



## RESEARCH LETTER

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## Key Points:

- Changes in seawater and sea spray composition did not strongly affect expected CCN concentrations
- Blooms may impact clouds more strongly through changes in aerosol flux or secondary chemistry
- Model parameterizations likely overestimate changes in cloud nuclei due to primary marine organics

## Supporting Information:

- Supporting Information S1

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## Phytoplankton blooms weakly influence the cloud forming ability of sea spray aerosol

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**Abstract** After many field studies, the establishment of connections between marine microbiological processes, sea spray aerosol (SSA) composition, and cloud condensation nuclei (CCN) has remained an elusive challenge. In this study, we induced algae blooms to probe how complex changes in seawater composition impact the ability of nascent SSA to act as CCN, quantified by using the apparent hygroscopicity parameter ( $\kappa_{\text{app}}$ ). Throughout all blooms,  $\kappa_{\text{app}}$  ranged between 0.7 and 1.4 (average  $0.95 \pm 0.15$ ), consistent with laboratory investigations using algae-produced organic matter, but differing from climate model parameterizations and *in situ* SSA generation studies. The size distribution of nascent SSA dictates that changes in  $\kappa_{\text{app}}$  associated with biological processing induce less than 3% change in expected CCN concentrations for typical marine cloud supersaturations. The insignificant effect of hygroscopicity on CCN concentrations suggests that the SSA production flux and/or secondary aerosol chemistry may be more important factors linking ocean biogeochemistry and marine clouds.

### 1. Introduction

Natural aerosol particles are responsible for the largest contribution to uncertainty in the aerosol indirect effect [e.g., Carslaw *et al.*, 2013; Tsigaridis *et al.*, 2013]. Understanding the properties and concentrations of aerosols that were dominant in the preindustrial atmosphere is key to understanding anthropogenic perturbations, since the relationship between aerosol and cloud droplet number concentrations is nonlinear; sensitivity of cloud droplet concentrations to present-day anthropogenic perturbations rests strongly on the preindustrial baseline [Ramanathan *et al.*, 2001]. Sea spray aerosol (SSA) is one of the most abundant types of natural aerosol globally and can play an important role in cloud formation and microphysics through their role as cloud condensation nuclei (CCN) [Feingold *et al.*, 1999; Gantt *et al.*, 2012; McCoy *et al.*, 2015; Twohy and Anderson, 2008].

Major ionic components of seawater ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$ ) have been found within marine cloud droplets and precipitation [Straub *et al.*, 2007; Twohy and Anderson, 2008; Woodcock, 1952], and SSA particles have been shown to influence the properties of marine stratocumulus clouds [Feingold *et al.*, 1999], especially in remote regions [Glantz, 2010]. While the chemical composition of SSA is highly complex [Quinn *et al.*, 2015], it is often roughly approximated as a mixture of inorganic and organic species [e.g., Roelofs, 2008], which can be modulated by marine microbial activity [Ault *et al.*, 2013; O'Dowd *et al.*, 2015; Wang *et al.*, 2015]. Using a simple two-component view of SSA composition and hygroscopicity, global model studies have shown that biogeochemical changes within the surface ocean can account for a change in marine CCN concentrations between  $-5\%$  and  $+50\%$ , depending on how aerosol mixing state and production flux are treated within the models in association with marine microbial activity [Meskhidze *et al.*, 2011; Tsigaridis *et al.*, 2013; Westervelt *et al.*, 2012]. SSA flux and chemical parameterizations would be most complete when informed by chemically and physically realistic experiments that control conditions around SSA particles specifically, yet attempt to approximate the complexity of marine biogeochemistry. The present study perturbed seawater chemistry through dynamic microbial ecosystem processes to examine chemically complex SSA particles [Lee *et al.*, 2015]. Using a plunging waterfall method, SSA particles were produced with physicochemical properties similar to those produced by breaking waves [Collins *et al.*, 2014; Stokes *et al.*, 2013].

The relative role of chemistry in determining CCN concentrations mostly centers on the magnitude of the change in  $\kappa_{\text{app}}$  compared with the magnitude of possible changes in the number size distribution of aerosol [Dusek *et al.*, 2006]. Rather than focusing on just the average composition of particles in the atmosphere, Wex *et al.* [2010a] illustrated conceptually that the mixing state of the chemical components of the aerosol population is a key component of the system, which has been shown in laboratory [Collins *et al.*, 2013; Schill *et al.*, 2015], field [Cubison *et al.*, 2008; Padro *et al.*, 2012], and modeling studies [Meskhidze *et al.*, 2011; Roelofs, 2008]. The strongest effect of composition in decreasing CCN activity occurs when the abundance of particle types, each with significantly different intrinsic hygroscopicity, vary with size and the less hygroscopic particles have smaller dry diameters than the more hygroscopic particles [Collins *et al.*, 2013; Wex *et al.*, 2010a].

