# What is the Source of Cloud Condensation Nuclei in the Marine Boundary Layer?

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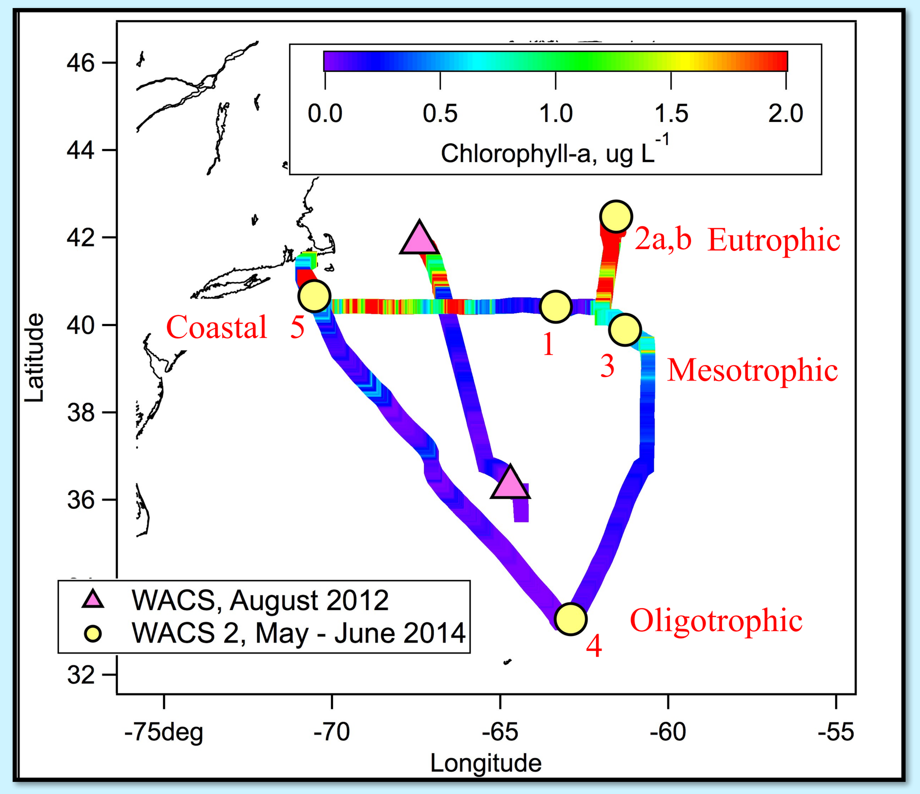
## Introduction

Potential sources of cloud condensation nuclei (CCN) to the marine boundary layer (MBL) include primary aerosol emitted directly from the ocean. Breaking waves on the ocean surface result in the entrainment of air bubbles that scavenge organic matter from seawater as they rise to the surface. When injected to the atmosphere, the bubbles burst and yield sea spray aerosol (SSA) composed of sea salt and organic matter. Other potential sources of CCN to the MBL are secondary aerosol formed in the free troposphere (e.g., sulfate derived from DMS) or transported in the free troposphere (e.g., continental aerosol) that is entrained into the lower atmosphere. Understanding the sources and properties of CCN to the MBL is required for accurately modeling its impact on marine boundary layer cloud properties and Earth's radiation balance.

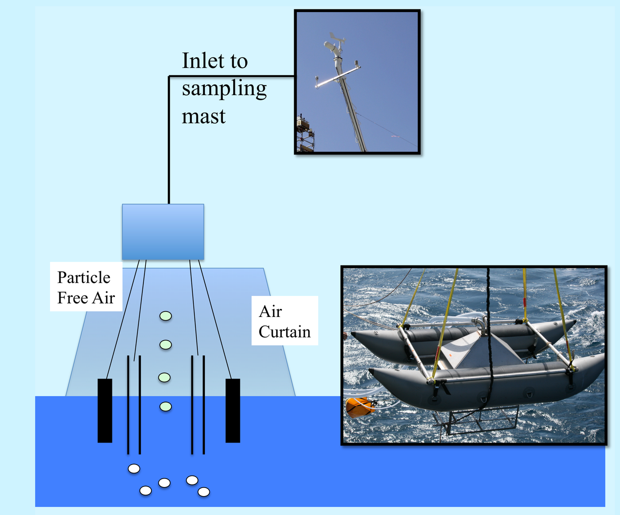
Recent research has employed "model ocean" sea spray aerosol generators to characterize the properties of freshly emitted SSA under relatively controlled conditions (e.g., Keene et al., 2007; Prather et al., 2013; Quinn et al., 2014). Here, we report measurements of SSA produced *in situ* with the Sea Sweep aerosol generator during two cruises in the North Atlantic, WACS and WACS 2. During both cruises, eutrophic and oligotrophic regions were targeted to assess the impact of local biological activity on SSA properties. In addition, during WACS 2, sustained periods of wind speeds greater than 10 m $s^{-1}$ were encountered which allowed for a comparison of the properties of SSA produced by the Sea Sweep generator and MBL ambient aerosol under high wind conditions.

