

# A Two-Component Parameterization of Marine Ice Nucleating Particles Based on Seawater Biology and Sea Spray Aerosol Measurements in the Mediterranean Sea

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**Abstract.** Ice nucleating particles (INP) have a large impact on the climate-relevant properties of clouds over the oceans. Studies have shown that sea spray aerosols (SSA), produced upon bursting of bubbles at the ocean surface, can be an important source of marine INP, particularly during periods of enhanced biological productivity. Recent mesocosm experiments using natural seawater spiked with nutrients have revealed that marine INP are derived from two separate classes of organic matter in SSA. Despite this finding, existing parameterizations for marine INP abundance are based solely on single variables such as SSA organic carbon (OC) or SSA surface area, which may mask specific trends in the separate classes of INP. The goal of this paper is to improve the understanding of the connection between ocean biology and marine INP abundance by reporting results from a field study and proposing a new parameterization of marine INP that accounts for the two associated classes of organic matter. The PEACETIME cruise took place from May 10 to June 10, 2017 in the Mediterranean Sea. Throughout the cruise, INP concentrations in the surface microlayer (INP<sub>SML</sub>) and in SSA (INP<sub>SSA</sub>) produced using a plunging aquarium apparatus were continuously monitored while surface seawater (SSW) and SML biological properties were measured in parallel. The organic content of artificially generated SSA was also evaluated. INP<sub>SML</sub> and INP<sub>SSA</sub> concentrations were found lower than in the literature, presumably due to the oligotrophic nature of the Mediterranean Sea. A dust wet deposition event that occurred during the cruise increased the INP concentrations measured in the SML by an order of magnitude, in line with increases of iron in the SML and bacterial abundances. Increases of INP<sub>SSA</sub> were not observed until after a delay of three days compared to increases in the SML, and are likely a result of a strong influence of bulk SSW INP for the temperatures investigated ( $T = -18^\circ\text{C}$  for SSA,  $T = -15^\circ\text{C}$  for SSW). Results confirmed that INP<sub>SSA</sub> are divided into two classes depending on their associated organic matter. Here we find that warm ( $T \geq -22^\circ\text{C}$ ) INP<sub>SSA</sub> concentrations are correlated with water soluble organic matter (WSOC) in the SSA, but also to SSW parameters (POC<sub>SSW</sub> and INP<sub>SSW,-16C</sub>) while cold INP<sub>SSA</sub> ( $T < -22^\circ\text{C}$ ) are correlated with SSA water-insoluble organic carbon (WIOC), and SML dissolved organic carbon (DOC) concentration. A relationship was also found between cold INP<sub>SSA</sub> and SSW nano- and micro-phytoplankton cell abundances, indicating that these species might be a source of water insoluble organic matter with surfactant properties and specific IN activities. Guided by these results, we formulated and tested multiple parameterizations for the abundance of INP in marine SSA, including a single component model based on POC<sub>SSW</sub> and a two-component model based on SSA WIOC and OC. We also altered two previous models based on SSA surface area and OC<sub>SSA</sub> content to account for oligotrophy of the Mediterranean Sea. We then compared these formulations with the previous models. These new parameterizations should improve attempts to incorporate marine INP emissions into numerical models.

## 43 1 Introduction

44 Ice nucleating particles are a subset of aerosol particles that are required for the heterogeneous nucleation of ice particles in  
45 the atmosphere. While extremely rare (Rogers et al., 1998), INP greatly control the ice content of clouds, which is crucial to a  
46 range of climate-relevant characteristics including precipitation onset, lifetime, and radiative forcing (Verheggen et al., 2007).  
47 Despite their importance, the knowledge of INP sources and concentrations, particularly in marine regions, remains low as  
48 evidenced by the large uncertainties in modelled radiative properties of clouds (McCoy et al., 2015; McCoy et al., 2016;  
49 Franklin et al., 2013).

50 While the ice nucleating (IN) ability of marine SSA particles is less efficient than their terrestrial counterparts (DeMott et  
51 al., 2016), modelling studies have shown that marine INP are of particular importance in part due to the lack of other INP  
52 sources in such remote regions (Burrows et al., 2013; Vergara-Temprado et al., 2017). For this reason, recent studies have  
53 been conducted to better understand which SSA particles contribute to the marine INP population as well as the relationship  
54 between SSA emission and ecosystem productivity. Results from these studies suggest that the IN ability of SSA is linked to  
55 the biological productivity of source waters, with higher productivity leading to greater IN activity (DeMott et al., 2016; Bigg,  
56 1973; Schnell and Vali, 1976). For example, it has been shown that both the cell surface and organic exudate of the marine  
57 diatom *Thalassiosira pseudonana* can promote freezing at conditions relevant to mixed-phase clouds (Knopf et al., 2011;  
58 Wilson et al., 2015). More recently, mesocosm studies on phytoplankton blooms using two separate in-lab SSA-generation  
59 techniques have furthered the understanding of the connection between ocean biology and the IN activity of SSA (McCluskey  
60 et al., 2017). In-depth chemical analysis of the artificially generated SSA during this set of experiments has revealed marine  
61 INP may be related to two classes of organic matter: a regularly occurring surface-active molecule type related to DOC and  
62 long-chain fatty acids, and an episodic heat-labile microbially-derived type (McCluskey et al., 2018b).

63 As the understanding of the connection between ocean biology and marine INP has improved, parameterizations for  
64 predicting marine INP abundance using readily available ocean parameters have been proposed. Wilson and co-authors  
65 (Wilson et al., 2015) identified a temperature-dependent relationship between TOC and ice nucleating entities (INE) number  
66 concentrations in the SML from samples collected in the North Atlantic and Arctic ocean basins. They then extended this  
67 relationship from the ocean to the atmosphere to predict the abundance of INP in SSA based on model estimates of marine  
68 organic carbon aerosol concentrations. The parameterization was tested for the first time on field measurements of marine  
69 aerosol over the North Atlantic at Mace Head and was found to overestimate INP abundance in pristine marine aerosol by a  
70 factor of 4 to 100 at -15°C and -20°C (McCluskey et al., 2018c). In the same study, a new parameterization based on SSA  
71 surface area and temperature was proposed (McCluskey et al., 2018c). However, this parameterization did not incorporate the  
72 recently observed heat labile organic INPs. Most recently, this parameterization was compared with observations of INP over  
73 the Southern Ocean, showing reasonable agreement between predictions and observations at -25°C (McCluskey et al., 2019).

74 Despite the recent progress made in the understanding of marine INP, there remains much room for improvement. To  
75 date, previous parameterizations have only been tested in the two field studies mentioned in the previous paragraph,  
76 underscoring the need for more real-world observations. Furthermore, the field studies conducted so far have taken place in  
77 regions of the ocean where biological productivity is high (i.e., North Atlantic and Southern Ocean). As modelling work has  
78 shown that the link between ocean biology and SSA organic content properties in oligotrophic waters differs from those in  
79 highly productive regions (Burrows et al., 2014) there is need for more measurements in waters with low primary productivity.  
80 Finally, despite the finding that marine INP may exist as two separate populations, no model has yet been proposed to account  
81 for this.

82 This paper addresses the current gaps in the knowledge of marine INP by 1) testing existing parameterizations of INP on  
83 a new set of field measurements by extending the current inventory of field measurements beyond eutrophic waters to more  
84 oligotrophic regions for the first time 2) improving the understanding of how INP in the SML and SSA are linked to both

85 seawater biological and SSA organic properties and 3) proposing a new parameterization based on the two-component nature  
86 of INP. Here we present results from the ProcEss studies at the Air-sEa Interface after dust deposition in the Mediterranean  
87 Sea (PEACETIME) cruise. The cruise took place in the central and western Mediterranean Sea from May 10 - June 10, 2017.  
88 Observations of INP concentrations both in the SML and SSA were compared with a suite of surface seawater, surface  
89 microlayer, and SSA properties to better determine how INP concentrations related to biology.

## 90 **2 Methods**

91 In the frame of the PEACETIME project (<http://peacetime-project.org/>), an oceanographic campaign took place aboard  
92 the French research vessel (R/V) ‘Pourquoi Pas?’ between May 10-June 10, 2017 with the purpose of investigating the  
93 processes that occur at the air-sea interface in the Mediterranean Sea. The cruise started in La Seyne, France and travelled in  
94 a clockwise fashion between 35° to 42° latitude and 0° to 20° longitude. The observations and process studies performed on  
95 board both in the whole water column and the atmosphere are described elsewhere (Freney et al., 2020). Here, we focus on the  
96 measurements conducted to describe the SML, SSW, and aerosol properties.