This study aims to constrain the CCN-derived hygroscopicity of SSA as a function of biological activity within a set of laboratory-generated marine phytoplankton bloom experiments [Lee *et al.*, 2015]. Approaching the highly complex chemical system of SSA in a top-down manner is useful for gaining an understanding of the ensemble effect of all chemical changes to the system with respect, in this case, to the phase of biological activity in the microcosm. While a predictive understanding of the cloud activity of SSA requires a detailed understanding of the physical chemistry of the activating droplet, this study aims to broadly characterize the response of the CCN derived hygroscopicity of SSA to marine microbial processes. The relative importance of particle hygroscopicity in driving expected CCN concentrations from nascent SSA in the marine boundary layer is discussed and compared with the current climate model paradigm.

## 2. Methods

### 2.1. Measurement of the Hygroscopicity Parameter

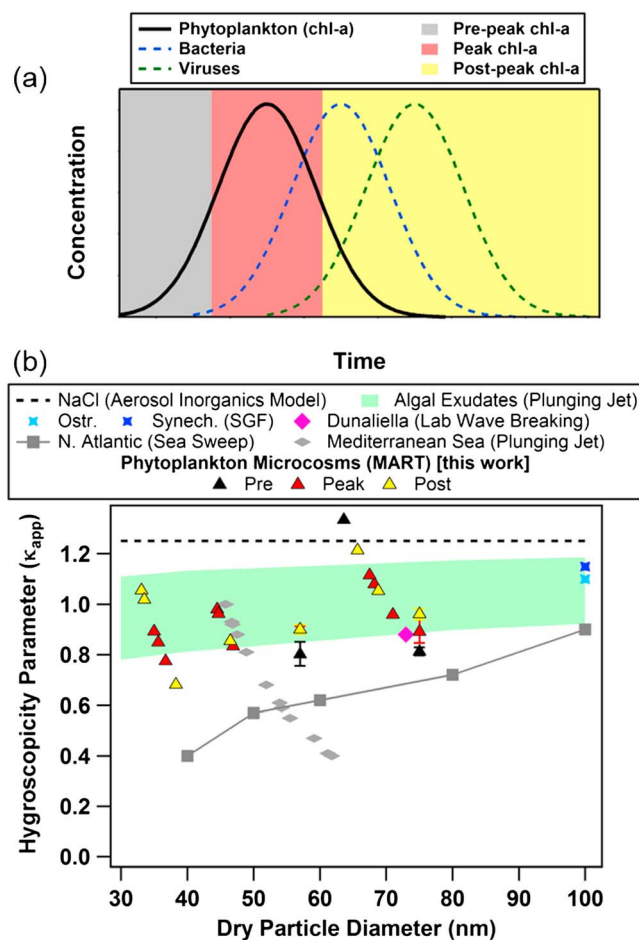
The hygroscopicity of nascent SSA particles was measured by using size-resolved CCN analysis. A dry, monodisperse aerosol is generated by selecting a specific size with an electrostatic classifier (TSI, Inc., Model 3080 L) operated with a sheath flow of 5 L/min and a total sample flow rate of 1 L/min. The monodisperse output of the electrostatic classifier was then split isokinetically to a continuous flow, stream-wise thermal gradient cloud condensation nucleus counter (CCNC; Droplet Measurement Technologies, Model CCN-100), and a condensation particle counter (TSI, Inc., Model 3010). The ratio of particles that activated into cloud droplets within the CCNC at a specified supersaturation ( $s$ ) was used to determine the activation diameter ( $D_{\text{act}}$ ) of the aerosol sample, where 50% of the particles are cloud-active. The  $D_{\text{act}}$  and  $s$  pairs determined by this method were used to calculate the hygroscopicity parameter ( $\kappa$ ) [Petters and Kreidenweis, 2007] using equation (1):

$$\kappa_{\text{app}} = \frac{4A^3 \sigma_{lv}^3}{27T^3 D_{\text{act}}^3 \ln^2(s)} \quad (1)$$

