Supplemental Information for “Phytoplankton Blooms Weakly Influence the Cloud Forming Ability of Sea Spray Aerosol”

Douglas B. Collins[1‡], Timothy H. Bertram[2], Camille M. Sultana[1], Christopher Lee[1], Jessica L. Axson[1,‖], Kimberly A. Prather[1,3,*]

[1]*Department of Chemistry and Biochemistry, University of California, San Diego;* [2]*Department of Chemistry, University of Wisconsin – Madison;* [3]*Scripps Institution of Oceanography, University of California, San Diego*

[‡]Now at: Department of Chemistry, University of Toronto

[‖]Now at: Department of Environmental Health Science, University of Michigan

*Corresponding Author: Kimberly A. Prather, kprather@ucsd.edu

Mailing Address: 9500 Gilman Drive M/C 0314, La Jolla, CA 92093-0314

1 Phytoplankton Microcosm Experiments

Protocols for conducting phytoplankton bloom experiments has been described in detail previously, including detailed measurements of biologically and chemically relevant seawater state parameters. [*Lee et al.*, 2015] This type of experiment was conducted to investigate the influence of dynamic biochemical processes on the properties of sea spray aerosol (SSA) as cloud condensation nuclei (CCN). Basic water measurements of chlorophyll and organic matter for three experiments presented in this study have been presented in Figure S1. Measurements of the CCN active fraction of particles for size- and supersaturation-selected SSA particles are presented in Figures S2 and S3.

Figure S1: Chlorophyll-a concentrations (green) and dissolved or total organic matter concentrations (black) in the seawater of three bloom experiments. CCN activity measurements for (a) are shown in Figure S3a-c, those for (b) are shown in Figure S3d-e, and those for (c) are shown in Figures 2 and S2. The shaded regions indicate the time periods in which SSA were generated and daily CCN measurements were conducted.