### 97 **2.1 Surface Seawater (SSW)**

98 SSW properties presented here were obtained from sampling at depths of 20 cm and 5 m. First, 21 parameters including  
99 various chemical properties, microbial assemblages, hydrological properties, and optical properties were monitored using the  
100 ship’s underway system that continuously collected seawater at 5 m under the ship using a large peristaltic pump (Verder VF40  
101 with EPDM hose). These measurements included counts of specific microbial classes (e.g., *Synechococcus*, *Prochlorococcus*,  
102 picoeukaryotes, nanoeukaryotes, microphytoplankton, high phycoerythrin containing cells, coccolithophores, cryptophytes), as  
103 well as seawater biovolume, chlorophyll-*a* (chl-*a*), and POC concentrations. Chl-*a* was determined from the particulate  
104 absorption spectrum line-height at 676 nm after adjusting to PEACETIME chl-*a* from high performance liquid chromatography  
105 (HPLC). POC was estimated from the particulate attenuation at 660 nm using an empirical relationship specific to  
106 PEACETIME ( $POC = 1405.1 \times c_p(660) - 52.4$ ). For enumeration of phytoplankton cells, an automated Cytosense flow  
107 cytometer (Cytobuoy, NL) operating at a time resolution of one-hour was connected to the continuous underway seawater  
108 system. Particles were carried in a laminar flow filtered seawater sheath fluid and subsequently detected with forward scatter  
109 and sideward scatter as well as fluorescence in the red (FLR > 652 nm) and orange (FLO 552-652 nm). Distinction between  
110 highly concentrated picophytoplankton and cyanobacteria groups and lower concentrated nano- and microphytoplankton was  
111 accomplished using two trigger levels (trigger level FLR 7.34 mV, sampling speed of  $4 \text{ mm}^3 \text{ s}^{-1}$  analysing  $0.65 \pm 0.18 \text{ cm}^3$  and  
112 trigger level FLR 14.87 mV at a speed of  $8 \text{ mm}^3 \text{ s}^{-1}$  analysing  $3.57 \pm 0.97 \text{ cm}^3$ ).

113 The second set of SSW measurements were made on seawater collected at ~20 cm depth from a pneumatic boat that was  
114 periodically deployed at a distance of 2 km from the R/V to avoid contamination. The SSW was manually collected using acid  
115 cleaned borosilicate bottles. From these discrete samples, microbial composition and cell abundance of the SSW was monitored  
116 as described in a companion paper (Tovar-Sanchez et al., 2019). Measurements included heterotrophic bacteria counts, high  
117 nucleic acid and low nucleic acid bacteria (HNA and LNA bacteria, respectively), total non-cyanobacteria like cells (NCBL),  
118 cyanobacteria like cells (CBL), and total phytoplankton concentration (NCBL+CBL). These were further segregated into size  
119 classes of small, medium, and large which roughly correspond to the pico-, nano-, and micro- size classifications from the  
120 underway measurements. Trace metals (i.e., Cd, Co, Cu, Fe, Ni, Mo, V, Zn, Pb) were analysed by inductively coupled plasma  
121 mass spectrometry, although here we only report on Fe. Finally DOC and marine gel-like particles, including abundance of  
122 transparent exopolymer particles (TEP) and Coomassie stainable particles (CSP) were also measured as described in literature  
123 (Engel, 2009).

## 124 2.2 Surface Microlayer

125 At the same time SSW samples were manually collected on the pneumatic boat, SML samples were also collected using  
126 a glass plate sampling method which has been previously described in the literature (Tovar-Sanchez et al., 2019). The glass  
127 plate was cleaned overnight with acid and rinsed with ultrapure Milli-Q water. Roughly 100 dips of the glass were conducted  
128 to collect 500 mL of SML water into 0.5 L acid cleaned low-density polyethylene plastic bottles. The samples were then  
129 acidified on board to pH<2 with ultrapure-grade hydrochloric acid in a class-100 HEPA laminar flow hood. The same  
130 measurements done for the SSW samples (see above, Section 2.1) were then made on the SML samples. Enrichment factor  
131 was calculated for relevant properties as the ratio of SML to SSW:

$$132 \quad EF = \frac{SML}{SSW}$$

133 In addition to biological measurements, concentrations of immersion freezing mode INP in SML samples (and a small  
134 number of SSW samples, n=4) were measured between May 22 - June 7 using an offline method described previously (Stopelli  
135 et al., 2014). Briefly, prior to acidification of the SML samples, additional aliquots were separated and stored in Corning  
136 Falcon 15 mL conical tubes and frozen at -20°C until analysis. Before INP measurement, each aliquot was gradually defrosted  
137 and distributed into an array of 26 Eppendorf tubes filled up to 200 µL. The array was then immersed inside an LED based Ice  
138 Nuclei Detection Apparatus (LINDA) and the number of ice nucleating particles per liter (INP/L) of SML water was following  
139 the method described in Stopelli et al. (2014) which was originally formulated by Vali (1971):

$$140 \quad \frac{INP}{volume} = \frac{\ln(N_{total}) - \ln(N_{unfrozen})}{V_{tube}}$$

141 where  $N_{total}$  is the total number of tubes,  $N_{unfrozen}$  the total number of unfrozen tubes, and  $V_{tube}$  the volume of sample in  
142 each tube. The number of unfrozen tubes is calculated by first blank correcting the number of frozen tubes, and then subtracting  
143 that value from the total number of tubes. We calculated uncertainty as the binomial proportion confidence interval (95%)  
144 using the Wilson score interval. Samples were not corrected for salinity in this study.

## 145 2.3 Artificially Generated Sea Spray Aerosol

146 Sea spray aerosols were generated using a sea spray generation apparatus which has been described previously (Schwier  
147 et al., 2015; Schwier et al., 2017). The characteristics of the setup were selected to mimic Fuentes et al. (2010). These  
148 parameters (water flow rates, plunging water depth, etc.) have been shown to mimic well nascent SSA. The apparatus consists  
149 of a 10 L glass tank with a plunging jet system. A continuous flow of seawater collected at 5 m depth using the ship's underway  
150 seawater circulating system (described above) was supplied to the apparatus. Particle free air was passed perpendicular to the  
151 water surface at a height of 1 cm to send a constant airflow across the surface of the water. Aerosols were then either dried  
152 with a 1 m long silica dryer for online instrumentation (see Section 2.3.3), with a 30 cm silica gel dryer cascade impactor  
153 sampling with subsequent chemical analysis, or were sampled directly from the sea spray generator onto filters for INP  
154 analysis.

### 155 2.3.1 Offline PM1 Filter Analysis

156 Aerosol particles were also sampled onto PM1 quartz fiber filters mounted on a 4-stage cascade impactor (10 LPM)  
157 on a daily basis (24-hour duration). Samples were then extracted in Milli-Q water by sonication for 30 minutes for the analysis  
158 of water-soluble components. Main inorganic ion abundance (i.e.,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ ,  $Na^+$ ,  $Cl^-$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) was analysed  
159 via ion chromatography. An IonPac CS16 3x 250 mm Dionex separation column with gradient methanesulfonic acid elution  
160 was used for cations, while an IonPac AS11 2 x 250 mm Dionex column with gradient potassium hydroxide elution was used  
161 for anions. Water soluble organic carbon (WSOC) and water insoluble organic carbon (WIOC) were also determined. WSOC  
162 was measured after water extraction using a high-temperature catalytic oxidation instrument (Shimadzu; TOC 5000 A). Total

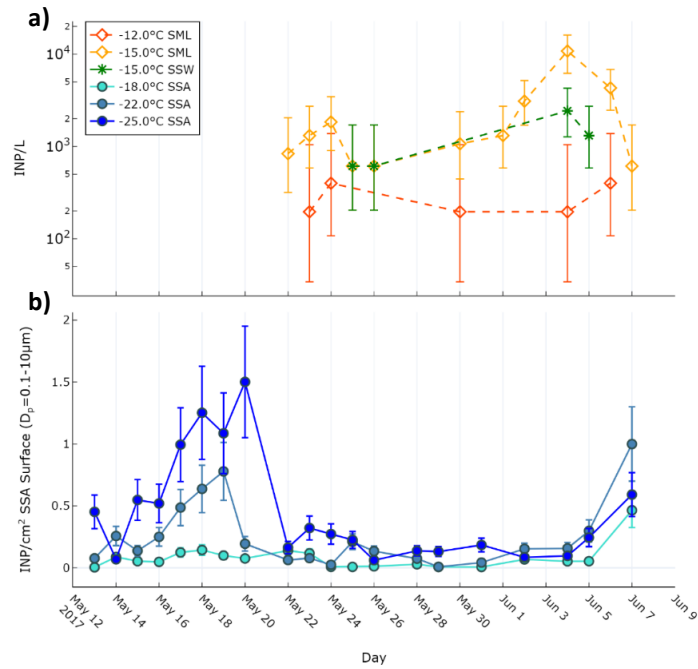
163 organic carbon (which we now refer to as OC), was measured using a Multi N/C 2100 elemental analyzer (Analytik Jena,  
164 Germany) with a furnace solids module. The analysis was performed on an 8 mm diameter filter punch, pre-treated with 40  
165  $\mu\text{L}$  of  $\text{H}_3\text{PO}_4$  (20% v/v) to remove contributions from inorganic carbon. WIOC was determined as the difference between OC  
166 and WSOC. Finally, we calculated organic mass fraction of SSA (OMSS) by taking the ratio of  $\text{OM}/(\text{OM}+\text{SeaSalt})$ , where  
167 OM is the sum of WSOM and WIOM, calculated as  $\text{WSOM} = \text{WSOC} \times 1.8$  and  $\text{WIOM} = \text{WIOC} \times 1.4$  and SeaSalt is the sum  
168 of inorganic ion abundance as determined above.