where  $A = 8.69251 \times 10^{-6} \text{ K m}^3 \text{ J}^{-1}$ ,  $\sigma_{lv}$  is the surface tension of the liquid/vapor interface of the droplet, and  $T$  is the temperature. This relatively simple formulation of the hygroscopicity parameter is an approximation [Petters and Kreidenweis, 2007, 2013], but deviations in  $\kappa$  derived from this calculation in comparison with numerical methods are much smaller than experimental uncertainties ( $\kappa \pm 10\%$ ). While  $\kappa$  strictly parameterizes only the Raoult's law term of the Kohler equation [Petters and Kreidenweis, 2007], the surface tension of the activating droplet is assumed to be constantly that of pure water ( $72 \text{ mN m}^{-1}$ ) for consistency across studies [e.g., Padro *et al.*, 2012; Sullivan *et al.*, 2009], as the surface tension of droplets at activation is difficult to quantify [Ruehl *et al.*, 2012]. Especially in cases where droplet surface tension is of potential importance to the observations,  $\kappa$  is often labeled as "apparent" ( $\kappa_{\text{app}}$ ) [Sullivan *et al.*, 2009] when surface tension is assumed constant. If changes in surface tension were to impact CCN activation, the coupled influence of the surface tension and solvent activity would be essentially lumped together within  $\kappa_{\text{app}}$ . The apparent hygroscopicity convention was adopted in this study in light of the high degree of chemical complexity and the relatively weak degree of physicochemical characterization of SSA particles to date [Quinn *et al.*, 2015].

### 2.2. Sample Preparation

This study evaluated the CCN activity of nascent SSA particles generated during a series of marine biological microcosm experiments. The methodology and detailed analysis of certain biological and chemical aspects of this type of experiment was described in detail by Lee *et al.* [2015], but a brief explanation will be given here. For each experiment, a sample of natural, coastal seawater was obtained, filtered by using 50  $\mu\text{m}$  Nitex mesh (Sefar Nitex 03-100/32), and allowed to equilibrate thermally with the laboratory overnight. The seawater



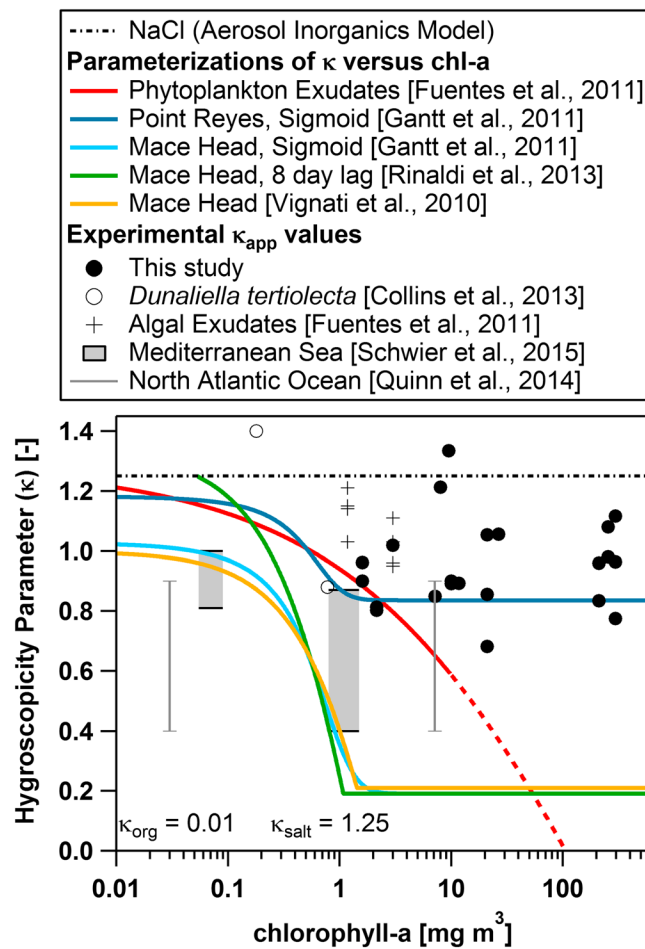
**Figure 1.** (a) General scheme for the growth of phytoplankton, bacteria, and viruses within a MART microcosm with prepeak chl *a*, peak chl *a*, and post-peak chl *a* periods labeled. (b) Hygroscopicity of nascent SSA particles from a variety of laboratory and field studies, segregated by dry particle diameter. Measurements presented in this study are shown as triangles; colors are coordinated with Figure 1a. The method by which the sample was generated is shown in parentheses. Data from the North Atlantic are from Quinn *et al.* [2014]; *Ostreococcus* (Ostr.) and *Synechococcus* (Synech.) are from Moore *et al.* [2011] (highest organic matter concentrations) and *Dunaliella tertiolecta* monoculture from Collins *et al.* [2013]. Shading for algal exudates from Fuentes *et al.* [2011] and Wex *et al.* [2010b] represents the range of values obtained from various algae utilized. Key details on each study are noted in the text.

