Phytoplankton Blooms Weakly Influence the Cloud Forming Ability of Sea Spray Aerosol

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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

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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 using the apparent hygroscopicity parameter (κ_{app}). Throughout all blooms, κ_{app} ranged between 0.7 – 1.4 (average 0.95 ± 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 κ_{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.

Index Terms: 0305 Aerosols and particles, 0315 Biosphere/atmosphere interactions, 0320 Cloud physics and chemistry, 0312 Air/sea constituent fluxes, 3311 Clouds and aerosols

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 pre-industrial atmosphere is key to understanding anthropogenic perturbations, since the relationship between aerosol and cloud droplet number concentrations is non-linear; sensitivity of cloud droplet concentrations to present-day anthropogenic perturbations rests strongly on the pre-industrial 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 (Na^+, K^+, Mg^{2+}, 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 κ_{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 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 using size-resolved CCN analysis. A dry, monodisperse aerosol is generated by selecting a specific size with an electrostatic classifier (TSI, Inc., Model 3080L) operated with a sheath flow of 5 liters per minute and a total sample flowrate of 1 liter per minute. 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 (CPC; 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_{act}) of the aerosol sample where 50% of the particles are cloud-active. The D_{act} and s pairs determined by this method were used to calculate the hygroscopicity parameter (κ) [*Petters and Kreidenweis*, 2007] using Equation 1:

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

where $A = 8.69251 \times 10^{-6}$ K m^3 J^{-1} and σ_{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 κ derived from this calculation in comparison with numerical methods are much smaller than experimental uncertainties ($\kappa \pm 10\%$). While κ 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 mN m^{-1}) for consistency across studies [e.g., *Padró 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, κ is often labeled as 'apparent' (κ_{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 κ_{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 using 50 µm Nitex mesh (Sefar Nitex 03-100/32), and allowed to equilibrate thermally with the laboratory overnight. The seawater 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 to and light was supplied continuously to (ca. 70 µE m^{-2} 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 mg m^{-3}, SSA particle generation was commenced. SSA was generated using the plunging waterfall mechanism of the MART [*Stokes et al.*, 2013] for two-hour periods, wherein the waterfall was 'pulsed' with a duty cycle of 4 seconds ON and 4 seconds OFF to simulate the episodic nature of a breaking wave in the open ocean [*Collins et al.*, 2014]. Six, 2 hour 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

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 Supplemental Information). Dry particle diameter and critical supersaturation pairs were used to calculate κ_{app} for a variety of time points along each bloom microcosm experiment. The data are separated into three general periods: pre-bloom (after nutrient addition), peak chl-a, and post-bloom (Figure 1a). Overall, κ_{app} averaged 0.95 ± 0.15 (1σ) 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), as expected based on the findings of *Fuentes et al.* [2010b]. The aforementioned *in situ* studies also disagree with one another with respect to the response of κ_{app} to biological activity metrics (e.g., chl-a): the observations of *Schwier et al.* [2015] indicate that κ_{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 κ_{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 κ_{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 κ_{app} were greater than 0.7 (c.f. Table 1, *Collins et al.* [2013] and references therein). It should be noted that the previous laboratory studies presented in comparison to the work described herein [*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 κ_{app} values of SSA produced from a stimulated dynamic ecosystem that was initiated from 50 μm 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 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 κ_{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 κ_{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] suggest that the specific chemical composition of organic matter may influence the relationship between κ_{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 µM 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 $\kappa_{app} = 0.7 – 1.4$.