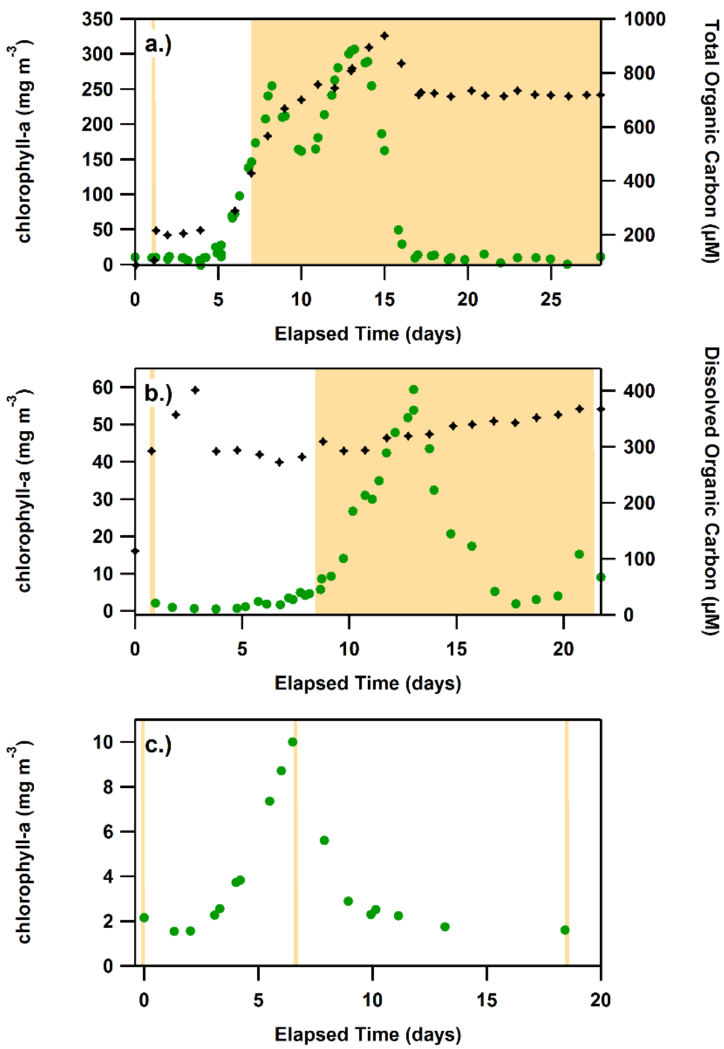


Figure S2: Supersaturation-resolved fraction of CCN active particles at specific dry particle sizes for aerosol produced in a MART using the 'Sea Sweep' diffusion stone [*Bates et al.*, 2012]. Critical supersaturations at each size are consistent with those determined by plunging waterfall on the same water samples. SSA generated by each method were generated using the same volume of seawater within a period of four hours. The mobility diameter (d_m) selected by the electrostatic classifier (see Section 2.1 of main text) is shown at the top of each panel, along with the corresponding physical diameter (d_p; shape factor = 1.06), which was used in Figure 1 and in the computation of κ_{app}.

