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Importance of Supermicron Ice Nucleating Particles in Nascent Sea Spray

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Key Points:

- Supermicron sea spray aerosols have higher ice nucleating particle (INP) concentrations at warm temperatures than submicron sea spray aerosols
- The higher concentrations of INPs in supermicron sea spray aerosols occur independent of phytoplankton bloom state
- The ice nucleating ability of a sea spray aerosol (SSA) is roughly proportional to the dry particle volume

Supporting Information:

- Supporting Information S1

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Abstract With oceans covering 71% of the Earth's surface, sea spray aerosol (SSA) particles play an important role in the global radiative budget by acting as cloud condensation nuclei and ice nucleating particles (INPs). By acting as INPs, SSA particles affect the structure and properties of mixed-phase clouds by inducing freezing at warmer temperatures than the homogeneous freezing temperature. Climate models that incorporate marine INPs use the emission of submicron SSA in INP parameterizations because these particles contain a higher fraction of organic mass. Here we show supermicron SSA particles, produced using a natural breaking wave analogue, are the major source of INPs throughout the lifecycle of a phytoplankton bloom. Additionally, supermicron SSA particles are shown to be more efficient INPs than submicron SSA particles, because they carry a greater number of ice active components. Thus, supermicron SSA needs to be incorporated in INP parameterizations for future climate models.

Plain Language Summary Clouds over high latitude oceans are a major source of uncertainty in global climate models. Sea spray aerosol (SSA) particles are the dominant source of cloud seeds over remote marine locations. Ice nucleating particles (INPs) initiate cloud freezing. Previous climate models approximated INPs released from oceans using the number of submicron SSA. However, field studies show supermicron particles are effective INPs over marine locations. This study was designed to understand the role of particle size for marine INPs in an isolated ocean/atmosphere laboratory setting. Two phytoplankton blooms were induced in seawater and a breaking wave proxy generated SSA. The ice nucleating activities of SSA particles in two size-segregated populations were measured. Throughout both blooms, supermicron SSA particles were the most ice active population. The efficiency of supermicron particles was still apparent after normalizing to particle surface area. Following normalization to aerosol volume, submicron and total particle populations were comparable, suggesting ice active components in SSA scale with particle volume in the observed temperature range (−26°C to −8°C). These results suggest that climate models use size-dependent INP activities for SSA. Proper representation of marine INPs will increase model accuracy of ice content in clouds and radiative forcing over high latitude oceans.

1. Introduction

Mixed-phase clouds, those containing both ice crystals and supercooled water, play a significant role in the global radiation budget due to their ubiquity, especially at high latitudes (Shupe et al., 2008). Aerosol particles affect mixed-phase cloud formation by acting as cloud condensation nuclei and ice nuclei. Ice nucleating particles (INPs) have been shown to glaciate mixed-phase clouds and change their radiative and physical properties (DeMott et al., 2010; Lohmann, 2002; Lohmann & Feichter, 2005). Without an effective particle upon which ice can form, water will remain supercooled in the atmosphere down to a temperature of −38°C, where homogeneous freezing occurs for dilute liquid aerosols (Heymsfield & Miloshevich, 1993). However, water will freeze in the atmosphere at temperatures as warm as −1°C with an effective INP (Després et al., 2012). Determining the freezing conditions of different INPs is important for understanding cloud glaciation influenced by different aerosol populations. It is believed that the primary mechanism for freezing in mixed-phase clouds is through immersion of INPs into supercooled water droplets, known as

the immersion freezing mode (Field et al., 2012; Hoose & Möhler, 2012; Murray et al., 2012; Westbrook & Illingworth, 2011).