The apparently small consequence of changing marine biological activity on the CCN-derived κ_{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 κ_{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^{-1} [*Moore et al.*, 2008], marine organic matter would, conversely, have an expected κ_{org} value of about 0.006 [Eq. 3, *Petters et al.*, 2009]. 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 µm 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 (σ_{lv}) due to the addition of surface active organic material would cause κ_{app} to remain higher than if only the solute properties of the organic component were acting on the system alone, as σ_{lv} is held at 72 mN m^{-1} in Equation 1 for κ_{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 σ_{lv} 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 κ_{app} during a subset of the bloom microcosm experiments. If such an increase in κ_{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 κ_{app} values from this study indicated that the apparent organic volume fraction ($\varepsilon_{app,org}$) of the SSA particles was less than 0.4 (D_p = 30 – 80 nm) (see Supplemental Information), whereas measured organic fractions approaching unity have been noted in nascent SSA particles with D < 200 nm [*Facchini et al.*, 2008; *Prather et al.*, 2013]. Such discord between CCN-derived organic content with more direct measures of CCN 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 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 κ_{app} values determined in this and similar studies superimposed on the assumed κ values as a function of chl-a concentration for a variety of organic mass fraction parameterizations (see Supplemental Information). Most parameterizations underestimated κ 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^{-3}, and most of the experimental data in this study had chl-a > 10 mg m^{-3} 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 3 vertical dashed lines that correspond to D_{act} for κ values of 1, 0.1, and 0.01, respectively. Changes in hygroscopicity which lead to changes in D_{act} that span the peak in the size distribution correspond to the highest sensitivity of N_{CCN} to changes in κ. Since the range of values measured in this study range was between κ_{app} = 0.7 – 1.4, a change in D_{act} (or κ_{app}) from one extreme of this range in κ_{app} to the other (blue vertical band in Figure 3) would not lead to a large changes in N_{CCN}. If SSA particle composition changed enough to shift the hygroscopicity through the whole range in κ_{app} observed in the phytoplankton bloom microcosm experiments described in this study (as a liberal estimate), the corresponding change in N_{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_{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 generated SSA from seawater in which a phytoplankton bloom was grown, similar to the present study. It was found that the production flux increased approximately 3-fold for particles with D_p < 200 nm during the bloom. Based on the κ_{app} values measured in this and comparable studies (Figure 1), the upper limit value of D_{act} for nascent SSA would be 125 nm (s_c = 0.1%, κ_{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 $D_p > D_{act}$ 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 using a pulsed plunging waterfall technique during a set of phytoplankton bloom microcosm experiments was quantified in this study. The overall value of κ_{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 κ_{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_{CCN} for typical marine cloud supersaturations. However, alterations to the SSA production flux for $D_p > D_{act}$ 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 κ_{app} associated with large increases in the organic matter concentration and/or status of biological activity of the seawater from which the SSA 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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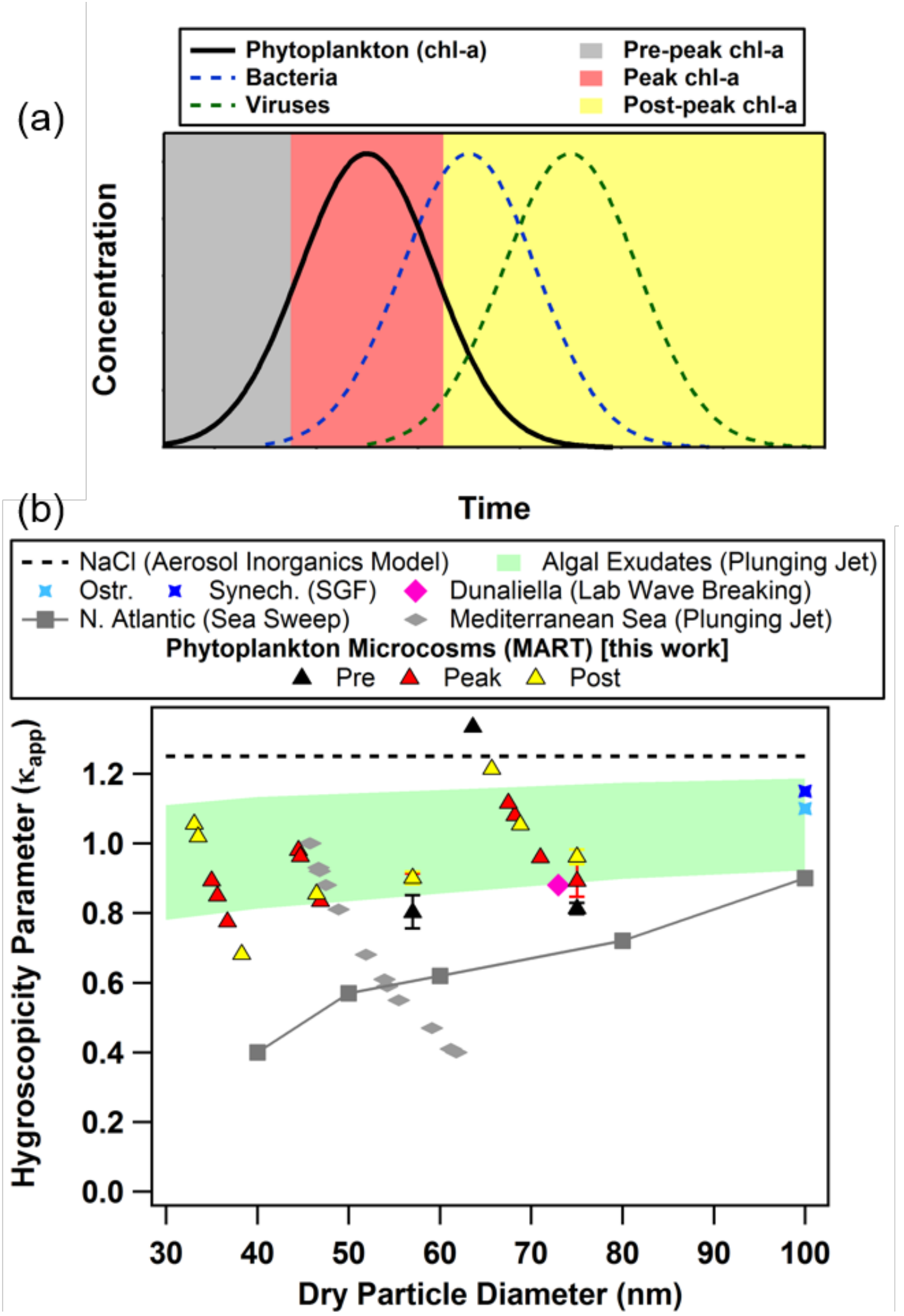
Figure 1: (a) General scheme for the growth of phytoplankton, bacteria, and viruses within a MART microcosm with Pre-peak chl-a, Peak chl-a, and Post-peak chl-a periods labeled. (b) Hygroscopicity of nascent SSA particles from a variety of laboratory and field studies, segregated by dry particle diameter. Measurements presented in this study are shown as triangles; colors are coordinated with (a). 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.