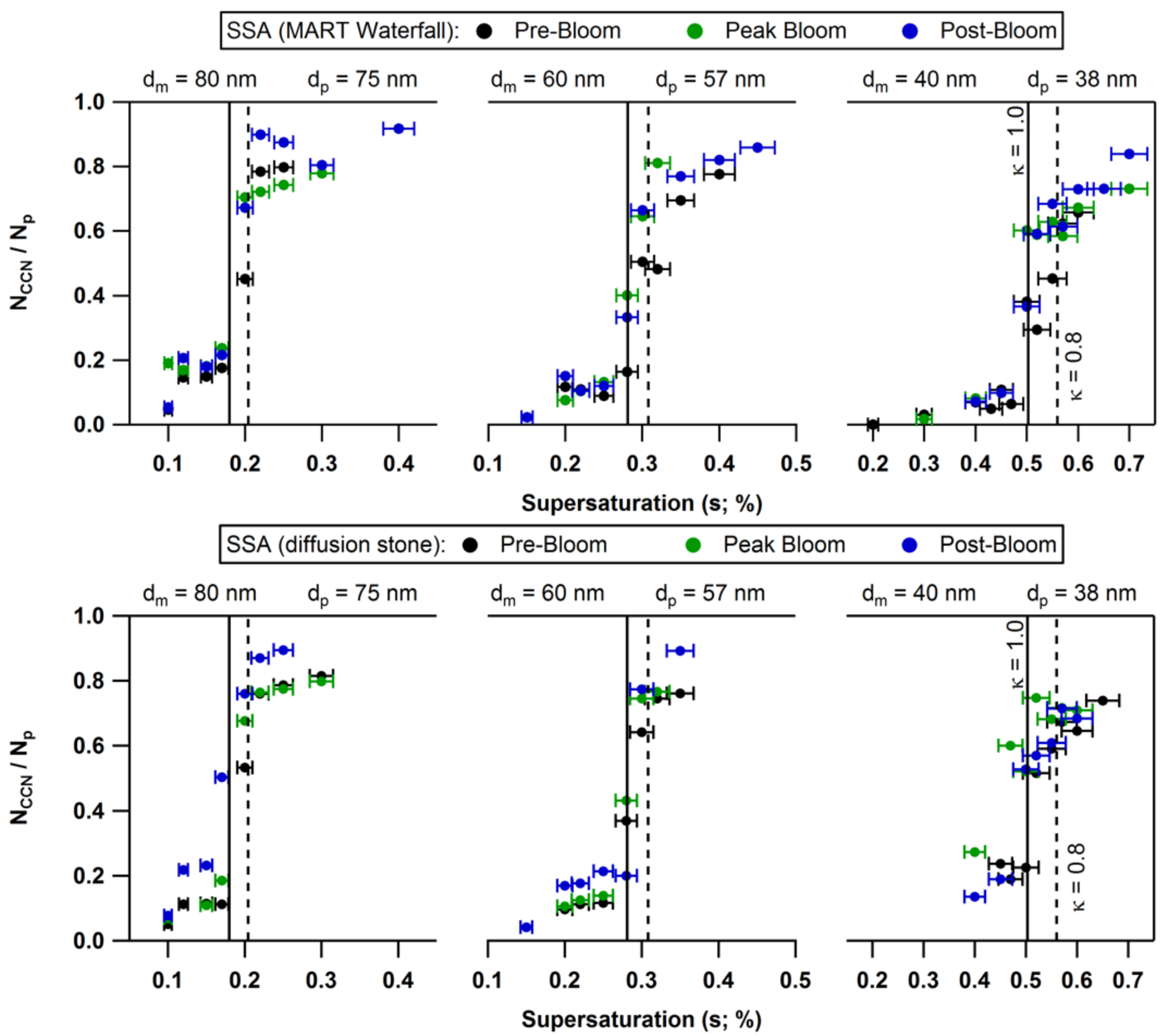


Figure S3: Size-resolved fraction of CCN active particles at specific supersaturations from two different phytoplankton bloom experiments. Seawater measurements for (a) – (c) are shown in Figure S1a, and seawater measurements for (d) and (e) are shown in Figure S1b. A sigmoid curve representing κ_{app} = 1.25 is shown for reference, with the limits of the shaded region showing activation curves of κ_{app} = 1 and κ_{app} = 1.5 for visual reference.

