Title

Sea Spray Aerosol: Where Marine Biology Meets Atmospheric Chemistry

Permalink

https://escholarship.org/uc/item/38z0m30w

Journal

ACS Central Science, 4(12)

ISSN

2374-7943

Authors

Schiffer, Jamie M
Mael, Liora E
Prather, Kimberly A
et al.

Publication Date

2018-12-26

DOI

10.1021/acscentsci.8b00674

Peer reviewed

Sea Spray Aerosol: Where Marine Biology Meets Atmospheric Chemistry

Jamie M. Schiffer,[†] Liora E. Mael,[†] Kimberly A. Prather,*,[†,‡] Rommie E. Amaro,*,[†]
and Vicki H. Grassian*,[†,‡,§]

[†]Department of Chemistry and Biochemistry and [§]Department of Nanoengineering, University of California, San Diego, 9500
Gilman Drive, La Jolla, California 92093-0378, United States
[‡]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093, United States

ABSTRACT: Atmospheric aerosols have long been known to alter climate by
scattering incoming solar radiation and acting as seeds for cloud formation. These
processes have vast implications for controlling the chemistry of our environment and
the Earth's climate. Sea spray aerosol (SSA) is emitted over nearly three-quarters of
our planet, yet precisely how SSA impacts Earth's radiation budget remains highly
uncertain. Over the past several decades, studies have shown that SSA particles are far
more complex than just sea salt. Ocean biological and physical processes produce
individual SSA particles containing a diverse array of biological species including
proteins, enzymes, bacteria, and viruses and a diverse array of organic compounds
including fatty acids and sugars. Thus, a new frontier of research is emerging at the
nexus of chemistry, biology, and atmospheric science. In this Outlook article, we
discuss how current and future aerosol chemistry research demands a tight coupling
between experimental (observational and laboratory studies) and computational
(simulation-based) methods. This integration of approaches will enable the systematic
interrogation of the complexity within individual SSA particles at a level that will enable prediction of the physicochemical
properties of real-world SSA, ultimately illuminating the detailed mechanisms of how the constituents within individual SSA
impact climate.
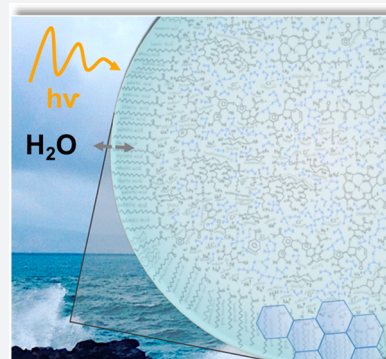
INTRODUCTION

The ocean represents one of the most abundant sources of
natural aerosols, termed sea spray aerosol (SSA).[1−4] SSA is
produced at the ocean surface and can be lofted into the upper
troposphere, where they contribute to the global radiation
budget. The scattering of solar radiation is one impact that
aerosols have on climate through aerosol−radiation inter-
actions, also known as the aerosol direct effect.[5] More
uncertainty relates to aerosol aerosol−cloud interactions, also
known as indirect effects, which include processes such as the
seeding of clouds.[5]

This Outlook first discusses the importance of defining how
the chemical and biological components of individual particles
within SSA guides the formation of clouds. We then explore
how the components within individual SSA particles are
controlled by marine biology and how this can be studied in
the laboratory. We end with a view toward the future of this
nexus of chemistry, biology, and atmospheric science, where
the integration of computational and experimental techniques
is poised to identify and characterize the molecules driving
climate-relevant properties within individual particles. We
propose that fully integrated computational and experimental
simulated models, coupled with big data analytics, will lead to a
greater understanding of sea spray aerosol effects on climate
and the environment.

MARINE BIOLOGY CONTROLS THE CHEMICAL COMPOSITION AND IMPACTS OF SEA SPRAY AEROSOL

SSA particles impact climate through the formation of cloud
condensation nuclei (CCN) and ice nuclei (IN), respectively.[6]
CCN are particles upon which water vapor condenses and
subsequently forms cloud droplets.[7−10] The hygroscopicity, or
ability of an individual particle to take up water and eventually
become a cloud droplet, is a function of particle size[7] and
composition which varies widely among individual particles
within the SSA population.[8] Particle size and composition are
in turn functions of biologically induced changes in the
seawater chemistry. Recent findings using atomic-force
microscopy (AFM) revealed that ensemble-average particle
growth factors decrease over a phytoplankton bloom, and then
increase again after the bloom.[11] This trend was attributed to
increases in surface-active species, such as long-chain fatty
acids and polysaccharides, which exhibit decreased hygro-
scopicity compared to free saccharides. SSA particles have
recently also been identified as a unique source of ice
nucleating particles; increase in IN activity after the peak of
a phytoplankton bloom demonstrates the impact of ocean
biology on ice nucleation in SSA.[12,13] Given that over half of

the Earth's surface is covered by ocean, the formation of IN, as well as CCN, from nascent SSA is an important area of ongoing investigation, and yet represents a large uncertainty in climate models.

> Recent findings using atomic-force microscopy (AFM) revealed that ensemble-average particle growth factors decrease over a phytoplankton bloom, and then increase again after the bloom

Beyond Sea Salt. The uncertainties associated with the formation of CCN and IN from SSA have in part stemmed from the incomplete modeling of SSA as a simple mixture of salts with water (Figure 1). Particle growth factors for nascent
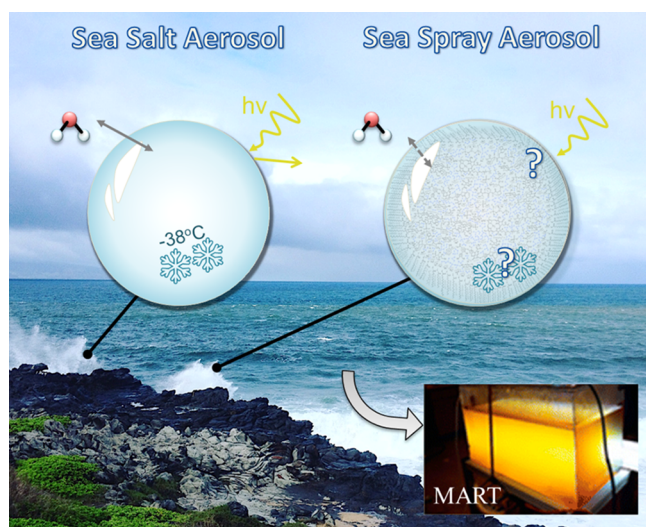
Figure 1. Hygroscopicity and ice nucleation of pure sea salt aerosols differs from that of sea spray aerosols, which affects how these aerosols seed clouds. To study the full complexity of nascent sea spray aerosols requires the bringing the ocean into the laboratory with the application of, for example, Marine Aerosol Reference Tanks (MARTs).

