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Connecting Chemistry and Climate through Aerosol Particles: Laboratory and Field Studies of Cloud Condensation Nuclei

A dissertation submitted in partial satisfaction of the requirements for the degree of

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in

Chemistry

by

Douglas Bradford Collins

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Professor Stanley J. Opella

2014
The Dissertation of Douglas Bradford Collins is approved, and is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2014
DEDICATION

To those that have supported, inspired, encouraged, and challenged...
EPIGRAPH

“When we try to pick out anything by itself, we find it hitched to everything else in the universe.”

*John Muir*

“If you can’t explain it simply, you don’t understand it well enough.”

*Albert Einstein*

“You play with the boat or the boat plays with you.”

*Marc-Oliver Klages*
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<tr>
<td>AR</td>
<td>Atmospheric River</td>
</tr>
<tr>
<td>ATOFMS</td>
<td>Aerosol Time-of-Flight Mass Spectrometer</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud Condensation Nuclei</td>
</tr>
<tr>
<td>CCNc</td>
<td>Cloud Condensation Nuclei Counter</td>
</tr>
<tr>
<td>CCSEM</td>
<td>Computer Controlled Scanning Electron Microscopy</td>
</tr>
<tr>
<td>chl-a</td>
<td>Chlorophyll-a</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation Particle Counter</td>
</tr>
<tr>
<td>CV</td>
<td>Central Valley (of California)</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analyzer</td>
</tr>
<tr>
<td>DMS</td>
<td>Dimethyl Sulfide</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved Organic Matter</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Analysis</td>
</tr>
<tr>
<td>GN</td>
<td>Giant (Cloud Condensation) Nuclei</td>
</tr>
<tr>
<td>MBL</td>
<td>Marine Boundary Layer</td>
</tr>
<tr>
<td>MOUDI</td>
<td>Micro-Orifice Uniform Deposit Impactor</td>
</tr>
<tr>
<td>MSA</td>
<td>Methane Sulfonic Acid</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near Edge X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>NPF</td>
<td>New Particle Formation</td>
</tr>
<tr>
<td>OC</td>
<td>Organic Carbon</td>
</tr>
<tr>
<td>OM&lt;sub&gt;aero&lt;/sub&gt;</td>
<td>Organic Matter in aerosols</td>
</tr>
<tr>
<td>OM&lt;sub&gt;sea&lt;/sub&gt;</td>
<td>Organic Matter in the ocean</td>
</tr>
<tr>
<td>PC</td>
<td>Pacific Cyclone</td>
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PSL……………………………………Polystyrene Latex (microspheres)
RH……………………………………Relative Humidity
RF……………………………………Radiative Forcing
SBJ……………………………………Sierra Barrier Jet
SEM……………………………………Scanning Electron Microscopy
SHS……………………………………Sloughhouse, CA
SMA……………………………………Secondary Marine Aerosol
SML……………………………………Sea Surface Microlayer
SOA……………………………………Secondary Organic Aerosol
SPD……………………………………Sugar Pine Dam (near Foresthill, CA)
SS………………………………………Sea Salt
SSA……………………………………Sea Spray Aerosol
STXM…………………………………Scanning Transmission X-ray Microscopy
TEM……………………………………Transmission Electron Microscopy
TOC……………………………………Total Organic Carbon
UF-ATOFMS………………………..Ultrafine Aerosol Time-of-Flight Mass Spectrometer
VOC……………………………………Volatile Organic Compound
## LIST OF SYMBOLS

- $a_w$.........................water activity
- $d$..............................aerosol diameter
- $d_a$............................aerodynamic diameter
- $d_{act}$.......................CCN activation diameter
- $d_{ae}$..........................area equivalent diameter
- $d_{dry}$.......................dry aerosol diameter
- $d_m$............................mobility diameter
- $d_{max}$......................upper limit diameter
- $d_{va}$.......................vacuum aerodynamic diameter
- $D$..............................droplet diameter
- $i$..............................van’t Hoff factor
- $m/z$..........................mass-to-charge ratio
- $M_w$..........................molecular weight of water
- $M_s$..........................molecular weight of solute
- $N_{CCN}$........................number concentration of CCN
- $OD_{pre}$......................pre-edge NEXAFS optical density
- $OD_{post}$......................post-edge NEXAFS optical density
- $p_w$..........................partial pressure of water vapor
- $p_w^*$........................equilibrium vapor pressure of water
- $r$..............................droplet radius
- $R$..............................universal gas constant
- $R_w$..........................gas constant for water vapor ($R/M_w$)
- $s$..............................supersaturation
$s_c$..........................critical supersaturation

$S$..........................saturation ratio

$T$..........................temperature

$T_{cf}$..........................CCNc chamber centerline flow temperature

$U$..........................wind speed

$U_{160}$..........................wind velocity component from 160° azimuth

$U_{250}$..........................wind velocity component from 250° azimuth

$V_w$..........................volume of water

$V_s$..........................volume of solute

$\Gamma$..........................surface excess

$\gamma$..........................activity coefficient

$\varepsilon$..........................volume fraction

$\kappa$..........................hygroscopicity parameter

$\lambda$..........................wavelength

$\rho_l$..........................density of water

$\rho_p$..........................aerosol particle density

$\rho_0$..........................reference density

$\sigma_{lv}$..........................liquid-vapor surface tension

$\phi$..........................dissolved volume fraction

$\chi$..........................dynamic shape factor
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ACKNOWLEDGEMENTS

This dissertation, the work it documents, and the perspective it provides would not be possible without the vision and training gained through my advisor, Prof. Kim Prather. Apart from being challenged to take on projects and roles that seem out of reach when started, I’ve learned to think broadly and include the big picture. I was told early that the best way to writing a good paper, is to read a lot of literature and have an understanding of the right questions. This key advice brought this dissertation to where it is today with a conceptual focus on making interdisciplinary connections. Kim always expected results which appeared in her email inbox to be fully vetted by the critical mind of each experimenter. Carefully considered analysis was often rewarded with a somewhat daunting, yet guiding list of open-ended questions that would spill back in a near stream of consciousness – often single ideas contained each in their own reply message, consistently ending in an ellipsis, but certainly all arriving back in my inbox within approximately four minutes of one another.

I would never have gotten to this point, of course, without the support, encouragement, and guidance afforded by my family and those that surrounded me in my early life. My parents have been nothing but supportive, through cross country moves, multiple grad schools, and sometimes totally unintelligible phone calls on Sundays about what I did (at work) that week. I’ve definitely started to see the impact each of them has made on my development to who I am today, and I’m thankful for each individual piece. They are responsible for setting up the litany of growing experiences that affect me to this day, including the many summers I enjoyed and grew at Cape Cod Sea Camps, which I think is one of the single most important and influential opportunities they ever afforded
me. They helped me through difficult attention deficit disorder and related issues, along with the sage advice and support of Dr. Bruce Roseman, who was not only a neurologist and mentor, but also a good friend, advocate, and role model. (He told me I needed to ‘save the world’ one day – that’s stuck with me always as I think of my future directions.) They put me through high school at Don Bosco Prep, ensuring I was in the most stimulating intellectual environment possible. Perhaps three of the most ‘legendary’ teachers at Bosco played key role in shaping my education there – Mr. Kevin Kilduff (Biology, Chemistry), Mr. Paul O’Connor (English), and Dr. Heidi Rohrs (German). These three seemed to know which students wanted more, I wasn’t the only one, and they had the unique ability to capture the attention of those students and help them feel like intellectualism was a good idea in a school that was quickly becoming a sports-focused powerhouse where thinking was not in great favor.

My time at Colgate changed the game, though, as college tends to do for many. I could define myself however I wanted. At the same time, the definitions that I thought were the ‘available options’ were totally out the window. It was 100% different culture from the one I grew up around in NJ. Colgate encourages students to learn by pushing them to challenge their teachers and mentors. If your teacher is stuck in what they know and how they think they know it, they’ll never help you learn anything new – hard questions are the heart of a good education. By my third year, I had come to realize the draw of environmental science, due to its pervasiveness and relevance to our lives. During those years I began to work with Profs. Keith Broekhuizen and Ephraim Woods in chemistry along with Prof. Karen Harpp in geology (who is an analytical chemist in disguise). While I didn’t have the top grades, they each seemed to know who I was better than I did. Karen
was a key driver in keeping my attention (as a chemist) in the earth sciences – truthfully she didn’t have to try all that hard – but was certain to always point out to me where the chemical sense fit in, helping me to remain curious in that way. I use what I learned from her just about every day now as an atmospheric chemist. While I thrived in geology, I actually struggled a bit with some of upper level chemistry. Prof. Woods was perhaps one of the best teachers I’ve ever worked with – through a very interesting way with words, he was able to make sense of initially obtuse topics as he taught thermodynamics. Some of the same tactics and explanatory style have entered my teaching ‘toolbox’ (a term he used often) when I not only teach others, but also when I try to teach myself something with which I’m having difficulty. Prof. Broekhuizen, as my research advisor, introduced me to the practical world of experimental physical and analytical chemistry. As was the policy at Colgate, he essentially taught me how to operate the setup I was meant to use, and essentially said, “Go at it.” Fostering independence and confidence in the laboratory setting is something I certainly credit to him. He was always there to help explain a new piece of the puzzle, but had the vision to make sure that I could make my own research decisions. After my time at Colgate, I transitioned to the University of New Hampshire, where I met some great people, learned a lot about the atmosphere, and had some really fun conversations with Dr. Karl Haase, my lab-mate and (coincidentally) house-mate, about new potential ways to measure things in the environment, using common sense to figure out how to fix household items, and many other abundantly nerdy things. During my year in New Hampshire, I began to develop a strong sense of what I wanted and needed in a graduate school – the only problem was, it wasn’t at UNH. My advisors, Prof. Barkley
Sive and Prof. Meg Greenslade, were more than supportive of my decision to continue my education elsewhere, and continue their support to this day, for which I am very grateful.

The two most important elements of a solid graduate education truly boil down to two things: resources and opportunity. Years spent working on a graduate degree are what the individual makes of them. The heights to which that individual can rise are often determined by their access to the best advice, environment, and tools. My graduate education at UCSD certainly has had each in good quality. Perhaps the best opportunity I was afforded is the ability to work within the emergent Center for Aerosol Impacts on Climate and the Environment (CAICE). Starting to work with the new Center in its Phase I stage during my third year at UCSD placed me in a veritable ball-pit of possibilities. Apart from the ability to work on developing the wave channel into an air-sea interaction facility, which we sometimes fondly called the ‘linear accelerator of sea spray particles’, at Scripps Institution of Oceanography and the early genesis of the now somewhat pervasive biological mesocosm and microcosm experiments, the most formative and important experience was my involvement in the proposal and review presentation process. This represented unprecedented access to the types of scientific, conceptual, and forward-thinking discussions that graduate students almost never experience. I owe a significant amount of my current ability to analyze data and generate new connections to my opportunities working with those who built CAICE from the ground up. The feverish support of those faculty members, like Professors Vicki Grassian, Tim Bertram, Grant Deane, Farooq Azam, Gil Nathanson, and Mario Molina, among several others, was both encouraging and confidence-building. Being able to stand in front of multiple NSF peer review panels, talk about both my research and my role as a graduate student within the
growing Center was of course a tangible opportunity that very few young scientists are afforded – one for which I am most grateful. I will remember the different approaches that the early high-level members of the Center used in their presentation style, the types of new directions they saw for CAICE science based on their current studies combined with inspiration from others in the room, and the special corner of science that truly is far closer to marketing and public relations.

Experimental efforts within CAICE were perhaps the most challenging I faced in all of graduate school. These experiments (documented in detail in this dissertation) exhibited a large number of degrees of freedom, even before the real chemical studies were undertaken. Dr. Rob Modini and Dr. Defeng Zhao worked very hard to make sure that the wave channel was characterized well, and that the data we got from it were of high quality. Their efforts were formative to the wave channel aerosol production studies performed thereafter, and to this day. Dr. Luis Cuadra-Rodriguez was an instrument-fixing guru – he always made careful measurements, which I tried to emulate. Dr. Tim Guasco kept things light in the lab, giving me perhaps the best Secret Santa gifts of anyone. Dr. Jess Axson made sure everyone was topped up on coffee, especially for the many consecutive 30-day phytoplankton bloom experiments we developed during her tenure in the lab. It’s been great to see Chris and Camille gain confidence and leadership skills, especially in the last 6 months or so – the lab will be in good hands! Mitch Santander, while quiet, makes very careful measurements and has really surprisingly hilarious comments when you don’t expect it. Josh Cox has been a really stellar undergrad, and I’m sure will do great things when he graduates, if not before!
My first draw to doing aerosol research at UCSD was the prospect of field work. Since most of my field projects were carried out prior to working with CAICE, they formed the basis of my training in making time-sensitive measurements in highly unconstrained environments. Field work, on the surface, seems like an act of making instruments behave for a period of weeks or months, all the while considering the measurements against the ambient conditions as you experience them and looking for reproducible trends. After a total of 2 months working at the SIO Pier with Cassie Gaston, Kaitlyn Suski, and Jack Cahill – it was clear that field work was more than meets the eye. Practical skills and problem solving were of paramount importance. Field laboratories are often makeshift shelters or mobile platforms which have large shifts in temperature and humidity. Stabilizing these variables is key for unadulterated datastreams. A thorough understanding of the instruments was also extremely important, as accurate troubleshooting is key for keeping downtime low and collateral damage limited. The ‘training’ field study at the SIO Pier helped set the stage for two deployments in the remote Sierra Nevadas which tested ingenuity, fortitude, driving abilities, and confidence.

Sugar Pine Dam, a remote field site near Foresthill, CA (just inside the border of Tahoe National Forest) at which I worked with Jessie Creamean during two consecutive winter seasons (2010 and 2011), joined by Liz Fitzgerald in the first year, and Jack Cahill during the second year. During the 2010 deployment, we were linked with a paired site in Mariposa, CA, where Melanie Zauscher, Kaitlyn, and Jack were stationed, along with Dr. Craig Corrigan (SIO) and Scott Noblitt (CSU), and finally Jake Lippman, who had the unenviable task of driving the length of the San Joaquin Valley every few days to transit between the two sites when needed. While the “Butterfly Crew” at Mariposa has one of
their less enjoyable field outings – Jack and Kaitlyn spent most of their time fixing SLY – most of the study at Sugar Pine was relatively smooth. We got snowed-out of our site a few times, which was good for precipitation sampling, we had a fair number of rain events, and everyone (myself included) found out that I was the doppelgänger of the 2010 Winter Olympic silver medal men’s singles figure skater, Russian ‘athlete’ Yevgeni Plushenko. Plushenko went on to do us both proud by publically slandering the American man who finally beat him for the gold medal, while disparaging the notion that he could have earned silver.

In 2011, we shared (the very cramped) mobile laboratory with Dr. Greg Roberts (SIO/Meteo France) and Dr. Scott Noblitt (CSU/SIO). Kaitlyn Suski and Dr. Alberto Cazorla were stationed at the airfield in Sacramento, as they were both involved with aircraft measurements of cloud droplet residues. They put in a huge effort in very difficult conditions, both on the ground and in the air! This second season was a record year for precipitation in the Sierra Nevadas – during our data workshop meeting in May, there was still many feet of snow at some of the observing sites. On several occasions, snowshoes were required to access our instruments at Sugar Pine, as the 1/4-mile access road to get there was behind a big yellow gate that played host to a few bullet-hole riddled signs. Rather than stepping ‘up’ into the trailer as we normally would, we were digging ramps down into the snow-bound lab. Greg’s natural ability to deal with the outdoors kept us in check. We had up to about 4 or 5 feet at one time, which was of course when one of JKE’s vacuum pumps decided to quit, forcing us to sled a new pump in from our spares storage back at the hotel. Luckily, Jack and Jessie decided to make use of the snowpack, building a very large snowball, which they ‘secretly’ (giggling loudly) propped in front of the Port-
o-John door while I was inside. My reaction, which was extremely calm in hindsight, was recorded on video by a very out-of-breath and self-proud Jack. I think it’s become clear that my field work was mostly associated with being made fun of by my lab-mates. It kept things interesting; we did a lot of laughing to keep morale up. I have to thank all of my field study compatriots for that.

Most recently, I was able to co-lead a field study with Dr. Andy Martin to Bodega Bay, CA, bringing along first-year grad students Hash Al-Mashat and Gavin “Lord Cromwell” Cornwell. We were joined by CSU scientists Dr. Ezra Levin and Christina McCluskey, who split the trip. Our kindness to the Oolok was rewarded with the 2 Hz foghorn soundings at end of Bodega Head, which wasn’t annoying at all while trying to sleep during the first week – although by the end, I was missing it. Hash and Gavin showed great fortitude, pushing through some pretty adverse instrument problems, including a trailer tire change on the way back to San Diego. I was flattered when Hash ‘thanked’ me for ensuring that their training throughout their first field project was all-encompassing.

I also want to be sure to thank Dr. Andy Ault, for continually reminding me during my first year that the problems I had with both the ATOFMS and Matlab were “user errors.” He was right, and those wise words are now known to come from my mouth for the benefit of new members of the lab. I’m still inspired by the way that Melanie Zauscher, Lindsay Hatch, and Meagan Moore always seemed to have the right question to ask during group meeting – I still ‘channel’ those types of thoughts when I’m listening to others. I have to thank Dr. Bob Moision and Dr. Alberto Cazorla for being awesome office mates.
who were very generous with their programming help in those early days of my time in the lab when Matlab was still something of a black box.

I’d like to thank my doctoral committee for their advice, comments, challenging questions, and support through my graduate career. I’ve had the chance to interact with some members more than others, but all have had an impact on my education. I’d like to be sure to thank our hard-working administrative assistants through the years, Paula Schachter, Carmen Alfaro, and most recently Krista Garcia, who are truly invaluable members of the group. Suzanne von Thaden, also a more recent addition to CAICE specifically, has brought a sense of refreshing urgency and business-like productivity to our academic environment, and has been a great person to work with and learn from.

Now, I look forward. I’ve not yet mentioned the most important person to come into my life: Sarah Smith, my bride-to-be. She has been nothing but supportive, understanding, and loving for the last four years, especially through the various intensive lab and field studies, late night writing sessions, and how I happen to sometimes ‘get involved’ at work. At the same time, she continually reminds me of how much more industrious, forward-thinking, affable, and brilliant she is compared to me; I absolutely admire her for each of those qualities and hope she never loses her Energizer-like drive. Overall, I don’t think I would have gotten through this experience without her, and I’m very excited that she’s agreed to spend her life with me so we can continue this journey together. It’s a good thing her class didn’t quite make it out of that CHEM 7L lab on time. Through her, I’ve also gained a group of really true friends in Alan, Abbas, and Sam, with whom I’ve had dinner at least once a week for four years. They are really are a lot more
like family than they are like friends. Friends don’t sit in the emergency room with your for four hours, trying desperately to crack a few jokes (most of which don’t land due to abject pain and inner frustration) while you wait to get a cast on the ankle you broke making an absolutely terrible slide during an intramural softball game – some family members aren’t even as loyal as that! The continually remind me what it means to feel a part of a close-knit group and also often remind me to loosen up and have a good time.


Phytoplankton Blooms. The dissertation author is the primary investigator and author of this paper.

Chapter 5 is in preparation for submission to *Geophysical Research Letters*: Collins, D.B. and K.A. Prather. Secondary marine aerosol formation during phytoplankton senescence. The dissertation author is the primary investigator and author of this paper.

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ABSTRACT OF THE DISSERTATION

Connecting Chemistry and Climate through Aerosol Particles: Laboratory and Field Studies of Cloud Condensation Nuclei

by

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Doctor of Philosophy in Chemistry

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The influence of aerosol particles on the Earth’s climate is a major driver of scientific uncertainty in assessing future conditions. The importance of aerosols in their role as cloud condensation nuclei (CCN) and ice nuclei (IN), known as the Aerosol Indirect Effect, is most poorly understood. The number concentration of CCN available to nucleate droplets can have important influences on cloud albedo, lifetime, and propensity to form precipitation. Natural sources are of particular importance, since the absolute influence of aerosols on cloud properties is highly sensitive to background concentrations of CCN.
before anthropogenic emissions. Chemical studies of sea spray aerosol (SSA) particles, the second most abundant type of natural aerosol globally, were conducted to better understand the influence of marine organic matter on CCN activity. While direct chemical measurements of aerosol particles with diameter \( d > 500 \) nm indicated that the production mechanism of SSA controls particle composition, especially with respect to the amount of organic matter transferred across the air-sea interface. CCN activity studies, on the other hand, showed a weak dependence on seawater organic matter concentration. The extent to which organic matter and sea salt were externally mixed for particles with \( d < 100 \) nm more strongly affected CCN activity than the overall volume fraction of organic matter in the population. Secondary aerosol formation, which was observed to be associated specifically with phytoplankton senescence in laboratory experiments could be an additional means of influencing marine clouds. Secondary aerosol were less CCN-active than SSA particles, but growth led secondary particles to contribute to CCN concentrations, and could potentially affect the formation of marine stratus clouds. Orographic clouds also form in pristine marine air masses over the Sierra Nevada Mountains. Below the marine clouds, highly CCN-active aerosols were redistributed by a barrier jet during winter storms and could influence rainfall in some regions of California. Overall, these studies show that chemistry is closely linked to climate through cloud droplet nucleation, and that studies of fundamental chemistry stemming from the complex systems described in this work could yield marked advances in scientific understanding of the indirect effect.
1. Introduction

Earth’s atmosphere consists of a wide variety of gaseous chemicals in which small liquid or solid particles are also suspended. Called an aerosol, this colloidal suspension of condensed phase particles within the continuous gas phase medium exists in highest concentration within the lowest ~10 km of the atmosphere [Seinfeld and Pandis, 2006]. Aerosol particles have been implicated in air pollution, visibility, human health, and have an important influence on the global climate [Pope and Dockery, 2006; Poschl, 2005; Stocker et al., 2013]. While to aerosol particles influence the climate through direct scattering and absorption of radiation (Section 1.3.1), a main focus of uncertainty in climate models is related to the ability to act as cloud condensation nuclei (CCN) – called the Aerosol Indirect Effect (Section 1.3.2). The role of chemistry as the ‘Central Science’ is accentuated through the Indirect Effect. Natural biological and geophysical processes interface with atmosphere and climate through physical chemistry at the heart of cloud droplet formation wherein aerosol particles act as condensation nuclei.

As an aerosol is a colloid, it is composed of a collection of individual particles. Each particle can often be distinguished by its chemical composition: the extent to which the individual particles in the aerosol population are chemically different from one another and/or fit into various chemical types is referred to as the ‘external’ mixing state. At the same time, individual particles can be mixtures of chemicals in and of themselves. The ‘internal’ mixing state is therefore characterized by the fractions of the individual particle’s mass that correspond to various compounds or chemical classes. The mixing state of aerosol particles, which is uniquely probed by analytical techniques that characterize
particles individually [Bzdek et al., 2012; Prather et al., 2008], has been shown to be important to the influence of aerosols on the environment [Posfai and Buseck, 2010], including their ability to act as CCN [Wex et al., 2010] or participate in heterogeneous chemical reactions with trace gases [Ault et al., 2014].

Throughout this dissertation, the confluence of chemistry and climatology within aerosol particles will become particularly evident. Figure 1.1 is a schematic that depicts the continuum that is the chemistry-climate spectrum. At the top of the diagram are fundamental parameters that describe the current global climate: Precipitation and Radiative Forcing. The latter, abbreviated RF herein, refers to the difference in radiant energy flux at the Earth’s surface between present day and pre-industrial times (before 1750 C.E.) [Stocker et al., 2013]. The influence of greenhouse gases on RF is largely understood. Far larger uncertainties exist in relation to the effects of aerosols on both RF and precipitation. Relationships extending from RF, to greenhouse gases, to the fundamental physical chemistry behind the molecular vibrations and rotations that give rise to the absorption of radiation in the atmosphere are relatively straightforward. Relationships between chemistry and climate through the ‘Aerosol’ channel appear much more complicated in comparison, reflecting the inherent complexity of molecular interactions in the condensed phase compared with the gas phase. Detailed relationships populate the center of the continuum, where chemistry and climate meet, while more general concepts that are fundamental to each field exist closer to the extents of each end member. While not all of these concepts will be discussed in this volume, attention will be focused on the importance of aerosols as CCN, their physicochemical properties, and the importance of CCN activity within both regional and global scale environmental issues.
1.1 Fundamentals of Cloud Droplet Nucleation

1.1.1 Köhler Theory

Cloud droplets nucleate in conditions where water vapor is supersaturated. The extent of supersaturation required to induce cloud droplet nucleation is determined by the properties of the potential CCN present. In general terms, the water vapor saturation ratio (S) is the ratio of the vapor pressure of water \( p_w \) to the equilibrium vapor pressure of water \( p_w^* \) at the given temperature (Equation 1.1)

\[
S = \frac{p_w}{p_w^*} \quad [1.1]
\]

While nucleation processes are often considered in terms of chemical kinetics, recent detailed studies of CCN activity indicate that any possible kinetic limitations to the accommodation of water during cloud droplet nucleation are insignificant [e.g., Moore et al., 2008; Padro et al., 2012]. These findings confirm applicability of the early work of Köhler, who expressed cloud droplet nucleation in terms of equilibrium thermodynamics. Köhler Theory (Equation 1.2) describes the dependence of S on the radius of an aqueous droplet (r) in equilibrium with the vapor [Kohler, 1936].

\[
S(r) = \left(1 - \frac{b}{r^3}\right) \exp\left(\frac{a}{r}\right)
\]

\[
a = \frac{2\sigma_{iv}}{\rho_i R_w T} \quad [1.2]
\]

\[
b = 3iM_w \frac{1}{4\pi\rho_i} \frac{m_s}{M_s}
\]
where \( i \) is the van’t Hoff factor, \( \rho_l \) is the density of the liquid, \( m_s \) is the mass of solute in the particle, \( \sigma_{lv} \) is the surface tension at the liquid-vapor interface, \( T \) is the temperature, \( M_w \) and \( M_s \) are the molar masses of the vapor and solute, respectively, and \( R_w \) is the gas constant for water vapor (\( R/M_w \)) [Curry and Webster, 1999]. The exponential term of Equation 1.2 describes the elevation of equilibrium vapor pressure over a curved surface (the Kelvin Effect), which becomes particularly important for aerosol particles with dry diameter (\( d_{dry} \)) less than 200 nm [McFiggans et al., 2006]. The parenthetical term is a form of Raoult’s Law, which describes the depression of equilibrium vapor pressure due to the presence of a solute. For particles where the Kelvin Effect term is appreciable (\( d_{dry} < 200 \text{ nm} \)), the Raoult’s Law term serves to dictate the partitioning of water between the vapor and the aqueous droplet. Figure 1.2 is a graphical representation of Equation 1.2, including curves corresponding to the Kelvin Effect and Raoult’s Law terms alone for comparison. In practical studies of CCN (and as shown in Figure 1.2), \( S \) is typically reported as the supersaturation percentage (\( s \)), according to Equation 1.2:

\[
S = (S - 1) \times 100 \quad [1.3]
\]

which is analogous to the use of RH in subsaturated conditions. The Köhler curve goes through a maximum at a value of \( s \) and \( r \), called the critical supersaturation (\( s_c \)) and the critical radius (\( r_c \)), which are characteristic of the nature of the solute and \( d_{dry} \).

### 1.1.2 The Hygroscopicity Parameter (\( \kappa \))

Chemistry enters the realm of CCN through the hygroscopicity of the solute and the surface tension at the liquid-vapor interface (\( \sigma_{lv} \)). It is possible to represent hygroscopicity, or the strength of the Raoult’s Law term in the Köhler equation, using a
single parameter (κ) [Petters and Kreidenweis, 2007]. By re-arranging Equation 1.2, the Köhler curve can be expressed in terms of the water activity (a_w):

\[ S = a_w \exp \left( \frac{4M_w \sigma_{lv}}{RT \rho_l D} \right) \quad [1.4] \]

where \( D = 2r \). Holding surface tension constant at the value for pure water (\( \sigma_{lv} = 0.072 \text{ N} \text{ m}^{-1}, T = 298.15 \text{ K} \)), one can encapsulate all of the effects of aerosol composition on CCN activation through apparent variations in \( a_w \). Petters and Kreidenweis [2007] introduced κ, which describes the water activity of the system by weighting the volume ratio of solute and water (\( V_s \) and \( V_w \), respectively):

\[ \frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \quad [1.5] \]

and has been shown to range from 0 to approximately 1.5 [Fuentes et al., 2011; Petters and Kreidenweis, 2007]. Incorporating Eq. 1.5 into Eq. 1.4 while assuming ideal solutions with additive component volumes, one obtains the governing equation for so-called κ-Köhler Theory:

\[ S(D) = \frac{D^3 - d_{dry}^3}{D^3 - d_{dry}^3 (1 - \kappa)} \exp \left( \frac{4M_w \sigma_{lv}}{RT \rho_l D} \right) \quad [1.6] \]

It is apparent that for a given \( d_{dry} \) and κ, the saturation ratio above the droplet can be determined. The desired measurement, therefore, is to find \( s_c \) for a sample while controlling \( d_{dry} \). If these two quantities are known, Equation 1.6 can be solved numerically by varying κ such that the maximum in \( S(D) \) is equivalent to the measured \( s_c \). The numerical solution converges when appropriate κ value for the \( s_c - d_{dry} \) pair has been
implemented. In this manner, the $\kappa$ can be thought of not only as a measure of aerosol hygroscopicity, but also a metric of apparent CCN activity (since $\sigma_v$ was assumed) [Petters and Kreidenweis, 2007; 2008; 2013], and will be used as such within this manuscript. CCN with multiple hygroscopic and fully water soluble solutes can be predicted using known $\kappa$ values for the each of the individual components. Assuming that the solutes do not interact (known as the Zdanovskii-Stokes-Robinson (ZSR) assumption [Stokes and Robinson, 1966]), a volume-additive mixing rule can be used [Petters and Kreidenweis, 2007](Equation 1.7).

$$\kappa = \sum_j \varepsilon_j \kappa_j \quad [1.7]$$

This mixing rule can be used in climate models to derive an average hygroscopicity for aerosol particles within the domain [Pringle et al., 2010], or alternatively, it can be used to back-calculate the volume fractions of each component within internally mixed aerosol [e.g., Quinn et al., 2014], perhaps described in simplified terms (e.g., salt + organics) or extended for any known mixing state for which $\kappa$ has been evaluated for each individual component.

1.1.3 Inclusion of Solubility

More complex adaptations to Köhler models have been developed in order to account for behavior associated with incomplete dissolution of solutes within an activating cloud droplet [Bilde and Svenningsson, 2004; Broekhuizen et al., 2004; Hori et al., 2003; Raymond and Pandis, 2003]. In a case such as this, it has been shown that quantitatively accounting for the solubility of each solute within the activating droplet allows for accurate
prediction of CCN activity [Bilde and Svenningsson, 2004]. This principle has been included in a more advanced version of the \( \kappa \)-Köhler model. Since \( \kappa \) represents a parameterization of the water activity within an activating cloud droplet, an adjustment can be made to this single parameter to account for only the dissolved material, rather than the total mass of the cloud droplet nucleus in the dry state. In practice, this can be achieved by including a factor representing the dissolved volume fraction (\( \phi \)) within the volume-additive mixing rule [Petters and Kreidenweis, 2008]:

\[
\kappa = \sum_j \varepsilon_j \kappa_j \phi_j \quad [1.8]
\]

\[
\phi_j = \frac{\left(\frac{D_j}{d_{j,\text{dry}}}\right)^3 - 1}{\varepsilon_j} C_{\text{sat},j} \quad [1.9]
\]

where \( C_{\text{sat}} \) is the equilibrium saturation concentration of the solute expressed in terms of volume of solute per volume of water, and the dissolved volume fraction (\( \phi \)) is forced to be \( \leq 1 \) when implemented in Equation 1.8.

Using the solubility-adapted \( \kappa \)-Köhler model, it is possible to conveniently explore the importance of weakly soluble materials chemical systems for which the physicochemical parameters required by the model can be prescribed, or at least assumed to reasonable accuracy. Sea spray aerosol particles that are produced at the ocean surface, for example, have been characterized as a mixture of sea salt and insoluble organic matter [e.g., Facchini et al., 2008]; measurements of aerosol particles enriched in marine organic matter (with little-to-no salt) have been shown to have weak hygroscopicity in laboratory experiments [Collins et al., 2013; Moore et al., 2008; Prather et al., 2013], perhaps
corroborating the qualitative ‘insoluble’ label despite the lack of a known $C_{sat}$ value for organic matter in the ocean (or in SSA particles). Figure 1.2(a,b) shows a comparison between the calculated $s_c$ for internally mixed salt/organic particles over a range of volumetric mixing ratios calculated using Equation 1.6. The dashed lines represent $s_c$ calculated by deriving $\kappa$ according to Equation 1.7, which assumes that the entire dry particle dissolves completely ($C_{sat} = \infty$). The solid lines use $\kappa$ values derived from Equation 1.8, with $C_{sat}$ for the salt fraction set to $1.6 \times 10^{-1}$ m$^3$ m$^{-3}$ (360 g kg$^{-1}$) and organics set to an arbitrarily low value of $1 \times 10^{-6}$ m$^3$ m$^{-3}$ (0.0013 g kg$^{-1}$). The solid and dashed curves are similar when the salt is > 10% of the (dry) particle by volume, but the calculated $s_c$ values begin to diverge as the mixing ratio becomes rich in the organic fraction. The weak solubility of the organic matter drives $s_c$ to higher values than those calculated using an assumption of infinite solubility, since a significantly smaller fraction of the particle dissolves, resulting in water activities that approach unity. As $a_w$ becomes close to 1, the Kelvin term dominates the behavior of the saturation ratio over the droplet (c.f. Equation 1.2), hence the trend of increasing $\Delta s_c$ with increasing organic fraction depends also on $d_{dry}$ (Figure 1.3). The percentage increase in $s_c$ associated with explicit accounting for solubility is also a function of the hygroscopicity of the weakly soluble component. It is interesting to notice that the solid curves in panels (a) and (b) of Figure 1.3 are the same; the stark differences observed in panels (c) and (d) are due to the differences in the dashed curves. The weak solubility is driving the behavior of the solid curves and the absolute calculated $s_c$ appears to be insensitive to the $\kappa$ value assigned to the organic fraction. Since $C_{sat}$ is set so low for the organic fraction, the influence of partial dissolution and dilution
through water uptake [Bilde and Svenningsson, 2004; Broekhuizen et al., 2004] is not relevant for this chemical system.

1.1.4 Surface Tension and Surfactant Partitioning

While simple inspection of the Equation 1.2 indicates that the liquid-vapor surface tension ($\sigma_{lv}$) plays an important role in CCN activation, systematic study of the impact of this parameter has only been conducted in the last 15 years [Facchini et al., 1999]. It is important to remember when considering surface tension, a concentration-dependent property of solutions, the physicochemical properties important to CCN activity must be evaluated under the conditions that exist at the activation point (when $s = s_c$, for instance) [Prisle et al., 2011; Ruehl et al., 2012]. The physical properties of modeled NaCl and malonic acid (MA) CCN with initial diameter ($d_{dry}$) of 45 nm are shown in Table 1.1, where the subscript ‘c’ denotes properties at the critical droplet activation point. The dependence of the volumetric growth factor ($V_c/V_{dry}$) on hygroscopicity is clearly significant ($\kappa_{NaCl} = 1.28$, $\kappa_{MA} = 0.22$), but overall, activating droplets can gain volume by a factor of up to $10^3$, significantly diluting the solute. Due to their amphiphilic nature, surfactants tend to partition to the air-liquid interface, thus exhibiting a relatively strong radial concentration gradient within the droplet. Some studies have argued that the partitioning of surface active compounds should be accounted for in Köhler models [Li et al., 1998; Prisle et al., 2008; Sorjamaa et al., 2004], but not all CCN activity findings require inclusion of this phenomenon in models to gain closure with measurements [Asa-Awuku et al., 2008; Broekhuizen et al., 2004; Frosch et al., 2011; Harmon et al., 2013; Moore et al., 2008].

