Reproducing the Chemical Complexity of Sea Spray Aerosols in a Laboratory Setting

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Supporting Information

MART photobioreactor microcosm method

The Southern California Coastal Ocean Observing System (www.sccoos.org), a seawater monitoring system off the coast of southern California, was used to monitor ocean conditions. When ocean condition parameters such as salinity, sea surface temperature, and chlorophyll-a concentration were within the location's monthly mean values, seawater was collected using a cleaned bucket tied to a hoist at the end of Scripps Pier (275 m offshore) located in Scripps Institution of Oceanography, University of California, San Diego. Seawater was filtered using 50 µm Nitex mesh prior to filling the MART. The 50 µm filtration removed any grazers that feed on phytoplankton without altering other microbial species. Fresh seawater was added to a MART system that had been previously cleaned with ethanol or isopropanol and triple rinsed with deionized water.

Once the MART was filled, control measurements utilizing the freshly collected seawater were performed, after which nutrients were added to the desired concentration. Another set of control measurements were performed immediately after nutrient addition to account for the change in seawater chemical composition due to the growth media. It was found empirically that longer periods of aerosol generation led to insignificant phytoplankton growth, likely due to phytoplankton cell damage in the centrifugal pump used to circulate water through the plunging waterfall aerosol generation apparatus.[1] Phytoplankton growth was initiated by illuminating the nutrient-doped seawater with two full spectrum fluorescent lamps (5700 K blackbody temperature; Full Spectrum Solutions, 205457). During this initial growth period, water was mixed and aerated by gently bubbling the sample by forcing particle-free air at 1 liter per minute

through 4-6 Tygon tubes (1/8 inch inside diameter) that were held on the bottom of the MART by glass weights.

Once sufficient phytoplankton cell density was reached, determined empirically to be approximately 12 mg chlorophyll m^{-3}, the bubbler system was removed and the MART was sealed. The headspace of the MART was then purged with particle-free air. With the MART purged of background particles, verified with a Condensation Particle Counter (TSI 3010), the aerosol measurements were performed as described in the methods section. Aerosols were generated with a two hours on, two hours off schedule. During aerosol generation, the waterfall was operated with a 4 seconds on and 4 seconds off duty cycle to simulate the episodic nature of natural breaking waves.[1-3] ATOFMS measurements were performed daily until at least one week past the return of chlorophyll-a concentrations to that of the freshly collected seawater, in order to capture chemical changes due to the biochemical processes associated with marine bacteria and viruses. Each microcosm experiment lasted about 24 to 28 days total.

In vivo chlorophyll-a measurements were made at least once daily, and samples of the bulk seawater for DOC, EEM measurements, and epifluorescence microscopy cell counts were taken once daily. Samples for EEM analysis were analyzed the day of sampling. EEM excitation and emission wavelengths ranged from 235-450 nm and 213-620 nm, respectively. EEM spectra were blank subtracted using ultrapure water. Spectra were also corrected for inner-filter effects and Rayleigh scatter masked (1^{st} and 2^{nd} order). To calibrate the EEM measurements, each spectrum was normalized to the area of the water Raman scatter peak at 350 nm taken daily and are reported in Raman Units (R.U.).[4-5] Bulk seawater samples for epifluorescence microscopy were taken daily, but SML and SSA particle samples for epifluorescence microscopy were taken every two days. Fluorescence microscopy samples were pipetted into sterile cryogenic vials and

preserved with glutaraldehyde (0.05% electron microscopy grade). After an incubation period of 15 minutes at approximately 4 ^{o}C, samples were flash frozen with liquid nitrogen and kept at -80 ^{o}C until analysis.

Date	*Chlorophyll-a (mg m^{-3})*	*Water Temp. (^{o}C)*	*Pressure (dbar)*	*Salinity (PSU)*	*Tank Notation*
7/11/13 12:00	0.837	21.0916	4.132	33.6435	A
9/10/13 18:00	2.029	17.2773	5.542	33.4388	D
11/7/13 15:00	3.709	15.8678	5.171	33.4449	B
12/1/13 12:00	n/a	n/a	n/a	n/a	C
1/5/2014 16:30	1.346	15.0671	5.116	33.5286	E
4/11/2014 12:00	4.491	14.3358	3.508	33.4264	F

Table S1. Select metrics for the chemical conditions of the coastal Pacific Ocean at the time of seawater collection for each experiment. Data from SCCOOS were not available for the 12/1/13 collection (Tank C).

