids with MSA.



Figure C.2 Comparison of $[B_{eff}]$ for the injections of amine/ammonia mixtures with organic acid mixtures. Red shows injections of a high concentration of amines ([DMA]+[TMA] = 67.5 pptv) and blue shows injections of a lower concentration of amines ([DMA]+[TMA] = 30.8 pptv). Squares indicate no added organic acids, while circles indicate organic acids are injected. Uncertainty bars represent the standard deviation in particle concentrations across the experiment.

Figure C.3 compares the uncorrected RH data to the corrected RH data. As seen in Figure

C.3, the corrected data bring all the $[B_{eff}]$ to similar values. The increase in uncertainty is related

to variations in estimated RH_{corr} and likely could be reduced with further experiments.



Figure C.3 Comparison of $[B_{eff}]$ at varying relative humidity. Black squares show uncorrected $[B_{eff}]$ values, while red triangles show the corrected $[B_{eff}]$ values. For the black squares, uncertainty represents the standard deviation in particle counts. For the red triangles, the uncertainty represents the standard deviation in the relative humidity correction factor (RH_{corr})

Figure C.4 shows the updated $[B_{eff}]$ calculations for Beijing China (Cai et al., 2021) with the updated k = 5.4×10^{-10} cm⁻³s⁻¹ for the steady-state model. For the steady-state case of the NPM, cluster balances through N₄ are set equal to zero and N_{4>} is removed. While values for $[B_{eff}]$ have changed when compared to Johnson & Jen (2022), the overall trends remain constant.



Figure C.4 Comparison of the weighted amine concentration and $[B_{eff}]$ for measurements in Beijing, China. Green squares show December measurements, red squares show November measurements, and black squares show December measurements.

Figure C.5 shows the comparison between measured and modeled nucleation rates for Beijing, China. Results indicate that $J_{1nm,modeled}$ is accurately capturing measured nucleation rates with an R²=0.997 and a slope of 0.55.



Figure C.5 Comparison of the measured and modeled nucleation rates for J_{1nm} .

Chapter 5: Conclusion and Future Work

6.1 Summary

Chapter 2 included the development and implementation of the NPM to describe sulfuric acid nucleation in the atmosphere. NPM was developed based on previous computational chemistry results that showed sulfuric acid-base nucleation has the highest probability of forming clusters in a 1:1 ratio of acid and base. NPM describes sulfuric acid nucleation with two precursor concentrations: sulfuric acid and an effective base concentration ([Beff]). [Beff] captures the effect of stabilizing compounds on sulfuric acid nucleation rates. [Beff] was determined from measured 1-nm particle concentrations, and its value depends heavily on the presence of strong stabilizing compounds, such as DMA and TMA, and their concentrations. NPM was also used to calculate [Beff] in various locations worldwide. Field measurements showed that NPM is capturing the differences between polluted and pristine environments based on the [Beff] in that region. [Beff] was also shown to correlate with the measured amine concentrations from a field campaign in Beijing, China.

Chapter 3 examines the chemical reactions of MSA-SA-amine/ammonia nucleation. Results showed that MSA allows for more unique chemical formation pathways for the formation of dimers, as shown by the MSA dimer and SA-MSA heterodimer. The fraction of [SA·SA], [MSA·MSA], and [SA·MSA] formed out of the total dimer concentration also indicates which base compounds are reacting more readily with MSA than others. Methylamine and dimethylamine react with SA and MSA to form relatively equal [MSA·SA] and [SA·SA], indicating that MSA readily reacts with MA and DMA. However, [MSA·SA] in the case of TMA is significantly lower than the [SA·SA], indicating that TMA is preferentially nucleating with SA. Insignificant changes to total dimer concentrations for ammonia indicate that any interactions between ammonia and MSA are likely negligible compared to SA and ammonia.

Particle measurements showed that while MSA enhances sulfuric acid nucleation in the case of MA, it may suppress nucleation in the case of SA-TMA. Introducing MA into the SA-MSA system saw an increase in particle concentrations at higher concentrations of MSA, whereas TMA saw a decrease in particle concentrations at high MSA concentrations. However, in the atmosphere, MSA concentration typically never surpasses that of SA, so while the laboratory results show suppression in the case of TMA, the TMA-MSA-SA suppression may be insignificant compared to the enhancement of TMA on SA nucleation.

Chapter 4 extends NPM developed in chapter 2 to capture $[B_{eff}]$ of higher order mixtures and determine the impacts of MSA in chapter 3 on $[B_{eff}]$. $[B_{eff}]$ has been shown to have a strong dependence on the concentration of strong SA nucleating compounds (DMA and TMA) even in complex mixtures of 9+ reactive compounds. Thus, high measured $[B_{eff}]$ in the atmosphere could indicate high concentrations of strong nucleating compounds. This dependence on strong nucleating compounds was also shown through the measurement of $[B_{eff}]$ of atmospheric air, which showed similar $[B_{eff}]$ to the lab generated amine mixtures. NPM was further expanded through RH experiments, that showed a correlation of increasing RH leading to a decrease in $[B_{eff}]$. Additionally, a correction factor (RH_{Corr}) was added to the NPM to account for changes in RH. Overall, this work showed that NPM can be used to make estimates of concentrations of potent nucleating compounds in a wide variety of climates and locations across the world.

Current nucleation models cannot predict nucleation rates accurately when applied to the atmosphere due to both model and instrumentation limitations. Additionally, measuring nucleation rates at a high spatial and temporal region is difficult due to instrumentation limitations. The work

in this thesis outlines a new approach to estimate concentrations of nucleation precursors and particle nucleation rates and detailed kinetics pathways for particle formation. NPM allows for estimation of precursor gases with the parameterized value $[B_{eff}]$. $[B_{eff}]$ has been shown to accurately capture the impact of mixtures of 8+ compounds and can also be corrected for impacts due to relative humidity. The NPM will profoundly impact global climate modeling and allow for more accurate predictions of weather and climate patterns. Future work will include high spatial and temporal measurements of $[B_{eff}]$ in diverse locations across the world.

6.2 Future Work

The NPM was developed and implemented in this work to estimate sulfuric acid nucleation precursor gas concentrations. The following knowledge gaps need to be further examined in the future:

- A field campaign where [B_{eff}] is directly measured for atmospheric air is needed understand the dependence of [B_{eff}] on emission sources. A mass spectrometer and an SMPS will also be required for the campaign to validate the NPM's results. The validation of NPM in the field is required for the successful implementation of NPM into larger global climate models.
- 2. Developing a new instrumentation technique for NPM to be used in the field will provide more accessible measurements. Currently, NPM is measured using a 1 m glass flow reactor. The size of the flow reactor would be cumbersome in the field and potentially introduce significant sources of contamination. A smaller flow reactor would allow more manageable and reliable measurements when determining [B_{eff}] directly for outdoor air.

