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Article

CAICE Studies: Insights from a Decade of Ocean–Atmosphere Experiments in the Laboratory

Published as part of the Accounts of Chemical Research special issue "New Frontiers in Chemistry–Climate Interactions".

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Cite This: *Acc. Chem. Res.* 2020, 53, 2510–2520

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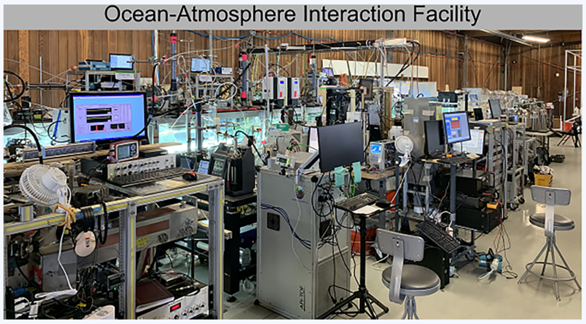
Ocean-Atmosphere Interaction Facility



CONSPECTUS: Ocean–atmosphere interactions control the composition of the atmosphere, hydrological cycle, and temperature of our planet and affect human and ecosystem health. Our understanding of the impact of ocean emissions on atmospheric chemistry and climate is limited relative to terrestrial systems, despite the fact that oceans cover the majority (71%) of the Earth. As a result, the impact of marine aerosols on clouds represents one of the largest uncertainties in our understanding of climate, which is limiting our ability to accurately predict the future temperatures of our planet. The emission of gases and particles from the ocean surface constitutes an important chemical link between the ocean and atmosphere and is mediated by marine biological, physical, and chemical processes. It is challenging to isolate the role of biological ocean processes on atmospheric chemistry in the real world, which contains a mixture of terrestrial and anthropogenic emissions. One decade ago, the NSF Center for Aerosol Impacts on Chemistry of the Environment (CAICE) took a unique ocean-in-the-laboratory approach to study the factors controlling the chemical composition of marine aerosols and their effects on clouds and climate. CAICE studies have demonstrated that the complex interplay of phytoplankton, bacteria, and viruses exerts significant control over sea spray aerosol composition and the production of volatile organic compounds. In addition, CAICE experiments have explored the physical production mechanisms and their impact on the properties of marine cloud condensation nuclei and ice nucleating particles, thus shedding light on connections between the oceans and cloud formation. As these ocean-in-the-laboratory experiments become more sophisticated, they allow for further exploration of the complexity of the processes that control atmospheric emissions from the ocean, as well as incorporating the effects of atmospheric aging and secondary oxidation processes. In the face of unprecedented global climate change, these results provide key insights into how our oceans and atmosphere are responding to human-induced changes to our planet.

This Account presents results from a decade of research by chemists in the NSF Center for Aerosol Impacts on Chemistry of the Environment. The mission of CAICE involves taking a multidisciplinary approach to transform the ability to accurately predict the impact of marine aerosols on our environment by bringing the full real-world chemical complexity of the ocean and atmosphere into the laboratory. Toward this end, CAICE has successfully advanced the study of the ocean–atmosphere system under controlled laboratory settings through the stepwise simulation of physical production mechanisms and incorporation of marine microorganisms, building to systems that replicate real-world chemical complexity. This powerful approach has already made substantial progress in advancing our understanding of how ocean biology and physical processes affect the composition of nascent sea spray aerosol (SSA), as well as yielded insights that help explain longstanding discrepancies in field observations in the marine environment. CAICE research is now using laboratory studies to assess how real-world complexity, such as warming temperatures, ocean acidification, wind speed, biology, and anthropogenic perturbations, impacts the evolution of sea spray aerosol properties, as well as shapes the composition of the marine atmosphere.

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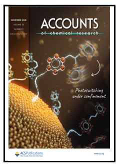
Received: August 4, 2020
Published: October 22, 2020



https://dx.doi.org/10.1021/acs.accounts.0c00504
Acc. Chem. Res. 2020, 53, 2510–2520