### 169 2.3.2 INP

170 INP concentrations were determined from filter-based samples of total suspended particles over a 24-hour duration daily  
171 or from the average of two filters (day and night). The concentration of INP in the SSA was determined for the condensation  
172 freezing mode using a Dynamic Filter Processing Chamber (DFPC), which has been used in multiple previous studies and  
173 found to agree well with other INP monitoring instruments (DeMott et al., 2018; Hiranuma et al., 2019; McCluskey et al.,  
174 2018c). A full description of the instrument can be found in the literature (DeMott et al., 2018). Briefly, bulk SSA formed  
175 using the plunging aquarium apparatus were impacted onto 47 mm nitrocellulose filters which were then placed on a metal  
176 plate coated with a smooth surface of Vaseline. Air entered the chamber and was sent through a cooling coil allowing it to  
177 become saturated with respect to water. Different supersaturations with respect to ice and liquid water can be obtained by  
178 controlling the temperatures of the filter and the air flowing across the filter. Filter air temperature combinations were set three  
179 different ways, all resulting in a supersaturation with respect to liquid water of 1.02. The filter temperatures were -18, -22, and  
180  $-25^\circ\text{C}$  (-15.9, -19.6, and  $-22.3^\circ\text{C}$  for air temperature). Under these conditions, condensation freezing is expected to be the  
181 dominant freezing mode for INP. It has been reported (Vali et al., 2015) that condensation freezing and immersion freezing  
182 are not distinguishable from one another. Filters were processed inside the DFPC for 15 minutes and monitored for formation  
183 of ice crystals upon activation of INPs. Based on sampling time and flow rate, the number of INP/volume were calculated. We  
184 report an uncertainty of  $\pm 30\%$  based on previous reports of the DFPC (DeMott et al., 2018).

### 185 2.3.3 Size Distribution Measurements

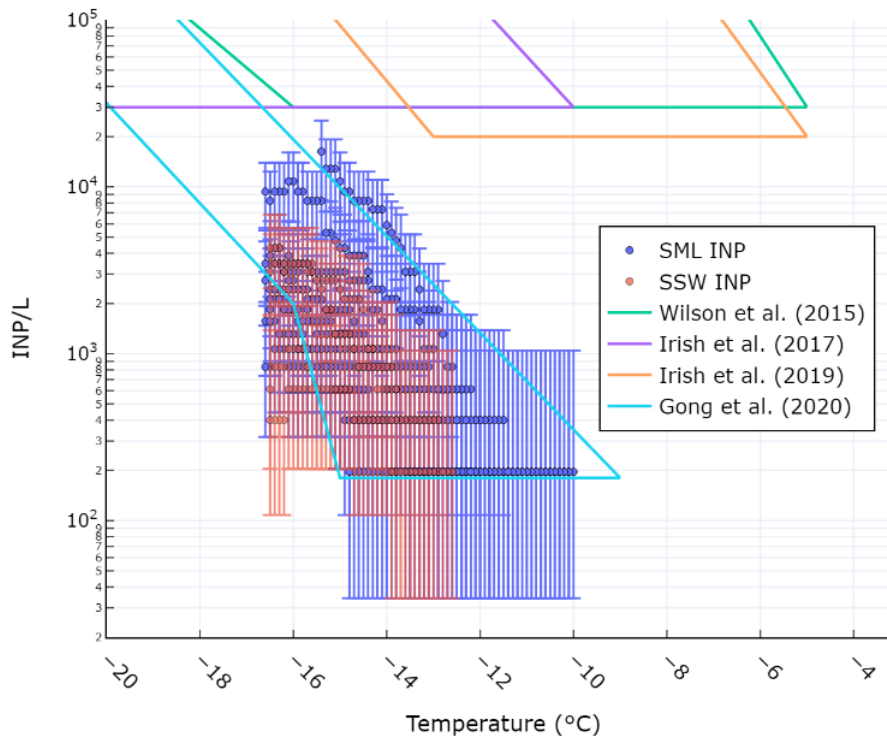
186 Particle size distribution and number concentrations of aerosols generated with the plunging apparatus were  
187 monitored using a custom-made differential mobility particle sizer (DMPS) preceded by a 1-micron size-cut impactor and X-  
188 ray neutralizer (TSI Inc.). Total counts from the DMPS system were checked using a condensation particle counter (CPC,  
189 TSI3010). Using the DMPS, a total of 25 size bins ranging between 10-500 nm (dry particle electrical mobility diameter) were  
190 scanned over a 10-minute time period. We then averaged the size distributions across each DFPC sampling period. For the  
191 purpose of the present study, surface area of SSA particles were calculated from the number size distributions by assuming  
192 spherical particles. Theoretical calculation of the number and surface area distributions for particles between .5-10  $\mu\text{m}$  was  
193 also carried out. The fit from our observed number size distributions from modes 1-4 agreed well with the fit of a sea spray  
194 aerosol source function consisting 5 lognormal modes based on in-situ particle number concentration measurements at Mace  
195 Head and open-ocean eddy correlation flux measurements from the Eastern Atlantic (Table S1) (Ovadnevaite et al., 2014). We  
196 took the ratio of mode 5 to mode 3 from this parameterization and applied it to our fit to calculate a fifth mode accounting for  
197 particles ranging in size between 500 nm and 10  $\mu\text{m}$ .



200 **Figure 1. a) INP concentrations observed during the PEACETIME cruise in the SML and SSW as measured using the LINDA**  
 201 **instrument. Error bars represent the binomial proportion confidence interval (95%) using the Wilson score interval. b) INP<sub>SSA</sub>**  
 202 **concentrations as observed by the DFPC normalized by SSA surface area. Error bars represent  $\pm 30\%$  uncertainty of the DFPC**  
 203 **instrument, as cited previously (DeMott et al., 2018).**

204 Ice nucleating particle characteristics were determined for the SSW, SML, and SSA. Figure 1a shows the concentration of  
 205 INP in the SML ( $\text{INP}_{\text{SML}}$ ) at two different temperatures ( $-12^\circ\text{C}$ ,  $-15^\circ\text{C}$ ) and in the SSW ( $\text{INP}_{\text{SSW}}$ ) at  $-15^\circ\text{C}$  as determined  
 206 using the LINDA instrument. An initial increase occurred on May 24 ( $1.8 \times 10^3$  INP/L at  $T = -15^\circ\text{C}$ ) relative to May 22 which  
 207 was then followed by a further increase on June 4 ( $1.1 \times 10^4$  INP/L at  $T = -15^\circ\text{C}$ ). The enhancement on June 4 occurred on the  
 208 same day as a dust deposition event which led to an enrichment of iron in the SML relative to the underlying water (see Section  
 209 3.2). While only four SSW samples were analysed for INP concentrations, they exhibited similar concentrations and trends to  
 210 those seen in the SML, with an observed maximum on June 4 ( $2.4 \times 10^3$  INP/L at  $T = -15.0^\circ\text{C}$ ). Based on these four samples, no  
 211 significant enrichment of INP was observed in the SML compared to SSW, except during the dust deposition event when the  
 212 SML concentration was enriched by a factor 4.5.

213 Figure 1b shows the concentration of ice nucleating particles in SSA ( $\text{INP}_{\text{SSA}}$ ) normalized by particle surface area for  
 214 particles with diameters smaller than  $10\ \mu\text{m}$  ( $0.1 < D_p < 10\ \mu\text{m}$ ) at three different temperatures as observed by the DFPC. It  
 215 should be noted that  $\text{INP}_{\text{SSA}}$  measurements were conducted at colder temperatures than for the  $\text{INP}_{\text{SML}}$  measurements due to  
 216 differences between the LINDA and DFPC instruments. In general, the highest concentrations of  $\text{INP}_{\text{SSA}}$  were observed at the  
 217 beginning of the voyage, with an initial value of  $0.45\ \text{INP}_{\text{SSA},-25^\circ\text{C}}/\text{cm}^2$  observed on May 13, increasing to a maximum observed  
 218 value of  $1.5\ \text{INP}_{\text{SSA},-25^\circ\text{C}}/\text{cm}^2$  on May 20. After May 20, a considerable drop in  $\text{INP}_{\text{SSA},-25^\circ\text{C}}$  concentrations was observed.  
 219 Concentrations remained at low, albeit with slight fluctuations, before increasing again to  $0.59\ \text{INP}_{\text{SSA},-25^\circ\text{C}}/\text{cm}^2$  on June 7. It is  
 220 also worth noting that the highest concentrations of INP active at  $-18^\circ\text{C}$  ( $\text{INP}_{\text{SSA},-18^\circ\text{C}}/\text{cm}^2$ ) were observed on this day. The  
 221 increase of INP concentrations around the time of the dust deposition event in early June is similar to the trend observed for  
 222 seawater INP, albeit with a lag of at least one day (no observations of  $\text{INP}_{\text{SSA}}$  were made on June 6).

