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Key Points:

- Marine plankton ecosystems do not directly affect sea spray aerosol
- Chemical transport and climate models do not need to incorporate plankton ecosystems in modeling sea spray aerosol

Supporting Information:

- Supporting Information S1

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Variability in Marine Plankton Ecosystems Are Not Observed in Freshly Emitted Sea Spray Aerosol Over the North Atlantic Ocean

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Abstract Sea spray aerosol (SSA) consists of both sea salt and organic components. These aerosols affect Earth's climate by scattering solar radiation and by altering cloud properties. Here we present observations of SSA particles generated at sea using an over-the-side bubbling system (Sea Sweep) and an onboard plunging wave mesocosm (Marine Aerosol Reference Tank—MART) during five cruises in the North Atlantic. The cruises were timed to sample different stages of the North Atlantic plankton bloom and included transects from the oligotrophic Sargasso Sea to the biologically productive western subarctic. The results show that the North Atlantic plankton bloom has little effect on the emission flux, organic fraction, or cloud condensation nuclei (CCN) activity of SSA, and therefore, plankton ecosystems do not need to be included in modeling aerosol indirect effects of primary SSA in global climate models or in chemical transport models.

Plain Language Summary Breaking waves on the ocean surface emit sea spray aerosol (SSA) to the atmosphere. These particles affect Earth's climate by scattering solar radiation and altering cloud properties (e.g., cloud brightness, extent, and rain). SSA consists of both sea salt and organic components. A key question in chemical transport and climate models is whether marine plankton ecosystems affect the organic component of SSA. The results presented here show that marine plankton ecosystems have little effect on SSA and that the ocean source of organic SSA comes from the large pool of dissolved organic carbon in the ocean. Chemical transport and climate models, therefore, can treat the ocean as a uniform organic SSA source, affected only by sea surface temperature.

1. Introduction

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 (Tseng et al., 1992; Lewis & Schwartz, 2004). When injected to the atmosphere, the bubbles burst and yield primary sea spray aerosol (SSA) consisting of sea salts and organic matter. The organic matter in SSA is highly enriched relative to its concentration in seawater (Barker & Zeitlin, 1972; Bates et al., 2012; Facchini et al., 2008; Hoffman & Duce, 1977; Keene et al., 2007; Quinn et al., 2014). SSA in the atmosphere scatters solar radiation (Quinn & Coffman, 1998), acts as cloud condensation nuclei (CCN) (Clarke et al., 2006; O'Dowd et al., 1999), and has a large impact on atmospheric chemistry through multiphase reactions (Keene et al., 2007; Zhou et al., 2008). Understanding the emission flux, composition, and CCN activity of SSA is required for accurately modeling the impact of SSA on direct radiative forcing, marine boundary layer (MBL) cloud properties, and tropospheric chemistry.

1.1. SSA Emission Flux

Early model parameterizations of the flux of SSA to the atmosphere assumed that SSA emissions were proportional to white cap coverage (Monahan et al., 1983) and could be described as a function of wind speed at a height of 10 m (Monahan & O'Muircheartaigh, 1986). Gong (2003) and Clarke et al. (2006) expanded this function to a size resolved number flux based on comparisons with field observations. Jaegle et al. (2011) further modified the source function by adding a dependence on sea surface temperature that improved comparisons between modeled SSA concentrations and in situ and remote sensing observations of aerosol mass (primarily sea salts) and aerosol optical depth thus constraining SSA direct radiative forcing.

