CHEMICAL REVIEWS

Chemistry and Related Properties of Freshly Emitted Sea Spray Aerosol

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1. INTRODUCTION

Aerosol particles that exist in the marine atmosphere are derived from both continental and oceanic sources. Since aerosol lifetimes and atmospheric transport times often are similar,[1] particles emitted from continental sources (fossil fuel combustion, biomass burning, dust, and biogenic emissions) can be transported great distances across ocean basins, either in the boundary layer or in the free troposphere. Marine vessel emissions also contribute to the aerosol burden over the oceans, particularly in coastal regions and major shipping lanes.[2] As a result, marine aerosol number and mass concentrations, chemical composition, and optical and cloud-nucleating properties vary with distance from shore and with the occurrence of transport events that carry continental emissions thousands of kilometers downwind. While acknowledging the complexity of the sources of aerosol in the marine atmosphere, this review focuses on freshly emitted, primary sea spray aerosol (SSA) generated at the ocean surface and factors affecting its composition and associated properties. This information is required for assessment and validation of model estimates of the atmospheric chemistry and climate impacts of SSA.

Wind-driven particle production at the ocean surface is one of the largest global sources of primary atmospheric aerosol on a mass concentration basis.[3,4] As a result, even in ocean regions impacted by continental sources, SSA can make a significant contribution to the total aerosol mass concentration under moderate to high wind speed conditions. At wind speeds greater than about 5 m·s^{-1}, breaking waves are formed on the ocean surface.[5] As waves break, air bubbles are entrained into ocean surface waters. These bubbles rise to the surface and burst, with each bubble producing up to hundreds of film drops in the nanometer to micrometer size range (see Figure 1).[6,7] Ambient measurements and laboratory studies indicate that the resulting SSA can have a trimodal size distribution for particles less than 10 μm in diameter, with modes centered around 0.02−0.05 μm, 0.1−0.2 μm, and 2−3 μm.[8,9] This multimodal behavior suggests that several mechanisms are involved in SSA production. Film drops form due to fragmentation of the thin fluid cap film of each bubble.[10] Cap films can be stabilized by surfactants, increasing their lifetime and affecting the bursting dynamics of collections of bubbles on the water surface.[11] Larger diameter particles are produced by collapse of the bubble cavity; it has been suggested that the material ejected into the atmosphere emanates from the inner gas−liquid
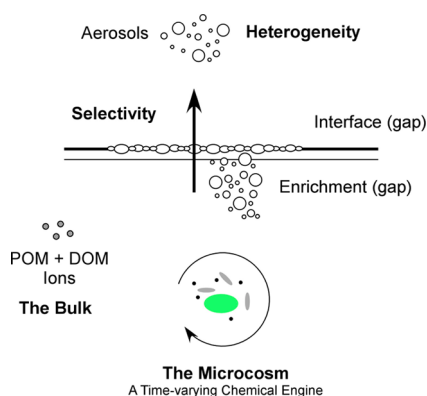
Figure 1. Representative diagram that underlies the fundamental processes that occur in wind-driven production of sea spray aerosol. Breaking waves entrain air bubbles into ocean surface waters. These bubbles scavenge organic matter as they rise to the surface. When they burst at the air—sea interface, they release a mixture of organic matter and inorganic sea salt, forming SSA. "The Microcosm" here describes dynamic microbial ecosystem processes and the interrelationships between dissolved organic matter (DOM), particulate organic matter (POM), and the biological material by which SSA composition is influenced. Large gaps exist in our knowledge regarding enrichment of organics, selectivity that occurs during the production of sea spray aerosol, and heterogeneity of individual sea spray aerosol particles. (Courtesy of Grant Deane, Scripps Institution of Oceanography).

80 interface of the rupturing bubble.[12] It is believed this process
81 leads to the formation of jet drops ranging in size from about 1
82 to 25 μm.[12] In addition, spume drops are torn directly from the
83 crests of waves when wind speeds reach 10 m·s^{-1} or more.[13]
84 Having diameters between tens of micrometers and several
85 millimeters, spume drops have very short atmospheric lifetimes
86 of seconds to minutes[14] and consequently are often not
87 included in considerations of atmospheric chemistry and/or
88 aerosol—climate interactions. Overall, SSA production depends
89 on bubble size distributions and lifetime, surface tension, and
90 cap film thickness.[15,16] Uncertainties surrounding production
91 mechanisms and associated controlling factors make this an
92 active and ongoing area of research.
93   A number of studies have reported the scavenging of surface-
94 active (i.e., surfactant) organic material from seawater by rising
95 bubbles.[17−22] Upon bursting at the ocean surface, the bubbles
96 release this organic material into the atmosphere along with
97 other seawater-dissolved and particulate organic material.
98 Laboratory experiments indicate that longer bubble rise
99 times,[19] faster bubbling rates, and smaller bubble sizes[20] result
100 in an enrichment in organic carbon relative to seawater in the
101 freshly emitted SSA. These results imply that the magnitude of
102 the incorporation of organic carbon (OC) into SSA varies with
103 turbulence in the upper ocean. The result is a complex,
104 multicomponent chemical mixture of particles ranging from
105 nanometers to micrometers in diameter.
106   SSA impacts the earth's radiation balance directly by
107 scattering incoming solar radiation and indirectly by acting as
108 cloud condensation nuclei (CCN) and altering cloud micro-
109 physical properties (e.g., cloud drop effective radius and
110 number concentration) and macrophysical properties (e.g.,
111 cloud lifetime and extent). Since the wavelength of solar
112 midvisible radiation is centered around 0.55 μm, the most
113 efficient particle size range for scattering light occurs between
114 0.2 and 1 μm. The peak in the SSA number concentration
115 occurs at the lower end of this size range. Although the majority

116 of the SSA mass occurs in particles with diameters larger than 1
117 μm, the large mass concentration of supermicrometer SSA
118 compensates for the low scattering efficiency of this size range.
119 In addition, if the supermicrometer SSA mass concentration is
120 large, it "tails" or extends into the submicrometer, more
121 optically active size range. Thus, SSA is the dominant
122 contributor to light scattering in the marine boundary layer
123 (MBL) for both the sub- and supermicrometer size ranges.[23−26]
124 Consistent with this analysis, model calculations indicate that,
125 on a global scale, yearly averaged direct radiative forcing by SSA
126 is equal to or greater in magnitude than forcing by natural
127 sulfate and soil dust.[27,28] Hence, SSA may be the most
128 important natural aerosol chemical component in the
129 atmosphere in terms of aerosol direct effects and scattering of
130 solar radiation.
131   While direct scattering of solar radiation in the MBL is
132 controlled by SSA mass concentrations, the indirect effects of
133 CCN on MBL cloud properties are influenced by the SSA
134 number concentrations. For a given supersaturation of water,
135 the CCN number concentration depends on the number of
136 particles that are sufficiently large with enough soluble species
137 to take up water vapor and activate to form cloud droplets.
138 Measurements suggest that the effective supersaturation of
139 MBL clouds ranges between approximately 0.1% and
140 0.4%,[29−32] although effective supersaturations up to 1% for
141 clean stratus clouds (CCN and total particle concentrations
142 <300 cm^{-3}) have been reported.[33] Particles larger than 300 nm
143 will activate regardless of chemical composition, but because of
144 their limited number, they do not contribute significantly to
145 CCN number concentrations (see Figure 2). For particles less