Sea spray aerosol (SSA) particles have been shown to be a major source of INPs in the marine atmosphere (DeMott et al., 2016; Wilson et al., 2015). SSA particles are considered to be the most likely source of INPs in remote marine locations, representing up to 80% of INPs over the high latitude oceans when dust is not present (Burrows et al., 2013; Vergara-Temprado et al., 2017). Ice nucleating entities (INEs) are the chemical species in seawater that are transferred into SSA particles and can form INPs. Potential species that act as INEs include proteins, carbohydrates, and cell fragments which, along with other organic species, are often enriched in the sea surface microlayer (SSML, Aller et al., 2005; McCluskey et al., 2018b; Schnell & Vali, 1976; Wilson et al., 2015). Wilson et al. (2015) studied INEs in various locations and found the organic-rich SSML contains more INEs that nucleate ice at warmer temperatures than bulk seawater. They showed that, upon filtration of the SSML and subsequent measurement of the ice nucleating ability of the filtrate, INEs in the SSML are likely submicron in size. Using a slightly different sampling method, measurements of the bulk seawater and the SSML in the Canadian Arctic by Irish et al. (2017) concluded that INEs were biological material with diameters between 0.2 and 0.02 μm, supporting the measurements made by Wilson et al. (2015).

Breaking waves form bubbles which burst at the ocean surface to produce SSA. When bubbles rupture, INEs can be transferred from seawater to the atmosphere and serve as INPs in SSA. There are two main SSA production mechanisms: (1) the retraction and fragmentation of the bubble cap, which ejects film drops and (2) the production of a fluid jet at the base of the bubble that fragments through a Plateau-Rayleigh instability and produces jet drops. These generation mechanisms produce droplets with different size distributions and distinct chemical compositions (Veron, 2015). Wang et al. (2017) investigated the impact of production mechanisms on submicron INP concentrations and found INPs generated by jet drops had higher concentrations than those generated by film drops, suggesting a potential size-differentiated distribution of INEs released in SSA particles. The compositional differences of SSA based on particle size, referred to as a size-resolved external mixing state, have motivated the study of the effect of SSA size on INP concentration. Previously, Rosinski et al. (1986, 1987) suggested that marine INPs were submicron in size based on physical and chemical analysis of filter-collected INPs. However, Schnell and Vali (1976) discovered a source of "ocean derived nuclei" from seawater INEs that were micron-sized and suggested that these nuclei were responsible for increased INPs over regions of elevated ocean productivity.

There has been a recent resurgence in the number of studies measuring the size of INPs in marine locations, which include anthropogenic and terrestrial sources in addition to SSA (Creamean et al., 2019; Ladino et al., 2019; Mason et al, 2015, 2016; McCluskey et al., 2018a, 2018c; Si et al., 2018). These studies often show that the majority of INPs are supermicron in scale. Although Ladino et al. (2019) hypothesized that some of the supermicron INPs observed could consist of marine biological particles, there may have been other sources, such as mineral dust or terrestrial biological aerosols, making it impossible to definitively determine the origin of the INPs.

The approach here uses a unique system to produce isolated, nascent SSA in a laboratory setting, which excludes all other sources of INPs, to measure the size-resolved ice nucleating activity for immersion freezing. Previously, DeMott et al. (2016) and McCluskey et al. (2017, 2018b) investigated INPs from SSA generated in the laboratory in a wave flume and a Marine Aerosol Reference Tank (MART, Stokes et al., 2013). DeMott et al. (2016) found INP concentrations from laboratory-generated SSA were consistent with concentrations measured in remote marine locations. McCluskey et al. (2017) investigated nascent SSA from mesocosm blooms and observed an increase in INP concentrations after the senescence of phytoplankton bloom biomass. Through chemical analysis of the SSA, McCluskey et al. (2018b) hypothesized two sources of marine INPs: molecular INEs in dissolved organic carbon, and INEs as particulate organic carbon derived from marine microbes. None of these studies reported the size-resolved ice nucleating activity of nascent SSA without the influence of other aerosols. As discussed earlier, the size differentiation of INPs is important for understanding the composition and factors controlling the ice nucleating abilities of SSA particles. Therefore, the size range for the most active INP population was measured over the course of two phytoplankton blooms in natural seawater to better understand how biology and physical production processes affect the ice nucleating ability of SSA.