3. NPM should be validated at a range of atmospherically relevant temperatures. The quantification of temperature effects for NPM will be an essential step for implementing NPM into global climate models. Like the RH effects described in Chapter 4, [B_{eff}] likely depends on the temperature during nucleation experiments. Temperature variations could be explored similarly to RH, where a temperature-controlled flow reactor is used to measure [B_{eff}] at various temperatures. This will allow for better implementation of NPM into earth systems models.

This thesis also explored the reaction kinetics of SA-MSA-amine/ammonia nucleation to better understand the chemical formation pathways that may occur in a marine atmosphere. The following knowledge gaps will need to be explored in the future:

- Measuring unique trimers and tetramers with the MCC will allow for a better understanding of the chemical formation pathways beyond the dimer. Likely, this would require specific tuning parameters on the MCC to measure larger clusters. Additionally, testing different reagent ionization molecules, such as iodine or other organic acids, that charge clusters differently than nitrate and acetate may allow for measuring previously undetected clusters.
- 2. Measurements of clusters with complex mixtures of amines could show what nucleation pathways will dominate. In this work, amines were injected one at a time; thus, the experiments did not match atmospheric conditions where all amines would be present simultaneously. If measurements were taken with multiple amines injected, this would provide valuable information about which amines may dominate the chemical reactions with MSA and SA. However, these measurements would require the above suggestion to be completed first. Measurement of more potential cluster types are necessary when

determining the specific chemical reactions various mixtures will take when forming stable clusters.

References

- Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim,
 A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E.,
 Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., ... Kirkby, J. (2013). Molecular understanding of
 sulphuric acid–amine particle nucleation in the atmosphere. *Nature*, 502(7471), 359–363.
 https://doi.org/10.1038/nature12663
- Ball, S. M., Hanson, D. R., Eisele, F. L., & McMurry, P. H. (1999). Laboratory studies of particle nucleation: Initial results for H2SO4, H2O, and NH3 vapors. *Journal of Geophysical Research: Atmospheres*, 104(D19), 23709–23718. https://doi.org/10.1029/1999JD900411
- Berresheim, H., Elste, T., Tremmel, H. G., Allen, A. G., Hansson, H.-C., Rosman, K., Dal Maso, M., Mäkelä, J. M., Kulmala, M., & O'Dowd, C. D. (2002a). Gas-aerosol relationships of H2SO4, MSA, and OH: Observations in the coastal marine boundary layer at Mace Head, Ireland. *Journal of Geophysical Research: Atmospheres,* 107(D19), PAR 5-1-PAR 5-12. https://doi.org/10.1029/2000JD000229
- Berresheim, H., Elste, T., Tremmel, H. G., Allen, A. G., Hansson, H.-C., Rosman, K., Dal Maso, M., Mäkelä, J. M., Kulmala, M., & O'Dowd, C. D. (2002b). Gas-aerosol relationships of H2SO4, MSA, and OH: Observations in the coastal marine boundary layer at Mace Head, Ireland. *Journal of Geophysical Research: Atmospheres*, 107(D19), PAR 5-1-PAR 5-12. https://doi.org/10.1029/2000JD000229
- Cai, R., Yan, C., Yang, D., Yin, R., Lu, Y., Deng, C., Fu, Y., Ruan, J., Li, X., Kontkanen, J., Zhang, Q., Kangasluoma, J., Ma, Y., Hao, J., Worsnop, D. R., Bianchi, F., Paasonen, P., Kerminen, V.-M., Liu, Y., ... Jiang, J. (2021).
 Sulfuric acid–amine nucleation in urban Beijing. *Atmospheric Chemistry and Physics*, 21(4), 2457–2468. https://doi.org/10.5194/acp-21-2457-2021
- Chen, H., & Finlayson-Pitts, B. J. (2017). New Particle Formation from Methanesulfonic Acid and Amines/Ammonia as a Function of Temperature. *Environmental Science & Technology*, 51(1), 243–252. https://doi.org/10.1021/acs.est.6b04173
- Chen, H., Varner, M. E., Gerber, R. B., & Finlayson-Pitts, B. J. (2016). Reactions of Methanesulfonic Acid with Amines and Ammonia as a Source of New Particles in Air. *The Journal of Physical Chemistry B*, 120(8), 1526–1536. https://doi.org/10.1021/acs.jpcb.5b07433

- Chen, M., Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., Zhao, J., & McMurry, P. H. (2012). Acid–base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer. *Proceedings of the National Academy of Sciences of the United States of America*, 109(46), 18713–18718. https://doi.org/10.1073/pnas.1210285109
- Chen, Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., Zhao, J., & McMurry, P. H. (2012). Acid-base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer. *Proceedings of the National Academy of Sciences*, 109, 18713–18718. https://doi.org/10.1073/pnas.1210285109
- Coffman, D. J., & Hegg, D. A. (1995). A preliminary study of the effect of ammonia on particle nucleation in the marine boundary layer. *Journal of Geophysical Research: Atmospheres*, 100(D4), 7147–7160. https://doi.org/10.1029/94JD03253
- Cree, C. H. L., Airs, R., Archer, S. D., & Fitzsimons, M. F. (2018). Measurement of methylamines in seawater using solid phase microextraction and gas chromatography. *Limnology and Oceanography: Methods*, 16(7), 411– 420. https://doi.org/10.1002/lom3.10255
- Dawson, M. L., Varner, M. E., Perraud, V., Ezell, M. J., Gerber, R. B., & Finlayson-Pitts, B. J. (2012). Simplified mechanism for new particle formation from methanesulfonic acid, amines, and water via experiments and ab initio calculations. *Proceedings of the National Academy of Sciences*, 109(46), 18719–18724. https://doi.org/10.1073/pnas.1211878109
- DePalma, J. W., Bzdek, B. R., Doren, D. J., & Johnston, M. V. (2012). Structure and Energetics of Nanometer Size Clusters of Sulfuric Acid with Ammonia and Dimethylamine. *The Journal of Physical Chemistry A*, 116, 1030–1040. https://doi.org/10.1021/jp210127w
- Dunne, E. M., Gordon, H., Kürten, A., Almeida, J., Duplissy, J., Williamson, C., Ortega, I. K., Pringle, K. J., Adamov,
 A., Baltensperger, U., Barmet, P., Benduhn, F., Bianchi, F., Breitenlechner, M., Clarke, A., Curtius, J.,
 Dommen, J., Donahue, N. M., Ehrhart, S., ... Carslaw, K. S. (2016). Global atmospheric particle formation
 from CERN CLOUD measurements. *Science*, *354*(6316), 1119–1124.
 https://doi.org/10.1126/science.aaf2649
- Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma,