Three laboratory-generated phytoplankton bloom microcosm experiments were conducted within a MART system from which size- and supersaturation-resolved CCN active fractions of SSA particles were quantified (see the supplemental information). Dry particle diameter and critical supersaturation pairs were used to calculate  $\kappa_{app}$  for a variety of time points along each bloom microcosm experiment. The data are separated into three general periods: prebloom (after nutrient addition), peak chl *a*, and postbloom (Figure 1a). Overall,  $\kappa_{app}$  averaged  $0.95 \pm 0.15$  ( $1\sigma$ ) with a range of 0.7–1.4 for all sizes studied (Figure 1b). Measurements of hygroscopicity in laboratory experiments utilizing complex organic matrices like the present study and that of Fuentes *et al.* [2011] lack full agreement with in situ SSA generation studies performed in the North Atlantic [Quinn *et al.*, 2014] and the Mediterranean Sea [Schwier *et al.*, 2015] (Figure 1b, gray markers). Differences in production method between this study and Quinn *et al.* [2014] were ruled out by direct comparison of the sintered diffusion stone [Bates *et al.*, 2012] and MART waterfall methods in the same seawater (Figure S2 in the supporting information), as expected based on the findings of Fuentes *et al.* [2010b]. The aforementioned in situ

sample was added to a Marine Aerosol Reference Tank (MART) [Stokes *et al.*, 2013], at which point control measurements were made. Guillard's *f/2* growth medium with sodium metasilicate [Guillard and Ryther, 1962] was added to the seawater, and light was supplied continuously ( $70 \mu\text{E m}^{-2} \text{s}^{-1}$ ) to stimulate algae growth. The seawater was mixed and aerated by introducing large bubbles of filtered air into the bottom of the tank through 3 mm diameter Tygon tubing. When the chlorophyll *a* (chl *a*) concentration in the seawater reached an empirically determined threshold of approximately  $12 \text{ mg m}^{-3}$ , SSA particle generation was commenced. SSA was generated by using the plunging waterfall mechanism of the MART [Stokes *et al.*, 2013] for 2 h periods, wherein the waterfall was "pulsed" with a duty cycle of 4 s ON and 4 s OFF to simulate the episodic nature of a breaking wave in the open ocean [Collins *et al.*, 2014]. Six, 2 h periods of SSA generation were performed each day until about 7 days past the time where chl *a* concentrations in the seawater bulk returned to baseline values. CCN activity measurements presented in this study were conducted at least 3 times and at most once per day during each microcosm experiment.

## 3. Results and Discussion

### 3.1. Hygroscopicity of Sea Spray From Laboratory Phytoplankton Blooms



**Figure 2.** Selected SSA organic mass fraction parameterizations based on measured ocean surface chl *a* concentration, translated into  $\kappa$  values (see supporting information). Measured  $\kappa_{app}$  values from this and prior studies of nascent SSA have been superimposed for comparison.

[Collins *et al.*, 2013; Fuentes *et al.*, 2011; Moore *et al.*, 2011; Wex *et al.*, 2010b] use algae-produced organic matter samples that were static in composition and produced in monoculture. Any chemical differences documented between samples in those studies are related to either organic matter concentration or source organism. In contrast, the present study differs importantly from previous efforts due to the use of the Microbial Loop to induce temporally dynamic organic matter composition changes in the seawater through natural biochemical interactions between marine organic matter and the biological community in the seawater [Azam *et al.*, 1983; Lee *et al.*, 2015]. Several groups have posited that chl *a* (a metric for phytoplankton biomass) may not be a universal basis for parameterizing the properties of nascent SSA [Quinn and Bates, 2011; Wang *et al.*, 2015] and that microbial processes are of great importance to shaping the composition and physicochemical properties of nascent SSA [Ault *et al.*, 2013; Collins *et al.*, 2013; O'Dowd *et al.*, 2015; Prather *et al.*, 2013; Wang *et al.*, 2015]. With such arguments in mind, the present study quantified the CCN-derived  $\kappa_{app}$  values of SSA produced from a stimulated dynamic ecosystem that was initiated from 50  $\mu\text{m}$  filtered coastal seawater. While phytoplankton exudate production was likely the most influential process controlling organic matter composition in monoculture-based studies [Collins *et al.*, 2013; Fuentes *et al.*, 2011; Moore *et al.*, 2011; Wex *et al.*, 2010b], the bloom microcosm experiments presented in this study include biochemical processes (e.g., enzyme activity) that influence the organic matter dynamics throughout this type of experiment [Riemann *et al.*, 2000]. Important organic matter processes include not only those associated with primary productivity, like exudate production, but also processes associated with algae senescence, such as predation by bacteria and viruses, heterotrophic bacterial productivity and