SSA deviate from pure salt particles,[14,15] a clear indication that SSA is composed of more than just sea salt. Results from laboratory studies demonstrate substantial particle-to-particle variability[16,17] and high organic composition.[17–19] The complexity of SSA is a function of the diversity of species from where SSA is derived, i.e., the ocean surface or the so-called sea surface microlayer (SSML).[20] The SSML even has its own microbiome.[21] Phytoplankton residing in the SSML contain mixtures of microscopic plants and photosynthetic cyanobacteria, and represent a food source for marine bacteria.[22] Microbial degradation of phytoplankton produces dissolved organic carbon consisting of refractory molecules that persist in the ocean for millennia, but when introduced to environmental conditions including solar radiation (Figure 1) can be removed from the ocean within 1.5 years.[23] Viruses as well as abiotic mechanisms also contribute to the production of organic carbon within the ocean by breaking down marine bacteria to release dissolved organic carbon.[24] Viruses are the last stage of the microbial loop,[25] with decline of viruses giving

way to the regrowth of phytoplankton, a process that is known to change the chemical makeup of ocean surfaces.[22,25,26] Poorly understood factors involved in the physical production of SSA coupled with these complex biological processes at ocean surfaces guide SSA's chemistry and impact on the environment in ways we are just beginning to uncover.

> Poorly understood factors involved in the physical production of SSA coupled with these complex biological processes at ocean surfaces guide SSA's chemistry and impact on the environment in ways we are just beginning to uncover

■ METHODS FOR STUDYING SSA CHEMISTRY AND SSA PROPERTIES

Bringing the Ocean-Atmosphere into the Laboratory. While field studies have measured the composition,[27] marine hygroscopicity,[15] and ice nucleating[28] ability of particles over the open ocean, it has become difficult to discern the sources of marine particles. Given that aerosol particles can be transported long distances in the atmosphere (including from Beijing to the continental U.S.),[29] particles measured in field studies can originate from an array of different sources.[30] Thus, in order to understand the impacts of SSA on our environment, the physical, biological, and chemical factors controlling the physiochemical complexity of SSA need to be isolated and studied under controlled conditions only possible in a laboratory setting. With the goal of recreating the chemical complexity of real world marine aerosols in the laboratory, mesocosm experiments probe how the microbial loop at the ocean surface effects the climate-relevant properties of SSA.[19,31]

On the small scale, Marine Aerosol Reference Tanks (MARTs)[32] are portable systems that have been specifically designed to mimic the same physical production mechanisms for SSA particles (Figure 1) and protocols have been developed for growing phytoplankton blooms to induce the same biochemical patterns present at ocean surfaces.[7,8,11,33–35] By being able to isolate SSA particles, they can be studied using an array of methods, revealing key insights into the transfer of fluorescent biological species from the ocean to the atmosphere,[31] uncovering the oxygen-to-carbon ratios as well as IN freezing temperatures within particles of different size regimes,[36] and even illuminating novel biological structures present in SSA from cryotransmission electron microscopy images.[37]
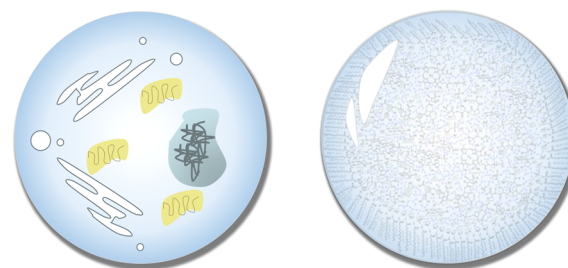
On a larger scale, mesocosm experiments conducted in a 3400 gallon channel waveflume containing natural seawater undergoing a phytoplankton bloom have provided a resource for measuring more representative real-world SSA.[12,13,36] Particle size distributions created by this wave channel match real world size and chemical distributions and are thus able to provide novel insight into the cloud-forming properties of these SSA.[38] Measurement of CCN during the phytoplankton bloom experiments revealed that the hygroscopicity of the SSA was lowest when heterotrophic bacteria levels were greatest.[38]

Additionally, measurements of IN during the phytoplankton bloom were consistent with ice nucleating particle (INP) measurements over the open ocean.[12] Increases in INPs active between −25 °C and −15 °C lagged behind the chlorophyll A peak of the phytoplankton bloom, but were in tandem with increases in heterotrophic bacteria activity.[13]

Molecular Model Systems. With the many different types of molecules now identified in the mesocosm experiments, arrays of SSA particles can be created wherein the complexity of modeled substituents can be carefully tuned, enabling a systematic interrogation of the effects of particular components on SSA properties. Key molecules elucidated from mesocosm experiments include dissolved organic carbon (DOC), particulate organic carbon (POC), and surface active molecules.[38] Experimentally, DOC species are separated from POC species using a 0.45 μm filter.[22] Thus, POC, which includes extracellular polymeric substances (EPS)[39] and cell debris, are much larger in size than DOC. These POC species are also most concentrated in the supermicrometer SSA particle sizes.[36] DOC species, including simple sugars, humic acids, and amino acids, are oxygen containing organics, and are most concentrated in the supermicrometer SSA particle sizes.[19,24,36] The surface active molecules measured within SSA include fatty acids, lipopolysaccharides, and amphiphillic proteins such as lipase,[40] and are most concentrated in the submicrometer SSA particles.[19,41−46]