## Western Atlantic Climate Studies: WACS and WACS 2




**Cruise tracks for WACS and WACS 2.** Cruise tracks are colored by surface seawater Chl-a concentrations. Station locations where freshly emitted SSA was generated are indicated by markers. At the coastal and eutrophic stations, deep nutrient rich waters were mixed to the surface leading to highly productive waters. Mesotrophic stations on the edge of the Gulf Stream were regions of moderate productivity. Oligotrophic stations in the Sargasso Sea were regions of very low biological productivity.

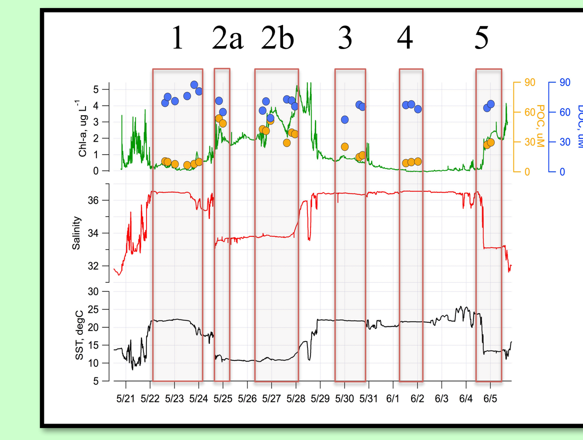
## Sea Sweep Generation of Nascent SSA




Bates et al., *JGR*, 2012

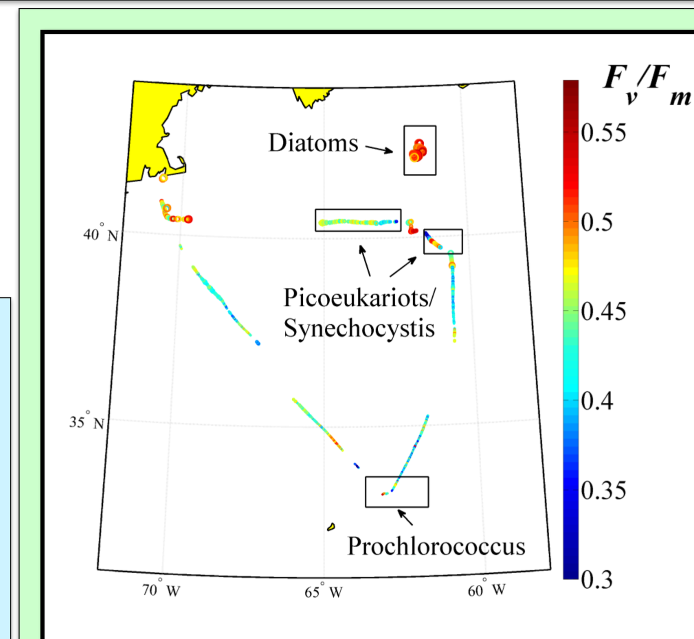
## WACS 2 Seawater Properties

**(Numbers indicate Sea Sweep Stations)**




Surface seawater Chl-a, salinity, and sea surface temperature for WACS 2. Also shown are surface seawater DOC and POC.