J., Kontkanen, J., Nieminen, T., ... Mentel, T. F. (2014). A large source of low-volatility secondary organic aerosol. *Nature*, *506*(7489), 476. https://doi.org/10.1038/nature13032

- Eisele, F. L., Lovejoy, E. R., Kosciuch, E., Moore, K. F., Mauldin, R. L., Smith, J. N., McMurry, P. H., & Iida, K. (2006). Negative atmospheric ions and their potential role in ion-induced nucleation. *Journal of Geophysical Research: Atmospheres*, 111(D4). https://doi.org/10.1029/2005JD006568
- Eisele, F. L., & Tanner, D. J. (1993). Measurement of the gas phase concentration of H2SO4 and methane sulfonic acid and estimates of H2SO4 production and loss in the atmosphere. *Journal of Geophysical Research: Atmospheres*, 98(D5), 9001–9010. https://doi.org/10.1029/93JD00031
- Elm, J. (2017). Elucidating the Limiting Steps in Sulfuric Acid–Base New Particle Formation. *The Journal of Physical Chemistry A*, 121(43), 8288–8295. https://doi.org/10.1021/acs.jpca.7b08962
- Elm, J. (2019). An Atmospheric Cluster Database Consisting of Sulfuric Acid, Bases, Organics, and Water. ACS Omega, 4(6), 10965–10974. https://doi.org/10.1021/acsomega.9b00860
- Elm, J. (2021). Clusteromics II: Methanesulfonic Acid–Base Cluster Formation. ACS Omega, 6(26), 17035–17044. https://doi.org/10.1021/acsomega.1c02115
- Elm, J. (2022). Clusteromics III: Acid Synergy in Sulfuric Acid–Methanesulfonic Acid–Base Cluster Formation. ACS Omega, 7(17), 15206–15214. https://doi.org/10.1021/acsomega.2c01396
- Elm, J., Jen, C. N., Kurtén, T., & Vehkamäki, H. (2016). Strong Hydrogen Bonded Molecular Interactions between Atmospheric Diamines and Sulfuric Acid. *The Journal of Physical Chemistry A*, 120, 3693–3700. https://doi.org/10.1021/acs.jpca.6b03192
- Elm, J., Passananti, M., Kurtén, T., & Vehkamäki, H. (2017). Diamines Can Initiate New Particle Formation in the Atmosphere. *The Journal of Physical Chemistry A*, 121(32), 6155–6164. https://doi.org/10.1021/acs.jpca.7b05658
- Erupe, M. E., Benson, D. R., Li, J., Young, L.-H., Verheggen, B., Al-Refai, M., Tahboub, O., Cunningham, V., Frimpong, F., Viggiano, A. A., & Lee, S.-H. (2010). Correlation of aerosol nucleation rate with sulfuric acid and ammonia in Kent, Ohio: An atmospheric observation. *Journal of Geophysical Research: Atmospheres*, *115*(D23). https://doi.org/10.1029/2010JD013942
- Flocke, F., Pfister, G., Crawford, J. H., Pickering, K. E., Pierce, G., Bon, D., & Reddy, P. (2020). Air Quality in the Northern Colorado Front Range Metro Area: The Front Range Air Pollution and Photochemistry Éxperiment

(FRAPPÉ). Journal of Geophysical Research: Atmospheres, 125(2), e2019JD031197. https://doi.org/10.1029/2019JD031197

- Fomete, S. K. W., Johnson, J. S., Casalnuovo, D., & Jen, C. N. (2021). A tutorial guide on new particle formation experiments using a laminar flow reactor. *Journal of Aerosol Science*, 157, 105808. https://doi.org/10.1016/j.jaerosci.2021.105808
- Fomete, S. K. W., Johnson, J. S., Myllys, N., & Jen, C. N. (2022). Experimental and Theoretical Study on the Enhancement of Alkanolamines on Sulfuric Acid Nucleation. *The Journal of Physical Chemistry A*, 126(25), 4057–4067. https://doi.org/10.1021/acs.jpca.2c01672
- Fomete, S. K. W., Johnson, J. S., Myllys, N., Neefjes, I., Reischl, B., & Jen, C. N. (2022a). Ion–Molecule Rate Constants for Reactions of Sulfuric Acid with Acetate and Nitrate Ions. *The Journal of Physical Chemistry* A, 126(44), 8240–8248. https://doi.org/10.1021/acs.jpca.2c02072
- Fomete, S. K. W., Johnson, J. S., Myllys, N., Neefjes, I., Reischl, B., & Jen, C. N. (2022b). Ion–Molecule Rate Constants for Reactions of Sulfuric Acid with Acetate and Nitrate Ions. *The Journal of Physical Chemistry* A, 126(44), 8240–8248. https://doi.org/10.1021/acs.jpca.2c02072
- Freshour, N. A., Carlson, K. K., Melka, Y. A., Hinz, S., Panta, B., & Hanson, D. R. (2014). Amine permeation sources characterized with acid neutralization and sensitivities of an amine mass spectrometer. *Atmospheric Measurement Techniques*, 7(10), 3611–3621. https://doi.org/10.5194/amt-7-3611-2014
- Froyd, K. D., & Lovejoy, E. R. (2003). Experimental Thermodynamics of Cluster Ions Composed of H2SO4 and H2O. 1. Positive Ions. *The Journal of Physical Chemistry A*, 107, 9800–9811. https://doi.org/10.1021/jp027803o
- Ge, X., Wexler, A. S., & Clegg, S. L. (2011). Atmospheric amines Part I. A review. Atmospheric Environment, 45(3), 524–546. https://doi.org/10.1016/j.atmosenv.2010.10.012
- Glasoe, W. A., Volz, K., Panta, B., Freshour, N., Bachman, R., Hanson, D. R., McMurry, P. H., & Jen, C. (2015). Sulfuric acid nucleation: An experimental study of the effect of seven bases. *Journal of Geophysical Research: Atmospheres*, 120(5), 1933–1950. https://doi.org/10.1002/2014JD022730
- Gordon, H., Kirkby, J., Baltensperger, U., Bianchi, F., Breitenlechner, M., Curtius, J., Dias, A., Dommen, J., Donahue,
 N. M., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Frege, C., Fuchs, C., Hansel, A., Hoyle, C. R.,
 Kulmala, M., Kürten, A., ... Carslaw, K. S. (2017). Causes and importance of new particle formation in the

present-day and preindustrial atmospheres. *Journal of Geophysical Research: Atmospheres*, *122*(16), 8739–8760. https://doi.org/10.1002/2017JD026844