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Attempts have been made to account for the flux of the organic fraction of SSA by using a scaling factor in the flux parameterization based on surface ocean chlorophyll concentration (Fuentes et al., 2010; Gantt et al., 2011; Gantt et al., 2015; Long et al., 2011; O'Dowd et al., 2008; Rinaldi et al., 2013; Vignatti et al., 2010). Chlorophyll *a* (Chl *a*) is attractive as a proxy for the organic fraction of SSA because it can be retrieved from satellite observations that offer global coverage of the world's oceans. Chl *a* is a measure of phytoplankton, or algal, biomass which contributes to the surface seawater pool of particulate organic carbon (POC). Measurements of ambient marine aerosol at coastal stations on Mace Head, Ireland (Cavalli et al., 2004; O'Dowd et al., 2004; Yoon et al., 2007), and Amsterdam Island (Sciare et al., 2009) show an increase in atmospheric organic carbon during periods of high upwind chlorophyll concentrations. However, recent direct measurements of SSA in the mid-North Atlantic Ocean comparing eutrophic (high Chl *a*) and oligotrophic (low Chl *a*) regions in the same season indicate that the organic fraction of SSA is not directly associated with chlorophyll and phytoplankton biomass (Keene et al., 2017; Quinn et al., 2014). The discrepancy between the ambient measurements of marine aerosol and the direct measurements of SSA is because the ambient aerosol has been impacted by atmospheric processing. The evidence for this is clearly seen in Figure 3 of O'Dowd et al. (2004) which shows two modes in the size distribution.

The marine ecosystem could affect the MBL aerosol concentration by altering the flux of SSA to the atmosphere. In microcosm studies, Fuentes et al. (2010) showed that the production of SSA was enhanced by the presence of diatomaceous exudate in seawater. Long et al. (2014) and Keene et al. (2017) presented data suggesting that sunlight-mediated biogenic surfactants in biologically productive waters increase the flux of SSA to the atmosphere. However, in laboratory studies, Modini et al. (2013) showed that surfactants decrease the number production flux of SSA. Alpert et al. (2015) showed an increase in the number flux of up to three times in actively growing bacteria and phytoplankton mesocosm experiments while Christiansen et al. (2019) showed a decrease in the number production flux with increases in algal biomass. Tyree et al. (2007) and Forestieri et al. (2018) reported mixed responses of the number production flux when including organic matter. This is clearly an area for further study.

1.2. SSA Composition and Its Contribution to the MBL CCN Population

SSA is thought to be a major contributor to the CCN population in the marine boundary layer (Cipriano et al., 1987; Clarke et al., 2006; Leck & Bigg, 2005; O'Dowd & Smith, 1993). More recent results indicate the SSA is only a significant contributor to CCN concentrations in the high southern latitudes (Quinn et al., 2017). The composition of SSA affects its ability to act as a CCN at supersaturations typical of MBL clouds (O'Dowd et al., 2004; O'vadnevaite et al., 2011). Direct impactor measurements of the size-resolved chemical composition of fresh SSA produced artificially by bubbling air through flowing North Atlantic seawater indicate the dry mass of particles with diameters less than 200 nm is dominated by organic compounds (e.g., Facchini et al., 2008; Keene et al., 2007; Quinn et al., 2014; Quinn et al., 2015). TEM-EDX measurements of SSA produced artificially with Pacific Ocean water from the Scripps Institute of Oceanography pier show a decrease in the number of internally mixed organic carbon/sea salt particles with decreasing particle diameter and an increase in pure organic carbon particles (Prather et al., 2013).

The source of the organic material in SSA is most likely the large pool of organic carbon in the oceans in the form of dissolved organic carbon (DOC) (Quinn et al., 2014). DOC is operationally defined in oceanography as the marine organic matter that can pass through a 0.2 μm filter and consists of dissolved compounds and colloidal particles small enough to pass through the filter (Carlson, 2002; Hansell & Carlson, 2015). Although DOC is autotrophically produced and microbially remineralized in the surface ocean, the production of semi-labile DOC that accumulates in the surface ocean is a small fraction of the DOC inventory. Hence, DOC concentrations are relatively constant in the surface ocean ranging from 70–80 $\mu\text{mol C kg}^{-1}$ in tropical and semitropical surface waters, 55–70 $\mu\text{mol C kg}^{-1}$ in temperate surface waters, and 45–55 $\mu\text{mol C kg}^{-1}$ in subpolar and polar waters (Hansell et al., 2009). DOC concentrations are generally an order of magnitude higher than POC concentrations.