2. Materials and Methods

2.1. Overview of the Experiment

SSA was generated during two mesocosm phytoplankton blooms from June 18, 2017 to June 29, 2017 and September 20, 2017 to October 13, 2017. Blooms were induced in an outdoor tank through the addition of nutrients and sodium silicate to seawater collected from the Pacific Ocean. Water from the tank was transferred to a MART to generate SSA. Sampling days were chosen based on chlorophyll-a concentrations, a common indicator of phytoplankton growth. SSA sampling was performed at three critical times during the phytoplankton bloom: before the peak, during the peak, and after the peak of the bloom during senescence.

A schematic of the experiment setup is shown in Figure S1. SSA particles generated in the MART were sent into two main sampling lines, one for characterization of the size distribution and the other for collecting SSA on filters for off-line processing of INP activity. SSA particles were dried with silica diffusion driers, to ensure the relative humidity was below the deliquescence point, prior to measuring the size distribution with a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer (APS). SSA particles for off-line processing were collected onto 0.2 μm polycarbonate filters for a period of 18 h at a flow rate of 4.5 L/min. After collection, the INPs were eluted off the filters with a milliQ water wash and subsequently measured with an automated ice spectrometer, with controlled cooling from −5°C to −35°C, to determine the immersion freezing temperatures of the samples (Beall et al., 2017). The SSA particles were divided into two size ranges before reaching the filters: submicron, which excluded droplets greater than 1 μm dry diameter, and total, which included all droplets produced (both supermicron and submicron). Particles were removed from the submicron SSA population using a custom impactor with a 50% collection efficiency cut-off at an aerodynamic diameter of 2 μm near 80% relative humidity (RH). Particles with aerodynamic diameters of 1 μm at 80% RH passed through with close to 0% collection efficiency and particles with 3 μm diameters had a 90% collection efficiency through this impactor. Assuming spherical particles, there is a factor of 2 size reduction upon desiccation (Lewis & Schwartz, 2004). Therefore, once dried, the aerosol physical diameter at 50% collection efficiency is approximately 1 μm. The supermicron particles removed by the custom impactor were not collected for analysis. Additionally, measurements of seawater chlorophyll-a concentration, and bacterial and viral concentrations were performed on each day. Further details on the methods are in the supporting information and the data is available at: https://doi.org/10.6075/J0GM85TV.

3. Results

3.1. Conditions for Mesocosm Phytoplankton Blooms

Two phytoplankton blooms, representative of the microbial communities off La Jolla, California at different times of the year, were induced (Figures 1a and 1b). Both blooms reached chlorophyll-a maximum values in the range of 0.1–10 μg/L, typical of moderate phytoplankton blooms in the Pacific Ocean (Coale et al., 1996; McClain, 2009; Wernand et al., 2013). The first phytoplankton bloom, induced during the summer, reached a maximum chlorophyll-a concentration of 8.79 μg/L, 4 days after spiking with F/100 nutrients. The second phytoplankton bloom, in the fall, showed a minor increase in chlorophyll-a fluorescence after spiking with F/100 nutrients but required an additional spike with F/20 nutrients on October 3, 2017 to achieve a full bloom, with a peak concentration of 4.48 μg/L. The two blooms showed similar abundances of both bacteria and viruses, consistent with previous observations in marine environments (Bergh et al., 1989; Hara et al., 1991). Bacterial concentrations during both blooms were on the order of 10^6 mL^{-1} while virus concentrations ranged from 10^7 to 10^8 mL^{-1}.

Phytoplankton blooms follow a typical pattern known as the microbial loop, where the breakdown of phytoplankton coincides with bacterial growth (Azam et al., 1983). After peaking, bacterial concentrations decline due to viral lysis (Wilhelm & Suttle, 1999). Both blooms followed this pattern, with bacterial populations tracking the chlorophyll-a growth with a slight delay (Figures 1a and 1b). The viral growth progressed after the peak in the bacterial concentrations and generally increased throughout the course of the bloom into senescence. Presuming INEs are biological in origin (Alpert et al., 2011; Irish et al., 2017; Knopf et al., 2011; McCluskey et al., 2018b; Wilson et al., 2015), the concentration of INEs is expected to change throughout these biological growth and degradation processes.