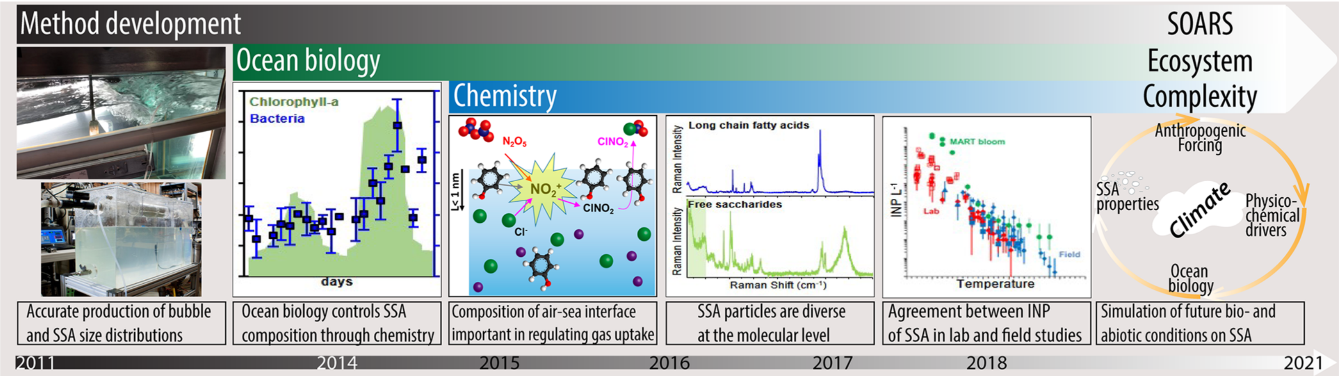


Figure 1. Timeline of CAICE achievements, through the innovation and development of a new ocean−atmosphere interaction facility and major experimental results obtained using these systems. CAICE seeks to accurately predict the impact of marine aerosols on our environment by bringing the full real-world chemical complexity to the laboratory. Toward this end, the team has successfully replicated the complexity of the ocean−atmosphere system, by accurately reproducing bubble and SSA size distribution and the microbiology of the system. The CAICE in-development SOARS simulator will assess the impact of the full system complexity on atmospheric chemistry. Adapted with permission from refs 2 and 20. Copyright 2015 American Chemical Society. (SSA, sea spray aerosols; IN, ice nucleation; SOARS, Scripps Ocean Atmosphere Research Simulator).

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■ INTRODUCTION

Marine aerosols constitute an important chemical link between the oceans and the atmosphere. Aerosols affect climate directly by scattering incoming solar radiation and indirectly by affecting cloud properties.[5] Aerosols can serve as cloud condensation nuclei (CCN), which influence the size and number of droplets in a cloud, thus affecting precipitation and interactions with radiation.[6,7] In addition, some aerosols may serve as ice nuclei (IN), facilitating the formation of ice crystals in mixed-phase clouds.[8,9] Aerosol−cloud interactions constitute the largest source of uncertainty in our understanding of the Earth's radiative budget,[10] with a large contribution from the understanding of natural aerosols.[11]

The climate impacts of marine aerosols are of particular interest, as oceans cover 71% of the Earth's surface. Primary sea spray aerosol (SSA) is generated by bubble-bursting at the ocean surface as a result of breaking waves. Secondary marine aerosol (SMA) is formed from the oxidation of volatile gases emitted from the oceans,[12] which can result in the formation of new particles through nucleation processes.[13,14] Alternatively, secondary species can condense onto existing particles in the marine atmosphere, such as SSA, influencing their chemical composition and properties.[15] Biological activity in seawater exerts significant control over the chemical composition of SSA,[16,17] as well as the emission of gas-phase precursors that form SMA.[18,19]

A major challenge in the study of marine aerosols and gases is disentangling the multitude of factors that influence their composition and properties: biological activity in seawater;