Mathematical treatment of partitioning and the resulting influence on both the Kelvin Effect and Raoult’s Law terms within Köhler Theory (Equation 1.2) focus on the
accounting for the surfactant concentration in the droplet bulk \cite{Prisle2011,Raatikainen2011} and the apparent effects of increasing water activity in the solution, since surfactant molecules which have partitioned to the surface are then not considered not to be solvated based on the Gibbs equation \cite{Donaldson2006,Holmberg2002}. Due to the large ratio of surface area-to-volume of activating cloud droplets, surface coverage of surfactants may be lower than for bulk solutions of the same concentration. In addition only some of the most recent theoretical assessments have explicitly included effects important to ionic surfactants in electrolyte solutions \cite{Petters2013}, which represents a large fraction of atmospheric aerosols, and dynamic surface tension \cite{Petters2013}, since growing droplets are likely not in thermodynamic equilibrium at or above the critical activation point. A technique for direct measurements of the surface tension of aerosol particles is a much needed development. Due to the infancy of the fundamental scientific understanding of surface tension in micrometer-sized droplets, any implication of surface tension on observed CCN activity in this manuscript is discussed only at a generalized level.

### 1.2 Sources of Atmospheric Aerosol Particles

In order to assess coupling of the Earth and atmosphere, aerosol particles included in climate models are typically linked back to their sources. Each aerosol source typically has a characteristic particle composition and/or size distribution, which is a direct link to the aerosol physicochemical properties (e.g., CCN activity, optical properties) of interest to climatologists. Two main classes of sources exist: ‘primary’ and ‘secondary’.
1.2.1 Primary Aerosol

Primary aerosol particles are emitted in a condensed phase directly from a source, typically at the Earth’s surface. Anthropogenic primary aerosol sources include fires, emissions from incomplete combustion, meat cooking, and metalworking, among others [Poschl, 2005; Prather et al., 2008]. Primary emissions from human activities are often associated with aerosols composed of organic material, due to the abundance of combustion-related or pyrogenic anthropogenic particle sources. Natural primary sources include sea spray aerosol production at the ocean surface [de Leeuw et al., 2011; Lewis and Schwartz, 2004], lofting of mineral dust particles in arid terrestrial regions [Ginoux et al., 2012], ash-producing volcanic eruptions [Langmann, 2014], and primary biological particle production from vegetation [Despres et al., 2012]. Mineral dust and sea spray aerosol have the two highest aerosol fluxes of any aerosol source on Earth [Andreae and Rosenfeld, 2008], and as such can be critically important to the global climate as discussed in detail (Section 1.3.3).

Sea spray aerosol (SSA), in particular, is a chemically rich system wherein fundamental chemistry is central not only to the properties and reactivity of nascent particles [Ault et al., 2013a; Gantt and Meskhidze, 2013], but also in the mechanism of particle generation via bubble bursting [Collins et al., 2014; Lewis and Schwartz, 2004]. The composition of SSA has long been known to be a mixture of sea salt and organic matter [Blanchard, 1964; Duce and Hoffman, 1976; Novakov et al., 1997], however a comprehensive analysis of the size-resolved composition and mixing state SSA particles has only recently been described in detail [Ault et al., 2013b; Prather et al., 2013] and continues to be topic of research that is of great importance to the field [Meskhidze et al.,
The incorporation of organic matter into SSA particles in the open ocean is thought to be a function of the biological activity in the region from which the particles were produced [O’Dowd et al., 2004]. This concept was derived from long term measurements on the coast of Ireland, which is said to probe SSA emissions from the North Atlantic up to 500 km offshore [Ceburnis et al., 2008]. Seasonal-scale trends in aerosol composition in both the northern and southern mid-latitudes are in general agreement with the concept that biological activity induces enhancements in the quantity of organic aerosol mass in the marine boundary layer (MBL) [Sciare et al., 2009; Yoon et al., 2007]. Investigations of the fundamental details behind the relationship between marine biological activity (tracked with ocean surface chlorophyll-a) and the production of organic-containing SSA have not found such a straightforward linear relationship [Quinn et al., 2014; Rinaldi et al., 2013].

Studies probing the fundamental physical chemistry of the organic matter transfer process across the air-sea interface are the subject of portions of this manuscript.

1.2.2 Secondary Aerosol

Secondary aerosol particles are produced by chemical reactions between gas molecules which result in products that have low vapor pressure products. The atmosphere is an oxidizing environment, which can facilitate the formation of both inorganic and organic aerosols. Combustion is a major source of both nitrogen oxides (NO$_x = NO + NO_2$) and SO$_2$ in the atmosphere, wherein each can be oxidized to HNO$_3$ and H$_2$SO$_4$, respectively. When NH$_3$ or amines are available (emitted from agricultural and industrial activities [Sorooshian et al., 2008]), nitric and sulfuric acids are neutralized to form the corresponding ammonium salts. Ammonium sulfate is thermodynamically favored, however, provided sufficient quantities of base along with cool temperatures and high
humidity, ammonium nitrate can also form in the aerosol phase [Seinfeld and Pandis, 2006; Stelson and Seinfeld, 1982]. The formation of high concentrations of nitrate and sulfate-rich secondary aerosol is common in the Central Valley (CV) of California [Chow et al., 2006; Whiteaker et al., 2002], especially in winter when frequent temperature inversions concentrate pollutants near the ground [Pun and Seigneur, 1999; Watson and Chow, 2002]. The meteorological and chemical environment in the CV leads to serious particulate matter formation episodes, routinely placing several cities in the region amongst the 10 most polluted cities in the United States [Nolen et al., 2014].

Sulfate aerosol can be formed over the oceans via oxidation of dimethyl sulfide (DMS) [e.g., Ayers and Gras, 1991; Charlson et al., 1987], a volatile metabolite produced by microbiological activity [Nguyen et al., 1988]. The influence of trace gas emissions from phytoplankton blooms are highly uncertain, with some evidence supporting their importance in forming secondary aerosol in the MBL [Woodhouse et al., 2013], while others downplay the impacts of biogenic secondary aerosol in favor of as yet weakly characterized contributions from sea spray [Leck and Bigg, 2005; Quinn and Bates, 2011].

Volatile organic compounds (VOCs) from both biogenic and anthropogenic sources can be oxidized by various reactive species in the atmosphere (e.g., O3, OH, ·NO3, ·Cl), leading to the formation of secondary organic aerosol (SOA) [Kroll and Seinfeld, 2008]. The formation of SOA is perhaps the most heavily studied aerosol formation pathway over the last decade. Despite the highly branched and complex organic reaction mechanisms involved in its formation, SOA can be quite adequately described by its physicochemical properties (e.g., volatility, water solubility) [Jimenez et al., 2009; Kroll
et al., 2011], allowing for a relatively concise organic aerosol classification scheme
[Murphy et al., 2014] compared to the wide array of distinguishable compounds that may
be present in SOA [Putman et al., 2012].

SOA formation over the oceans is more weakly characterized than in continental
regions and has seen considerable debate in the literature, especially in the last decade
[Arnold et al., 2009; Hu et al., 2013; Meskhidze and Nenes, 2006; 2010], as most prior
work had focused on sulfate aerosol as the sole secondary particle type with an oceanic
source. At the heart of the weak characterization of SOA in the MBL is the overall poor
understanding of biogenic VOC fluxes across the air-sea interface [Carpenter et al., 2012].
The ocean has been shown to be a source of various VOCs, including isoprene [Shaw et
al., 2010], monoterpenes [Yassaa et al., 2008], aliphatic amines [Van Neste et al., 1987],
DMS [Nguyen et al., 1988], and halocarbons [Zhou et al., 2005]. Chemical mechanisms
including all of these trace gas classes have been invoked to explain secondary aerosol
formation in the marine environment in the literature, but specific processes have not
necessarily been assigned to sources with predictable or sensible global spatial orientation
in the environment [Dawson et al., 2012; Hoffmann et al., 2001; Hu et al., 2013; Meskhidze
and Nenes, 2006].

It has been suggested that marine secondary aerosol formation can be initiated
through new particle formation (NPF) in the free troposphere followed by downward
mixing back into the MBL [Clarke et al., 1998; Russell et al., 1998], suggesting that the
condensation sink near the ocean surface is too high to allow nucleation to take place
[Kulmala et al., 2004]. Early studies of marine secondary aerosol implicated DMS as a
precursor to sulfate aerosol [Bates et al., 1987; Charlson et al., 1987; Clarke et al., 1998; Quinn et al., 1993], to which the traditional H$_2$SO$_4$-based NPF mechanism could be easily applied [Sipila et al., 2010; Weber et al., 1996]. However, many recent measurements in the MBL indicate the prevalence of not only sulfate, but also nitrogen-containing organic material [Dall'Osto et al., 2012; Decesari et al., 2011; Mueller et al., 2009; Sorooshian et al., 2009] and the oxidation products of isoprene and monoterpenes [Bikkina et al., 2014; Hu et al., 2013] in secondary marine aerosol. Measurements of ultrafine particles during nucleation events have uncovered the importance of amines in addition to sulfuric acid in early particle growth [Bzdek et al., 2014; Smith et al., 2010] in agreement with fundamental chemical studies [Almeida et al., 2013]. In addition, Bork et al. [2014] have used computational studies to indicate that methanesulfonic acid (MSA), a commonly-occurring oxidation product of DMS [Saltzman et al., 1983], has the potential to enhance the formation of molecular clusters at the earliest stages of NPF and Dawson et al. [2012] have shown that MSA and alkyl amines can initiate particle formation through a ternary mechanism with water. Microbiological processes are known to induce the production of DMS [Zubkov et al., 2001] and aliphatic amines [Kiene and Hoffmann Williams, 1998; Lidbury et al., 2014], perhaps even during similar or coincident biochemical processes, although the air-sea flux of the amines is highly uncertain. In sum, there is great potential that NPF in marine regions is underestimated, especially over regions where biological activity is elevated.

1.3 Aerosol Particles and Climate

The global radiation budget, which exerts principal energetic control on the climate, is balanced by atmospheric agents that can reject and/or trap energy within the Earth
system. Greenhouse gases are well known to absorb infrared energy emitted by the Earth, trapping energy within the atmosphere. Atmospheric aerosols, on the other hand, are mostly implicated in scattering sunlight back to space, imparting a ‘cooling’ effect on the global climate system \cite{Satheesh and Moorthy, 2005; Stocker et al., 2013}. Aerosol particles participate in the radiation balance in two major ways: the ‘direct’ and ‘indirect’ aerosol effects.

### 1.3.1 Aerosol Direct Effect

The direct aerosol effect includes the interactions of light and aerosol particles through scattering and absorption. Light scattering by aerosol particles with diameters on the same length scale as the wavelength of interest are governed by Mie Theory. The scattering efficiency increases as a function of particle diameter ($d$) and depends also on refractive index, which is dictated by its composition \cite{Seinfeld and Pandis, 2006}. Aerosol size can also depend on the ambient relative humidity in tandem with the hygroscopicity of the particle \cite{Martin, 2000}, and therefore so too does the scattering efficiency \cite[e.g.,][]{Zieger et al., 2013}. Aerosol absorption, on the other hand, is dictated almost exclusively by aerosol composition \cite{Andreae and Gelencser, 2006; Flores et al., 2014; Laskin et al., 2010}. The total light absorption of aerosol particles, particularly those composed of combustion-derived black carbon (or soot), can be enhanced by the presence of a weakly-absorbing coating \cite{Lack et al., 2012; Moffet and Prather, 2009}. The role of this mixing state effect on light absorption has, however, not been observed in every case \cite{Cappa et al., 2012}, so further study to understand the fundamentals of this process is ongoing.
1.3.2 Aerosol Indirect Effect

The aerosol indirect effect encompasses a variety of interactions that aerosols have with altering clouds properties in their role as CCN [Lohmann and Feichter, 2005; McFiggans et al., 2006], to be discussed in detail in Sections 1.3.2.1 and 1.3.2.2. The indirect effect contains the largest uncertainty in global radiative forcing (RF) of any climate forcing category [Stocker et al., 2013; Storelvmo et al., 2009]. Indirect effect RF uncertainty is of such a significant magnitude that it precludes validation of climate sensitivity (the warming associated with a doubling of CO$_2$) using measured warming, which is a key gap in advancing quantitative predictions of the changing climate [Kiehl, 2007]. Overall, gaining a better understanding of the fundamental sources and activities of CCN in the environment will help lead to improved model estimates of the indirect effects of aerosols [Carslaw et al., 2013; Ghan et al., 2013].

1.3.2.1 Clouds and Radiation

Once the CCN activity of aerosols is known, these parameters can be then incorporated into global climate models [Pringle et al., 2010] to study the influence of aerosols on clouds in the global system. Originally studied in marine stratocumulus clouds, adding CCN to existing clouds allows the available liquid water to redistribute amongst the now greater number of particles available, reducing the average cloud drop size. Clouds with greater number concentrations of cloud droplets have higher albedo [Twomey, 1977] and a longer lifetime [Albrecht, 1989], both of which decrease the overall solar radiation flux at the Earth’s surface. Overall, increased number concentrations of CCN active aerosols in the atmosphere, especially in locations not heavily affected by urban pollution
[Andreae, 2007; Carslaw et al., 2013], are critically important to the radiation balance in the atmosphere through the indirect effect.

1.3.2.2 Aerosol-Cloud-Precipitation Interactions

The indirect aerosol effect is not limited to the influences of clouds on the radiation budget. Liquid clouds that have smaller average droplet sizes also have a weakened ability to induce the autoconversion of cloud droplets to hydrometeors, effectively suppressing or delaying precipitation [Rosenfeld et al., 2008b]. Reductions in precipitation due to anthropogenic pollution aerosols being ingested into typically pristine clouds, especially in orographic systems, have been recorded in a variety of locales [Jirak and Cotton, 2006; Rosenfeld, 2000; Rosenfeld and Givati, 2006; Rosenfeld et al., 2008a; Rosenfeld et al., 2007; Saleeby et al., 2011]. A duality is observed in aerosol-cloud-precipitation interactions, however. In deep convective systems, ingestion of high concentrations of CCN tend to enhance precipitation [Koren et al., 2012; Rosenfeld et al., 2008b], rather than the suppression effect discussed earlier. This is thought to be due, in part, to a select subset of aerosol particles (based on their composition) that can act as ice crystal nuclei [DeMott et al., 2010; Murray et al., 2013] since ice formation in clouds is a common driver of the formation of precipitation-sized hydrometeors [Pruppacher and Klett, 1997]. The influence of natural aerosols on precipitation enhancement in California’s Sierra Nevada Mountains [Creamean et al., 2013], for instance, are in contrast to the precipitation suppressing effects of local pollution sources [Fan et al., 2014]. While aerosol-cloud-precipitation interactions involving natural mineral dust and biological aerosols over the Sierra Nevada Mountains initiate precipitation within the California watershed, anthropogenic pollution from highly developed regions along the west coast of the United
States may be working to suppress precipitation [Fan et al., 2014; Rosenfeld et al., 2008a; Rosenfeld et al., 2014], potentially affecting the region’s water and energy supplies. Therefore, understanding the fundamental influence of aerosols on clouds in regions such as California, where water supply planning depends heavily on quantitative precipitation forecasts for a small number of storms each year [Dettinger et al., 2011], is critical for public policy and resource management.

1.3.3 Importance of Natural Aerosols in Understanding the Changing Climate

Natural aerosol particles represent the constant background signal upon which aerosol particles from anthropogenic activities are superimposed. In terms of the indirect effect, this superposition of anthropogenic particle effects on top of the effects due to natural aerosols is non-linear [Menon et al., 2002; Ramanathan et al., 2001]. The differential impact of anthropogenic aerosols on clouds in the present day climate relies critically on the quality of CCN concentration hindcasting for pre-industrial times (i.e. – pre-1750); the climate effects of natural aerosol particles are a main driver of uncertainty in the indirect effect within climate models [Carslaw et al., 2013]. Controlled studies of aerosol particles from natural sources in their nascent physicochemical state, like SSA particles [e.g., Prather et al., 2013], are therefore important for making improvements in the scientific understanding of both the pre-industrial atmosphere and the natural processes that persist through to the present day [Andreae, 2007; Satheesh and Moorthy, 2005; Tsigoridis et al., 2013].
1.4 Characterization of Aerosol Particles

Technological advancement in the chemical analysis of micrometer and nanometer-sized particles has taken significant strides within the past two decades [Bzdek et al., 2012; Prather et al., 2008; Pratt and Prather, 2012a; b]. Many of these techniques are based on mass spectrometry, due to its low detection limit and high throughput, although techniques involving spectroscopic principles like fluorescence [Pohlker et al., 2012] and laser-induced breakdown spectroscopy [Hahn, 2009] are developing. Real-time measurements of aerosols can be conducted for bulk samples as well as individual particles [Pratt and Prather, 2012a], which can be used in a complimentary manner [Drewnick et al., 2008], yield even more comprehensive results when combined with microspectroscopic analysis in an offline manner [e.g., Prather et al., 2013]. In relation to aerosol interactions with clouds, number concentrations of particles with various compositions and cloud droplet or ice crystal nucleation capacities are most important. Hence, single-particle chemical analysis, which can provide number-weighted fractions of aerosol types, are particularly useful. This section will focus on techniques that educate the chemistry involved in aerosol-cloud interactions.

1.4.1 Cloud Condensation Nuclei

Since physicochemical requirements exist for aerosols to act as CCN, it is possible to analyze an aerosol sample for the fraction of CCN-active particles. By carefully controlling the supersaturation of water vapor in air that is in contact with the aerosol sample, the number of particles that have grown to cloud droplet size (greater than 3 times larger than the size of the aerosol that acted as the nucleus) can be counted. In practice, an instrument called a continuous-flow streamwise thermal-gradient CCN counter, now
commercially-available and commonly referred to simply as a CCN counter (CCNc) [Lance et al., 2006; Roberts and Nenes, 2005; Rose et al., 2008], has become near standard practice for particle chemistry and aerosol-cloud interaction studies during the last decade.

Briefly, the CCNc operates by precisely controlling the saturation ratio \( S \) of water vapor in a cylindrical continuous flow chamber. This is achieved by applying an increasing thermal gradient along the length of the chamber, wherein the walls are continuously wetted with pure water. The chamber houses two concentric laminar air flows, a centerline flow containing the aerosol sample, and a particle-free sheath flow. The temperature of the air within the centerline flow \( T_{cf} \) is equal to the temperature of the wall \( T_1 \) at some point upstream since air is flowing through the chamber and there is a finite amount of time required for heat to diffuse radially. Similarly, \( p_w \) at any point along the centerline of the chamber represents \( p_w^* \) at the temperature of the wall \( T_2 \) from which the water vapor originated. When an increasing temperature gradient is applied along the length of the chamber such that \( T_2 > T_1 \) (remembering that \( T_1 = T_{cf} \)), at the centerline \( p_w(T_2) > p_w^*(T_{cf}) \), therefore \( S > 1 \) at the centerline (and the supersaturation \( s \) > 0, cf. Equations 1.1 and 1.3). The temperature difference between \( T_2 \) and \( T_1 \) drives the extent to which \( s > 0 \), so \( s \) is adjusted by changing the temperature gradient.

Aerosol particles flowing along the centerline of the chamber serve as condensation nuclei for the supersaturated water vapor according to Köhler Theory (Section 1.1). Particles that are CCN active at a particular \( s \) are counted by an optical particle counter, which measures the number concentration and size distribution of the droplets. By operating the CCNc in parallel with a condensation particle counter (CPC), which provides
the total number concentration of aerosol particles in the sample, the fraction of total aerosol that were CCN-active at a given $s$ can be obtained.

In order to probe the influence of chemistry on CCN activity, or to conversely probe the hygroscopicity of the aerosol, the effect of aerosol size on its ability to act as a cloud droplet nucleus can be removed by measuring the CCN activity of particles of a known size [e.g., Moore et al., 2010; Petters et al., 2007]. To achieve this, the CCNc and CPC are set to sample in parallel after aerosol particles are desiccated and size-selection is performed using a differential mobility analyzer (DMA) [Knutson and Whitby, 1975]. By systematically increasing $s$ within the CCN counter, an activation curve can be constructed by plotting the fraction of CCN-active particles as a function of $s$, which typically follows a cumulative Gaussian distribution function. The value of $s$ at which 50% of the particles are CCN active is designated as the critical supersaturation ($s_c$). Knowledge of $s_c$ and $d_{dry}$ (selected using the DMA) permits evaluation of the hygroscopicity parameter, $\kappa$ (Section 1.1.2) [Petters and Kreidenweis, 2007]. Similarly, this procedure can be conducted using a single setting of $s$ and stepping or smoothly scanning [Moore et al., 2010] through settings of $d_{dry}$ to find the size at which 50% of particles are CCN-active ($d_{act}$). Once the $\kappa$ value for various types of aerosol particles are known, these parameters can then be applied to aerosols from different sources within detailed models of the atmosphere so that aerosol-cloud interactions can be studied in a larger scale [e.g., Pringle et al., 2010; Westervelt et al., 2012].
1.4.2 Chemical Analysis of Individual Aerosol Particles

Early studies of aerosol chemical composition utilized sampling methodologies that involved collecting many particles onto a filter or other separation device before analysis. While this method was, and is still, sufficient for many types of detailed offline chemical analysis [Pratt and Prather, 2012b], the specific information about the mixing state of the aerosol particles is not accessible by this type of ‘bulk’ sampling method. The interactions between aerosols and clouds, as discussed in Section 1.3.2, are rooted in the number-weighted concentration of aerosol particles that can act as CCN, rather than the mass-weighted concentrations of aerosols returned by bulk analysis [Andreae and Rosenfeld, 2008]. The distinction between the mass and number concentrations of particles is especially important for the small aerosol particles \(d < 200\) nm [McFiggans et al., 2006]; particles in this size regime are far more numerous in the atmosphere than particles with \(d > 200\) nm, but carry very little mass [Seinfeld and Pandis, 2006]. One will also note that this size regime is also that in which CCN activity is most sensitive to particle composition [Dusek et al., 2006; McFiggans et al., 2006]. Chemical analysis of individual particles provides the advantage of directly characterizing the number-weighted fraction of different types of particles in the atmosphere [Prather et al., 2008].

The chemical composition of aerosol particles studied in this manuscript were measured using aerosol time-of-flight mass spectrometry (ATOFMS) [Prather et al., 1994]. This technique allows for the measurement of both the size and chemical composition of individual aerosol particles in real time [Noble et al., 1994; Nordmeyer and Prather, 1994]. Subsequent developments based on the first ATOFMS instrument now allow for the simultaneous measurement of both positive and negative mass spectra on a
portable platform [Gard et al., 1997], have the ability to measure individual particles as small as 80 nm [Su et al., 2004], retrieve aerosol optical properties [Moffet and Prather, 2005], and a recent major re-design for operation on research aircraft [Pratt et al., 2009].

While the details of the instrumental design and operating principles are covered thoroughly in the literature [Gard et al., 1997; Prather et al., 1994; Pratt et al., 2009; Su et al., 2004], a brief description will be provided here. Aerosol particles are introduced through an inlet into a set of differentially pumped vacuum chambers, each separated by a skimmer such that a collimated beam of particles is formed. Each particle travels through the instrument at its terminal velocity, which is characteristic of its vacuum aerodynamic diameter ($d_{va}$). This terminal velocity is measured using the time required for each particle to transit the beams of, and scatter the light from, two orthogonally-oriented continuous wave diode pumped solid state lasers (50 mW, $\lambda = 532$ nm) placed 6 cm apart. The particle velocity-to-aerodynamic diameter relationship is calibrated empirically using an array of polystyrene latex (PSL) microspheres of known diameter. The particle velocity information is then further utilized to synchronize a shot from a pulsed, frequency-quadrupled Nd:YAG laser ($\lambda = 532$ nm, 1.3 mJ, 7 ns pulse width), which serves to desorb the condensed phase aerosol particle into the gas phase and simultaneously ionize the molecules. Both positive and negative ions are then extracted into two reflectron time-of-flight mass spectrometers oriented antiparallel to one another, wherein the mass-to-charge ratios of the ions generated from the particles are measured.

When sampling ambient air in field locations, ATOFMS is able to provide the size-resolved chemical mixing state of aerosol particles between $d_{va} = 0.08 – 3 \mu m$, when
instruments with different inlet configurations [Gard et al., 1997; Su et al., 2004] are used in parallel. Positive ion mass spectra typically indicate the source of each particle in the environment, while the negative mass spectrum normally contains more information on its chemical aging history. For instance, a ‘sea salt’ positive ion mass spectrum would contain ion markers for Na$^+$, K$^+$, and Na$_2$Cl$^+$, among others, and would not typically change when subjected to reaction with reactive nitrogen in the atmosphere. On the other hand, the negative ion mass spectrum would contain a large ion marker for Cl$^-$ for freshly emitted sea salt, while chloride would be replaced by NO$_2^-$ and NO$_3^-$ ion markers after heterogeneous uptake of reactive nitrogen species in polluted coastal environments [Ault et al., 2013a; Ault et al., 2014; Gard et al., 1998; Ryder et al., 2014].

Single-particle mass spectrometry, like ATOFMS, is increased in analytical power when used in parallel with other chemical or physicochemical analysis techniques. Recent studies have used ATOFMS to analyze individual particles which nucleate ice crystals [Corbin et al., 2012], in parallel with spectromicroscopy techniques for detailed chemical analysis of SSA particles [Ault et al., 2013a; Ault et al., 2014; Collins et al., 2014; Prather et al., 2013], and has been used in parallel with ensemble aerosol chemical composition measurements to maximize the complementarity of each technique [Dall’Osto et al., 2013; Decesari et al., 2011], among other synergistic approaches.

The ability to directly measure both the internal and external mixing states of particles within a given sample is a powerful and unique capability of analytical techniques that can characterize particles individually [Posfai and Buseck, 2010; Prather et al., 2008]. The influence of mixing state on the CCN activity of aerosols has been well documented
in the literature [Broekhuizen et al., 2006; Collins et al., 2013; Padro et al., 2012; Wex et al., 2010] and the characterization of the mixing state of aerosols from various sources is still a critical issue within model studies [Bauer et al., 2008; Mann et al., 2014], especially with respect to the Indirect Effect [Meskhidze et al., 2011; Westervelt et al., 2012].

1.5 Interactions of Aerosols and Clouds: Outstanding Questions

As discussed in detail within Section 1.3.2, the interactions of aerosols with clouds can be broken down into two sections: (1) influences of aerosols on cloud radiative properties and (2) aerosol-cloud-precipitation interactions.

1.5.1 Marine Aerosols and CCN Activity

The influences of aerosol particles on the radiative properties of clouds are limited by the size distributions and number concentrations of particles in the pre-industrial (natural background) atmosphere and the CCN activities of particles from each of the various natural sources [Carslaw et al., 2013; Ghan et al., 2013; Menon et al., 2002; Ramanathan et al., 2001]. Hence, detailed studies of the flux, composition, and associated CCN-activity of natural aerosols, like SSA, are necessary. To this end, the total flux and size resolved composition of aerosols are critical pieces of information [Gantt and Meskhidze, 2013; Westervelt et al., 2012]. In order to experimentally access nascent SSA particles, controlled methods of aerosol production must accurately reproduce natural aerosol production mechanism(s) [de Leeuw et al., 2011; Lewis and Schwartz, 2004] are needed, however, currently there is not a widely-utilized standard method for generating SSA particles under controlled conditions [e.g., Fuentes et al., 2010]. Recently, SSA production and composition studies have been conducted in a large linear wave channel
[Prather et al., 2013], from which a promising benchtop-scale SSA generator has recently been developed to facilitate controlled bubble and SSA production studies [Stokes et al., 2013]. These types of devices which mimic the bubble size distributions of breaking waves in the open ocean [Deane and Stokes, 2002] can help address uncertainties in the transfer of organic matter across the air-sea interface within SSA. The enrichment of organic matter in SSA is thought to be associated with marine biological activity [O’Dowd et al., 2004], which is supported by agreement between parameterized model simulations and seasonal-scale measurements [Tsigaridis et al., 2013]. However, the relationship between chlorophyll-a and organic matter in SSA (used in aforementioned parameterizations) suffers from limited understanding at a fundamental level, as correlations in time series measurements show a time lag between the signals [Rinaldi et al., 2013] and recent in situ shipboard measurements show no difference in organic enrichment between nascent SSA samples \((d < 100 \text{ nm})\) from oligotrophic and eutrophic regions [Quinn et al., 2014].

Secondary marine aerosol has been suggested to strongly influence marine cloud properties, due to their large number concentrations and likely association with phytoplankton blooms [Kruger and Grassl, 2011; Meskhidze and Nenes, 2006]. Since field measurements of marine aerosol cannot unequivocally extricate changes in the primary and secondary sources of ocean-derived aerosols [Shank et al., 2012; Sorooshian et al., 2009], studies of the influence of trace gas-to-particle nucleation in the absence of SSA particles are necessary to carry out in a controlled laboratory environment. Since nature of marine secondary aerosol is difficult to tie to a single trace gas source [Quinn and Bates, 2011], and oceanic emission of reactive gases is not near complete [Carpenter et al., 2012], top down experiments exploring the formation of aerosols in relation to complex biological
systems are likely of high utility at present to place constraints on these biosphere-atmosphere interactions.

Overall, the outstanding questions that relate to the impacts of marine aerosol particles on climate can be summarized:

1. What is the characteristic number size distribution of SSA particles and how might the distribution change in response to changes in biological activity in the ocean?
2. Using an SSA generator which reproduces the physical processes involved in forming a breaking wave, can the composition of SSA from natural seawater be reproduced for detailed laboratory studies?
3. What is the influence of biological activity on the CCN activity of SSA particles? How do different types of microbes (bacteria, phytoplankton, etc.) influence the physicochemical properties of SSA? How might aerosol mixing state play a role?
4. What controls the transfer of organic material across the air-sea interface?
5. What qualities of marine biological activity are important to the formation of biogenic secondary aerosol formation in the marine boundary layer?

1.5.2 Aerosols, Clouds, and Precipitation in California

Aerosol-cloud-precipitation interactions apply most often at regional scales. The suppression (or delay of onset) of precipitation by entrainment of pollution aerosols into clouds has been observed consistently in a variety of locations, especially in systems where orographic forcing in important to precipitation formation [Jirak and Cotton, 2006;
Rosenfeld, 2000; Rosenfeld and Givati, 2006; Rosenfeld et al., 2008a; Rosenfeld et al., 2007; Saleeby et al., 2011]. Recently, however, aircraft ATOFMS measurements paired with chemical measurements of precipitation have uncovered the role of natural mineral dust and biological aerosol in the enhancement of precipitation in mixed-phase orographic clouds by initiating ice nucleation [Ault et al., 2011; Creamean et al., 2013]. The Sierra Nevada Mountains now exhibit a possible competition: the precipitation suppressing or delaying effects of the abundant pollution aerosol produced just to windward of the mountain range during the cool season, or the precipitation enhancing effects of trans-Pacific transported mineral dust and biological aerosol [Fan et al., 2014]. Since the effects of aerosols on the ultimate quantity of precipitation that falls on the windward slope of the Sierra Nevada Range are highly uncertain, ground-based measurements in this region must focus on the abundance and physicochemical properties of locally-sourced pollutant aerosols, so that they can be accurately represented in regional-scale weather models. Accurate quantitative precipitation estimates [Matrosov et al., 2014] are critical for driving real-time water management decisions [Ralph et al., 2013; White et al., 2013] during the few, yet significant, precipitation events that occur in California each year [Dettinger et al., 2011].

Science questions concerning the role of aerosols in modulating precipitation in the western United States can be summarized:

1. What are the sources of aerosol particles that can be ingested into orographic clouds over the Sierra Nevada Mountains?
2. What meteorological factors influence the spatial distribution of aerosol particles during winter storms?

3. What is the composition, CCN activity, and size distribution of aerosol particles observed in regions where orographic precipitation forms?

1.6 Synopsis and Goals of the Dissertation

This dissertation discusses the sources and properties of aerosol particles in the context of their influence on cloud albedo and mixed phase precipitation. In this way the importance of natural aerosols, SSA in particular, will be explored in the Chapters 2 – 5, while Chapter 6 documents a more applied approach to studying the properties of cloud-active aerosol through fieldwork. Specifically, Chapter 2 will discuss the production of SSA particles in the laboratory utilizing both a linear wave channel and a Marine Aerosol Reference Tank. Similarities and differences between the size-differentiated compositions of SSA particles produced by breaking waves, a plunging waterfall, and gas forced through sintered glass filters followed differences in the number size distributions of particles, indicating that the SSA production mechanism not only controls the size, but also the composition of the aerosol. Chapter 3 discusses the CCN activity of SSA particles generated during a heterotrophic bacteria-rich mesocosm experiment conducted in a wave channel. The relative abundance of small ($d < 100$ nm) particles with weak hygroscopicity was observed to suppress CCN activity to unprecedented levels for laboratory-generated SSA. Chapter 4 extends the study of SSA from biologically-active seawater, instead probing aerosol generated from seawater containing a phytoplankton bloom. CCN activity was remarkably consistent, with $\kappa > 0.8$ throughout all experiments. Chapter 5 moves into biogenic secondary aerosol formation occurring during phytoplankton senescence.
Aerosol nucleation spontaneously occurred only while chlorophyll-a was decreasing in the phytoplankton bloom microcosm, leading to a high number concentration of particles which had a hygroscopicity resembling secondary organic aerosol measured in terrestrial environments. Future directions in the study of the fundamental chemistry involved in the CCN activation of SSA particles and the proclivity for secondary aerosol formation to take place over phytoplankton blooms is discussed in Chapter 7. Chapter 6 switches to the atmosphere in the remote Sierra Nevada Mountains, where meteorological conditions are observed to significantly change the composition of aerosols observed. The confluence of pollutant aerosol from local sources in the CV and marine aerosol transported with the onshore flow of an Atmospheric River was observed during storms. The coincident observation of these two types of particles not observed outside of stormy periods perhaps indicated that these the polluted CV air and the more pristine AR mixed over the windward slope of the Sierra Nevada Mountains, providing a mechanism for the delivery of anthropogenic aerosols to low level orographic clouds in this region. Advances in coupling meteorological measurements with aerosol chemistry measurements and modeling is discussed in Chapter 7.