The effect of organic matter on CCN activity has been studied in marine aerosol generation experiments. The addition of micro- and nano-gel colloidal matter at concentrations similar to an intense algal bloom reduced the CCN activity of the primary marine aerosol by 5–24% (Fuentes et al., 2011). Other aerosol generation experiments, however, found little change in CCN activity in algal bloom conditions (Collins et al., 2016; Schwier et al., 2015).

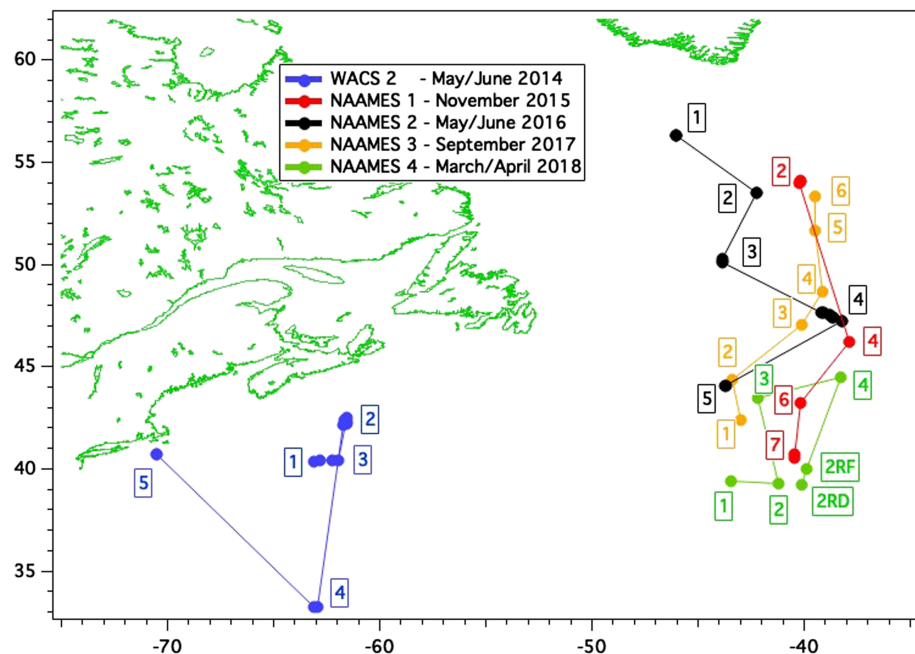


Figure 1. Station locations during the five cruises. Sea Sweep was only deployed at four stations during NAAMES-1 due to adverse weather.

2. Results and Discussion

2.1. Field Studies

The WACS-2 cruise in May 2014 sampled both northern, colder, moderately productive waters of the western North Atlantic and the warmer waters of the Sargasso Sea, a region of typically low productivity (Figure 1). Chlorophyll concentrations were highest at Station 2 (mean $> 2.0 \text{ mg m}^{-3}$), intermediate at Stations 1, 3, and 5 ($0.3\text{--}0.7 \text{ mg m}^{-3}$), and lowest at Station 4 (0.1 mg m^{-3}). The phytoplankton community at the northern stations was dominated by coccolithophores with dinoflagellates and green algae as lesser components. At Station 4 picocyanobacteria and small green algae predominated (Aller et al., 2017).