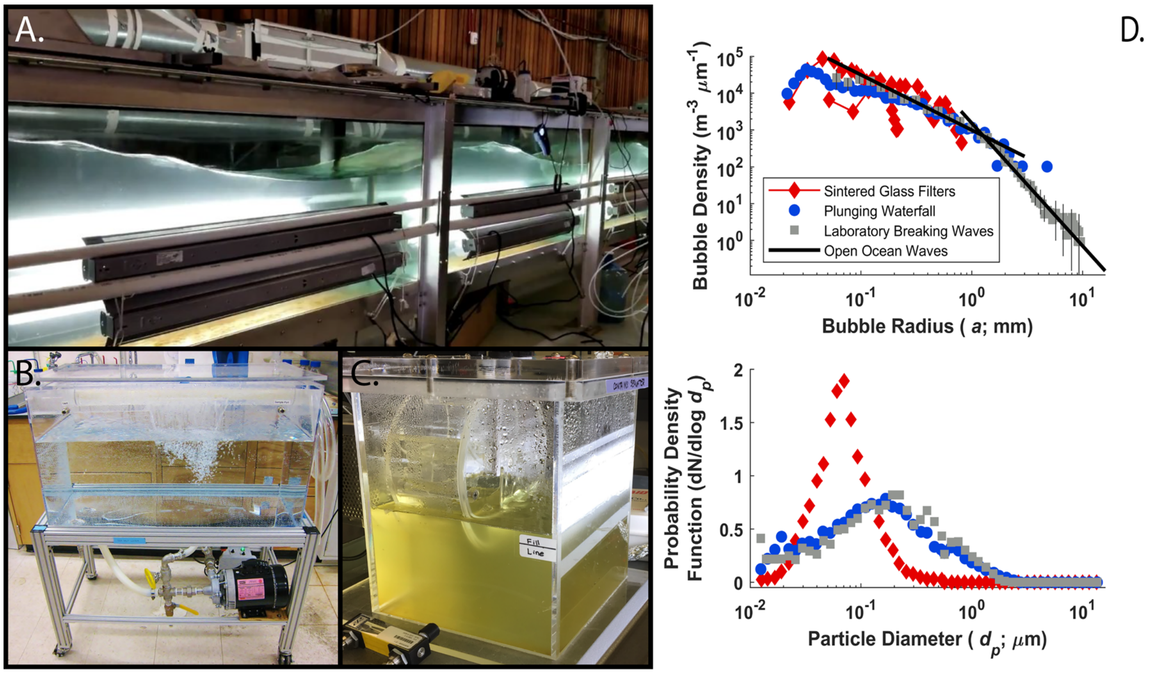

Figure 2. CAICE's ocean–atmosphere simulators: 13000 L wave channel (A), 210 L Marine Aerosol Reference Tank - MART (B), and 19 L miniMART (C). Panel D shows the bubble size distributions and normalized aerosol size distributions with laboratory and plunging waterfall in reference to open ocean waves. Reproduced with permission from ref 20. Copyright 2015 American Chemical Society.

transport of terrestrial and anthropogenic aerosols and gases to marine regions; heterogeneous and photochemical aging processes; physical parameters such as wind speed, temperature, and relative humidity; and secondary aerosol formation and growth processes. These numerous confounding variables make it challenging to disentangle the individual contributions from each of these processes, which impedes our ability to model and predict the properties of marine aerosols. Ocean–atmosphere experiments conducted in the laboratory have the significant advantage of allowing for the isolated study of individual processes that control marine aerosol composition, properties, and production flux. Here, we discuss ocean–atmosphere experiments addressing the aforementioned challenges. Through the implementation of technologies designed to produce marine aerosols as naturally as possible, we outline the various directions of new inquiry opened by the ocean–atmosphere experimental approach, as well as the successes already achieved (Figure 1). Lastly, we introduce the future of ocean–atmosphere experiments through the lens of an under-development facility that seeks to improve upon previous designs and allows for the study of external perturbations on the natural marine environment including high speed winds and cold ocean temperatures.

■ MAKING WAVES: SEA SPRAY AEROSOL GENERATION

Multiple CAICE innovations have advanced our understanding of atmospheric chemistry through ocean-in-the-laboratory approaches. Initial experiments focused on using accurate production methods to generate realistic SSA in controlled laboratory settings. In the past, many studies have used sintered glass filters to produce SSA by forcing air through the filters to produce bubbles, which rise to the surface and burst, producing SSA.[20,21] However, a major drawback of these methods is that they produce a very narrow range of bubble sizes, which skews the resulting SSA size distribution and produces a persistent surface foam.[22] In order to produce realistic SSA, it is necessary to simulate the action of real breaking ocean waves, which intermittently entrain air beneath the ocean surface via the action of plunging sheets of water, producing a wide range of bubble sizes. To accurately capture this process in the laboratory, CAICE has pioneered the use of wave channels for laboratory studies of marine aerosols.[1] Traditionally used for experiments in physical oceanography, these large channels often hold over 10000 L of seawater and produce waves using computer-controlled reciprocating paddles (Figure 2A), which send artificial waves to break on an artificial beach. To facilitate studies of marine aerosols, CAICE researchers transformed an existing wave channel into an ocean–atmosphere simulator by sealing it with lids to create an enclosed headspace along the full length of the channel. Clean, particle-free air is provided to the headspace by a specialized filtration system. These modifications have enabled the study of sea spray aerosol generated by real breaking waves in natural seawater under the cleanest possible conditions, isolated from anthropogenic and terrestrial influences. An advantage of their large size, wave channels allow for many analytical instruments in the same location to sample both seawater properties and gases and aerosols in the headspace. These large-scale experiments have discovered numerous processes that govern and contribute to the transfer of molecules from the ocean to the atmosphere.[2,23]

Despite serving as the "gold standard" for ocean–atmosphere experiments, drawbacks of the use of wave channels are the size and cost, which limit widespread usage. This has been addressed by the development of smaller SSA generation devices that produce realistic bubble and aerosol size distributions without requiring the use of a full-sized wave channel. The Marine Aerosol Reference Tank (MART) is a CAICE-developed 210 L acrylic tank that generates an intermittent plunging sheet of water to produce a bubble plume that replicates the size distribution and has a temporal evolution similar to bubble plumes measured in the ocean and in wave tanks (Figure 2B).[24] These bubbles rupture at the water surface, producing SSA closely matching the size distribution produced by breaking waves in wave channels and the natural environment (Figure 2D). The enclosed MART headspace, containing both aerosols and gases, can then be sampled by various offline and online methods at particle concentrations (~500 particles/cm^3) needed for most measurement techniques. Replication of the proper SSA size distribution has been a crucial advancement in answering questions such as the impact of changing biology on SSA flux and hygroscopicity.[25] Other questions, difficult to study in the field, such as the influence of seawater temperature on SSA production, have also been investigated using the MART.[26] Natural or artificial seawater added to the MART can be biologically stimulated through nutrient and culture additions to grow a representative range of natural marine microorganisms. The versatility of the MART as an accurate SSA production device makes it useful for investigations of not only the influences of ocean biology but the physiochemical properties of aerosols as well.[27−29] The MART has been widely adopted as the *de facto* method for generating realistic SSA size distributions and has been utilized by researchers outside of CAICE for studies on physical production mechanisms,[30] health effects,[31,32] and ship-based measurements of marine aerosols.[33]