1.7 Acknowledgements

Olivia Ryder is acknowledged for assisting in the editing of this chapter.
## 1.8 Tables

**Table 1.1**: Physical properties of a NaCl particle at the CCN activation point.

<table>
<thead>
<tr>
<th></th>
<th>$s_c$ (%)</th>
<th>$d_{dry}$ (nm)</th>
<th>$D_c$ (nm)</th>
<th>$D_c/d_{dry}$</th>
<th>$SA_c/SA_{dry}$</th>
<th>$V_c/V_{dry}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.39</td>
<td>45</td>
<td>197</td>
<td>8.76</td>
<td>77</td>
<td>671</td>
</tr>
<tr>
<td>Malonic Acid</td>
<td>0.85</td>
<td>45</td>
<td>180</td>
<td>4</td>
<td>16</td>
<td>64</td>
</tr>
</tbody>
</table>
1.9 Figures

Figure 1.1: Schematic depicting the fundamental connections between chemistry and climate, focusing on the channel through CCN activity. The bold connections are discussed in detail throughout this dissertation. Dotted arrows pointing toward the ‘climate’ end-member represent side effects induced by changes in the parameters represented by more fundamental chemistry. The detailed relationships populating the center of the diagram tend to collapse into more general concepts (shown in red) toward each end member.
Figure 1.2: (a.) Graphical representation of the Kohler equation along with the Kelvin and Raoult terms individually. (b.) Hygroscopicity parameter isopleths in terms of $d_{dry}$ and $s_c$. 
**Figure 1.3:** Comparison of modeled $s_c$ as a function of salt volume fraction ($\varepsilon_{salt}$) for particles of two different dry sizes and two different assumed organic hygroscopicities. In panels (a.) and (b.), solid lines represent calculated $s_c$ as a function of $\varepsilon_{salt}$, while explicitly treating the solubility of each component, while the dashed curves assume all components are infinitely soluble in water. Panels (c.) and (d.) show the ratio of the solid curve to the dashed curve in (a.) and (b.) respectively, stressing the fact that the effect of including weak solubility is more pronounced for compounds that have greater hygroscopicity and provide the assumed $\kappa$ and $C_{sat}$ values used in each set of calculations.
1.10 References


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2. Direct Aerosol Chemical Composition Measurements to Evaluate the Physicochemical Differences between Controlled Sea Spray Aerosol Generation Schemes

2.1 Synopsis

Controlled laboratory studies of the physical and chemical properties of sea spray aerosol (SSA) must be underpinned by a physically and chemically accurate representation of the bubble mediated production of nascent SSA particles. Bubble bursting is sensitive to the physicochemical properties of seawater. For a sample of seawater with constant composition, any important differences in the SSA production mechanism are projected into the composition of the aerosol particles produced. Using direct chemical measurements of SSA at the single-particle level, this study presents an inter-comparison of three laboratory-based, bubble-mediated SSA production schemes: gas forced through submerged sintered glass filters (‘frits’), a pulsed plunging waterfall apparatus, and breaking waves in a wave channel filled with natural seawater. The size-resolved chemical composition of SSA particles produced by breaking waves is more similar to particles produced by the plunging waterfall than those produced by sintered glass filters. Aerosol generated by disintegrating foam produced by sintered glass filters contained a larger fraction of organic enriched particles and a different size-resolved elemental composition, especially in the 0.8 – 2 μm dry diameter range. Interestingly, chemical differences between the methods only emerged when the single-particle chemical analysis was size segregated; averaging the elemental composition of particles across all sizes masked the differences between the SSA samples. When dried, SSA particles generated by the sintered
glass filters had the highest fraction of particles with spherical morphology compared to the more cubic structure expected for pure NaCl particles, which can be attributed to the presence of additional organic carbon. In addition to an inter-comparison of three SSA production methods, the role of the episodic or ‘pulsed’ nature of the waterfall method on SSA composition was undertaken. In organic-enriched seawater, the continuous operation of the plunging waterfall mechanism resulted in the accumulation of surface foam and an over-expression of organic matter in SSA particles compared to those produced by a pulsed plunging waterfall. Throughout this set of experiments, comparative differences in the SSA number size distribution were coincident with differences in aerosol composition, indicating that the production mechanism of SSA exerts important controls on both the physical and chemical properties of the resulting aerosol with respect to both the internal and external mixing state of the particles. This study provides insight into the inextricable physicochemical differences between each of the bubble-mediated SSA generation mechanisms tested and the aerosol particles that they produce, and also serves as a guideline for future laboratory studies of SSA particles.

2.2 Introduction

Understanding the production and characteristics of natural atmospheric aerosol particles is critical for constraining their influence on our global climate [e.g., Carslaw et al., 2013; Charlson et al., 1992; Ghan et al., 2013; Lohmann and Feichter, 2005; Menon et al., 2002; Ramanathan et al., 2001; Tsagaridis et al., 2013] and for the accurate prediction of chemical processes in the atmosphere [Andreae and Crutzen, 1997; Brown and Stutz, 2012]. Sea spray aerosol (SSA) particles, which are ejected from the ocean surface through the disintegration of whitecap foam [Blanchard and Woodcock, 1957; de
Leeuw et al., 2011; Lewis and Schwartz, 2004], represent one of the most dominant types of natural atmospheric aerosol [Andreae and Rosenfeld, 2008]. The production flux and physicochemical properties of SSA that are emitted over the wide range of possible oceanic conditions are not sufficiently constrained for proper inclusion in climate models [de Leeuw et al., 2011; Gantt and Meskhidze, 2013; Lewis and Schwartz, 2004; Quinn and Bates, 2011; Tsiganidis et al., 2013].

While SSA has long been known to consist of both inorganic salts and organic material [Blanchard, 1964; Duce and Hoffman, 1976; Novakov et al., 1997], field studies during the past decade have suggested that the organic fraction of marine aerosol is enhanced when the particles are ejected from seawater that is host to elevated biological activity [e.g., O’Dowd et al., 2004]. Seasonal trends in organic aerosol mass supporting the influence of biological activity on SSA composition have been observed in the northern and southern mid-latitudes [Sciare et al., 2009; Yoon et al., 2007], but ambient studies cannot always unambiguously assign changes in the composition of SSA to specific primary, secondary, anthropogenic, and/or continental sources [Shank et al., 2012; Sorooshian et al., 2009].

Laboratory studies are quite commonly conducted to generate and study nascent SSA that is uncontaminated by particles found in the marine boundary layer that are produced by other sources. These studies produce SSA from disintegrating foam in natural seawater or proxy materials mainly by means of sintered glass bubblers or plunging water jets [Bates et al., 2012; Fuentes et al., 2010b; Hultin et al., 2010; Keene et al., 2007; Park et al., 2014; Sellegri et al., 2006; Tyree et al., 2007]. Since it is well known that SSA is
produced by the bursting of air bubbles at the sea surface [e.g., Blanchard and Woodcock, 1957; de Leeuw et al., 2011; Lewis and Schwartz, 2004], the differences between generation methods for SSA in the laboratory differ primarily by the method of bubble production. Recent reports indicate that pneumatic atomization does not produce particles of similar physical or chemical properties to those generated by bubble bursting [Fuentes et al., 2010b; Gaston et al., 2011]. Until recently, two different bubble production techniques have been utilized for laboratory studies of aerosol composition: (1) air (or N₂) forced through sintered glass filters [Cloke et al., 1991; Fuentes et al., 2010b; Keene et al., 2007; Park et al., 2014; Sellegri et al., 2006; Tyree et al., 2007; Wise et al., 2009], and (2) impinging water jets [e.g., Cipriano et al., 1983; Fuentes et al., 2010b; Hultin et al., 2010; Sellegri et al., 2006]. A new approach introduced by Prather et al. [2013] produces SSA using reproducible breaking waves in a linear wave channel filled with natural, filtered seawater. While laboratory waves may not reproduce all of the factors that lead to SSA production over the ocean, they do produce bubble size distributions that compare favorably with those measured in whitecaps [Deane and Stokes, 2002]. Consequently, aerosol generation by the wave breaking method provides the closest proxy to natural SSA currently available in a controlled environment.

Experiments to compare the characteristics of aerosols produced using sintered glass filters, plunging water jets or waterfalls, and breaking waves have shown that each has a distinctly different and characteristic size distribution [Fuentes et al., 2010b; Prather et al., 2013; Sellegri et al., 2006; Stokes et al., 2013]. Some inter-comparison studies have investigated water uptake properties of the aerosol as indirect measures of composition [Fuentes et al., 2010b; King et al., 2012], however, the findings of each study depend on
the specific operating conditions of each bubble-mediated aerosol generation method tested. In this study, direct chemical measurements of SSA generated using sintered glass filters and a plunging waterfall were compared against SSA produced by laboratory breaking waves to investigate the importance of reproducing various physical elements of the wave breaking process in the generation of nascent SSA in the laboratory. The impact of continuous bubble production, which can result in the accumulation of foam at the water surface several bubble layers thick, on the composition of SSA is also discussed.

2.3 Experimental Methods

Two sets of experiments were conducted: (1) the inter-comparison experiments to compare the production of SSA between sintered glass filters, a plunging waterfall, and breaking waves, and (2) the foam production experiments to study the effects of pulsed versus continuous foam production. The inter-comparison experiments were staged in the glass-walled wave channel in the SIO Hydraulics Laboratory, while the foam production experiments were carried out using a Marine Aerosol Reference Tank. The methodologies of both studies are described in this section.

2.3.1 Sea spray generation methods inter-comparison

Sea spray aerosol particles were generated using sintered glass filters, a plunging waterfall, and breaking waves in a 33x0.5x0.6 meter (length-width-water depth, 9900 L) glass-walled wave channel managed by the Hydraulics Laboratory at Scripps Institution of Oceanography (SIO), which has been recently adapted for ocean-atmosphere interaction studies [Prather et al., 2013], and is shown schematically in Figure 2.1. Prior to each experiment, the wave channel was filled with natural, coastal seawater from 275 m offshore.
and approximately 4 meters below the low tide line at the SIO Pier (La Jolla, CA; 32° 52.0’ N, 117° 15.4’ W). Detailed information on the seawater delivery system to the wave channel facility is provided by Prather et al. [2013]. All SSA generation methods tested in these inter-comparison experiments were operated using the same sample of seawater within 24 hours of filling the wave channel to ensure that the biogeochemical state of the seawater closely represented the natural seawater supply and chemical changes in the seawater itself were minimized. Sweep air that was filtered and scrubbed of reactive trace gases was supplied to the wave channel headspace continuously with a linear velocity of approximately 6 cm/s. Bubbles were generated using each of the three methods approximately 1 meter upstream of the sampling manifold, giving a particle residence time in the headspace of the wave channel of approximately 17 seconds.

2.3.1.1 Controlled breaking waves

Individual breaking waves were generated by a computer-controlled hydraulic paddle. The breaking waves were formed when a train of wave pulses of varying amplitude and speed generated at one end of the channel focus and superimpose to form a plunging breaker at a set location along the wave channel’s long axis. This hydraulic-paddle induced wave production at the SIO Hydraulics Laboratory wave channel facility is described in detail elsewhere [Callaghan et al., 2013; Deane and Stokes, 2002]. Waves were generated with a maximum frequency of 1 min⁻¹. Bubbles entrained in the water column by the wave breaking event penetrated to approximately at cm below the water surface. The lack of background particle contamination was verified every 5 minutes by generating a wave pulse train with an amplitude insufficient to induce a wave breaking event to ensure that the wave generation mechanism did not contaminate the sample.
2.3.1.2 Plunging waterfall

Specifically designed as a physical mimic to wave breaking, a plunging waterfall apparatus was implemented to generate aerosol in the same location of the wave channel where wave breaking occurs. In this technique, seawater was recirculated from the wave channel through a centrifugal pump to a horizontal slotted cylinder approximately 40 cm above the water surface. The recirculating flow to the waterfall apparatus was modulated with a 6 sec on/ 6 sec off cycle that allowed the foam patch at the waterfall impinging location to decay before plunging resumed. As a result of the modulated flow, the waterfall swept across a 30 x 50 cm patch of the wave channel surface, disturbing the surface and forming bubbles throughout the swept area. This system is based on the same design criteria used to engineer the plunging waterfall system in the Marine Aerosol Reference Tank described by Stokes et al. [2013].

2.3.1.3 Sintered glass filters

The setup utilized in this inter-comparison was similar to that implemented by Keene et al. [2007] and is identical to that utilized by Prather et al. [2013]. The distance from the top of the sintered glass filter, where bubbles are released into the water, to the water surface was approximately 35 cm, which is smaller than the 115 cm rise distance used by Keene et al. [2007]. Nitrogen gas was forced through two sintered glass filters of porosity ‘A’ (145-174 μm pore diameter) and four of porosity ‘E’ (4-8 μm pore diameter). Each set of glass filters of a particular porosity was supplied a total of 0.5 liters per minute N₂ gas, so that the gas flux for the two sets of bubble sizes was equal.
2.3.2 Foam production experiments

The impact of standing foam on SSA composition was investigated using the plunging waterfall mechanism in a Marine Aerosol Reference Tank (MART) system [Stokes et al., 2013]. The plunging waterfall utilized in the inter-comparison experiment performed in the wave channel (Section 2.3.1.2) is mechanistically similar to the aerosol generation system implemented in the MART. The plunging waterfall was operated in two modes: ‘continuous’ and ‘pulsed’. While in ‘continuous’ mode, the waterfall was continuously generated by recirculating water from the bottom of the tank to the waterfall apparatus suspended above the water surface through a centrifugal pump. In ‘pulsed’ mode, the recirculation flow to the waterfall apparatus was modulated with a 4 sec on, 4 sec off pattern. During the ‘on’ cycle, the flow rate of water was approximately 40 liters per minute.

Seawater for MART-based experiments was collected from the ocean surface 275 m offshore at the end of Scripps Pier, slightly different from the source of seawater used in the inter-comparison experiments. Results utilizing this unaltered seawater condition are labeled ‘Natural Seawater’ in Section 2.4.2. In order to perform this foam production experiment with high organic matter concentrations, the natural seawater sample was augmented with Guillard’s f/2 media (including 13 mg/L Na₂SiO₃; Aquatic EcoSystems, Inc., Apopka, FL) and was continuously supplied with cool white light (~100 μE m⁻², 6500 K; Phillips Alto II, F32T8/DX), allowing an unconstrained phytoplankton bloom to take place over the course of one to two weeks, in which the large majority of the autotrophic biomass consisted of diatoms. Proliferation of heterotrophic bacteria was observed upon phytoplankton senescence in agreement with the canonical view of biological processes
active within the microbial loop \cite{Pomeroy2007}. Chlorophyll-a concentrations reached as high as 140 mg m$^{-3}$ and then subsided to 20 mg m$^{-3}$, at which time the foam production experiments were conducted (Section 3.2). Autotrophic organisms, the abundance of which is indicated through the chlorophyll-a concentration, are well known to exude organic material, increasing the organic matter concentration in the seawater throughout the bloom lifetime. Heterotrophic organisms (e.g., bacteria, grazers) then process these organic exudates \cite{Ogawa2001,Teeling2012}, chemically altering the dissolved organic matter produced by the autotrophic biomass. This method of enriching the seawater with organic matter allows natural dynamic ecosystem processes to shape the composition of the organic matter in the seawater, similar to the types of interactions found in natural phytoplankton blooms \cite{Azam2007,Pomeroy2007,Teeling2012}. While the total chlorophyll-a concentration in these experiments is an indirect indicator of the autotrophic biomass, it is notable that various controlled SSA generation studies have shown that the amount of organic matter imparted to SSA is only a weak function of the seawater chlorophyll concentration, and depends instead on the amount and composition of organic matter in the seawater \cite{Ault2013,Collins2013,Park2014,Prather2013,Quinn2014}. Total organic carbon (TOC) concentrations in the seawater were measured by the high temperature combustion method (Shimadzu Scientific Instruments) after acidifying the sample with 12N hydrochloric acid. While the exact molecular identity of the organic compounds in the seawater in these experiments was not known, the composition of the seawater utilized in this experiment can be reasonably expected to be more chemically similar to regions of the ocean that are naturally organic matter-enriched than a salt water
mixture doped with organic proxy molecules. This experiment therefore also benefits from naturally accurate influences of organic matter physicochemical properties on bubble physics and sea surface microlayer properties.

2.3.3 Aerosol measurements

All aerosol measurements were conducted after passing the sample through silica gel diffusion driers to attain a relative humidity of < 15%. Number size distributions of aerosol particles were measured using a scanning mobility particle sizer (SMPS) for particles with mobility diameters \(d_m\) between 0.013 and 0.7 um, and an aerodynamic particle sizer (APS) for particles with an aerodynamic diameters \(d_a\) between 0.6 and 20 um. Size distributions from these two different instruments, with different aerosol size metrics were unified by converting both \(d_m\) and \(d_a\) to the physical diameter \(d_p\) according to Equations 2.1 and 2.2 [DeCarlo et al., 2004], assuming all particles were spherical and had a density \(\rho_p\) of 1.8 g cm\(^{-3}\) [Zelenyuk et al., 2007] and a reference density \(\rho_0\) of 1 g cm\(^{-3}\).

\[
d_p = d_m \quad [2.1]
\]

\[
d_p = d_a \left(\frac{\rho_0}{\rho_p}\right)^{\frac{1}{2}} \quad [2.2]
\]

Since particles were dried prior to sampling, the spherical particle assumption may not be accurate in all cases. SSA is an external mixture of particles with different compositions [Collins et al., 2013; Prather et al., 2013], including size dependent differences in
Caution is therefore encouraged when making quantitative comparisons between SSA size distributions reported using different methods.

The size resolved chemical composition of SSA was characterized by aerosol time-of-flight mass spectrometry (ATOFMS). Two ATOFMS instruments were used in parallel: one was fitted with a converging nozzle inlet [Gard et al., 1997] and measured particles with vacuum aerodynamic diameters ($d_{va}$) between 0.5 – 3 μm, while a second, using an aerodynamic lens inlet [Su et al., 2004], measured particles with $d_{va}$ between 0.1-2.5 μm. In both ATOFMS instruments, particles transmitted through the inlet reach a size-dependent terminal velocity in a differentially pumped vacuum chamber, where they intersect two continuous wave lasers (532 nm; 50 mW) positioned at a fixed distance along the flight trajectory. The light scattered as the particle intersects each beam is collected and the time between each set of light scatter pulses is used to determine the velocity of each particle. Particle velocities are converted to $d_{va}$ using a calibration curve generated using polystyrene latex (PSL) spheres of known diameter (density = 1.05 g cm$^{-3}$). In order to make convenient correspondence with the number size distributions presented herein, $d_{va}$ was converted to $d_p$ using the density of PSL in this case for $\rho_0$ (Equation 2.3); however, caution in making comparisons is again encouraged due to the inherent morphology and density assumptions required for conversions between size metrics.

$$d_p = d_{va} \frac{\rho_0}{\rho_p} \quad [2.3]$$

The measured particle velocity is also used to trigger a pulsed, Q-switched Nd:YAG laser (266 nm; 1.3 mJ; 7 ns) that intersects each particle in the ion source region of the mass
spectrometer, where particle desorption and ionization occur using a single laser pulse. Positive and negative ion time-of-flight mass spectra are obtained for each particle. Information about the ATOFMS is provided in greater detail in prior publications [Gard et al., 1997; Su et al., 2004]. ATOFMS data were post-processed using the YAADA toolkit (http://www.yaada.org) for Matlab (The Math Works, Inc.). Particles were classified according to their mass spectral signatures using a neural network algorithm, Art-2a [Song et al., 1999] with a vigilance factor of 0.85 and a learning rate of 0.05. The resulting clusters were then refined by regrouping with a threshold of 0.90. Five distinct particle types (Figure 2.2) were formed by manually based on their characteristic mass spectra based on the classifications described by [Prather et al., 2013].

In addition to in situ single-particle composition measurements using ATOFMS, SSA samples were collected for offline analysis by scanning electron microscopy (SEM). Aerosol samples were deposited on silicon wafer substrates using a micro-orifice uniform deposit impactor (MOUDI; MSP Corporation). SEM images were collected using a Hitachi S-4800 Scanning Electron Microscope with a 5 kV accelerating voltage and a 9.2-9.6 mm working distance. Single particle analysis was performed using computer controlled SEM combined with an IXRF Systems energy dispersive x-ray (EDX) spectrometer (CCSEM/EDX). EDX data were analyzed with Iridium Ultra software (IXRF Systems) for automated particle analysis. The computer controlled system analyzes the sample on a field-by-field basis. Once particles are identified in a field of view, the software acquires an x-ray spectrum for each particle. X-ray spectra were acquired for 20 seconds at a beam current of 15 μA and an accelerating voltage of 5 kV. Particle size was
determined by automated measurement of the area of each particle. The area equivalent diameter \((d_{ae})\) was then calculated using Equation 2.4:

\[
d_{ae} = \left( \frac{4A}{\pi} \right)^{\frac{1}{2}} \tag{2.4}
\]

where \(A\) is the geometric area of the particle in the image. Conversion of \(d_{ae}\) to \(d_p\) for particles deposited on MOUDI substrates are associated with uncertainty in particle shape. The shape of particles deposited on a substrate depends on viscosity and surface tension [O’Brien et al., 2014], neither of which are known for SSA. Consequently, particle sizes within the CCSEM/EDX analysis were not converted to \(d_p\).

In total, 2187 particles with \(d_{ae}\) between 0.3 and 3 μm were analyzed. Any particle intersected by the boundary of the image was neglected to ensure that only particles that were completely imaged are included in the analysis. All measured particles were segregated into size bins for analysis. The number of particles analyzed in each size bin for each aerosol generation method can be found in Table 2.1.

2.4 Results

2.4.1 SSA generation method inter-comparison and particle composition

The physicochemical properties of SSA particles have been associated with the physical characteristics of bubbles in many prior publications [e.g., Blanchard and Woodcock, 1957; de Leeuw et al., 2011; Fuentes et al., 2010b; King et al., 2012; Lewis and Schwartz, 2004; Sellegrí et al., 2006], however, direct comparison with SSA produced by a breaking wave in the laboratory, assumed to be a good proxy for nascent sea spray, has only recently been realized [Prather et al., 2013]. The physicochemical characteristics of
aerosol production from bubble bursting have been linked not only to the size distribution of SSA [Fuentes et al., 2010b; Prather et al., 2013; Sellegri et al., 2006], but also to the water uptake properties of SSA particles [Fuentes et al., 2010b; King et al., 2012]. This study extends prior investigations by directly probing the influence of bubble bursting mechanisms on the detailed composition of SSA particles using direct chemical measurements at the single-particle level.

As discussed earlier, aerosol particles were generated using breaking waves, a plunging waterfall, and sintered glass filters in natural seawater. The laboratory breaking waves used here have bubble size distributions that are representative of those observed in open-ocean waves [Deane and Stokes, 2002] and particles from the breaking waves are taken to be the best proxy for oceanic SSA. As discussed by [Prather et al., 2013], the number size distribution of SSA particles derived from sintered glass filters had a modal diameter of approximately 60 nm, whereas the plunging waterfall and wave breaking particles exhibit modal diameters of approximately 190 and 200 nm, respectively (Figure 2.3). The differences in size distribution shape and modal diameter suggest that the dominant SSA production mechanism of SSA from the sintered glass filters could be different from SSA produced by wave breaking and the plunging waterfall. On the other hand, differences in the number size distribution of aerosols produced by each method could feasibly result from simple scaling of aerosol sizes to the bubble sizes (as is accepted for the jet droplet mechanism, [Lewis and Schwartz, 2004]), since bubbles from the sintered glass filters did not produce bubbles larger than 1 mm [Prather et al., 2013]. If this were the case, the size-resolved composition and mixing state of the SSA produced by each method would be expected to be identical.
2.4.1.1 Mixing state measurements by ATOFMS

Sea spray aerosol is composed of a mixture of aerosol particles that are chemically distinct, yet fall into several defined types: this is referred to as the ‘external’ mixing state. For this inter-comparison, the chemical mixing state of 47,927 individual SSA particles generated by controlled breaking waves, plunging waterfall, and sintered glass filters were measured using ATOFMS. The particles were grouped into four types previously described by Prather et al. [2013]: sea salt (SS), sea salt with organic carbon (SS-OC), biological (Bio), and organic carbon-dominated (OC). A fifth type labeled “Other” contains Art-2a clusters with minor contributions and/or are attributed to contamination from lab air. A representative dual-polarity mass spectrum for each particle type is provided in Figure 2.2. The SS type is characterized by prominent ion markers for Na and Cl, with smaller contributions from other inorganic species known to exist in seawater (e.g., K, Ca, Mg). The SS-OC type is characterized by a larger ratio of organic marker ions (CN\textsuperscript{-} and CNO\textsuperscript{2-}, for example) to chloride. In addition, the contribution of salt ion clusters (NaCl\textsubscript{2}\textsuperscript{-}, MgCl\textsubscript{3}\textsuperscript{-}) is greater in the SS-OC type than in the SS type, and the total absolute intensity of these mass spectra were smaller than for SS. Particles within the SS-OC type had a similar size distribution to SS-OC particles measured by transmission electron microscopy with energy dispersive x-ray analysis (TEM-EDX) in prior studies of nascent SSA produced by wave breaking [Ault et al., 2013; Prather et al., 2013]. It is notable that both the SS and SS-OC types have different size distributions and mass spectral signatures, yet both contain markers for organic material (e.g., CN\textsuperscript{-}). The ‘Biological’ (Bio) particle type is characterized by the presence of positive ion markers for Mg, Ca, and transition metals with organic nitrogen, phosphate, and carbohydrate negative ion markers [Guasco
et al., 2013; Pratt et al., 2009]. The ‘Organic-Carbon Dominated’ (OC) particle type has a large Ca ion marker, with Na also present but to a smaller degree than in the SS and SS-OC types. The negative ion spectrum contains markers for organic nitrogen, carbohydrates, phosphate, and chloride. The presence of Ca in this particle type is in correspondence with CCSEM/EDX analysis presented below and discussed further in Section 2.4.1.2 in the context of the marine organic matter literature.

Particles with $d_{va} > 1 \mu m$ were characterized by large number fractions of SS and Bio particles, while particles with $d_{va} < 1 \mu m$ were dominated by SS-OC and OC particles. The size-resolved chemical composition of SSA produced by each of the bubble generation methods shown in Figure 2.3a is shown alongside the corresponding number size distributions for each method in Figure 2.3b. The sampling efficiency for particles with $d_{va} > 1 \mu m$ in these experiments was greater than for particles with $d_{va} < 1 \mu m$. Therefore, the ability of the ATOFMS to chemically speciate particles at sizes approaching $d_{va} = 0.1 \mu m$ was dependent on the number concentration of particles present at that size. The sintered glass filters produce approximately 10-fold higher size-resolved number concentrations than the other two methods (Figure 2.3b).

The fraction of OC particles is higher for all measured sizes in the sintered glass filter-generated SSA particles compared to wave breaking, whereas the overexpression of OC particles from the plunging waterfall is more moderate. A slightly larger number fraction of biological particles with $d_{va} > 1 \mu m$ was also observed in the aerosol generated by plunging waterfall and sintered glass filters, compared with wave breaking. Overall, the fraction of organic and biological SSA particles generated in these experiments
increases with a distinct trend: wave breaking < plunging waterfall < sintered glass filters. This trend is especially evident in the super-micron size range, which is also the size range containing the majority of the chemically characterized particles in this study. These ATOFMS results indicate that the size-resolved composition of SSA is directly affected by the physical mechanisms of bubble generation.

2.4.1.2 Elemental composition measurements by electron microscopy

Further single-particle composition measurements were conducted CCSEM/EDX, which allowed for quantitative chemical analysis of individual particles with $d_{ae} = 0.3 – 3 \mu m$. Figure 2.4 compares the enrichment of three different elements ($X = Mg, K, and Ca$) relative to Na from a collection of individual SSA particles sampled from each of the three generation methods. The comparison is presented as the size-resolved ratio of $X/Na$ for aerosol particles generated using the plunging waterfall (Figure 2.4a) and sintered glass filter (Figure 2.4b) schemes, divided by the size-resolved $X/Na$ ratio for SSA generated by wave breaking (the reference case). A value of 1 in Figure 2.4 means that there is no difference between the $X/Na$ ratio in the SSA generated by the methods being compared. The chemical composition as determined by CCSEM/EDX is very similar across all sizes between the plunging waterfall and wave breaking SSA particles. In contrast, SSA generated by the sintered glass filter method shows ratios of Mg/Na, K/Na, and Ca/Na compared to wave breaking SSA that are much greater than 1 for particles with $d_{ae} = 1 – 1.5 \mu m$, indicating an enrichment of those ions in supermicron particles. In particles with $d_{ae} < 0.8 \mu m$, these ionic species are depleted relative to wave-generated SSA, shown by $X/Na$ ratios less than 1. It is important to note that the enhancement and depletion of $X/Na$ ratios relative to wave-generated particles only emerges when their size resolved
composition is measured. Despite the significant deviations from unity observed in the size-resolved particles produced by the sintered glass filter, all three of the elemental ratio comparisons are close to unity when averaged over all particle sizes (Figure 2.4, insets). This disparity between the two means of analysis highlights the importance of making size-resolved single particle measurements due to inherent chemical heterogeneity in an externally mixed aerosol.

Common results from both ATOFMS and CCSEM/EDX analyses are the enrichment of Mg, Ca, and K in SSA generated by sintered glass filters in supermicron particles. ATOFMS measurements show that these cations are mainly localized to OC and biological SSA particles (Figure 2.2). The tendency for inorganic cations to coordinate, or strongly associate, with organic and biological material in the ocean and in SSA particles has long been recognized [e.g., Duce and Hoffman, 1976]. Divalent cations, such as Mg$^{2+}$ or Ca$^{2+}$, have the ability to stabilize organic supramolecular structures [Verdugo, 2012] and coordinate surface active organic ligands at interfaces [Casillas-Ituarte et al., 2010]. Magnesium has been shown to be a good tracer for SSA produced from bacteria-rich seawater [Guasco et al., 2013] and has been observed in aerosol over the ocean in association with biological activity [Gaston et al., 2011]. Hence, the enrichment of Ca, Mg, and K in the $d_{ae} = 1 – 1.5 \ \mu m$ size range in the CCSEM/EDX analysis is in good agreement with the ATOFMS results, which show an increased fraction of OC and biological particles from the sintered glass filter-generated SSA in this same size range, relative to wave production. The depletion of Mg, K, and Ca in particles with $d_{ae} < 0.8 \ \mu m$ observed by CCSEM/EDX suggests that smaller particles have chemical trends opposite those with $d_{ae} > 1 \ \mu m$. ATOFMS measurements did not achieve sufficient sampling
statistics for detailed comparative analysis. Consequently, any suppression of organic matter in the $d_{ae} = 0.1 – 0.8$ μm size range could not be dually corroborated and should be a topic of future work.

2.4.1.3 Internal mixing state of SS-OC particles

The trend of increasing organic matter enrichment in SSA by plunging waterfall and sintered glass filters compared to wave breaking is not restricted to the variety of particle types observed. Individual types of SSA particles, described in Section 2.4.1.1, often contain mixtures of chemicals within each particle; this is referred to as the ‘internal’ mixing state. The size-resolved fraction of particles containing sea salt mixed with organic carbon (SS-OC) does not appear to change significantly across the three methods (Figure 2.3), however, the amount of organic matter in SS-OC particles is different for each bubble generation method. Figure 2.5 shows the fraction of SS-OC particles that contain mass spectral markers for organic matter, binned by the area under each ion marker peak (an indicator of the quantity of each species in the particle). The fraction of particles that contain NaCl and each organic marker, as well as the organic ion marker peak area, increase with the same pattern as described previously: breaking waves < plunging waterfall < sintered glass filters. Therefore, even within the SS-OC particle type, organic matter is enriched in SSA particles generated by sintered glass filters, while the plunging waterfall produced only a moderate enrichment in organic matter compared to breaking waves.

Morphological details of individual particles were measured using SEM images, examples of which are shown in Figure 2.6. The particle cores (which consist mainly of
salts) are more rounded in the sintered glass filter sample, compared with the plunging waterfall and wave breaking samples. Differences in the morphologies of vacuum dried SSA particles generated by each method were quantified using a circularity parameter, \( C \), which was calculated for nearly 100 particles with \( d_{ae} \) between 0.380 – 2.6 μm from each generation method using Equation 2.5.

\[
C = \frac{4\pi A}{P^2} \tag{2.5}
\]

where \( A \) is the geometric area of an individual particle and \( P \) is its perimeter. Particles were counted as either spherical, if \( C \) was within 10% of the value for an ideal sphere (\( C = 1.00 \pm 0.10 \)), or were counted as cubic if \( C \) was within 10% of the value for an ideal cube (\( C = 0.79 \pm 0.08 \)). Only the ‘core’ of each particle was accounted for in the circularity determination; ‘shadows’ observed around the particles were neglected. It was found that 56% of the SSA particles generated by sintered glass filters were classified as spherical under vacuum, whereas 44% of the SSA particles generated by the plunging waterfall and 32% of the SSA particles generated by wave breaking were classified as spherical. Less than 1% of the particles measured were characterized as neither spherical nor cubic. For particles that are composed of a mixture of sea salt and organic matter (e.g., SS-OC particles), it has been shown previously that increasing circularity is associated with a greater organic/inorganic volume mixing ratio as cubic crystallization is inhibited [Ault et al., 2013; Laskin et al., 2012]. Hence, agreement was observed between the SEM morphology analysis and single particle analysis by ATOFMS: sea spray particles generated by the sintered glass filter method contain the most organic matter in this inter-
comparison, followed by particles generated by plunging waterfall, with SSA particles from breaking waves containing the least amount of organic matter.

2.4.2 Continuous foam formation and SSA composition

Natural SSA is mainly produced by whitecaps in the ocean, which are episodic in nature [de Leeuw et al., 2011]. The visible white area on the sea surface during and subsequent to a wave breaking episode is due to the presence of foam, a collection of bubbles floating at the air-sea interface, each separated from the next by a thin liquid film [Bikerman, 1973]. Whitecap foam persistence, measured in terms of its exponential decay time, lies mostly in the range of 2 – 4 seconds, occasionally extending to times as long as 10 seconds [Callaghan et al., 2012]. The discrete, episodic nature of wave breaking in the natural environment and in wave channel experiments reported here (mimicked also by the duty cycle of the plunging waterfall) is in contrast to the behavior of continuously-generated bubble plumes from sintered glass filters. Continuous production of bubbles results in a persistent surface foam, which has been implicated in alterations to SSA production mechanisms [Keene et al., 2007; Tyree et al., 2007] and water uptake properties [King et al., 2012]. These observations led to the investigation of the role of time-modulated (or ‘pulsed’) versus continuous bubble generation on particle production. Using a MART system [Stokes et al., 2013], which produces aerosol through a plunging waterfall apparatus similar to that implemented in the wave channel inter-comparison experiments described above, the sensitivity of SSA composition to the intermittent nature of the plunging waterfall was tested using both unamended natural seawater ([TOC] = 85 μM) and organic-enriched natural seawater ([TOC] = 400 μM) as described in Section 2.3.2.
2.4.2.1 Size distributions

The number size distributions of SSA particles were observed to be the nearly identical (within 1σ) between the pulsed and continuous plunging protocols when implemented using unamended natural seawater (Figure 2.7a). However, a significant change in the shape of the SSA number size distribution was observed when comparing pulsed and continuous plunging waterfall protocols in organic-enriched natural seawater (Figure 2.7b). The concentration of particles with $d_p < 0.05 \, \mu m$ and $d_p > 0.3 \, \mu m$ were lower, while concentrations of particles with $d_p = 0.05 - 0.125 \, \mu m$ were higher for continuous plunging when compared with pulsed plunging in the same seawater. Continuous plunging resulted in a tank-wide layer of foam that accumulated on the water surface, whereas surface foam had a patchy character when the plunging waterfall was pulsed at 4 second intervals. The reduced concentration of particles with $d_p > 0.3 \, \mu m$ during continuous plunging could be due to the weakened jet droplet production and will be discussed in further detail in Section 2.5.3.