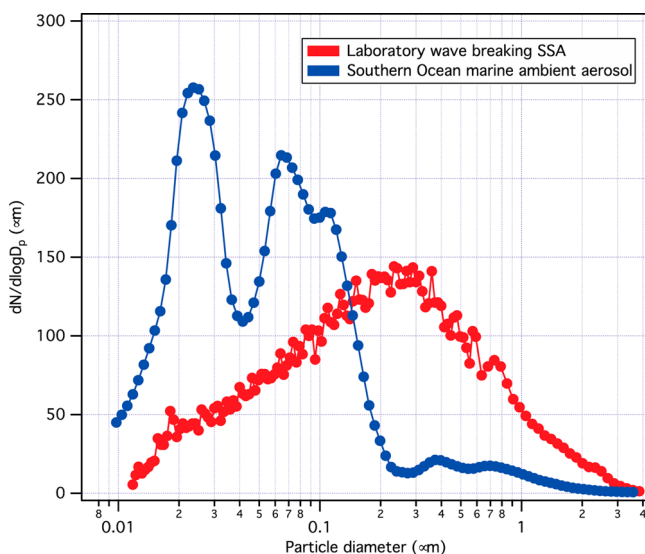**Figure 2.** Comparison of number size distributions of ambient open ocean aerosol measured over the Southern Ocean during remote marine conditions[44] and SSA particles generated by laboratory breaking waves.[43] Both are shown for relative humidity (RH) of 15%.

146 than 300 nm in diameter, chemical composition affects the
147 critical diameter (D_c) for activation to a cloud droplet (the size
148 at which 50% of particles activate at a given supersaturation)
149 through the molecular weight, degree of dissociation, density,
150 and solubility of the solute, along with the surface tension of
151 the aqueous droplet at the point of nucleation. For soluble
152 compounds that do not appreciably affect droplet surface
153 tension, Köhler theory[34] predicts D_c values between about 40

154 and 300 nm for water vapor supersaturations of 0.1–0.4%. D_c
155 can be as small as 20–30 nm at 1% supersaturation. Hence,
156 particles less than 300 nm in diameter will determine the CCN
157 concentration in the remote MBL. Under certain conditions,
158 SSA larger than about 1 μm in diameter may act as so-called
159 "giant CCN" and/or ice nuclei; the influence of aerosols on
160 clouds through these two pathways may affect precipitation
161 rates and the magnitude of the local aerosol indirect effect.[35−37]
162   MBL ambient aerosol is a mixture of freshly emitted SSA,
163 particles of continental and marine origin that have been mixed
164 into the MBL from the free troposphere, and particles of
165 various ages and origins that have been chemically
166 modified.[38−40] For example, soon after emission, with the
167 exact time scale depending on the species and processes
168 involved, secondary organic reaction products derived from the
169 oxidation of precursor gases can condense onto freshly emitted
170 SSA.[41] In addition, the enriched organic matter in freshly
171 emitted SSA can react photochemically, resulting in a loss of
172 particulate organic species and the production of volatile, low-
173 molecular-weight organic compounds.[42] This complex mixture
174 of aerosols and the processing that occurs in the marine
175 atmosphere make it impossible to characterize freshly emitted
176 SSA through measurements of ambient marine aerosol. For
177 example, Figure 2 shows the differences in aerosol number size
178 distribution observed for SSA particles generated from breaking
179 waves in the laboratory[43] and for ambient aerosol measured
180 over the Southern Ocean during remote marine conditions as
181 indicated by low radon concentrations (<100 mBq·m^{-3}) and
182 low total particle number concentration (<500 cm^{-3}).[44] In
183 contrast to the monomodal freshly emitted SSA size
184 distribution, the ambient marine aerosol distribution is bimodal
185 in the submicrometer size range. This shape is typical of marine
186 aerosol and indicates that it has undergone coalescence and
187 solute condensation in cloud, growing the smaller Aitken mode
188 particles into the accumulation mode size range.[29] Accumu-
189 lation mode particles can also "accumulate" mass over the
190 course of their lifetime through the condensation of gas-phase
191 species out of cloud. In addition, ambient aerosol is subject to
192 loss processes including sedimentation of larger particles.
193   Studies aimed at characterizing the properties of freshly
194 emitted SSA have been performed by generating SSA from
195 seawater while avoiding interferences from gas- and particle-
196 phase species in the marine atmosphere. These studies include
197 generation of SSA from natural seawater in both field[16,45−48]
198 and laboratory settings.[19,43,49−59] Chemical measurements
199 indicate that the enrichment of organic carbon relative to
200 seawater is highest for the smallest particle size ranges
201 measured ($D_{p,aero,60\%RH} \lesssim 180$ nm),[45,47,49,52] which correspond
202 to the size range that dominates the MBL CCN population. If
203 the ocean-derived organic species incorporated into SSA
204 suppress surface tension, they may reduce the supersaturation
205 required for the SSA to activate into cloud droplets.[55,60] In
206 addition, photochemical processing of organic compounds
207 within SSA solutions is likely a significant source of OH and
208 other radicals, which can lead to low-molecular-weight reaction
209 products including carboxylic acids, ketones, and alcohols.[42]
210   Previous reviews of the state of knowledge on sea spray
211 aerosol have focused on production fluxes and mecha-
212 nisms[5,12,61,62] and on physical and chemical properties.[5,63]
213 This review will focus on the results of field and laboratory
214 experiments that have been performed to characterize the
215 properties of freshly emitted SSA, with a strong emphasis on
216 the organic fraction.

2. SEAWATER ORGANIC CARBON POOL

217 The ocean contains one of the largest reservoirs of reactive
218 organic carbon on Earth.[64] This carbon pool is operationally
219 divided into particulate organic carbon (POC), which is large
220 enough in size to be retained on a filter with pore sizes ranging
221 from 0.2 to 0.7 μm, and dissolved organic carbon (DOC),
222 which consists of colloidal particles small enough to pass
223 through a filter (e.g., vesicles,[65] gel-like particles,[66,67] and
224 viruses[68]) and dissolved compounds.[64,69] POC includes
225 phytoplankton, zooplankton, bacteria, and detritus and makes
226 up only ~3% of the ocean's total organic carbon (TOC).[64] At
227 the molecular level, DOC is composed of a mixture of
228 biopolymers including polysaccharides, proteins, nucleic acids,
229 and lipids.[70] Figure 3 displays the known components of the
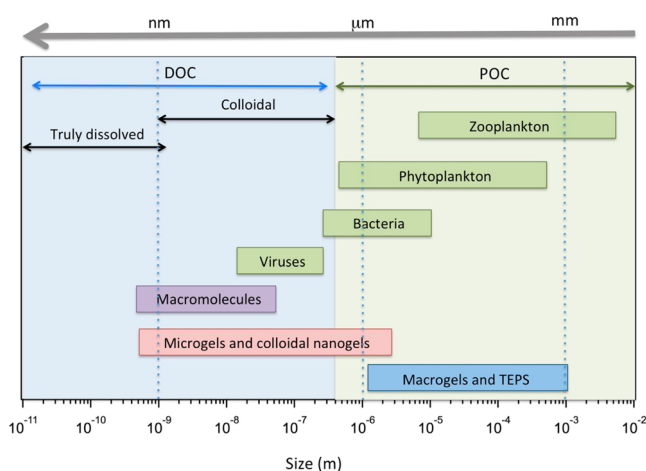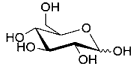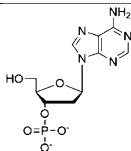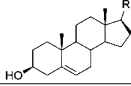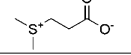230 seawater organic carbon pool as a function of size.