Chemical Complexity. What becomes clear almost immediately from the above review of the molecular and biological species involved is how complex the chemical makeup is within SSA and at these particles' surfaces. In fact, the complexity within SSA mirrors, in many ways, the complexity within our own cells (Figure 2). Just as the shape of a cell is defined by the formation of a membrane of lipids and other amphiphillic macromolecules, so too do SSA have a surface composed of lipids and amphiphilic macromolecules. Other similarities between cells and SSA include the presence of internal vacuoles or lipid vesicles[37] and the guidance of pH and salt concentration on chemical reaction pathways within cells and, most likely, also within SSA. Given the similarities between cells and SSA, computational and experimental methods that have been applied to the study of cells and molecules within cells are now poised to provide new insights into the chemistry within SSA. Among these methods, measurements that are often performed on single cells can be used to understand single aerosol particles. These methods are likely to provide new insights into climate relevant properties of aerosols, especially in light of particle-to-particle variability and scarcity of INPs in our troposphere (e.g., only one in 10^6 aerosols are INPs).[47]

Single Particle Experimental Techniques. New single particle techniques (Figure 3) for probing the impact of chemical composition on SSA hygroscopicity, surface tension, and immersion ice nucleation can be used to build up single particle model systems of increasing complexity. Atomic force microscopy coupled with IR spectroscopy (AFM-IR)[11,48] are examples of tools for single particle measurements of size as a function of relative humidity and surface tension of deposited particles (Figure 3a). Recent findings with the continuous flow stream-wise thermal gradient chamber (CFSTGC)[33] have revealed significant reductions on the surface tension of model aerosols composed of NaCl coated by fatty acid mixtures,[33,49] and support literature that suggests surface partitioning of organic molecules can impact particle hygroscopicity.[50]
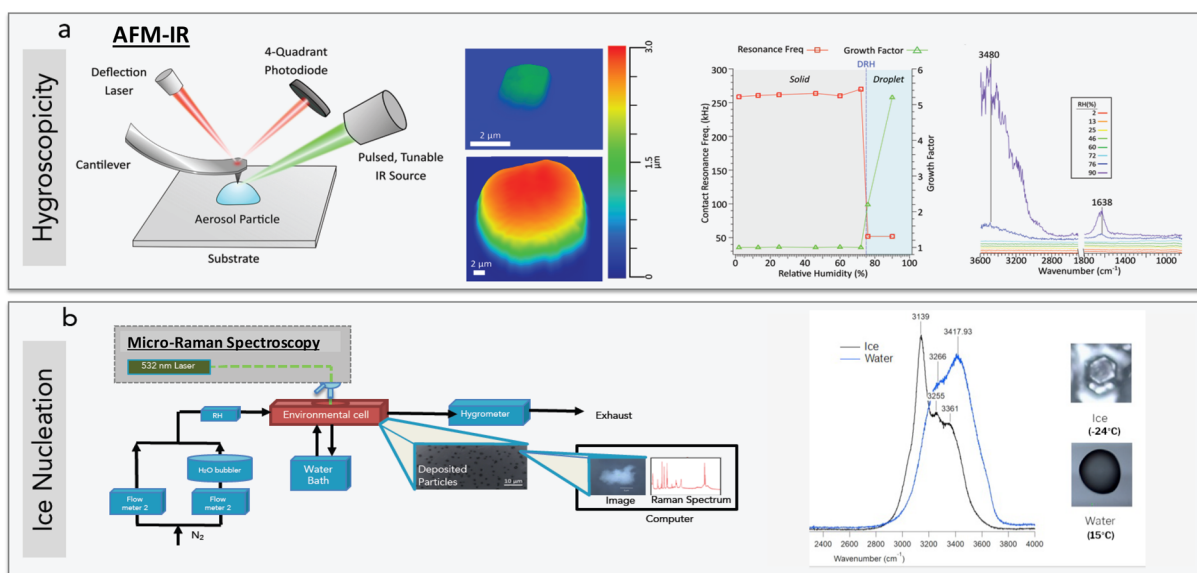

Cell	Sea Spray Aerosol
The presence of a **cell membrane** to protect the cell and act as a control for the passage of materials and shape of the cell. Proteins are bound to cell membrane to help with this process.	The presence of **fatty acids and other lipids that coat the surface**. Lipids can alter heterogeneous pathways into the cell, and are likely to interact with amphiphillic proteins like lipase which get out into SSA.
Formation of **lipid rafts** at the membrane surface effects the fluidity of the cell membrane.	Formation of **lipid islands** at the surface, and the absence of them, can tune SSA hygroscopicity.
Vacuoles and golgi bodies: coordinate transfer of materials inside and outside of the cell	The presence of **internal vesicles** (Patterson *et al* 2016): function unknown.
Mitochondria and Chloroplasts: the endosymbiotic hypothesis suggests that these organelles descend from prokaryotic cells.	The presence of **entire bacterial cells** within super micron SSA (Patterson *et al* 2016) transferred from sea surface microlayer
Slight changes in **pH and salt concentrations** can alter cellular function and also lead to functional responses like action potentials in neurons.	Large changes in **pH and salt** concentrations are expected as particles age and may alter enzymatic pathways and surface chemistry (Schiffer *et al*).

Figure 2. (Left column, top to bottom) The characteristics of a cell including the presence and structure of the outer membrane, presence of interior membranes, presence of bacterial derivatives, and the impacts of pH and salt on cellular chemistry. (Right column) The analogous traits found within sea spray aerosols.

