

Supporting Information

Variability in Marine Plankton Ecosystems are not Observed in Freshly Emitted Sea Spray Aerosol

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Methods:

SSA Generation

SSA was generated with the PMEL Sea Sweep (Bates et al., 2012). Sea Sweep generates SSA *in-situ* by producing bubbles 0.75 m below the sea surface alongside the ship. A curtain of particle free air prevents ambient air from entering the stainless steel hood above the bubbles. The nascent SSA particles produced when the bubbles burst at the ocean surface are drawn from the hood to aerosol instruments aboard the ship. With the ship slowly moving through the water (0.5 knots), the bubbled water is constantly replenished.

Sea Sweep consists of a frame of stainless steel (ss) flatbar 0.61 m wide, 0.91 m long, and 0.91 m high (Figure 4). The upper 0.15 m (stern) and 0.46 m (port and starboard sides, bow) of the frame are covered with ss sheet metal. The top is enclosed with a ss sheet metal hood in a cone shape extending 0.3 m above the frame. The Sea Sweep frame is supported by two inflatable pontoon floats 3 m long attached to aluminum tubing. The frame is adjusted in the pontoons so that the opening at the stern is 1.0 cm above the water under calm conditions.

Three hoses are attached to the Sea Sweep cone top. One hose (1.3 cm ID) provides compressed air at a flow of 50 L min^{-1} to two ss diffusion stones (200 μm porosity, 2.54 cm diameter, 30 cm long). The diffusion stones are horizontally mounted on the bottom of the Sea Sweep frame 0.75 m below the sea surface. A second hose (5.1 cm ID) provides a laminar flow air curtain directed downward at the bow and stern ends of the frame. A blower is used to produce a flow of $2 \text{ m}^3 \text{ min}^{-1}$ of particle-free air (charcoal and hepa filtered) to form this curtain. The curtain and side walls prevent ambient air from entering the Sea Sweep. The curtain provides an outward flow of about $1 \text{ m}^3 \text{ min}^{-1}$ (1 m sec^{-1} face velocity) and a dilution flow to the bubbled air in the enclosed space under the hood. The third hose (5.1 cm ID) brings $1 \text{ m}^3 \text{ min}^{-1}$ of Sea Sweep “sample” air (bubble and dilution flow) to the aerosol sampling mast 18 m above the sea surface. This is the same mast and flow rate used during ambient air sampling. The transmission efficiency of the sampling mast for particles with aerodynamic diameters less than $6.5 \mu\text{m}$ (the largest size tested) is greater than 95% [Bates et al., 2002]. To check for particle losses, simultaneous measurements of the aerosol number size distribution resulting from bubbled seawater were made at the top of the Sea Sweep cone and at the base of the sampling mast with two Aerodynamic Particle Sizers (APS). These measurements showed no measurable

loss of particles in either the hose or the mast for an aerodynamic diameter range of 0.9 to 7.0 μm . The Sea Sweep “blank” is tested with the blower flow on and the bubbler flow off.

The Marine Aerosol Reference Tank (MART) was used to generate SSA aboard the ship. The MART system is designed to mimic the bubble plume, foam, and aerosol generating mechanisms that occur during wave breaking at the ocean surface (Stokes et al., 2013). The system includes a flow-controlled closed-loop seawater circulation system that draws water from the tank bottom, a waterfall at the top of the tank to produce a plunging sheet that hits the surface water and produces a bubble plume, and an air-tight headspace for controlled aerosol sampling. The system was operated with 120 L of water and 60 L of headspace with the wave on for 10 sec and off for 5 sec. The water and air flows were controlled and monitored volumetrically so that a number production flux could be calculated. The air flow exiting the MART was dried using nafion driers. Uncontaminated sea water from the bow inlet (nominally 5 m below the surface) was pumped to the MART at 6 L min⁻¹. Water exited the tank from a vertical drain pipe that maintained the water level at the 120 L mark. More details about the specifications and operation of the MART can be found in Stokes et al. (2013). One advantage of the MART over Sea Sweep is that the water and air flows can be controlled to directly compare the number production fluxes along the cruise track. Sea Sweep provides a large aerosol number/mass flux for analysis by multiple instruments but does not capture all the bubbles generated and thus can not be used to measure the number production flux.