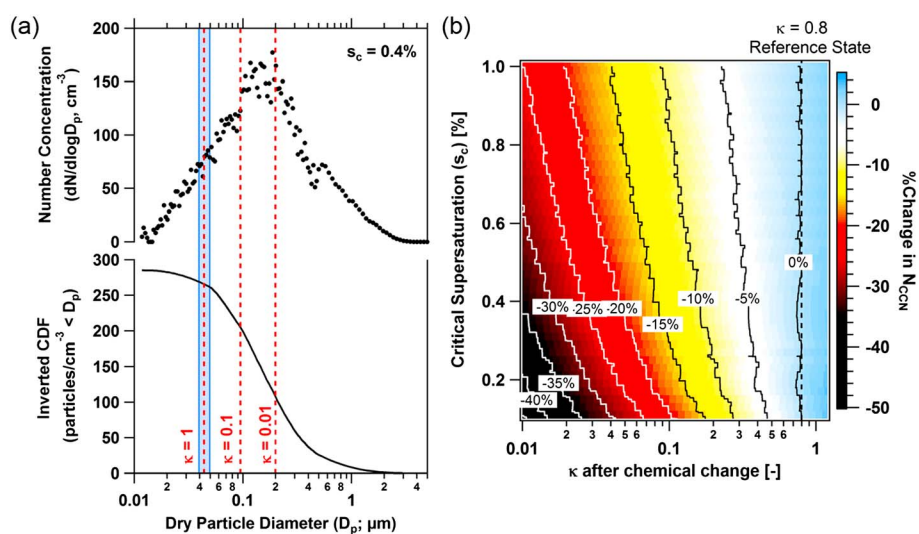
studies also disagree with one another with respect to the response of  $\kappa_{app}$  to biological activity metrics (e.g., chl *a*): the observations of Schwier *et al.* [2015] indicate that  $\kappa_{app}$  of SSA was only slightly less sensitive to biological activity than current parameterizations [e.g., Gantt *et al.*, 2011; Rinaldi *et al.*, 2013] would have predicted, whereas Quinn *et al.* [2014] observed little-to-no relationship between chl *a* and  $\kappa_{app}$  for freshly produced SSA. Discrepancies between studies using natural seawater could be ascribed to regional differences in organic matter composition and/or microbial community composition.

The range of  $\kappa_{app}$  values obtained in this study agrees well with other laboratory studies of SSA generated from chemically complex, algae-dominated seawater samples (Figure 2) [Collins *et al.*, 2013; Fuentes *et al.*, 2011; Moore *et al.*, 2011; Wex *et al.*, 2010b]. For particles with  $D_p < 120$  nm, all studies on such systems to date have indicated that the CCN-derived  $\kappa_{app}$  were greater than 0.7 [cf. Collins *et al.*, 2013, Table 1, and references therein]. It should be noted that the previous laboratory studies presented in comparison to the work described herein

metabolism, cell lysis, and bacterial enzyme activity [Azam and Malfatti, 2007; Pomeroy et al., 2007]. Using a similar chemical system, prior laboratory studies have shown that bacterial processing could be important to SSA composition, mixing state, and physicochemical properties [Ault et al., 2013; Collins et al., 2013; Prather et al., 2013; Wang et al., 2015]. In particular, Collins et al. [2013] showed that bacterial growth on ZoBell media in natural seawater was associated with a major decrease in CCN-derived  $\kappa_{\text{app}}$ , yet additions of algae monocultures to both bacteria-rich seawater and fresh coastal seawater yielded much smaller depressions of SSA hygroscopicity, similar to the present study. Bacterial processing of ZoBell media, rich in peptone and yeast extract, appears to have had a stronger effect on  $\kappa_{\text{app}}$  of SSA than did bacterial degradation of natural algae-produced organic matter, known to be rich in carbohydrates. Comparison of these two mesocosm/microcosm studies, along with the aforementioned comparison between the present study and those of Schwier et al. [2015] and Quinn et al. [2014], suggests that the specific chemical composition of organic matter may influence the relationship between  $\kappa_{\text{app}}$  and marine microbial activity.