The correlation of changes in the size distribution for $d_p < 0.05 \, \mu m$ with particles having $d_p > 0.3 \, \mu m$ suggests a physical link between the production mechanism of SSA particles in each of these size ranges. The presence of a significant surface foam layer appeared to enhance the production of SSA with $d_p = 0.05-0.125 \, \mu m$, suggesting that cap film breakup plays a significant role in the production of SSA particles in this limited size range. Hence, this type of deliberate foam accumulation experiment is a potentially useful tool for isolating the production mechanism of SSA particles via thin fluid film fragmentation for more detailed studies.
2.4.2.2 Chemical composition

The chemical composition of SSA produced via continuous and pulsed plunging, showed indistinguishable differences when generated from unaltered natural seawater (Figure 2.8a, c). However, continuous plunging in organic-enriched natural seawater was associated not only with a change in the SSA particle size distribution (Figure 2.7), but also with more organic matter in SSA particles sampled by ATOFMS (Figure 2.8b). For instance, the fraction of SS-OC particles measured by ATOFMS that contained organic carbon markers, as well as the area under the organic carbon marker peaks in the SS-OC particles’ mass spectra, was substantially higher in SSA produced by continuous plunging, as compared to pulsed plunging in organic-enriched seawater (Figure 2.8). This finding is in general agreement with the response of CCN activity to foam buildup in a similar type of laboratory experiment utilizing sodium laurate as a surface-active chemical proxy for dissolved organic matter [King et al., 2012]. Achieving similar results to those of King et al. [2012] in this study with only 1% of the concentration of organic material reinforces the critical importance of the naturally complex chemical composition of organic matter used to alter the seawater in this and other recent laboratory SSA experiments [Ault et al., 2013; Collins et al., 2013; Fuentes et al., 2010a; Moore et al., 2011; Prather et al., 2013]. The differences observed in SSA composition between the pulsed and continuous plunging modes explored here stress the importance of preserving the transient nature of surface foam inherent to the wave breaking process in the production of SSA in the laboratory when concentrations of organic matter in the seawater are elevated.
2.5 Discussion

Direct chemical measurements of laboratory-produced SSA at the single particle level described in this study indicate that the physical mechanism for bubble generation is inherently linked to particle composition. In this section, a variety of hypotheses are provided for the results of this study, which are discussed in the context of the existing literature. Each concept discussed below is shown schematically in Figure 2.9.

2.5.1 Bubble-Mediated Surfactant Transport

As described in detail above, the size-resolved chemical composition of SSA generated by sintered glass filters contains a larger number fraction of OC particles in the super-micron size range than are found in SSA from breaking waves (Figure 2.3). In addition, particles within the SS-OC type, which do not show as significant a change in number fraction as the OC particles, still undergo an enrichment in organic matter from sintered glass filter production, as compared to SSA from wave breaking and plunging waterfall (Figure 2.5). As discussed by Prather et al. [2013], the bubble size distribution produced by the sintered glass filter setup did not produce bubbles with radius > 1 mm. Sub-surface bubbles are known to scavenge surface active material from the water column and transport the organics to the sea surface [Liss, 1975]. Since the efficiency of surfactant scavenging by rising bubbles increases as bubble radius decreases [Blanchard, 1975], a greater degree of surfactant scavenging in bubble plumes generated by sintered glass filters is expected as compared to plumes generated by wave breaking or plunging waterfall, assuming the same gas flux rate for all systems, but weighted toward smaller bubbles in the case of the frit. On the whole, the process of surfactant transport toward the air-sea interface would result in the accumulation of organic matter in the sea surface microlayer
(SML) [Keene et al., 2007], which is a layer of material at the air-sea interface up to 1 mm thick that is typically highly enriched in dissolved and particulate organic material in the open ocean [Aller et al., 2005; Carlson, 1983; Cunliffe et al., 2011; Liss and Duce, 1997]. Some sintered glass filter aerosol generators have been designed to mitigate the over-expression of organics in the SML by continuously refreshing the surface of the seawater subjected to bubbling [Bates et al., 2012; Keene et al., 2007; Modini et al., 2010]; this design feature was not explicitly tested in this study. Wurl et al. [2011] show that the SML exists on the ocean surface for wind speeds up to 10 m/s (global ocean mean wind speed is approximately 6 m/s), so the existence of the SML is relevant for many instances of wave-induced bubble and foam production. At the same time, dynamic physical processes at the ocean surface can exert control on the thickness and extent of the SML [Cunliffe et al., 2013], so limiting organic matter enrichment at the sea surface is likely important for SSA production studies and likely bears on the results of the inter-comparison experiment within this study. Surface active material is well known to be important to foam lifetime; a recent study discussed its potential influence on whitecap decay time measurements near the east coast of the United States [Callaghan et al., 2012], which was then explicitly tested in laboratory studies of bubble decay times [Callaghan et al., 2013; Modini et al., 2013]. Still, studies have not explored the extent to which organic-enriched surface microlayers that exist in laboratory-scale SSA generators represent the range of environments in the open ocean. Important considerations for future SSA production studies include surfactant solubility, quantitative analysis of surface/bulk mixing, the dilation, compression, and packing of surfactant molecules, along with the already recognized role of sub-surface bubble scavenging. As reviewed by de Leeuw et al. [2011], the impact of bubble rise
distance could be a contributing factor in organic matter transport from the water column to the air-sea interface [Blanchard, 1975; Blanchard and Syzdek, 1972; 1975], although a recent theoretical assessment conflicts with these results [Fuentes et al., 2010b]. While our study did not systematically test the bubble transit distance as a contributing factor in SSA organic matter content, we note that the transit distance of bubbles from breaking waves in this set of experiments (which includes a downward and upward path) was similar to that of the sintered glass filter bubble plume (upward path only), since the penetration depth of the wave was about half the depth of the sintered glass filter setup.

2.5.2 Surface water mixing

In the breaking wave and plunging waterfall mechanisms, mixing of sea surface material back into the water column is a phenomenon that counteracts bulk-to-surface transport of surface active organic matter by the rising bubble plume. Vertical mixing of surface water was observed concurrently with air entrainment and bubble generation in prior wave channel studies of plunging breakers [Rapp and Melville, 1990], and is expected to translate to bubble entrainment by the plunging waterfall due to the similarity of the bubble formation processes between these two SSA generation methods. The lack of mixing of the organic-enriched SML back into the water column, as is likely the case for sintered glass filters due to the lack of surface penetration, could also contribute to the observed enhancements of organic matter in SSA relative to wave breaking, as described above. The results provided in this study suggest that generating aerosol using a technique where surface-active organic material is mixed back into the water column provides a similar mitigation of organic enrichment in the SML. Based on this explanation, the
composition of SSA from the plunging waterfall suggests that the surface water mixing regime lies between that of wave breaking and sintered glass filters.

### 2.5.3 Foam layer accumulation

The impact of a layer of accumulated, persistent foam on SSA production was investigated by comparing the size distribution and composition of SSA produced from the plunging waterfall in pulsed and continuous operation. The two operation modes produced SSA differently only while the seawater was enriched with organic matter ([TOC] = 400 μM), and a persistent layer of foam was observed on the water surface.

The transient nature of surface foam in natural wave breaking has been discussed in the context of a continuous plunging water jet technique [Fuentes et al., 2010b], where the bubble plume and foam on the water surface is allowed to decay as it moves away from the jet impingement location. The continuous production of bubbles that have a size distribution closely mimicking that within oceanic breaking waves in an experiment utilizing a plunging water technique may closely approximate wave breaking SSA composition at mean TOC concentration (60-85 μM), but not when using seawater that is enriched with organic matter (Figure 2.7 and Figure 2.8). Addition of soluble surfactants to salt water is known to increase bubble lifetime [Modini et al., 2013], and can lead to more persistent whitecap foam following a breaking wave event [Callaghan et al., 2013].

The properties of persistent foam are temporally dynamic. Foam cell size distributions are subject to fluid film rupture, which gives rise to processes which can both coarsen the foam by coalescence [e.g., Colin, 2012] and cause foam fining through daughter bubble production [Bird et al., 2010]. Direct measurements of aerosol production with
quantitative measurements of foam properties have not been shown in the literature to date, however, results shown in Section 2.4.2, along with those reported by King et al. [2012], indicate that foam properties can exert a significant influence on the physical and chemical characteristics of SSA.

As bubbles age on the seawater surface, the cap films are known to drain and thin; these types of time-dependent processes have been shown to influence aerosol production in single bubble experiments [Modini et al., 2013]. In this study, the production of SSA particles from persistent foam that is greater than one bubble layer thick (continuous plunging, high [TOC]) was associated with increased organic matter in the particles compared to SSA generated from the bursting of bubbles while a less pronounced foam layer existed (pulsed plunging, low [TOC]; Figure 2.8). We hypothesize that foam bubble bursting could (1) preferentially produce particles that are more enriched in organic matter than free bubbles bursting at the air-sea interface due to bubble cap film draining and thinning processes, and/or (2) droplets produced by the bursting of thin fluid films (film drops) are inherently enhanced in organics as a result of their production mechanism. While these hypotheses are not mutually exclusive and the former would require further detailed measurements, the latter concept is supported by the coincidence of the accepted film droplet size distribution [e.g., de Leeuw et al., 2011; Lewis and Schwartz, 2004] and the size-resolved enhancement of organic matter in nascent, submicron SSA particles [e.g., Facchini et al., 2008; Gantt and Meskhidze, 2013; Keene et al., 2007; Prather et al., 2013].

The existence of a layer of foam on the seawater surface was also associated with a change in the shape of the SSA size distribution (Figure 2.7). The low concentrations of
SSA particles with $d_p > 0.3$ μm is perhaps indicative of reduced aerosol production by the jet droplet mechanism, based on particle size [de Leeuw et al., 2011; Lewis and Schwartz, 2004]. The existence of the foam layer on the seawater surface may be capable of prohibiting or curtailing jet droplet production by assimilating rising bubbles into the foam layer prior to rupture. The mechanism for jet droplet formation via rapid retraction of the surface water within the cavity of a bursting bubble is likely to be impossible in the absence of a continuous liquid phase beneath it, as in a foam that is greater than one bubble layer thick. In addition, we suggest that jet droplets that may have formed beneath the foam layer would have been sequestered by the overlying foam, causing a reduction in jet droplet introduction to the air above the foam (Figure 2.9, inset). In either case, the reduced influence of particles with $d_p > 0.3$ μm on SSA when a persistent layer of foam was observed clearly links a change in SSA production with surface foam accumulation.

### 2.6 Conclusions

Due to uncertainties in the projections of global climate which stem from natural aerosol sources, detailed studies of SSA in controlled environments approximating pre-industrial conditions are of great importance [Ghan et al., 2013; Menon et al., 2002; Tsigaridis et al., 2013]. At the same time, controlled laboratory studies that utilize physicochemically accurate SSA production taking into account realistic biogeochemical systems are critical for developing an understanding of natural geochemical and geophysical interactions that influence the global climate system. It has been shown in this study that the composition of laboratory-generated SSA was inherently sensitive to the physicochemical environment (controlled by the bubble production mechanism) in which bubbles were generated and allowed to burst. In addition, the pulsed or periodic nature of
bubble production was important in controlling the transfer of organic matter to SSA via surface foam accumulation when high concentrations of organic matter are present in the seawater. Based on the results presented in Section 2.4.2, it is also shown that SSA production studies with accumulated foam layers can be a useful tool in enhancing the formation of SSA via thin fluid film rupture.

When compared with wave breaking and plunging waterfall in this study, the sintered glass filter apparatus produced a different bubble size distribution and different surface foam accumulation properties. The modal diameter and shape of the sintered glass filter aerosol number size distribution are also clearly distinguishable from the plunging waterfall and wave breaking size distributions. Size-resolved, single-particle chemical composition measurements of SSA particles produced by the sintered glass filters showed a larger contribution of OC from supermicron particles compared with both plunging waterfall and wave breaking. While it has been established that the similarity of the bubble size distribution in laboratory SSA generators to that in the open ocean is an important factor [Fuentes et al., 2010b; Prather et al., 2013], these authors suspect that turbulent mixing of the organic-enriched surface microlayer back into the water column by the breaking waves and plunging waterfall, and perceived lack thereof by the sintered glass filters, may play an added role in the results presented in the inter-comparison portion of this study (Section 2.4.1). The natural conformity of the physical and chemical environment for bubble generation and bursting are critical for an accurate reproduction of SSA generation in the laboratory. It is possible that a careful re-design of the sintered glass filter setup used in this study could allow for SSA production that more closely matches the wave breaking method described in this study. In general, new SSA generation
schemes should not only replicate the bubble size distribution of open ocean waves, but also the inherently turbulent and discrete nature of the wave breaking process.

The correspondence of similarities and differences in both the size distribution and chemical composition of SSA particles generated by the methods explored in this study stresses the inherent coupling between the SSA production mechanism and its composition. Hence, this study indicates that the similarity of the number size distribution of laboratory-generated SSA to the best available reference (e.g., laboratory breaking waves) can be utilized as a first-order check on SSA composition. This study takes important steps toward bringing the marine environment into the laboratory by evaluating the natural fidelity of the starting material utilized for many chemical and physical studies of SSA particles through a critical inter-comparison of various SSA generation mechanisms.

2.7 Acknowledgements

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### 2.8 Tables

**Table 2.1**: Number of particles analyzed by CCSEM/EDX in each size bin for samples collected from each aerosol generation method.

<table>
<thead>
<tr>
<th>$D_{proj}$ (μm)</th>
<th>Sintered Glass Filters</th>
<th>Plunging Waterfall</th>
<th>Wave Breaking</th>
</tr>
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<tbody>
<tr>
<td>0.3-0.4</td>
<td>166</td>
<td>171</td>
<td>54</td>
</tr>
<tr>
<td>0.4-0.5</td>
<td>76</td>
<td>75</td>
<td>41</td>
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<tr>
<td>0.5-0.6</td>
<td>29</td>
<td>42</td>
<td>37</td>
</tr>
<tr>
<td>0.6-0.7</td>
<td>17</td>
<td>37</td>
<td>31</td>
</tr>
<tr>
<td>0.7-0.8</td>
<td>13</td>
<td>49</td>
<td>28</td>
</tr>
<tr>
<td>0.8-0.9</td>
<td>38</td>
<td>48</td>
<td>32</td>
</tr>
<tr>
<td>0.9-1.0</td>
<td>31</td>
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<td>6</td>
</tr>
<tr>
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<td><strong>678</strong></td>
<td><strong>963</strong></td>
<td><strong>546</strong></td>
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</tbody>
</table>
Figure 2.1: Schematic of the linear wave channel with interchangeable bubble generation apparatuses for SSA production. Each of these bubble generation mechanisms were tested within the wave channel within 24 hours, and with the same natural seawater sample.
Figure 2.2: Representative mass spectra for each of the particle types described in this study.
Figure 2.3: (a.) Size resolved chemical composition of SSA particles measured by ATOFMS for each bubble/aerosol generation method noted in white text. The grayscale bar at the top of each panel indicates the number of particles sampled in each size bin. (b.) Number size distributions measured by SMPS and APS, corresponding with the data shown in (a.). Seawater for inter-comparison experiments conducted in the wave channel was obtained from Scripps Pier, as discussed in the text. The sintered glass filter method generates a significantly different number size distribution of SSA particles as well as shows an enhancement in organic-rich particles in the $d_{va} = 0.8$–$2 \mu m$ range, when compared with the other two generation methods. The second axis in (a.) labelled ‘Physical Diameter’ is provided for comparison with (b.), noting that $d_{va}$ is the size metric directly measured by ATOFMS.
Figure 2.4: Elemental composition of particles produced via (a.) plunging waterfall (PW) and (b.) sintered glass filters (SGF), compared to particles produced via wave breaking (WB). The comparison is made using the ratio of the EDX intensities (counts per second) for Mg, K, and Ca referenced to Na in SSA particles. Deviation from unity indicates differences in chemical composition. The number of particles in each size bin can be found in Table 2.1.
Figure 2.5: Color-stack plots showing ATOFMS ion markers for organic nitrogen (CN\textsuperscript{-}), oxygenated organic carbon (CH\textsubscript{3}COO\textsuperscript{-}), and phosphate (PO\textsubscript{3}\textsuperscript{2-}) considering only particles composed of an internal mixture of sea salt and organic compounds (SS-OC). The vertical axis indicates the fraction of SS-OC particles whose mass spectrum includes each marker with the color indicating the peak area of the marker. Notice that from left-to-right, a larger fraction of SS-OC particles contain these organic/biomolecule marker ions; the peak area also increases, suggesting that each particle contains more of each chemical species moving from left-to-right.
Figure 2.6: SEM images of particles generated by each of the three laboratory SSA generation mechanisms considered in this study (two images shown for each case). All samples are dried in the vacuum of the SEM during the analysis process. The increased circularity of the particle cores is visible when comparing the sintered glass filter SSA samples to the plunging waterfall and wave breaking samples.
Figure 2.7: Number size distributions for MART-generated SSA particles using continuous (red) and pulsed (black) plunging waterfall modes (±1σ error bars). The change in the shape of the size distribution is clearly evident between the continuous and pulsed plunging cases when the seawater is enriched with organic matter. Concentrations of particles with $d_p > 0.3 \, \mu m$ and $d_p < 0.05 \, \mu m$ are smaller during continuous plunging indicating a change in the SSA particle production mechanism due to the over-production of foam.
Figure 2.8: (a, b) Comparison of color-stack plots generated by sampling SSA produced by a plunging waterfall under ‘continuous’ bubble generation versus ‘pulsed’ (4 sec on/off) bubble generation. Large differences in SSA composition are observed when seawater organic matter concentrations are high ([TOC] = 400 μM), coinciding with major differences in surface foam accumulation between the generation modes. Only SS-OC particles are considered in (a) and (b). On the right, (c.) shows a matrix of pie charts indicating the fractional contribution of each of the particle types to SSA from both pulsed and continuous plunging with both low (85 μM) and high (400 μM) organic matter concentrations in the seawater.
Figure 2.9: Process diagram of SSA production depicting phenomena described in Section 2.5.
2.10 References


Rapp, R. J., and W. K. Melville (1990), Laboratory Measurements of Deep-Water Breaking Waves, Philos T Roy Soc A, 331(1622), 735-&.


3. Impact of Marine Biogeochemistry on the Chemical Mixing State and Cloud Forming Ability of Nascent Sea Spray Aerosol

3.1 Synopsis

The composition and properties of sea spray aerosol, a major component of the atmosphere, are controlled by marine biological activity, however the scope of impacts that ocean chemistry has on the ability for sea spray aerosol to act as cloud condensation nuclei (CCN) is not well understood. In this study, we utilize a mesocosm experiment to investigate the impact of marine biogeochemical processes on the composition and mixing state of sea spray aerosol particles with diameters < 0.2 μm produced by controlled breaking waves in a unique ocean-atmosphere facility. An increase in relative abundance of a distinct, insoluble organic particle type was observed after concentrations of heterotrophic bacteria increased in the seawater, leading to an 86 ± 5% reduction in the hygroscopicity parameter (κ) at 0.2% supersaturation. Aerosol size distributions showed very little change and the submicron organic mass fraction increased by less than 15% throughout the experiment; as such, neither of these typical metrics can explain the observed reduction in hygroscopicity. Predictions of the hygroscopicity parameter that make the common assumption that all particles have the same bulk organic volume fractions lead to over-predictions of CCN concentrations by 25% in these experiments. Importantly, key changes in sea spray aerosol mixing state that ultimately influenced CCN activity were driven by bacteria-mediated alterations to the organic composition of seawater.
3.2 Introduction

Atmospheric aerosols are known to play a significant role in forcing global climate directly through the scattering and absorption of solar radiation, and indirectly by altering cloud microphysics and albedo [Forster et al., 2007]. Aerosol particles induce indirect effects through their ability to act as cloud condensation nuclei (CCN) in air that is supersaturated with respect to water vapor; the ability of an individual particle to do so depends on its size and chemical composition. Wettable particles with a dry diameter \(d_{\text{dry}}\) > 0.2 \(\mu\)m will activate at climatically relevant supersaturations (< 1%) almost regardless of their composition, while those containing highly soluble material may act as CCN with \(d_{\text{dry}}\) as small as 0.05 \(\mu\)m [Andreae and Rosenfeld, 2008; McFiggans et al., 2006]. As such, the composition of aerosol particles, particularly those with \(D_{\text{dry}} < 0.2 \mu\)m, can play an important role in determining the number concentration of sub-cloud CCN, which, combined with the dynamic nature of cloud supersaturation, is thought to ultimately determine the impact of aerosol particles on cloud drop size and number concentration [Hegg et al., 2012].

A unifying explanation of the production and activity of CCN in the marine boundary layer (MBL) is not well established [Meskhidze et al., 2011; Pierce and Adams, 2006]. Using the hygroscopicity parameter, \(\kappa\), for CCN activity comparisons [Petters and Kreidenweis, 2007], the global average value for the MBL is 0.72 ± 0.24 based on model simulations [Pringle et al., 2010] with individual in situ reports as low as \(\kappa = 0.17-0.3\) (off the Southern California coast) [Furutani et al., 2008] and as high as \(\kappa = 1.15-1.4\) (tropical Atlantic) [Good et al., 2010]. Factors that contribute to this variability include the chemical
nature and mixing state of nascent sea spray aerosol (SSA), secondary chemical alterations to SSA during its residence time in the MBL, and the influence of continental/anthropogenic aerosols advected to marine regions [Furutani et al., 2008; Kaku et al., 2006; Langley et al., 2010; Sorooshian et al., 2009]. Anthropogenic and continental impacts on CCN activity in marine regions are particularly evident in the comparison of the hygroscopicity parameter in the North Atlantic ($\kappa = 0.59\pm0.18$) with that over the Southern Ocean ($\kappa = 0.92 \pm 0.09$) [Pringle et al., 2010], since anthropogenic impacts on atmospheric composition are less pronounced in the Southern Hemisphere on average [Chung and Seinfeld, 2002; Wofsy et al., 2011], indicating that anthropogenic influences tend to reduce the aerosol hygroscopicity in the MBL. Table 3.1 provides a review of a number of reports of CCN activity measurements from both laboratory and field studies (including this work). The assessment of modern anthropogenic aerosol impacts on cloud properties depend critically on the concentrations of natural aerosol [Lohmann and Feichter, 2005; Menon et al., 2002], although this information has been difficult to assess [Andreae, 2007], stressing the importance of detailed characterization of the sources and properties of natural aerosol particles.

The production of SSA accounts for a large fraction of the total atmospheric burden of natural aerosol due to the vast extent of the Earth’s oceans and the widespread strength of SSA production at the sea surface [Andreae and Rosenfeld, 2008; de Leeuw et al., 2011]. Particles directly ejected from the ocean with diameters of approximately 1 micron and larger are composed largely of salts, whereas particles smaller than 1 micron are more numerous [de Leeuw et al., 2011] and have been characterized as increasingly rich in organic matter ($\text{OM}_{\text{aero}}$) with decreasing diameter on both mass [Facchini et al., 2008;
Keene et al., 2007; O'Dowd et al., 2004] and number fraction basis [Ault et al., 2013; Prather et al., 2013]. Since cloud properties are sensitive to sub-cloud aerosol number concentrations, understanding the production flux and CCN activity of these small, organic-enriched particles is of critical importance to predictions of cloud albedo and lifetime [Lohmann and Feichter, 2005]. In particular, knowing whether the chemical components of the aerosol are mixed together in the same particle (internally mixed) or exist in separate particles (externally mixed) can play a major role in model predictions of CCN number concentrations [Meskhidze et al., 2011; Wex et al., 2010a]. Some laboratory and field studies of SSA have reported an internally mixed aerosol population [Fuentes et al., 2011; Kammermann et al., 2010], while others provide evidence of distinct, externally mixed sub-populations of particles [Bigg and Leck, 2008; Hawkins and Russell, 2010; Hultin et al., 2010; Murphy et al., 1998; Prather et al., 2013].

Laboratory bubble bursting experiments indicate that nascent SSA from unaltered seawater exhibits $\kappa$ values between 1.2-1.5, which are close to the value for pure NaCl ($\kappa = 1.25-1.3$), but well above many field observations (Table 3.1). The composition of seawater and the resulting SSA are not globally homogeneous, however. Seasonal phytoplankton blooms that lead to regionally elevated dissolved and particulate organic matter (OM$_{sea}$) concentrations in the ocean [Ducklow et al., 1995], have been associated with reports of strong enhancements in the organic mass fraction of submicron aerosol [O'Dowd et al., 2004; Yoon et al., 2007] at Mace Head, Ireland. Subsequent investigations into the influence of organic material on the CCN activity of sea salt/organic mixtures have mostly utilized model chemical systems (e.g., oleic acid, amino acids, surfactants) to simulate varying concentrations of OM$_{sea}$ that is ejected from the ocean, showing modest
reductions in CCN activity with the addition of organics in many cases [Frosch et al., 2011; King et al., 2012; Moore et al., 2011; Schwier et al., 2011]. This weak influence of organics is likely related to the dominant effect of the highly water-soluble inorganic components on the CCN activation of internally mixed salt/organic particles [Bilde and Svenningsson, 2004; Broekhuizen et al., 2004], the lack of long range molecular order in the organic films [Davies et al., 2013], and the relatively low viscosity of the organic proxies [Bones et al., 2012; Shiraiwa et al., 2011].

Recent laboratory studies of the influence of organic matter on the water uptake properties of SSA have begun to utilize more representative chemical proxies for dissolved organic matter (DOM), which is the dominant reservoir for reduced carbon in the ocean [Hansell et al., 2009] and is operationally defined as the organic fraction of seawater that can pass through a filter (pore size ranges 0.2-0.7 μm). Aerosolized DOM from two different marine environments showed different reductions in CCN activity when mixed with salts, likely resulting from their differing chemical compositions [Moore et al., 2008]. Studies that utilize phytoplankton exudates (i.e. – phytoplankton culture filtrate) as DOM proxies [e.g., Fuentes et al., 2010] have concluded that the CCN activity of SSA can be reduced by 5-24% with organic carbon concentrations in the parent seawater up to ~7 times mean oceanic levels, depending on which organism produced the exudate material. This observed reduction in CCN activity corresponded to an OM\textsubscript{aero} fraction of 30-40% by volume [Fuentes et al., 2011; Wex et al., 2010b] (Table 3.1 b-c).

In order to connect field and laboratory investigations of SSA production and physicochemical properties, a prescriptive relationship for including SSA organics in models has been proposed and investigated, linking the total submicron mass fraction of
SSA with satellite-observable chlorophyll-\(a\) (chl-\(a\)) in the surface ocean [Albert et al., 2012; O’Dowd et al., 2008; Vignati et al., 2010], although this relationship is not well understood. The uncertainties associated with this initially proposed relationship have prompted the suggestion that a sea spray OM\(_{\text{aero}}\) parameterization may be improved through the inclusion of carbon sources apart from primary production (\(e.g.,\) heterotrophic bacteria, protozoa) [Quinn and Bates, 2011]. The concentration of heterotrophic bacterial biomass, for instance, is less variable than that of phytoplankton across the spectrum of eutrophic, mesotrophic, and oligotrophic regimes (5x\(10^5\) – 5x\(10^7\) cells mL\(^{-1}\)) [Cho and Azam, 1990; Li, 1998]. Marine heterotrophic bacteria play a key role in the structuring of microbial ecosystems [Azam and Malfatti, 2007; Pomeroy et al., 2007] and influence the composition of oceanic DOM [Coble, 2007; Jiao et al., 2010; Ogawa et al., 2001], which could, in turn, exert control over the physicochemical properties of SSA.

This study explores the coupled impact of marine heterotrophic bacterial activity and OM\(_{\text{aero}}\) mixing state on the CCN activity of SSA. Taking advantage of the ability to produce sea spray aerosol using physically realistic breaking waves in a laboratory setting, the impact of seawater biological and chemical conditions were fully isolated over a range of organic matter concentrations and biogeochemical conditions. Rather than utilizing only phytoplankton-produced exudates as a controllable DOM surrogate, these experiments were carried out with the goal of exploring the impact of a broader marine biogeochemical system on SSA properties. Specifically, the mixing state of submicron SSA was investigated in an effort to probe the impact of external mixing on CCN activity and the relative response of the OM\(_{\text{aero}}\) mass fraction to the observed changes in aerosol water uptake.
3.3 Experimental Methods

3.3.1 Aerosol Generation

Measurements of aerosol properties were made during an intensive experiment organized by the Center for Aerosol Impacts on Climate and the Environment (CAICE). A novel ocean-atmosphere chamber was developed utilizing an existing glass-walled, 33x0.5x0.5 meter (length-width-water depth, 8250 L) linear wave channel at the Hydraulics Laboratory at Scripps Institution of Oceanography (http://hydraulicslab.ucsd.edu) [Prather et al., 2013]. Bubble size distributions generated by controlled breaking waves in this facility have been previously validated against measurements of open ocean waves [Deane and Stokes, 2002]. Seawater was drawn from approximately 13 ft below the low-tide line 900 ft offshore at Scripps Pier (La Jolla, CA; 32° 52.0’ N, 117° 15.4’ W), passed through two No. 12 crystal sand bed filters to remove macroscopic organisms and debris, and was delivered directly to the wave channel. The temperature of the seawater was measured throughout the experiments. After each new fill of natural seawater, the temperature started at the ambient ocean temperature (16°C) and equilibrated over time to room temperature (20°C). Temperature changes in this range would not likely affect SSA production [Zabori et al., 2012]. The total organic carbon, chlorophyll-a, trace metal, and nutrient concentrations within the seawater were all observed throughout the experiment. Further detailed chemical analysis of the organic fraction was not carried out. Inorganic nutrient concentrations remained low and nearly invariant throughout the experiments.

The 33m-long wave channel was fitted with a 4-stage air handling system to remove volatile organic compounds, nitrogen and sulfur oxides, and aerosol particles prior to
entering the headspace of the wave channel, and is shown schematically in Figure 3.1. SSA was generated continuously in the sealed wave channel through the breaking of sinusoidal wave pulses on an artificial shoal with a frequency of 0.6 Hz or through a pulsed plunging waterfall technique, which involves the intermittent gravitational impingement of a waterfall in the wave channel at 6 second intervals to produce sea spray, similar to the system described by Stokes et al. [2013]. Number size distributions and chemical mixing state of sea spray aerosol particles generated by wave breaking and plunging waterfall methods have been determined to agree well with one another [Collins et al., 2014; Prather et al., 2013].

3.3.2 Measurement Techniques

Nascent SSA was sampled approximately 2 meters downstream of the breaking wave location through 1/2” stainless-steel tubing to a laminar flow manifold, where the aerosol was diverted to an array of on-line and off-line measurement techniques. A schematic of the experimental setup is provided in the Supplemental Information.

3.3.2.1 Chemical Measurements of Sea Spray Aerosol Particles

Single particle measurements of aerosol chemical composition were obtained from both real-time and offline techniques. Size-resolved chemical composition of individual sea spray aerosol particles with dry (RH = 15%) vacuum aerodynamic diameters ($d_{va}$) between 0.3 – 1 µm was measured with Ultrafine Aerosol Time-of-Flight Mass Spectrometry (UF-ATOFMS) [Su et al., 2004], which obtains the aerodynamic diameter and laser desorption/ionization (266 nm, ~1.3 mJ, 7 ns pulse) dual-polarity mass spectrum for each particle sampled. Analysis of this large dataset is performed with the aid of the
YAADA toolkit (http://www.yaada.org) for MATLAB (The Math Works, Inc.). Data are reported here as 15-minute average mass spectral peak areas normalized to the total area of the mass spectrum from which they were obtained.

Samples were collected using a micro-orifice uniform deposit impactor (MOUDI; MSP Corp. Model 100) sampling air at 30 LPM at ca. 60% relative humidity, with 50% aerodynamic cut-off diameters at 1.0, 0.53, 0.30, 0.18, 0.09, and 0.05 µm for offline microscopy analysis. Aerodynamic diameter bins generated by MOUDI cut-offs have been shown to agree well with independent particle size measurements by electron microscopy [Ault et al., 2013]. Aerodynamic diameters were converted to equivalent spherical diameter in order to calculate size distributions for each particle type. For this conversion, the salt and non-salt fractions were assigned densities of 1.8 and 1.35 g mL$^{-1}$ [Kuwata et al., 2012; Zelenyuk et al., 2007] and dynamic shape factors of 1.08 and 1 [Hinds, 1999], respectively. A growth factor of 1.6 was then used to convert the diameter at 60% RH to a dry diameter for comparisons and calculations involving aerosol size distributions (Sections 3.3.5 and 3.3.6). Aerosol samples were deposited on 400 mesh Carbon Type B/Formvar TEM grids (Ted Pella Inc., part number 01814-F). Transmission electron microscopy with energy dispersive x-ray analysis (TEM-EDX) measurements were collected on a JEOL 2100f field emission TEM operated at an accelerating voltage of 200 kV with a Gatan high angle annular dark field (HAADF) detector and a Nanotrace EDX detector. In addition to TEM-EDX, scanning transmission x-ray microscopy (STXM) and near edge x-ray absorption fine structure (NEXAFS) data from the carbon K-edge, sulfur L-edge, and chlorine L-edge were collected at the Advanced Light Source at Lawrence Berkeley National Laboratory [Kilcoyne et al., 2003; Moffet et al., 2010]. Submicron SSA was classified into particle
types based on elemental composition (EDX), inorganic/organic ratio and molecular information (STXM-NEXAFS), and morphological analysis of single particles (TEM). In addition, STXM-NEXAFS was used to quantify the (dry) organic volume fractions of internally mixed salt/organic aerosol particles. The inorganic and organic portions of the particles were mapped using the pre- and post-edge optical densities at the carbon K-edge in the x-ray absorption spectrum at each pixel [Moffet et al., 2010]. It was assumed that the particles were composed of organic material having an O:C:H ratio of 0.67:1:1.67 mixed with sodium chloride. The pre-edge (278 eV) optical density ($OD_{pre}$) can be expressed as:

$$OD_{pre} = \mu(278)_{NaCl} \rho_{NaCl} t_{NaCl} + \mu(278)_{org} \rho_{org} t_{org} \quad [3.1]$$

and the post-edge (320 eV) optical density ($OD_{post}$) is expressed similarly:

$$OD_{post} = \mu(320)_{NaCl} \rho_{NaCl} t_{NaCl} + \mu(320)_{org} \rho_{org} t_{org} \quad [3.2]$$

Using the measured optical densities, calculated atomic cross sections ($\mu$) [Henke et al., 1993], and densities ($\rho_{org} = 1.35 \text{ g cm}^{-3}$, $\rho_{NaCl} = 2.16 \text{ g cm}^{-3}$) the thickness of the NaCl ($t_{NaCl}$) and organic ($t_{org}$) are determined. Since the x-ray beam cross sectional area remains constant, the volume fraction of organic matter ($\varepsilon_{org}$) within the sample column (represented as an individual pixel) can be calculated as

$$\varepsilon_{org} = \frac{t_{org}}{t_{org} + t_{NaCl}} \quad [3.3]$$

### 3.3.2.2 Physical Measurements of Sea Spray Aerosol Particles

Aerosol size distributions were measured at a relative humidity of 15 ± 10% using a Scanning Mobility Particle Sizer (SMPS; TSI Inc. Model 3936) and an Aerodynamic
Particle Sizer (APS; TSI Inc. Model 3321). SMPS measured particles with diameters of 0.011-0.6 µm. APS measurements were adjusted from $d_a$ to physical diameter ($d_p$) assuming an effective density of 1.8 g mL$^{-1}$ [Zelenyuk et al., 2007]. Sizes measured by the APS (after adjustment) that overlap the capabilities of the SMPS ($d_p < 0.6$ µm) were truncated. After density adjustment, the largest size measured by the APS was 11 µm.