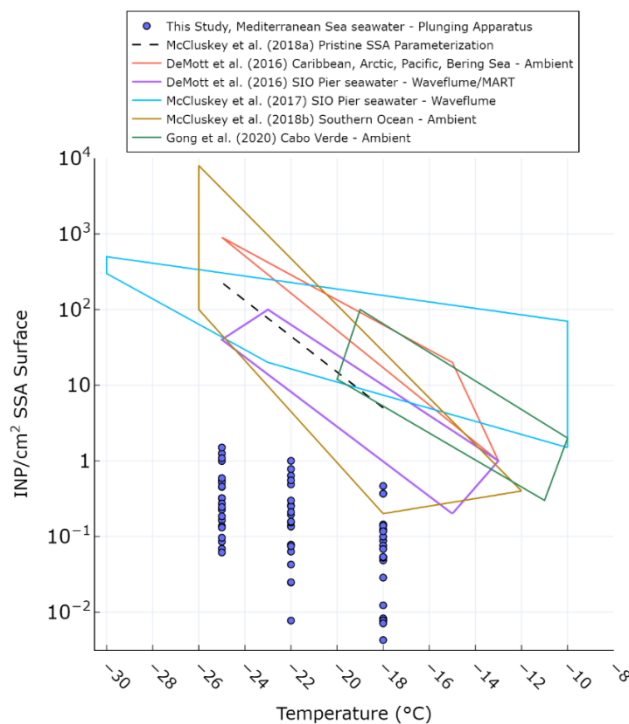


223 **Figure 2. Comparison of observed SSW (blue markers) and SML (red markers) INP concentrations with previous studies. Error**  
 224 **bars represent the binomial proportion confidence interval (95%) using the Wilson score interval.**

225 Figure 2 shows the comparison of observed INP concentrations at various temperatures in the SML and SSW with  
 226 those reported in previous studies. The concentrations we report here are lower than those from Arctic seawater samples  
 227 reported by Irish et al. (2017; 2019) and from Arctic and North Atlantic seawater samples reported in Wilson et al. (2015).  
 228 The difference can likely be attributed to the fact that eutrophic Arctic and North Atlantic seawater is more biologically active  
 229 than the oligotrophic Mediterranean Sea. Our values agree well with those reported by Gong et al. (2020) who calculated INP  
 230 concentrations in mid-latitude seawater off the coast of Cabo Verde. The authors of that study also posited that the low INP  
 231 concentrations relative to Irish et al. (2017; 2019) and Wilson et al. (2015) was due to the lower biological activity of the  
 232 oligotrophic seawater near Cabo Verde.

233 Figure 3 compares the INP per cm<sup>2</sup> of SSA surface during the PEACETIME cruise with values reported in previous  
 234 studies. DeMott et al. (2016) reported INP concentrations from ambient measurements over the Caribbean, Arctic, Pacific, and  
 235 Bering Sea. DeMott et al. (2016) and McCluskey et al. (2017) both reported INP concentrations from separate experiments in  
 236 which SSA was artificially generated using nutrient-spiked seawater collected off the Scripps Institute of Oceanography (SIO)  
 237 Pier with either a marine aerosol reference tank (MART) or an indoor waveflume. McCluskey et al. (2018a) reported ambient  
 238 INP concentrations measured over the Southern Ocean. Finally, Gong et al. (2020) reported INP concentrations as measured  
 239 off the coast of Cabo Verde. Our observed values are below those in all studies cited. The differences in our values compared  
 240 to those in the literature can be attributed to a number of factors, including differences in trophic state of source waters,  
 241 influences from terrestrial sources, and differences in INP analysis instruments. For example, Gong et al. (2020) state that  
 242 most INPs observed in their study were from dust particles, rather than sea spray. Gong et al. (2020) also calculated a theoretical  
 243 INP concentration based on the ratio of NaCl mass to INP in air and seawater (not shown in Figure 3). When we perform the  
 244 same calculation using observed NaCl values in SSA and salinity measurements of underway seawater, we find that the  
 245 INP/NaCl in the SSA is ~3000 times higher than in the SML. This is an important conclusion and points to the need for caution  
 246 when using the Gong et al. (2020) approach for calculating a contribution of SSA-derived INP in ambient air aerosols in future  
 247 studies. We note that studies in which seawater has been spiked with nutrients (McCluskey et al., 2017; McCluskey et al.,  
 248 2018b; DeMott et al., 2016) are expected to have higher levels of biological activity than those observed in the Mediterranean  
 249 and other oligotrophic regions. Since the departure of the PEACETIME INP in SML and SSW to the literature values is of the

250 same order of magnitude as the departure of the PEACETIME INP in SSA to the literature, it is reasonable to attribute the low  
251 INP<sub>SSA</sub> values to the oligotrophic nature of the Mediterranean seawater.



252 **Figure 3. INP/cm<sup>2</sup> SSA surface ( $0.1 < D_p < 10 \mu\text{m}$ ) at various temperatures as measured by the DFPC during the PEACETIME**  
253 **cruise (blue circles) compared with values reported in the literature. SSA were generated by continuously passing seawater from**  
254 **the ship's underway system into a plunging apparatus. Error bars are not shown as the uncertainty is smaller than the data points.**

### 255 3.2 Correlations between INP and Biogeochemical Conditions

256 As described in the methods section, various seawater biogeochemical properties were monitored throughout the voyage  
257 for the SSW and SML. Plots of selected continuous measurements from the R/V's underway sampling system and discrete  
258 measurements from the pneumatic boat of relevant biogeochemical values are found in the supporting information (Figure S1  
259 and Figure S2, respectively). Biogeochemical properties are described in more detail in our companion papers (Freney et al.,  
260 2020; Tovar-Sanchez et al., 2019) and seawater gel properties will be discussed in an upcoming paper. Here, we present a  
261 broad summary of observed conditions.

262 In general, surface waters were characterized by oligotrophic conditions as expected for the season. Bacteria  
263 concentrations ranged between  $2 \times 10^5$  and  $7 \times 10^5$  cells/mL in the SSW and were greatest at the start and end periods of the  
264 voyage. NCBL abundance followed a similar trend and ranged between  $4.0 \times 10^2$ – $4.0 \times 10^3$  cells/mL. Observed DOC values  
265 ranged between 700–900  $\mu\text{gC/L}$  and POC between 42–80  $\mu\text{gC/L}$  and were within the range of expected values for the  
266 oligotrophic Mediterranean (540–860  $\mu\text{gC/L}$  for DOC and 9.6–104  $\mu\text{gC/L}$  for POC) (Pujo-Pay et al., 2011). SSW TEP  
267 concentrations ranged between  $1.2 \times 10^6$  and  $1.1 \times 10^7$  particles/L, with CSP between  $5.6 \times 10^6$  and  $9.3 \times 10^6$  particles/L, and will  
268 be discussed in a future paper.

269 Enrichment factors (EF) in the SML relative to the SSW remained low with an average of 1.10 for DOC, 1.07 for bacteria,  
270 and 1.17 for NCBL. As POC was not measured in the SML, we cannot report its EF. TEP was typically enriched relative to  
271 the SSW, with an average EF of 4.5, while CSP EF was on average 2.7. Of importance, the dust deposition event that occurred  
272 on June 4 lead to a drastic increase in SML dissolved iron relative to the SSW (EF ~800). This deposition event had important  
273 impacts on the biology of the surface seawaters, which is the focus of another paper (Freney et al., 2020). As a result, TEP EF  
274 increased to 17, bacteria EF increased to 1.5, and NBCL to 2.4. We next discuss the correlations between INP abundances and  
275 biogeochemical properties in the following sections.

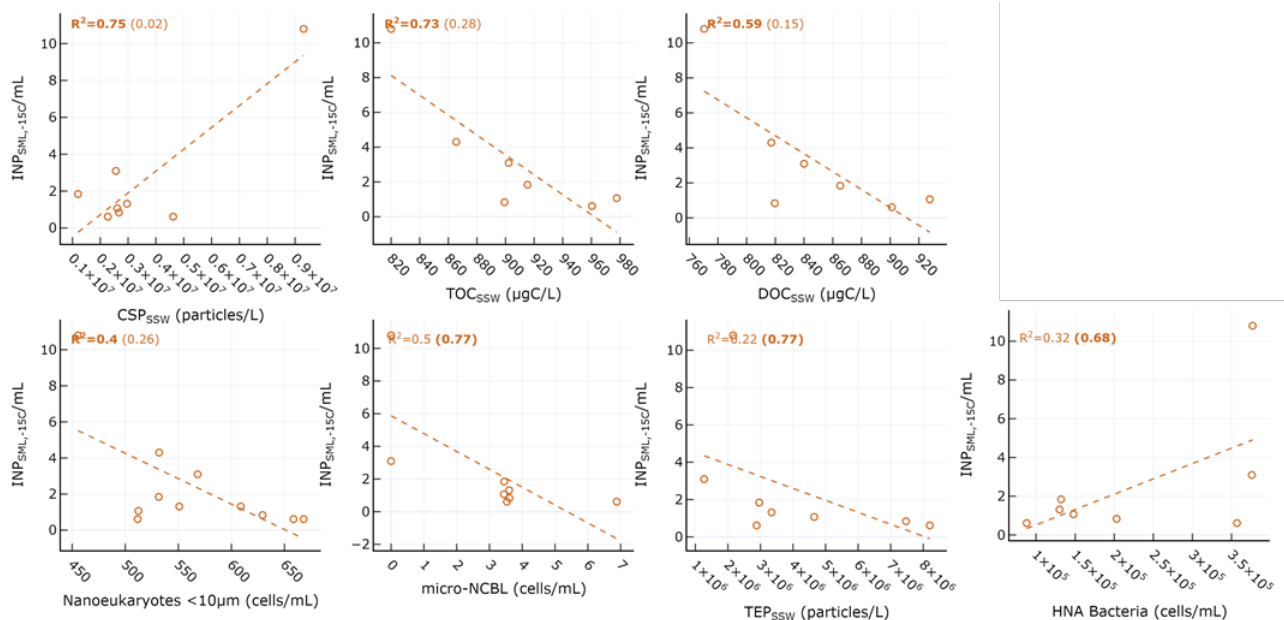


276 **3.2.1 Correlations Between INP<sub>SML</sub> Abundance and Seawater Properties**