An undesirable side effect of the centrifugal pump currently used in the MART is the potential to physically damage the marine microorganisms via pump shear, which distorts the biological communities toward the most hardy species.[27] To facilitate smaller scale experiments and preserve fragile microorganisms, a smaller MART that uses a gentler plunging mechanism was developed. The miniMART features a 19 L acrylic tank where a small plunging waterfall is generated through the action of a water wheel (Figure 2C).[34] Similarly, bubble plumes and short-lived foams are generated that produce bubble size distributions and sea spray aerosol closely matching the size distribution found in the natural ocean. Through the miniMART, multiple findings regarding the behavior of surface partitioned organics, marine enzymes, and ice nuclei have been obtained.[35] The wave channel, MART, and miniMART represent the ability to perform ocean−atmosphere experiments across 4 orders of magnitude of water volume, giving massive flexibility toward the design of experiments that vary in scale, expense, and complexity. Trade-offs in constraints involving the air flow, number of SSA produced, ease of cleaning, experimental footprint, transport of water, and other logistical factors must be considered. At the wave channel level, the operational environment and level of effort is similar to that of a field campaign, whereas the miniMART can be easily used to conduct smaller scale experiments by a single investigator in the laboratory.

■ BUILDING THE BIOLOGICAL COMPLEXITY OF OCEAN−ATMOSPHERE SIMULATIONS

The initial ocean−atmosphere experiments conducted in CAICE focused on accurately producing SSA in the laboratory, with regards to both size distributions and chemical complexity. This was accomplished initially using a wave channel to generate realistic SSA from natural seawater and later by the development of the MART and miniMART. Following the development of physical production methods, the next goal of CAICE was to understand how biological activity in the oceans modulates and controls the properties of SSA. To this end, a novel mesocosm experiment was conducted in the wave channel to simulate the biological and chemical complexity of the real ocean.[1] During this 5-day mesocosm, cultures of marine phytoplankton and bacteria were added to the seawater in the wave channel. The major findings of this study in 2011 were that biogenic organic species have profound impacts on the chemical composition and properties of SSA. However, as the cultures were added to the seawater sequentially, this experiment did not adequately simulate the full progression of a real oceanic phytoplankton bloom. The next major ocean−atmosphere experiment within CAICE was the Investigation into Marine Particle Chemistry and Transfer Science (IMPACTS) experiment in 2014. During this campaign, a phytoplankton bloom was induced in natural seawater by adding nutrients to the wave channel and measuring the evolution of SSA composition and properties over the full bloom life cycle. A major goal was to replicate the microbial loop, a process that occurs naturally in the oceans wherein marine phytoplankton, bacteria, and viruses interact dynamically over the course of a bloom cycle.[36]

During IMPACTS, marked differences were observed in SSA properties over two subsequent blooms, including the aerosol composition, organic speciation, and ice nucleating particle (INP) production, which has been attributed to differences in the phytoplankton and bacterial dynamics in the system.[2] Enzymes, specifically lipase, produced by marine microorganisms were found to transform the available pool of aqueous organic carbon to a more soluble state.[2] The effects of the microbial transformation of marine organic carbon were later observed in the composition of aerosols produced through wave breaking. Specifically, the fraction of aliphatic-rich SSA was observed to be enhanced during periods of high phytoplankton productivity and low bacterial activity. This trend was found to be reversed in cases where phytoplankton activity was high with commensurately high bacterial activity. This discovery stimulated further research into the role of lipase as an effector of aerosol composition inside individual droplets, uncovering a new mechanism for the transformation of organic compounds after aerosolization.[37] These results together advance an important narrative that the competition between phytoplankton production and bacterial degradation exerts control over the composition of marine aerosols, which contrasts with attempts to predict aerosol composition using chlorophyll-a (chl-a) alone.[38,39]

Beyond their influence on the array of organic matter, the diversity of marine bacteria and viruses aerosolized from IMPACTS seawater was characterized using state-of-the-art sequencing approaches.[40] This research uncovered new information about specific microorganisms that are preferentially transferred from seawater to aerosols, while also connecting the physiochemical structure of the microorganisms to their efficiency of aerosolization. Aerosolized taxa also included notable species of infectious concern such as *Legionella*, *E. coli*, *Corynebacterium*, and *Mycobacterium*. The implications of taxon-specific aerosolization from marine environments are multifold, where ice nucleation efficiency of different marine organisms can influence cloud formation and certain taxa may have significant impacts on human health. These findings highlight how biological complexity in the oceans affects marine aerosol composition and atmospheric chemistry.