CCN number concentrations ($N_{CCN}$) were measured with a miniaturized stream-wise thermal-gradient cloud condensation nuclei counter (CCNc) [Roberts and Nenes, 2005]. Briefly, this technique exposes particles to an environment supersaturated with respect to water vapor, in which a subset of the particles activate to form cloud drops and are then counted using an optical particle counter. The CCNc sampled aerosol in parallel with a water-based condensation particle counter (CPC; TSI, Inc. Model 3781) to evaluate total aerosol concentrations, and was operated at a constant supersaturation ($s$) of 0.2 ± 0.02%, which is similar to conditions found in marine stratocumulus cloud decks [e.g., Hudson, 1983]. In order to connect CCN measurements with the chemical composition of the particles, the hygroscopicity parameter ($\kappa$) was calculated based on the critical activation diameter ($d_{act}$) and $s$ using code implemented in the R language (http://atofms.ucsd.edu/content/code) based on the work of Petters and Kreidenweis [2007]. Calculations assumed the surface tension of water (72 mN m$^{-1}$). $d_{act}$ was determined by integrating the aerosol size distribution such that:

$$\int_{d_{act}}^{d_{max}} n(d_p) dd_p = N_{CCN}$$  \[3.4\]

where $d_p$ is the physical aerosol diameter in micrometers, $N_{CCN}$ is the number concentration of cloud active aerosol at $S = 0.2\%$, $n(d_p)$ is the number size distribution of dry particles,
and $d_{\text{max}}$ is the upper limit diameter measured by the APS. The hygroscopicity parameter is reported as the calculated $\kappa$ value for the mean $d_{\text{act}}$ based on 30-minute averaged size distributions and $N_{\text{CCN}}$. The $\kappa$ value obtained for un-amended seawater using this technique (Table 3.1a) was validated with prior measurements performed by our group by using size-selected monodisperse aerosol populations, and directly measuring the fraction of active CCN as a function of dry diameter. A lower limit uncertainty in $\kappa$ was determined by accounting for systematic biases in the size distribution (due to under-counting). The SMPS-derived size distribution was scaled to the largest ratio of all integrated size distributions and parallel CPC measurements made during these experiments ($N_{\text{SMPS}+N_{\text{APS}}}/N_{\text{CPC}} = 0.85$), from which $d_{\text{act}}$ and $\kappa$ were re-calculated. Uncertainty in $\kappa$ is reported as the value corresponding to $\pm 2\sigma$ of the 30-minute $d_{\text{act}}$ determinations within each reported data point, or the $\kappa$ value obtained from aforementioned counting corrections, whichever accounts for a larger deviation from the mean.

### 3.3.2.3 Seawater Measurements

Seawater chl-$a$ was measured in real time using a WET Labs ECO Triplet customizable fluorometer. Samples for seawater total organic carbon (TOC) analysis were collected from the upper $\sim$5 cm of the tank, transferred (unfiltered) to combusted 40 mL glass vials, and immediately acidified to pH 2 with trace metal free 12N HCl. Analysis was later performed by high temperature combustion (Shimadzu Scientific Instruments). TOC concentrations were linearly interpolated when needed for comparison with other variables (e.g., CCN activity). Water samples for cell counts were obtained using sterile plastic pipettes, immediately fixed with paraformaldehyde, and flash frozen in liquid
nitrogen. Heterotrophic prokaryotic cell (bacteria and archaea) abundance was quantified by flow cytometry at the University of Hawaii SOEST Flow Cytometry Facility, and will be referred to simply as bacteria herein.

### 3.3.3 Preparation and Addition of Biological and Organic Matter

The organic matter content of the seawater in these experiments was modulated through two means: addition of pre-concentrated algae monoculture and ‘mesocosm’ growth of bacteria. An algae-only experiment utilized a monoculture of a common marine green microalgal species (*Dunaliella tertiolecta*) grown in Guillard’s “f” media diluted by a factor of 2 (i.e. – f/2 media) [Guillard and Ryther, 1962]. Direct lighting was not delivered to the culture after being added to the wave channel, therefore sustained primary production during SSA generation was not expected.

In a separate experiment which began after the wave channel was again filled with fresh unamended seawater, a bacterial ‘mesocosm’ was initiated through the coincident addition of whole surface seawater from Scripps Pier (collected manually), a polyculture of three bacterial isolates (*Alteromonas TW2, TW7, [Bidle and Azam, 2001]*) and *AltSIO* [Pedler et al., 2014]) grown on ZoBell media (5 g peptone and 1 g yeast extract L⁻¹) [Oppenheimer and ZoBell, 1952], and an aliquot of sterile ZoBell growth media. Further additions of bacteria and ZoBell were performed over the ensuing 2.7 days, maintaining high levels of heterotroph-dominated biological activity with low chl-a concentrations. The community of bacteria that grew in the mesocosm was not controlled or speciated. The initial seawater contained a natural assemblage of bacteria and the added cultures of *Alteromonas* spp. bacteria (Table 3.2) each contained less than 10% of the total number of bacteria already present in the mesocosm, similar to the proportion of *Alteromonas* to total...
heterotrophic bacteria found in a phytoplankton bloom in the North Pacific [Tada et al., 2011]. A final aliquot of ZoBell media, a culture of the heterotrophic bacterium *Pseudoalteromonas atlantica* (strain 19262), and a culture of *Dunaliella tertiolecta* (green algae) were added to the wave channel, bringing chl-\(a\) concentrations up to 5.5 mg m\(^{-3}\). Due to the large volume of the wave channel, the volume of added organic and biological material did not significantly alter the final volume of the mixture. The details of each addition, labeled A1-A4, are shown in Table 3.2 and Figure 3.2. The unfettered growth of a natural assemblage of bacteria found in seawater is a key element of this mesocosm experiment, setting it apart from studies involving single biological or chemical components. The highly coupled biogeochemical interactions in this type of experiment allow naturally complex assemblages of biological and chemical species to interact.

3.4 Results and Discussion

3.4.1 Sea Spray from Unaltered Seawater

Oceanic dissolved organic carbon (DOC; a standard metric for seawater DOM content) typically has a concentration < 80 \(\mu\)M in vast regions of the ocean during non-phytoplankton bloom conditions [Hansell et al., 2009]. The physicochemical properties of aerosol generated within this condition are particularly relevant for regions where biological activity is not elevated, and also acts as a baseline control for experiments conducted with higher biological activity and organic carbon concentrations. Measurements of CCN activity of SSA derived from breaking waves in unaltered coastal seawater (TOC = 69 ± 2 \(\mu\)M, chl-\(a\) = 0.18 ± 0.03 mg m\(^{-3}\)) yielded \(\kappa = 1.4 (+0.3, -0.7)\). It is notable that this hygroscopicity parameter value is similar to published values for artificial seawater and other inorganic proxies [Fuentes et al., 2011; Niedermeier et al.,]
2008], but is higher than many field observations made in the marine boundary layer (κ ~ 0.72; Table 3.1f) [Allan et al., 2008; Bougiatioti et al., 2009; Furutani et al., 2008; Good et al., 2010; Hudson, 2007; Martin et al., 2011; Mochida et al., 2011; Moore et al., 2012; Pringle et al., 2010]. This difference is attributed to the inability of ambient aerosol measurements in the MBL to fully de-convolute influence from secondary marine, continental, and/or anthropogenic sources [Shank et al., 2012; Sorooshian et al., 2009].

3.4.2 Sea Spray from Phytoplankton-rich Seawater

In order to draw initial parallels with studies that utilized phytoplankton exudates to simulate marine DOM [Fuentes et al., 2011; Wex et al., 2010b], the seawater was spiked with a culture of Dunaliella tertiolecta. As a result of the phytoplankton addition to the seawater, the chl-a concentration in the seawater increased from 0.1 mg m⁻³ to 0.78 mg m⁻³, which is comparable to a spring phytoplankton bloom in the North Atlantic [Martinez et al., 2011], while the concentration of bacteria remained stable (1±0.2 x 10⁶ cells/mL⁻¹) at levels commonly found in the coastal ocean [Li, 1998]. We found a 37% reduction from the values of unaltered coastal seawater in CCN-derived hygroscopicity with the unfiltered phytoplankton culture used in this study (κ = 0.88 (+0.34, -0.23), TOC = 120-127 μM). This value is a comparable suppression in CCN activity to that found using filtered phytoplankton cultures as a proxy for DOM enrichment [Fuentes et al., 2011; Wex et al., 2010b]. For a given concentration of phytoplankton and/or organic matter, deviations in κ values obtained in these and other similar experiments are likely attributable to differences in the chemical composition of OMsea produced by each species [e.g., Kujawinski, 2011] and/or differences in the culture growth conditions. For instance, Fuentes et al. [2011] observed species-dependent deviations in the critical supersaturation of up to 25% for size-
resolved SSA particles derived from artificial seawater doped with exudates from four different types of phytoplankton. The influence of whole phytoplankton cells on CCN activity in these experiments was unlikely since the *Dunaliella tertiolecta* cells are far larger than $d_{acq}$ at $S = 0.2\%$ (cellular equivalent spherical diameter $\sim 8 \mu m$) [Stramski *et al.*, 1993] and thus would not influence the determination of the hygroscopicity parameter.

### 3.4.3 Impact of Bacteria on Sea Spray Aerosol

Marine bacteria are known to chemically alter the organic matter composition of seawater [Coble, 2007; Gruber *et al.*, 2006; Jiao *et al.*, 2010; Ogawa *et al.*, 2001], therefore an evaluation of the impact of bacterial processes on SSA composition and CCN activity must be made by continuously monitoring changes in aerosol properties, along with changes in biological metrics in the seawater. Coincident time-resolved measurements of single particle chemical composition, CCN, chlorophyll concentration, and bacterial abundance in the seawater during the mesocosm experiment are presented in Figure 3.2a-c, demonstrating the interplay between marine biogeochemistry, aerosol composition, and CCN activity. Using the CNO$^-$ ion ($m/z = -42$) as a marker for organic nitrogen species in the UF-ATOFMS mass spectra, inclusion of the peptide-rich ZoBell media in SSA is observed immediately following each addition of this material to the seawater in the wave channel (Figure 3.2c). Figure 3.3 summarizes the hygroscopicity parameters ($\kappa$) of all experiments presented herein with respect to seawater TOC, compared with the results of Fuentes *et al.* [2011], who utilized phytoplankton exudates as a DOM proxy. SSA hygroscopicity was reduced by 42% to $\kappa = 0.81$ (+0.33, -0.40) (Figure 3.2 and Figure 3.3, period Z1) in association with the initial addition of bacteria culture, ZoBell media, and unfiltered seawater (A1) at $t = 0.6$ days. The TOC concentration in the seawater after this
initial addition averaged 89 μM, approximately 20 μM higher than the unaltered seawater control, which is slightly higher than typical springtime regional averages [Sohrin and Sempere, 2005], but is well below values observed at the ocean surface in regions of high biological activity [Engel et al., 2012]. This initial suppression of aerosol hygroscopicity after A1 is attributed primarily to the influence of just the ZoBell media on the OM$_{aero}$ content. Similar to the case with the phytoplankton-only experiment described above, all bacteria added at $t = 0.6$ days are large enough to be CCN active at $S = 0.2\%$ regardless of any chemical effect (average diameter of 0.9 μm) should they be ejected as whole cells, and as such would be insignificant in CCN-derived hygroscopicity parameter measurements.

CCN-derived hygroscopicity was further reduced to $\kappa = 0.14 \pm 0.04 – 0.21 (+0.06, -0.05)$ (Figure 3.2 and Figure 3.3, triangles) at $t = 1.25$ days ($\Delta t = 0.65$ days after A1), coincident with an increase in seawater bacteria concentration and a reduction in aerosol-phase organic nitrogen, measured by UF-ATOFMS (cf. Figure 3.2, periods Z1-Z2). The change in organic nitrogen could indicate bacterial assimilation of peptide or amino acid components of ZoBell media. This $86 \pm 5\%$ reduction in $\kappa$ from the base seawater case with only 110 μM TOC starkly contrasts prior laboratory studies which indicate relatively modest reductions in CCN activity even with >500 μM dissolved organic carbon in the seawater [Frosch et al., 2011; Fuentes et al., 2011; Schwier et al., 2011; Wex et al., 2010b]. The chemical properties of the SSA that led to the large change in CCN activity will be further explored in Section 3.4.5. To date, this represents the largest observed change in CCN activity for ocean-relevant TOC (50-120 μM) [Engel et al., 2012; Sohrin and
Semper, 2005] and heterotrophic bacteria concentrations (approx. 5x10^5 – 5x10^7 cells/mL) [Cho and Azam, 1990; Li, 1998]. Teeling et al. [2012] recently observed heterotrophic bacteria concentrations of ~3.6x10^6 cells mL^-1 in the North Sea following periods of high photosynthetic biological activity (high chl-a), which acted as the carbon source for the observed surge in bacterial growth in that locale. While the labile organic carbon source in this study was ZoBell growth media, the change in bacterial abundance in this mesocosm experiment was similar to that observed by Teeling et al. [2012] and may have produced SSA with similar properties.

The reduction in CCN activity upon the increase in bacterial abundance and depletion of organic nitrogen was attributed to the bacteria-mediated chemical degradation of ZoBell media, which consists predominantly of peptides. In addition, the chemical composition of DOM in the wave channel was also likely impacted by senescent phytoplankton cells, based on the observed reduction in chl-a (Figure 3.2a). The correlation between the observed changes in UF-ATOFMS and CCN-derived hygroscopicity measurements with changes in the concentration of bacterial and phytoplankton biomass in the seawater suggests that the combined effect of the complex biogeochemical interactions occurring in this simulated post-phytoplankton bloom regime influences the physicochemical properties of SSA. Other similar mesocosm experiments have found that bacterial abundance tends to increase as phytoplankton bloom activity begins to subside [Smith et al., 1995], which was also found to be associated with an increase in bacterial surface enzyme activity (which would lead to chemical transformation of OM_{sea}), colonization of phytoplankton particulates, and changes in bacterial community composition [Riemann et al., 2000]. A recent field study also indicated that sequential
changes in bacterial community composition occur as a result of growth substrate changes in the ocean [Teeling et al., 2012]. The results presented in this work, coupled with an understanding of biogeochemical dynamics in the mesocosm, demonstrate that the physicochemical properties of SSA, at least in this study, are strongly affected by the chemical composition of OM_{sea} and that biologically-mediated changes in organic matter composition can significantly influence the mixing state and overall CCN activity of SSA.

### 3.4.4 Phytoplankton Addition After Bacterial Growth

The hygroscopicity parameter did not show significant changes after the addition of phytoplankton to the mesocosm (Figure 3.2, after A4). Curiously, the relatively weak dependence of $\kappa$ on TOC after A4 was qualitatively similar to experiments where phytoplankton exudates dominate the composition of DOM described in Section 3.3.3 and in prior studies [Fuentes et al., 2011; Wex et al., 2010b]. Since the chemical composition of DOM that has been influenced by marine bacteria differs from that of freshly produced DOM by photoautotrophs [e.g., Shimotori et al., 2012], the observed differences in $\kappa$ with respect to TOC between heterotrophic (bacteria-dominated; mesocosm pre-A4) and autotrophic (phytoplankton-dominated; algae-only experiment and mesocosm post-A4) regimes suggests that the chemical composition of OM_{sea} is driving the enrichment and/or physicochemical nature of OM_{aero}. Bacterial processing of DOM with little-to-no change in TOC in these experiments ($\text{TOC}_{Z2} - \text{TOC}_{Z1} = 0 \mu\text{M}$) shows a stronger effect on the CCN activity of SSA ($\kappa_{Z2} - \kappa_{Z1} = -0.6$) than large changes in TOC when non-degraded phytoplankton exudates are added to the seawater ($\text{TOC}_{Z4} - \text{TOC}_{Z2} = 324 \mu\text{M}$, $\kappa_{Z4} - \kappa_{Z2} = -0.09$). Two physical possibilities could have forced the observed reduction in $\kappa$: (1) the
influence of bacteria-processed OM$_{\text{sea}}$ could be enhancing the formation of a distinct population of insoluble organic particles, similar to those observed by Facchini et al. [2008], or (2) the OM$_{\text{sea}}$ associated with bacterial activity is more hydrophobic than OM$_{\text{sea}}$ derived from phytoplankton exudates, which have been shown to be rich in carbohydrates [e.g., Aluwihare and Repeta, 1999], in which case this chemical change to OM$_{\text{sea}}$ would then be simply transferred to OM$_{\text{aero}}$ upon SSA production. These options are investigated through a closure study of CCN activity below.

3.4.5 CCN Activity and Mixing State

Since CCN activity is driven by both size and chemical composition, closure between theoretical and observed CCN can be achieved if the role of size and chemical composition are accurately represented in the theoretical prediction. Despite induced changes in the organic and biological content of the seawater in these experiments, the measured size distributions of nascent SSA, shown in Figure 3.4, did not indicate significant systematic variability such that the reduction in CCN activity could be explained on the basis of particle size. Prior studies have reported changes in the size distribution of nascent SSA as a function of OM$_{\text{sea}}$ concentration [e.g., Fuentes et al., 2010; King et al., 2012; Sellegri et al., 2006]. Our experiments are possibly limited by low concentrations, especially for $d_p < 0.1 \, \mu m$. The lack of significant change in size distributions during these experiments demonstrates the impact of aerosol chemical composition and mixing state on the CCN activity measurements presented herein.

Most studies that strive for CCN closure utilize bulk chemical analysis to drive predictive calculations based on the known hygroscopicity of various substances [e.g., Broekhuizen et al., 2006; Martin et al., 2011]. Often, the incorporation of external mixing
assumptions are required to gain closure due to the importance of the number concentration-weighted mixing state of particles rather than widely used bulk aerosol mass concentration measurement techniques [Wex et al., 2010a]. Two major, distinct particle types occupy the submicron size range of SSA in these experiments [Ault et al., 2013; Prather et al., 2013]. Each of these distinct particle types was identified using TEM-EDX and STXM-NEXAFS analysis for diameters < 0.3 \( \mu m \): an internally mixed salt/organic particle type (SS-OC) and an insoluble organic type that contains small amounts of inorganic sulfur (OC), along with a fraction labeled ‘Other’ which contains particles identified as contaminants [Ault et al., 2013]. Prather et al. [2013] show that the OC type in these experiments was correlated with a population of particles that had a subsaturated hygroscopic growth factor < 1.2 (RH = 93%), and is thus descriptively labeled ‘insoluble’ here. After stimulated bacterial growth, the OC type began to dominate at \( d_p < 0.2 \mu m \) and down to 0.03 \( \mu m \). Figure 3.5 shows the size resolved submicron chemical composition as observed by TEM-EDX for each of the four periods, Z1-Z4 as reported by Ault et al. [2013]. In addition, the organic volume fraction within the SS-OC type was analyzed by STXM-NEXAFS. Spatial maps of \( t_{org} \) and \( t_{NaCl} \) were generated using the methods outlined in Section 3.3.2.1 (Figure 3.6a,b), which were then transformed to organic volume fraction maps using Equation 3.3 (Figure 3.6c). Frequency distributions of the volume fractions (\( \varepsilon_{org} \)) for whole individual particles were derived from the spatial maps and are shown in Figure 3.6d.

In order to bring closure to the changes in relative abundance of each type and illustrate their changes in number concentration constrained by the size distributions (which remained largely unchanged throughout all of the experiments), three lognormal
modes were fitted to the size distribution for each of the four periods, Z1-Z4 (Figure 3.7b). Since the two main particle types (SS-OC, OC) were distinct in composition, it is expected that each should exist with its own lognormal distribution of sizes. Mode 1, with the smallest modal diameter, is considered to consist entirely of the OC type, while the two larger modes (Modes 2 and 3) were considered to be comprised of SS-OC particles based on the size-resolved trend in the TEM-EDX analysis (Figure 3.7a). The height of Mode 1 was constrained such that the re-constructed fraction of SS-OC (Figure 3.7a, red line) came into agreement with the TEM-EDX observations for each of the four cases. The change in magnitude of Mode 1 in relation to Modes 2 and 3 illustrate that underlying changes in the relative abundances of the particle populations occurred despite the lack of significant alterations in the measured size distribution magnitude and/or shape. Figure 3.7 shows that the insoluble organic particle type (Mode 1) increases relative to the SS-OC type upon the growth of bacteria (between periods Z1 and Z2). Due to the fact that the shape and magnitude of the size distributions did not change significantly, the SS-OC particle type appears to have been replaced by OC particles at smaller sizes with changing bacterial abundance in the seawater.

In order to illustrate the importance of external mixing to CCN activity in these experiments, the predicted hygroscopicity parameter ($\kappa_{\text{pred}}$) values are calculated using the simplifying assumption that the population is completely internally mixed and that the salt and organic components do not interact with one another in the mixture. The size-resolved chemical mixing state provided by TEM-EDX and STXM-NEXAFS observations allowed for the calculation of the ensemble submicron organic volume fraction assuming that the OC type is entirely organic and volume fractions for the SS-OC type were derived from
the STXM-NEXAFS analysis (Figure 3.5 and Figure 3.6). The Zdanovskii-Stokes-
Robinson mixing rule [Stokes and Robinson, 1966] was used to generate $\kappa_{\text{pred}}$ using
Equation 3.5:

$$\kappa_{\text{pred}} = \varepsilon_{\text{salt}} \kappa_{\text{salt}} + \varepsilon_{\text{org}} \kappa_{\text{org}}$$  \[3.5\]

where $\varepsilon_{\text{salt}}$ and $\varepsilon_{\text{org}}$ are the bulk volume fractions of salt and organic material, $\kappa_{\text{salt}}$ is
assigned a value of 1.25 (see Table 3.1a), and $\kappa_{\text{org}}$ is assigned a value of 0.006 [Moore et
al., 2008]. The modal organic volume fraction based on STXM-NEXAFS measurements
was used for $\varepsilon_{\text{org}}$, with the remainder of the volume assigned to $\varepsilon_{\text{salt}}$. For period Z3,
insufficient statistics precluded construction of a histogram; the value of $\varepsilon_{\text{org}}$ is estimated
to be 0.45. These data were not available for period Z4 and are omitted. Figure 3.8 shows
the results of this calculation for periods Z1-Z3, compared with the measured values of $\kappa$
during each of these timeframes. The value of $\kappa_{\text{pred}}$ deviates positively from the
measurements after the growth of bacteria, when the OC type dominates the size
distribution at $d_p < 0.2 \ \mu m$ (Figure 3.7, periods Z2-Z4), stressing that accurate
characterization of mixing state in this case is critical to predicting CCN activity. The use
of $\kappa_{\text{pred}}$ based on the assumption of internal mixing in this case would overpredict CCN
concentrations ($s = 0.2\%$) by approximately 25% for periods Z2 and Z3. The OC particle
type, while not contributing significant aerosol volume (or mass) to the submicron particle
population, has a large impact on $\kappa$ due to the sensitivity of this parameter to the number
concentration and hygroscopicity of each particle type. The number concentration of less
hygroscopic OC particles is higher than that of salt-containing aerosol in the smallest sizes,
forcing $d_{\text{act}}$ to become larger (and $\kappa$ to become smaller) as bacterial abundance increases
and OM$_{sea}$ composition is influenced. Hence, these results indicate that bacterial growth in the seawater altered the physicochemical properties of OM$_{sea}$ in a way that influenced the mixing state and CCN activity of nascent SSA.

### 3.4.6 Organic Mass Fraction

In order to compare these results with prior studies of the variability of OM$_{aero}$ with seawater composition, the bulk submicron organic mass fraction of SSA was calculated. Figure 3.9 shows the calculated bulk organic mass fractions for each sample timeframe (Z1-Z3) as a function of chl-a in comparison with parameterized datasets from the literature. Aerosol number size distributions were determined for each of the two main particle types based on sigmoid curves fit to the size-resolved TEM-EDX and STXM-NEXAFS number fractions of SS-OC particles (Figure 3.5 and Figure 3.7). Aerosol mass fractions are determined using an organic matter density of 1.35 g mL$^{-1}$ [Kuwata et al., 2012] and a salt density of 1.8 g mL$^{-1}$ [Zelenyuk et al., 2007]. The organic volume fraction of SS-OC particles was determined by calculating the organic and salt thickness maps based on STXM-NEXAFS measurements of single particle composition of approximately 300 particles in each time period (Figure 3.6). The OC type was taken to be 100% organic for the purposes of this analysis, and due to the presence of some inorganic material may produce an upper limit estimate. For samples collected during Z1 and Z2, frequency distributions of individual particle organic volume fraction values were obtained (Figure 3.6d). Insufficient data were available to generate a reliable histogram for Z3 in this manner; the estimated range reported herein was based on a limited dataset.

It is important to note that changes in the organic mass fraction are small (<15%; Figure 8), despite more prominent changes in the fractional contribution of each particle
type by number, since the insoluble organic sub-population of particles exists mainly in the smaller size range (<0.2 μm; Figure 3.7). The relative invariance of the OM\textsubscript{aero} mass fraction between periods Z1 and Z2, which corresponds to a large reduction in κ, emphasizes that the enhancement of a sub-population of small, less hygroscopic particles can exert a strong influence on CCN activity, but may not be clearly resolved by aerosol mass measurements. As shown in Figure 3.7 and Figure 3.8, changes in κ are driven in this case by the relative abundances of two different particle types, each containing OM\textsubscript{aero}, but with drastically different hygroscopicity, despite only minor changes in the total mass concentration of organic material present in the SSA particle population.

Published parameterizations of the submicron OM\textsubscript{aero} mass fraction based on oceanic chl-a concentrations [Fuentes et al., 2011; Gantt et al., 2011; Vignati et al., 2010] are superimposed on the mass fraction calculations given in Figure 3.9. The mixing ratio of organic matter within the SS-OC type, due to its dominance in particles with d > 0.2 μm, exerts most of the organic mass variability in SSA overall. Prior studies have reported bulk organic mass fractions as high as 77-80% [Facchini et al., 2008; Keene et al., 2007] and as low as ~4% [Modini et al., 2010] in SSA generated from natural seawater samples. The ensemble submicron organic mass fraction in these experiments was approximately 35-40% for periods Z1 and Z2 (Figure 3.9). The OM\textsubscript{aero} mass fractions found in this work deviate positively from published parameterizations at low values of chl-a. This is likely due to the fact that the addition of organic matter to the seawater at A1 did not include the addition of phytoplankton (and hence chl-a), and in fact, significant phytoplankton senescence was observed (shown as a decay in chl-a; Figure 3.2). The modal organic volume fraction within the SS-OC particles increased between Z1 and Z2 (Figure 3.6d) as
chl-a decreased, opposite the expected trend based on current parameterizations [Fuentes et al., 2011; Gantt et al., 2011; Vignati et al., 2010], which do not consider possible differences in the SSA composition between increasing and decreasing chl-a trends. In a natural phytoplankton bloom ecosystem, such as those studied biologically by Teeling et al. [2012] or Smith et al. [1995], autotrophic activity imparts DOM to the seawater, followed by increases in the populations of heterotrophic organisms (e.g., bacteria). The experiments reported herein suggest that marine biogeochemical interactions in the post-bloom period induce changes in the chemical mixing state and CCN activity of SSA. We emphasize that in these experiments, CCN activity changed without increasing chl-a or the bulk submicron OM\textsubscript{aero} fraction. Instead, the importance of the relative abundances of distinct particle types with significantly different compositions and hygroscopicity were observed.

3.5 Implications for Clouds and Climate in Marine Environments

Biological processes actively and dynamically influence the chemical composition of oceanic DOM. Associated with organic matter-producing autotrophic microbes (e.g., phytoplankton) through the microbial loop [Pomeroy et al., 2007], heterotrophic bacteria and their associated enzymes serve as the primary reactive surface responsible for chemical transformation of DOM [Azam and Malfatti, 2007; Jiao et al., 2010]. While the molecular-level details have not been thoroughly characterized to date, bacterial activity is known to alter the chemical composition of DOM [Coble, 2007; Flerus et al., 2012; Gruber et al., 2006; Kujawinski et al., 2009]. In stark contrast with laboratory sea spray experiments that use phytoplankton exudates as an OM\textsubscript{sea} chemical proxy [Fuentes et al., 2011; Wex et al., 2010b], the results presented in this study demonstrate the importance of including a more
holistic representation of the biological complexity of marine microbial assemblages. Since the ratio of bacterial production to phytoplankton production in the ocean varies based on environmental conditions [e.g., Hoppe et al., 2002], the localized biogeochemical state of the ocean will likely influence the CCN properties of nascent SSA through differing compositions of OM\textsubscript{sea}. The ratio of bacterial carbon to phytoplankton carbon increases almost asymptotically as chl-\textit{a} concentration approaches zero in the ocean, owing to the relatively stable abundance of marine heterotrophic bacterial biomass ($5 \times 10^5$ – $5 \times 10^7$ cells mL$^{-1}$) [Cho and Azam, 1990]. This emphasizes the significant influence that heterotrophic bacteria can exert on the composition of OM\textsubscript{sea} through their ability to consume, utilize, and produce DOM, thus impacting the composition, mixing state, and cloud activity of SSA independently of phytoplankton abundance as estimated by chl-\textit{a} concentrations.

Recent global modeling efforts have used the OM\textsubscript{aero} – chl-\textit{a} relationship to derive aerosol composition (with hygroscopicity assumptions) [Meskhidze et al., 2011; Westervelt et al., 2012] due to the near global coverage of satellite-derived oceanic chl-\textit{a} measurements. While this approach may closely approximate OM\textsubscript{aero} mass fractions in some regions, the results of this study indicate that more detailed information may be necessary for the derivation of CCN concentrations. Still, aerosol mixing state information has been shown to be crucial in constraining marine CCN concentrations [Meskhidze et al., 2011]; experimental evidence for the importance of external mixing to the CCN properties of nascent SSA is provided herein. Due to the lack of significant changes in the size distribution despite the increasing relative abundance of a distinct insoluble organic particle type (Figure 3.7), enrichment of OM\textsubscript{aero} resulting from elevated oceanic biological activity appears to replace salt-containing particles in this experiment with concomitant changes in
OM\textsubscript{sea}. This type of behavior has been shown in model simulations to reduce globally averaged CCN concentrations compared to cases where the SSA source function disregards organic matter [Westervelt \textit{et al.}, 2012]. The size dependence of the insoluble organic particle type supports observations of decreasing hygroscopicity with decreasing particle size [Kaku \textit{et al.}, 2006] and likely plays a strong role in buffering aerosol-mediated changes in cloud microphysics due to the dynamic nature of water vapor supersaturation within marine stratocumulus clouds [Hegg \textit{et al.}, 2012]. The observed close connection of the CCN activity of SSA to heterotrophic bacterial activity within a dynamic microbial ecosystem stresses the climatic influence of biosphere/atmosphere coupling. Investigations into the physicochemical properties of SSA that are integrated with detailed marine microbiological and chemical analyses will further elucidate the interactions between marine biogeochemical processes and climate-relevant aerosol properties.

### 3.6 Acknowledgements

This work was funded through the Center for Aerosol Impacts on Climate and the Environment (CAICE), a National Science Foundation Phase I Center for Chemical Innovation (CHE-1038028). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. F. Azam was supported by grants from NSF OCE0962721 and the Gordon and Betty Moore Foundation Marine Microbial Initiative. The authors would like to thank all investigators involved in the CAICE intensive campaign, with special thanks to Christopher Cappa, Grant Deane, Dale Stokes, John Seinfeld, Scott Hersey, Wilton Mui, and Michelle Kim for their valuable
contributions. Nathan Schoepp and William Lambert provided algae cultures through the San Diego Center for Algae Biotechnology (SD-CAB) greenhouse facility. The Bartlett Lab at Scripps Institution of Oceanography supplied the culture of *Pseudoalteromonas atlantica*. Dave Aglietti, John Lyons, Paul Harvey, and Charles Coughran of the Scripps Institution of Oceanography Hydraulics Laboratory provided valuable assistance and expertise. The authors also thank the anonymous reviewers for their highly constructive comments. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

### Table 3.1: Selected hygroscopicity parameter values from the literature.

<table>
<thead>
<tr>
<th>Author, Year</th>
<th>$\kappa$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(a.) Unaltered Natural Seawater and Inorganic Proxies</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collins et al. [this work]</td>
<td>1.4 (+0.3, -0.7)</td>
<td>Natural seawater, sand filtered</td>
</tr>
<tr>
<td>King et al. [2012]</td>
<td>1.25, 1.08</td>
<td>NaCl and Artificial seawater, respectively</td>
</tr>
<tr>
<td>Fuentes et al. [2011]</td>
<td>1.3–1.5</td>
<td>&quot;Seawater proxy&quot; no organics; $\kappa$ depends on $a_w$</td>
</tr>
<tr>
<td>Niedermeier et al. [2008]</td>
<td>1.3$^a$, 1.05–1.25$^a$</td>
<td>NaCl$_{aq}$, Natural seawater (various locations)</td>
</tr>
<tr>
<td>Petters and Kreidenweis [2007]</td>
<td>1.28</td>
<td>Calculated: Aerosol Inorganic Model</td>
</tr>
<tr>
<td><strong>(b.) Wave channel experiments [Collins et al., this work]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seawater + algae culture</td>
<td>0.88 (+0.34, -0.23)</td>
<td>Dunaliella tertiolecta</td>
</tr>
<tr>
<td>Mesocosm (pre-growth)</td>
<td>0.81 (+0.33, -0.40)</td>
<td>Alteromonas spp. + ZoBell</td>
</tr>
<tr>
<td>Mesocosm (post-growth)</td>
<td>0.14 (+0.04, -0.05)</td>
<td>Alteromonas spp. + ZoBell</td>
</tr>
<tr>
<td>Mesocosm (with algae)</td>
<td>0.12 (+0.02, -0.03)</td>
<td>Alteromonas spp. + ZoBell + Dunaliella tertiolecta</td>
</tr>
<tr>
<td><strong>(c.) Phytoplankton exudates in seawater proxy [Fuentes et al., 2011]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thalassiosira rotula</td>
<td>1.21, 1.11</td>
<td>Average $\kappa$ values:</td>
</tr>
<tr>
<td>Chaetoceros sp.</td>
<td>1.03, 0.95</td>
<td></td>
</tr>
<tr>
<td>Emiliania huxleyi</td>
<td>1.14, 0.96</td>
<td>175 $\mu$M and 512 $\mu$M DOC, respectively</td>
</tr>
<tr>
<td>Phaeocystis cf. globosa</td>
<td>1.15, 1.03</td>
<td></td>
</tr>
<tr>
<td><strong>(d.) Phytoplankton exudate mixtures [Wex et al., 2010b]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thalassiosira rotula</td>
<td>1.1</td>
<td>Mixtures contained exudates from all types listed in varying proportions; entries identified by dominant exudate source; all cited $\kappa$ values are averaged across various $a_w$ conditions</td>
</tr>
<tr>
<td>Chaetoceros sp.</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>Emiliania huxleyi</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>Phaeocystis cf. globosa</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td><strong>(e.) Other relevant model and natural systems</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>King et al. [2012]</td>
<td>~1.25$^a$</td>
<td>60g NaCl + 1 g sodium laurate, aqueous</td>
</tr>
<tr>
<td>Frosch et al. [2011]</td>
<td>~0.2$^a$</td>
<td>0.27g NaCl + 1 g sodium laurate, aqueous</td>
</tr>
<tr>
<td>Moore et al. [2011]</td>
<td>0.57</td>
<td>50% oxalic acid, 50% NaCl</td>
</tr>
<tr>
<td>Moore et al. [2011]</td>
<td>0.38</td>
<td>80% oxalic acid, 20% NaCl</td>
</tr>
<tr>
<td>Schwier et al. [2011]</td>
<td>1.1$^a$</td>
<td>&gt;bilayer oleic acid on NaCl$_{aq}$</td>
</tr>
<tr>
<td></td>
<td>1.3$^a$</td>
<td>&gt;bilayer sodium dodecyl sulfate on NaCl$_{aq}$</td>
</tr>
<tr>
<td></td>
<td>1.187</td>
<td>NaCl + 0.001M sodium oleate</td>
</tr>
<tr>
<td></td>
<td>0.869</td>
<td>NaCl + 0.01M sodium oleate</td>
</tr>
<tr>
<td><strong>(f.) 'Clean Marine' field observations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moore et al. [2012]</td>
<td>0.15–0.2</td>
<td>Aircraft; Coastal Southern California</td>
</tr>
<tr>
<td>Martin et al. [2011]</td>
<td>0.33–0.50</td>
<td>Ship; Arctic summer (range: 0.09–0.61)</td>
</tr>
<tr>
<td>Mochida et al. [2011]</td>
<td>~0.6</td>
<td>Ship; Subarctic North Pacific</td>
</tr>
<tr>
<td>Good et al. [2010]</td>
<td>1.15–1.40</td>
<td>Ship; Tropical Atlantic</td>
</tr>
<tr>
<td>Allan et al. [2008]</td>
<td>0.6 ± 0.2</td>
<td>Puerto Rico</td>
</tr>
<tr>
<td>Furutani et al. [2008]</td>
<td>0.17–0.3$^a$</td>
<td>Ship; Coastal Southern California</td>
</tr>
<tr>
<td>Hudson [2007]</td>
<td>0.87 ± 0.24</td>
<td>Aircraft; near Antigua Island</td>
</tr>
</tbody>
</table>