	Molar Concentration	
Components	f/2 (M)	f/20 (M)
$NaNO_3$	8.82×10^{-4}	8.82×10^{-5}
$NaH_2PO_4 \cdot H_2O$	3.62×10^{-5}	3.62×10^{-6}
$Na_2SiO_3 \cdot 9H_2O$	1.06×10^{-4}	1.06×10^{-5}
$FeCl_3 \cdot 6H_2O$	1.17×10^{-5}	1.17×10^{-6}
$Na_2EDTA \cdot 2H_2O$	1.17×10^{-5}	1.17×10^{-6}
$CuSO_4 \cdot 5H_2O$	3.93×10^{-8}	3.93×10^{-9}
$Na_2MoO_4 \cdot 2H_2O$	2.60×10^{-8}	2.60×10^{-9}
$ZnSO_4 \cdot 7H_2O$	7.65×10^{-8}	7.65×10^{-9}
$CoCl_2 \cdot 6H_2O$	4.20×10^{-8}	4.20×10^{-9}
$MnCl_2 \cdot 4H_2O$	9.10×10^{-7}	9.10×10^{-8}
Thiamine HCl (vit. B_1)	2.96×10^{-7}	2.96×10^{-8}
Biotin (vit. H)	2.05×10^{-9}	2.05×10^{-10}
Cyanocobalamin (vit. B_{12})	3.69×10^{-10}	3.69×10^{-11}

Table S2. Tabulated concentrations of nutrients in the final volume of seawater for higher concentration (f/2) and lower concentration (f/20) nutrient additions. $Na_2SiO_3 \cdot 9H_2O$ is not part of the ProLine nutrient mix, and was added separately.

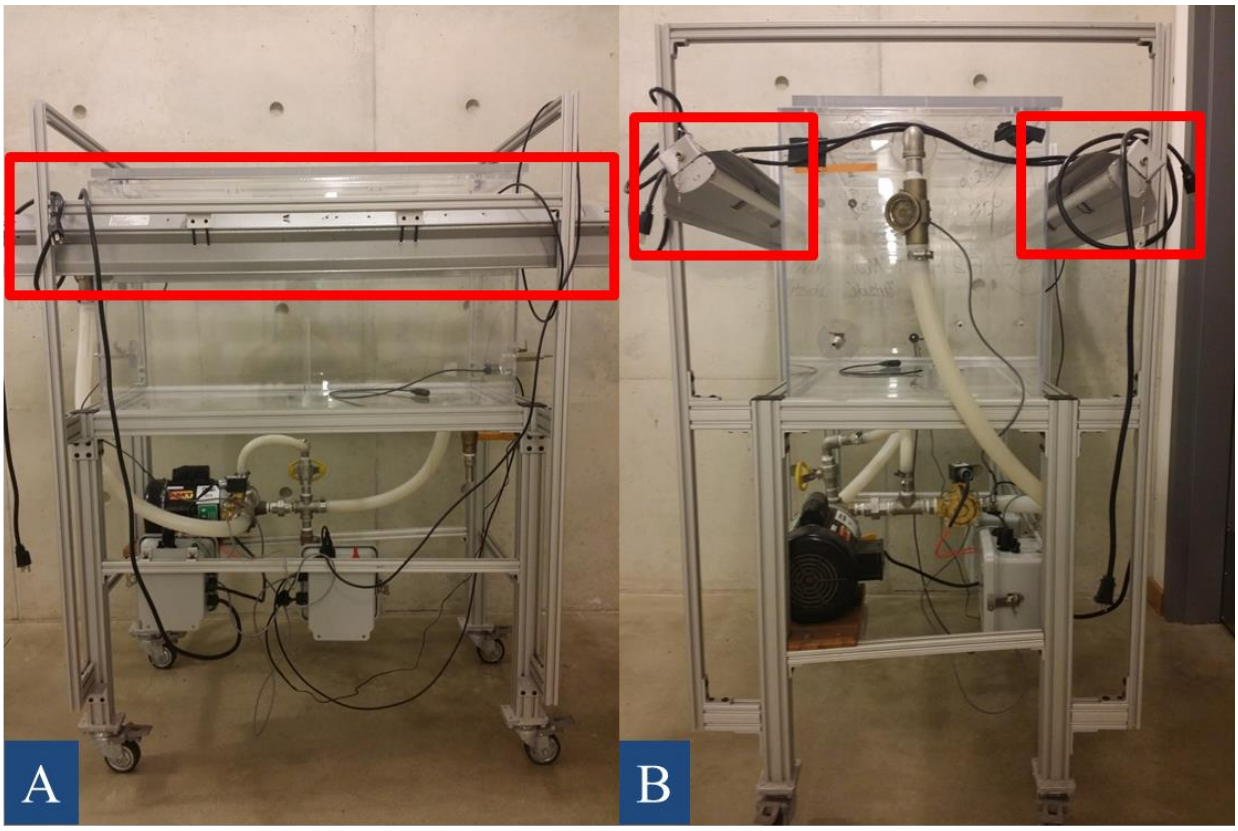

Figure S1. Picture of modified MART photobioreactor. Highlighted boxes are two fluorescent glow light fixtures that provide necessary illumination for growth of autotrophic microorganisms. A. front view and B. side view.