Further experiments simulating the influence of biological complexity on SSA properties have been conducted using MARTs. The Biological Effects on Air−Sea Transfer (BEAST) experiment investigated the influence of marine bacteria and viruses on SSA composition and organosulfur gas production. Results from BEAST have provided insight on the bacterial turnover of marine saccharides and their transfer to the aerosol phase.[41] In the same experiment, the production of non-dimethyl sulfide organosulfur gases, methanethiol, and dimethyl disulfide was found to be significantly enhanced, with flux ratios of (MeSH + DMDS/DMS) that ranged from 0.2 to 35, significantly higher than those observed in field studies.[42] The unexpected production of these reactive gases was connected to both the turnover in bacterial assemblages and possible changes in metabolic pathways influencing the transformation of these dissolved gases. These findings have further reinforced the importance of accounting for the community structure and activity of marine microorganisms.

PROBING THE CHEMICAL COMPLEXITY OF SEA SPRAY AEROSOL

The ability to produce realistic SSA in the laboratory from natural seawater across a wide range of biological conditions, with no contamination from terrestrial gases and aerosols, has greatly expanded our understanding of the chemical complexity of SSA. Studies have investigated the chemical composition of freshly emitted SSA, including morphology and structure, individual particle mixing state, and reactivity with atmospheric trace gases. Early results from wave channel experiments indicated that SSA is an external mixture, made up of four distinct particle types including sea salt, mixed sea salt/organic, organic, and biological particles. In a landmark study on the composition of SSA, the presence of whole bacteria, viruses, phytoplankton, and marine vesicles was discovered using cryo-electron microscopy performed on MART and wave channel generated aerosols.[43] The molecular diversity of SSA has also been shown to be sensitive to biological activity and vary over time in response to the dynamics of phytoplankton and heterotrophic bacteria in seawater.[23]

Results from laboratory ocean–atmosphere experiments within CAICE have shown that nascent SSA is enriched with organic compounds relative to both bulk seawater and the sea surface microlayer (SSML). For example, saccharides were observed to be enriched in sub-micrometer SSA from 14- to 1314-fold relative to seawater.[44] Analysis of SSA by high resolution mass spectrometry has shown that the molecular composition of nascent SSA is size dependent and that organic surfactants such as fatty acids are selectively transferred to smaller particles.[45] Further studies have shown that the size-selective transfer of organic material from seawater to the aerosol phase is largely driven by the mechanics of bubble bursting. Briefly, the bursting of the bubble cap produces film drops, which are enriched with hydrophobic materials that partition to the air–water interface, while jet drops are produced by the collapse of the bubble cavity. These two different SSA production mechanisms result in an externally mixed aerosol population, with two distinct chemical compositions.[1] While it was previously believed that film drops contributed primarily to the sub-micrometer aerosol and jet drops contributed to the super-micrometer mode, CAICE experiments have shown that jet drops can produce up to 43% of sub-micrometer SSA.[46]

The mixing state and chemical complexity of SSA have been shown to have a significant influence over heterogeneous reactions with atmospheric trace gases. These findings have significant implications for atmospheric chemistry and climate models, as many currently approximate the properties of SSA as those of pure NaCl. The reactions of SSA with reactive nitrogen species (i.e., N_2O_5, HNO_3) have been of particular interest, given their impact on the global NO_x budget. CAICE laboratory studies of the reaction between individual nascent SSA particles and nitric acid have shown a wide range of behavior, from no reaction to complete reaction, due to both particle type and heterogeneity within individual particles.[47] The analysis of individual SSA particles using transmission electron microscopy (TEM) has shown that particles undergo ion redistribution after reaction with nitric acid, which indicates that particle structure plays an important role in controlling heterogeneous reactivity.[28]

In addition, studies on the reactive uptake of N_2O_5 by laboratory-generated SSA have also been conducted within CAICE.[29] These experiments used a MART to generate SSA from both natural ocean water and artificial seawater, which was sequentially doped with molecular mimics of seawater organics, and found that organic films do not impede the reactive uptake of N_2O_5 at high relative humidity. Studies on the uptake N_2O_5 at the air–sea interface have found that aromatic compounds (i.e., phenol and humic acid) present at an air–liquid interface can suppress the yield of $ClNO_2$ by acting as competitive reactants with chloride.[48] Notably, the usage of low-complexity seawater mimics failed to reproduce the uptake properties observed both in the field and with MART generated aerosols, showing the need for experiments that maintain the high complexity of the marine environment. These results highlight the utility of ocean–atmosphere simulators, which can be used to generate model SSA containing selected compounds in order to simplify and understand the specific variables that contribute to the full complexity of the real environment.