277 **Table 1. Correlation statistics between INP<sub>SML,-15C</sub> and seawater properties in the SML and SSW, where p is the p-value test for**  
 278 **significance and r is the Pearson correlation coefficient. Values in parentheses are calculated for days before the dust deposition**  
 279 **event (i.e., days before June 4). Values that are not statistically significant ( $p > .05$ ) are italicized.**

Variable	$p_{\text{all days}} (p_{\text{pre-dust}})$	$r_{\text{all days}} (r_{\text{pre-dust}})$
<b>SSW</b>		
CSP	0.005 (0.78)	0.87 (-0.15)
TOC <sub>SSW</sub>	0.015 (0.36)	-0.85 (-0.53)
DOC <sub>SSW</sub>	0.045 (0.52)	-0.76 (-0.39)
Nanoeukaryotes <10 $\mu\text{m}$	0.038 (0.20)	-0.63 (-0.51)
Micro-NCBL	0.051 (0.021)	-0.70 (-0.88)
TEP	0.25 (0.022)	-0.46 (-0.88)
Bacteria HNA	0.14 (0.043)	0.57 (0.83)
<b>SML</b>		
Dissolved Iron	.0000021 (.012)	0.99 (0.91)
TEP EF	0.00032 (0.42)	0.95 (0.41)
Total Bacteria EF	0.00075 (0.82)	0.93 (-0.12)
CSP	0.0053 (0.25)	0.87 (-0.56)
Total NCBL	0.0053 (0.34)	0.87 (0.48)
Pico-NCBL	0.0088 (0.43)	0.84 (0.40)
Total Bacteria	0.016 (0.17)	0.81 (0.64)
Phytoplankton (NCBL+CBL)	0.021 (0.68)	0.78 (-0.22)
NCBL EF	0.022 (0.92)	0.78 (0.054)
DOC EF	0.041 (0.38)	0.78 (-0.51)
Nano-NCBL	0.027 (0.42)	0.77 (0.41)
Bacteria HNA	0.012 (0.068)	0.83 (0.78)
Bacteria LNA	0.037 (0.54)	0.74 (0.32)
TOC <sub>SML</sub>	0.50 (0.020)	0.31 (-0.93)

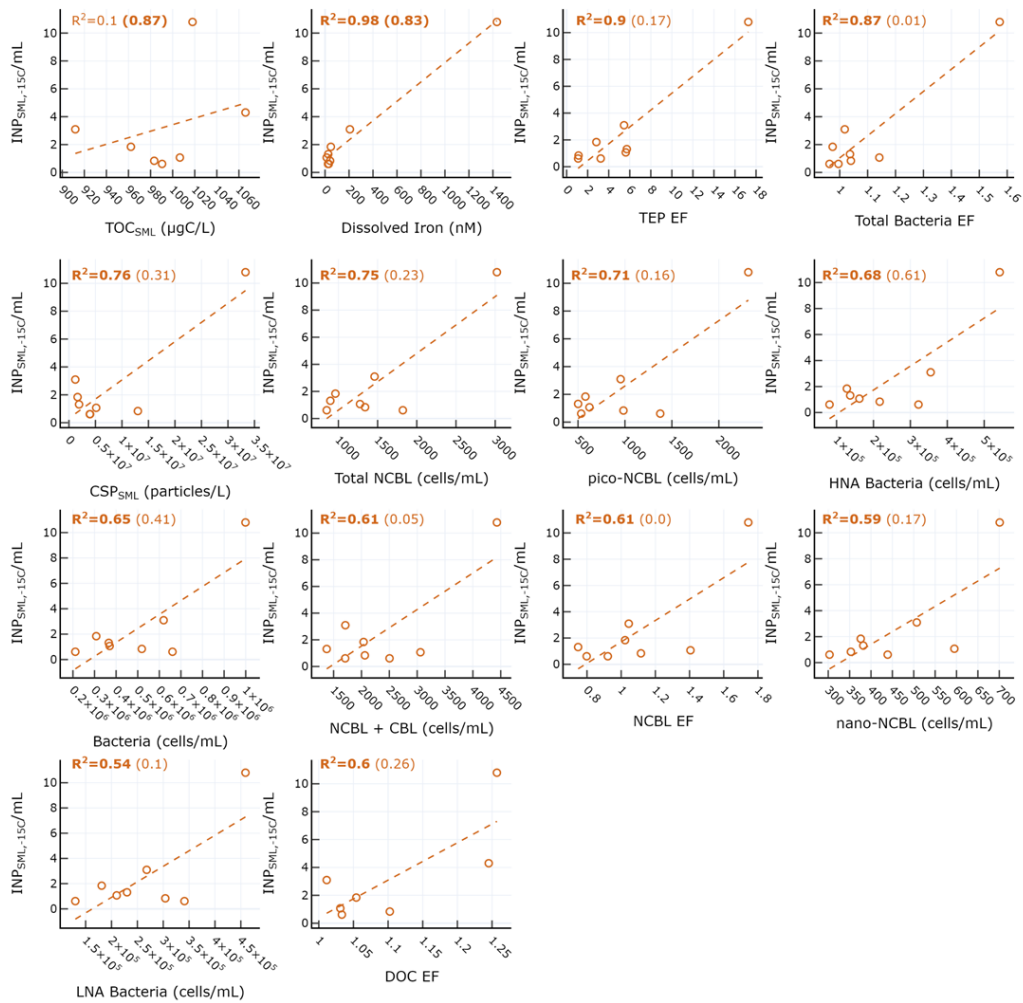
280  
 281 Table 1 shows the correlation statistics between INP<sub>SML,-15C</sub> and selected observed seawater properties (SSW and  
 282 SML), calculated either for all days of the PEACETIME experiment or only for days before the dust deposition event (i.e.,  
 283 days before June 4). Relationships are only listed in Table 1 if they were significant ( $p < .05$ ) for either all days or pre-dust only  
 284 days. Figure 4 shows the corresponding scatterplots of INP<sub>SML,-15C</sub> abundance and SSW properties. We note a statistically  
 285 significant correlation between INP<sub>SML,-15C</sub> and CSP ( $r=0.87$ ) as measured from the underway system. When considering only  
 286 days before the dust deposition event, INP<sub>SML,-15C</sub> were significantly correlated with HNA bacteria ( $r=0.83$ ) while the  
 287 correlation with CSP is no longer statistically significant. INP<sub>SML,-15C</sub> are actually negatively correlated with most of the  
 288 measured SSW properties either when excluding the dust event (for micro-NCBL<sub>SSW</sub> and TEP<sub>SSW</sub>) or due to the dust event (for  
 289 TOC<sub>SSW</sub>, DOC<sub>SSW</sub> and nanoeukaryotes cell abundances). This points to a non-proportional transfer of each species from the  
 290 bulk seawater to the SML relative to one another. Given the high p-values and weak correlation coefficients, it appears to be  
 291 difficult to reliably relate INP<sub>SML</sub> to properties of the underlying SSW. Rather, we posit that INP in the SML are more reliably  
 292 dictated by SML properties, as shown in the following paragraph.



293 **Figure 4. Scatter plot of INP in the SML and various biogeochemical parameters in the SSW.  $R^2$  for all days are shown in each plot,**  
 294 **with  $R^2$  calculated for only days before the dust event shown in parentheses. Statistically significant relationships are shown in bold.**

295 Figure 5 shows scatterplots of statistically significant relationships between  $INP_{SML,-15C}$  concentrations and various SML  
 296 properties.  $INP_{SML,-15C}$  were most strongly positively correlated with dissolved iron ( $r=0.99$ ), TEP EF ( $r=0.95$ ), and bacteria  
 297 EF ( $r=0.93$ ). However, these relationships are skewed by the outlier due to the drastic increase in iron observed on June 4  
 298 (Figure S2a) from the dust deposition event, as described previously. It is difficult to discriminate between the dust and  
 299 biological impact on the  $INP_{SML,-15C}$ , as dust is known to have good INP properties while also being capable of fertilizing the  
 300 surface ocean with dissolved iron, leading to concomitant increases in biological activity. It is also possible that the dust  
 301 deposition led to increased abundance of terrestrial OC, which would exhibit different INP activity. When considering days  
 302 before the dust event,  $INP_{SML,-15C}$  is only significantly correlated with dissolved iron ( $r=0.91$ ) and TOC in the SML ( $r=-0.93$ ).  
 303 We note that while no longer statistically significant for pre-dust days, moderate correlations were still observed between  
 304  $INP_{SML,-15C}$  and total NCBL ( $r=0.48$ ), HNA bacteria ( $r=0.78$ ), and total bacteria ( $r=0.64$ ). Previous reports examining the  
 305 correlation between INP and microbial abundance have yielded mixed results. For example, a report of INP in Arctic SML  
 306 and SSW found no statistically significant relationship between the temperature at which 10% of droplets had frozen and  
 307 bacteria or phytoplankton abundances in bulk SSW and SML samples (Irish et al., 2017). However, recent mesocosm studies  
 308 using nutrient-enriched seawater found that INP abundances between  $-15^{\circ}C$  and  $-25^{\circ}C$  in the aerosol phase were positively  
 309 correlated with aerosolized bacterial abundance (McCluskey et al., 2017).