In general agreement with the bloom experiments presented herein, a recent study by Schill et al. [2015] showed a lack of change in the CCN-derived hygroscopicity of SSA for experiments wherein various representative proxy compounds for marine organic matter were sequentially added to a MART containing artificial seawater, resulting in an ultimate organic matter concentration of 350  $\mu\text{M}$ C. The final concentration of this “artificial bloom” experiment was similar to the total organic carbon concentration found in the phytoplankton bloom experiments in the present study (Figure S1). Overall, studies using state-of-the-art SSA production methods that range from additions of a few simple proxy compounds to those utilizing complex, phytoplankton-based organic systems have illustrated a common range of CCN-derived hygroscopicity for freshly emitted SSA particles between  $\kappa_{\text{app}} = 0.7\text{--}1.4$ .

The apparently small consequence of changing marine biological activity on the CCN-derived  $\kappa_{\text{app}}$  of SSA in this study may be related to the mechanism of organic enrichment in SSA particles [Quinn et al., 2015; Russell et al., 2010; Wang et al., 2015]. The insoluble and/or amphiphilic nature of the organic components of SSA [Facchini et al., 2008] have led to model studies assigning  $\kappa_{\text{org}} < 0.1$  [Meskhidze et al., 2011; Westervelt et al., 2012]. In the surface ocean, about 60–75% of organic molecules are less than 1 kDa [Benner, 2002]. With an average molecular weight cited around 4370 kg kmol<sup>-1</sup> [Moore et al., 2008], marine organic matter would, conversely, have an expected  $\kappa_{\text{org}}$  value of about 0.006 [Petters et al., 2009, equation (3)]. The bubble-mediated SSA production process is well known to be chemically selective [e.g., Hoffman and Duce, 1976], and it has been shown that SSA has a different composition than the seawater from which it formed [Quinn et al., 2015]. Detailed chemical studies have shown that the composition of SSA particles with  $D_p < 1 \mu\text{m}$  is dominated by fatty acids [e.g., Cochran et al., 2016; Frossard et al., 2014; Wang et al., 2015], suggesting that the surface tension of droplets formed from SSA particles could be smaller than that of pure water. Decreased surface tension ( $\sigma_{\text{IV}}$ ) due to the addition of surface active organic material would cause  $\kappa_{\text{app}}$  to remain higher than if only the solute properties of the organic component were acting on the system alone, as  $\sigma_{\text{IV}}$  is held at 72 mN m<sup>-1</sup> in equation (1) for  $\kappa_{\text{app}}$  by definition. To be clear, the true role of surface tension in cloud droplet activation is under current scrutiny [e.g., Farmer et al., 2015; Petters and Kreidenweis, 2013; Prisle et al., 2008; Ruehl et al., 2016]. The potential importance of  $\sigma_{\text{IV}}$  for SSA particle CCN activation is suggested based on current knowledge of particle composition and the repeated experimental determinations of hygroscopicity in this study with elevated marine organic matter present. Close inspection of the findings of one experiment in this study (Figures 2 and S2) reveals a 12–18% increase in  $\kappa_{\text{app}}$  during a subset of the bloom microcosm experiments. If such an increase in  $\kappa_{\text{app}}$  was due to changes in droplet surface tension, it would align with the increasing prevalence surface active compounds during the “peak chl *a*” and “post senescence” periods of algae blooms [Cochran et al., 2016; Zutic et al., 1981]. Overall, an analysis of the  $\kappa_{\text{app}}$  values from this study indicated that the apparent organic volume fraction ( $\epsilon_{\text{app,org}}$ ) of the SSA particles was less than 0.4 ( $D_p = 30\text{--}80 \text{ nm}$ ) (see the supporting information), whereas measured organic fractions approaching unity have been noted in nascent SSA particles with  $D < 200 \text{ nm}$  [Facchini et al., 2008; Prather et al., 2013]. Such discord between CCN-derived organic content and more direct measures of SSA organic content could indicate the influence of surface tension on cloud droplet activation. Generally speaking, the senescent period of an algae bloom is characterized by a high diversity of biogeochemical processes within microbial ecosystems [Azam and Malfatti, 2007; Pomeroy et al., 2007], which has been shown to have important impacts on the composition and the enrichment of organic matter in SSA