For IN relevant measurements at the single particle level, new applications of experimental and computational methods to increasingly complex SSA model systems allow for a better understanding of the role of chemical complexity in ice nucleation (Figure 3). Pure water undergoes homogeneous freezing at 235 K. Different methods can use this as a baseline to compare the freezing of more complex chemical mixtures. For example, the cryogenic refrigerator applied to freezing test (CRAFT) system allows for the evaluation of deposited particles over a wide temperature range in supermicron-sized particles from 240 to 273 K.[51] Similarly, micro-Raman spectroscopy of individual particles has been coupled to an environmental cell to study water uptake and ice nucleation behavior from 225 to 245 K on the full range of model to complex systems from simple model sea-salt particles to particles collected directly from the ocean-atmosphere facility.[52]

Measurements from single-particle techniques now provide the necessary data to construct computational atomic-scale three-dimensional structural models of SSA, and subsequently probe their time-dependent phase and morphological changes with physics-based approaches, such as coarse-grained[53] and all-atom molecular dynamics simulations.[54] Already from computational chemistry research, atomic level simulations of surface active species like palmitic acid on salt subphase have elucidated the interplay between organic and inorganic fractions as they contribute to particle hygroscopic growth and reveal how water can promote the formation of fatty acid

Figure 3. Examples of some methods to study substrate-deposited particles for (a) water uptake and hygroscopic growth (see ref 48 for more details) and (b) ice nucleation of individual sea spray aerosol particles. The importance of these techniques is that they provide measurements of atmospheric processes (hygroscopicity, IN activity, etc.) with added chemical information from vibrational spectroscopy.

islands at particle surfaces.[55] All-atom molecular dynamics simulations of DOC, such as polysaccharides, reveal the role of hydrogen bonds in establishing the structures of these molecules that ultimately allow them to take up water in the aerosol form.[56] Most recently, all-atom molecular dynamics simulations of lipase at lipid surfaces have revealed how enzymes can disrupt and alter the structure and dynamics of the lipids at the air–water interface. While these studies have investigated the nature of specific model systems, future computational work will need to match the sharp increase in chemical complexity that has been observed experimentally in order to more rigorously characterize how these many different species contribute to the chemistry of SSAs.

> Already from computational chemistry research, atomic level simulations of surface active species like palmitic acid on salt subphase have elucidated the interplay between organic and inorganic fractions as they contribute to particle hygroscopic growth and reveal how water can promote the formation of fatty acid islands at particle surfaces

■ OUTLOOK

Toward Automation, Molecular Networks and Big Data in SSA Chemistry. Given the advances in single-particle SSA methods and the similarities between SSA and cells, new advances in SSA chemistry will likely stem from the increasing application of high-throughput, high resolution methods and big data, just as has been taking place in the cell biology community.[57] For example, single particle methods discussed

above can be combined with ultrahigh resolution mass spectrometry methods for identifying the molecular constituents that contribute to environmentally relevant signatures, such as high IN temperatures or distinct particle growth factors (Figure 4). Automated methods and microfluidic devices, long
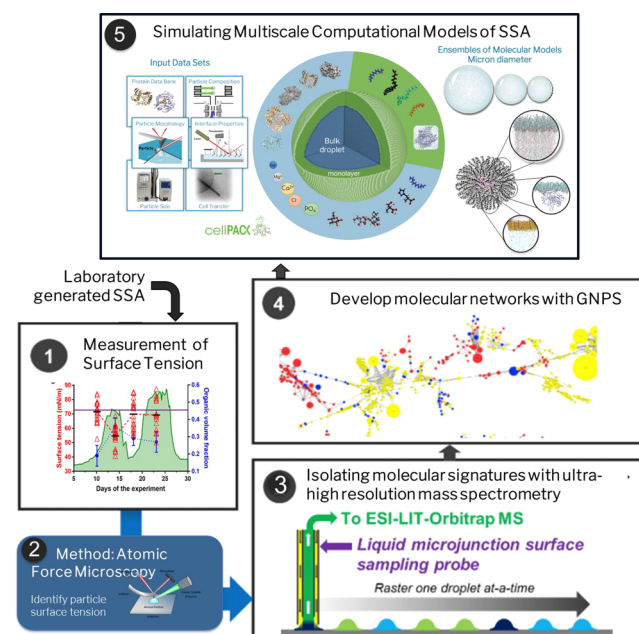
Figure 4. Futuristic workflow for connecting atomic-level mechanisms with environmentally relevant properties of SSA. Results from hygroscopic growth experiments[16] (1) can be coupled with (2) AFM-IR (or micro-Raman) measurements to understand single particle CCN and IN chemical characteristics, over the growth of a phytoplankton bloom. Single particle surface tension with AFM (or other methods to measure surface tension) can then be linked with (3) high resolution mass spectrometry to (4) construct molecular networks with GNPS and finally (5) use these molecular networks to construct atomic level molecular dynamics simulations of full aerosol particles.

used in the cell and systems biology communities, can be adapted for the study of phase behavior within single particles.[58] Measurements of molecular constituents and phase behavior can be organized within molecular networks, using tools like Global Natural Products Social (GNPS) molecular networking infrastructure,[59] to understand how chemistry guides the indirect effects of SSA, and thus define the impacts of ocean biology on our environment.

Multiscale Computational Models. Ostensibly, these molecular network data sets will provide sufficient input for the construction of atomic-level computational models of aerosol particles (Figure 4). The future of computational SSA research will borrow tools from cellular biology and biophysics, the same tools which have been used to uncover the atomic-level dynamics within entire virus particles (which, notably, are roughly the same size as the most chemically active SSA particles).[60−62] Molecular dynamics simulations can take an atomic-level model of SSA and step the atoms through time, illuminating the precise mechanisms by which molecules organize, interact with liquid water, and nucleate ice. Just as has been done in drug discovery fields, multiscale structure-based simulations can provide atomic level information about the drivers of structure−activity relationships as it relates to climate impacts that is currently not possible with experiment alone (Figure 4).[63,64]

CONCLUSIONS

While an integrated experimental and computational approach that connects climate-relevant properties of SSA with atomic and molecular-level structures may be on the horizon, a number of challenges must be overcome to achieve this end. Storing and mining of the large, diverse data sets currently being generated will involve translating methods already developed in the big data community to SSA.[65−67] Additionally, in order to address the complexity associated with particle-to-particle variability, reliable automation of the creation and investigation of complex SSA model systems in the lab will need to mirror the automated techniques that have been applied to the study of cells, and is in fact already under way.[54,64] Validation and application of computational chemistry force fields that simultaneously represent the correct surface tension of water,[65−67] capture the properties in high salinity environments,[51,68] and are compatible with state of the art force fields for sugar, proteins, and lipids will need to be tested.[69,70] Finally, direct comparisons between laboratory and computational findings with real world measurements will be key to further progress in this field, and likely require the development of even more rigorous laboratory systems capable of mimicking real world conditions, including the incorporation of atmospheric polutants and solar impacts.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: vhgrassian@ucsd.edu.
*E-mail: ramaro@ucsd.edu.
*E-mail: kprather@ucsd.edu.