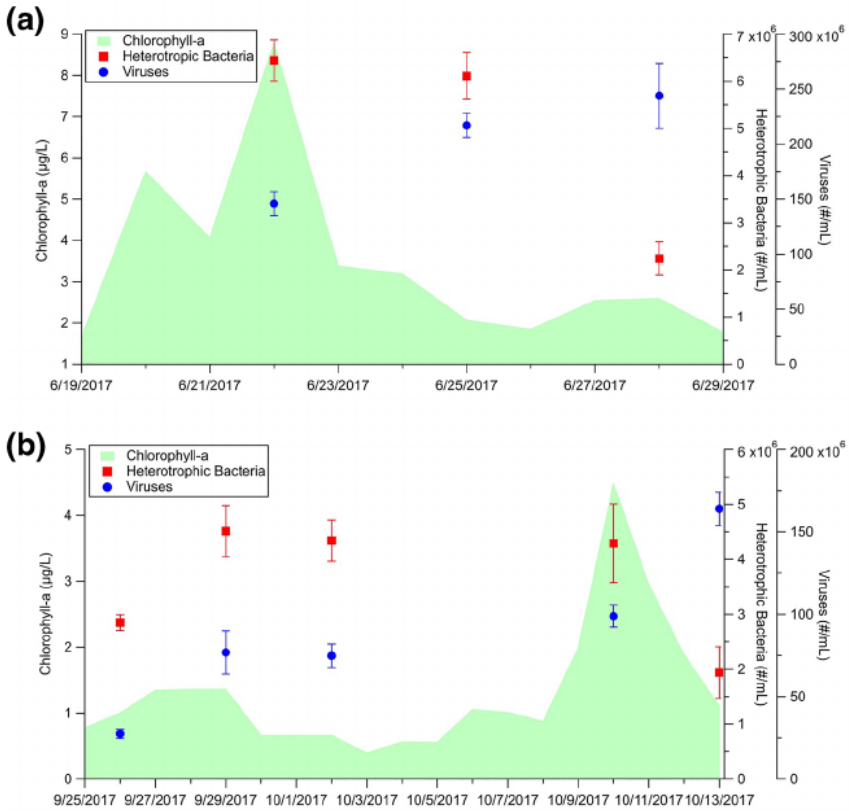

Figure 1. Temporal profiles of chlorophyll-a concentration, bacteria, and virus concentrations in seawater for (a) Bloom 1 and (b) Bloom 2.

3.2. Measured INP Concentrations

Figure 2 compares the INP concentrations of total SSA to submicron SSA for both blooms. The INP concentrations for total SSA were typically a factor of 10 higher than those measured for submicron SSA, demonstrating a larger abundance of species that form INPs in the supermicron SSA population. On October 2, 2017 the submicron INPs reached their highest concentrations and fell in the lower range of observed total

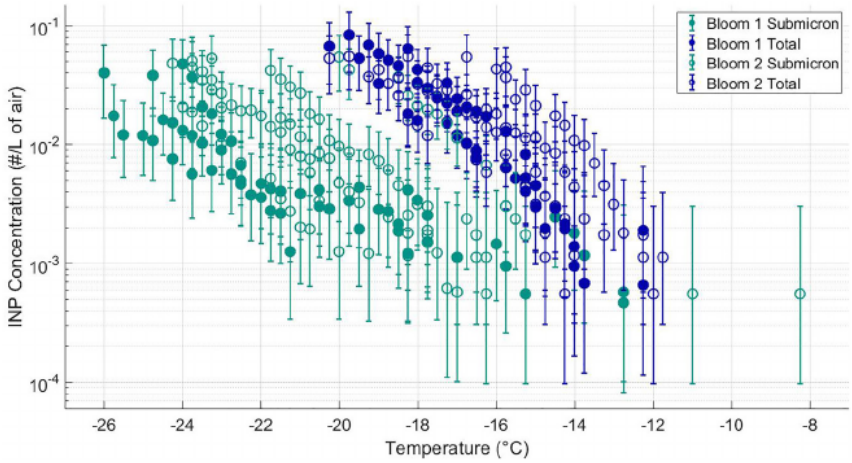

Figure 2. Ice nucleating particle (INP) concentrations for submicron (teal) and total (navy) sea spray aerosol (SSA) populations plotted for both Bloom 1 (closed marker) and Bloom 2 (open marker).