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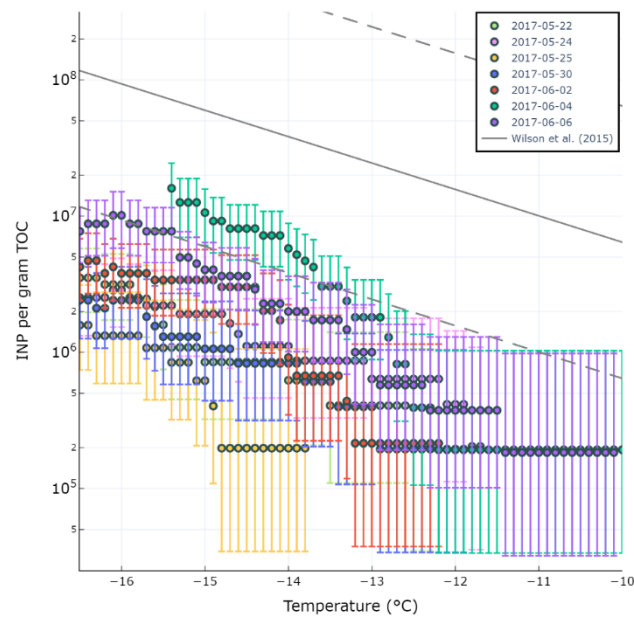


312 **Figure 5. Scatter plot of INP in the SML and various biogeochemical properties in the SML.  $R^2$  for all days are shown in each plot,**  
 313 **with  $R^2$  calculated for only days before the dust event shown in parentheses. Statistically significant  $R^2$  values are shown in bold.**

314 A previous study by Wilson and co-authors presented an INP parameterization (hereafter termed W15) based on a  
 315 positive relationship between seawater TOC and INP abundance in Arctic, North Pacific, and Atlantic SML and SSW (Wilson  
 316 et al., 2015). Total organic carbon in the SML ( $TOC_{SML}$   $\mu gC/L$ ), derived here as the sum of POC in the SSW ( $POC_{SSW}$ ) and  
 317 DOC in the SML ( $DOC_{SML}$ ), was poorly correlated with  $INP_{SML,-15C}$  ( $r=0.31$ ,  $p=0.50$ ). Figure 7 shows the observed  $INP_{SML,-15C}/TOC_{SML}$   
 318 ratio (INP per gram of TOC) for various temperatures and days of the experiment compared with the W15  
 319 parameterization (grey line). Our results show observed  $INP_{SML}/TOC_{SML}$  ratios below those expected by the model proposed  
 320 by W15, indicating the  $TOC_{SML}$  in Mediterranean waters is less IN active at these temperatures than predicted by the W15  
 321 parameterization.

322 In agreement with our findings, a recent study found that the W15 model over-predicted observed INP concentrations  
 323 in the aerosol phase during two separate mesocosm experiments (McCluskey et al., 2017) by assuming the INP/TOC ratio in  
 324 the SML was preserved in the aerosol phase. The authors of that study speculated that the overprediction by the W15 model  
 325 was due to the fact that it does not account for the complex transfer mechanism of organic matter from the SML to the aerosol  
 326 phase. Our results here show that the overprediction by W15 persists even when calculating INP in the SML and therefore the  
 327 overprediction may be due to other factors beyond the transfer of organic matter from the SML to the atmosphere. We stress  
 328 however, that the TOC value used in this study was derived using  $DOC_{SML}$  and  $POC_{SSW}$  values as POC measurements in the  
 329 SML were not conducted. As there typically exists an enrichment of organic matter in the SML relative to the bulk seawater,  
 330 it is possible that the  $POC_{SSW}$  we used to calculate  $TOC_{SML}$  was below the actual POC content in the SML, thus underestimating  
 331  $TOC_{SML}$ . However, if this was the case, a higher abundance of  $TOC_{SML}$  would only further increase the overprediction of W15

332 relative to our observations. Finally, it is possible that the oligotrophic nature of Mediterranean waters results in a pool of TOC  
 333 with a different chemical composition than what is observed in more biologically productive waters such as the Arctic and  
 334 Atlantic. For example, the pool of TOC during this study was dominated by DOC and featured low POC content, presumably  
 335 due to low biological productivity.



336 **Figure 6. Observed INP/TOC ratio in the SML during PEACETIME experiment for different temperatures. The gray line is the fit**  
 337 **from Wilson et al., 2015.**

338 In summary,  $INP_{SML,-15C}$  increased with SML microbial cell counts (e.g., NCBL and heterotrophic bacteria),  $F_{eSML}$   
 339 and  $DOC_{EF}$  during a dust deposition event, but were overall not correlated with TOC nor DOC in the SML. Compared to  
 340 previous studies, the INP/TOC ratio observed in the Mediterranean is low. We surmise that the overprediction of INP/TOC by  
 341 the model may either be caused by a different relationship between INP and TOC at warmer temperatures, or possibly be due  
 342 to the chemical characteristics of TOC in the oligotrophic Mediterranean. This complicated relationship between seawater  
 343 TOC and  $INP_{SML}$  highlights the need for further studies focused on the chemical composition of DOC and POC in bulk SSW  
 344 and SML. Further experiments during low and high biological productivity are needed in controlled environments to better  
 345 determine under what conditions (oligotrophic and eutrophic) and location in the water column (i.e., bulk SSW vs SML) TOC,  
 346 bacteria, and phytoplankton are linked to INP across a range of temperatures. Finally, regardless of the exact mechanism, the  
 347 impact of dust deposition on  $INP_{SML,-15C}$  is fairly large, as we observe an increase of by  $INP_{SML,-15C}$  by almost an order of  
 348 magnitude during the dust event. This impact may have climate implications if  $INP_{SML,-15C}$  were efficiently transferred to the  
 349 sea spray.

### 350 3.2.2 Correlations Between $INP_{SSA}$ Abundance and Observed SSA and Seawater Conditions

351 In the following section, we compare  $INP_{SSA}$  at various temperatures with seawater and SSA properties. Submicron  
 352 particle concentrations ranged between 1000-3000 particles/cm<sup>3</sup> (Figure S3) and its dependence of seawater biology is further  
 353 explored in a separate manuscript (Sellegrri et al. under revision). For comparison with seawater properties,  $INP_{SSA}$  was first  
 354 normalized by SSA particle surface area ( $0.1 < D_p < 10 \mu m$ , Figure S4)(see methodology in Section 2.3.1 for estimation of  
 355 SSA surface area for particles larger than  $D_p=500$  nm).

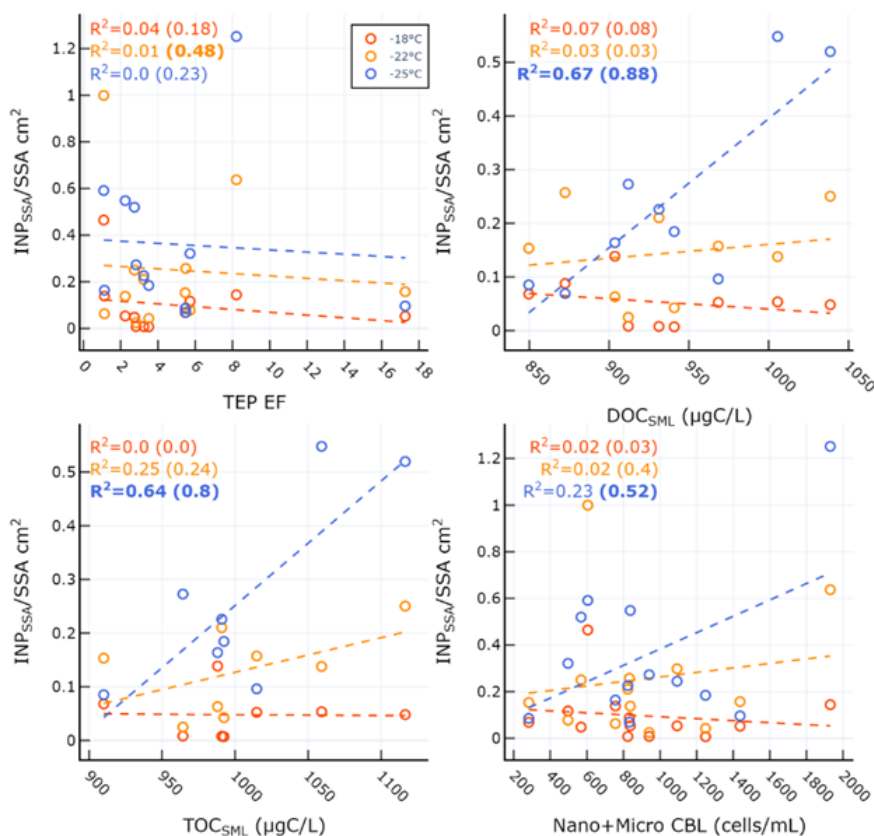
356 Table 2 shows the correlation statistics between  $INP_{SSA}$  normalized by SSA particle surface area and select conditions  
 357 in the SML for relationships that were statistically significant. Figure 7 shows the corresponding scatter plots for these  
 358 relationships. We also tested for correlations on days not affected by the dust event (i.e., days before June 4), and their statistics  
 359 are shown in parentheses in Table 2 and Figure 7. Surprisingly, there were no significant correlations between  $INP_{SSA,-18C}$  and

360 conditions in the SML, including TEP and CSP abundance and enrichment factors, bacteria abundance and enrichment factors,  
 361 nor with  $INP_{SML}$  as measured by the LINDA instrument. This is somewhat unexpected considering INP in the SML at  $-15^{\circ}C$   
 362 was correlated with SML phytoplankton and bacteria counts, which are all expected to transfer efficiently from the SML to  
 363 the aerosol phase, an assumption widely used in the modelling community. Similarly,  $-22^{\circ}C$   $INP_{SSA}$  had no significant  
 364 correlations with SML variables, except for TEP EF which was positively correlated ( $r=0.69$ ) when only considering days  
 365 before the dust deposition event. At  $-25^{\circ}C$ ,  $INP_{SSA}$  were found to be significantly correlated with  $DOC_{SML}$  and  $TOC_{SML}$  on all  
 366 days ( $r=0.82$  and  $r=0.81$  for DOC and TOC, respectively). When examining only pre-dust event days, the significant  
 367 correlations included DOC enrichment as well as nano- and micro-CBL.