Figure 3. Size scale of organic carbon components in seawater. Material retained by seawater filtration at 0.2 μm pore size is regarded as particulate organic carbon. The fraction that passes through the filter is labeled as dissolved organic carbon and includes colloidal and truly dissolved materials. Macromolecules include humic substances and high molecular weight DOM. Adapted from Verdugo et al.[67]

231   The microbial food web is the dominant source and chemical
232 processor of oceanic DOC. Exopolymer substances (EPS)
233 secreted by phytoplankton are taken up and enzymatically
234 degraded by marine heterotrophic bacteria.[71−75] In addition,
235 grazing of bacteria by higher heterotrophic organisms trans-
236 forms organic carbon within the food web, influencing its
237 composition.[71,75,76] Overall, marine heterotrophic bacteria can
238 transform DOC into organic compounds that have long
239 lifetimes in the ocean (also known as recalcitrant or refractory
240 carbon)[74,77,78] and therefore have a molecular structure distinct
241 from more labile forms.[79]
242   As stated above, the primary source of DOC in ocean surface
243 waters is the microbial food web. Additional processes that
244 control the distribution and loss of DOC from surface waters
245 include vertical mixing and horizontal advection,[80] reactivity of
246 algal-derived DOC,[81] accommodation of DOC by particulates
247 with subsequent sinking,[82] and UV oxidation and volatilization
248 at the ocean surface.[42,83] As a result, the distribution of DOC in
249 surface waters in any given region can be decoupled from local
250 biological production.
251   Only about 15% of seawater DOC has been identified at the
252 molecular level due to low concentrations (total DOC
253 concentrations in surface seawater range between 60 and 90

Table 1. Classes of Compounds and Materials Found in Marine Organic Matter, Their Subsurface Concentrations, and Enrichment Factors in Sea Surface Microlayer and Sea Spray Aerosol Particles[a]

Component	Metric	Surface Seawater Conc.	Enrichment Factor SSML	Enrichment Factor SSA	Example Molecule	Ref
DOC	passed through 0.7 µm filter (µM)	60 - 90	1-2 [S,G]	See Figure 4		70,94-96
POC	collected by 0.7 µm filter (µM)	2-7 (1 - 800)	~4 (1.3 – 38) [S,G]	See Bacteria and Virus-like Particles		95,97-98
Carbohydrates	carbohydrate (µM C glucose equiv.)	10 - 25	1.3 – 3 [S,G]	Detected[a], No EF[b]		70,94,97,99
	hydrolyzable neutral sugars (µM)	0.2 – 0.8			[poly-saccharide]	70
	hydrolyzable amino sugars (µM)	0.042 – 0.094			[peptidoglycan]	70
Proteins, Peptides, Amino Acids	Dissolved combined amino acids (µM)	0.2 – 1	1.9 [S]	1.2-20	see PDB ID: 1RBL	70,100-102
Fatty Acids	solvent extractable lipids (µM)	0.0002 – 0.0007	3.5 [S]	Detected[a], No EF[b]		103
Nucleic Acids (DNA, RNA)	(ug L^{-1})	1 – 30				104-105
Sterols, Hopanoids	total dissolved sterols in lipid extract (ug L^{-1})	0.5 – 7.7	2 (0.2 – 8) [S]	Detected[a], No EF[b]		106
Organosulfur	DMSP (µM)	0.0076	1.85 (0.81-4.6) [S]	Detected[a], No EF[b]		59,107
CDOM	Absorbance at 350nm (m^{-1})	0.014-0.05	1.3-4 [S]			95-96,108
Bacteria	(cells mL^{-1})	1.1 x 10^6	1 – 2, 6 [S,G]	10		97,101,109
Virus-Like Particles (VLP)	(mL^{-1})	2.2 x 10^6	1.5, 7 [S]	10		101,109
Microgels	(as TEP; mL^{-1})	10^6 - 10^{12}	1.3 – 5 [G,S]	Detected[a]		66,97,110

[a]Has been reported to be detected in SSA. [b]No EF$_{OC}$ has been reported. SSML sampling methods:[97] [S] screen or mesh, [G] glass slide. Enrichment factor (EF) here refers to the ratio of SSML or SSA concentration relative to the subsurface concentration

µM) and a lack of methods with the required sensitivity.[70] Carbohydrates, existing in a combined or polysaccharide form, make up the largest identified fraction (10–15%).[70] Other classes of compounds that have been identified include neutral sugars, amino acids, amino sugars, and lipids (Table 1).[84−87] In addition to molecular-level analysis, solid-phase extraction has been used to isolate and characterize the humic fraction of DOC. Humic substances, defined as dissolved organic matter (DOM) that is retained on XAD-2 or XAD-8 resins under acidic conditions, make up 5−25% of surface seawater DOC.[88] High-molecular-weight DOM, defined as DOM that is retained by an ultrafiltration membrane with 1 nm pore size and a 1000 Da cutoff, makes up 25−40% of surface ocean DOC.[88]

Studies of the composition of marine DOM using high-resolution mass spectrometry appear to be a promising and helpful direction.[79,89,90] Electrospray ionization (ESI), a soft ionization technique that ionizes polar compounds in aqueous solutions, followed by injection into a high-resolution mass spectrometer, allows for the detection of individual molecules within an organic mixture. For example, a combination of ESI and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been used to investigate molecular-level changes in ocean DOM resulting from microbial and photochemical processes.[89]

Over the past decade, hydrogels have been increasingly recognized as a significant component of seawater.[66,67] Polymeric DOM is composed of hydrophobic and amphiphilic chains. The polymers can be coordinated by cations available in seawater and form nanogels (100−150 nm) through ionic and/or hydrophobic interactions. Nanogels then anneal, forming microscopic transparent exopolymeric particles (TEP) ranging in size from less than 2 µm to greater than 100 µm.[91,92] Continued agglomeration of colloidal DOM into particulate organic matter (POM) can result in meter-sized macrogels.[93] It has been estimated that bulk seawater contains 700 Gt of DOC, 3 Gt of POC, and 70 Gt of hydrogels including 10 Gt of microscopic gels.[66]

The sea surface microlayer (SSML), operationally defined as the top 1−1000 µm of surface waters, serves as the boundary layer interface between the ocean and atmosphere.[111] As such, it has received attention due to its potential role in enriching organic matter in SSA. The composition of organics in the

SSML varies with microbial community composition but, in general, is dominated by carbohydrates with smaller contributions from proteins and lipids. SSML enrichment factors for DOC, total dissolved carbohydrates (TDC), chromophoric dissolved organic matter (CDOM), POC, and TEP have been reported, based on simultaneous sampling of SSML and underlying subsurface waters, and are summarized in Table 1. In general, SSML enrichments have been found to be low for DOC (<2) relative to subsurface water for both coastal and open ocean regions.[70,94−96,112,113] TDC and CDOM SSML enrichments are also less than 2 except in regions of visible slicks, which result from organic matter enrichments above some threshold. TDC and CDOM SSML enrichment factors have been found to be up to 3, on average, in slicks.[113] Some studies have noted that the enrichment of nitrogen-containing material is higher than that of carbohydrates and hydrocarbons, but the identity of these compounds has not been not fully elucidated.[99] SSML enrichment of POC is higher than that of TOC, ranging from 1.3 to 38.[95,96]