CLIMATE-RELEVANT PROPERTIES OF MARINE AEROSOLS

Aerosol–cloud interactions are the largest source of uncertainty in our understanding of the climate system.[49] The oceans have been identified as a major source of ice nucleating particles (INPs); however, terrestrial contributions from dust and other sources dominate in regions where there is long-range transport of these aerosols, including over the oceans.[50,51] Marine INPs are now known, partially due to findings by CAICE, to be excellent ice nucleators; however the rarity of marine INPs (about 5 in 10^5 particles at −30 °C) makes understanding their composition very difficult.[4] In order to study marine INPs, measurements must be conducted in extremely remote sampling locations. By isolating ocean from terrestrial influences in the laboratory, it was possible to definitively identify and measure the properties of INPs emitted from the oceans.[4,52] The usage of more representative SSA production techniques like the MART and wave channel have shown that the production method is important to INP release.[4] Further studies on marine INPs have focused on developing a molecular-level understanding of the sources of these particles and how they are influenced by the activity of different marine microorganisms such as phytoplankton and bacteria.[53,54]

Laboratory ocean–atmosphere experiments have lent clarity to the debate over what drives the correlations between cloud droplet number and seawater chlorophyll-a concentrations observed in remote sensing studies.[55] It was hypothesized that biological activity in seawater could either affect the CCN activity and production flux of SSA, or it could result in increased SMA formation. Research within CAICE has shown that biological activity in seawater has a weak effect on the CCN activity of freshly emitted SSA and that the observed changes cannot account for the observed influence on cloud properties.[56] Using a miniMART, Forestieri and co-workers observed a strong relationship between SSA production and water temperature for artificial seawater, which is consistent with parametrizations in the literature.[26] However, for natural seawater, they observed seemingly random, irreproducible variability in SSA production, which evolved over the course of several days. This variability was attributed to temporal changes in the water composition, possibly related to organic or biological components of the natural seawater not present in the artificial mimics. While some conflicting data regarding SSA flux has been reported,[26,57−59] recently Bates and co-workers utilized a MART deployed during a ship-based study in the North Atlantic and concluded that variability in the flux of SSA was not linked to the activity of marine phytoplankton.[33] In summary, influence of biological activity on SSA flux, and by extension CCN concentrations, remains highly uncertain.

Further experiments within CAICE have shown that the changes in SSA flux and hygroscopicity during a phytoplankton bloom cycle cannot explain the observed correlations between chl-a and cloud properties. During four subsequent phytoplankton bloom cycles, we found a weakly negative correlation between the flux of SSA from a MART (as evidenced by the integrated number concentrations) and the seawater chl-a concentrations, a proxy for biological activity (Figure 3a). In addition, the shape of the size distribution remained relatively constant throughout the experiments (Figure S1). While some variability is observed in the production of SSA during these experiments, it does not appear to be driven by phytoplankton alone. In addition, no correlation was observed between chl-a and the apparent hygroscopicity parameter, which remained relatively unchanged over the course of all four bloom cycles ($\kappa_{app} = 1.02 \pm 0.04$, Figure 3b). In summary, while there appears to be some degree of natural variability in both the flux and hygroscopicity of SSA, ocean−atmosphere experiments using MARTs have conclusively shown that this variability is not directly related to marine phytoplankton concentrations, as indicated by the chl-a concentrations. The relative insensitivity of SSA flux and hygroscopicity to biological activity suggests that the observed correlations between cloud properties and phytoplankton blooms is driven by secondary aerosol formation, either through the formation of new SMA particles or the condensation of secondary species onto existing particles, thus increasing their size and ability to act as CCN.

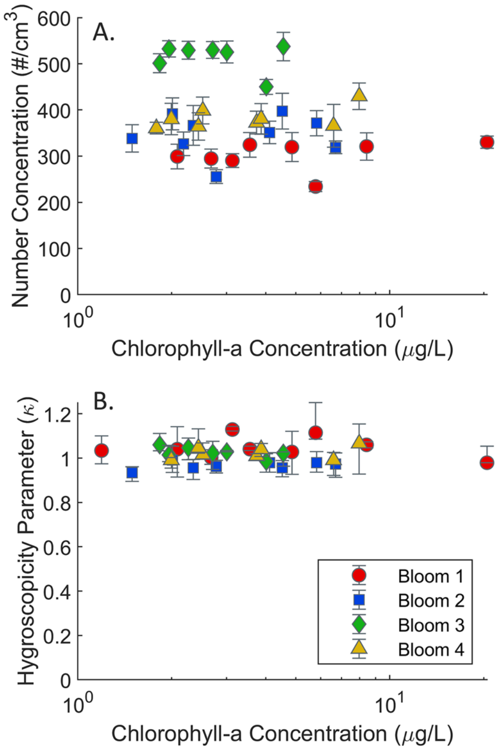

Figure 3. (a) Number concentrations of MART-generated SSA versus seawater chl-a concentrations during four phytoplankton bloom experiments. As the air flow rate through the MART headspace is kept constant, the number concentration is directly proportional to the flux of SSA. (b) Apparent hygroscopicity parameters (k_{app}) of MART-generated SSA during the four phytoplankton bloom experiments. These results show the relative insensitivity of both SSA flux and CCN activity with regards to biological activity in seawater, as represented by the chl-a concentrations. Detailed methods and experimental details are reported in the Supporting Information, as well as the daily data (Figure S2 and S4), aerosol size distributions (Figure S1), and CCN activation curves (Figure S4).