368 **Table 2. Correlation statistics between  $INP_{SSA}$  and properties in the SML, where p is the p-value test for significance and r is the**  
 369 **Pearson correlation coefficient. Values in parentheses are calculated for days before the dust deposition event (i.e., days before June**  
 370 **4). Values that are not statistically significant ( $p > .05$ ) are italicized.**

Variable	$p_{all\ days}$ ( $p_{pre-dust}$ )	$r_{all\ days}$ ( $r_{pre-dust}$ )
<b><math>-18^{\circ}C</math></b>		
<i>No significant correlations</i>		
<b><math>-22^{\circ}C</math></b>		
TEP EF	<i>0.81</i> (0.026)	<i>-0.078</i> (0.69)
<b><math>-25^{\circ}C</math></b>		
$DOC_{SML}$	0.0073 (0.00054)	0.82 (0.94)
$TOC_{SML}$	0.017 (0.0066)	0.81 (0.89)
DOC EF	<i>0.46</i> (0.014)	<i>0.28</i> (0.81)
Nano+Micro CBL	<i>0.10</i> (0.019)	<i>0.47</i> (0.72)

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372 **Figure 7. Scatter plots of  $INP_{SSA}$  normalized by SSA particle surface area at three temperatures and select conditions in the SML**  
 373 **for relationships that were statistically significant. Corresponding correlation parameters are reported Table 2.  $R^2$  values for all**  
 374 **days are shown in each plot, with  $R^2$  values for days not including the dust deposition event (i.e., days before June 4) in parentheses.**  
 375  **$R^2$  for statistically significant relationships are shown in bold.**

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**Table 3. Correlation statistics between  $INP_{SSA}$  and properties in the SSW, where  $p$  is the  $p$ -value test for significance and  $r$  is the Pearson correlation coefficient. Values in parentheses are calculated for days before the dust deposition event (i.e., days before June 4). Values that are not statistically significant ( $p > .05$ ) are italicized.**

Variable	$p_{all\ days} (p_{pre-dust})$	$r_{all\ days} (r_{pre-dust})$
<b>-18°C</b>		
POC <sub>SSW</sub>	<i>0.46 (0.0064)</i>	<i>0.18 (0.63)</i>
DOC <sub>SSW</sub>	<i>0.16 (0.020)</i>	<i>-0.51 (-0.79)</i>
<b>-22°C</b>		
Nanoeukaryotes <10µm	0.014 (0.050)	-0.53 (-0.48)
Prochlorococcus	0.36 (0.000019)	0.23 (0.89)
POC <sub>SSW</sub>	0.29 (0.037)	0.25 (0.54)
Coccolithophores	0.72 (0.035)	0.084 (0.51)
Micro-NCBL	0.14 (0.0088)	0.43 (0.77)
<b>-25°C</b>		
Nanoeukaryotes <10µm	0.0055 (0.0040)	-0.58 (-0.66)
Prochlorococcus	0.00076 (0.00015)	0.72 (0.84)
Coccolithophores	0.031 (0.042)	0.47 (0.50)
Cryptophytes	0.028 (0.050)	0.48 (0.48)
Micro-NCBL	0.0012 (0.0049)	0.79 (0.81)
Nano-NCBL	0.048 (0.058)	0.56 (0.62)

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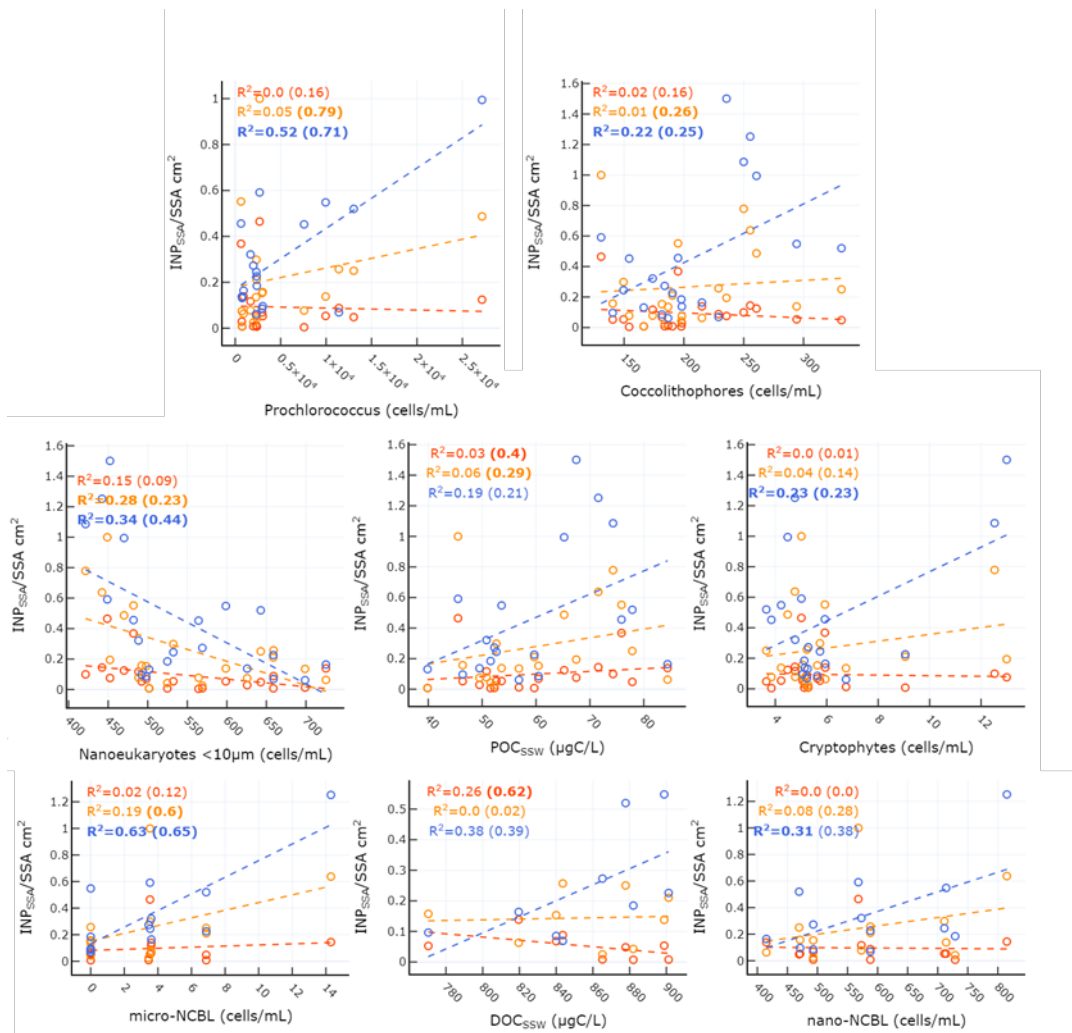
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Table 3 and the corresponding scatter plots in Figure 8 show that a weak correlation exists between  $INP_{SSA}$  active at -18°C and POC<sub>SSW</sub> for all days, but becomes significant and strong for days not including the dust event. This points to the possible interference of a different class of organic carbon (e.g., terrestrial OC) or the introduction of some other IN active material (e.g., dissolved iron) which masks the impact of the original pool of POC<sub>SSW</sub> on INP concentrations.  $INP_{SSA,-18C}$  are also significantly correlated  $INP_{SSW,-16C}$ , (results not shown) but with a sample size of  $n=4$  this finding requires further validation. Nonetheless, this result could indicate that  $INP_{SSA}$  at this temperature come from the bulk water rather than the SML.  $INP_{SSA}$  at -22°C show a slightly weaker, yet still significant correlation with POC<sub>SSW</sub> than  $INP_{SSA}$  at -18°C on pre-dust days ( $r=0.54$ ). Additionally, they have a correlation with Prochlorococcus, coccolithophores, and micro-NCBL. This finding is in agreement with a recent study in which particles generated from lysed Prochlorococcus cultures exhibited good ice nucleating capabilities, albeit at much colder temperatures than observed in our study (i.e.,  $T < -40°C$ ) (Wolf et al., 2019).  $INP_{SSA}$  at -25°C were correlated with similar variables as  $INP_{SSA}$  at -22°C, with the exception POC<sub>SSW</sub>. Furthermore, the correlations with the various microbial categories was stronger for  $INP_{SSA}$  at -25°C than at warmer temperatures, indicating these parameters are more associated with cold INP. Interestingly,  $INP_{SSA,-25C}$  was not correlated with DOC<sub>SSW</sub>, yet was correlated with DOC<sub>SML</sub> (Table 2), potentially indicating an important step in the process of transfer of IN active DOC material to the atmosphere is its prior enrichment at the SML.