**Figure 3.** (a) Number size distribution of nascent SSA from wave breaking (top) and the “inverted” cumulative distribution (CDF) of the same data (bottom). The inverted CDF is the integral of the size distribution between a size ( $D_p$ ) and the upper limit of the distribution. When evaluated at the activation diameter ( $D_{act}$ ), the inverted CDF represents the number concentration of CCN expected ( $N_{CCN}$ ). The vertical red dashed lines indicate  $D_{act}$  for a  $\kappa$  value that is labeled at the base of the figure when  $s_c = 0.4\%$ . The blue shaded band indicates the full range of  $\kappa_{app}$  values (0.7–1.4) observed in the MART microcosm bloom experiments. (b) Percentage change in total  $N_{CCN}$  for the wave breaking size distribution when considering a hypothetical change in hygroscopicity from a reference state of  $\kappa = 0.8$  to the value shown on the horizontal axis. The contour lines are superimposed to help guide the eye; the line color changes from black to white only to maximize contrast.

particles [Lee *et al.*, 2015; O’Dowd *et al.*, 2015], including an enrichment of fatty acids in the aerosol [Cochran *et al.*, 2016; Wang *et al.*, 2015].

### 3.2. Comparison With Primary Marine Organic Aerosol Parameterizations

Ambient aerosol measurements in the marine boundary layer have suggested a relationship between biological activity in the surface ocean and the organic mass fraction of marine aerosol [O’Dowd *et al.*, 2004]. Analysis of submicron aerosol organic mass fraction data from coastal sites, mainly focused on a single long-term sampling effort at Mace Head, Ireland, has produced a series of proposed relationships between chl *a* and the submicron organic matter fraction in SSA [Fuentes *et al.*, 2010a; Gantt *et al.*, 2011; O’Dowd *et al.*, 2008; Rinaldi *et al.*, 2013; Vignati *et al.*, 2010]. Global models use these source function parameterizations to derive not only the organic fraction of SSA but also can further calculate physicochemical property parameters from the known organic mass fraction in the aerosol, provided some assumptions. As discussed above, the hygroscopicity parameter can be derived from the organic volume fraction of the aerosol. Figure 2 shows the  $\kappa_{app}$  values determined in this and similar studies superimposed on the assumed  $\kappa$  values as a function of chl *a* concentration for a variety of organic mass fraction parameterizations (see the supporting information). Most parameterizations underestimated  $\kappa$  in comparison with experiments at nearly all chl *a* concentrations studied experimentally. It should be noted that most of the parameterizations were derived from conditions where chl *a* < 5 mg m<sup>-3</sup>, and most of the experimental data in this study had chl *a* > 10 mg m<sup>-3</sup> due to technical considerations [Lee *et al.*, 2015]. Still, the CCN activity of SSA in these experiments was not well approximated by the existing organic mass fraction parameterizations. Bulk composition data (and parameterizations derived therefrom) may not be suited to predict the properties of nascent SSA particles as CCN. Unpredicted CCN behavior could result from uncertainties in the interactions of SSA particles with water during cloud droplet activation [Moore *et al.*, 2011; Ovadnevaite *et al.*, 2011] or the insensitivity of aerosol mass measurements to detailed chemical changes in aerosols at CCN-relevant sizes.

### 3.3. Sea Spray Aerosol Size Distributions and CCN Concentrations

In order to connect (intensive) aerosol physicochemical properties with the (extensive) expected CCN number concentrations ( $N_{CCN}$ ) at a particular supersaturation, one must closely inspect the size distribution of particles [Dusek *et al.*, 2006]. Figure 3 shows the size distribution and size-resolved cumulative distribution

function (CDF) of SSA generated by a laboratory breaking wave, which is nearly identical in shape to the aerosol size distribution generated by the plunging waterfall within the MART [Collins *et al.*, 2014; Stokes *et al.*, 2013]. Superimposed on the size distribution are three vertical dashed lines that correspond to  $D_{\text{act}}$  for  $\kappa$  values of 1, 0.1, and 0.01, respectively. Changes in hygroscopicity which lead to changes in  $D_{\text{act}}$  that span the peak in the size distribution correspond to the highest sensitivity of  $N_{\text{CCN}}$  to changes in  $\kappa$ . Since the range of values measured in this study range was between  $\kappa_{\text{app}} = 0.7\text{--}1.4$ , a change in  $D_{\text{act}}$  (or  $\kappa_{\text{app}}$ ) from one extreme of this range in  $\kappa_{\text{app}}$  to the other (blue vertical band in Figure 3) would not lead to a large changes in  $N_{\text{CCN}}$ . If SSA particle composition changed enough to shift the hygroscopicity through the whole range in  $\kappa_{\text{app}}$  observed in the phytoplankton bloom microcosm experiments described in this study (as a liberal estimate), the corresponding change in  $N_{\text{CCN}}$  would be less than 3% for supersaturations relevant to marine clouds ( $s_c \leq 1\%$ ). Hence, based on these experiments, one would expect the composition of nascent SSA particles to have a small effect on  $N_{\text{CCN}}$  over the ocean.