ORCID
Liora E. Mael: 0000-0003-1073-9717
Rommie E. Amaro: 0000-0002-9275-9553
Vicki H. Grassian: 0000-0001-5052-0045

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Holmes, N. S. A Review of Particle Formation Events and Growth in the Atmosphere in the Various Environments and Discussion of Mechanistic Implications. *Atmos. Environ.* **2007**, *41*, 2183−2201.

(2) Satheesh, S. K.; Krishna Moorthy, K. Radiative Effects of Natural Aerosols: A Review. *Atmos. Environ.* **2005**, *39*, 2089−2110.

(3) Turpin, B. J.; Saxena, P.; Andrews, E. Measuring and Simulating Particulate Organics in the Atmosphere: Problems and Prospects. *Atmos. Environ.* **2000**, *34*, 2983−3013.

(4) Andreae, M. O.; Rosenfeld, D. Aerosol-Cloud-Precipitation Interactions. Part 1. The Nature and Sources of Cloud-Active Aerosols. *Earth-Sci. Rev.* **2008**, *89*, 13−41.

(5) Meyer, L.; Rajendra, K. P. IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change; PCC: Geneva, Switzerland; pp 1−151.

(6) Haywood, J.; Boucher, O. Estimates of the Direct and Indirect Radiative Forcing Due To Tropospheric Aerosols: A Review. *Rev. Geophys.* **2000**, *38*, 513−543.

(7) Laskina, O.; Morris, H. S.; Grandquist, J. R.; Qin, Z.; Stone, E. A.; Tivanski, A. V.; Grassian, V. H. Size Matters in the Water Uptake and Hygroscopic Growth of Atmospherically Relevant Multicomponent Aerosol Particles. *J. Phys. Chem. A* **2015**, *119*, 4489−4497.

(8) Schill, S. R.; Collins, D. B.; Lee, C.; Morris, H. S.; Novak, G. A.; Prather, K. A.; Quinn, P. K.; Sultana, C. M.; Tivanski, A. V.; Zimmermann, K.; Cappa, C. D.; Bertram, T. H. The Impact of Aerosol Particle Mixing State on the Hygroscopicity of Sea Spray Aerosol. *ACS Cent. Sci.* **2015**, *1* (3), 132−141.

(9) Grützun, V.; Knoth, O.; Simmel, M. Simulation of the Influence of Aerosol Particle Characteristics on Clouds and Precipitation with LM-SPECS: Model Description and First Results. *Atmos. Res.* **2008**, *90*, 233−242.

(10) Kaufman, Y. J.; Tanré, D.; Boucher, O. A Satellite View of Aerosols in the Climate System. *Nature* **2002**, *419*, 215−223.

(11) Estillore, A. D.; Morris, H. S.; Or, V. W.; Lee, H. D.; Alves, M. R.; Marciano, M. A.; Laskina, O.; Qin, Z.; Tivanski, A. V.; Grassian, V. H. Linking Hygroscopicity and the Surface Microstructure of Model Inorganic Salts, Simple and Complex Carbohydrates, and Authentic Sea Spray Aerosol Particles. *Phys. Chem. Chem. Phys.* **2017**, *19*, 21101−21111.

(12) DeMott, P. J.; Hill, T. C. J.; McCluskey, C. S.; Prather, K. A.; Collins, D. B.; Sullivan, R. C.; Ruppel, M. J.; Mason, R. H.; Irish, V. E.; Lee, T.; Hwang, C. Y.; Rhee, T. S.; Snider, J. R.; McMeeking, G. R.; Dhaniyala, S.; Lewis, E. R.; Wentzell, J. J. B.; Abbatt, J.; Lee, C.; Sultana, C. M.; Ault, A. P.; Axson, J. L.; Martinez, M. D.; Venero, I.; Santos-Figueroa, G.; Stokes, M. D.; Deane, G. B.; Mayol-Bracero, O. L.; Grassian, V. H.; Bertram, T. H.; Bertram, A. K.; Moffett, B. F.; Franc, G. D. Sea Spray Aerosol as a Unique Source of Ice Nucleating Particles. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 5797−5803.

(13) McCluskey, C. S.; Hill, T. C. J.; Malfatti, F.; Sultana, C. M.; Lee, C.; Santander, M. V.; Beall, C. M.; Moore, K. A.; Cornwell, G. C.; Collins, D. B.; Prather, K. A.; Jayarathne, T.; Stone, E. A.; Azam, F.; Kreidenweis, S. M.; DeMott, P. J. Dynamic Link between Ice Nucleating Particles Released in Nascent Sea Spray Aerosol and Oceanic Biological Activity during Two Mesocosm Experiments. *J. Atmos. Sci.* **2017**, *74*, 151−166.

(14) Bertram, T. H.; Cochran, R. E.; Grassian, V. H.; Stone, E. A. Sea Spray Aerosol Chemical Composition: Elemental and Molecular

Mimics for Laboratory Studies of Heterogeneous and Multiphase Reactions. *Chem. Soc. Rev.* **2018**, *47*, 2374−2400.