- Hanson, D. R., Bier, I., Panta, B., Jen, C. N., & McMurry, P. H. (2017). Computational Fluid Dynamics Studies of a Flow Reactor: Free Energies of Clusters of Sulfuric Acid with NH3 or Dimethyl Amine. *The Journal of Physical Chemistry A*, 121(20), 3976–3990. https://doi.org/10.1021/acs.jpca.7b00252
- Hanson, D. R., Burkholder, J. B., Howard, C. J., & Ravishankara, A. R. (1992). Measurement of hydroxyl and hydroperoxy radical uptake coefficients on water and sulfuric acid surfaces. *The Journal of Physical Chemistry*, 96, 4979–4985. https://doi.org/10.1021/j100191a046
- Hanson, D. R., & Eisele, F. L. (2002a). Measurement of prenucleation molecular clusters in the NH₃, H₂SO₄, H₂O system. J. Geophys. Res., 107, 4158. https://doi.org/10.1029/2001jd001100
- Hanson, D. R., & Eisele, F. L. (2002b). Measurement of prenucleation molecular clusters in the NH3, H2SO4, H2O system. Journal of Geophysical Research: Atmospheres, 107(D12), AAC 10-1-AAC 10-18. https://doi.org/10.1029/2001JD001100
- Hanson, D. R., McMurry, P. H., J., Tanner, D., & Huey, L. G. (2011). Ambient Pressure Proton Transfer Mass Spectrometry: Detection of Amines and Ammonia. *Environmental Science & Technology*, 45, 8881–8888. https://doi.org/10.1021/es201819a
- Hatakeyama, S., & Akimoto, H. (1983). Reactions of hydroxyl radicals with methanethiol, dimethyl sulfide, and dimethyl disulfide in air. *The Journal of Physical Chemistry*, 87(13), 2387–2395. https://doi.org/10.1021/j100236a029
- Hatakeyama, S., Okuda, M., & Akimoto, H. (1982). Formation of sulfur dioxide and methanesulfonic acid in the photooxidation of dimethyl sulfide in the air. *Geophysical Research Letters*, 9(5), 583–586. https://doi.org/10.1029/GL009i005p00583
- Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kürten, A., Hansel, A., & Curtius, J. (2016). Characterization of the mass-dependent transmission efficiency of a CIMS. *Atmos. Meas. Tech.*, 9(4), 1449–1460. https://doi.org/10.5194/amt-9-1449-2016
- Henschel, H., Kurtén, T., & Vehkamäki, H. (2016). Computational Study on the Effect of Hydration on New Particle Formation in the Sulfuric Acid/Ammonia and Sulfuric Acid/Dimethylamine Systems. *The Journal of Physical Chemistry. A*, 120(11), 1886–1896. https://doi.org/10.1021/acs.jpca.5b11366

- Henschel, H., Navarro, J. C. A., Yli-Juuti, T., Kupiainen-Määttä, O., Olenius, T., Ortega, I. K., Clegg, S. L., Kurtén, T., Riipinen, I., & Vehkamäki, H. (2014). Hydration of Atmospherically Relevant Molecular Clusters: Computational Chemistry and Classical Thermodynamics. *The Journal of Physical Chemistry A*, *118*, 2599–2611. https://doi.org/10.1021/jp500712y
- Hering, S. V., Lewis, G. S., Spielman, S. R., Eiguren-Fernandez, A., Kreisberg, N. M., Kuang, C., & Attoui, M. (2017). Detection near 1-nm with a laminar-flow, water-based condensation particle counter. *Aerosol Science and Technology*, 51(3), 354–362. https://doi.org/10.1080/02786826.2016.1262531
- Hering, S. V., Stolzenburg, M. R., Quant, F. R., Oberreit, D. R., & Keady, P. B. (2005). A Laminar-Flow, Water-Based Condensation Particle Counter (WCPC). Aerosol Science and Technology, 39(7), 659–672. https://doi.org/10.1080/02786820500182123
- Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., Seibert, J. J., Vu, L., Andres, R. J., Bolt, R. M., Bond, T. C., Dawidowski, L., Kholod, N., Kurokawa, J., Li, M., Liu, L., Lu, Z., Moura, M. C. P., O'Rourke, P. R., & Zhang, Q. (2018). Historical (1750–2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS). *Geoscientific Model Development*, *11*(1), 369–408. https://doi.org/10.5194/gmd-11-369-2018
- Iida, K., Stolzenburg, M. R., McMurry, P. H., & Smith, J. N. (2008). Estimating nanoparticle growth rates from sizedependent charged fractions: Analysis of new particle formation events in Mexico City. *Journal of Geophysical Research: Atmospheres*, 113(D5). https://doi.org/10.1029/2007JD009260
- Jen, C. N., Bachman, R., Zhao, J., McMurry, P. H., & Hanson, D. R. (2016). Diamine-sulfuric acid reactions are a potent source of new particle formation. *Geophysical Research Letters*, 43(2), 867–873. https://doi.org/10.1002/2015GL066958
- Jen, C. N., Hanson, D. R., & McMurry, P. H. (2015). Towards Reconciling Measurements of Atmospherically Relevant Clusters by Chemical Ionization Mass Spectrometry and Mobility Classification/Vapor Condensation. Aerosol Science and Technology, ARL, 49, i–iii. https://doi.org/10.1080/02786826.2014.1002602
- Jen, C. N., McMurry, P. H., & Hanson, D. R. (2014). Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine. *Journal of Geophysical Research: Atmospheres*, 119(12), 7502–7514. https://doi.org/10.1002/2014JD021592