$^a$$\kappa$ calculated from reported $D_{acf}/S$ pairs. $^b$Large positive deviations in $\kappa$ for highest water activity ($a_w$) are omitted here. $^c$Mobile sampling platforms (e.g., aircraft) are noted where applicable.
### Table 3.2: Mesocosm experiment additions

<table>
<thead>
<tr>
<th>ID</th>
<th>Time (days)</th>
<th>Material Added</th>
<th>Quantity(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Seawater</td>
<td>8250 L</td>
</tr>
<tr>
<td>A1</td>
<td>0.6</td>
<td><em>Alteromonas</em> spp. bacteria</td>
<td>1x10(^{10}) cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Whole Seawater</td>
<td>100 L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZoBell media</td>
<td>18 g C</td>
</tr>
<tr>
<td>A2</td>
<td>1.9</td>
<td><em>Alteromonas</em> spp. bacteria [ZoBell media (in culture)]</td>
<td>4.5x10(^{12}) cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[13.5 g C]</td>
</tr>
<tr>
<td>A3</td>
<td>2.6</td>
<td>ZoBell media</td>
<td>15 g C</td>
</tr>
<tr>
<td>A4</td>
<td>2.8</td>
<td>ZoBell media</td>
<td>15 g C</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>P. atlantica</em> bacteria</td>
<td>1x10(^{11}) cells</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Dunaliella tertiolecta</em> algae</td>
<td>1x10(^{11}) cells</td>
</tr>
</tbody>
</table>

\(^a\)Quantities are approximate.
3.8 Figures

Figure 3.1: Schematic of the wave channel experimental setup. All SSA samples were drawn from the headspace of the wave channel at the same height (relative to the water surface) and at the same distance (~2 meters) from the wave breaking region. Clean air was delivered to the channel by aluminum ducts and a 4-stage air purification system.
Figure 3.2: Temporal profile of (a.) TOC and chl-a in the seawater, (b.) the hygroscopicity parameter ($\kappa$) of SSA, and (c.) 15-minute averaged SSA-bound organic nitrogen (UF-ATOFMS) juxtaposed with the concentration of bacteria in seawater for the mesocosm experiment. Error bars on the time axis of (b.) represent the averaging time for each determination. See text for discussion of uncertainty in $\kappa$. Vertical dashed lines denote additions of biological and/or organic material to the wave channel corresponding to those listed in Table 3.2. A1 denotes the initial major addition of *Alteromonas* spp. bacteria, ZoBell media, and unfiltered seawater. Note that the CNO$^-$ signal increases upon each addition of fresh ZoBell media and/or seed cultures that contain as yet un-degraded media. The periods Z1-Z4 were chosen to overlap with samples analyzed by TEM-EDX and STXM-NEXAFS and are described in detail. The phytoplankton-only experiment (Section 3.4.2) is not shown.
**Figure 3.3**: Scatter plot of $\kappa$ values related to the (a.) total organic carbon content of the seawater from which the SSA were derived, compared with a study utilizing phytoplankton culture exudates as a DOM proxy. Labels Z1-Z4 correspond to the shaded time periods in Figure 3.2.
Figure 3.4: Aerosol size distributions used for CCN activity determinations in this study on (a.) linear and (b.) logarithmic scales. Note that neither the magnitude nor shape of the SMPS-derived size distribution changed significantly throughout this set of experiments. Since all particles sampled by the APS would theoretically act as CCN based on their large size alone [McFiggans et al., 2006], total particle concentration for \(d_p = 0.6 - 11 \mu m\) is shown at right for simplicity. The top axis shows the size scale converted to the \(r_{80}\) particle size metric used in many sea spray flux studies [de Leeuw et al., 2011; Lewis and Schwartz, 2004].
**Figure 3.5:** Size-resolved fraction of mixed salt/organic (SS-OC) particles derived from TEM-EDX and STXM-NEXAFS observations. The remainder of the particles in this size range are taken to be of the primarily organic type. These data are reproduced as blue bars in Figure 3.7. Detailed explanation of TEM-EDX and STXM-NEXAFS measurements are provided by *Ault et al.* [2013].
**Figure 3.6:** Spatial maps of SSA particles analyzed by STXM-NEXAFS showing (a.) the thickness of organic material ($t_{OC}$), (b.) thickness of inorganic material ($t_{NaCl}$), and (c.) spatially resolved organic volume fraction. (d.) Normalized frequency distribution of organic volume fractions ($\varepsilon_{org}$) for individual SSA particles collected during periods Z1 and Z2.
Figure 3.7: (a.) TEM-EDX size resolve number fractions of particles superimposed with a fit of the size resolved SS-OC fraction and the size-resolved fraction of Mode 2+Mode 3 particles. The sigmoid fits to the TEM-EDX data were used for interpolation in ensemble volume and mass fraction calculations. All four of the sigmoid fits are shown superimposed on one another Figure 3.5. (b.) The size distributions for each of the four periods are fitted with three log-normal component distributions. Mode 1 represents the insoluble organic particle type, while Modes 2 and 3 represent the SS-OC particles. The height of Mode 1 was constrained by the mixing state observations made by TEM-EDX, as described in the text.
Figure 3.8: Predicted $\kappa$ based on the assumption of volume-weighted internal mixing (Eq. 4.5) compared with measured values. Note that the predicted $\kappa$ only over-estimates hygroscopicity when the less hygroscopic Mode 1 particles begin to outnumber the more hygroscopic Mode 2 particles (Figure 3.7) through the influence of bacterial activity on the seawater organic composition. Data for Z4 are omitted here since organic volume fractions derived from STXM-NEXAFS data were unavailable.
Figure 3.9: Submicron OM$_{aero}$ mass fraction is calculated considering two particle types observed by microscopy: a mixed salt/organic type and a separate insoluble organic type. The vertical bars indicate the range of submicron OM$_{aero}$ mass fraction values expected based on the distribution of organic volume fractions in the SS-OC particle type observed by STXM-NEXAFS (Figure 3.6). The mode of the distribution of organic volume fractions is shown by the filled circles. A statistically valid histogram could not be generated for Z3, so only the estimated range is indicated. Filled triangles show the calculated OM$_{aero}$ mass fraction when neglecting OM in the SS-OC particle type, indicating the organic mass contained in only the insoluble organic type. Published parameterizations of the OM$_{aero}$ – chl-α relationship are superimposed for direct comparison.
3.9 References


Bidle, K. D., and F. Azam (2001), Bacterial Control of Silicon Regeneration from Diatom Detritus: Significance of Bacterial Ectohydrolases and Species Identity, *Limnol. Oceanogr.*, 46(7), 1606-1623.


4. Consistency in Cloud Droplet Activation of Sea Spray Aerosol Produced from Phytoplankton Blooms

4.1 Synopsis

Sea spray aerosol (SSA) particles are one of the most abundant types of natural aerosol particles globally, impacting the climate through both direct light scattering and through their role as cloud condensation nuclei (CCN). The ability for aerosol particles to act as CCN is controlled by their physicochemical properties, so understanding the variations in composition of these particles is key for constraining the impact of ocean-derived CCN on marine clouds. SSA particle composition has been associated with the extent of biological activity in the seawater from with the particles were produced, but fundamental physical and chemical findings have been inconsistent. By inducing phytoplankton growth in a Marine Aerosol Reference Tank (MART) coupled with the use of an SSA production method that closely resembles laboratory breaking waves, it was determined that the overall CCN activity of SSA is largely invariant with respect to bloom state and dissolved organic carbon concentration over the range of conditions studied. Hygroscopicity parameter ($\kappa$) values for the SSA were consistently greater than 0.8, with a weak size dependence for particles with diameter ($d_p$) of 38 – 75 nm. Similar results were obtained for particles generated with a diffusion stone, which produces a different bubble size distribution from the plunging waterfall typically used in the MART. A sample of foam was collected at the end of a bloom experiment and aerosolized using an atomizer and had $\kappa = 0.75 – 0.8$, only slightly lower than the SSA particles produced throughout the rest of the study ($\kappa = 0.8 – 1$). For $\kappa = 0.8$, the organic fraction of an assumed internal
mixture of salt and organics is about 40%. The consistency in CCN activity observed in these experiments perhaps suggests that this mixing ratio of 40% organic/60% salt is a sort of upper limit, even for the foam sample which could have been enriched in organic matter up to 100 fold over the organic concentration in the bulk seawater. The results are discussed in the context of the production mechanism of SSA and the possible importance of surface tension.

4.2 Introduction

Assessments of the global climate are limited by scientific understanding of the influence of natural aerosols on the radiation balance [Andreae, 2007]. The relative influence of natural aerosols on the formation of clouds, called the Aerosol Indirect Effect, is of particularly large uncertainty. Aerosol particles act as the nuclei for cloud droplets: the aerosol particles capable of nucleating a cloud are called cloud condensation nuclei (CCN). Since the dependence of cloud droplet number concentrations on CCN number concentrations has a logarithmic shape, the sensitivity of cloud microphysical properties to the anthropogenic CCN emissions varies with the pre-industrial CCN concentration. Hence, controlled studies of the emissions and properties of nascent, natural aerosol particles is key to our understanding of the human impact on climate.

The ocean is one of the two most abundant sources of natural particles globally, with vast remote regions that are, even today, minimally influenced by anthropogenic emissions. Sea spray aerosol (SSA) particles are produced by the ocean when wind stress on the sea surface induces the formation of waves, which upon reaching a crest and breaking, entrain air into the upper mixed layer of the ocean [de Leeuw et al., 2011]. The
bubbles formed by this air entrainment rise through the water column to the air-sea interface and eventually burst, ejecting a number of aerosol particles into the atmosphere. Two main aerosol production mechanism are recognized to occur during a bubble bursting event, reviewed in detail by Lewis and Schwartz [2004]. First, the fluid film that forms the ‘cap’ of the bubble thins through drainage of liquid toward its margins, and at some critical thickness, ruptures. The fragmentation of this film creates droplets that are ejected (often called ‘film droplets’), typically at a low azimuthal angle and are thought to have diameters \((d) < 1 \text{ \(\mu\)m} \text{[Resch and Afeti, 1992]}. \) After the cap film ruptures, the remaining bubble cavity collapses on itself, creating a reactionary jet of water protruding from the center of where the bubble once resided on the water surface. The water that makes up this jet is thought to derive from a thin layer that once made up the inner wall of the bubble. The breakup of the jet as it rises forms droplets of a variety of sizes, some too large to have reasonable lifetimes and impact within the atmosphere, but overall mostly thought to have \(d > 1 \text{ \(\mu\)m}. \) Importantly the size of the bursting bubble controls the importance of each part of the mechanism, with larger bubbles (radius > 1 mm) having a larger contribution from film droplet production, while bubbles at the small end of the size spectrum \((r < 0.5 \text{ mm})\) are thought to produce exclusively jet droplets. Hence the shape of the bubble size distribution is of critical importance to the nature of the SSA number size distribution \([Prather et al., 2013]\).

The composition of SSA particles, while long simplified in large-scale models as ‘sea salt’ or sodium chloride (NaCl), has actually been known for many years [e.g., Blanchard, 1964] to be a mixture of inorganic salts, organic compounds, and biological material \([Ceburnis et al., 2008; Kuznetsova et al., 2005; Novakov et al., 1997; O’Dowd et]
The size-differentiated composition of SSA particles has been characterized. Particles with $d < 1 \mu m$ exhibit a significant enrichment (by mass) of organic matter relative to salt [Ceburnis et al., 2008; O'Dowd et al., 2004]. Recent studies have confirmed that SSA at any given size is a mixture of various types of particles. Sea salt particles with little-to-no organic material can be separated from particles dominated by organic material [Bigg and Leck, 2008] (called an external salt/organic mixture), or salts and organics can be mixed internally (existing within the same particle) [Ault et al., 2013; Prather et al., 2013]. Primary biological particles are yet another distinct particle type, occurring mostly at $d > 1 \mu m$, containing either viable, vegetative, or fragmented bacteria and viruses [Aller et al., 2005]. The properties of SSA particles, including their size distribution, composition, and physicochemical properties have been shown to be a function of the composition of the seawater from which they were generated.

In order to extend SSA composition to global climate models, attempts at parameterizing the emissions of organic matter from the ocean based on observables from space-borne instruments, allowing wide spatial coverage. While perhaps an indirect physical connection exists, several studies have attempted to utilize ocean surface chlorophyll-a as a metric from which to derive source functions for organic matter in SSA particles [Gantt et al., 2011; Long et al., 2011; O'Dowd et al., 2008; Vignati et al., 2010]. This relationship was based initially on the observed correlation between biological activity in the North Atlantic and the size-resolved mass fraction of organic matter in aerosol collected at a coastal site with clean marine backward parcel trajectories [O'Dowd et al., 2004], which was echoed by seasonal scale measurements in both the northern and
southern mid-latitudes [Sciare et al., 2009; Yoon et al., 2007]. Finer scale investigations on the relationship between chlorophyll-a and the production of organic-enriched SSA particles have been inconsistent, however. In situ observations on shipborne campaigns have shown evidence of organic matter in SSA particles, but correlations with chlorophyll-a are either weak or non-existent [Gaston et al., 2011; Quinn et al., 2014]. Reanalysis of the initial North Atlantic coastal dataset revealed that correlations between chlorophyll-a and organic aerosol mass improved when a time-delay was inserted into the signal [Rinaldi et al., 2013]. The general discrepancy between in situ measurements and those that integrate over larger temporal and spatial scales indicates that biogeochemical nuance may link the production of organic-enriched SSA and the occurrence of elevated microbiological activity in the ocean.

As noted earlier, the impact of natural aerosol particles on the indirect effect is a major source of uncertainty in global climate simulations [Carslaw et al., 2013; Tsigaridis et al., 2013]. Incorporating the dependence of CCN activity on the composition of SSA particles could help constrain the influence of natural aerosols on the climate. A promising direction forward may be to generate hygroscopicity predictions based on the aforementioned organic mass fraction parameterization(s). To this end, the hygroscopicity parameter (κ), which can be calculated based on measurements of CCN activity [Petters and Kreidenweis, 2007], has been used to generate global hygroscopicity parameter coverage [Pringle et al., 2010]. Laboratory-generated SSA particles from natural seawater or artificial proxies tend to yield hygroscopicity parameter (κ) values between 1 – 1.5 [Collins et al., 2013; Fuentes et al., 2011; King et al., 2012; Moore et al., 2011; Niedermeier et al., 2008; Wex et al., 2010], which includes the theoretical value for NaCl
When seawater or artificial proxies were doped with organic material in order to evaluate the concomitant change in CCN-derived hygroscopicity, results mostly lie within the range $\kappa = 0.8 - 1.25$ [Collins et al., 2013; Fuentes et al., 2011; King et al., 2012; Moore et al., 2011; Wex et al., 2010]. Field measurements of ambient aerosol in the marine boundary layer (MBL) often yield $\kappa = 0.1 - 0.6$ [e.g., Allan et al., 2008; Furutani et al., 2008; Martin et al., 2011; Mochida et al., 2011] with some measurements in the $\kappa = 0.85 - 1.4$ range [Good et al., 2010; Hudson, 2007]. A global model study indicated that the average hygroscopicity of particles in the MBL was $\kappa = 0.59$ in the North Atlantic although higher ($\kappa = 0.92$) over the Southern Ocean [Pringle et al., 2010]. This was explained by the weaker overall anthropogenic influence on the atmosphere in the Southern Hemisphere [Chung and Seinfeld, 2002], suggesting perhaps that the hygroscopicity of true natural aerosol is more similar to the measurements of SSA produced in controlled laboratory settings.

Assuming characteristic hygroscopicity values for the salt and organic portions of an assumed population of uniform, internally mixed salt/organic particles, applying a volumetric mixing rule [Petters and Kreidenweis, 2007] to the organic matter parameterizations based on chlorophyll-a yields the curves presented in Figure 4.1. For the parameterizations based on the Mace Head, Ireland (North Atlantic) dataset, the calculated $\kappa$ values fall almost entirely below the range of values measured for natural seawater and seawater proxies, and extends all the way to $\kappa = 0.2$ when the parameterizations saturate at an organic mass fraction of 76% [Vignati et al., 2010]. It is interesting to note that the parameterization based on the Point Reyes dataset (Pacific coast
of California) [Gantt et al., 2011] agrees better with the range of κ values reported for nascent SSA produced in laboratory experiments (shaded regions).

In order to study the fundamental connection, if any, between CCN activity and biological activity in the surface ocean, this study will generate aerosol from phytoplankton bloom microcosms grown in the laboratory. While it is still uncertain whether chlorophyll-a is a good proxy for organic matter in SSA, and perhaps also its CCN activity, the phytoplankton are used here also as synthesizers of organic matter in proper proportions to replicate the chemical complexity of organic matter found in the open ocean. In addition, these experiments are conducted in seawater that contain natural assemblages of bacteria and viruses, which couple with the phytoplankton through ecosystem processes [Pomeroy et al., 2007] that dynamically shape the composition of both dissolved and particulate organic matter [Azam and Malfatti, 2007; Kujawinski, 2011]. These experiments represent the first measurements of the CCN activity of SSA produced from seawater that contains a phytoplankton bloom in a controlled environment.

4.3 Experimental Methods

In order to test the influence of seawater organic matter concentration and composition on the properties of SSA particles, a phytoplankton blooms were reproduced in the laboratory in microcosm experiments. The results presented in this study are from three different microcosm growth experiments from the months of September 2013 (Expt. 1), January 2014 (Expt. 2), and July 2014 (Expt. 3). Experiments 1 and 2 were conducted in parallel with a variety of other measurements to be presented in separate manuscripts,
while Experiment 3 was conducted as a comparison of the CCN activity of SSA particles generated by two different bubble-generation methods.

4.3.1 Preparation and Growth of Phytoplankton Microcosms

Seawater was obtained from the surface of the coastal Pacific Ocean at Scripps Pier (La Jolla, CA; 32° 52.0’ N, 117° 15.4’ W), 275 meters from the shoreline. Collected seawater was passed through 100 μm Nitex mesh to prevent larger organisms from being present within the microcosm experiment. Seawater was shielded from direct sunlight after collection, and was allowed to thermally equilibrate with the laboratory for 24 hours. Phytoplankton growth in the natural seawater samples was stimulated under constant light (~100 μE m⁻² s⁻¹, 5700 K) through the addition of Guillard’s “f” growth medium diluted by a factor of 2 (f/2; Aquatic EcoSystems, Apopka, FL). Phytoplankton cell abundance was measured in real time using chlorophyll-a fluorescence (AquaFluor, Turner Designs). Total organic carbon (TOC) and dissolved organic carbon (DOC; filtered, 0.2 μm pore size) in the seawater was measured by the high temperature combustion method (Shimadzu Scientific Instruments). Temporal profiles of chlorophyll-a and TOC (or DOC) are provided in Figure 4.2.

4.3.2 Aerosol Generation

Microcosm experiments were conducted within a Marine Aerosol Reference Tank [Stokes et al., 2013], which utilizes a pulsed plunging sheet of water to produce bubbles, from which SSA are generated. The chemical and physical properties of SSA particles generated by this plunging waterfall method compare well to SSA produced by breaking waves in a laboratory wave channel [Collins et al., 2014; Prather et al., 2013; Stokes et al.,]
Once phytoplankton growth was initiated, SSA particles were produced only after chlorophyll-a fluorescence reached approximately 100 fluorescence units. Subsequent operation of the plunging waterfall was restricted to a 2-hour duty cycle in order to limit damage to the phytoplankton through shear stress imparted by the centrifugal pump used to circulate water through the waterfall apparatus. The MART waterfall aerosol generation apparatus was used to make SSA in each of the experiments presented here.

Sea spray aerosol was also generated through a bubble-bursting method wherein bubbles were generated at the bottom of the MART by forcing purified air through a stainless steel diffusion stone and were then allowed to rise to the surface of the water and burst; an identical method to that described and used by Bates et al. [2012]. Based on a prior inter-comparison of the chemical properties of aerosols generated by various methods, it was hypothesized that the similarity of the diffusion stone to the sintered glass filter method investigated by Collins et al. [2014] would result in SSA that was over-expressed in organic matter. It should be noted, however, that the aforementioned inter-comparison study of laboratory SSA generation methods investigated particles with $d_p > 100$ nm, and did not evaluate the influence of bubble generation mechanism on aerosol composition for particle sizes relevant to the current study ($d_p < 100$ nm). Consequently, it is not known whether SSA generation methods similar to the diffusion stone or sintered glass filters produce aerosol with $d_p < 100$ that have a different composition from SSA generated by other methods (e.g., MART plunging waterfall). The dearth of chemical information about SSA particles with sizes important to CCN activity ($d_p < 100$ nm) is emblematic of a similarly weak understanding, and need for further fundamental study, of
the production mechanism and enrichment of organics in of SSA particles all sizes [Gantt and Meskhidze, 2013; Lewis and Schwartz, 2004; Meskhidze et al., 2013].

4.3.3 Cloud Condensation Nuclei Measurements

CCN activity was measured by evaluating the fraction of total aerosol particles that could act as CCN while controlling the diameter of dry particles \(d_{dry}\) and the supersaturation \(s\) to which the particles were subjected. The goal of these measurements is to evaluate the water uptake properties of SSA particles using the hygroscopicity parameter \(\kappa\), which can be calculated using the critical supersaturation \(s_c\) for a known dry particle diameter \(d_{dry}\), assuming that the surface tension is that of pure water \(\sigma_{lv} = 0.072 \text{ N m}^{-1}\) [Petters and Kreidenweis, 2007]. The aerosol sample was dried using silica gel diffusion driers, bringing the relative humidity (RH) of the sample air below 25%. The dried particles were then pass through a Kr-85 bipolar charger, wherein a known distribution of both positive and negative charge is imparted to the aerosol [Wiedensohler and Fissan, 1990]. The particles are then size selected using a Differential Mobility Analyzer (DMA; TSI, Inc.), which selects positively charged aerosol particles based on their mobility within an electric field [Knutson and Whitby, 1975]. Aerosol sizes selected by the DMA are known as mobility diameters \(d_m\), which are equal to the physical diameter \(d_p\) when particles are perfect spheres. A recent study by Wex et al. [2010] indicates that the shape factor \(\chi\) for SSA can be represented as \(\chi = 1.06\), resulting in a \(d_p\) which is approximately 6% smaller than the corresponding \(d_m\) [DeCarlo et al., 2004]. Substituting the corrected \(d_p\) for \(d_m\) in analytical hygroscopicity parameter calculations (Eq. 10, [Petters and Kreidenweis, 2007]) leads to \(\kappa\) values that are 1.2 times higher than if \(d_m\) was utilized as \(d_{dry}\), irrespective of supersaturation. Hence, in this study \(d_{dry} = d_p\) after adjustment using
the aforementioned shape correction. The number concentration of CCN \( (N_{CCN}) \) was measured using a continuous-flow streamwise thermal gradient CCN counter (CCNc; Droplet Measurement Technologies) \cite{Roberts2005}, while total aerosol particle concentrations \( (N_p) \) were measured by a condensation particle counter (TSI, Inc.). The supersaturation within the CCNc is controllable with variation of approximately 5\% (conservatively) \cite{Rose2008}. This setup was operated in two different (equivalent) modes: (1) stepping through an array of \( d_{dry} \) at constant \( s \) and (2) stepping through an array of \( s \) at constant \( d_{dry} \). Mode 1 was used for routine analysis of SSA particles throughout the course of a phytoplankton bloom within the microcosm (Expts. 1 and 2) and Mode 2 was used specifically to probe the size-resolved hygroscopicity of SSA between \( d_m = 40 – 80 \) nm (Expt. 3).

4.4 Results

4.4.1 CCN Activity of Nascent SSA during Phytoplankton Blooms

Model predictions of primary marine aerosol properties in the MBL, based on the parameterized flux of sea spray organics \cite{ODowd2008} and measured hygroscopicity of isolated marine organic matter \cite{Moore2008}, inherently predict that the CCN activity of SSA particles generated within a phytoplankton bloom region should be lower than for SSA particles generated in an oligotrophic region \cite{Meskhidze2011, Westervelt2012} (c.f. Figure 4.1) These experiments, conducted in a background aerosol-free environment within the MART, can help constrain the impact of phytoplankton blooms on the CCN activity of SSA emitted in these regions.
It has been suggested that DOC is an important source of carbon in SSA particles [Fuentes et al., 2011; Quinn et al., 2014; Russell et al., 2010], so alterations to DOC concentrations of the magnitude observed in this study should influence the composition and CCN activity of particles produced with the MART in these experiments. The fraction of CCN-active SSA particles were measured as a function of size, and are shown for two supersaturation settings for Experiments 1 and 2 in Figure 4.3. No systematic change in hygroscopicity was observed at s = 0.2%, 0.4%, or 0.6%. The shoulder in the s = 0.2% curves obtained during Experiment 2 was due to the presence of particles that passed through the DMA with greater than 1 positive charge [Petters et al., 2007]. Data from these two experiments was collected using a different DMA and charge neutralizer system, which may explain the discrepancy in the presence of the multiple charge shoulder. The dashed sigmoid curve corresponds to the hygroscopicity of NaCl (κ = 1.25) [Petters and Kreidenweis, 2007], and the shaded region represents the range of hygroscopicity parameter values that have been reported for laboratory-generated SSA particles (κ = 1 – 1.5) at mean seawater organic matter concentrations (~70 μM C) or using inorganic seawater proxies [Collins et al., 2013; Fuentes et al., 2011; King et al., 2012; Niedermeier et al., 2008]. The differential particle size analysis of CCN activity at s = 0.2% lies mostly within the range of reported values for SSA that were not organic-enriched, while the higher supersaturations indicate the possibility that particles with \(d_{dry} < 50\) nm may have weaker hygroscopicity than inorganic salt aerosol. The importance of mixing state for SSA particles with \(d_p < 50\) nm has been observed previously [Collins et al., 2013]. Overall, the lack of a systematic change in hygroscopicity with respect to the biological state of the bloom (and the associated changes in DOC) was remarkable. If SSA particles within this
size range \((d_p = 30 – 80\, \text{nm})\) were experiencing an enrichment in organic matter as seawater DOC increased, then the physicochemical consequences of increasing the fraction of organic matter in SSA particles must be compensated by other factors.

SSA composition is known to be a strong function of particle size; the organic/salt mass ratio increases as particle diameter decreases [Ceburnis et al., 2008; O’Dowd et al., 2004] and a distinct population of organic-dominated particles (not internally mixed with sea salt) are prevalent when \(d < 100\, \text{nm}\) [Ault et al., 2013; Prather et al., 2013]. A recent shipborne study in the North Atlantic measured the size-resolved CCN activity of SSA [Quinn et al., 2014] that was artificially generated at the sea surface by forcing air through a set of stainless steel diffusion stones placed below the sea surface [Bates et al., 2012]. The generated aerosol exhibited \(\kappa \sim 0.4\) at \(d_m = 40\, \text{nm}\), increasing monotonically with particle diameter up to \(\kappa \sim 0.85\) at \(d_m = 100\, \text{nm}\), which the authors related to size dependent variations in the volume fraction of organic matter within the particles [Quinn et al., 2014]. Size-resolved CCN activity of SSA particles generated by the plunging waterfall in the MART was explored in Experiment 3, wherein measurements from before nutrient addition, at peak chlorophyll-a, and after phytoplankton senescence were compared. Figure 4.4 shows the CCN active fraction of particles at three different settings for \(d_{dry}\), while performing CCN activity measurements using Mode 2 (Section 4.3.3). To give a reference point, vertical lines corresponding to \(s_c\) at each \(d_{dry}\) associated with \(\kappa = 1\) (solid) and \(\kappa = 0.8\) (dashed) have been added. In each case, \(s_c\) corresponds to \(\kappa\) values between 0.8 and 1, and may increase slightly with increasing \(d_p\). The increasing \(\Delta s\) between \(\kappa = 0.8\) and \(\kappa = 1\) as \(d_p\) decreases may play a role in that assessment, however. It appears that \(s_c\) for the ‘Pre-Bloom’ condition (natural seawater before nutrient addition) is consistently
higher than $s_c$ measured during or after the bloom at each size, but the differences may not be statistically significant considering a 5% uncertainty in $s$ within the CCNc chamber. It is certain though, that variation in CCN-derived hygroscopicity with respect to particle size was weak at best in all experiments presented in this study. It is important to reiterate that the biological nature of each bloom conducted in this study was unconstrained, apart from the removal of organisms and particulate/suspended material using 100 μm mesh. Seawater TOC concentrations in these experiments were between 110 – 950 μM, wider than the range of some similar laboratory studies (0-512 μM) [Fuentes et al., 2011; Wex et al., 2010], and higher than those sampled by [Quinn et al., 2014] (74-108 μM) in the North Atlantic. While the experiments may not represent exact replicates, the similarity of the CCN activity results speaks to the expected consistency of the CCN activity of nascent SSA produced within phytoplankton blooms in the ocean. The range of hygroscopicity measured in all experiments here was similar to the results of experiments in which the exudates from phytoplankton or cyanobacteria cultures were systematically added to seawater or a synthetic proxy [Collins et al., 2013; Fuentes et al., 2011; Moore et al., 2011].

4.4.2 Sensitivity of CCN Activity to Generation Method

The shipborne study of generated aerosol at the sea surface by Quinn et al. [2014] used an SSA generation method that does not produce a bubble size distribution that is similar to the MART plunging waterfall. Bubble sizes generated by the stainless steel diffusion stone are dictated by its porosity, which is uniform and monodisperse. Deviations in the bubble size distribution are known to translate to differences in the SSA size distribution [Fuentes et al., 2011; Lewis and Schwartz, 2004], and could be a key factor leading to observed differences in aerosol composition between different laboratory-based
SSA generation methods [Collins et al., 2014]. In Experiment 3, a comparison between the CCN activity of SSA generated by the MART waterfall [Stokes et al., 2013] and the stainless steel diffusion stone [Bates et al., 2012] was conducted before bloom growth, at peak algae density, and after chl-a returned to the baseline. Similar to Figure 4.4, the size dependence of CCN-derived hygroscopicity of diffusion stone-generated SSA was weak, with $s_c$ for each size lying between that corresponding to $\kappa = 1$ and $\kappa = 0.8$ (Figure 4.5). In addition to the added vertical lines marking reference points for $\kappa$, the $s_c$ values for each size reported by Quinn et al. [2014] has been added to Figure 4.5 to show the stark difference in size dependent hygroscopicity between the two studies, which is especially evident at $d_m = 40$ nm ($d_p = 38$ nm).

4.4.3 Influence of Sea Foam

After phytoplankton senescence, persistent foam was observed on the seawater surface within the MART during, and persisting after, aerosol generation in all bloom experiments. Subsurface bubbles are known to transport surface active material from the water column to the air-sea interface and into SSA particles [Blanchard, 1964]. In addition, foam generation has long been used in industrial settings to fractionate surface active material (e.g, surfactant, protein) in aqueous media [Lemlich and Lavi, 1961; Li and Stevenson, 2012]. Liquid foam is formed when sufficient surface active material is present to help stabilize thin fluid films that act as the barriers between neighboring gas bubbles [Bikerman, 1973]. Enrichment of a particular surface active species within a foam is a function of the specific surface area of the foam and the surface excess of the organic material of interest. The enrichment ratio of surface active material in the foam, defined as the ratio of the concentration of surfactant in the foamate (condensed phase material
within the foam) to the concentration of surfactant in the bulk, of approximately $10^2$ are common in natural systems [Li and Stevenson, 2012]. Exploiting the chemically fractionated nature of the foam formed at the end of the phytoplankton bloom microcosm in Experiment 2, the foamate was collected using a glass beaker and was then aerosolized using a Collison atomizer. The aerosol generated from the foamate sample had a CCN activity that is essentially indistinguishable from the CCN activity of atomized seawater that was collected near the bottom of the MART (Figure 4.6). The activation diameters determined for the two samples at $s = 0.6\%$ correspond to $\kappa = 0.75 - 8$. Using the Zdanovskii-Stokes-Robinson approximation which state that solutes do not interact and impart deviations from solution ideality [Stokes and Robinson, 1966], the volume-additive mixing rule (Equation 3.1) was used to determine the organic volume fraction of the aerosol, assuming that all particles were identical internal mixtures of salt and organic matter [Petters and Kreidenweis, 2007].

$$\varepsilon_{org} = \frac{\kappa - \kappa_{salt}}{\kappa_{org} - \kappa_{salt}}$$ \[3.1\]

The organic volume fraction ($\varepsilon_{org}$) of the aerosol is between $0.36 - 0.4$, for $\kappa_{org} = 0.006$ [Moore et al., 2008] and $\kappa_{salt} = 1.25$ [Niedermeier et al., 2008; Petters and Kreidenweis, 2007]. This is a similar $\varepsilon_{org}$ to those derived from other hygroscopicity ($\varepsilon_{org} = 0.08 - 0.37$) [Fuentes et al., 2011] and spectromicroscopy ($\varepsilon_{org} = 0.35-0.4$) [Collins et al., 2013] measurements of organic-enriched SSA particles generated in the laboratory. Noting that the hygroscopicity of SSA particles shown in Figure 4.4 have $\kappa \sim 0.8$, the volumetric
mixing rule dictates that the organic volume fraction of the foamate sample was similar to that of SSA generated by bubble bursting.

4.5 Discussion

4.5.1 The Sea Surface Microlayer and Aerosol Production

SSA particles and sea foam are both formed as a result of bubbles rising to the air-water interface, where an interaction with the sea surface microlayer (SML) takes place. The SML is a layer of concentrated organic and biological material at the air-sea interface which is typically thought to be up to 1 mm thick [Cunliffe et al., 2013; Liss and Duce, 1997], and has been suggested to play an important role in both SSA [Gantt et al., 2011; Leck and Bigg, 2005; Quinn and Bates, 2011] and foam production [Druzhkov et al., 1997]. Sea foam is formed at the sea surface when groups of bubbles coalesce and have sufficiently stable thin fluid film boundaries to enable their persistence over time [Bikerman, 1973]. In the ocean, foam decay times have been observed between 4 – 10 seconds [Callaghan et al., 2012] and are a function of surfactant concentration in the seawater [Callaghan et al., 2013; Modini et al., 2013]. Upon bubble bursting, the fragmentation of the thin films that act as the barrier between the gas within the bubble and the atmosphere has been implicated as an SSA particle production mechanism, although mechanistic understanding is limited [Lewis and Schwartz, 2004]. Thin film fragmentation, known as ‘film drop’ production, can lead to SSA particles with $d_p < 1 \mu m$ [Resch and Afeti, 1992]. A recent study showed that concentrations of SSA particles with $d_p = 50 – 300 \text{ nm}$ were enhanced when a thick bed of foam covered nearly the whole surface of the seawater within a MART [Collins et al., 2014], suggesting that the bursting of foam
bubbles led to the production of particles in this defined size range. The similarity in hygroscopicity between the aerosolized foamate sample and SSA particles produced by bubble bursting reported in Section 4.4.3 perhaps provides further physicochemical evidence for a link between the existence of foam on the sea surface and the formation of SSA particles with $d_p < 100$ nm. In addition, it could provide evidence for a chemical connection between the SML and SSA, lending to the concept that a chemical selection process exists in the formation mechanism of SSA particles [Schmitt-Kopplin et al., 2012]. Thus, the suggested [Gantt et al., 2011; Saltzman, 2013], and in some cases demonstrated [Aller et al., 2005; Kuznetsova et al., 2005], importance of the SML in directing the composition and mixing state of SSA particles may help explain similarities between CCN activity and direct chemical composition measurements made on nascent SSA produced in two regions of the ocean that have vastly different trophic states [Quinn et al., 2014].