INP concentrations. However, on this day, there were also elevated total INP concentrations and supermicron INPs remained the most abundant. Fisher's exact test was used to compare the significance of the INP concentrations for the total and submicron particle populations for each sampling day of both blooms (Fisher, 1922). The higher INP concentrations observed in total SSA were statistically significant (p-value <0.05) at all times throughout both blooms, independent of the stage of the bloom lifecycles.

The warmest temperatures at which significant differences occurred between total and submicron INP activities ranged from −14°C to −17°C (Table S1). At these mid-level temperatures and colder, total INPs were significantly higher in concentration. McCluskey et al. (2017) observed an increase in INP concentrations between temperatures of −15°C and −25°C after the peak of a phytoplankton bloom. Our results show that the predominant INP source in this temperature range was from supermicron particles. There were two observations, at −8°C and −11°C, of warm submicron INPs. Both data points were considerably warmer than the other submicron INP temperatures, indicating they may have been from a distinct source of biological INEs or, more likely, random variability or potential contamination. However, these two outliers did not represent the majority of the INP populations measured or change the conclusion that supermicron INPs dominate in the mid to cold temperatures.

3.3. Calculated Number and Volume Site Densities

The number site density, n_s, is often used to describe the efficiency of a single INP type by normalizing the INP concentration to the total dry aerosol surface area, calculated from the number size distribution (Figures S2a and S2b). The number site density has been used to parameterize INP concentrations from size distributions of SSA and dust INP types in an atmospheric model (McCluskey et al., 2019). In this study, we used the number site density to compare how efficient total INP and submicron INP populations were to one another. As shown in Figure 3a, the number site densities for both submicron and total aerosols fell within the values for lab generated SSA previously reported by DeMott et al. (2016). However, the total particles generally showed larger number site densities compared to submicron particles, indicating that submicron SSA particles are less efficient INPs in primary SSA. Additionally, this figure shows the range of number site density values measured by McCluskey et al. (2018c) for INPs collected in clean marine air masses at the Mace Head Research Station in Ireland.

Figure 3a shows the total INP number site densities measured in this laboratory study fell within the range of number site densities measured for ambient SSA. Total INP number site densities occurred at the upper end of those measured at Mace Head. This could be because marine events with enhanced INPs were excluded from the values reported by McCluskey et al. (2018c). This difference may also reflect the influence of atmospheric processes on INPs in the real atmosphere, such as aerosol scavenging through wet and dry deposition and/or secondary reactions. The results of this study are consistent with recent ambient observations suggesting supermicron sized particles play a major role acting as marine INPs.

After normalizing to the surface area, supermicron INPs had moderately higher number site densities compared to submicron particles. A subsequent normalization of the ice active sites to aerosol volume showed submicron and total particle populations had comparable volume site densities, v_s (Figure 3b). A linear fit was generated using the volume site density data from both blooms based on the following equation: $\log_{10}(v_s) = a \cdot T + b$, where v_s is the volume site density (cm^{-3}) and T is the freezing temperature (°C). The fit parameters (±95% confidence intervals) based on this equation were −0.18 (±0.02) and 2.41 (±0.27), respectively, with a coefficient of determination of 0.71. This relationship supports the idea that the number of entrained INEs scales with SSA volume. Supermicron particles, which have larger volumes, therefore likely contain more INEs than submicron SSA particles.