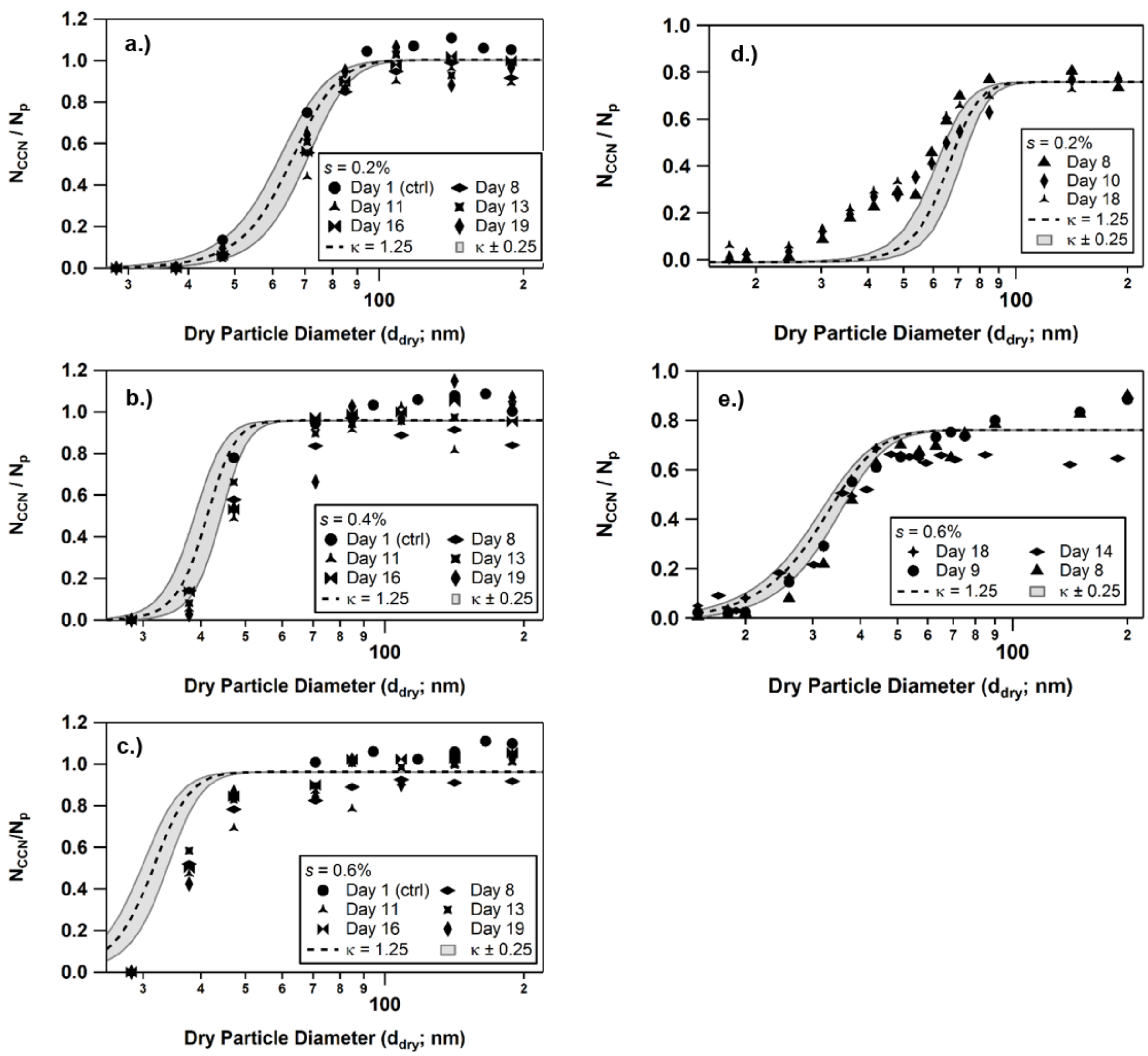


Table S1: Tabulated CCN-derived hygroscopicity data used within Figures 1 and 2. Experiment ID corresponds to the panel label in Figure S1. Days Elapsed reflects the number of days elapsed in the experiment at the time of measurement since the addition of growth media.

Activation Diameter (D_{act}; nm)	Critical Supersaturation (s_c; %)	κ_{app}	Chlorophyll-a (mg m^{-3})	Experiment ID [Fig S1]	Days Elapsed
63.6	0.2	1.334	9.52	A	1
68.2	0.2	1.08	254.56	A	8
44.5	0.4	0.98	254.56	A	8
71	0.2	0.959	210.5	A	11
46.9	0.4	0.834	210.5	A	11
44.7	0.4	0.963	296.5	A	13
36.7	0.6	0.775	296.5	A	13
67.5	0.2	1.116	296.5	A	13
68.8	0.2	1.054	21	A	16
46.5	0.4	0.855	21	A	16
38.3	0.6	0.682	21	A	16
65.65	0.2	1.213	8	A	19
35.6	0.6	0.849	7.15	B	8
35	0.6	0.893	11.71	B	9
33.1	0.6	1.056	26.55	B	14
33.5	0.6	1.019	3	B	18
57	0.304	0.802	2.15	C	0
75	0.2	0.813	2.15	C	0
57	0.287	0.9	9.99	C	6
75	0.19	0.891	9.99	C	6
57	0.287	0.9	1.6	C	18
75	0.184	0.961	1.6	C	18

2 CCN-Derived Hygroscopicity Parameter and Relationship to Organic Volume Fraction

Hygroscopicity parameter values can be translated to organic volume fraction using the linear mixing rule as follows [*Petters and Kreidenweis*, 2007]:

$$\kappa_{app} = \kappa_{salt}\varepsilon_{app,salt} + \kappa_{org}\varepsilon_{app,org} \qquad [S1]$$

where κ_{salt} and κ_{org} represent the intrinsic hygroscopicities of the salt and organic SSA components, respectively, and ε represents the volume fraction of each component if all particles are assumed to have an identical, average mixed salt/organic composition. It is important to note that all quantities inferred from κ_{app} must also be considered 'apparent', hence the use of the ε_{app} notation in Equation S1. Table S2 shows the values of $\varepsilon_{app,org}$ for a range of κ_{org} between 0.001 – 0.1. As a point of reference, *Westervelt et al.* [2012] assigned κ_{org} = 0.09 for marine organics in their model based on a laboratory study by *Moore et al.* [2008]. A prior study reported measurements of ε_{org} from a collection of individual SSA particles, showing ε_{org} ~ 0.4. CCN-derived $\varepsilon_{app,org}$ (s_c = 0.2%) showed agreement with directly-measured ε_{org} when a large fraction of SSA particles with D_p < 120 nm were salt/organic internal mixtures [*Collins et al.*, 2013]. CCN-derived $\varepsilon_{app,org}$ was less than 0.4 for all samples in the present study, which is within the range of volume fractions shown in the literature (ε_{org} = 0.3 – 0.7) [e.g., *Burrows et al.*, 2014; *Collins et al.*, 2013; *Fuentes et al.*, 2011; *O'Dowd et al.*, 2004; *Quinn et al.*, 2014; *Schill et al.*, 2015; *Schwier et al.*, 2015]. It is important to reiterate that the $\varepsilon_{app,org}$ values here are 'apparent'. The influence of surface tension may play a role in determining the 'true' hygroscopicity parameter, along with the inherent dependence of $\varepsilon_{app,org}$ on the value of κ_{app}, and to a lesser degree the choice of κ_{org}. Should surface tension depression play an important role in the cloud droplet activation of SSA particles, the 'true' κ value would be lower than κ_{app}, and the associated ε_{org} value would be higher than $\varepsilon_{app,org}$.