Wurl et al.[113,114] reported the persistence of TDC and CDOM SSML enrichments at wind speeds up to 9.6 m·s^{-1}, the highest winds encountered, indicating a lack of SSML dispersion under moderate wind conditions. The persistence of the CDOM SSML enrichment, even with a short lifetime with respect to photochemical transformation and degradation,[115] suggests that it is continually being supplied from subsurface waters to the SSML. In contrast, a negative correlation was reported between TEP SSML enrichment and wind speed, indicating a removal of TEP through deep bubble mixing or bubbles bursting at the ocean surface. Transport of TEP from the SSML to the atmosphere within SSA particles produced by bubble bursting is supported by Leck and Bigg,[116] who observed organic microcolloids surrounded by transparent material assumed to be exopolymer gel that is prevalent in the SSML.

Measurements off Long Island, NY, revealed SSML enrichment factors of bacteria and viruses relative to subsurface waters on the order of 5 and 7, respectively.[109] In addition, measurements of bacteria and viruses in SSA (1.2−20 μm in diameter at ambient RH) allowed for the assessment of enrichment factors relative to both the SSML (∼5) and subsurface waters (∼10). The greater enrichment of organic and/or biological material in SSA compared to SSML samples supports the concept that the SSML is a mechanistic intermediate for the transfer of condensed-phase material from the ocean to the atmosphere. Table 1 shows subsurface concentrations and enrichment factors for many classes of dissolved and particulate organics in the SSML and in SSA (relative to the subsurface concentration where known). The amount and type of organic molecules in SSA that are derived from the subsurface versus SSML remains an open question.

3. GENERATION OF FRESHLY EMITTED SEA SPRAY AEROSOL

Characterization of freshly emitted SSA requires production, sampling, and analysis methods that can generate and allow isolation of these particles, preventing them from being modified by ambient gases and particles. Two approaches to SSA generation have been developed. Bubbles can be generated in situ in ocean surface waters while the resulting SSA is drawn into shipboard instrumentation.[46] Alternatively, seawater can be pumped into a ship or laboratory where it is bubbled in a tank or generator to produce SSA.[16,43,48,49,58] Although the use of tanks removes the seawater from its natural physical environment, it allows for the systematic change of seawater properties (e.g., temperature, dissolved oxygen, salinity, biological composition) to study the effects on SSA flux[48,49,117−119] and composition.[43,50,51,53]

3.1. Field Measurements

An SSA generator known as Sea Sweep,[46] the only method currently reported to follow the first approach, generates SSA in situ by producing bubbles 0.75 m below the sea surface alongside a ship. A curtain of particle-free air prevents ambient air from entering the stainless steel hood above the bubbles. The freshly emitted SSA produced when the bubbles burst at the ocean surface is drawn from the hood to aerosol instruments aboard the ship. With the ship moving through the water, the bubbled water is being constantly replenished. The more common approach for shipboard measurements is to pump seawater to the ship and generate SSA onboard.[16,48] A bubble generator designed to model ocean-atmosphere processes that result in the production of SSA has been deployed on ships.[16,49,120] The volume of the generator, seawater flow rate, and location of the frits used to form bubbles in the generator are such that the average injection depth and lifetimes of the bubbles are representative of average conditions for the surface ocean. Other shipboard methods for generating SSA have included the use of a tank continuously replenished with seawater and bubble production by an impinging water jet.[45,48]

3.2. Laboratory Measurements

Generation of SSA from natural and artificial seawater has been performed for several decades in the laboratory to characterize the chemical and physical properties of SSA.[9,16,43,46−51,53−55,58,59,119−128] In addition, the formation and properties of bubbles in seawater have been probed to better understand their roles in the bubble bursting process and their influence on SSA properties.[9,15,43,51,127] For example, the bubble size distribution plays a key role in SSA production since bubble size at the time of bursting dictates the relative number of SSA produced from film droplets versus jet droplets.[10,126,129] In most field and laboratory experiments, SSA production involves bubbles that have been generated by forcing pure air (or N_2) through submerged sintered filters or diffusers, which are also known as frits,[19,46,49,53−55,58,127,130] or by impinging a water jet or waterfall on the surface of seawater, or an artificial seawater proxy solution, in a tank.[9,45,48,51,128] Both of these methods have been recently tested against laboratory breaking waves,[43,51] with the impingement of falling water showing a greater similarity to breaking waves than does the sintered glass filter technique. While the details of these and other investigations will be discussed below, it is important to stress that the method by which SSA particles are generated has been shown to influence their physical[9,127] and chemical[51] properties.

Recently, freshly emitted SSA has been generated by breaking waves in a 33-m-long wave channel apparatus[43] in which reproducible breaking waves yield bubble size distributions similar to those observed in the open ocean.[131] In addition, the wave channel apparatus mimics the physical processes of mixing and air entrainment that occur when waves break in the open ocean.[132] A generation technique for SSA has been developed that is based on the wave channel using a pulsed plunging waterfall and has been used to physically mimic breaking waves. The plunging waterfall apparatus includes not

only the sheetlike shape of an open ocean wave, which impacts the seawater surface with gravitational acceleration, but also the episodic (or "pulsed") nature of bubble production by waves in the open ocean and a "sweeping" action in which bubbles are produced by impingement of water over a given area of the seawater surface.[128] Physical properties of the plunging waterfall, such as plunging jet/sheet surface roughness[133] or the dissipation rate of turbulent kinetic energy,[134] have an important influence on the bubble plume and the subsequent surface foam. Each of these factors can be modulated by natural variations in the marine environment, such as changes in water temperature or composition.[135]

A recent study[43,51] using the wave channel apparatus compared bubble size distributions generated by sintered glass filters and a pulsed plunging waterfall. The pulsed plunging waterfall was found to produce a bubble size distribution that most closely matches that of breaking waves generated from both laboratory and open ocean measurements.[123,131,136,137] Most significantly, bubble size distributions produced with the pulsed plunging waterfall replicated[43] the shape of the distribution around the Hinze scale (a_H)[131] (Figure 4a), the size known to provide the greatest contribution to whitecap foam formation, which is an important driver of SSA production at the ocean surface.[5,12] Sintered glass filters produced a bubble size distribution similar in shape to the pulsed plunging waterfall and laboratory breaking waves in the 0.02–1.4 mm bubble size range.[43,51] However, they did not produce bubbles larger than 1.4 mm. As a result, the SSA number size distributions generated by sintered glass filters were found to have a smaller submicrometer modal diameter than those generated by the plunging waterfall and breaking wave methods (Figure 4b,c).[43]

SSA chemical composition and related properties may also vary depending on the production method. However, a direct comparison of bubble bursting methods indicates that subsaturated water uptake properties show only slight differences.[9] These small differences could be due to differing organic matter transfer properties of the various bubbling methods. Similarly, the CCN activity of submicrometer SSA particles (water uptake under supersaturated conditions) has been found to be nearly indistinguishable between methods,[9] unless a thick foam is formed on the water surface.[138] Direct chemical analysis of particles with diameters closer to 1 μm, however, shows a strong sensitivity to bubble generation mechanism, suggesting perhaps that the chemical composition of these larger particles is more sensitive to differences in bubble generation mechanism in laboratory chambers,[51] although a study of submicrometer particle composition with a similar level of detail is warranted.