3.4. INE Transfer to INP

INE concentrations measured during the second bloom using immersion freezing are reported for bulk seawater and SSML samples (Figures 4a and 4b). INE concentrations in the microlayer were greater than those in the bulk seawater, a trend reported in previous studies (Irish et al., 2017; McCluskey et al., 2018b; Wilson et al., 2015). The concentrations of INEs in the SSML and bulk seawater fall within those reported for seawater from the Pacific Ocean (McCluskey et al., 2018b). The number of INEs increased over the

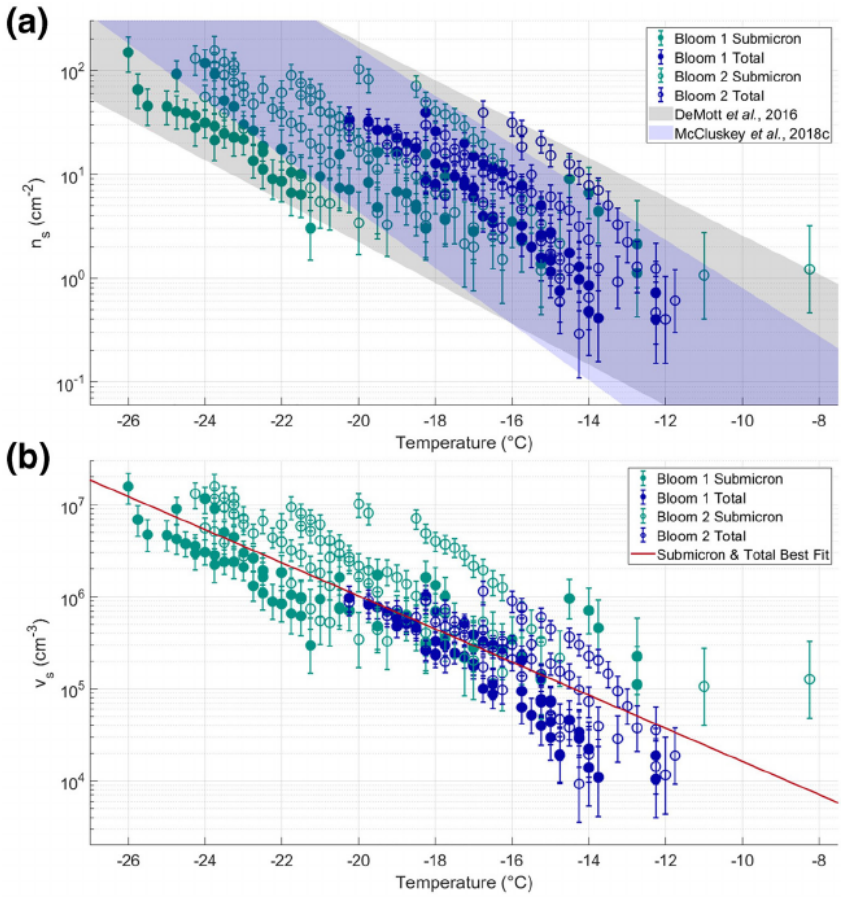

Figure 3. (a) Number site densities of the submicron (teal) and total (navy) populations plotted against freezing temperatures for Bloom 1 (closed markers) and Bloom 2 (open markers). For reference, the ranges are plotted for laboratory SSA values from DeMott et al. (2016) and ambient values by McCluskey et al. (2018c). (b) Volume site densities of submicron and total populations plotted against freezing temperatures for Bloom 1 and Bloom 2. A best fit ($R^2 = 0.71$) is shown for the combined total and submicron data from both blooms with the following equation: $\log_{10}(v_s) = -0.18\ T + 2.41$, where v_s is the volume site density (cm^{-3}), and T is temperature (°C).

course of the phytoplankton bloom, which corresponded with the observed increase in total INP concentrations at the end of the bloom (Figure 4c); more INEs in the bulk was consistent with more INPs in the SSA. However, the lack of a clear trend between INE and INP concentrations suggests an increase in the number of INEs alone was not sufficient to explain the observed INP concentration behavior. We speculate that unidentified processes influence the selection of INEs into SSA particles. Although INEs were not size selected in our seawater samples, previous studies found that INEs within the SSML and bulk are between 0.02 and 0.2 μm (Irish et al., 2017; McCluskey et al., 2018b; Wilson et al., 2015). Additionally, these studies demonstrated that the INEs are likely biological in nature. It is known that bubbles scavenge both biological and surface-active particles, resulting in an enrichment of these species at the sea surface (Blanchard et al., 1981; Cunliffe et al., 2013; Weber et al., 1983). Previously, Rastelli et al. (2017) showed supermicron SSA particles contain a higher overall abundance of biological species compared to submicron SSA particles. Furthermore, submicron jet drops were shown to have higher ice nucleating activity than submicron film drops; likely due to the different production mechanisms and different chemical compositions (Wang et al., 2017). A majority (60%–80%) of all submicron SSA particles are film drops (Wang et al., 2017), whereas jet drops are believed to comprise a majority of SSA particles with diameters from 1 to 25 μm (80% RH) (de Leeuw et al., 2011). Therefore, we suggest scavenging of INEs in surface-active material through rising bubbles and subsequent airborne transfer in supermicron sized SSA, likely through jet drops, as an important mode of transport (Figure S3).