(15) Swietlicki, E.; Hansson, H. C.; Hämeri, K.; Svenningsson, B.; Massling, A.; Mcfiggans, G.; Mcmurry, P. H.; Petäjä, T.; Tunved, P.; Gysel, M.; Topping, D.; Weingartner, E.; Baltensperger, U.; Rissler, J.; Wiedensohler, A.; Kulmala, M. Hygroscopic Properties of Submicrometer Atmospheric Aerosol Particles Measured with H-TDMA Instruments in Various Environments - A Review. *Tellus, Ser. B* **2008**, *60* (3), 432−469.

(16) Sultana, C. M.; Collins, D. B.; Prather, K. A. Effect of Structural Heterogeneity in Chemical Composition on Online Single-Particle Mass Spectrometry Analysis of Sea Spray Aerosol Particles. *Environ. Sci. Technol.* **2017**, *51*, 3660−3668.

(17) Cochran, R. E.; Laskina, O.; Jayarathne, T.; Laskin, A.; Laskin, J.; Lin, P.; Sultana, C.; Lee, C.; Moore, K. A.; Cappa, C. D.; Bertram, T. H.; Prather, K. A.; Grassian, V. H.; Stone, E. A. Analysis of Organic Anionic Surfactants in Fine and Coarse Fractions of Freshly Emitted Sea Spray Aerosol. *Environ. Sci. Technol.* **2016**, *50*, 2477−2486.

(18) Tervahattu, H.; Hartonen, K.; Kerminen, V.; Kupiainen, K.; Aarnio, P.; Koskentalo, T.; Tuck, A.; Vaida, V. New Evidence of an Organic Layer on Marine Aerosols. *J. Geophys. Res.* **2002**, *107*, 1−8.

(19) Wang, X.; Sultana, C. M.; Trueblood, J. V.; Hill, T. C. J.; Malfatti, F.; Lee, C.; Laskina, O.; Moore, K. A.; Beall, C. M.; McCluskey, C. S.; Cornwell, G. C.; Zhou, Y.; Cox, J. L.; Pendergraft, M.; Santander, M. V.; Bertram, T. H.; Cappa, C. D.; Azam, F.; DeMott, P. J.; Grassian, V. H.; Prather, K. A. Microbial Control of Sea Spray Aerosol Composition: A Tale of Two Blooms. *ACS Cent. Sci.* **2015**, *3*, 124−131.

(20) Wurl, O.; Ekau, W.; Landing, W. M.; Zappa, C. J. Sea Surface Microlayer in a Changing Ocean − A Perspective. *Elem. Sci. Anthr.* **2017**, *5*, 31.

(21) Biteen, J. S.; Blainey, P. C.; Cardon, Z. G.; Chun, M.; Church, G. M.; Dorrestein, P. C.; Fraser, S. E.; Gilbert, J. A.; Jansson, J. K.; Knight, R.; Miller, J. F.; Ozcan, A.; Prather, K. A.; Quake, S. R.; Ruby, E. . T. D. Tools for the Microbiome: Nano and Beyond. *ACS Nano* **2016**, *10*, 6−37.

(22) Azam, F.; Malfatti, F. Microbial Structuring of Marine Ecosystems. *Nat. Rev. Microbiol.* **2007**, *5*, 782−791.

(23) Shen, Y.; Benner, R. Mixing It up in the Ocean Carbon Cycle and the Removal of Refractory Dissolved Organic Carbon. *Sci. Rep.* **2018**, *8*, 1−9.

(24) Blanchard, D. C. Jet Drop Enrichment of Bacteria, Virus, and Dissolved Organic Material. *Pure Appl. Geophys.* **1978**, *116*, 302−308.

(25) Pomeroy, L. R.; Williams, P. J.; Azam, F.; Hobbie, J. E. The Microbial Loop. *Oceanography* **2007**, *20*, 28−33.

(26) Allison, S. D. Cheaters, Diffusion and Nutrients Constrain Decomposition by Microbial Enzymes in Spatially Structured Environments. *Ecol. Lett.* **2005**, *8*, 626−635.

(27) Heintzenberg, J.; Covert, D. C.; Van Dingenen, R. Size Distribution and Chemical Composition of Marine Aerosols: A Compilation and Review. *Tellus, Ser. B* **2000**, *52*, 1104−1122.

(28) Huang, W. T. K.; Ickes, L.; Tegen, I.; Rinaldi, M.; Ceburnis, D.; Lohmann, U. Global Relevance of Marine Organic Aerosols as Ice Nucleating Particles. *Atmos. Chem. Phys.* **2018**, *18*, 11423−11445.

(29) Gu, X.; Bao, F.; Cheng, T.; Chen, H.; Wang, Y.; Guo, H. The Impacts of Regional Transport and Meteorological Factors on Aerosol Optical Depth over Beijing, 1980−2014. *Sci. Rep.* **2018**, *8*, 5113.

(30) Jaenicke, R. Chapter 1 Tropospheric Aerosols. In *Annual Cloud-Climate Interactions*; 1993; pp 1−31.

(31) Lee, C.; Sultana, C. M.; Collins, D. B.; Santander, M. V.; Axson, J. L.; Malfatti, F.; Cornwell, G. C.; Grandquist, J. R.; Deane, G. B.; Stokes, M. D.; Azam, F.; Grassian, V. H.; Prather, K. A. Advancing Model Systems for Fundamental Laboratory Studies of Sea Spray Aerosol Using the Microbial Loop. *J. Phys. Chem. A* **2015**, *119*, 8860−8870.

(32) Stokes, M. D.; Deane, G. B.; Prather, K.; Bertram, T. H.; Ruppel, M. J.; Ryder, O. S.; Brady, J. M.; Zhao, D. A Marine Aerosol Reference Tank System as a Breaking Wave Analogue for the Production of Foam and Sea-Spray Aerosols. *Atmos. Meas. Tech.* **2013**, *6*, 1085−1094.