3.3. Considerations for Wave Breaking Proxies

Wave breaking is an inherently episodic phenomenon. In most cases, bubble plumes entrained in the surface ocean fully decay via bursting before more bubbles are entrained in the same volume of seawater.[139] Based on observations at a coastal location, the decay time of oceanic whitecap foam ranges from 0.2 to 10 s,[139] with the decay time depending on the concentration and composition of surface-active compounds.[15,140] Foam has been observed to form in SSA generators that contain high concentrations of surface-active material, sometimes becoming a thick cap on the water surface throughout the tank.[49,51,138] Persistent foam on the water surface in laboratory SSA generators has been shown to
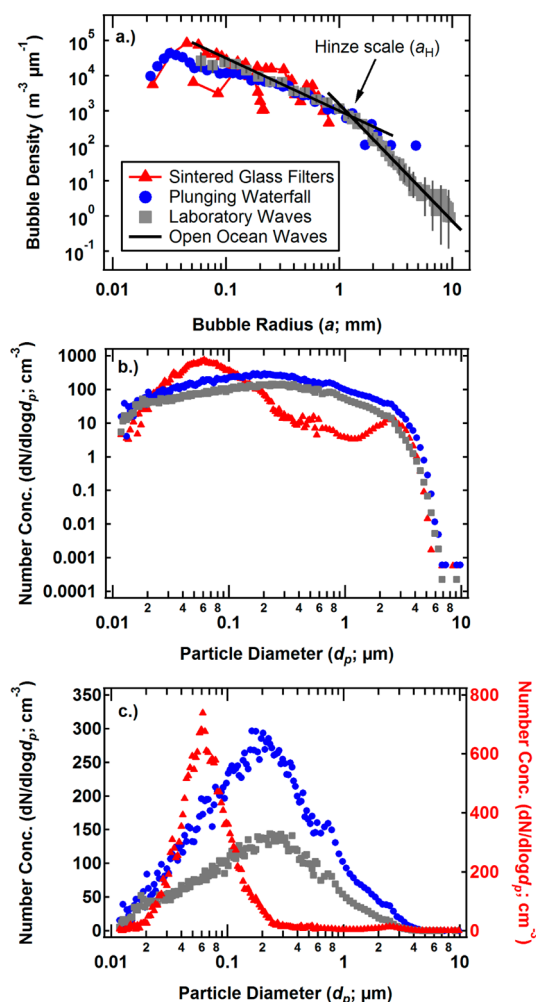
Figure 4. (a) Normalized bubble size distribution from sintered glass filters, laboratory breaking waves, and plunging waterfall.[43] The solid line refers to the shape of the bubble size distribution of waves in the open ocean.[131] (b) Number size distributions of SSA generated by each of the three methods are shown on a log–log scale to emphasize the difference in modal diameter and submicrometer size distribution shape.[43,51] The shape of the size distributions from breaking waves and plunging waterfall are similar. (c) Sintered glass filters, which produce a different size distribution of bubbles (i.e., lacking bubbles with diameters greater than 1.4 mm), yield SSA with a different number size distribution shape. The sintered glass filters distribution corresponds to the right-hand vertical axis.

influence the total aerosol concentration,[16,49,138] induce a change in the shape of the number size distribution,[51,138] decrease CCN activity,[138] and increase organic content[51] of aerosol particles formed through bubble bursting. By allowing bubble plumes to decay to some extent before bubble generation is resumed, the formation of foam can be reduced but not fully eliminated.[51] Refreshing the air–water interface by circulating seawater through the tank and allowing surface water to spill off into a drain[49,58] can reduce or even preclude the formation of foam. Further measurements are required to assess the environmental relevance of aerosol production in SSA generators under varying foam presence, extent, and morphology. Since foam forms and is stabilized by the presence of surface-active compounds,[11] measurements of surface tension and surfactant concentrations, such as those recently reported by Long et al.,[16] would help to constrain realistic foam

conditions in laboratory experiments and help give SSA production physicochemical context.

4. SIZE-DEPENDENT ENRICHMENT OF ORGANIC MATTER

The enrichment of organic material in SSA is often defined as

$$EF_{OC} = \frac{OC_{SSA}/Na_{SSA}}{OC_{seawater}/Na_{seawaterr}} \qquad (1)$$

where EF_{OC} is the enrichment factor of organic carbon in sea spray aerosol relative to that in seawater, OC_{SSA} and Na_{SSA} are the concentrations of organic carbon and Na^+ in sea spray aerosol, and $OC_{seawater}$ and $Na_{seawater}$ are the corresponding concentrations in seawater.[19,45,47,49] Several studies have reported values of EF_{OC} for freshly emitted SSA that was generated from natural seawater with techniques able to eliminate any influence of ambient constituents.[19,45,47,49]

Hoffman and Duce[19] reported EF_{OC} for bulk SSA (D_p < 20 μm at 48−79% RH) produced from seawater collected from Narragansett Bay and the Sargasso Sea. Values averaged 250 ± 145 and 74 ± 27 for the productive waters of Narragansett Bay and oligotrophic waters of the Sargasso Sea, respectively.[19] The authors hypothesized that the larger EF_{OC} values for the Narrangansett Bay SSA were due to more surface-active organics in the seawater relative to the Sargasso Sea. When surface-active material was added to the natural seawater, it was found that the OC to Na^+ ratio increased dramatically, confirming that surfactant material in seawater has a significant influence on the organic content of SSA.

Keene et al.[49] measured size-segregated EF_{OC} for SSA derived from Sargasso Sea water. Values were found to increase with decreasing particle size such that sub-1 μm and sub-0.18 μm diameter SSA (79% RH) had EF_{OC} on the order of 10^3 and 10^4, respectively (Figure 5). These values are 1 (sub-1 μm) and 2 (sub-0.18 μm) orders of magnitude greater than the sub-20 μm value reported by Hoffman and Duce[19] due to inorganic sea salt dominating bulk SSA mass.

Submicrometer (60% RH) EF_{OC} values for a range of biological activity (as indicated by chlorophyll a) in California coastal waters were on the order of 1000.[47] The same SSA generator (Sea Sweep[46]) was used in the western North Atlantic to characterize freshly emitted SSA generated from the eutrophic, biologically productive waters of Georges Bank and oligotrophic, nonproductive waters of the Sargasso Sea. Sub-1 μm and sub-0.18 μm (60% RH) EF_{OC} values were on the order of 10^3 and 10^4, respectively, with values derived from the oligotrophic seawater being slightly higher (Figure 5). Measurements by Facchini et al.[45] in the northeast Atlantic during a plankton bloom resulted in EF_{OC} values of 10^4 and 10^5 for sub-1 μm and sub-0.25 μm SSA, respectively (Figure 5).