Table S2: Calculated apparent organic volume fractions ($\varepsilon_{app,org}$) using a range of κ_{org} values.

κ_{app}	κ_{salt}	κ_{org}	$\varepsilon_{app,org}$
0.8	1.25	0.1	0.39
0.8	1.25	0.01	0.36
0.8	1.25	0.001	0.36

3 Determination of Hygroscopicity from Organic Mass Fraction Parameterizations

Various studies have established parameterizations of the organic mass fraction of SSA particles based on the chlorophyll-a concentration in the surface ocean [*Fuentes et al.*, 2011; *Gantt et al.*, 2011; *O'Dowd et al.*, 2008; *Rinaldi et al.*, 2013; *Vignati et al.*, 2010]. The organic mass fraction of nascent sea spray aerosol (Figure S4a) can be translated into the hygroscopicity parameter given certain assumptions.

1. The aerosol population is treated as a homogenous set of particles that contain both salt and organic material as an internal mixture.
2. An intrinsic hygroscopicity parameter for each component is known.
3. The water uptake properties of the aerosol behave as a linear combination of its two components.

Since the linear mixing model for κ_{app} (Equation S1) assumes volume additivity, the organic mass fraction (f_{org}) should be converted into organic volume fraction (ε_{org}) using Equation S2:

$$\varepsilon_{org} = \frac{f_{org}}{\left(f_{org} + (1 - f_{org})\left(\frac{\rho_{org}}{\rho_{salt}}\right)\right)} \qquad [S2]$$

where ρ_{org} and ρ_{salt} are the densities of the organic and salt fractions, respectively. In this study, $\rho_{org} = 1.4$ g cm^{-3} and $\rho_{salt} = 2.2$ g cm^{-3}; the results of this conversion are shown in Figure S4b.

The intrinsic κ values for each component were then selected in accordance with the known value for sea salt-dominated aerosol (κ_{salt} = 1.25; c.f. Table 1, [*Collins et al.*, 2013]) and an estimated value for marine-derived organic matter that has been used in model studies (κ_{org} = 0.01; [e.g., *Westervelt et al.*, 2012]). A simple sensitivity analysis was conducted on the intrinsic hygroscopicity of the organic fraction (Figure S5) where κ_{org} was assigned values of 0.1 and 0.001, similar to the calculation in Table 1. Since κ_{salt} is large and ε_{org} is less than 0.8 in all of the parameterizations, the choice of κ_{org} has a minimal impact on the overall findings.

Figure S4: (a) Selected primary organic mass fraction parameterizations from the literature. The parameterization by [*Fuentes et al.*, 2011] is shown for [chl-a] < 10 mg m^{-3} as a solid line, and has been extrapolated (dashed line) beyond the range shown by the original authors to accommodate the wide range of chl-a concentrations explored in the present study. (b) Organic mass fraction has been translated to organic volume fraction (ε_{org}) according to Equation S2.