- Jen, C. N., Zhao, J., McMurry, P. H., & Hanson, D. R. (2016). Chemical ionization of clusters formed from sulfuric acid and dimethylamine or diamines. *Atmospheric Chemistry and Physics*, 16(19), 12513–12529. https://doi.org/10.5194/acp-16-12513-2016
- Jiang, J., Chen, M., Kuang, C., Attoui, M., & McMurry, P. H. (2011). Electrical Mobility Spectrometer Using a Diethylene Glycol Condensation Particle Counter for Measurement of Aerosol Size Distributions Down to 1 nm. Aerosol Science and Technology, 45, 510–521. https://doi.org/10.1080/02786826.2010.547538
- Johnson, J. S., & Jen, C. N. (2022). A sulfuric acid nucleation potential model for the atmosphere. *Atmospheric Chemistry and Physics*, 22(12), 8287–8297. https://doi.org/10.5194/acp-22-8287-2022
- Johnson, J. S., & Jen, C. N. (2023). Role of Methanesulfonic Acid in Sulfuric Acid–Amine and Ammonia New Particle Formation. ACS Earth and Space Chemistry. https://doi.org/10.1021/acsearthspacechem.3c00017
- Johnson, M., Sanders, R., Avgoustidi, V., Lucas, M., Brown, L., Hansell, D., Moore, M., Gibb, S., Liss, P., & Jickells, T. (2007). Ammonium accumulation during a silicate-limited diatom bloom indicates the potential for ammonia emission events. *Marine Chemistry*, 106(1), 63–75. https://doi.org/10.1016/j.marchem.2006.09.006
- Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., & Worsnop, D. R. (2010). A high-resolution mass spectrometer to measure atmospheric ion composition. *Atmos. Meas. Tech.*, *3*, 1039–1053. https://doi.org/10.5194/amt-3-1039-2010
- Kawamura, Kimitaka., & Kaplan, I. R. (1987). Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. *Environmental Science* & *Technology*, 21(1), 105–110. https://doi.org/10.1021/es00155a014
- Kerminen, V.-M., Chen, X., Vakkari, V., Petäjä, T., Kulmala, M., & Bianchi, F. (2018). Atmospheric new particle formation and growth: Review of field observations. *Environmental Research Letters*, 13(10), 103003. https://doi.org/10.1088/1748-9326/aadf3c
- Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kurten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., ... Kulmala, M. (2011). Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature*, 476, 429–433. http://www.nature.com/nature/journal/v476/n7361/abs/nature10343.html#supplementary-information

- Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., ... Curtius, J. (2016). Ion-induced nucleation of pure biogenic particles. *Nature*, *533*(7604), 521–526. https://doi.org/10.1038/nature17953
- Kuang, C. (2018). A diethylene glycol condensation particle counter for rapid sizing of sub-3 nm atmospheric clusters. Aerosol Science and Technology, 52(10), 1112–1119. https://doi.org/10.1080/02786826.2018.1481279
- Kuang, C., McMurry, P. H., McCormick, A. V., & Eisele, F. L. (2008). Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations. *Journal of Geophysical Research: Atmospheres*, *113*(D10209). https://doi.org/10.1029/2007jd009253
- Kuang, C., Riipinen, I., Sihto, S. L., Kulmala, M., McCormick, A. V., & McMurry, P. H. (2010). An improved criterion for new particle formation in diverse atmospheric environments. *Atmos. Chem. Phys.*, 10, 8469– 8480. https://doi.org/10.5194/acp-10-8469-2010
- Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petaja, T., Sipila, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Jarvinen, E., Aijala, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkila, J., ... Worsnop, D. R. (2013). Direct Observations of Atmospheric Aerosol Nucleation. *Science*, *339*(6122), 943–946. https://doi.org/10.1126/science.1227385
- Kulmala, M., Laaksonen, A., & Pirjola, L. (1998). Parameterizations for sulfuric acid/water nucleation rates. *Journal of Geophysical Research: Atmospheres*, 103(D7), 8301–8307. https://doi.org/10.1029/97JD03718
- Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W., & McMurry, P. H. (2004). Formation and growth rates of ultrafine atmospheric particles: A review of observations. *Journal of Aerosol Science*, 35, 143–176. http://dx.doi.org/10.1016/j.jaerosci.2003.10.003
- Kupiainen-Määttä, O., Olenius, T., Korhonen, H., Malila, J., Dal Maso, M., Lehtinen, K., & Vehkamäki, H. (2014). Critical cluster size cannot in practice be determined by slope analysis in atmospherically relevant applications. *Journal of Aerosol Science*, 77, 127–144. http://dx.doi.org/10.1016/j.jaerosci.2014.07.005
- Kupiainen-Määttä, O., Olenius, T., Kurtén, T., & Vehkamäki, H. (2013). CIMS Sulfuric Acid Detection Efficiency Enhanced by Amines Due to Higher Dipole Moments: A Computational Study. *The Journal of Physical Chemistry A*, 117(51), 14109–14119. https://doi.org/10.1021/jp4049764
- Kürten, A., Bergen, A., Heinritzi, M., Leiminger, M., Lorenz, V., Piel, F., Simon, M., Sitals, R., Wagner, A. C., & Curtius, J. (2016). Observation of new particle formation and measurement of sulfuric acid, ammonia, amines and highly oxidized organic molecules at a rural site in central Germany. *Atmospheric Chemistry and Physics*, 16(19), 12793–12813. https://doi.org/10.5194/acp-16-12793-2016
- Kürten, A., Bianchi, F., Almeida, J., Kupiainen-Määttä, O., Dunne, E. M., Duplissy, J., Williamson, C., Barmet, P., Breitenlechner, M., Dommen, J., Donahue, N. M., Flagan, R. C., Franchin, A., Gordon, H., Hakala, J., Hansel, A., Heinritzi, M., Ickes, L., Jokinen, T., ... Curtius, J. (2016). Experimental particle formation rates spanning tropospheric sulfuric acid and ammonia abundances, ion production rates, and temperatures. *Journal of Geophysical Research: Atmospheres, 121*(20), 12,377-12,400. https://doi.org/10.1002/2015JD023908
- Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., ... Curtius, J. (2014). Neutral molecular cluster formation of sulfuric acid–dimethylamine observed in real time under atmospheric conditions. *Proceedings of the National Academy of Sciences*, *111*(42), 15019–15024. https://doi.org/10.1073/pnas.1404853111
- Kürten, A., Li, C., Bianchi, F., Curtius, J., Dias, A., Donahue, N. M., Duplissy, J., Flagan, R. C., Hakala, J., Jokinen, T., Kirkby, J., Kulmala, M., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Onnela, A., Rissanen, M. P., Simon, M., Sipilä, M., ... McMurry, P. H. (2018). New particle formation in the sulfuric acid–dimethylamine–water system: Reevaluation of CLOUD chamber measurements and comparison to an aerosol nucleation and growth model. *Atmospheric Chemistry and Physics*, 18(2), 845–863. https://doi.org/10.5194/acp-18-845-2018
- Kurtén, T., Loukonen, V., Vehkamäki, H., & Kulmala, M. (2008). Amines are likely to enhance neutral and ioninduced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia. *Atmospheric Chemistry and Physics*, 8(14), 4095–4103. https://doi.org/10.5194/acp-8-4095-2008
- Larriba, C., Hogan, C. J., Attoui, M., Borrajo, R., Garcia, J. F., & de la Mora, J. F. (2011). The Mobility–Volume Relationship below 3.0 nm Examined by Tandem Mobility–Mass Measurement. *Aerosol Science and Technology*, 45, 453–467. https://doi.org/10.1080/02786826.2010.546820