A complete description of the NAAMES study can be found in Behrenfeld et al. (2019). Briefly, four NAAMES field campaigns (labeled NAAMES 1–4) were conducted between 2015 and 2018, with each campaign targeting specific events in the annual phytoplankton cycle. Primary ship sampling stations during each cruise (Figure 1) were distributed latitudinally roughly along the 40°W longitude. The timing of events in the annual phytoplankton cycle varies with latitude, so this distribution of sampling stations ensured a broad range of ecosystem states within each ~ 1 month cruise. NAAMES 1 was conducted in November and targeted the early-winter transition event initiating the annual phytoplankton blooming phase (Behrenfeld & Boss, 2018). Chlorophyll concentrations along the main science transect were low during this cruise (mean $= 0.3 \text{ mg m}^{-3}$), and phytoplankton communities, while taxonomically diverse, were numerically dominated by cyanobacteria (*Prochlorococcus* and *Synechococcus*) and picoeukaryotes. NAAMES 2 was conducted in May and June and targeted the annual bloom climax period. Chlorophyll concentrations during this cruise were the highest of all the NAAMES cruises (mean $> 2.0 \text{ mg m}^{-3}$), and phytoplankton communities were dominated by small cells ($< 20 \mu\text{m}$) with a greater contribution from pico- and nano-eukaryotic phytoplankton than in November. The September NAAMES 3 cruise occurred during the declining phase of the phytoplankton annual cycle, with low chlorophyll concentrations (typically $< 0.5 \text{ mg m}^{-3}$) in strongly stratified surface layers. Phytoplankton communities for this cruise were also dominated by smaller cells with a notable contribution from dinoflagellates. The NAAMES 4 cruise in March and April was centered on the accumulation phase of the annual phytoplankton cycle. Chlorophyll concentration and phytoplankton community composition were highly variable spatially during this cruise. While the phytoplankton community predominantly consisted of small cells, patches of diatoms were observed, however rarely, between core stations along the main science transect.