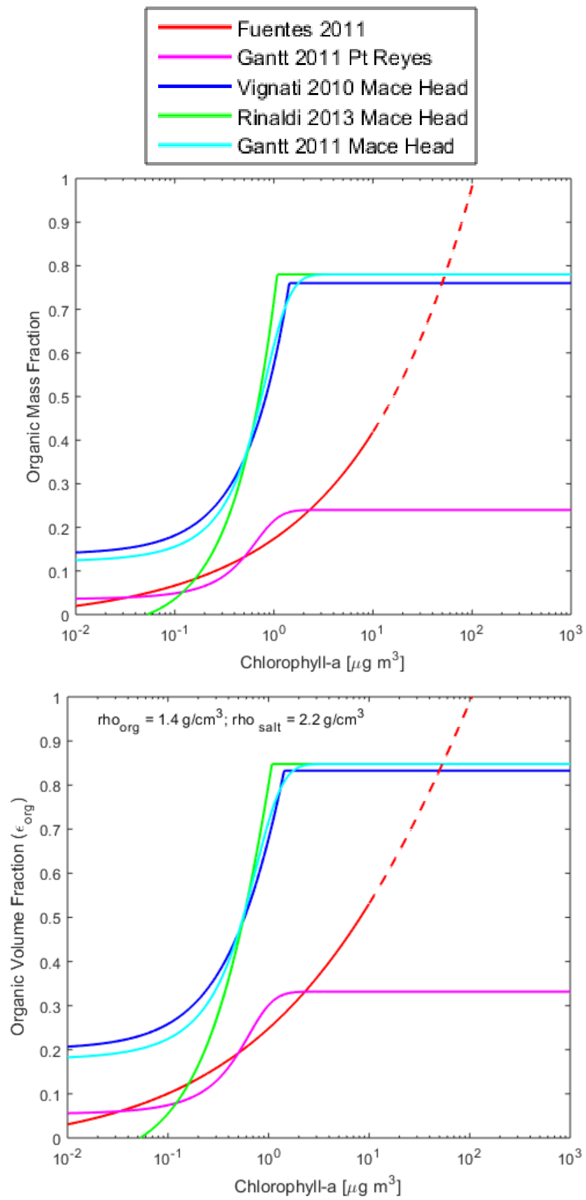
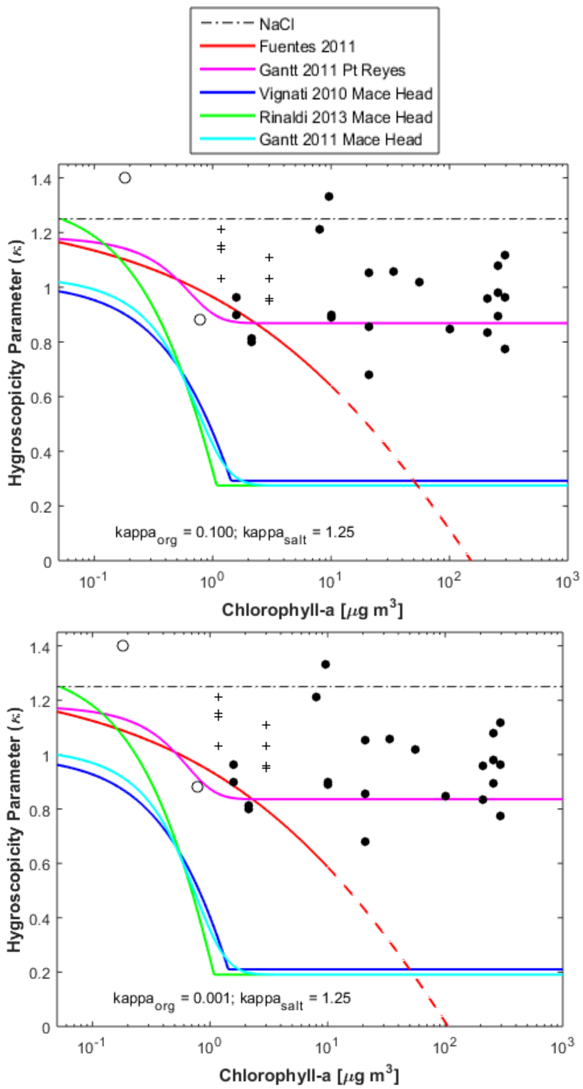


Figure S5: Sensitivity analysis of the comparison between the model parameterizations and measured κ_{app} when varying κ_{org}. As in Figure 3, solid circles are data reported in this study, open circles are from the algae-only experiment in [*Collins et al.*, 2013], and crosses are from [*Fuentes et al.*, 2011].



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