All measurements of freshly emitted SSA indicate that OC is enriched in all size ranges with respect to seawater and that the smallest analyzed size fraction has the largest enrichment. High OC enrichments occur in regions of both eutrophic and oligotrophic surface seawater. That said, comparisons of SSA OC concentrations and EF_{OC} between experiments is complicated by the different methods used for analysis of OC concentration. EF_{OC} values from Quinn et al.[47] for California coastal and North Atlantic waters are based on total OC_{SSA} determined from thermal-optical analysis. Values from Keene et al.[49] for the Sargasso Sea are based on combustion of the water-extractable fraction of organic carbon (WEOC). Values from Facchini et al.[45] for the North Atlantic are based on the water-insoluble organic carbon fraction (WIOC) derived from the difference between total organic carbon (TOC) determined by thermal-optical analysis and water-soluble organic carbon (WSOC) determined by a liquid TOC analyzer. In addition, Collins et al.[51] reported that sintered glass filters produce aerosol containing a larger fraction of organic-enriched particles (0.8−2.0 μm size range) than either the pulsed plunging waterfall or breaking waves in a wave channel. A dedicated intercomparison study of methods is required to fully understand the method-dependent biases associated with the reported OC concentrations and EF_{OC}.

5. PROPERTIES OF FRESHLY EMITTED SEA SPRAY AEROSOL

5.1. Organic Composition

A variety of methods, each providing unique information, has been used to characterize the organic composition of SSA. Proton nuclear magnetic resonance (^{1}H NMR) spectroscopic measurements of the submicrometer fraction of freshly emitted SSA generated in the northeastern Atlantic show a dominant aliphatic composition, including (a) hydroxylated moieties of sugars, esters, and polyols; (b) aliphatic groups adjacent to carbonyls, amides, and acids; and (c) aliphatic chains with terminal methyls, typical of lipids.[45] High-resolution aerosol mass spectrometer (AMS; Aerodyne Research, Inc.) measurements of SSA in coastal California waters show that the organic fraction contains nonoxygenated hydrocarbon classes (40−70%, average = 58%) of which approximately 50% are unsaturated hydrocarbons.[46] Oxygenated hydrocarbons account for 28−58% (average ∼40%) of the organic mass. Fourier transform infrared (FTIR) spectroscopy measurements suggest the submicrometer organic carbon mass composition is 53% hydroxyl, 33% alkane, and 14% amine.[46] Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and NMR spectroscopy of freshly emitted SSA from the Angola Basin (south Atlantic) show CHO, CHNO, and CHOS type compounds.[59,107] NMR spectrometry also shows the presence of acrylic acid (a breakdown product of dimethylsulfoniopro-
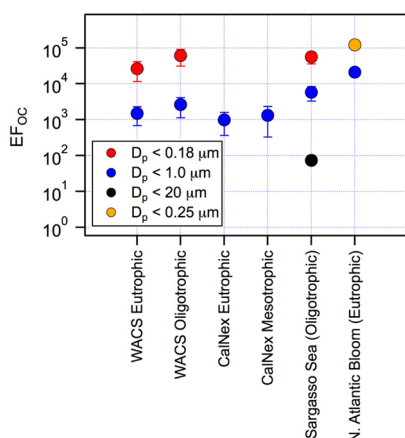
Figure 5. Organic enrichment factors (EF_{OC}), as micrograms of carbon, for freshly emitted SSA relative to seawater for WACS, CalNex,[47] Sargasso Sea,[19,49] and a North Atlantic plankton bloom region.[45] WACS, CalNex, and Sargasso Sea values (D_p < 20 μm) are based on measurement of total OC; Sargasso Sea values (D_p < 0.18 and 1.0 μm) are based on water-extractable OC; and North Atlantic values are based on water-insoluble OC.

pionate (DMSP) in the freshly emitted aerosol.[59,107] These measurements are consistent with the composition of dissolved organic carbon (DOC) in the ocean that includes polysaccharides, proteins, nucleic acids, and lipids[66,141] (see section 2 for a description of seawater DOC).

5.2. Mixing State

Based on the analysis of individual particles by online single-particle mass spectrometry and offline spectrochemical imaging and microanalysis of substrate deposited particles, SSA generated in the wave channel apparatus can be broken down into four main particle types: sea salt (SS), sea salt with organic carbon (SS-OC), organic carbon (OC), and biological (Bio).[43] The relative abundance of these particle types is size-dependent, with organic-containing types generally becoming more prevalent with decreasing size (Figure 6), similar to the
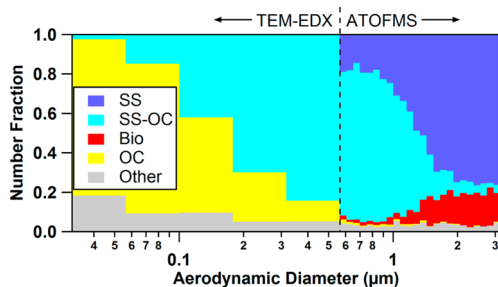
Figure 6. Size-resolved chemical composition from 30 nm to 3 μm of individual SSA particles generated in the Scripps Institution of Oceanography ocean-atmosphere wave channel. Particles are divided into four distinct chemical types as described in the text. Adapted from Prather et al.[43]

findings of size-segregated bulk chemical composition measurements.[45,49,142] Bio and SS particle types dominate the number fraction of the largest size range analyzed (2–3 μm in diameter). SS-OC dominates from 200 nm to 1 μm, and OC particles dominate at sizes below approximately 200 nm.

SS and SS-OC particles are characterized by dominant contributions from Na, Cl, Mg, and K, which are abundant inorganic components of seawater. In addition to these inorganic components, SS-OC particles also contain up to about 30–40% (v/v) organic matter.[50,143] OC particles contain Ca and Mg, which are known to form complexes with natural organic ligands[124,144] and help organize organic-dominated supramolecular structures in seawater.[66] The remaining particle type, Bio, is biological in nature and is thought to consist of either whole or fragmented bacterial cells on the basis of aerosol particle size and studies of controlled bacteria culture additions to seawater.[43,145] This particle type has been associated with known single-particle mass spectrometric markers for biological material, including phosphate, organic nitrogen, and Mg.[146,147] Additionally, Bio particles are often associated with transition metals as a result of sequestration and chelation by biological components.[145] Transition metals associated with Bio-type particles may play a role in the atmospheric chemistry and climate effects of SSA particles.