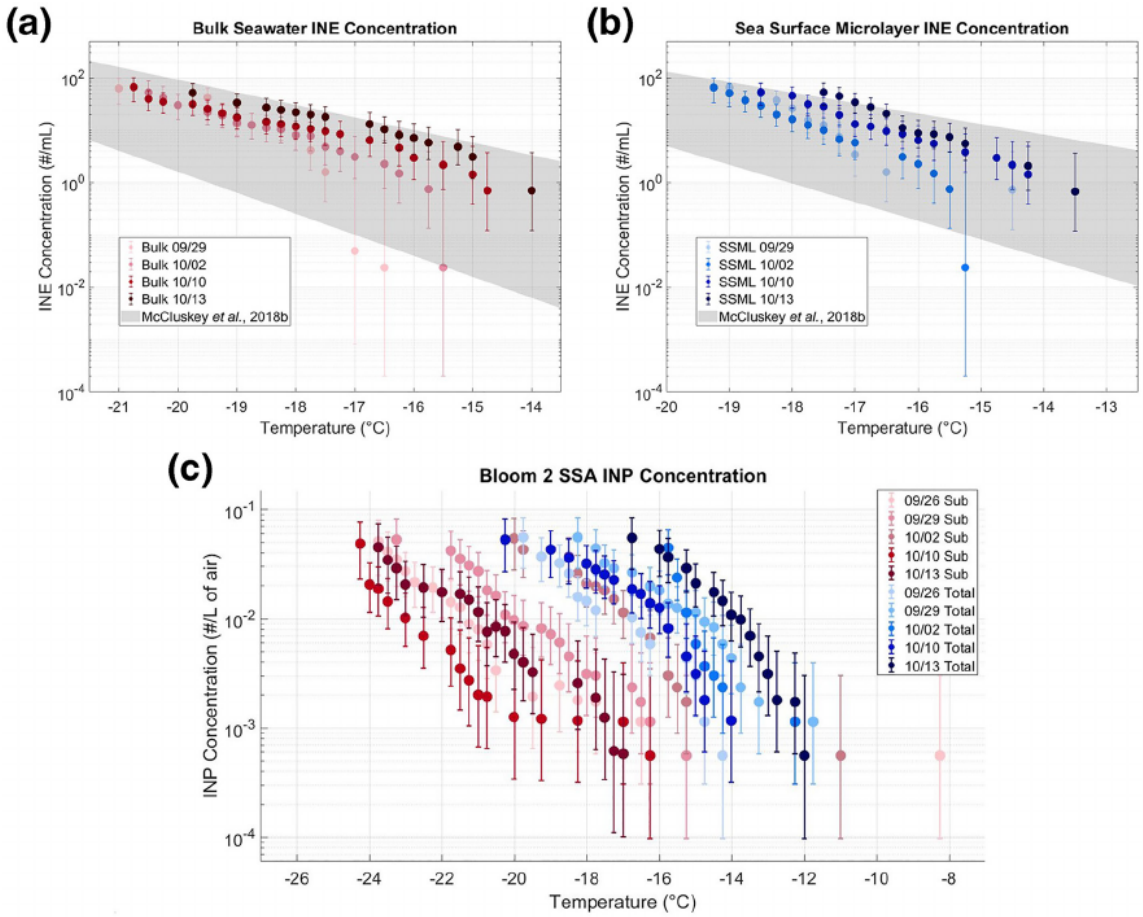

Figure 4. Daily INE concentrations in (a) bulk seawater; and (b) sea surface microlayer (SSML) during Bloom 2. (c) Daily INP concentrations for Bloom 2 submicron (red) and total (blue) particles. For reference, the range of INE concentrations from bulk seawater and the SSML measured by McCluskey et al. (2018b) are included.