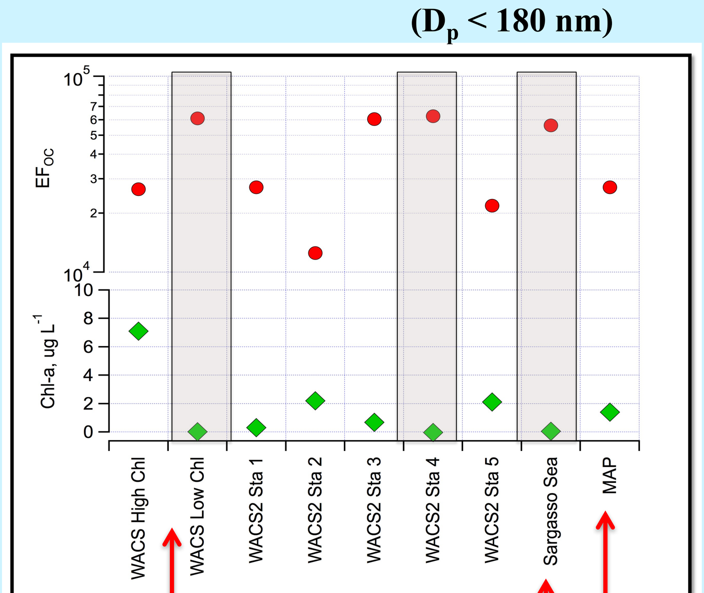
## Photophysiological parameters of phytoplankton




Horizontal distribution of photophysiological parameters of phytoplankton measured using a Fluorescence Induction and Relaxation instrument (Gorbunov and Falkowski, 2005). $F_v/F_m$ represents the photochemical efficiency of the phytoplankton. The size of the data points represents relative chlorophyll a fluorescence (proxy for phytoplankton biomass). Measurements were carried out at night to avoid the effects of high light stress. Variations in $F_v/F_m$ are driven by variability in nutrient limitation.
Also shown are estimates of the variability in phytoplankton communities at the different Sea Sweep stations.

## SSA organic carbon enrichment factors

**($D_p$ < 180 nm)**

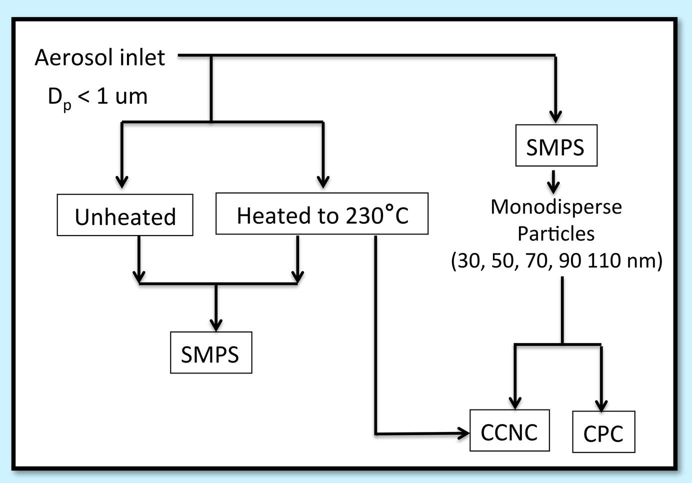



Large organic enrichments in low-chlorophyll Sargasso Seawater reveals a pool of surface seawater organic matter that is not directly associated with Chl *a* and phytoplankton biomass, but is available for incorporation into nascent SSA.

Quinn et al., 2014 Keene et al., 2007 Facchini et al., 2008

$$EF_{OC} = \frac{[(OC\ as\ C) / Na^+]_{SSA}}{[(TOC\ as\ C) / Na^+]_{seawater}}$$

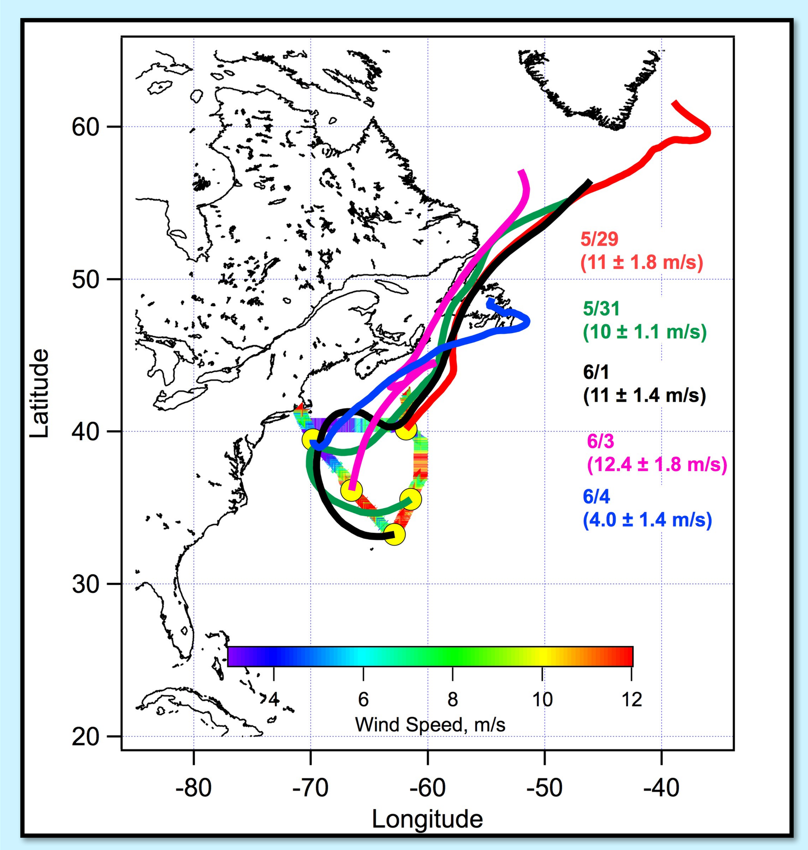
## Sampling scheme for aerosol volatility and CCN-activity as a function of particle size