Spectroscopic chemical analysis of individual particles can yield important information on the molecular composition of individual particles and the mixing state of various classes of chemicals. For instance, the association of organic matter with Mg in particles with diameters between 30 and 550 nm has been ascertained through chemical imaging of individual

particles by scanning or transmission electron microscopy (SEM or TEM) with energy-dispersive X-ray analysis (EDX).[52,148] In order to gather more information about the organic components of SSA, electron microscopic analysis can be performed in parallel with scanning transmission X-ray microscopy (STXM) with near-edge X-ray absorption fine structure (NEXAFS).[149] Combined STXM–NEXAFS and TEM–EDX analysis of OC particles has shown that this type is characterized by a lack of chloride, a preponderance of carbonyls, and inorganic species like Ca, K, and Mg.[52] The carbonyls could indicate the importance of protein and/or fatty acid aggregates as the source of this particle type.[100,150]

Micro-Raman spectroscopy can also nondestructively resolve information about the organic chemical structures within particles in the 300–4000 nm diameter size range as well as select inorganic components (e.g., sulfate, carbonate) and even the hydration state of crystalline particles. Sulfate has been observed in particles by electron microscopy with EDX, STXM–NEXAFS, and Raman spectroscopy. Raman analysis indicated that sulfate in freshly emitted SSA samples was localized to particles with diameters mostly larger than 2 μm, while the aliphatic carbon signal was increasingly prevalent as particle size decreased toward 300 nm.[148] Often individual particle spectra showed the presence of both organics and sulfate. An example of this is shown in Figure 7 for a 2 μm
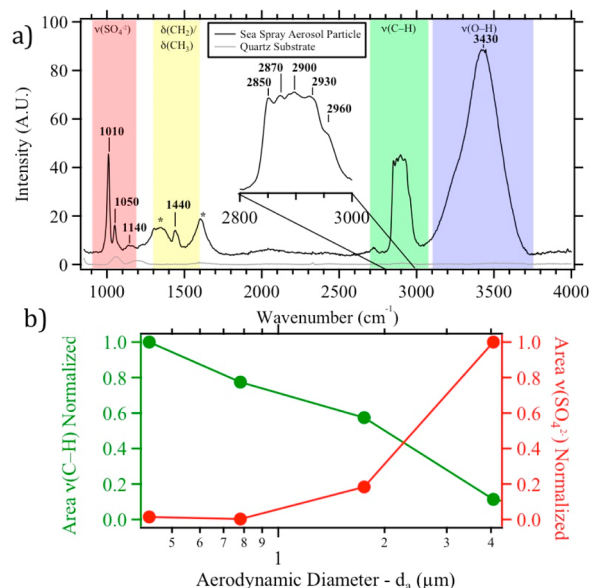
Figure 7. (a) Raman spectra of a 2 μm SSA particle (with inset of C–H stretching region). Bands associated with various vibrational modes and different functional groups are labeled. (b) Normalized integrated area of Raman bands for $\nu(SO_4^{2-})$ and $\nu(C-H)$ modes, as a function of particle size. Reprinted with permission from Ault et al.[148] Copyright 2013 Royal Society of Chemistry.

diameter particle that shows both sulfate peaks and C–H stretches associated with aliphatic hydrocarbons. The relative areas of the sulfate peak near 1010 cm^{-1} and the C–H stretching region around 2900 cm^{-1} shown as a function of particle size demonstrate that the sulfates are mostly in the larger particles and the organic compounds dominate at smaller particle sizes. Signals referring to amino acids along with fatty acids and lipids have been observed in particles, although heterogeneity exists between the Raman spectra collected for different particles collected in a single sample.[148] In addition,

surface-sensitive spectroscopy studies have indicated that interfacial C−H and O−H stretches exist, but alkyl chains are disordered on the surface,[151] perhaps allowing for the penetration of reactive gas molecules, contrary to the setup of some laboratory studies that utilize single, well-ordered monolayers of surface-active compounds to simulate SSA particle surfaces.[152,153]

5.3. Volatility

Heating of atmospheric aerosols is used to infer aerosol chemical composition.[8,154,155] Atmospheric aerosol heated to 230 °C causes ammonium nitrate, ammonium sulfate, and volatile organics to evaporate, leaving behind nonvolatile organics, sea salt, elemental carbon, and dust.[8] Heating freshly emitted SSA generated at the ocean surface by use of Sea Sweep to 230 °C volatilizes only a small fraction of the organic carbon (<10%).[46] The lack of volatility of SSA at 230 °C is consistent with the colloidal nature of a portion of seawater organic matter[66] (see section 2). It has been hypothesized that aggregates of seawater organic matter, bound together by phytoplankton exudates, are injected into the atmosphere through bubble bursting.[156] Once in the atmosphere, the colloidal exopolymer gels that bind the aggregates together are degraded by ultraviolet light and acidification. These exopolymer gels have been described as insoluble, thermally stable, and highly hydrated.[45,156]

5.4. Hygroscopicity

Measurements of the subsaturated hygroscopic growth factor (HGF) of SSA generated in situ at the ocean surface by use of Sea Sweep at 90% RH for diameters of 50, 100, and 145 nm yield a single mode in the frequency distribution that is 10% less hygroscopic than aerosol generated from artificial seawater in the laboratory.[46,143] Organic enrichment of artificial seawater in laboratory experiments achieves similar results to field studies.[143,157] The relatively large HGFs are consistent with a high enrichment in organic matter similar in composition to seawater colloidal exopolymer gels. The lack of two modes indicates that either all the SSA organics and sea salt are internally mixed at these diameters or the externally mixed particles (OC and SS-OC particles, see Figure 6) are similar in their hygroscopicity.

5.5. Cloud Condensation Nuclei Activity

The CCN activation ratio, which indicates the fraction of total particles that take up water and form CCN, has been measured for SSA generated in situ at the ocean surface by use of Sea Sweep.[47] The difference in the measured CCN activation ratio of SSA and aerosol generated from a NaCl solution was used to estimate a supersaturated hygroscopicity parameter.[158] SSA with a dry diameter of 100 nm was found to be about 30% less CCN-active than the NaCl calibration aerosols, while 40 nm particles were 70% less CCN-active. With decreasing particle size, the SSA became less like NaCl due to an increase in the volume fraction of OC. The volume fraction of OC increased from 40% for 100 nm particles to 80% for 40 nm particles.[47]

Laboratory studies with large perturbations in seawater organic content also show that very high organic enrichments can affect SSA CCN activity in some cases. When the hygroscopicity parameter[158] was used to quantify CCN activity, a decrease of 9−37% was observed with addition of phytoplankton exudates (512 μM C) or DOC-rich algae cultures to seawater,[50,143] although minimal changes in CCN activity under similar chemical conditions have also been reported.[55] In a different laboratory experiment, heterotrophic bacteria were allowed to grow on peptone and yeast extract as a nutrient source. The CCN activity of SSA produced from this seawater was observed to decrease by 86%. This change in CCN activity was driven by a large increase in the number fraction of OC particles with dry diameters between 30 and 200 nm.[50] The change in CCN activity was likely a result of the mixing state of SSA. It has been hypothesized that aerosol mixing state can have a particularly strong control over the CCN activity of SSA particles,[50] and that changes in internally mixed volume fractions of salts and organics may have a smaller impact.[159]

5.6. Ice Nucleation Activity

The heterogeneous ice nucleation (IN) activity of isolated freshly emitted SSA particles using realistic aerosol generation methods has not been reported in the literature. Only a few studies have published ice nucleating particle (INP) concentrations within the MBL[160−163] or in controlled marine aerosol generation experiments.[164] Marine diatoms may influence heterogeneous ice nucleation in SSA particles;[165−167] however, the flux of such large plankton cells into the atmosphere is likely quite small due to their large size compared to the SSA number size distribution. On the basis of limited experimental data, recent model studies suggest that the contribution of INP to the MBL from SSA could be important climatologically, especially in mixed-phase clouds[168] and over the Southern Ocean.[169] In terrestrial systems, some biological particles (e.g., certain bacteria) have been characterized as highly IN-active, initiating ice nucleation at temperatures as warm as −5 °C.[170,171] In comparison, mineral dust (widely accepted as a significant type of INP) has been shown to initiate ice nucleation at approximately −20 °C,[171] although less efficient nucleation has been observed at warmer temperatures.[172,173] Biological particles have been observed in SSA,[43,145] including both bacteria and viruses,[56,109,174] for which the IN activity is unknown yet potentially important. Overall, studies of IN activity in aerosol particles have shown a high degree of chemical selectivity,[166,173,175−177] although the fundamental process of heterogeneous freezing in the atmosphere has yet to be elucidated.