4. Conclusions

Laboratory measurements comparing the ice nucleating activities of submicron versus total SSA particles in an isolated ocean/atmosphere study show supermicron SSA particles are the dominant source of INPs in nascent SSA. We show INPs in supermicron SSA have higher ice nucleation active site densities when normalized by surface area compared to INPs in submicron SSA. When the active sites were normalized to aerosol volume, submicron and total SSA populations showed comparable results, suggesting the transfer of INEs into SSA scales with particle volume. These measurements support the conclusion that supermicron SSA particles are the main source of INPs released from the ocean and marine INEs are predominantly transferred into these particles because they represent the bulk of SSA volume. The dominance of supermicron INPs in nascent SSA is consistent with prior studies, which quantified the important role of supermicron INPs in ambient environments but were unable to unambiguously show that SSA particles led to the observed difference in activity. This laboratory study is the first to clearly show that supermicron SSA particles represent a key source of nascent INPs in marine environments. A caveat to this conclusion is that the ice nucleating properties of aged SSA are potentially quite different from the nucleating properties of the nascent SSA studied here. Assuming this is not the case, factors leading to changes in SSA production or biological processes resulting in an increased flux of supermicron SSA particles are likely to have a strong impact on marine clouds and climate.

A question remains as to which physical mechanism produces supermicron INPs. As discussed herein, SSA particles are produced via two bubble-bursting mechanisms: (1) the breakup of a jet formed at the

base of a bursting bubble producing jet drops and (2) the fragmentation of the retracting bubble cap film producing film drops. Current wisdom is that most supermicron SSA particles, and therefore supermicron INPs, are produced via jet drops (Lewis & Schwartz, 2004). Additionally, it has been proposed that INEs are enriched in jet drops relative to film drops. Wang et al. (2017) analyzed the ice nucleating activity of submicron SSA and, upon normalization to the total aerosol surface area and volume, found INP concentrations from jet drops were greater than those from film drops. They suggested the observed dominance of INPs in submicron jet drops could be explained if the jet drop production mechanism concentrates INEs more than film drop production. Unlike the study by Wang et al. (2017), which used bubble generators, the results shown here on SSA generated using a breaking wave analogue do not suggest enhancement of INEs in supermicron particles after normalization to aerosol volume. However, the dominance of supermicron INPs indicates that jet drops serve as an efficient transfer method of INEs into SSA particles for the observed temperature regime (−26°C to −8°C).

Previous studies aimed at representing marine INPs in global climate models assumed all marine INPs were derived from submicron SSA particles (Burrows et al., 2013; Huang et al., 2018; Vergara-Temprado et al., 2017). McCluskey et al. (2019) found model-observation closure for marine INPs using ice nucleating site densities that included all aerosol particle sizes. However, they highlighted the critical need for studies that resolve the size-dependence of marine aerosol composition on INP efficiency. Here, supermicron particles represent the major fraction of INPs in nascent SSA during two phytoplankton blooms. These results suggest that existing marine INP parameterizations need to include supermicron marine INPs in global climate models. Additionally, based on the volume scaling shown in this analysis, models should consider parameterizing INPs in SSA based on active sites normalized to dry particle volume as opposed to surface area. Without accounting for the impact of supermicron INPs, this study predicts an underestimation of the number of marine INPs by a factor of 10, which will lead to a subsequent misrepresentation of the effects on the global radiative budget. Future work focused on the composition of INEs and their transfer to the marine atmosphere as INPs will benefit model simulations of aerosol impacts on clouds and climate over remote marine locations, especially over the Southern Ocean.

Data Availability Statement

All data supporting the conclusions are publicly available from the UC San Diego Library Digital Collections at: https://doi.org/10.6075/J0GM85TV.

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