- Lee, S.-H., Gordon, H., Yu, H., Lehtipalo, K., Haley, R., Li, Y., & Zhang, R. (2019a). New Particle Formation in the Atmosphere: From Molecular Clusters to Global Climate. *Journal of Geophysical Research: Atmospheres*, 124(13), 7098–7146. https://doi.org/10.1029/2018JD029356
- Lee, S.-H., Gordon, H., Yu, H., Lehtipalo, K., Haley, R., Li, Y., & Zhang, R. (2019b). New Particle Formation in the Atmosphere: From Molecular Clusters to Global Climate. *Journal of Geophysical Research: Atmospheres*, 124(13), 7098–7146. https://doi.org/10.1029/2018JD029356
- Lee, Y. H., Pierce, J. R., & Adams, P. J. (2013). Representation of nucleation mode microphysics in a global aerosol model with sectional microphysics. *Geoscientific Model Development*, 6(4), 1221–1232. https://doi.org/10.5194/gmd-6-1221-2013
- Lehtipalo, K., Ahonen, L. R., Baalbaki, R., Sulo, J., Chan, T., Laurila, T., Dada, L., Duplissy, J., Miettinen, E., Vanhanen, J., Kangasluoma, J., Kulmala, M., Petäjä, T., & Jokinen, T. (2022). The standard operating procedure for Airmodus Particle Size Magnifier and nano-Condensation Nucleus Counter. *Journal of Aerosol Science*, 159, 105896. https://doi.org/10.1016/j.jaerosci.2021.105896
- Lehtipalo, K., Yan, C., Dada, L., Bianchi, F., Xiao, M., Wagner, R., Stolzenburg, D., Ahonen, L. R., Amorim, A., Baccarini, A., Bauer, P. S., Baumgartner, B., Bergen, A., Bernhammer, A.-K., Breitenlechner, M., Brilke, S., Buchholz, A., Mazon, S. B., Chen, D., ... Worsnop, D. R. (2018). Multicomponent new particle formation from sulfuric acid, ammonia, and biogenic vapors. *Science Advances*, 4(12), eaau5363. https://doi.org/10.1126/sciadv.aau5363
- Li, H., Ning, A., Zhong, J., Zhang, H., Liu, L., Zhang, Y., Zhang, X., Zeng, X. C., & He, H. (2020). Influence of atmospheric conditions on sulfuric acid-dimethylamine-ammonia-based new particle formation. *Chemosphere*, 245, 125554. https://doi.org/10.1016/j.chemosphere.2019.125554
- Liang, Y., Jen, C. N., Weber, R. J., Misztal, P. K., & Goldstein, A. H. (2021). Chemical composition of PM_{2.5} in October 2017 Northern California wildfire plumes. *Atmospheric Chemistry and Physics*, 21(7), 5719–5737. https://doi.org/10.5194/acp-21-5719-2021
- Loukonen, V., Kurtén, T., Ortega, I. K., Vehkamäki, H., Pádua, A. a. H., Sellegri, K., & Kulmala, M. (2010). Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water – a computational study. *Atmospheric Chemistry and Physics*, 10(10), 4961–4974. https://doi.org/10.5194/acp-10-4961-2010

- McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., Kurtén, T., Kulmala, M., & Vehkamäki, H. (2012). Atmospheric Cluster Dynamics Code: A flexible method for solution of the birth-death equations. *Atmospheric Chemistry and Physics*, 12(5), 2345–2355. https://doi.org/10.5194/acp-12-2345-2012
- McMurry, P. H., & Eisele, F. L. (2005). Preface to topical collection on new particle formation in Atlanta. *Journal of Geophysical Research: Atmospheres*, 110(D22). https://doi.org/10.1029/2005JD006644
- McMurry, P. H., Fink, M., Sakurai, H., Stolzenburg, M. R., Mauldin, R. L., Smith, J., Eisele, F., Moore, K., Sjostedt, S., Tanner, D., Huey, L. G., Nowak, J. B., Edgerton, E., & Voisin, D. (2005). A criterion for new particle formation in the sulfur-rich Atlanta atmosphere. *Journal of Geophysical Research: Atmospheres*, *110*(D22). https://doi.org/10.1029/2005JD005901
- Merikanto, J., Napari, I., Vehkamäki, H., Anttila, T., & Kulmala, M. (2007). New parameterization of sulfuric acidammonia-water ternary nucleation rates at tropospheric conditions. *Journal of Geophysical Research: Atmospheres*, 112(D15). https://doi.org/10.1029/2006JD007977
- Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., & Carslaw, K. S. (2009). Impact of nucleation on global CCN. Atmospheric Chemistry and Physics, 9(21), 8601–8616. https://doi.org/10.5194/acp-9-8601-2009
- Murphy, D. M., & Fahey, D. W. (1987). Mathematical treatment of the wall loss of a trace species in denuder and catalytic converter tubes. *Analytical Chemistry*, *59*, 2753–2759. https://doi.org/10.1021/ac00150a006
- Myllys, N., Chee, S., Olenius, T., Lawler, M., & Smith, J. (2019). Molecular-Level Understanding of Synergistic Effects in Sulfuric Acid–Amine–Ammonia Mixed Clusters. *The Journal of Physical Chemistry A*, 123(12), 2420–2425. https://doi.org/10.1021/acs.jpca.9b00909
- Myllys, N., Ponkkonen, T., Passananti, M., Elm, J., Vehkamäki, H., & Olenius, T. (2018). Guanidine: A Highly Efficient Stabilizer in Atmospheric New-Particle Formation. *The Journal of Physical Chemistry A*, 122(20), 4717–4729. https://doi.org/10.1021/acs.jpca.8b02507
- Narukawa, M., Kawamura, K., Takeuchi, N., & Nakajima, T. (1999). Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires. *Geophysical Research Letters*, 26(20), 3101–3104. https://doi.org/10.1029/1999GL010810
- Olenius, T., Halonen, R., Kurtén, T., Henschel, H., Kupiainen-Määttä, O., Ortega, I. K., Jen, C. N., Vehkamäki, H., & Riipinen, I. (2017). New particle formation from sulfuric acid and amines: Comparison of

monomethylamine, dimethylamine, and trimethylamine. *Journal of Geophysical Research: Atmospheres*, *122*(13), 7103–7118. https://doi.org/10.1002/2017JD026501