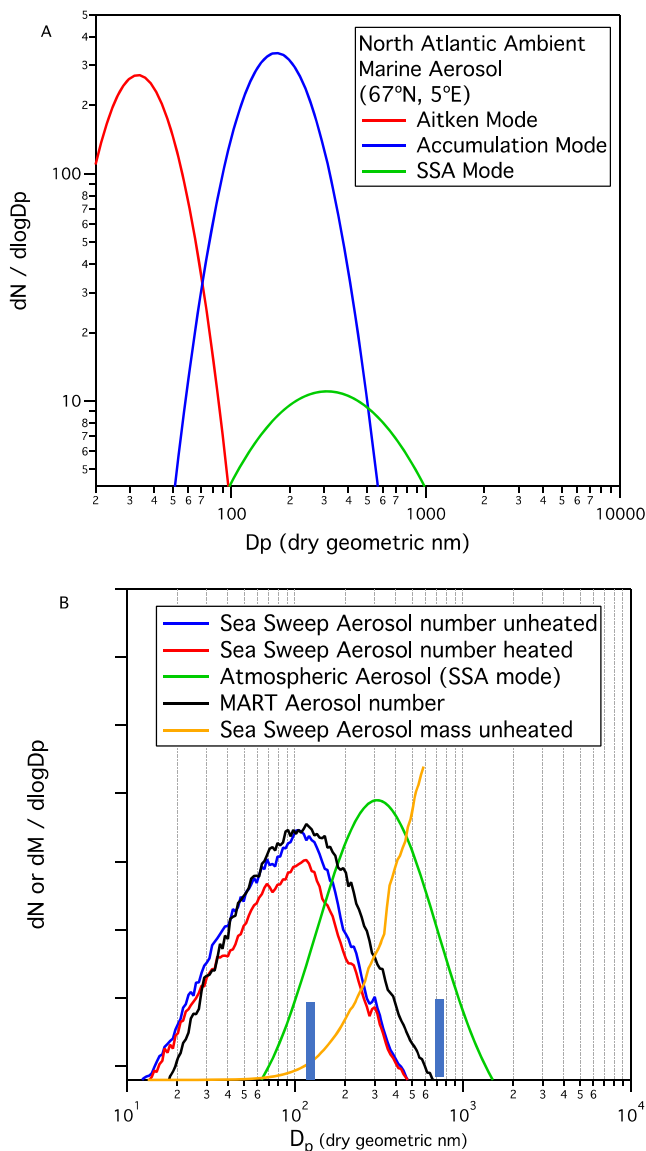


Figure 2. Ambient aerosol number size distribution over the North Atlantic Ocean showing the dominant three modes (a). The ambient aerosol SSA number mode with the Sea Sweep and MART SSA number distributions superimposed (b). Also shown in (b) is the calculated Sea Sweep mass mode. The vertical black arrows show the sub 180 nm and sub 1.1 μm (aerodynamic diameter) impactor cutoffs converted to geometric diameter. The Y axis is arbitrary because the size distributions have been shifted vertically to allow direct comparison. The atmospheric aerosol SSA mode shown here is a representative ambient size distribution from NAAMES (Saliba et al., 2019, Figure S28).

2.2. SSA Size Distributions

A typical number size distribution of marine boundary layer atmospheric aerosols over the remote ocean includes three modes: an Aitken, an accumulation, and a SSA mode (Figure 2a) (Bates et al., 2002). Sea Sweep and MART sample freshly emitted SSA before it reacts in the atmosphere and before it mixes with aerosols from other sources. The number size distributions generated from the two sampling methods were very similar (Figure 2b) capturing the smaller SSA mode particles. The size distributions generated with Sea Sweep using smaller frits (2 μm) result in smaller modal diameters (Bates et al., 2012); however, the 200 μm frits produce a size distribution very similar to that generated with MART which presumably captures film and jet droplets (Wang et al., 2017). Neither Sea Sweep nor MART produce number size distributions that span the full range of that produced in ambient seawater (Figure 2b). The larger SSA (>200 nm diameter) are all sufficiently large to act as CCN at supersaturations >0.1%. The smaller (<200 nm diameter) more organic rich (see below) SSA are the ones that have the potential to affect CCN activity. The impactor samples collected during the cruises (sub 180 nm and sub 1.1 μm aerodynamic diameter) captured the smaller half of the distribution and the total distribution. Most of the aerosol mass was contained in the larger half of the distribution (Figure 2b).

2.3. SSA Composition

FTIR analysis of all four NAAMES campaigns and WACS2 showed that the particulate organic matter (POM) in the sub 1.1 μm Sea Sweep SSA was comprised mostly of hydroxyl groups (80 \pm 17%) followed by alkane groups (12 \pm 13%) and amine groups (8 \pm 5%) consistent with a carbohydrate-like composition seen previously (Russell et al., 2010). SSA organic matter has been shown to be water insoluble, consisting in part of polysaccharides with long hydrophobic aliphatic chains (Bates et al., 2012; Facchini et al., 2008; Quinn et al., 2014). The SSA particles sampled with Sea Sweep were not volatile at 230 $^{\circ}\text{C}$ (Figure 2b) which is consistent with a microcolloidal aggregate composition of the organic matter (Bigg & Leck, 2008; Leck & Bigg, 2005).

FTIR measurements were used to derive a SSA POM/OC ratio for each cruise. Details of the measurements reported in this paper can be found in the Supporting Information. Values of the POM/OC ratio ranged from 2.71 to 3.46. The POM dry mass fraction (POM/(POM + sea salt)) was 20 \pm 6% for the sub 1.1 μm size fraction and 86 \pm 2% for the sub 180 nm size fraction (Figure 3a) during the five cruises. No significant differences were observed between cruises. The high organic mass fractions for sub 180 nm SSA and the lower organic mass fractions for sub 1.1 μm SSA are consistent with previous studies that have shown that the dry mass of SSA with diameters less than 200 nm is dominated by organic compounds (e.g., Facchini et al., 2008; Keene et al., 2007; Quinn et al., 2014; Quinn et al., 2015) and support the hypothesis (Kieber et al., 2016; Quinn et al., 2014) that the organic component of the SSA comes from a large pool of refractory seawater DOC that is relatively uniform in time and space (Hansell et al., 2009).