For comparison of:

- Generated Sea Sweep SSA
- Ambient aerosol sampled during high wind conditions
- Volatility and CCN measurements were made on both monodisperse and bulk submicrometer aerosol

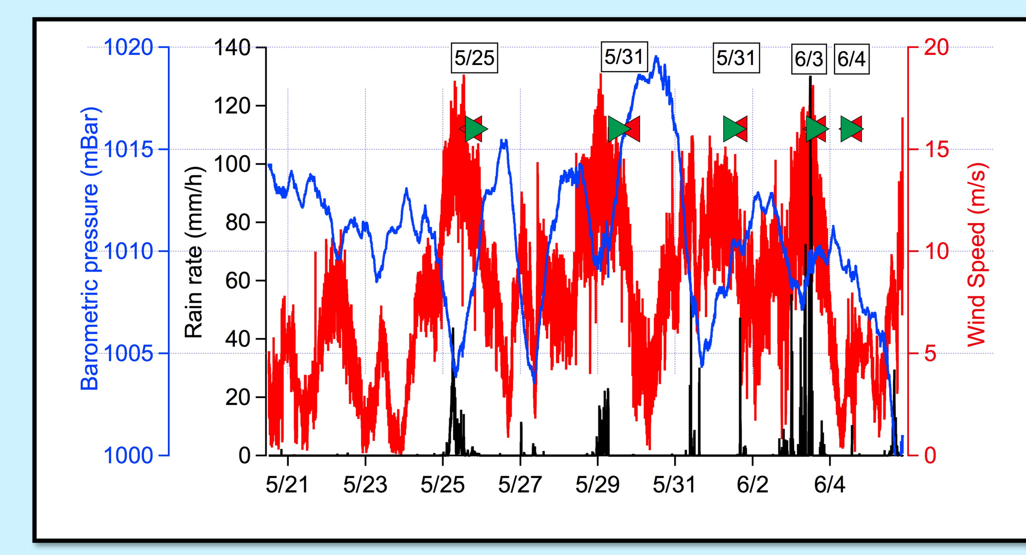
## Calculated back trajectories for ambient samples collected under high wind speed conditions




Average wind speeds over the periods of sample collection are shown along with HYSPLIT 5-day back trajectories for a starting altitude of 100 m asl.

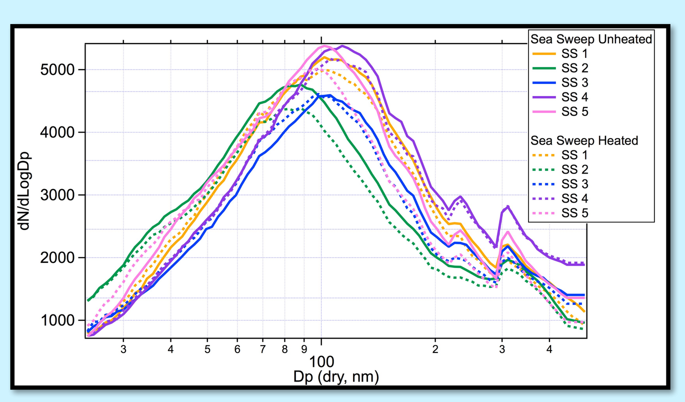
(www.arl.noaa.gov/HYSPLIT_info.php)

## Meteorological conditions during ambient sampling




Periods of sampling during high winds are indicated by the green (start) and red (stop) triangles. Ambient sampling on 6/4 was during low wind speed and continental aerosol for comparison.