- Olenius, T., Kupiainen-Määttä, O., Ortega, I. K., Kurtén, T., & Vehkamäki, H. (2013). Free energy barrier in the growth of sulfuric acid–ammonia and sulfuric acid–dimethylamine clusters. *The Journal of Chemical Physics*, *139*. https://doi.org/doi:http://dx.doi.org/10.1063/1.4819024
- Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., & Vehkamäki, H. (2012). From quantum chemical formation free energies to evaporation rates. *Atmospheric Chemistry and Physics*, 12(1), 225–235. https://doi.org/10.5194/acp-12-225-2012
- Panta, B., Glasoe, W. A., Zollner, J. H., Carlson, K. K., & Hanson, D. R. (2012). Computational Fluid Dynamics of a Cylindrical Nucleation Flow Reactor with Detailed Cluster Thermodynamics. *The Journal of Physical Chemistry A*, 116, 10122–10134. https://doi.org/10.1021/jp302444y
- Pöschl, U., Canagaratna, M., Jayne, J. T., Molina, L. T., Worsnop, D. R., Kolb, C. E., & Molina, M. J. (1998). Mass Accommodation Coefficient of H2SO4 Vapor on Aqueous Sulfuric Acid Surfaces and Gaseous Diffusion Coefficient of H2SO4 in N2/H2O. *The Journal of Physical Chemistry A*, *102*(49), 10082–10089. https://doi.org/10.1021/jp982809s
- Ranjithkumar, A., Gordon, H., Williamson, C., Rollins, A., Pringle, K., Kupc, A., Abraham, N. L., Brock, C., & Carslaw, K. (2021). Constraints on global aerosol number concentration, SO₂ and condensation sink in UKESM1 using ATom measurements. *Atmospheric Chemistry and Physics*, 21(6), 4979–5014. https://doi.org/10.5194/acp-21-4979-2021
- Riccobono, F., Rondo, L., Sipilä, M., Barmet, P., Curtius, J., Dommen, J., Ehn, M., Ehrhart, S., Kulmala, M., Kürten,
 A., Mikkilä, J., Paasonen, P., Petäjä, T., Weingartner, E., & Baltensperger, U. (2012). Contribution of sulfuric
 acid and oxidized organic compounds to particle formation and growth. *Atmospheric Chemistry and Physics*,
 12(20), 9427–9439. https://doi.org/10.5194/acp-12-9427-2012
- Riccobono, F., Schobesberger, S., Scott, C. E., Dommen, J., Ortega, I. K., Rondo, L., Almeida, J., Amorim, A.,
 Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R.
 C., Franchin, A., Hansel, A., Junninen, H., ... Baltensperger, U. (2014). Oxidation Products of Biogenic
 Emissions Contribute to Nucleation of Atmospheric Particles. *Science*, *344*, 717–721.
 https://doi.org/10.1126/science.1243527

- Riipinen, I., Sihto, S. L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V. M., Laaksonen, A., & Lehtinen, K. E. J. (2007). Connections between atmospheric sulphuric acid and new particle formation during QUEST III-IV campaigns in Heidelberg and Hyytiälä. *Atmos. Chem. Phys.*, 7, 1899–1914. https://doi.org/10.5194/acp-7-1899-2007
- Rozaini, M. Z. H. (2012). The Chemistry of Dicarboxylic Acids in the Atmospheric Aerosols. *Atmospheric Aerosols Regional Characteristics Chemistry and Physics*. https://doi.org/10.5772/50127
- Saltzman, E. S., Savoie, D. L., Zika, R. G., & Prospero, J. M. (1983). Methane sulfonic acid in the marine atmosphere. *Journal of Geophysical Research: Oceans, 88*(C15), 10897–10902. https://doi.org/10.1029/JC088iC15p10897
- Sauer, J. S., Simkovsky, R., Moore, A. N., Camarda, L., Sherman, S. L., Prather, K. A., & Pomeroy, R. S. (2021). Continuous measurements of volatile gases as detection of algae crop health. *Proceedings of the National Academy of Sciences*, 118(40), e2106882118. https://doi.org/10.1073/pnas.2106882118
- Semeniuk, K., & Dastoor, A. (2018). Current state of aerosol nucleation parameterizations for air-quality and climate modeling. *Atmospheric Environment*, 179, 77–106. https://doi.org/10.1016/j.atmosenv.2018.01.039
- Sihto, S. L., Kulmala, M., Kerminen, V. M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., & Lehtinen, K. E. J. (2006). Atmospheric sulphuric acid and aerosol formation: Implications from atmospheric measurements for nucleation and early growth mechanisms. *Atmos. Chem. Phys.*, *6*, 4079–4091. https://doi.org/10.5194/acp-6-4079-2006
- Simon, M., Heinritzi, M., Herzog, S., Leiminger, M., Bianchi, F., Praplan, A., Dommen, J., Curtius, J., & Kürten, A. (2016). Detection of dimethylamine in the low pptv range using nitrate chemical ionization atmospheric pressure interface time-of-flight (CI-APi-TOF) mass spectrometry. *Atmospheric Measurement Techniques*, 9(5), 2135–2145. https://doi.org/10.5194/amt-9-2135-2016
- Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L., Hyvärinen, A.-P., Lihavainen, H., & Kulmala, M. (2010). The Role of Sulfuric Acid in Atmospheric Nucleation. *Science*, 327, 1243–1246. https://doi.org/10.1126/science.1180315
- Sipilä, M., Sarnela, N., Jokinen, T., Junninen, H., Hakala, J., Rissanen, M. P., Praplan, A., Simon, M., Kürten, A., Bianchi, F., Dommen, J., Curtius, J., Petäjä, T., & Worsnop, D. R. (2015). Bisulfate – cluster based atmospheric pressure chemical ionization mass spectrometer for high-sensitivity (< 100 ppqV) detection

of atmospheric dimethyl amine: Proof-of-concept and first ambient data from boreal forest. *Atmospheric Measurement Techniques*, 8(10), 4001–4011. https://doi.org/10.5194/amt-8-4001-2015

- Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Mann, G. W., & Sihto, S.-L. (2006). The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales. *Atmospheric Chemistry and Physics*, 6(12), 5631–5648. https://doi.org/10.5194/acp-6-5631-2006
- Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Sihto, S.-L., Riipinen, I., Merikanto, J., Mann, G. W., Chipperfield, M. P., Wiedensohler, A., Birmili, W., & Lihavainen, H. (2008a). Contribution of particle formation to global cloud condensation nuclei concentrations. *Geophysical Research Letters*, 35(6), L06808. https://doi.org/10.1029/2007GL033038
- Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Sihto, S.-L., Riipinen, I., Merikanto, J., Mann, G. W., Chipperfield, M. P., Wiedensohler, A., Birmili, W., & Lihavainen, H. (2008b). Contribution of particle formation to global cloud condensation nuclei concentrations. *Geophysical Research Letters*, 35(6). https://doi.org/10.1029/2007GL033038
- Takahashi, K., Kasahara, M., & Itoh, M. (1975). A kinetic model of sulfuric acid aerosol formation from photochemical oxidation of sulfur dioxide vapor. *Journal of Aerosol Science*, 6(1), 45–55. https://doi.org/10.1016/0021-8502(75)90041-5
- Titcombe, M. E. (2012). New particle formation: Sulfuric acid and amine chemical nucleation, photochemical reaction chamber studies and the laboratory cluster-CIMS [Ph.D]. University of Minnesota Twin Cities.
- Vehkamäki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M., & Laaksonen, A. (2002). An improved parameterization for sulfuric acid–water nucleation rates for tropospheric and stratospheric conditions. *Journal of Geophysical Research: Atmospheres*, 107(D22), AAC 3-1-AAC 3-10. https://doi.org/10.1029/2002JD002184
- Viggiano, A. A., Perry, R. A., Albritton, D. L., Ferguson, E. E., & Fehsenfeld, F. C. (1982). Stratospheric negativeion reaction rates with H2SO4. J. Geophys. Res., 87, 7340–7342. https://doi.org/10.1029/JC087iC09p07340
- Viggiano, A. A., Seeley, J. V., Mundis, P. L., Williamson, J. S., & Morris, R. A. (1997). Rate Constants for the Reactions of XO₃⁻ (H₂O) n (X = C, HC, and N) and NO₃⁻ (HNO₃) n with H₂SO₄: Implications for Atmospheric Detection of H₂SO₄. *The Journal of Physical Chemistry A*, 101(44), 8275–8278. https://doi.org/10.1021/jp971768h