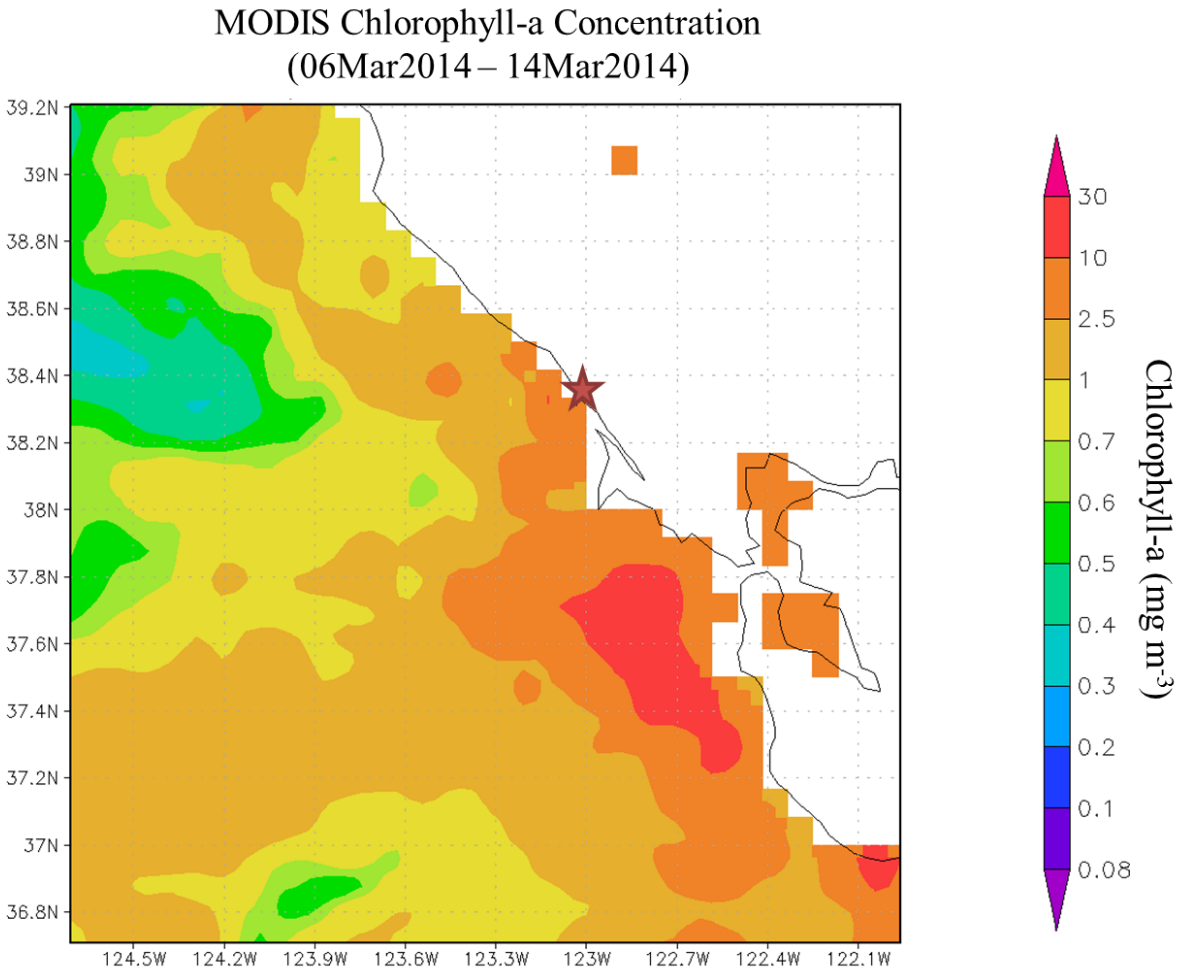

Figure S2. Satellite-derived ocean surface chlorophyll-a concentration (MODIS) in the vicinity of Bodega Bay, CA (red star). Chlorophyll-a concentration near the sampling location is ~ 2 mg m^{-3}. Wind direction and velocity measured at the time of sampling (313 ± 6 degrees 12.3 ± 1.7 m s^{-1}) suggest the air sampled is of primarily marine origin.