The POM dry mass fraction was correlated with sea surface temperature (SST) (Figure 3b). SST affects bubble size, number and bursting, and the production of SSA (Salter et al., 2014). Salter et al. (2014) have shown a decrease in entrainment with increasing SST as well as a decrease in the ratio of 100 nm SSA to 375 nm SSA. Results from Sea Sweep deployments during NAAMES 2 (Figure 3c) are consistent with Salter et al. (2014). Although the particle mode diameter remains constant during the

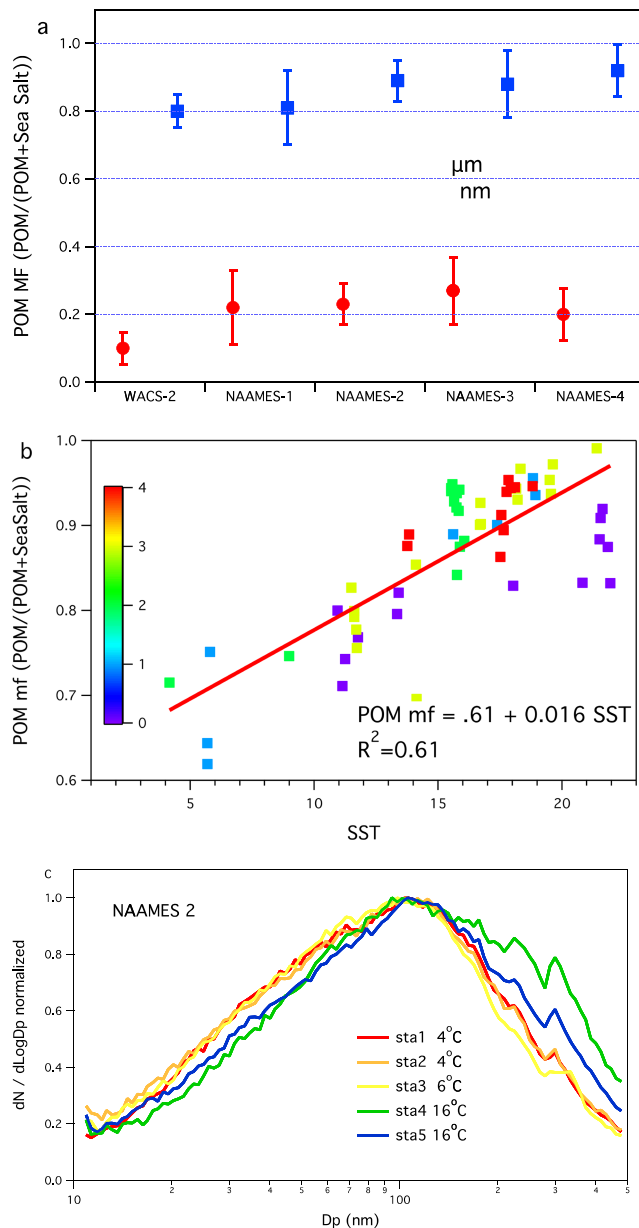


Figure 3. (a) Sea Sweep generated SSA sub 180 nm and sub 1.1 μm particulate organic matter (POM) mass fractions. POM was calculated as organic carbon times a campaign averaged POM/OC value based on the FTIR data. POM comprised $20 \pm 6\%$ (mean \pm standard deviation) of the sub 1.1 μm mass and $86 \pm 2\%$ of the sub 180 nm mass during the five cruises. (b) Sub 180 nm POM mass fractions versus sea surface temperature. The points are colored by cruise number with WACS-2 being 0. (c) NAAMES-2 Sea Sweep number size distributions.

cruise, at higher temperatures there are fewer small particles and more larger particles. How this relates to the POM mass fraction SST correlation, however, is not clear from the results of this study.