- Wang, C.-Y., Jiang, S., Liu, Y.-R., Wen, H., Wang, Z.-Q., Han, Y.-J., Huang, T., & Huang, W. (2018). Synergistic Effect of Ammonia and Methylamine on Nucleation in the Earth's Atmosphere. A Theoretical Study. *The Journal of Physical Chemistry A*, 122(13), 3470–3479. https://doi.org/10.1021/acs.jpca.8b00681
- Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., & Jefferson, A. (1996). Measured atmospheric new particle formation rates: Implications for nucleation mechanisms. *Chemical Engineering Communications*, 151, 53–64. https://doi.org/10.1080/00986449608936541
- Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., & Jefferson, A. (1997a). Measurements of new particle formation and ultrafine particle growth rates at a clean continental site. *Journal of Geophysical Research: Atmospheres*, 102(D4), 4375–4385. https://doi.org/10.1029/96JD03656
- Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., & Jefferson, A. (1997b). Measurements of new particle formation and ultrafine particle growth rates at a clean continental site. *Journal of Geophysical Research: Atmospheres*, 102(D4), 4375–4385. https://doi.org/10.1029/96JD03656
- Weber, R. J., McMurry, P. H., Mauldin, L., Tanner, D. J., Eisele, F. L., Brechtel, F. J., Kreidenweis, S. M., Kok, G. L., Schillawski, R. D., & Baumgardner, D. (1998). A study of new particle formation and growth involving biogenic and trace gas species measured during ACE 1. *Journal of Geophysical Research: Atmospheres*, 103, 16385–16396. https://doi.org/10.1029/97JD02465
- Xie, H.-B., Elm, J., Halonen, R., Myllys, N., Kurtén, T., Kulmala, M., & Vehkamäki, H. (2017). Atmospheric Fate of Monoethanolamine: Enhancing New Particle Formation of Sulfuric Acid as an Important Removal Process. *Environmental Science & Technology*, 51(15), 8422–8431. https://doi.org/10.1021/acs.est.7b02294
- Yao, L., Garmash, O., Bianchi, F., Zheng, J., Yan, C., Kontkanen, J., Junninen, H., Mazon, S. B., Ehn, M., Paasonen,
 P., Sipilä, M., Wang, M., Wang, X., Xiao, S., Chen, H., Lu, Y., Zhang, B., Wang, D., Fu, Q., ... Wang, L.
 (2018). Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. *Science* (*New York, N.Y.*), 361(6399), 278–281. https://doi.org/10.1126/science.aao4839
- Yu, F., & Luo, G. (2009). Simulation of particle size distribution with a global aerosol model: Contribution of nucleation to aerosol and CCN number concentrations. *Atmospheric Chemistry and Physics*, 9(20), 7691– 7710. https://doi.org/10.5194/acp-9-7691-2009

- Yu, F., Nadykto, A. B., Herb, J., Luo, G., Nazarenko, K. M., & Uvarova, L. A. (2018). H₂SO₄-H₂O-NH₃ ternary ionmediated nucleation (TIMN): Kinetic-based model and comparison with CLOUD measurements. *Atmospheric Chemistry and Physics*, 18(23), 17451–17474. https://doi.org/10.5194/acp-18-17451-2018
- Yu, H., McGraw, R., & Lee, S.-H. (2012). Effects of amines on formation of sub-3 nm particles and their subsequent growth. *Geophysical Research Letters*, 39, L02807. https://doi.org/10.1029/2011GL050099
- Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., & Molina, M. J. (2004). Atmospheric New Particle Formation Enhanced by Organic Acids. *Science*, 304(5676), 1487–1490. https://doi.org/10.1126/science.1095139
- Zhao, B., Shrivastava, M., Donahue, N. M., Gordon, H., Schervish, M., Shilling, J. E., Zaveri, R. A., Wang, J., Andreae, M. O., Zhao, C., Gaudet, B., Liu, Y., Fan, J., & Fast, J. D. (2020). High concentration of ultrafine particles in the Amazon free troposphere produced by organic new particle formation. *Proceedings of the National Academy of Sciences*, 117(41), 25344–25351. https://doi.org/10.1073/pnas.2006716117
- Zhao, J., Eisele, F. L., Titcombe, M., Kuang, C., & McMurry, P. H. (2010). Chemical ionization mass spectrometric measurements of atmospheric neutral clusters using the cluster-CIMS. *Journal of Geophysical Research: Atmospheres*, 115(D8). https://doi.org/10.1029/2009JD012606
- Zhao, J., Khalizov, A., Zhang, R., & McGraw, R. (2009). Hydrogen-Bonding Interaction in Molecular Complexes and Clusters of Aerosol Nucleation Precursors. *The Journal of Physical Chemistry A*, 113(4), 680–689. https://doi.org/10.1021/jp806693r
- Zhao, J., Ortega, J., Chen, M., McMurry, P. H., & Smith, J. N. (2013). Dependence of particle nucleation and growth on high-molecular-weight gas-phase products during ozonolysis of α-pinene. *Atmospheric Chemistry and Physics*, 13(15), 7631–7644. https://doi.org/10.5194/acp-13-7631-2013
- Zollner, J. H., Glasoe, W. A., Panta, B., Carlson, K. K., McMurry, P. H., & Hanson, D. R. (2012). Sulfuric acid nucleation: Power dependencies, variation with relative humidity, and effect of bases. *Atmos. Chem. Phys.*, *12*, 4399–4411. https://doi.org/10.5194/acp-12-4399-2012