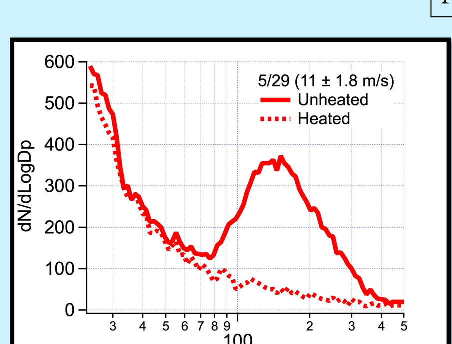
## Unheated and heated (230° C) sea spray and ambient aerosol number size distributions

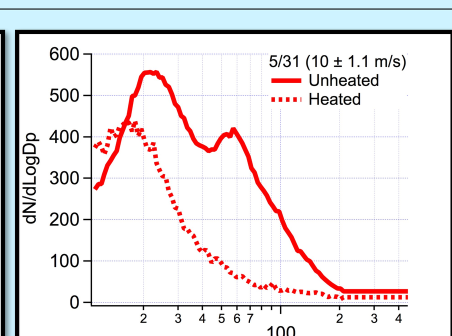


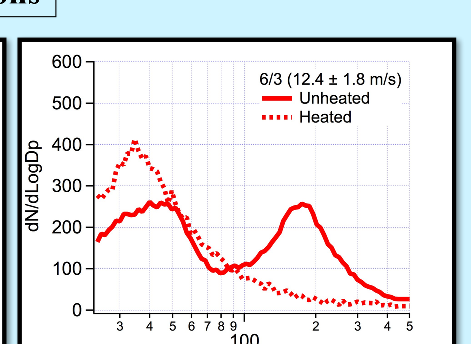

**Sea Sweep size distributions**:

- The magnitude of the distribution is a function of the bubbling rate through Sea Sweep.
- Heated and unheated generated SSA are similar indicating most of the SSA is refractory at 230C.
- SS2 (the eutrophic station) has the smallest modal diameter and an additional mode at ~ 40 nm.

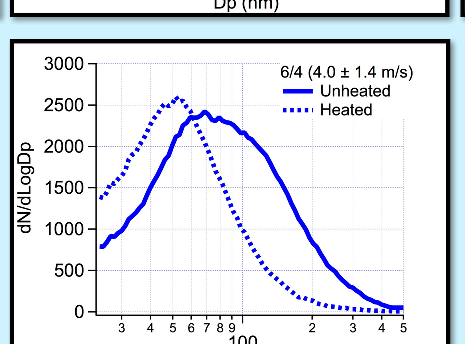
**Ambient aerosol size distributions**



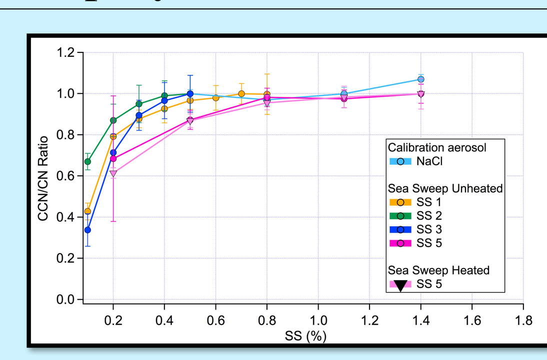



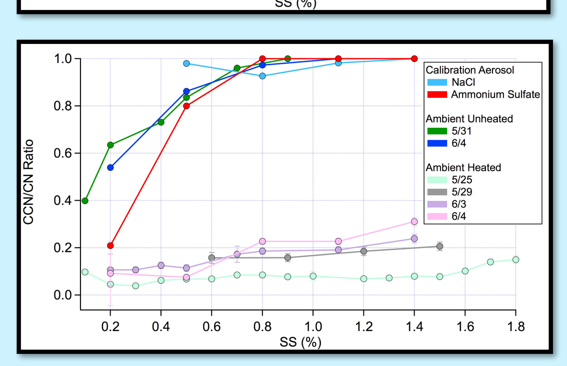

Heating the ambient high wind aerosol drives off the accumulation mode $SO_4^=$ leaving behind a non-volatile Aitken mode. Is it primary SSA?