Sea Sweep Aerosol Sampling

Aerosol sampling inlet. The bottom 1.5 meters of the sampling mast and the humidity controlled chamber at the base of the mast containing the impactors and sizing instruments were

heated or cooled to establish a stable reference relative humidity (RH) for the sample air of \approx 60%. A stable reference RH allows for constant instrumental size segregation and results in chemical, physical, and optical measurements that are directly comparable. A reference RH of 60% was chosen because it is above the crystallization humidity of most aerosol components and component mixtures (Carrico et al., 2003). Twenty one 1.6 cm outer diameter stainless steel tubes extended into the heated portion of the mast. These were connected to the aerosol instrumentation and impactors with conductive silicon tubing to prevent electrostatic loss of particles or stainless steel tubing for the lines to the impactors used for collection of carbonaceous aerosol.

Aerosol chemical composition. Samples using seven-stage and two-stage multi-jet cascade impactors (Bernier et al., 1979) were used to determine sub-180 nm and sub-1.1 μm concentrations of inorganic ions. The 50% aerodynamic cutoff diameters of the impactors, $D_{50,\text{aero}}$, were 180 nm and 1.1 μm . The RH of the sampled air stream was measured a few cm upstream from the impactors.

Sub-180 nm and sub-1.1 μm concentrations of Cl^- , NO_3^- , SO_4^{2-} , methanesulfonate (MSA^-), Na^+ , NH_4^+ , K^+ , Mg^{+2} , and Ca^{+2} were determined by ion chromatography (IC) (Quinn et al., 1998). Non-sea salt SO_4^{2-} , K^+ , Mg^{+2} , and Ca^{+2} concentrations were calculated by subtracting the sea-salt concentration (based on Na^+ concentrations and the ratio of the ion to sodium in seawater) from the total ion concentration. Sea salt aerosol concentrations were calculated as $\text{Na}^+ \times 3.26$ where 3.26 is the seawater ratio of $(\text{Na}^+ + \text{Cl}^- + \text{K}^+ + \text{Mg}^{+2} + \text{Ca}^{+2} + \text{SO}_4^{2-} + \text{HCO}_3^-) / \text{Na}^+$ (Holland, 1978).

Sub-180 nm and sub-1.1 μm samples were collected on pre-combusted quartz fiber filters using 3 and 2 stage impactors for organic carbon (OC) and elemental carbon (EC) analysis

(Bates et al., 2004). A charcoal diffusion denuder was deployed upstream of the impactors to remove gas phase organic species. A backup filter was used for the OC blank to correct for any remaining gas phase organic species. OC and EC concentrations were determined with a Sunset Laboratory thermal/optical analyzer. Three temperature steps were used to evolve OC under O₂ free conditions for quantification. The first step heated the filter to 230°C; the second step heated the filter to 600°C; and the final step heated the filter to 870°C. There was no measurable carbonate carbon in the Sea Sweep samples which would have appeared in the final heating step. After cooling the sample down to 550°C, a He/O₂ mixture was introduced and the sample was heated in four temperature steps to 910°C to drive off EC. The transmission of light through the filter was measured to correct the observed EC for any OC that charred during the initial stages of heating. There was no measurable EC in the Sea Sweep samples.

Sub-1.1 μm particles were collected on 37 mm Teflon filters for organic functional group analysis. After collection, the filters were frozen to prevent losses due to desorption or reaction, and transported back to San Diego for analysis by Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectra were analyzed using an automated algorithm that includes baselining, peakfitting, and integrating at specific peak locations to quantify organic functional group mass associated with major carbon bond types based on the method outlined by Maria et al. [2002] and revised by Russell et al. [2009]. Concentrations were calculated by dividing the mass of each functional group measured for each filter by the total volume of air sampled through the filter. Functional groups that were quantified include hydroxyl (including alcohol, COH), alkane (CCH), and amine (CNH₂). Carbonyl (C = O), carboxylic acid (COOH), aromatic, alkene (C = CH), organosulfate and organonitrate functional groups were below the detection limit for all filters collected from Sea Sweep.