4.5.2 Insensitivity of Observed Hygroscopicity to Biological Activity

The CCN-derived hygroscopicity of SSA particles with $d_p = 38 – 75$ nm measured in this study was insensitive to the magnitude of chlorophyll-a in seawater from which the aerosol was produced with TOC concentrations between 110 – 950 $\mu$M. Current model parameterizations of SSA organics predict that the organic mass fraction of submicron particles should increase as a function of chlorophyll-a concentration in the surface ocean [e.g., Gantt et al., 2011; O’Dowd et al., 2008]. Extension of such an organic matter enhancement to the physicochemical properties of SSA suggests that hygroscopicity should decrease as surface ocean chlorophyll increases, although the nature of the changes in modeled CCN activity have been shown to be somewhat complex and subject to underlying assumptions about the aerosol mixing state [Meskhidze et al., 2011; Westervelt
et al., 2012]. Fundamentally, relating the hygroscopicity of SSA to the mixing state of an assumed internal mixture of salt and organic matter relies on predictable, ideal behavior of inorganic salts and organic compounds in aqueous solution. Full treatment of the solubility of activating cloud droplets has allowed Köhler models to account for the effects partial dissolution of some organic compounds [Bilde and Svenningsson, 2004; Broekhuizen et al., 2004; Hori et al., 2003; Raymond and Pandis, 2003], and has helped bound the range of solubility wherein this effect is important [Petters and Kreidenweis, 2008]. Chemical interactions between salts and carboxylic acids, and perhaps also with fulvic acids, have been proposed to explain anomalously low CCN activities in some experiments [Frosch et al., 2011], so these types of solution non-idealities would not explain the consistently high CCN activities observed in the current study.

CCN activity analysis of the foamate sample, which is likely to be highly enriched in organic matter due to chemical fractionation [Li and Stevenson, 2012], may provide a clue for the physical constraints on the system. Since the foamate sample was aerosolized using an atomizer, a uniform internally mixed aerosol containing the components of the sample can be expected. As reported in Section 4.4.3, the CCN activity analysis indicated that $\varepsilon_{\text{org}} = 0.36 – 0.4$, similar to $\varepsilon_{\text{org}}$ values for nascent SSA particles generated by bubble bursting techniques utilized in the laboratory [Collins et al., 2013; Fuentes et al., 2011]. The similarity between these values is striking, and perhaps suggests a strong chemical link between the SML and SSA. Since the SML is enriched in organic matter, but not exclusively composed of organic molecules [Cunliffe et al., 2013], the organic/salt ratio of fractionated SML may control the mixing ratio within SSA particles. The ocean surface may be physicochemically incapable of producing aerosol that has a larger organic/salt
volume ratio than 0.4. Still, the production of particles in which the organic fraction dominates have been observed [Ault et al., 2013; Bigg and Leck, 2008]. In laboratory wave channel experiments, these organic-dominated particles had a distinct number size distribution mode around $d_p = 100$ nm and exhibited weak hygroscopicity [Collins et al., 2013]. The production of small organic-dominated particles, which was likely not important within the current study, is likely related to the composition of the organic matter in seawater, rather than the total quantity of organic carbon. Understanding the differences in the physicochemical properties of the seawater and SML between cases where weakly-hygroscopic SSA particles are and are not produced will help ascertain predictive power. Overall, it seems that changes in the production of organic-dominated particles could be the only means of attaining $\kappa < 0.8$ for nascent SSA particles.

### 4.5.3 Surface Tension and CCN Activity of Sea Spray Aerosol

A long discussed competitor to the reduction of CCN activity by organic enrichment is the expected change in surface tension [e.g., Facchini et al., 1999]. Within the Kohler equation, the surface tension acts on the Kelvin Effect term, reducing the barrier to droplet nucleation by decreasing the energy required for the droplet to grow. Based on parameterized relationship between chlorophyll-a and the organic matter fraction of SSA [Gantt et al., 2011; O'Dowd et al., 2008; Vignati et al., 2010], and its predicted hygroscopicity (Figure 4.1), a surface tension of 0.0455 N m$^{-1}$ at droplet activation would be required to bring the predicted organic mass fraction (based on chlorophyll-a) and the observed CCN activity in this experiment into agreement. According to the surface tension dependence on the concentration of marine organic matter presented by Moore et al. [2008], the aforementioned surface tension depression translates a solution with
approximately 360 μM organic carbon, which is very similar to the range of seawater DOC concentrations achieved in Experiment 2. Considering the relatively large uncertainties inherent to the SSA organic fraction parameterization [Albert et al., 2012], the questionable applicability of the organic matter data used in this brief calculation due to its collection at significant depth in the ocean [Moore et al., 2008], and the fact that surfactant partitioning [Sorjamaa et al., 2004] is not considered, the rough agreement between the calculated organic matter concentration required for surface tension depression and that of the seawater is remarkable and worthy of more detailed study and direct measurements. The detailed chemistry driving the influence of surfactants on the CCN activity is highly uncertain, with recent studies actually adding complexity [Frosch et al., 2011; Harmon et al., 2013; Prisle et al., 2008] rather than converging on a consensus, so a further discussion here is perhaps preemptive.

The transfer of marine organic matter to SSA particles is equally as uncertain as the importance of surface tension; in fact, the two factors are likely to be highly coupled. Studies of the chemical composition of SSA produced during the phytoplankton bloom experiments described herein showed that organic matter was incorporated into SSA particles after the peak in chlorophyll-a (Sultana et al., in preparation). Bacteria also tend to proliferate as phytoplankton senescence occurs, due to the availability of labile substrates [Pomeroy et al., 2007]. The production of highly surface active molecules has also been associated with marine bacteria [Das et al., 2010], which aligns with the observed production of persistent foam at the end of each bloom experiment. If the transfer of organic matter proceeds as a result of surfactant accumulation within the SML, this could suggest that the observed transfer of organic matter by direct chemical analysis represents
highly surface active compounds which simultaneously add organic mass to the SSA
particles and cause compensating changes in droplet surface tension.

4.6 Conclusions

The variation of CCN activity of nascent SSA particles generated from a three
separate, unconstrained phytoplankton blooms that stimulated in a laboratory chamber
weak or even non-existent. Size-differentiated determinations of the $s_c$ prior to, at the peak
of, and after senescence of a bloom showed a consistently weak size dependence to
hygroscopicity between $d_p = 38$-$75$ nm. The hygroscopicity parameter derived from a
sample of foamate produced at the end of a bloom experiment showed little difference from
a simultaneously-collected sample of the seawater from which the foam was generated.
The similarities between the foamate and SSA particles generated when the seawater
suggests a common physicochemical link via the SML. Surface tension effects are a
plausible explanation for the weak changes in CCN activity. Further study on the nature
of surfactant production during blooms, their surface activity, and the ultimate impact of
surface partitioning of these molecules on the CCN activity of SSA particles is a promising
direction for continuing research.

4.7 Acknowledgements

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4.8 Figures

**Figure 4.1**: Calculated hygroscopicity parameter values corresponding to parameterizations of SSA organic mass fraction over a range of ocean surface chlorophyll-a. The vertical axis on the right corresponds to the organic volume fraction used to derive $\kappa$, based on the assumed component hygroscopicities specified in the inset. The shaded regions correspond to the range of $\kappa$ values observed for SSA produced in laboratory experiments as discussed in the text; the two ranges overlap between $\kappa = 1 – 1.25$. 
Figure 4.2: Temporal profiles of chlorophyll-a, measured by fluorescence, and the concentration of organic carbon in the seawater for (a.) Experiment 1, (b.) Experiment 2, and (c.) Experiment 3. Due to high loadings observed in Expt. 1, organic matter sampling was changed such that DOC was measured for Expts 2 and 3. Samples were collected during Expt 3, but data are not available. Shaded regions indicate time periods where SSA was being produced and sampled on a 2-hour duty cycle, as described in Section 4.3.2.
Figure 4.3: CCN activity of SSA particles from (a.) Expt. 1 at $s = 0.2\%$, (b.) Expt. 1 at $s = 0.4\%$, (c.) Expt. 2 at $s = 0.2\%$, and (d.) Expt. 2 at $s = 0.6\%$. Aerosols were generated in a MART using the plunging waterfall mechanism throughout the growth and senescence of phytoplankton blooms. Schematic sigmoid curves correspond to $\kappa = 1.25 \pm 0.25$, which represents the range of CCN-derived hygroscopicity values for laboratory-generated SSA and SSA proxies in the absence of biological or artificial organic enrichment.
**Figure 4.4**: CCN activation curves for MART-generated SSA particles with $d_{\text{dry}}$ of 75, 57, and 38 nm for each of the three phytoplankton bloom conditions (c.f. Figure 4.2). Each CCN activity curve is shown with a sigmoidal fit. Vertical lines, shown for reference, indicate $s_c$ corresponding to $\kappa = 1.0$ (solid) and $\kappa = 0.8$ (dashed) for each $d_{\text{dry}}$. Error bars indicate $s \pm 5\%$. 
**Figure 4.5**: CCN activation curves for SSA particles generated by the diffusion stone with \( d_{dry} = 75, 57, \) and \( 38 \) nm for each of the three phytoplankton bloom conditions (c.f., Figure 4.2). Vertical lines indicate \( s_c \) corresponding to \( \kappa = 1.00 \) (solid) and \( \kappa = 0.80 \) (short dashes) for each color coded \( d_{dry} \). Each of the conditions indicates that \( k \) for the SSA was close to 0.8. These results are compared to those reported by Quinn et al. [2014] by showing \( s_c \) values reported therein using vertical lines with longer dashes.
Figure 4.6: CCN activity of aerosol generated from a sample of seawater collected near the tank bottom and sample of surface foam collected from off the water surface within a MART. The samples were collected simultaneously 12 days after the peak in chlorophyll-a fluorescence (Expt. 2). Both samples were aerosolized using a Collison atomizer. Values of $d_{act}$ are reported as the size at the half maximum value of a sigmoid fit to the data.
4.9 References


DeCarlo, P. F., J. G. Slowik, D. R. Worsnop, P. Davidovits, and J. L. Jimenez (2004), Particle Morphology and Density Characterization by Combined Mobility and


5. Formation and CCN Activity of Secondary Marine Aerosols

Associated with Phytoplankton Senescence

5.1 Synopsis

Marine phytoplankton have long been thought to have an impact on clouds, but studies linking chlorophyll-a and cloud properties report inconsistent results. In this study, we explore biosphere-atmosphere coupling by stimulating phytoplankton growth in the laboratory. Secondary aerosol formation initiated spontaneously during phytoplankton senescence. The hygroscopicity parameter (κ) of the secondary aerosol particles was similar to that of organic aerosol (κ = 0.22 [+0.13] [-0.08]), suggesting that the formation and growth mechanisms of secondary aerosol involved the condensation of organic vapor. Comparing with prior studies of natural marine aerosol, κ values as low as 0.2 have only been observed when an external mixture of salt-containing and water insoluble particle types exists (Chapters 3 and 4). The phase of autotrophic biological activity (growth vs senescence), which could simply be an indirect indicator of key heterotrophic biological activity, within phytoplankton blooms appears to be important to their influence on the abundance and cloud activity of natural aerosols in the marine environment.

5.2 Introduction

A complete understanding of the abundance and characteristics of natural atmospheric aerosol particles is of critical importance to reducing uncertainty in radiative forcing assessments [Andreae, 2007; Carslaw et al., 2013]. The marine boundary layer (MBL) is host to a large mass of primary sea spray aerosol (SSA) particles [de Leeuw et al., 2011] along with a significant contribution from secondary marine aerosol (SMA)
[Rinaldi et al., 2010], which form through chemical reactions of traces gases. Most SMA particles have long been thought to form as a result of the oxidation of dimethyl sulfide (DMS), an prevalent volatile metabolite produced by marine microorganisms [Charlson et al., 1987; Nguyen et al., 1988]. SMA could then play a role in aerosol indirect effects (e.g., cloud albedo and lifetime) by acting as cloud condensation nuclei (CCN) [Albrecht, 1989; Twomey, 1974]. Changes in cloud properties over phytoplankton blooms have been observed by remote sensing [Kruger and Grassl, 2011; Lana et al., 2012; Meskhidze and Nenes, 2006; 2010], but simple correlations between chlorophyll-a and key cloud properties are not effective in all cases [Miller and Yuter, 2008], suggesting subtlety within the relationship. An understanding of the system with increased biogeochemical resolution is needed to address the problem from a more fundamental level.

Kruger and Grassl [2011], using remote sensing measurements, documented increasing CCN concentrations with decreasing wind speeds toward 5 m s$^{-1}$, which is roughly the lower limit for wave breaking and SSA production [de Leeuw et al., 2011]. Simply put, the lack of primary (sea spray) aerosol in low wind conditions leads to the logical conclusion that secondary aerosol are most likely contributing to the noted trend in CCN. Moreover, when SSA concentrations are low the condensation sink will also be low, providing conditions conducive to aerosol nucleation and secondary aerosol formation. In the marine environment, significant effort has been applied to understanding secondary sulfate aerosol, due the prevalence and known biological source of trace DMS in the MBL [Ayers and Gras, 1991; Charlson et al., 1987]. Biogenic volatile organic compounds (BVOC), and the secondary organic aerosol (SOA) that arise due to their oxidation, are heavily studied in the context of the terrestrial biosphere [e.g., Scott et al., 2014], but are
weakly characterized in the MBL. Alkyl amines [Mueller et al., 2009; Sorooshian et al., 2009; Van Neste et al., 1987], isoprene [Shaw et al., 2010], monoterpenes [Yassaa et al., 2008], and their respective condensed phase products [Bikkina et al., 2014; Dall’Osto et al., 2012; Decesari et al., 2011; Facchini et al., 2008; Hu et al., 2013] have been observed in the MBL, yet large uncertainties exist in oceanic emissions estimates of BVOCs [Carpenter et al., 2012; Gantt et al., 2009; Luo and Yu, 2010]. As a consequence of the weak characterization of secondary aerosol processes in the MBL, the uncertainty in radiative forcing from indirect effects due to SMA over the ocean is large [Carslaw et al., 2013]. A better understanding of the biogeochemical conditions that lead to secondary aerosol formation in the remote MBL is therefore essential to improving radiative forcing estimates from global models.

Biogeochemical influences on marine aerosol may be nuanced beyond the level of high or low biological activity; correlations in long-term measurements of organic matter in marine aerosol collected in the North Atlantic are improved when a time delay between the signals is included [Rinaldi et al., 2013], suggesting that peak primary productivity may not equate with peak organic aerosol production [Quinn et al., 2014]. Marine heterotrophic bacterial activity has been implicated in alterations to SSA properties in laboratory experiments [Prather et al., 2013a; Prather et al., 2013b], which is likely associated with the critical role of bacteria in shaping the composition of marine organic matter already recognized within in the global carbon cycle [Jiao et al., 2010; Kujawinski, 2011]. At the intersection of the marine ecosystems and the atmosphere, this study shows that SMA formation can be governed by the biological state of a phytoplankton bloom, investigates the CCN activity of SMA and SSA particles derived from seawater containing stimulated
biological activity, and provides insight from a fundamental level on the connections between marine microbiology and the CCN activity of marine aerosols.

### 5.3 Experimental Methods

Phytoplankton growth was induced within a Marine Aerosol Reference Tank (MART), which utilizes a plunging waterfall apparatus to generate bubbles in a tank of natural seawater, resulting in the production of SSA via bubble bursting \cite{Stokes:2013}. Prior studies have indicated that the plunging waterfall apparatus produces SSA particles with a similar number size distribution \cite{Prather:2013b} and size-resolved chemical composition \cite{Collins:2014} to laboratory breaking waves. Natural seawater was obtained from the end of Scripps Pier (La Jolla, CA; 32° 52.0’ N, 117° 15.4’ W) after macroscopic organisms were removed via a No. 12 crystal sand bed filter. Approximately 100L of seawater was added to the MART, in which Guillard’s f medium \cite{Guillard:1962} diluted by a factor of 2 (f/2, with Na$_2$SiO$_3$; ProLine, Apopka, FL) was used to induce a diatom bloom under continuously illuminated conditions (Phillips Alto II F32T8/DX, 6500K) with a photon flux of approximately 120 μmol m$^{-2}$ s$^{-1}$. The biological community composition of the bloom was not constrained or actively controlled in order to allow dynamic ecosystem interactions within the microbial loop \cite[e.g.,][]{Pomeroy:2007} to take place in the most natural manner possible. The plunging waterfall was activated for 2 hour on/off cycles in order to limit damage to the phytoplankton community by means of the centrifugal pump used to re-circulate water through the waterfall apparatus. The MART headspace was purged with HEPA-filtered air at 4 liters per minute, giving a residence time in the headspace of approximately 23 minutes (neglecting interactions with tank surfaces) \cite{Stokes:2013}.
All aerosol sampling was conducted at low relative humidity (RH = 15±10%) by passing the sample through two silica gel diffusion driers immediately after being drawn out of the MART headspace. Number size distributions of particles with diameters \(d\) ranging 11 – 600 nm were sampled with a scanning mobility particle sizer (SMPS; TSI, Inc. Model 3080/3010). CCN concentrations were obtained using a stream-wise thermal gradient CCN counter (CCNc; Droplet Measurement Technologies, Model CCN-100) [Roberts and Nenes, 2005] at a constant supersaturation \(s\) of 0.16% in parallel with a condensation particle counter (CPC; TSI, Inc. Model 3010) used to measure total aerosol number concentrations \(d > 10\) nm). The fraction of CCN active particles was calculated as the ratio of the CCN concentration to total aerosol concentration. Size-resolved CCN active fractions were obtained by drying the aerosol using two silica gel diffusion driers (RH = 15±10%), then passing the sample through an electrostatic classifier (TSI, Inc., Model 3080) ahead of the CCNc and CPC. The sheath:sample flow ratio in the electrostatic classifier was set to 5:1 for the CCN measurements. Size resolved CCN active fraction data were normalized [Rose et al., 2008] and activation diameters \(d_{act}\) were determined by the inflection point of a sigmoidal fit to the data. Uncertainty in \(d_{act}\) was assessed by weighting the sigmoid fit by the standard deviation of the CCN active fraction data. Hygroscopicity parameter \(\kappa\) values were derived based on measured \(d_{act}\) and \(S\) in the CCNc column [Petters and Kreidenweis, 2007].

5.4 Results

During typical operation, the plunging waterfall of the MART is activated to produce SSA particles with a 2 hour on/off duty cycle, as described in Section 5.3. The operating parameters of the MART (waterfall flow rate, waterfall height, tank water
volume, water and air temperature) are held constant during these experiments, and as such, the production of SSA is most sensitive to induced chemical/biological changes to the seawater in the tank. This results in a relatively consistent temporal pattern in aerosol size distributions (Figure 5.1).

At peak prokaryotic cell density, the unconstrained phytoplankton bloom that was stimulated in the MART reached a chlorophyll-a concentration of 173 mg m\(^{-3}\). As chlorophyll-a concentrations began to subside, total concentrations of aerosol increased in the headspace above the seawater, especially when the plunging waterfall was not operating and SSA particles were absent (Figure 5.2). During the period shown in Figure 5.2, the aerosol number concentration was approximately 50% higher when plunging waterfall-mediated SSA production was turned off compared to when SSA was being generated. CCN concentrations, on the other hand, followed temporal trends in SSA particles, suggesting that a significant fraction of particles residing in the MART headspace while the plunging waterfall was active had critical supersaturations \((s_c) < 0.16\%\), commensurate with the properties of nascent SSA particles [e.g., Prather et al., 2013a]. Therefore, SMA formation was initiated after the subsidence of SSA concentrations caused a reduction in the condensation sink. SMA production persisted for approximately 20 hours (Figure 5.1), during which time an acrid odor was observed in the headspace above the seawater, suggesting the presence of appreciable concentrations of biogenic trace gases that could potentially serve at SMA precursors. Formation of small particles \((d < 30\text{ nm})\) was observed each time total aerosol surface area was reduced upon the cessation of SSA generation, such as in the transition from P2 to P3. These events have
‘banana’-shaped temporal size distribution trends similar to those observed during new particle formation (NPF) in the atmosphere [Kulmala et al., 2013].

Number size distributions obtained during the three periods defined above are compared with that of SSA generated within the MART in the absence of SMA formation (Figure 5.4). The total concentration of particles during SMA formation was 3-fold higher than that during SSA production via plunging waterfall. The modal diameter of the SMA-affected size distributions (red, green, and blue) never exceeded 70 nm. Comparing the shapes of the ‘SSA+SMA’ and ‘SSA only’ size distribution in Figure 5.4 shows that the SMA population is superimposed upon the SSA population (c.f., $d > 300$ nm), suggesting that the SMA and SSA particles were externally mixed. The mode of the population shifted to smaller diameters for both ‘SMA only’ (P1: 53 nm, P3: 66 nm) and ‘SSA+SMA’ (65 nm) cases compared to the nascent SSA modal diameter (89 nm). This suggests that the formation of SMA particles persisted throughout the SSA generation period (P2), although to a somewhat lesser extent as described above. The modal aerosol diameter increased from P1 to P3, indicating a changing growth process over the course of phytoplankton senescence, since the particle residence time was not altered throughout the experiment. The larger modal diameter of the SMA particles was reflected by a doubling of CCN concentrations at $s = 0.16\%$ between P1 and P3.

Size-resolved CCN activity was measured for the SSA+SMA period between 17:00 and 19:00, and for the SMA only period between 19:00 and 21:00. The $d_{act}$ values at $S = 0.16\%$ measured under each of the two conditions were not significantly different (Figure 5.5); for SMA particles in the absence of SSA, $\kappa = 0.22$ (+0.13, -0.08). The hygroscopicity
of SMA particles in this study are generally consistent with that of secondary organic aerosol (SOA) [e.g., Liu and Wang, 2010] and lies within the range of $\kappa$ values for particles with $d_{\text{act}} \sim 130$ nm in the MBL [Hegg et al., 2012]. SMA particles were observed to age over time in this study, increasing in size over a period of hours (Figure 5.4), similar to SOA from continental and/or terrestrial sources. As such, SMA particles were able to contribute to CCN concentrations at $s = 0.16\%$ during P3 despite weak hygroscopicity. In the atmosphere, particle lifetimes are much longer than the residence time in the MART headspace (~23 min), so presumably the size (and perhaps also the hygroscopicity) of SMA particles would continue to increase, which could substantially influence CCN concentrations over some parts of the ocean.

5.5 Discussion

The timing of SMA formation with respect to the biological status of the phytoplankton bloom may be particularly telling of the importance of marine biogeochemistry and associated trace gas exchange across the air-sea interface. DMS has received particular attention in the literature due to its abundance in the marine atmosphere and suggested role in the global climate [e.g., Charlson et al., 1987]. Emissions of DMS from biologically productive seawater have been linked preferentially to phytoplankton senescence, rather than growth phases [Kameyama et al., 2011; Nguyen et al., 1988]. A major biochemical pathway for DMS production is associated with enzymatic degradation of its precursor dimethylsulfoniopropionate (DMSP) [Steinke et al., 2000], which can be brought on by predation and/or grazing of phytoplankton by bacteria [e.g., Zubkov et al., 2001]. The production of SMA during phytoplankton senescence in these experiments is likely associated with the oxidation of DMS to $\text{H}_2\text{SO}_4$ and/or methanesulfonic acid (MSA).
In addition to sulfur compounds, alkyl amines have been implicated in NPF [Almeida et al., 2013; Dawson et al., 2012; Smith et al., 2010] and SOA formation [Angelino et al., 2001]. Several studies have linked organic nitrogen to secondary aerosol in the MBL near locations characterized by high biological activity [Dall’Osto et al., 2012; Decesari et al., 2011; Facchini et al., 2008; Mueller et al., 2009; Sorooshian et al., 2009]. The biogenic precursors to gas-phase alkyl amines in the marine environment are not well known, but may include the breakdown of glycine betaine [Kiene and Hoffmann Williams, 1998] and/or trimethylamine oxide (TMAO) [Lidbury et al., 2014], analogous to the production of DMS from DMSP. The seawater concentrations of each of these alkyl amine precursors is associated with primary production; the growth of heterotrophic bacteria has been shown to be specific to the availability of labile substrates typically produced by autotrophs [Teeling et al., 2012], resulting in (volatile) metabolite production. Quantitative predictions of the impact of amines on aerosol in the MBL are limited by technical challenges posed with measuring alkyl amines in the gas phase [Carpenter et al., 2012], although a limited number of methylamine concentrations in the MBL are available [Gibb et al., 1999; Van Neste et al., 1987]. Further study of the sources of marine biogenic amines and their flux across the air-sea interface is necessary to understand the relationship between biological activity and SMA formation.

The current understanding of NPF chemistry invokes the importance of a sulfur-containing acid (H₂SO₄ or MSA), ammonia or amines, and organic compounds [Bzdek et al., 2014; Dawson et al., 2012; Kulmala et al., 2013]. The hygroscopicity of ammonium sulfate and alkylaminium sulfates have been inferred to be similar (κ_{sulf} = 0.61) [Lavi et al., 2014], so in order to gain closure with CCN-derived hygroscopicity measured here (κ =
0.22), an internal mixture of alkylammonium sulfate and organics \( (\kappa_{\text{org}} = 0.10) \) would need to contain approximately 75% organic matter by volume [Petters and Kreidenweis, 2007]. Organic compounds are important during the growth phase of new particle formation [Kulmala et al., 2013; Wang et al., 2010]; a recent study indicates that extremely low volatility organics (including nitrogen-substituted compounds) contribute to more than half of particle growth up to 20 nm [Bzdek et al., 2014]. In this study, \( d_{\text{act}} \) at \( S = 0.16\% \) was 134 nm, so while the predicted organic fraction at 20 nm already aligns reasonably well with the observed CCN-derived hygroscopicity of SMA particles in this study, further growth by the mechanism described by Bzdek et al. [2014] would not have led to significant alterations in hygroscopicity. MSA and/or \( \text{H}_2\text{SO}_4 \) should also contribute to growth processes, simply referencing their Henry’s Law constants [Sander, 1999] and propensity for existing in the condensed phase. A consistent sulfur/organic mixing ratio during particle growth would provide a similarly consistent hygroscopicity [Bzdek et al., 2014; Dall'Osto et al., 2012].

The source of condensed phase organics in this system may not be significantly different from the range of biogenic volatile organic compounds (BVOC) available during continental SOA formation. Both isoprene and monoterpenes are known to be emitted from the ocean in association with primary production [e.g., Carpenter et al., 2012; Shaw et al., 2010]. Trace gas measurements performed in the headspace of phytoplankton cultures indicate that diatoms (the dominant autotrophs involved in this study) tend to produce more isoprene than other types of phytoplankton [Gantt et al., 2009; Shaw et al., 2003], but the range of BVOCs and their source strengths are not well defined. However,
the CCN-derived hygroscopicity observed in the current study strongly suggests that low-volatility biogenic organic vapors contributed to SMA formation.

Recent studies of the CCN activity of nascent SSA particles generated under controlled conditions from natural seawater indicate that their hygroscopicity is high, consistently reporting $\kappa > 1$ [Fuentes et al., 2011; Niedermeier et al., 2008], similar to NaCl. In cases where salts and organics are thought to be internally mixed, organic-driven suppressions in CCN activity can be accounted for assuming an organic/salt mixing ratio of between 30% and 80% [Fuentes et al., 2011; Quinn et al., 2014]. CCN-derived hygroscopicity values for nascent SSA from stimulated phytoplankton blooms within a MART, as described in Section 5.3, have been observed to be stable over a range of biological conditions (Figure 5.6). The results of SMA particle analysis combined with studies in the literature highlight the importance of externally mixed populations of salt-rich and weakly hygroscopic particles on the CCN activity of natural marine aerosol. CCN activity of SSA generated from seawater that was host to bacterially degraded growth media was also driven by the changing abundance of an insoluble, externally mixed particle type [Prather et al., 2013a]. Similarly, the appearance of externally mixed particles with weak hygroscopicity imparted a strong suppression of CCN activity during aerosol nucleation in the open ocean [Dall'Osto et al., 2012]. The range of $\kappa$ values accessed by externally mixed marine aerosols is much lower than for aerosols that are internally mixed (Figure 5.7). Consistency in $\kappa$ for marine aerosol that lacks significant contributions from external mixing of organics and/or the strong size dependence of SSA particles with weak hygroscopicity [Prather et al., 2013a] may help explain the relatively consistent
relationship between total aerosol and cloud droplet number concentrations in marine stratocumulus [Hegg et al., 2012].

5.6 Conclusions

The role of biological activity in the surface ocean with respect to the formation of CCN-active secondary aerosol in the MBL is a significant source of uncertainty in radiative forcing assessments [Carslaw et al., 2013]. Results presented in this study help to constrain the biological conditions most likely to lead to SMA formation, suggesting the importance of phytoplankton senescence on the proclivity for secondary aerosol chemistry to proceed and SMA particles to form. CCN-derived hygroscopicity of SMA particles reported in this work indicates the presence of a significant volume fraction of organic matter in the particles. Both MSA and alkyl amines are likely candidates for enhanced air-sea exchange and SMA formation during phytoplankton senescence as both are products of the breakdown of prevalent cellular osmolytes [Carpenter et al., 2012], and have been implicated in aerosol nucleation [Almeida et al., 2013; Dawson et al., 2012]. In addition a recent computational study has suggested that MSA could enhance molecular cluster formation compared to bimolecular nucleation by H$_2$SO$_4$ and dimethylamine [Bork et al., 2014], suggesting that some open ocean nucleation could be an underestimated source of marine aerosol. This study indicates that rather than just the absolute phytoplankton biomass, as is typically tracked using a scalar value for the chlorophyll-a concentration, the biological state of the cells within the phytoplankton bloom (e.g., growth, senescence) is an important factor when considering the flux of SMA precursors and aerosol formation. The CCN activity of external mixtures of aerosol that result from SMA formation in the marine environment are likely to be low even when SSA are present, considering the weak
hygroscopicity of the abundant newly formed secondary particles. Hence, the history of a phytoplankton bloom may be a better metric for potential SMA formation and subsequent cloud microphysical modification than the instantaneous measurement of total autotrophic biomass.

5.7 Acknowledgements

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5.8 Figures

**Figure 5.1**: Temporal plot of aerosol number size distributions measured by SMPS and seawater chlorophyll-a concentration measured by fluorescence.

**Figure 5.2**: Temporal profile of total aerosol and CCN number concentrations in the headspace of the MART. The CCN Fraction, defined as the ratio of the CCN concentration to the total aerosol concentration are shown in black in the top panel. SSA generation in the MART was modulated on a 2-hour cycle and is denoted by the dotted vertical lines. Note that total aerosol concentrations are highest and CCN Fraction is lowest while sea spray generation was not active.
Figure 5.3: Detailed view of SMA formation during period P3. The shape of the temporal changes in aerosol size distribution (top) indicates that aerosol nucleation was occurring upon the cessation of SSA generation at 15:00.
Figure 5.4: Number size distributions of aerosol particles measured by SMPS during each of the SMA-affected periods shown in Figure 5.2. A number size distribution for SSA generated in the MART in the absence of SMA formation is shown in black.
Figure 5.5: Size-resolved CCN active fractions of particles for SMA and SSA+SMA conditions. Determination of $d_{act}$ and $\kappa$ are described in Section 5.3. Error bars indicate the standard deviation (±1σ) in the CCN Active Fraction measured at each size, and are reflected in the uncertainties in both $d_{act}$ and $\kappa$. 

Supersaturation = 0.16%

- SMA + SSA
- SMA
- Sigmoid Fit: SMA

$d_{act} = 134 \pm 19$ nm
$\kappa = 0.22 (+0.13, -0.08)$
Figure 5.6: Size-resolved CCN activity of nascent SSA produced during the growth phase, and after the senescent phase of a phytoplankton bloom. The crosses represent points that are contaminated with multiple charged particles selected by the DMA [Petters et al., 2007].
Figure 5.7: Summary of hygroscopicity parameter (κ) values for natural marine aerosol generated in laboratory experiments. κ values for both SSA and SMA produced during phytoplankton growth experiments described in this work are compared with literature values for SSA produced from unamended natural seawater, seawater proxy amended with diatom exudate [Fuentes et al., 2011], and seawater after bacterial processing of ZoBell growth media [Prather et al., 2013a](c.f. Table 1 therein). The gray bar labeled ‘phytoplankton bloom’ includes values for κ during periods of phytoplankton growth and after cellular senescence (Figure 5.6). Bars with diagonal line pattern are samples that contain an externally mixed population of weakly soluble particles.
5.9 References


6. Redistribution of Natural and Anthropogenic Aerosol in California during Winter Storms

6.1 Synopsis

The impact of aerosols on wintertime orographic cloud systems associated with the Sierra Nevada Mountains in California has been linked to concentrations of cloud condensation nuclei (CCN), which act as the seeds for cloud droplets, immediately below cloud base. Distinct changes in the size distribution, CCN activity, and composition of aerosol particles were observed at a ground-based measurement site on the windward slope of the Sierra Nevadas during major winter storms in association with evolving meteorological conditions. Initiating approximately 6-12 hours prior to precipitation, aerosol concentrations increased by at least a factor of 10 over the course of 3 hours. The particles in these events were chemically distinct from typical aerosol observed at this remote mountain site, and were similar to the composition of particles influenced by sources and secondary chemistry in the Central Valley, located at the windward base of the Sierra Nevada Mountains. This distinct particle type contained nitrate, sulfate, amines and organic carbon and was observed to nucleate cloud droplets at supersaturations (s) less than 0.076%, which is lower than those commonly attributed to orographic clouds. The Sierra Barrier Jet (SBJ), a strong southeast-to-northwest wind feature that forms at the windward base of Sierra Nevadas during storms, was temporally associated with the observation of highly CCN-active particles from the Central Valley in three separate cases. Traditional conceptual models would implicate the Central Valley secondary (S-CV) aerosol in seeding orographic clouds. On the contrary, an influx of marine aerosol to the
measurement site was associated with southwesterly atmospheric river (AR) flow which was decoupled from the boundary layer, lifted up and over the polluted SBJ, and was principally responsible for orographic cloud formation over the Central Sierra Nevadas. The importance of identifying the sources of aerosols throughout the various elements of the complex meteorological scenario in this orographic system is key for fully understanding precipitation formation processes.

6.2 Introduction

The stability and predictability of water resources are among the most salient environmental issues in the western United States, especially in the state of California. Winter-time orographic precipitation is a key source of fresh water to this region, but with a relatively small number of wet days every year, the input of just a few storms annually can have a large impact on the overall water budget for the year [M Dettinger et al., 2011]. Precipitation formed through orographic lifting over the Sierra Nevada Mountains has long been studied meteorologically [e.g., Kingsmill et al., 2013; Marwitz, 1987a; Pandey et al., 1999], with only recent work taking a concerted focus on the impact of aerosol particles on cloud properties and precipitation [e.g., Creamean et al., 2013; Fan et al., 2014; Rosenfeld et al., 2008a].

Aerosols have a variety of impacts on clouds through serving as cloud condensation nuclei (CCN) [Andreae and Rosenfeld, 2008]. Studies of persistent maritime cloud decks show that the addition of submicron CCN (diameter < 1.0 µm) to preexisting clouds causes the average cloud droplet size to decrease, inducing an increase in shortwave cloud albedo [Twomey, 1974] and a reduction in the autoconversion rate of cloud droplets to hydrometeors [Albrecht, 1989]. On the other hand, adding large, hygroscopic particles to
clouds, like sea spray particles, can initiate precipitation [Feingold et al., 1999; Rosenfeld et al., 2002]. In practice, conflicting observations of rainfall suppression and enhancement as a result of submicron CCN entrainment in precipitation systems have been reported [Koren et al., 2012; Rosenfeld et al., 2007]. The apparent discrepancy is thought be mostly attributable to the extent of convection and glaciation within the cloud system [Rosenfeld et al., 2008b]. For mixed-phase orographic clouds, like those observed above the Sierra Nevada Mountains, the impact of increasing the CCN number concentrations available for cloud droplet formation is thought to amount to a reduction in precipitation (of both snow and rain) on the windward slope [Borys et al., 2003; Jirak and Cotton, 2006; Rosenfeld et al., 2008a; Saleeby et al., 2011]. The reduction in cloud droplet radius associated with a greater number concentration of CCN leads to weaker riming of hydrometeors [Borys et al., 2003], reducing fall speed and causing precipitation to spill over the crest of the mountain range [Saleeby et al., 2011].