■ BEYOND PRIMARY SSA: MARINE GAS EMISSIONS AND ATMOSPHERIC REACTIONS

CAICE ocean−atmosphere experiments have, in the past, primarily focused on the factors controlling the properties of freshly emitted SSA; however, in the real marine atmosphere, SSA particles are transformed by aging processes, such as photochemistry, oxidation, and reactions with trace gases. Understanding how the composition and properties of SSA transform over hours, days, or even weeks of atmospheric processing is critical for accurately representing them within climate models. In addition, the oceans are a source of volatile organic compounds (VOCs), which may lead to the formation of secondary marine aerosol. While a great deal of attention has been paid to the formation of sulfate aerosols from dimethyl sulfide oxidation, the role of other reactive trace gases that may contribute to secondary aerosol formation in the marine atmosphere have not been fully explored. Currently, a major research focus within CAICE is determining the biotic and abiotic factors that control the production of marine VOCs, as well as the properties and composition of secondary aerosols formed from their oxidation and their potential impacts on cloud properties and climate.

Future steps toward replicating the real marine atmosphere in the laboratory have been the incorporation of oxidation and atmospheric aging processes. To accomplish this, Potential Aerosol Mass Oxidative Flow Reactors (PAM-OFRs) have been coupled with both MARTs and the wave channel to generate secondary marine aerosol and simulate the aging of primary SSA. The PAM-OFR system has been described elsewhere.[60,61] Briefly, the OFR uses UV lamps (λ = 185 and 254 nm) to generate high concentrations of OH radical, which react with the sampled air as it flows through the reactor. This results in the formation of new particles, as well as the oxidation of primary aerosols. In contrast to environmental chambers, the short residence time (~100−300 s) allows for the near real-time measurements of secondary aerosol formation and aged SSA on a dynamic system such as a phytoplankton bloom, which can evolve and change rapidly. Previously, the PAM-OFR has been primarily used to study terrestrial and anthropogenic systems;[62] however, results from CAICE have shown the utility of this technique for the study of marine systems.[63,64] The adoption of OFRs for marine aerosol research has pushed the boundaries of ocean-in-the-laboratory experiments and allowed us to further

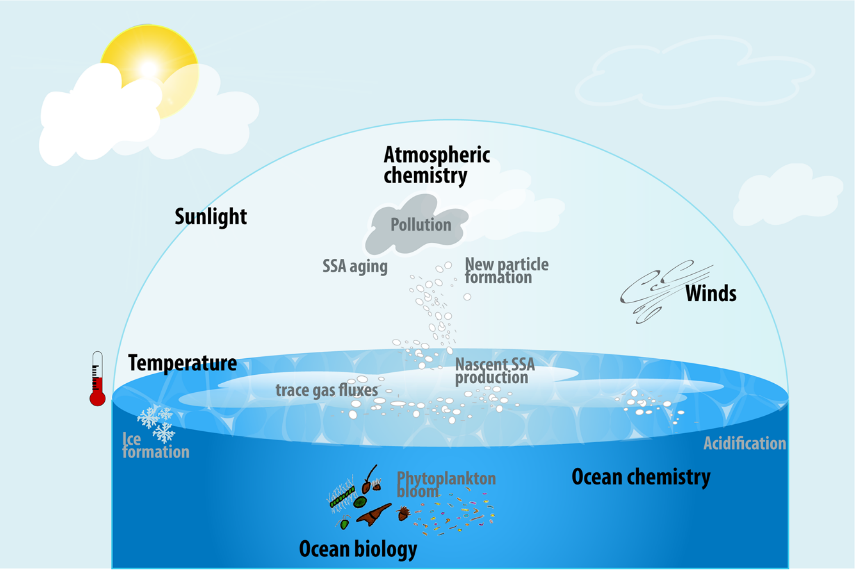

Figure 4. Representation of the Scripps Ocean Atmosphere Research Simulator (SOARS), which enables simulation of biotic, as well as physical and nonbiotic chemical, processes of the marine environment within the laboratory. The facility will provide the possibility to modulate the light intensity (through artificial lights and natural lights), temperature of the atmosphere and water (with the ability to form sea-ice), wind and waves, ocean biology (e.g., inducing a phytoplankton bloom, manipulating bacterial and viral populations), ocean chemistry (e.g., ocean acidification), and the atmospheric composition through aging of sea spray aerosol and trace gases in the smog chamber.

probe the links between biological activity in the ocean and atmospheric chemistry.