Figure 2: Selected SSA organic mass fraction parameterizations based on measured ocean surface chl-a concentration, translated into κ values (see Supporting Information). Measured κ_{app} values from this and prior studies of nascent SSA have been superimposed for comparison.

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 κ value that is labeled at the base of the figure when s_c = 0.4%. The blue shaded band indicates the full range of κ_{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 κ = 0.8 to the value shown on the horizontal axis. Contour lines are superimposed to help guide the eye; line color changes from black to white only to maximize contrast.



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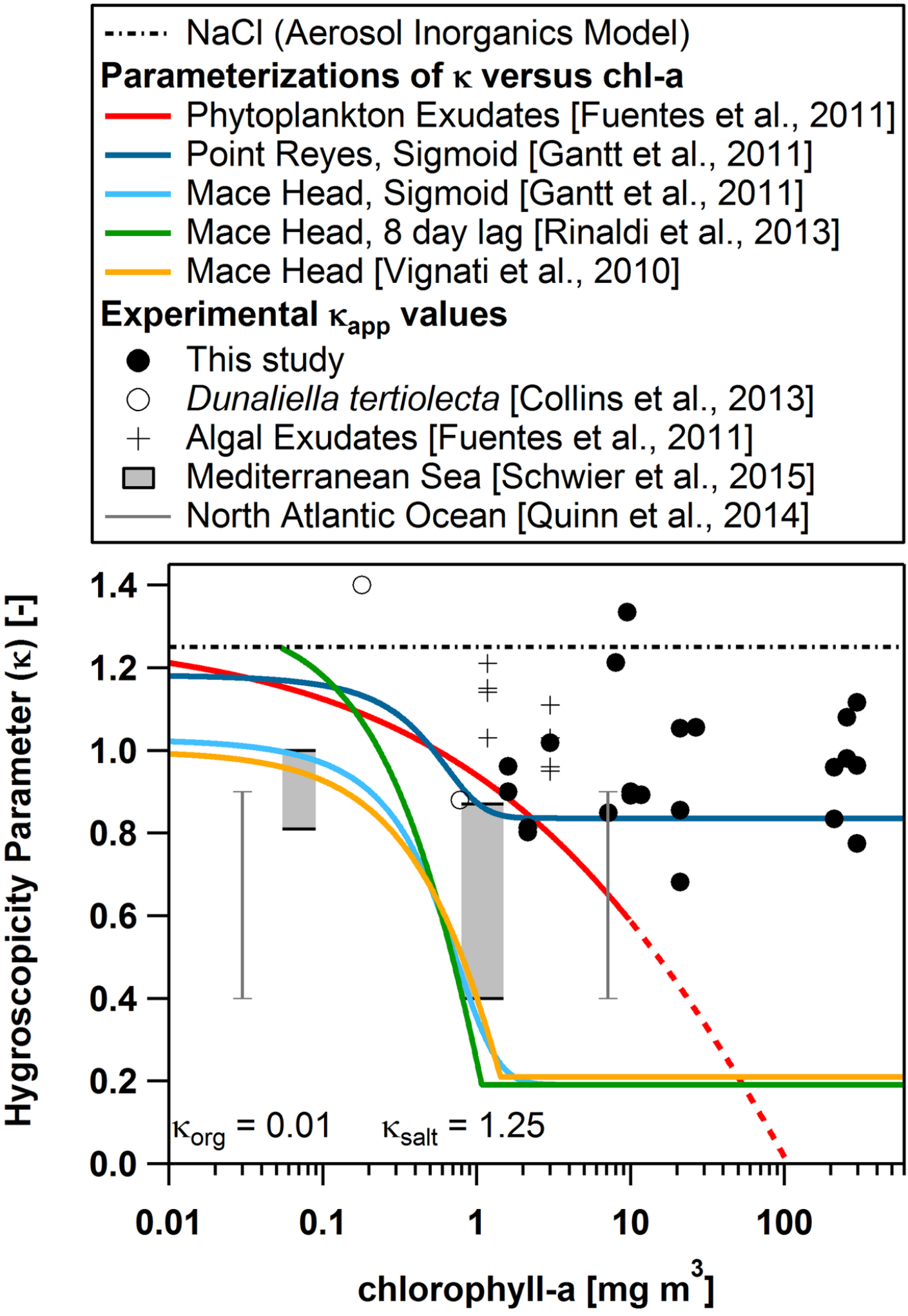