6. FLUX OF SEA SPRAY AEROSOL TO THE ATMOSPHERE

Most model parametrizations of the flux of SSA to the atmosphere assume that SSA emissions are proportional to whitecap coverage[13] and can be described as a function of wind speed at a height of 10 m.[178] Gong[179] and Clarke et al.[8] expanded this function to a size-resolved number flux based on comparisons with field observations. Jaegle et al.[180] further modified the source function by adding a dependence on sea surface temperature that improved comparisons with in situ and remote sensing observations. More recently, attempts have been made to account for the flux of the organic fraction of SSA by using a scaling factor in the flux parametrization based on surface ocean chlorophyll concentrations.[117,181−184] However, chlorophyll is able to explain only a fraction of the variance of organic content of ambient marine aerosol that is assumed to originate from the ocean,[47] most likely because chlorophyll is a tracer for only a small fraction of the ocean carbon pool as discussed above. Large EF$_{OC}$ in oligotrophic waters indicate a source of organic carbon that is not directly associated with chlorophyll and phytoplankton biomass but is available for

incorporation in SSA. That said, sunlight-mediated surfactants produced in biologically productive waters do affect the production efficiency (number of particles per unit volume of air detrained) of SSA.[16] In addition, laboratory experiments have shown a link between the number fraction of organic carbon particles in the 60−180 nm size range and heterotrophic biological activity.[43,52] Recently Burrows et al.[185] have parametrized SSA using a competitive Langmuir adsorption equilibrium at bubble surfaces. This approach is an initial step in linking ocean biogeochemistry and aerosol chemical composition in earth system models utilizing the concepts of fundamental physical chemistry.

The SSA number flux is dominated by particles containing organic carbon. The SSA number size distribution has a dominant mode centered around 100 nm.[8,118,186] If the organic fraction of the mass concentration of particles with diameters <180 nm is 55%,[47] the number fraction in this size range is >55% since the smallest sizes are predominantly OC-type particles (Figure 5). Similar or higher mass fractions of freshly emitted organic particles in this size range have been observed by Keene et al.[49] and Facchini et al.,[45] although laboratory studies indicate organic/salt fractions less than 40%.[50,143] For wind speeds of 5−15 m/s, the number flux of SSA particles is roughly 10−100 cm^{-2}·s^{-1}.[8,187] If a 1 km boundary layer height and a 5-day lifetime for SSA are assumed, this range in the number flux of SSA would support a background number concentration of 40−400 particles·cm^{-3}.

The SSA mass flux is dominated by inorganic sea salts with 99% of the mass in a size range with (dry) diameters greater than 1 μm.[180] Most of the mass less than 1 μm is from the tail of the sea salt mass distribution centered around 3 μm.[188] If 5% of the submicrometer SSA mass is organic,[47] based on the model results of Jaegle et al.,[180] the SSA organic flux is approximately 3 Tg C·year^{-1}. Other model estimates for submicrometer SSA organic flux range from 2 to 298 Tg C·year^{-1}.[182−184]

Clarke et al.[8] estimate that in regions with little continental impact, the SSA flux contributes 5−90% of the CCN in the marine boundary layer, with the remainder coming from the free troposphere via entrainment. In regions with little continental impact, many of the free troposphere particles result from gases that are emitted from the ocean and oxidized in the free troposphere.[8] Thus, it is of interest to compare the gas and particulate fluxes of organic carbon from the ocean to the atmosphere. The dominant organic carbon gas-phase emission from the ocean to the atmosphere is in the form of dimethylsulfide (DMS).[189] The DMS flux has been extensively studied over the past 25 years and is estimated at 19 Tg C·year^{-1} (25 Tg S·year^{-1}).[189] DMS is a major source of sulfate aerosol globally[190] but is also oxidized to methanesulfonic acid (MSA). If the average molar ratio of MSA/SO$_4^{2-}$ from DMS oxidation is 0.2,[191] DMS oxidation contributes about 0.6 Tg C to secondary organic aerosol via MSA. Most of the carbon associated with DMS will be oxidized to CO$_2$ and will not contribute to aerosol mass.[1] Similarly, the ocean flux of CH$_4$ to the atmosphere (0.3 Tg C·year^{-1})[192] will not contribute to aerosol mass. Facchini et al.[193] and Müller et al.[194] have reported monomethylammonium, dimethylamine, and diethylamine in submicrometer particles over the north Atlantic and at Cape Verde, respectively. The combined concentrations were an order of magnitude less than that of MSA, suggesting an amine carbon flux from the ocean of roughly 0.06 Tg C·year^{-1}. Isoprene and monoterpene emissions from the ocean may contribute up to 1 Tg C·year^{-1} to the atmosphere.[195] The fraction of this gas-phase carbon that is converted to atmospheric particulate carbon is quite uncertain and the atmospheric oxidation products, most likely oxalate, make up only a few percent of the submicrometer OC aerosol.[41] Although the sum of these potential secondary sources of organic carbon from the ocean is highly uncertain, it is likely to be at the very lower end of the range of the SSA primary source.

7. FUTURE DIRECTIONS

Much remains to be learned about the connections between seawater properties (DOC composition, local biological activity, surfactants, etc.) and the composition of SSA. Many important questions remain, including the following:

(1) How do physical production mechanisms influence the chemical composition of sub- and supermicrometer SSA?

(2) How are production mechanisms influenced by the biological and chemical properties of seawater and the SSML?

(3) What role do subsurface seawater and the SSML play in determining the composition of SSA?

(4) What are the specific classes of organic molecules in the SSML and SSA?

(5) What major classes of organic compounds move from bulk surface seawater and/or the SSML to SSA particles?

(6) Does the existence of a particular organic compound class in the SSML and/or SSA change as a function of the biogeochemical state of the seawater?

(7) What model compounds can be used in fundamental laboratory studies to better understand the physicochemical properties of SSA?

(8) How can the flux of SSA, including the organic fraction, best be parametrized in global-scale models to most accurately reflect the enrichment and climate impacts of organics in SSA?

(9) What is the role of gas-phase organic species emitted from the ocean in forming new aerosol or contributing to the growth of existing marine aerosol? How does the magnitude of this source of carbon to the atmosphere compare to the source of carbon from primary SSA production?

A combination of field and laboratory observations are required to answer these questions and inform and improve climate models. The most transformational results will be obtained by including the results from both the oceanic and atmospheric communities in observational and modeling efforts.

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Notes

The authors declare no competing financial interest.

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Douglas B. Collins received a B.A. in chemistry from Colgate University in 2008 and continued to the University of California at San Diego for an M.S. and Ph.D. in atmospheric and analytical chemistry, completed in 2014. His graduate work focused on the importance of aerosol chemistry and mixing state on the cloud nucleating properties of aerosols, including detailed studies of the production and physicochemical properties of sea spray aerosol. Douglas is currently a postdoctoral fellow at the University of California at San Diego with plans to pursue aerosol–climate interactions through remote measurements of the atmosphere.

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