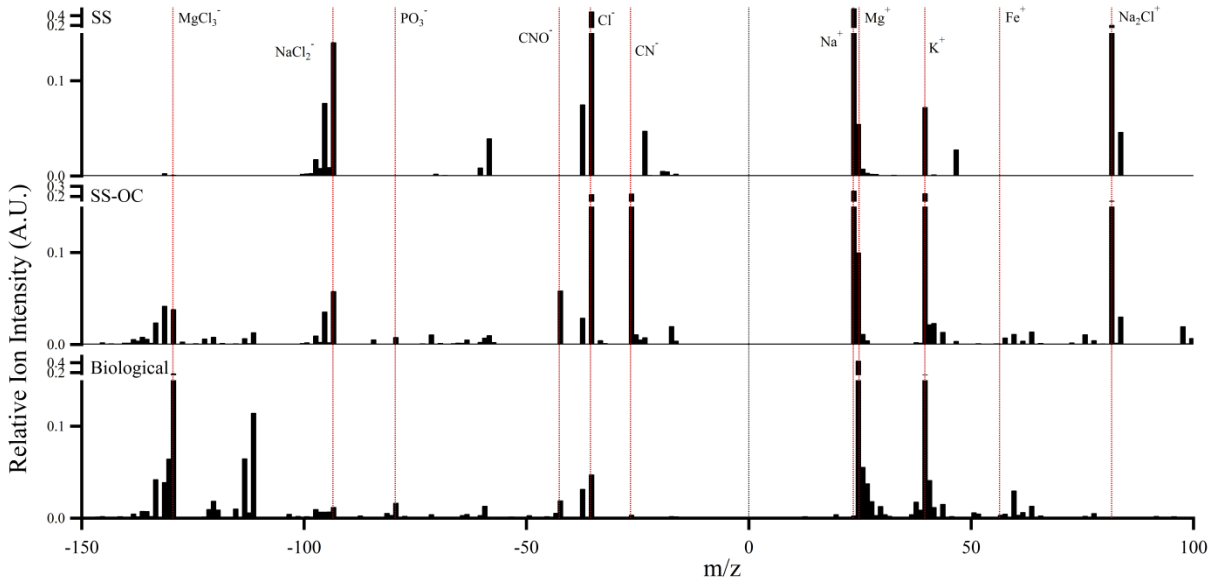

Figure S3. Representative dual polarity mass spectra of 3 main particle types from ATOFMS observed in the microcosm experiments. From top to bottom panels, sea salt (SS), sea salt-organic carbon (SS-OC), and Biological type particle spectra are shown respectively.

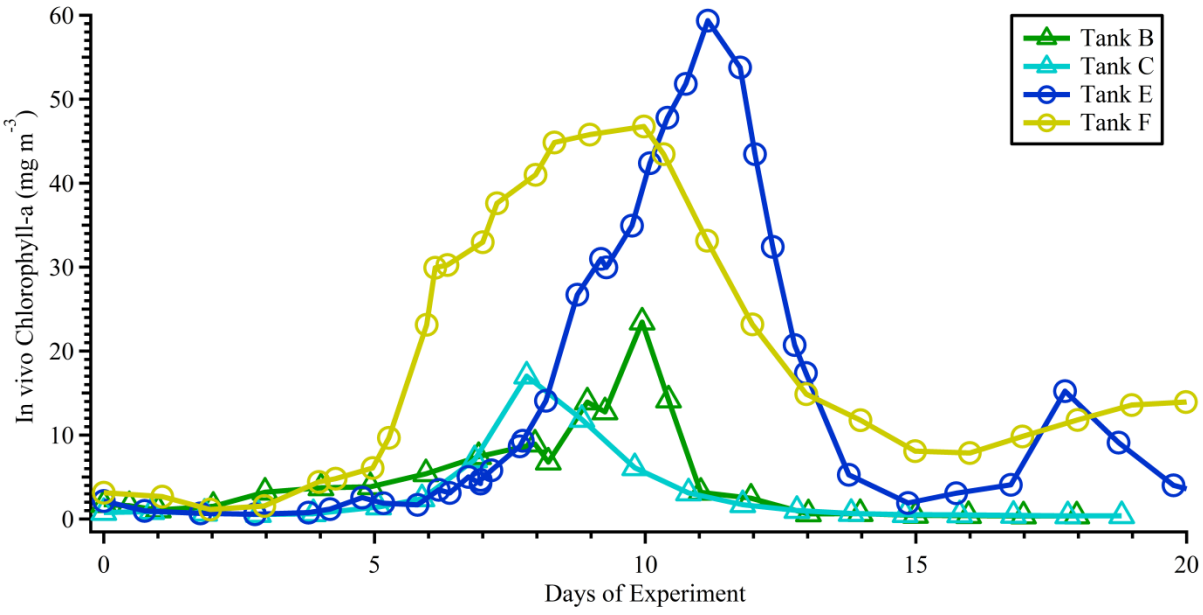

Figure S4. Compilation of absolute chlorophyll-a concentrations (mg m^{-3}) for four phytoplankton microcosms in this study (Tanks B, C, E, and F). Data from tanks A and D are not shown as the calibration for the chlorophyll-a concentration calculation during these two microcosms was not reliable. Initial chlorophyll-a concentrations for the two microcosms were provided by SCCOOS (Table S1).

References

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