(33) Forestieri, S. D.; Cornwell, G. C.; Helgestad, T. M.; Moore, K. A.; Lee, C.; Novak, G. A.; Sultana, C. M.; Wang, X.; Bertram, T. H.; Prather, K. A.; Cappa, C. D. Linking Variations in Sea Spray Aerosol Particle Hygroscopicity to Composition during Two Microcosm Experiments. *Atmos. Chem. Phys.* **2016**, *16*, 9003−9018.

(34) Kreidenweis, S. M.; Asa-Awuku, A. Aerosol Hygroscopicity: Particle Water Content and Its Role in Atmospheric Processes. In *Treatise on Geochemistry*, Holland, H. D.; Turekian, K. K., Eds.; Elsevier: Oxford, 2014; pp 331−361.

(35) Pham, D. Q.; O'Brien, R.; Fraund, M.; Bonanno, D.; Laskina, O.; Beall, C.; Moore, K. A.; Forestieri, S.; Wang, X.; Lee, C.; Sultana, C.; Grassian, V. H.; Cappa, C. D.; Prather, K. A.; Moffet, R. C. Biological Impacts on Carbon Speciation and Morphology of Sea Spray Aerosol. *ACS Earth Sp. Chem.* **2017**, *1*, 551−561.

(36) Wang, X.; Deane, G. B.; Moore, K. A.; Ryder, O. S.; Stokes, M. D.; Beall, C. M.; Collins, D. B.; Santander, M. V.; Burrows, S. M.; Sultana, C. M.; Prather, K. A. The Role of Jet and Film Drops in Controlling the Mixing State of Submicron Sea Spray Aerosol Particles. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 6978−6983.

(37) Patterson, J. P.; Collins, D. B.; Michaud, J. M.; Axson, J. L.; Sultana, C. M.; Moser, T.; Dommer, A. C.; Conner, J.; Grassian, V. H.; Stokes, M. D.; Deane, G. B.; Evans, J. E.; Burkart, M. D.; Prather, K. A.; Gianneschi, N. C. Sea Spray Aerosol Structure and Composition Using Cryogenic Transmission Electron Microscopy. *ACS Cent. Sci.* **2016**, *2*, 40−47.

(38) Prather, K. A.; Bertram, T. H.; Grassian, V. H.; Deane, G. B.; Stokes, M. D.; Demott, P. J.; Aluwihare, L. I.; Palenik, B. P.; Azam, F.; Seinfeld, J. H.; Moffet, R. C.; Molina, M. J.; Cappa, C. D.; Geiger, F. M.; Robe, D. Bringing the Ocean into the Laboratory to Probe the Chemical Complexity of Sea Spray Aerosol. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 7550−7555.

(39) Liu, L.; Huang, Q.; Zhang, Y.; Qin, B.; Zhu, G. Excitation-Emission Matrix Fluorescence and Parallel Factor Analyses of the Effects of N and P Nutrients on the Extracellular Polymeric Substances of Microcystis Aeruginosa. *Limnologica* **2017**, *63*, 18−26.

(40) Schiffer, J. M.; Luo, M.; Dommer, A. C.; Thoron, G.; Pendergraft, M.; Santander, M. V.; Lucero, D.; Pecora De Barros, E.; Prather, K. A.; Grassian, V. H.; Amaro, R. E. Impacts of Lipase Enzyme on the Surface Properties of Marine Aerosols. *J. Phys. Chem. Lett.* **2018**, *9*, 3839−3849.

(41) Aller, J. Y.; Radway, J. C.; Kilthau, W. P.; Bothe, D. W.; Wilson, T. W.; Vaillancourt, R. D.; Quinn, P. K.; Coffman, D. J.; Murray, B. J.; Knopf, D. A. Size-Resolved Characterization of the Polysaccharidic and Proteinaceous Components of Sea Spray Aerosol. *Atmos. Environ.* **2017**, *154*, 331−347.

(42) Kuznetsova, M.; Lee, C.; Aller, J. Characterization of the Proteinaceous Matter in Marine Aerosols. *Mar. Chem.* **2005**, *96*, 359−377.

(43) Trueblood, J. V.; Estillore, A. D.; Lee, C.; Dowling, J. A.; Prather, K. A.; Grassian, V. H. Heterogeneous Chemistry of Lipopolysaccharides with Gas-Phase Nitric Acid: Reactive Sites and Reaction Pathways. *J. Phys. Chem. A* **2016**, *120*, 6444−6450.

(44) Nguyen, Q. T.; Kjær, K. H.; Kling, K. I.; Boesen, T.; Bilde, M. Impact of Fatty Acid Coating on the CCN Activity of Sea Salt Particles. *Tellus, Ser. B* **2017**, *69*, 1304064.

(45) Mochida, M.; Kitamori, Y.; Kawamura, K.; Nojiri, Y.; Suzuki, K. Fatty Acids in the Marine Atmosphere: Factors Governing Their Concentrations and Evaluation of Organic Films on Sea-Salt Particles. *J. Geophys. Res. Atmos.* **2002**, *107*, AAC 1-1.

(46) Cochran, R. E.; Laskina, O.; Trueblood, J. V.; Estillore, A. D.; Morris, H. S.; Jayarathne, T.; Sultana, C. M.; Lee, C.; Lin, P.; Laskin, J.; Laskin, A.; Dowling, J.; Qin, Z.; Cappa, C. D.; Grassian, V. H. Molecular Characterization of Sea Spray Particles: Influence of Ocean Biology on Particle Composition and Interaction with Water. *Chem.* **2017**, *2*, 655−667.

(47) Demott, P. J.; Prenni, A. J.; Liu, X.; Kreidenweis, S. M.; Petters, M. D.; Twohy, C. H.; Richardson, M. S. Predicting Global

Atmospheric Ice Nuclei Distributions and Their Impacts on Climate. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 11217−11222.

(48) Or, V. W.; Estillore, A. D.; Tivanski, A. V.; Grassian, V. H. Lab on a Tip: Atomic Force Microscopy - Photothermal Infrared Spectroscopy of Atmospherically Relevant Organic/Inorganic Aerosol Particles in the Nanometer to Micrometer Size Range. *Analyst* **2018**, *143*, 2765−2774.