2.4. SSA Number Production Flux

The effect of the marine ecosystem on the SSA number production flux was studied during NAAMES 3 and 4 using the MART. Day was defined as 4 hr following sunrise through 2 hr following sunset, and night was defined as the 6 hr preceding sunrise following the time convention employed by Long et al. (2014). Long et al. (2014) and Keene et al. (2017) showed that the number production flux increased during daytime hours at a station on Georges Bank with very high chlorophyll concentrations ($5\text{--}8\text{ mg m}^{-3}$). They attributed this difference to sunlight-mediated biogenic surfactants. Fuentes et al. (2010) showed a decrease in SSA size and an increase in number production flux in microcosm experiments with diatomaceous exudate DOC concentrations $>175\ \mu\text{M}$. The effect was only observable with very high DOC concentrations and with diatomaceous exudate. They concluded that the effect would only be significant in regions of very high biological activity that were dominated by diatom algal populations.

The sea spray number production fluxes during NAAMES 3 and 4 were very similar between stations and cruises (Figure 4). No differences between day and night production fluxes were observed during NAAMES. The integrated number concentration from the number size distributions during both NAAMES cruises varied by only 16% which is within the uncertainties of the flow rates. This invariance in integrated number concentration was observed despite significant differences between NAAMES 3 and 4 in chlorophyll concentrations, plankton community composition, and opposing phases of the annual plankton cycle (Behrenfeld et al., 2019; see section 2.1). Unfortunately MART was not available during the bloom-climax NAAMES 2 cruise when chlorophyll concentrations were the highest.

2.5. CCN Activity

Most SSA are sufficiently large ($>75\text{ nm}$ diameter) to act as CCN at supersaturations $>0.25\%$. At 50 nm the critical supersaturation of Sea Sweep samples (0.27–0.32%) was only slightly higher than pure NaCl particles (Figure 5). This small depression in CCN activity was previously observed in mesocosm studies by Fuentes et al. (2011) (at OC concentrations $<300\ \mu\text{M}$) and Collins et al. (2016). Collins et al. (2016) concluded that these small changes in CCN activity would induce less than a 3% increase in expected CCN concentrations for typical marine cloud supersaturations. Note that the CCN/CN curves in Figure 5 are much steeper than those reported by Quinn et al. (2014) for WACS-1. It is critical to thoroughly dry the aerosol before it enters the CCN instrument. The SSA was not sufficiently dry during the WACS-1 measurements.

2.6. Implications for Chemical Transport and Climate Models

The WACS-2 and four NAAMES cruises in the northwestern Atlantic encompassed a wide range in phytoplankton biomass and a broad diversity of plankton communities. Nevertheless, our research shows that the size resolved organic mass fractions of SSA produced by Sea Sweep are relatively invariant between the five cruises. The number production fluxes measured using MART and the CCN activity of Sea Sweep generated SSA were also relatively invariant. We conclude that seasonal differences in plankton ecosystems in the North Atlantic Ocean have little effect on MBL CCN concentrations and