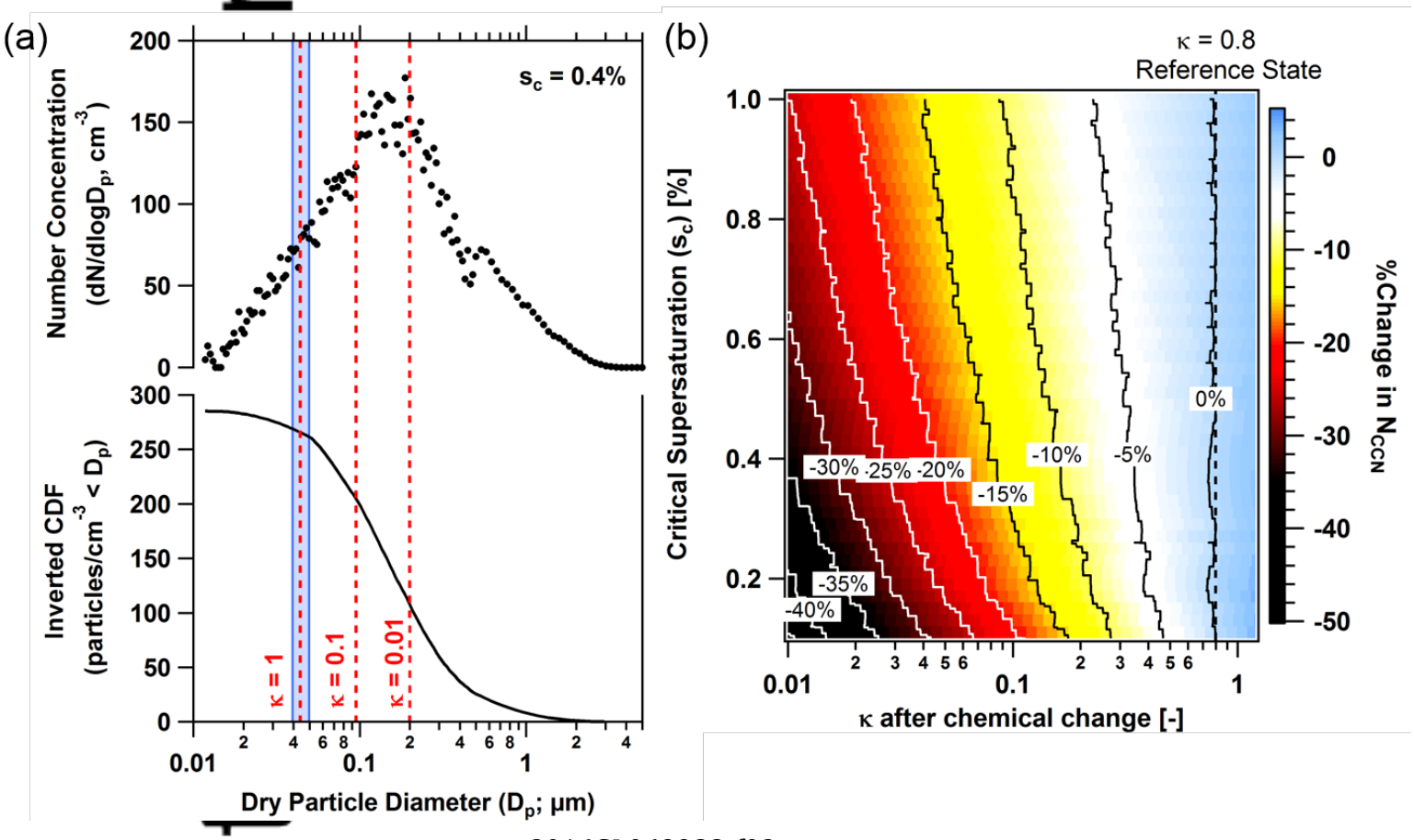

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