Observations of the suppression of orographic precipitation by regional air pollution [Jirak and Cotton, 2006; Rosenfeld et al., 2007; Saleeby et al., 2011] is of particular interest as clearly identifiable sources of aerosol often exist, providing relatively clear targets for mitigation. As such, central California is perhaps an ideal case study: the Sierra Nevada Mountains act as both an orographic barrier that forces the formation of precipitation [Dettinger et al., 2004] and as the eastern boundary of a large basin (the ‘Central Valley’) that plays host to persistent aerosol pollution [Watson and Chow, 2002]. In addition, orographic precipitation in the Sierra Nevada represents a significant source of the region’s annual water supply [M Dettinger et al., 2011]; understanding the interplay of regional air pollution and the water supply could be critical for hydrologic management.
While the importance of aerosols on the formation of orographic precipitation has been stressed by various research groups, little focus has been placed on the meteorological influence on the ability of aerosol particles from various sources to be entrained in clouds.

Prior studies of aerosol-cloud-precipitation interactions in central California link changes in cloud microphysics to concentrations of CCN immediately below cloud base (‘sub-cloud’) [Rosenfeld and Givati, 2006; Rosenfeld et al., 2008a]. These studies suggest that the source of sub-cloud CCN is the often highly polluted Central Valley (CV). Comprehensive study of the influence of boundary layer structure during non-storm periods on pollutant concentrations in the CV indicate that the persistence of low level temperature inversions during the winter season [Bianco et al., 2011] concentrate pollutants near the surface of the CV [Pun and Seigneur, 1999; Watson and Chow, 2002]. During the late stages of winter storms in the central CV, cloud properties can be influenced by additions of sub-cloud CCN, causing precipitation to be suppressed over the Sierra Nevada [Rosenfeld et al., 2014]. However, the coupling of the polluted boundary layer within the CV and the clouds which form during earlier, more heavily precipitating periods of the storms may not have similar coupling, based on kinematic analysis [Kingsmill et al., 2013].

Pacific cyclones are known to initiate distinctive flow features upon landfall in California, particularly during wintertime [Neiman et al., 2010], when the precipitation in California is at its highest [MD Dettinger et al., 2011]. A low level jet, termed the ‘Sierra Barrier Jet’ (SBJ), can form at the windward base of the Sierra Nevada Mountains [Marwitz, 1987b; Parish, 1982] as a result of ‘blocked flow’ at the orographic barrier when low-level stratification is strong and buoyancy is limited. The weakening Coriolis force
associated with slowing onshore flow and the orientation of the rangefront dictate that the resulting barrier jet flow is directed toward 340° azimuth (Figure 6.1) [Kim and Mahrt, 1992; Neiman et al., 2002]. The importance of barrier jets in modulating the magnitude and distribution of precipitation has been highlighted by recent studies [Lundquist et al., 2010; Neiman et al., 2010], including impacts on mesoscale water vapor transport [Kim and Kang, 2007; Rotunno and Ferretti, 2001; Smith et al., 2010]. Similar to its ability to transport water vapor, the SBJ could entrain and transport both gaseous and particulate pollutants that often exist in high concentrations in the Central Valley during winter [Chow et al., 2006; Watson and Chow, 2002]. Transport through the moisture and pollutant-laden SBJ could not only influence the ability of pollutants to be entrained in orographic clouds in the Central Sierra Nevadas (or lack thereof), as discussed in this study, but also could influence the formation of precipitation in the northern section of the CV, where the SBJ is eventually forced over an orographic barrier [Kingsmill et al., 2013; Neiman et al., 2013]. High pollutant aerosol concentrations in the CV and the occurrence of SBJs could be further coincident due to the mutual importance of low-level atmospheric stability to their formation.

The SBJ was shown to be associated with 60% of the cool season precipitation from 2000-2007, indicating the relatively common formation of this feature in association with winter storms [Neiman et al., 2010]. The onshore (mostly southwesterly) flow observed during landfalling Pacific cyclones, which can be associated with filaments of poleward water vapor transport called Atmospheric Rivers (ARs) [Neiman et al., 2008; Ralph et al., 2004; Zhu and Newell, 1998], was recently shown to ride up and over the SBJ, while the SBJ flow itself increases in altitude as it travels north [Kingsmill et al., 2013], where it is
eventually forced over the Trinity Alps and the southern Cascade Range which form northern boundaries of the CV, perhaps more directly influencing the formation of precipitation at those topographic barriers [Neiman et al., 2013]. Since the storms originate over the remote Pacific Ocean, one may expect the air masses associated with these storms to contain aerosol particles that originate from marine regions, whereas the SBJ flow may be expected to entrain pollutant aerosols that are abundant in the CV, but this chemical distinction has not been documented. Since the SBJ and AR are thought to contain (with observational evidence shown herein) such strikingly different concentrations of CCN, the extent to which the each of these air masses influences the concentration of CCN introduced to the low-level orographic clouds could influence the efficacy of precipitation formation through the seeder-feeder mechanism [Choularton and Perry, 1986; Saleeby et al., 2009].

This study will evaluate the influence of the terrain-parallel SBJ and onshore AR-associated air masses on the chemical and physical properties of atmospheric aerosols observed at ground-level in the Sierra Nevada Mountains. Discussion will focus on the ability for aerosols to trace the evolution of meteorological factors important to this orographic precipitation system. In addition, the potential for aerosols to influence precipitation in this system will be discussed based on observations of pollutant-rich and clean marine air within the orographic precipitation systems reported in this study.

6.3 Methods

6.3.1 The CalWater Field Campaign

Field measurements were made in the Sierra Nevada Mountains as part of the CalWater field campaign, which combined detailed aerosol chemical and physical
measurements with regionally distributed radar and surface meteorological observations to investigate the role of aerosols in orographic precipitation formation over the Sierra Nevada Mountains. Here, we present observations for 4 storms occurring between 13 February and 4 March 2011. Ground-based aerosol and precipitation sampling was conducted at Sugar Pine Dam (SPD) (39.13° N, 120.80° W; 1066 m MSL) in the central Sierra Nevada (Figure 6.1). The field site was located approximately 10 km from major anthropogenic sources.

6.3.2 Instrumental Configuration

A range of aerosol physical and chemical properties were measured during CalWater. Size distributions of aerosols with mobility diameters \( d_m \) between 0.01-0.6 μm were obtained using a Scanning Mobility Particle Sizer (SMPS; Model 3080/Model 3010, TSI Inc.) and aerosols with aerodynamic diameters \( d_a \) between 0.5-20 μm were measured with an Aerodynamic Particle Sizer (APS; Model 3321, TSI Inc.) at ambient relative humidity (RH = 10 – 97%). In order to relate the different size metrics measured by the SMPS and APS, the physical diameter \( d_p \) was used [DeCarlo et al., 2004]. For spherical particles, \( d_m \) is equal to \( d_p \), while \( d_a \) depends on particle density according to Equation 6.1.

\[
d_p = d_a \left( \frac{\rho_0}{\rho_p} \right)^{1/2} \quad [6.1]
\]

Particles measured by APS and reported in this study in terms of \( d_p \) are assumed to be spherical with a density \( \rho_p \) of 1.6 g cm\(^{-3}\), which is similar to reported densities of particles close to this size range [Vaden et al., 2011]; the reference density \( \rho_0 \) was 1 g cm\(^{-3}\). Number concentrations of CCN \( (N_{CCN}) \) were obtained using a miniaturized stream-wise
thermal gradient CCN counter (CCNc) [Roberts and Nenes, 2005], which was operated by continuously scanning a range of supersaturations \((s)\), but only \(s = 0.076\%\) and \(0.206\%\) are reported in this work. Measurements of size-resolved, single-particle chemical composition were obtained using an Ultrafine Aerosol Time-of-Flight Mass Spectrometer (UF-ATOFMS) equipped with an aerodynamic lens inlet to measure particles with vacuum aerodynamic diameter \((d_{va})\) between 0.08-1.0 μm [Su et al., 2004]. Dual-polarity mass spectra were obtained for individual particles and those with similar spectral patterns were grouped using a neural network clustering algorithm (ART-2a) [Song et al., 1999]. Each resulting cluster was chemically classified according to its representative positive and negative ion mass spectra, allowing the clusters to be further grouped into particle types.

Meteorological observations were made through the NOAA Hydrometeorology Testbed (http://hmt.noaa.gov). Precipitation rate was measured at SPD using a heated-funnel tipping bucket precipitation gauge. Time- and altitude-resolved profiles of horizontal winds were measured using a 915-MHz wind profiling radar [Carter et al., 1995; Weber et al., 1993] stationed at Sloughhouse, CA (SHS; 38.50° N, 121.21° W; 50m MSL) located approximately 76 km SW of SPD. The wind velocity was separated into terrain parallel \((U_{160};\) coming from 160° azimuth) and terrain normal components \((U_{250};\) coming from 250° azimuth) (Figure 6.1).

6.4 Results and Discussion

6.4.1 Episodes of Highly Active CCN

Several short episodes showing at least a 10-fold increase in particle concentrations with \(d_p > 0.2\ \mu m\) were observed at SPD. The increase in aerosol number concentration preceded precipitation events by 6-12 hours and reached peak concentrations in less than
3 hours (Figure 6.2). Decreasing aerosol concentrations were likely due to below-cloud scavenging in the local environment and/or in the particle source region; environmental implications for this observation are discussed in Section 6.4.4. Throughout these events, distinct changes in the aerosol size distribution, single particle composition, and CCN activity were observed.

A detailed view of the physicochemical characteristics of an exemplary aerosol episode measured at SPD on 14 February 2011 is shown in Figure 6.3. Relatively high ambient concentrations of particles with \(d_p > 0.2\ \mu m\) are observed at the sampling site during these episodes, lending to an increase in \(N_{CCN}\) at \(S = 0.076\%\) [Andreae and Rosenfeld, 2008; Dusek et al., 2006]. Aerosol chemical composition obtained using UF-ATOFMS indicated that a unique particle type contributed between 30-50\% of all particles measured by UF-ATOFMS during these pre-frontal episodes. This particle type was characterized as a highly aged secondary aerosol consisting of nitrate \((m/z\ 30, m/z\ -46, m/z\ -62)\), sulfate \((m/z\ -97)\), nitric \((m/z\ -125)\) and sulfuric \((m/z\ -195)\) acids, ammonium \((m/z\ 18)\) and organic carbon \((m/z\ 12, 27, 29, 43)\) (Figure 6.4). A similar chemical signature was prevalent in ATOFMS measurements at Bakersfield, CA in the southern CV during the winter [Whiteaker et al., 2002], and so is denoted as S-CV (‘Secondary – Central Valley’) hereafter. Notably, the S-CV particle type was rarely observed at SPD apart from periods in which precipitation was imminent. Ammonium nitrate-containing particulate matter, which forms through a secondary (gas-to-particle) formation process, makes up a substantial fraction of total particulate matter in the CV during the cool season due to widespread emissions of gas-phase ammonia and nitrogen oxides [Chow et al., 2006; Pun and Seigneur, 1999], cool ambient temperatures, high relative humidity [Stelson and
Seinfeld, 1982], and persistent valley-wide temperature inversions [Watson and Chow, 2002]. Amines (m/z 58) were also observed within S-CV particles, further suggesting that emissions from the abundant agricultural activities in the Central Valley [Sorooshian et al., 2008] influenced the chemical fingerprint of this particle type, and help to define its source region.

If one was to consider the S-CV particle type to have the average hygroscopic properties of its dominant inorganic components (50:50 ratio or NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$), the minimum size particle that such a particle could nucleate a cloud droplet at S = 0.076%, called the activation diameter ($d_{ac}$), is 155 nm based on κ-Köhler Theory [Petters and Kreidenweis, 2007]. Since nearly all of the S-CV particles observed during the study period were larger than 200 nm (Figure 6.4d), the variation in the number concentration of particles of this type was a driver of intermittent highly CCN activity of aerosols observed at SPD. Taken as a whole, these observations suggest that approaching frontal systems were likely responsible for transporting Central Valley pollutant aerosols to the remote, upslope regions of the Sierra Nevada at ground-level that are typically not subject to particulate air pollution during winter.

6.4.2 Correlation of Pollutant Transport with SBJ Formation

The temporal association between the aerosol pollution episodes with precipitation (Figure 6.2) suggested that a feature of approaching frontal systems is associated with the observed aerosol pollution episodes at SPD. Through inspection of hourly wind profiles at SHS, the existence of barrier jet conditions (vertically contiguous $U_{160}$ velocity > 10 m s$^{-1}$) shown in Figure 6.5, is temporally correlated with the observation of S-CV aerosol at
ground level. The correlation of temporally distinct terrain parallel flow events along the windward slope of the Sierra Nevada and episodes of S-CV aerosol detection at SPD support the concept of CV pollution transport within the SBJ. This leads to northward transport of pollutants formed in the southern CV, possible impacts on the formation of precipitation at the northern extent of the CV, and transport of pollutants up the windward slope of the Sierra Nevada Mountains along the ground. While these pollutant-rich SBJ is thought to be segregated from low-level orographic clouds associated with the over-riding AR [Kingsmill et al., 2013], a regularly occurring mechanism for pollutant transport in this manner has implications for wet deposition of pollutants in ecologically pristine mountain environments.

6.4.3 Marine Aerosol and Storm Passage

Shortly before and during light precipitation at SPD, an increase in the number concentration of sea salt particles was observed by UF-ATOFMS (Figure 6.6). The marine particle number concentrations increased even during the onset of light precipitation, where scavenging and wet deposition would be expected to suppress aerosol concentrations. Overall, the temporal trends in marine particles correlate with the descending lower extent of terrain-normal \( (U_{250}) \) winds aloft. The air characterized by the vertically contiguous \( U_{250} \) velocities shown in Figure 6.6 is also commonly parallel to the flow of landfalling ARs [Ralph et al., 2004]. Recently, it has been shown that this AR flow is lifted up and over the SBJ before continuing over the Sierra Nevada range crest, acting as the principally responsible kinematic mechanism for the formation of orographic precipitation [Kingsmill et al., 2013; Neiman et al., 2013]. Surface winds within Pacific cyclones, in general, are greater than the threshold for open ocean wave breaking and aerosol production \((U > 5 \text{ m})\).
leading to the production and entrainment of sea spray aerosol particles within these storms. Transport of sea salt aerosol to inland locations during precipitation events has been observed previously in California [Noble and Prather, 1997; Whiteaker et al., 2002]. Similar observations of marine aerosol in association with a descending AR above the Sierra Nevadas in this study suggests that a microcosm of the marine atmosphere was associated with the AR flow as it rode up and over the SBJ and was lifted at the orographic barrier. Marine air intrusions to the Sierra Nevada Range (approximately 300 km from the coastline) may be particularly strong near SPD in association with moisture transport to the Central Sierra Nevadas through the Carquinez Strait that has been observed during AR storms [Neiman et al., 2013]. In addition, Rosenfeld et al. [2014] have shown through aircraft observations that clouds upwind of the coastal margin are characteristic of typical marine clouds, producing drizzle by warm rain processes. After transiting California, however, clouds associated with the same air mass did not precipitate due to the added continental aerosol that were acting as CCN. It is important to note that this study of cloud ‘continentalization’ did not focus on time periods in which the kinematic scheme was necessarily similar to that discussed in this work and described in detail by Kingsmill et al. [2013].

Sea spray aerosol, produced by bubbles bursting at the air-sea interface, include particles that range in composition from containing mostly sea salt to other types which contain biological and/or organic material derived from the surface ocean [Gantt and Meskhidze, 2013; Prather et al., 2013]. While many types of continental aerosol contain organic compounds, sodium chloride-rich particles are a more unique tracer for the ocean as an aerosol source. Ocean-derived aerosols observed at SPD included into two sea salt-
containing particle types, called Sea Salt (SS) and Aged SS in this study. The representative mass spectrum for each particle type (Figure 6.4b,c) contained ion markers for nitrate \((m/z -46, -62)\) with suppressed or even entirely missing markers for chloride \((m/z -35, -37)\) due to well-known heterogeneous chemical processes in which nitrate replaces chloride in sea salt aerosol particles [Finlayson-Pitts et al., 1989; Gard et al., 1998; Vogt et al., 1996]. Aged SS particles observed at SPD also contained markers for sulfate \((m/z -80, -97)\) and oxalate \((m/z -89)\), indicating that these particles were more chemically aged than the SS type. The Aged SS type was temporally correlated with the S-CV type when SS was also detected (Figure 6.6), indicating that gaseous pollutants co-transported with S-CV particles within the SBJ may be responsible for the transformation of SS to Aged SS.

When viewed as chemical tracers, the temporal trends of the S-CV and SS particle types suggests that when the polluted SBJ is beneath the cleaner marine AR flow, the two orthogonal, stratified air masses must mix to some extent, particularly with respect to the observation of marine particles from the over-riding AR at ground level (below the SBJ). Evidence of nitrate replacement of chloride is present in both the SS and Aged SS types, but a larger fraction of marine particles fit into the SS type than into the Aged SS type, indicating that the marine air was advected to SPD by means of the AR without significant chemical influence from the polluted boundary layer.

Marine particle concentrations measured by UF-ATOFMS were similar for the first two episodes (Figure 6.6 a,b) while concentrations were much lower for the third episode during initial frontal passage around 00:00 PST on 2 March (Figure 6.6c). This discrepancy could be due to the sharp gradient in wind direction with height during this case, perhaps indicating particularly strong stratification between the SBJ and AR air.
masses. The differences in stratification could also be an indicator for mixing between the polluted SBJ and marine-influenced AR, suggesting that assessments of SBJ and AR mixing may be more subtle than previously thought. Mixing of the SBJ and AR is not only required for detection of marine aerosol at ground level, but also suggests that the pollutant aerosol carried by the SBJ could be introduced to the AR aloft; this has implications for introduction of highly active CCN to the orographic clouds, since the cross-barrier AR flow is principally responsible for the formation of orographic precipitation [Neiman et al., 2013]. Further in situ study of this system is required to assess microphysical impacts of regional pollutant aerosol on orographic clouds by this mechanism.

Sea spray aerosol, of which sea salt is a significant component [Prather et al., 2013], is often considered a good source of ‘giant nuclei’ (GN) [Johnson, 1982] due to the relatively large number concentration of water-soluble particles with $d_p > 1 \mu m$ [de Leeuw et al., 2011]. The large size of droplets formed by GN are particularly amenable to enhancing cloud droplet collection and coalescence processes that are associated with the initiation of precipitation [Rosenfeld et al., 2002], even when CCN concentrations are high and precipitation would be suppressed [Feingold et al., 1999]. In the mixed-phase system over the Sierra Nevadas in the winter, GN transported inland from the marine environment by ARs may facilitate warm rain production during periods where the onshore flow is decoupled from the boundary layer [Rosenfeld et al., 2014], or expedite riming of ice crystals when the seeder-feeder mechanism is active [Creamean et al., 2013]. The addition of anthropogenic ($d_p < 1 \mu m$) CCN to orographic clouds, as studied at a location ~1000 km inland from the Sierra Nevadas, would suppress or delay precipitation [Saleeby et al., 2011]. With the abundance of SS particles within the AR above the Sierra Nevadas, which
are relatively proximal to the Pacific coastline, the influence of GN may compete with the influence of added CCN with $d_p < 1 \mu m$, but detailed model studies are likely required to assess this possibility.

6.4.4 Seasonality and Breadth of Impact

The observation that the SBJ is important for increasing pollutant aerosol concentrations in remote mountain regions suggests that this terrain parallel flow feature acts as a commonly occurring mechanism for the transport of CCN to normally pristine regions. The frequency and strength of the SBJ is greatest in the winter months [Neiman et al., 2010] which is coincident with the highest concentrations of particulate matter in the southern part of the CV [Chow et al., 2006], stressing the broad importance of the SBJ for re-distributing pollutant aerosols that could ultimately impact cloud properties and precipitation in California.

The reduction in S-CV aerosol concentrations upon the initiation of precipitation indicates that below-cloud scavenging and wet deposition of these pollution particles were important. Due to the close association of the barrier jet with precipitation [Neiman et al., 2010], wet deposition of the pollutants introduced to normally clean mountain regions is likely important in a majority of SBJ cases overall. Ecological studies have shown that deposition of pollutants to surface water, especially nitrogen species, is significant in locations like the Sierra Nevada [Baron et al., 2011]. While inorganic nitrogen deposition in the Sierra Nevada is typically lower in winter than in summer, the systematic transport of pollutants to sensitive ecosystems upslope in winter just ahead of precipitation provides a concerted mechanism for pollutant deposition in groundwater and in the snowpack. Measurable changes in freshwater ecosystems have been observed as a result of reactive
nitrogen deposition [Jassby et al., 1994]. The SBJ could be a significant participant in the delivery of aerosol \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) to mountain lakes through its implication here in the transport and subsequent wet deposition of key anthropogenic pollutants.

6.5 Conclusions

Low level jets at topographic barriers are known to affect precipitation through modulating orographic forcing and water vapor transport. This study adds an additional dimension: regional redistribution of pollution aerosols. Aerosol redistribution associated with winter storms in California is associated with the formation of the SBJ, which transports aerosols produced in the often heavily polluted southern CV toward the northern part of the valley and along ground-level within the Central Sierra Nevada Mountains. The terrain-normal AR flow (from 250° azimuth) over the Sierra Nevadas delivered mostly pristine marine aerosol to the measurement site approximately 200 km inland, indicating that the prevailing orographic flow is dominated by marine air and likely contains a significant quantity of GN. Mixing of the AR flow and the barrier jet was not observed to be constant across all cases and could be related to the vertical gradient between \( U_{160} \) and \( U_{250} \) component wind velocities. Similar conditions are likely to exist in other locations where highly polluted population centers exist upwind of orographic barriers. While this study does not take into account in situ observations of microphysics and cloud drop residual chemistry, these types of studies could be readily connected with this mechanistic view of aerosol redistribution in the context of frontal passage.
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6.7 Figures

Figure 6.1: (a.) Shaded topographic map of the study region with each of the measurement sites labeled. (b) A schematic elevation cross section along 250°-70° azimuth is shown with the SBJ labeled. The markers along the line representing the terrain schematically indicate the position of the wind profiling radar at SHS and the aerosol measurement site at SPD; the sites are not located exactly along this transect. The symbol within the SBJ indicates that its flow direction is into the page. Illustration is not to scale. Prevailing winds are westerly.
Figure 6.2: Time series of size distributions for $d_p > 450$ nm measured using an APS and precipitation measured with a tipping bucket rain gauge.
Figure 6.3: A detailed temporally-resolved characterization of one aerosol episode observed at SPD: (a.) $N_{CCN}$ at two different supersaturations, (b.) aerosol number size distributions for $d_p = 0.45-4.5 \, \mu m$ measured with an APS, (c.) aerosol number size distributions from $d_p = 0.11-0.6 \, \mu m$ measured with an SMPS, (d.) precipitation rate at ground level measured with a tipping bucket rain gauge and the frequency of S-CV aerosol detection by UF-ATOFMS. $N_{CCN}$ at $s = 0.076\%$ increases due to higher loadings of larger aerosol, temporally correlated with the appearance of the S-CV particle type, suggesting a CV source for highly active CCN.
Figure 6.4: Representative positive and negative mass spectra for the (a.) S-CV, (b.) sea salt, (c.) aged sea salt. Some ion markers described in the text are not labeled. (d.) The submicron size distribution of each particle type determined by UF-ATOFMS, depicted as a fraction of all particles analyzed during the study.
Figure 6.5: Temporally-resolved precipitation rate (top), vertical wind profiles of $U_{160}$ at SHS (middle), and the frequency of S-CV particle detection by UF-ATOFMS at SPD (bottom). Secondary pollutant particle concentrations from the CV are observed when the SBJ is active prior to and during breaks in precipitation.
Figure 6.6: Temporally-resolved precipitation rate (top), vertical wind profiles of $U_{250}$ at SHS (middle), and the frequency of marine particle detection (SS + Aged SS) by UF-ATOFMS at SPD with S-CV particle detection frequency included for comparison (bottom). (a., b.) Sea salt particles increase in abundance as frontal passage occurs. Note that aerosol are scavenged by hydrometeors, leading to reduced total particle concentrations during precipitation. (c.) The lack of a large change in sea salt particle abundance around 00:00 on 2 March may be due to the strong vertical gradient in $U_{250}$, resulting in a lack of significant mixing between the terrain normal flow and air sampled at the ground level.
6.8 References


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7. Conclusions and Future Work

This dissertation has shown, through the ability of aerosol particles to act as cloud condensation nuclei (CCN), that the Earth’s climate has a tight connection to fundamental chemistry, especially that which occurs in the condensed phase. The research documented herein has shown that geophysical processes, such as oceanic bubble bursting, can control the chemical properties of the sea spray aerosol (SSA) that are produced. Similarly, the nature of biogeochemical interactions with organic matter in seawater can have a strong influence on the mixing state and CCN activity of SSA that is produced. Over the course of the studies presented here, it has been ascertained that the chemical determination of the extent of external mixing of organic and salt-containing particles is likely more important to deriving CCN concentrations within an aerosol population than the overall organic volume or mass fraction. The influence of biological activity showed little effect on the CCN activity of SSA, but the potential for secondary aerosol to form over blooms indicates more far-reaching influences on CCN concentrations and marine cloud microphysics. Orographic cloud systems over the Sierra Nevada Mountains, which are approximately 300 km from the coastline of the Pacific Ocean, form in a pseudo-marine environment, wherein aerosols generated in the marine boundary layer (MBL) are carried inland. This marine-dominated air mass has been in this work to chemically interact with the pollutant-bearing Sierra Barrier Jet at the windward base of the mountain range, indicating the possibility of pollutant aerosol entrainment into the cross-barrier flow as it is forced aloft. Overall, chemical studies of CCN-active aerosol particles at the intersection of the geophysics, biology, and meteorology has allowed for new insights that could not precipitate without cross-disciplinary connections.
7.1 Sea Spray Aerosol Particle Production: Chemistry and Physics

The production of SSA particles at the air-sea interface has been shown by the studies here to be an issue of chemistry, as much as it is an issue of geophysics [de Leeuw et al., 2011; Lewis and Schwartz, 2004]. Through inter-comparison experiments, the importance of the physical production mechanism of SSA on its composition was clearly shown through direct chemical measurements of individual aerosol particles. The composition, mixing state, and morphology were all been shown to be strong functions of the mechanism of bubble production. In addition, the formation of thick foam on the water surface was also shown to enrich the aerosol in organic matter and change the size distribution of SSA particles produced. This result mainly has implications for other laboratory studies of SSA particles generated from organic-rich seawater in which high concentrations of surfactants can induce foaming at the water surface. CCN activity was not shown to be altered by the use of different bubble/aerosol generation methods, even when foaming was observed after a phytoplankton bloom had peaked and subsided.

7.2 Mixing State and Solution Chemistry of CCN Activity of SSA Particles

Several chapters within this dissertation have focused on the CCN activity of SSA particles, especially those generated under conditions of elevated biological activity and/or enriched organic content. The overall CCN activity of the SSA population has been shown to be strongly influenced by the mixing state of particles with diameter \((d) < 100\) nm. SSA particles in this smallest section of the size distribution are characterized by an external mixture of salt-containing and organic-dominated particles. Organic particles exhibited weak hygroscopicity, and upon increasing in relative abundance after bacterial degradation of a growth medium that was added to the seawater, strong suppression of CCN activity
was observed. This contrasts with the weak dependence of CCN activity on the biological state of unconstrained phytoplankton blooms, which exhibited consistent CCN activity despite large (approx. 3-fold) increases in organic matter concentration within the seawater. Secondary aerosol was observed to form in response to phytoplankton senescence (to be discussed in detail in the next section), which had an effect on CCN activity which was similar in nature to that observed during the bacteria growth experiment. The hygroscopicity of the secondary aerosol was similar to that of secondary organic aerosol observed in continental environments, and dominated the number concentration of particles in the chamber. Hence, relatively high and consistent CCN activity ($\kappa > 0.8$) was observed, except when it was confirmed that salt-containing SSA particles were externally mixed with weakly hygroscopic (organic) aerosols with $d < 100$ nm. Climate models including the transfer of marine organic matter into the atmosphere have pointed to the importance of aerosol mixing state [Meskhidze et al., 2011; Westervelt et al., 2012], which has been confirmed experimentally in these studies.

7.3 Biogenic Marine Secondary Aerosol Formation

The influence of the marine biosphere on cloud albedo has been a topic of scientific inquiry for about three decades [Charlson et al., 1987; Meskhidze and Nenes, 2006; Quinn and Bates, 2011]. Still, the nature of the link between marine microbiological activity and changes in CCN concentrations through secondary aerosol formation have not been unequivocally addressed [Arnold et al., 2009; Miller and Yuter, 2008; Quinn and Bates, 2011]. In this dissertation, it was shown through a controlled phytoplankton bloom experiment, that secondary aerosol can form spontaneously in association with the senescence of phytoplankton. During senescence, the flux of gases containing reduced
sulfur, organic nitrogen, and/or hydrocarbons increased, leading to spontaneous particle nucleation. The CCN activity of these particles was low, but grew over time as the modal diameter of the number size distribution increased, indicating that CCN-active secondary marine aerosol were produced in direct association with biological activity. I hypothesize that bacterial degradation of phytoplankton and associated metabolites [Smith et al., 1995; Teeling et al., 2012; Zubkov et al., 2001] was a major factor in these observations, which provides constraints for studies of marine secondary aerosol formation in the MBL.

7.4 Ongoing and Future Work

7.4.1 Sea Spray Aerosol Production and Phytoplankton Blooms

The perceived importance of the biological state of phytoplankton blooms with respect to their impact on atmospheric chemistry is not only intriguing, but critical to understanding the aerosol indirect effect with greater quantitative certainty [Carslaw et al., 2013; Rap et al., 2013]. I plan to extend the systematic study of secondary aerosol formation in the marine environment using controlled atmospheric chamber studies wherein the concentrations of oxidants, photon flux, temperature, and/or humidity can be prescribed. Currently the understanding of the connection between the marine biosphere and the atmosphere is uncertain [Quinn and Bates, 2011]. The generality of initial correlations between cloud properties and ocean surface chlorophyll-a [Kruger and Grassl, 2011; Meskhidze and Nenes, 2006] has been questioned, showing weak or no correlation in several other regions [Miller and Yuter, 2008], along with complications from atmospheric dynamics, which can swamp the chemical signal and make in situ measurements difficult to assess [Sorooshian et al., 2009]. The results reported in Chapter
5 lend credence to the studies linking biological activity to cloud properties via secondary aerosol formation, so rather than focus on the apparent lack of generality as a drawback to the studies that do document correlations, it is productive to instead see this discrepancy as a sign of biogeochemical nuance. A main theme of Chapter 5 is the strong association of secondary aerosol production with phytoplankton senescence. Since the ensemble of biogeochemical interactions within the marine ecosystem are importantly related to primary productivity [Riemann et al., 2000; Smith et al., 1995; Teeling et al., 2012; Zubkov et al., 2001], it is important to also separate the phases of bloom growth, senescence, and dormancy in our studies of atmospheric couplings to this biological system. In this way, laboratory studies of secondary aerosol formation over phytoplankton blooms could help constrain the conditions in which changes in cloud properties are likely to occur, helping to focus the generalization of biological couplings to the aerosol indirect effect [Carslaw et al., 2013; Rap et al., 2013].

A recent review of the marine aerosol formation literature has pointed away from the importance of biogeochemical interactions on secondary aerosol formation overall, instead suggesting that SSA production is responsible for possible changes in cloud properties [Quinn and Bates, 2011]. Controlled studies in the laboratory can again shed considerable light on this question. Size-resolved aerosol fluxes generated within a MART during phytoplankton blooms could simply indicate whether SSA number concentrations increase or decrease as a function of chlorophyll-a or other biological parameters, similar to studies which have used known compounds to change organic matter concentrations in seawater or proxy solutions [King et al., 2012; Sellegri et al., 2006]. Coupling this information with constraints on the secondary aerosol formation potential of phytoplankton
blooms could tell an important story about changes in aerosol and CCN concentrations in phytoplankton bloom (Quinn and Bates, 2011) regions.

7.4.2 Physical Chemistry of Cloud Droplet Solutions

As discussed in Section 1.1.4 and highlighted again in Section 4.5.3, the fundamental physical chemistry occurring within activating cloud droplets is a topic in great need of fundamental study. Surfactant effects in micrometer-sized droplets have been suggested to be different from bulk solutions owing to the significantly different surface/volume ratios [Li et al., 1998; Prisle et al., 2008; Sorjamaa et al., 2004], but some studies find closure between measurements and model calculations using surfactant concentration dependence curves generated from bulk samples (Szyskowski-Langmuir isotherms) [Broekhuizen et al., 2004; Moore et al., 2008]. Studies are now limited by the dearth of direct surface tension measurement technologies for droplets on the micrometer scale [Petters et al., 2013; Ruehl et al., 2012], and inferences about surface tension are difficult using CCN activity measurements due to the complication of simultaneous changes in solution activity [Li et al., 1998; Sorjamaa et al., 2004]. In addition, the solubility of a surfactant can have important implications for changes in both water activity and concentration-dependent surface tension [Donaldson and Vaida, 2006; Holmberg et al., 2002].

7.4.3 Aerosols and California Hydrology

A major factor limiting our ability to adequately model the impacts of pollutant aerosol on orographic clouds that are formed as a result of cross-barrier flow (often associated with an Atmospheric River (AR)) characterized by a strong marine influence is
direct evidence of coupling between the polluted boundary layer and Sierra Barrier Jet (SBJ). Radar studies of the dynamics and kinematics of these storm systems suggests that the SBJ and AR did not interact during a case study in 2011 [Kingsmill et al., 2013], except that the SBJ can control precipitation forcing by acting as a dynamic barrier [Lundquist et al., 2010]. The results in Chapter 6 suggest otherwise, showing a correlation between chemically aged sea salt and secondary pollutant aerosol from the Central Valley. Direct measurements of aerosol chemical composition over the Sierra Nevada Mountains and of cloud droplet residues near cloud base could help enlighten the possibility of systematic introduction of highly CCN-active pollutant aerosol into orographic clouds during winter storms, as suggested previously [Rosenfeld et al., 2008a].

While the SBJ flows parallel to the Sierra Nevada Mountains, this jet of air is lifted at the northern extent of the Central Valley. Chapter 6 shows that the SBJ is highly polluted, which could act as a natural contrast to the clouds that are formed from pristine marine air over the Central Sierra Nevadas. Cloud droplet sizes over the Southern Cascades should be on average smaller than those in low level orographic clouds over the Sierra Nevadas based on assumptions derived from aerosol data collected during SBJ events, suggesting that precipitation formation should be less efficient through collision-coalescence and riming of primary ice crystals [Borys et al., 2003; Rosenfeld et al., 2008b; Saleeby et al., 2011]. Also, since anthropogenic aerosols are also not thought to be particularly effective ice nuclei [DeMott et al., 2010], the likelihood of finding clouds over the Southern Cascades that contain significant quantities of supercooled liquid droplets is high. Comparing the Southern Cascade orographic system with that over the Central Sierra Nevada Mountains may help provide fundamental insights on the impact of anthropogenic
pollution on clouds and precipitation, as well as practical insights for water managers in the state [White et al., 2013].

7.5 References


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