As CAICE research has shown that the controlling influence of biological activity on marine aerosol formation involves secondary processes, new ways to understand the production of marine gases have become essential. A particular advantage of ocean–atmosphere experiments is the lack of solar flux and oxidants, which can break down volatile gases very quickly. For example, during BEAST, the lack of these factors in the MART allowed for effective measurement of methanethiol and dimethyl disulfide, gaseous species that have high absorption and $^{\bullet}$OH reactive cross sections that keep their steady state concentrations low in the natural environment. Future CAICE ocean–atmosphere experiments will continue to take advantage of this property to better understand the production of labile volatile species far more difficult to observe in the natural environment. Additionally, community structure, stress, solar irradiation, signaling, grazing, nutrient availability, and other factors are relevant and important to the production of gases by microorganisms in the marine environment.[65,66] The role of bacteria in the formation of marine alkyl nitrate production was a significant CAICE finding enabled by the usage of ocean–atmosphere analogs.[67] By eliminating solar flux, this production was narrowed down to the marine organisms present, something not yet demonstrated in field studies. The role of metabolic partitioning along multiple pathways that lead to the production of marine gases, especially organosulfur species, is a central focus of CAICE, as the production of these gases in the marine environment is both highly variable and poorly understood.[68] Building a comprehensive list of marine VOCs and their relative fluxes at different biological states is a key CAICE focus that is currently under investigation. Furthermore, given the vast wealth of biological speciation data obtained during large mesocosm experiments, connecting the production of marine gases to specific biological actors is a new research area within CAICE.

■ OUTLOOK

Over the past decade, CAICE studies of isolated ocean–atmosphere interactions have greatly expanded our understanding of marine aerosols and their complex chemical properties. These experiments bridge the gap between field observations and traditional laboratory studies by building up real-world complexity under controlled conditions. New directions in marine aerosol research have been opened by findings using the unique ocean–atmosphere in the laboratory approach, including investigations into enzyme-aerosol activity, formation of unique vesicle macrostructures, heterogeneous reactions, and detection of previously under-appreciated reactive biogenic gas phase species.[28,37,43,67]

The Sea Spray Chemistry and Particle Evolution (SeaSCAPE) campaign was the most recent CAICE study conducted using a wave channel. This campaign focused on simulating atmospheric oxidation processes on both SSA and gases emitted from seawater during a phytoplankton bloom cycle. In addition to the oxidation experiments, comprehensive measurements were made of nascent SSA. Briefly, these measurements include aerosol chemical composition, size distributions, phase and morphology, hygroscopicity, IN activity, and trace gas speciation. The SeaSCAPE campaign will directly measure how rapid atmospheric processing transforms the properties of marine aerosols, enabled by laboratory ocean–atmosphere experiments. While significant progress has been made, critical gaps remain in our ability to fully simulate the marine environment, such as capturing the full temporal scale of oxidation and aging processes. These challenges must be addressed by modeling and the development of new innovative experimental proxies.

Future ocean–atmosphere experiments in CAICE will take the next step and center around the development of the Scripps Ocean Atmosphere Research Simulator (SOARS), shown in Figure 4. Once completed (planned by summer 2021), this first-of-its-kind facility will enable unique multidisciplinary experiments simulating a wide range of biological, physical, and chemical factors which influence the marine atmosphere. As a fully temperature-controlled wind-wave channel, SOARS will provide control of waves, windspeed (up to gale force winds), diurnal light cycling, and both water and air temperature (from polar to tropical conditions). An integrated environmental reaction chamber will allow for the simulation of atmospheric oxidation and aging of particles and gases under both pristine and polluted conditions. The ability to simulate these different physical and chemical processes under controlled conditions in the laboratory will allow for experiments that simulate the full complexity of the real marine environment. Experiments using the SOARS facility will explore the full extent of biological influence on marine aerosol production and properties under past and future climate scenarios. In addition, this facility will allow for studies of how anthropogenic air and water pollution, climate change, and ocean acidification affect ocean biology and the marine atmosphere.

It is critical to develop tools for improving our understanding of the impacts of natural ecosystems as the Earth undergoes unprecedented change. Over the past decade, CAICE has developed unique infrastructure and positioned itself at the forefront in innovating a range of ocean−atmosphere experimental systems and analytical methods to directly unravel the impacts of humans and natural emissions on the marine atmosphere.

FUTURE RESEARCH CHALLENGES AND PRIORITIES

- Integrative approach: Use CAICE lab observations to explain field study results.
- Understanding how a changing ocean microbiome will lead to changes in atmospheric composition and climate.
- Addressing how future changes in ocean temperatures and climate will impact ocean biology emissions and in turn atmospheric composition and climate.
- Using CAICE findings to improve air quality and climate model predictions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.accounts.0c00504.

Methods and experimental details for bloom experiments, SSA size distributions, CCN activation curves, and time series of SSA number concentrations and hygroscopicity parameters. (PDF)

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Notes

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ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation through the Center for Aerosol Impacts on the Chemistry of the Environment, an NSF Center for Chemical Innovation (CHE-1801971).

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