(49) Morris, H. S.; Grassian, V. H.; Tivanski, A. V. Humidity-Dependent Surface Tension Measurements of Individual Inorganic and Organic Submicrometre Liquid Particles. *Chem. Sci.* **2015**, *6*, 3242−3247.

(50) Ruehl, C. R.; Wilson, K. R. Surface Organic Monolayers Control the Hygroscopic Growth of Submicrometer Particles at High Relative Humidity. *J. Phys. Chem. A* **2014**, *118*, 3952−3966.

(51) Tobo, Y. An Improved Approach for Measuring Immersion Freezing in Large Droplets over a Wide Temperature Range. *Sci. Rep.* **2016**, *6*, 1−9.

(52) Schill, G. P.; De Haan, D. O.; Tolbert, M. A. Heterogeneous Ice Nucleation on Simulated Secondary Organic Aerosol. *Environ. Sci. Technol.* **2014**, *48*, 1675−1682.

(53) Qiu, Y.; Molinero, V. Morphology of Liquid-Liquid Phase Separated Aerosols. *J. Am. Chem. Soc.* **2015**, *137*, 10642−10651.

(54) Reinhardt, A.; Doye, J. P. K. Homogeneous TIP4P/2005 Ice Nucleation at Low Supercooling. *J. Chem. Phys.* **2013**, *139*, 096102.

(55) Lovric, J.; Duflot, D.; Monnerville, M.; Toubin, C.; Briquez, S. Water Induced Organization of Palmitic Acid at the Surface of a Model Sea Salt Particle: A Molecular Dynamics Study. *J. Phys. Chem. A* **2016**, *120*, 10141−10149.

(56) Sun, L.; Li, X.; Hede, T.; Tu, Y.; Leck, C.; Agren, H. Molecular Dynamics Simulations Reveal the Assembly Mechanism of Polysaccharides in Marine Aerosols. *Phys. Chem. Chem. Phys.* **2014**, *16*, 25935−25941.

(57) Dolinski, K.; Troyanskaya, O. G. Implications of Big Data for Cell Biology. *Mol. Biol. Cell* **2015**, *26*, 2575−2578.

(58) Nandy, L.; Dutcher, C. S. Phase Behavior of Ammonium Sulfate with Organic Acid Solutions in Aqueous Aerosol Mimics Using Microfluidic Traps. *J. Phys. Chem. B* **2018**, *122*, 3480−3490.

(59) Mohimani, H.; Gurevich, A.; Mikheenko, A.; Garg, N.; Nothias, L.-F.; Ninomiya, A.; Takada, K.; Dorrestein, P. C.; Pevzner, P. A. Dereplication of Peptidic Natural Products through Database Search of Mass Spectra. *Nat. Chem. Biol.* **2017**, *13*, 30−37.

(60) Tarasova, E.; Farafonov, V.; Khayat, R.; Okimoto, N.; Komatsu, T. S.; Taiji, M.; Nerukh, D. All-Atom Molecular Dynamics Simulations of Entire Virus Capsid Reveal the Role of Ion Distribution in Capsid's Stability. *J. Phys. Chem. Lett.* **2017**, *8*, 779−784.

(61) Freddolino, P. L.; Arkhipov, A. S.; Larson, S. B.; McPherson, A.; Schulten, K. Molecular Dynamics Simulations of the Complete Satellite Tobacco Mosaic Virus. *Structure* **2006**, *14*, 437−449.

(62) Perilla, J. R.; Hadden, J. A.; Goh, B. C.; Mayne, C. G.; Schulten, K. All-Atom Molecular Dynamics of Virus Capsids as Drug Targets. *J. Phys. Chem. Lett.* **2016**, *7*, 1836−1844.

(63) Amaro, R. E.; Mulholland, A. J. Multiscale Methods in Drug Design Bridge Chemical and Biological Complexity in the Search for Cures. *Nat. Rev. Chem.* **2018**, *2*, 0148.

(64) Ieong, P. U.; Sørensen, J.; Vemu, P. L.; Wong, C. W.; Demir, O.; Williams, N. P.; Wang, J.; Crawl, D.; Swift, R. V.; Malmstrom, R. D.; Altintas, I.; Amaro, R. E. Progress towards Automated Kepler Scientific Workflows for Computer-Aided Drug Discovery and Molecular Simulations. *Procedia Comput. Sci.* **2014**, *29*, 1745−1755.

(65) Purawat, S.; Cowart, C.; Amaro, R. E.; Altintas, I. Biomedical Big Data Training Collaborative (BBDTC): An Effort to Bridge the Talent Gap in Biomedical Science and Research. *Procedia - Procedia Comput. Sci.* **2016**, *80*, 1791−1800.

(66) Wang, J.; Crawl, D.; Altintas, I.; Li, W. Big Data Applications Using Workflows for Data Parallel Computing. *Comput. Sci. Eng.* **2014**, *16*, 11−21.

(67) Alma'abadi, A. D.; Gojobori, T.; Mineta, K. Marine Metagenome as a Resource for Novel Enzymes. *Genomics, Proteomics Bioinf.* **2015**, *13*, 290−295.

(68) Metcalf, A. R.; Narayan, S.; Dutcher, C. S. A Review of Microfluidic Concepts and Applications for Atmospheric Aerosol Science. *Aerosol Sci. Technol.* **2018**, *52*, 310−329.

(69) Javanainen, M.; Lamberg, A.; Cwiklik, L.; Vattulainen, I.; Ollila, O. H. S. Atomistic Model for Nearly Quantitative Simulations of Langmuir Monolayers. *Langmuir* **2018**, *34*, 2565−2572.

(70) Espinosa, J. R.; Vega, C.; Sanz, E. Ice − Water Interfacial Free Energy for the TIP4P, TIP4P/2005, TIP4P/ Ice, and MW Models as Obtained from the Mold Integration Technique. *J. Phys. Chem. C* **2016**, *120*, 8068−8075.