Aerosol number size distributions One of the 21 mast tubes was used to supply air to a thermodenuder (Wehner et al., 2002) Scanning Mobility Particle Sizer (SMPS) system. The 30 L min⁻¹ flow-passed through a submicrometer impactor at 60% RH and was then subsampled at 5 L min⁻¹ each into two 2.2 cm ID tubes, one at ambient temperature and one heated to 230°C. The heated section was 0.61 m long resulting in a residence time in the heated tube of 2.8 s. At the end of the heated tube, the flow passed through a perforated stainless steel tube (0.55 m) surrounded by a sheet of carbon-impregnated paper to remove the reactive gas phase species. The heated and unheated airflows were then isokinetically subsampled at the centerline at 2.0 L min⁻¹ and passed through nafion driers before entering the SMPS (TSI 3080 coupled to a TSI 3010 CN counter). A valve switched between the heated and unheated flows every 5 minutes. The dried aerosol (<30%RH) was charged with Po²¹⁰ charge neutralizers. The SMPS operated with a sample flow rate of 1 L min⁻¹ and a sheath air flow rate of 10 L min⁻¹ and measured the dry size distribution from 20-500 nm. Mobility distributions were collected every 2-minutes. The mobility distributions were inverted to a number distribution assuming a Fuchs-Boltzman charge distribution from the charge neutralizer. Tests with ammonium sulfate aerosol showed a complete removal of aerosol particle number in the thermodenuder.

Cloud condensation nuclei concentrations. A Droplet Measurement Technologies (DMT) CCN Counter (CCNC) [Roberts and Nenes, 2005; Lance et al., 2006] was used to determine CCN concentrations at supersaturations in the range 0.1% to 1%. The CCNC was operated in two modes – either sampling bulk sub-1 µm aerosol or monodisperse aerosol. For the sampling of bulk sub-1 µm aerosol, each supersaturation was sampled for 5 min. The first 2 or 3 minutes (depending on supersaturation) of each 5 min period was discarded so that only periods with stable supersaturations were included in the data analysis. For the sampling of

monodisperse aerosol, an SMPS was used to size-select dry diameter particles in the size range of 50-150 nm diameter, which were then sampled in parallel by the CCNC and a TSI 3010 particle counter. In this case, each supersaturation was sampled for 10 to 15 minutes while the range of monodisperse diameters was cycled through. The sampling time depended on supersaturation and the number of diameters sampled. Only the monodisperse sampling is reported here. The CCN counter was calibrated before and during the experiment as outlined by Lance et al. (2006). An $(\text{NH}_4)_2\text{SO}_4$ aqueous solution was atomized with dry air, passed through a diffusional drier, diluted and then introduced to a SMPS (TSI). The resulting monodisperse aerosol stream was sampled simultaneously by the CCN counter and a TSI 3010 particle counter in order to determine the average activated fraction (CCN/CN). This procedure was repeated for a range of particle sizes and instrumental supersaturations. Using this procedure, the instrument supersaturation was equal to the critical supersaturation of the particle obtained from the activation curve for an activated fraction of 50%. The critical supersaturation for a given particle size was calculated from Kohler theory (e.g., Fitzgerald and Hoppel, 1984).

MART Aerosol Sampling

MART was sampled with a CCN counter (described above) and a Scanning Mobility Particle Sizer (SMPS) (TSI 3080 coupled to a TSI 3010 CN counter). The dried aerosol (<30%RH) was charged with Po^{210} charge neutralizers. The SMPS operated with a sample flow rate of 0.82 L min^{-1} and a sheath air flow rate of 8.2 L min^{-1} and measured the dry size distribution from 20-500 nm. Mobility distributions were collected every 2-minutes. Data reduction was the same as for the SMPS described above. MART was deployed only on NAAMES 3 and 4.