If biogeochemically induced changes in SSA particles were to have a significant impact on cloud properties in remote marine regions [e.g., McCoy *et al.*, 2015; Quinn and Bates, 2011], it is most likely derived from changes in the size-resolved emission rate of particles [Alpert *et al.*, 2015; Fuentes *et al.*, 2010a] or through biogenic secondary processes acting on primary SSA [Charlson *et al.*, 1987; Lana *et al.*, 2012]. Size-resolved studies of the production flux of SSA particles have been done previously [de Leeuw *et al.*, 2011; Lewis and Schwartz, 2004] with results that vary to a degree that can strongly influence the findings of global model studies [Tsigaridis *et al.*, 2013]. Alpert *et al.* [2015] recently used a plunging water jet system to generate SSA from seawater, in which a phytoplankton bloom was grown, similar to the present study. It was found that the production flux increased approximately threefold for particles with  $D_p < 200$  nm during the bloom. Based on the  $\kappa_{\text{app}}$  values measured in this and comparable studies (Figure 1), the upper limit value of  $D_{\text{act}}$  for nascent SSA would be 125 nm ( $s_c = 0.1\%$ ,  $\kappa_{\text{app}} = 0.7$ ). An increase in SSA flux such as that observed by Alpert *et al.* [2015] would therefore translate to an increased flux of CCN as well. Fuentes *et al.* [2010a] and Schwier *et al.* [2015] also showed that regions of the ocean with higher chl *a* led to a greater production flux of particles during in situ controlled SSA production experiments using plunging water jet systems. It should be noted that recent studies have shown that the formation of a thick foam within laboratory SSA generators through continuous bubble production (like the continuous plunging water jet apparatus) can strongly influence the size distribution and composition of the aerosol when seawater organic matter concentrations are high [Collins *et al.*, 2014; King *et al.*, 2012]. The “pulsed” operation of the MART used in this study reduces the buildup of foam by mimicking the episodic behavior of waves in the open ocean [Collins *et al.*, 2014]. None of the aforementioned SSA flux studies gave an explicit characterization of foam within the SSA generator during organic matter-dependent flux studies; future studies are encouraged to monitor surface conditions. Still, increasing concentrations of particles with  $D_p > D_{\text{act}}$  would explain a primary marine contribution to correlated chl *a* and cloud drop number concentrations that have been noted in the Southern Ocean [e.g., McCoy *et al.*, 2015; Meskhidze and Nenes, 2006], especially considering the small changes in hygroscopicity observed herein.

#### 4. Conclusions

The range of CCN-derived hygroscopicity for nascent SSA particles generated in a controlled environment by using a pulsed plunging waterfall technique during a set of phytoplankton bloom microcosm experiments was quantified in this study. The overall value of  $\kappa_{\text{app}}$  was observed to remain greater than 0.7 for all experiments, with an average of 0.95. In general, these results compare well with chemically simpler laboratory studies, in which SSA particles were generated from seawater samples doped with algae-produced organic matter, suggesting that overall impacts of biological activity on SSA  $\kappa_{\text{app}}$  values are relatively weak. The shape of the size distribution from a breaking wave (and from the MART plunging waterfall) dictates that changes in hygroscopicity within the range observed in this study would only account for up to 3% change in  $N_{\text{CCN}}$  for typical marine cloud supersaturations. However, alterations to the SSA production flux for  $D_p > D_{\text{act}}$  could help explain observed correlations between biological activity and cloud properties in remote oceanic regions. This is especially evident in light of the relatively small changes in  $\kappa_{\text{app}}$  associated with large increases in the organic matter concentration and/or status of biological activity of the seawater from which the SSAs were generated. Continued characterization of the SSA production flux under different marine biogeochemical states using state-of-the-art SSA generators is warranted. Careful accounting of the production

of foam within such generators is highly recommended to ensure that conditions for SSA production are well characterized. Chemically characterized effects on the size-resolved number flux of particles from the ocean and reconciliation of the discrepancies between production of SSA from in situ studies and those from laboratory experiments should be priorities for the field.

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