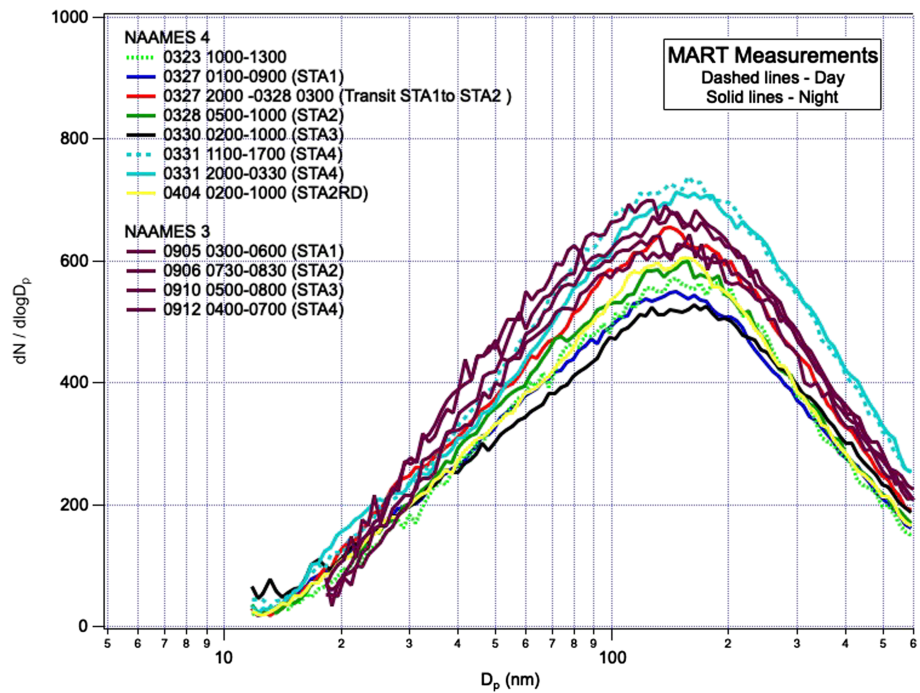


Figure 4. Dried number size distributions sampled from MART during NAAMES 3 and 4.

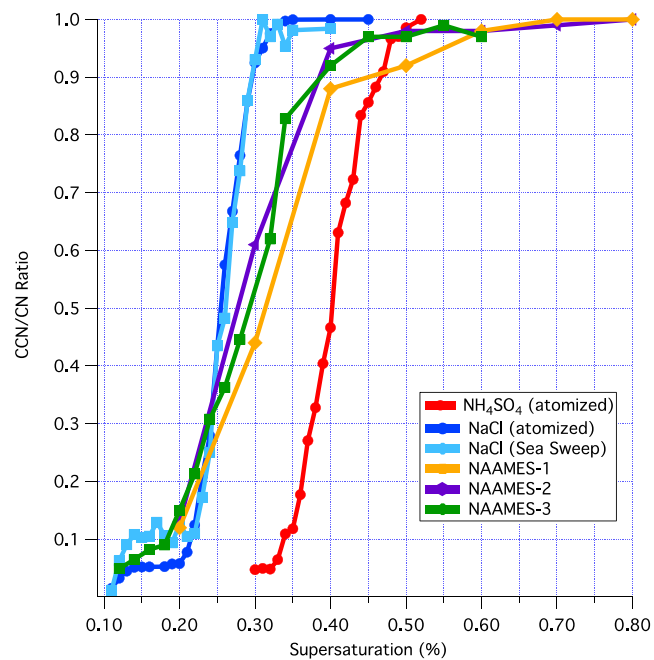


Figure 5. Critical supersaturations for 50 nm particles. The instrument is calibrated with atomized ammonium sulfate and sodium chloride. SSA produced with Sea Sweep in a bin of sodium chloride showed the same CCN/CN values as atomized sodium chloride. The NAAMES samples averaged over each cruise were identical within the uncertainties of the measurements. The critical supersaturation of the NAAMES samples were slightly depressed from pure sodium chloride.

thus need not be included in modeling atmospheric organic carbon or CCN concentrations. These measurements should be repeated in other ocean basins to test whether this conclusion can be extrapolated globally.

Data Availability Statement

All data are available on the NASA data servers accessible through <https://naames.larc.nasa.gov> and the NOAA PMEL atmospheric chemistry data server accessible through <https://saga.pmel.noaa.gov>.

Author Contributions

T. B. P. Q., L. R., and M. B. designed the study. All authors contributed to data collection and analysis. T. B. interpreted the results and wrote the manuscript with contributions and input from all authors.

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Erratum

In the originally published version of this article, the supporting information file was omitted. This error has since been corrected, and the present version may be considered the authoritative version of record.