Heating the ambient continental aerosol drives off the $SO_4^=$, leaving behind a non-volatile core.

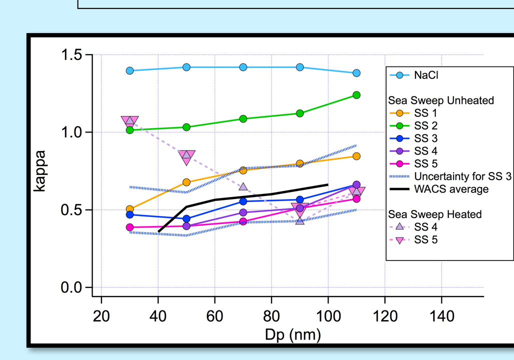
## Unheated and heated CCN activity ratios for bulk sub-1 µm sea spray and ambient aerosol

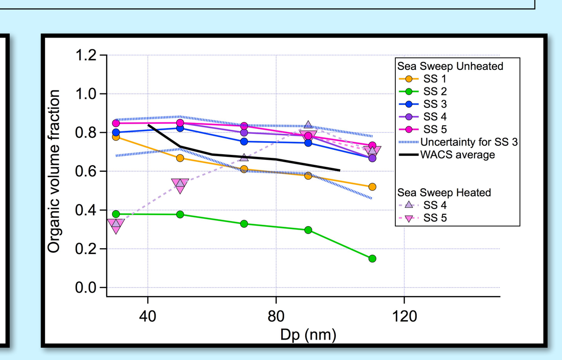


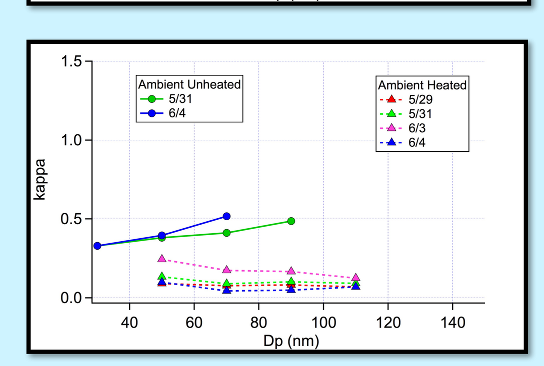



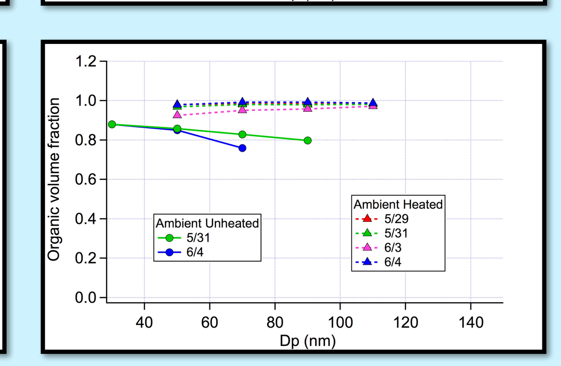

- Heated and unheated generated SSA are similar in their CCN activity for the bulk sub-1 µm size range.
- Heated ambient aerosol (i.e., the non-volatile Aitken mode) is much less CCN active than the unheated aerosol.

## Unheated and heated kappa and organic volume fractions for monodisperse sea spray and ambient aerosol




- The upper plots show Sea Sweep (heated and unheated) kappa hygroscopicity parameter and calculated organic volume fraction. The lower plots show the same for ambient aerosol.
- SSA generated in the most eutrophic seawater is least enriched in organics and the most hygroscopic.
- The ambient heated aerosol sampled during high wind speed conditions appears to be organic (not sea salt) and the organic fraction is less hygroscopic than that of generated sea spray aerosol.

## Conclusions

- There is a pool of organic carbon in surface seawater that is not directly associated with local biological activity but is available for incorporation into freshly generated SSA.
- However, during periods of high wind speed, the majority of CCN in the marine boundary layer appear to not be primary sea spray aerosol.
- Next steps are to include aerosol chemical composition from AMS and FTIR measurements in the analysis as well as additional seawater parameters.
- Similar measurements (volatility, CCN activity, chemical composition) of ambient aerosol during high wind conditions are needed in other ocean regions to assess the magnitude of the contribution of primary SSA to MBL CCN.

**References**

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