397 **Figure 8. Scatter plots of  $INP_{SSA}$  normalized by SSA particle surface area at three temperatures and select conditions in the SSW**  
 398 **for relationships that were statistically significant. Corresponding correlation parameters are reported Table 3.  $R^2$  values for all**  
 399 **days are shown in each plot, with  $R^2$  values for days not including the dust deposition event (i.e., days before June 4) in parentheses.**  
 400  **$R^2$  for statistically significant relationships are shown in bold.**

401 Table 4 and Figure 9 show the significant correlations between  $INP_{SSA}$  and SSA properties. A positive correlation was observed  
 402 between  $INP_{SSA,-18C}$  and SSA organic carbon (OC) as well as the ratio of SSA water-soluble organic carbon to organic carbon  
 403 (WSOC/OC). The correlation between WSOC/OC and  $INP_{SSA,-18C}$  makes sense given the finding that  $INP_{SSA,-18C}$  was correlated  
 404 with  $POC_{SSW}$ . A higher WSOC/OC value would suggest a higher fraction of soluble organics which would be expected to  
 405 transfer to the atmosphere from the bulk SSW rather than the SML due to their high solubility.

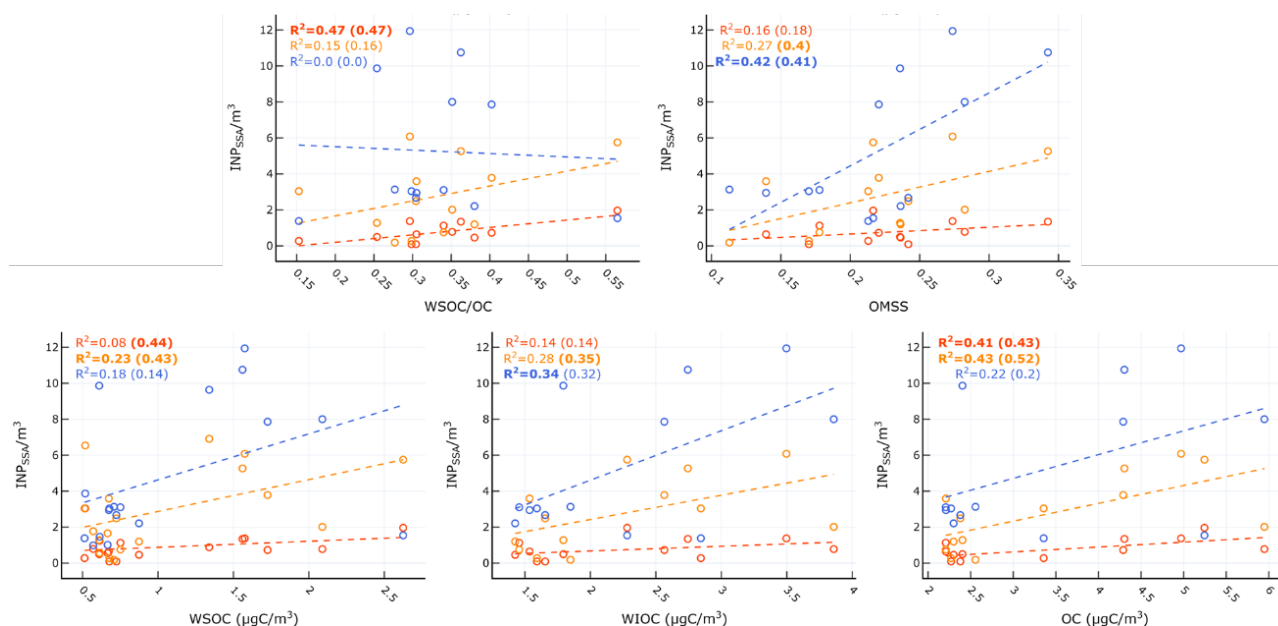
406 **Table 4. Correlation statistics between  $INP_{SSA}$  and SSA properties, where p is the p-value test for significance and r is the Pearson**  
 407 **correlation coefficient. Values in parentheses are calculated for days before the dust deposition event (i.e., days before June 4).**  
 408 **Values that are not statistically significant ( $p > .05$ ) are italicized.**

Variable	$p_{all\ days}$ ( $p_{pre-dust}$ )	$r_{all\ days}$ ( $r_{pre-dust}$ )
<b>-18°C</b>		
WSOC/OC	0.0099 (0.014)	0.68 (0.68)
OC	0.018 (0.021)	0.64 (0.65)
WSOC	<i>0.25</i> (0.0074)	<i>0.29</i> (0.66)
<b>-22°C</b>		
WSOC	0.042 (0.0082)	0.48 (0.65)
OC	0.015 (0.0080)	0.66 (0.72)
WIOC	<i>0.061</i> (0.043)	<i>0.53</i> (0.59)
OMSS	<i>0.066</i> (0.028)	<i>0.52</i> (0.63)
<b>-25°C</b>		
WIOC	0.037 ( <i>0.057</i> )	0.58 ( <i>0.56</i> )
OMSS	0.016 (0.025)	0.65 (0.64)



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Figure 9 and Table 4 also show that  $INP_{SSA,-25C}$  had a significant correlation with WIOC and organic mass fraction of sea spray (OMSS) ( $r=0.58$  and  $r=0.65$ , respectively). As mentioned above,  $INP_{SSA,-25C}$  was found to be correlated with various microbes in the SSW, specifically Prochlorococcus, coccolithophores, and nano- and micro-NCBL. Phytoplankton are known for their ability to produce extracellular polymeric substances (Thornton, 2014), and a previous mesocosm experiment showed microbially-derived long-chain fatty acids were efficiently ejected from the seawater as SSA, increasing the fraction of highly-aliphatic, WIOC (Cochran et al., 2017). A separate manuscript discusses the trend and controls on SSA chemical composition, linking the different classes of organic carbon in submicron SSA to seawater chemical and biological properties (Freney et al., 2020). In this work, OMSS was linked to  $POC_{SSW}$  and the coccolithophores cell abundance in the SSW. In light of this and given the correlation of  $INP_{SSA,-25C}$  with seawater microbial abundance and with SSA OMSS and WIOC, it seems likely that  $INP_{SSA}$  at this temperature are related to the exudates of phytoplankton which are concentrated at the SML and then emitted into the SSA as WIOC.



432 **Figure 9. Scatter plots of  $INP_{SSA}$  at three temperatures and SSA properties for relationships that were statistically significant.**  
433 **Corresponding correlation statistics are reported Table 2.  $R^2$  values for all days are shown in each plot, with values calculated pre-**  
434 **event (i.e., days before June 4) in parentheses. Statistically significant values are shown in bold.**

435 To summarize the results thus far, we have found evidence for the existence of two classes of INP in SSA with  
436 separate sources: 1) a class of INP related to POC in the bulk SSW and SSA WSOC and 2) a class of INP related to microbial  
437 abundance and POC in the SSW, DOC in the SML, and WIOC in SSA. These findings of a two-component marine INP  
438 population agree with a recent study which also reported on the existence of dual classes of INP emitted as SSA during two  
439 mesocosm experiments, described as: 1) particulate organic carbon INP coming from intact cells or IN-active microbe  
440 fragments and 2) dissolved organic carbon INP composed of IN-active molecules enhanced during periods when the SML is  
441 enriched with exudates and cellular detritus (McCluskey et al., 2018b). However, in contrast to that study, we report here the  
442 existence of separate temperature regimes at which each INP class is active. Here, the first class of INP consists of INP that  
443 are more active at warmer temperatures ( $T=-18^{\circ}C$ ) while the second class of INP are active at colder temperatures ( $T=-25^{\circ}C$ ).  
444 INP at  $T=-22^{\circ}C$  correlates with items from both warm and cold categories.

#### 445 4 Proposal of New INP Parameterization and Comparison with Previous Models

446 To date, parameterizations for the estimation of INP in SSA have not incorporated the knowledge of a two-component  
447 INP population. Rather, they have predicted INP based on OC or SSA surface area (W15 and MC18, respectively). To improve



448 upon existing models, we formulated various parameterizations consisting of different time periods, features, and number of  
 449 components for temperature ranges. Predictor features were chosen based upon their correlation with INP concentrations as  
 450 described in the previous section. Single component parameterizations in which INP across all three temperatures were linked  
 451 with the same features were compared with two-component parameterizations in which INP were split into warm and cold  
 452 categories, each having their own predictor features. Finally, we developed and compared altered versions of the W15 and  
 453 MC18 models to account for the oligotrophic seawater of the Mediterranean Sea, as the existing models were formulated from  
 454 observations of eutrophic waters. Each parameterization was recalculated using data across all days of the cruise as well as for  
 455 only days before the dust deposition event in order to determine the impact of the dust event on the ability to predict INP. The  
 456 complete set of parameterizations and their associated fit metrics ( $R^2$  and  $R_{adj}^2$ ) are given in Table S2.

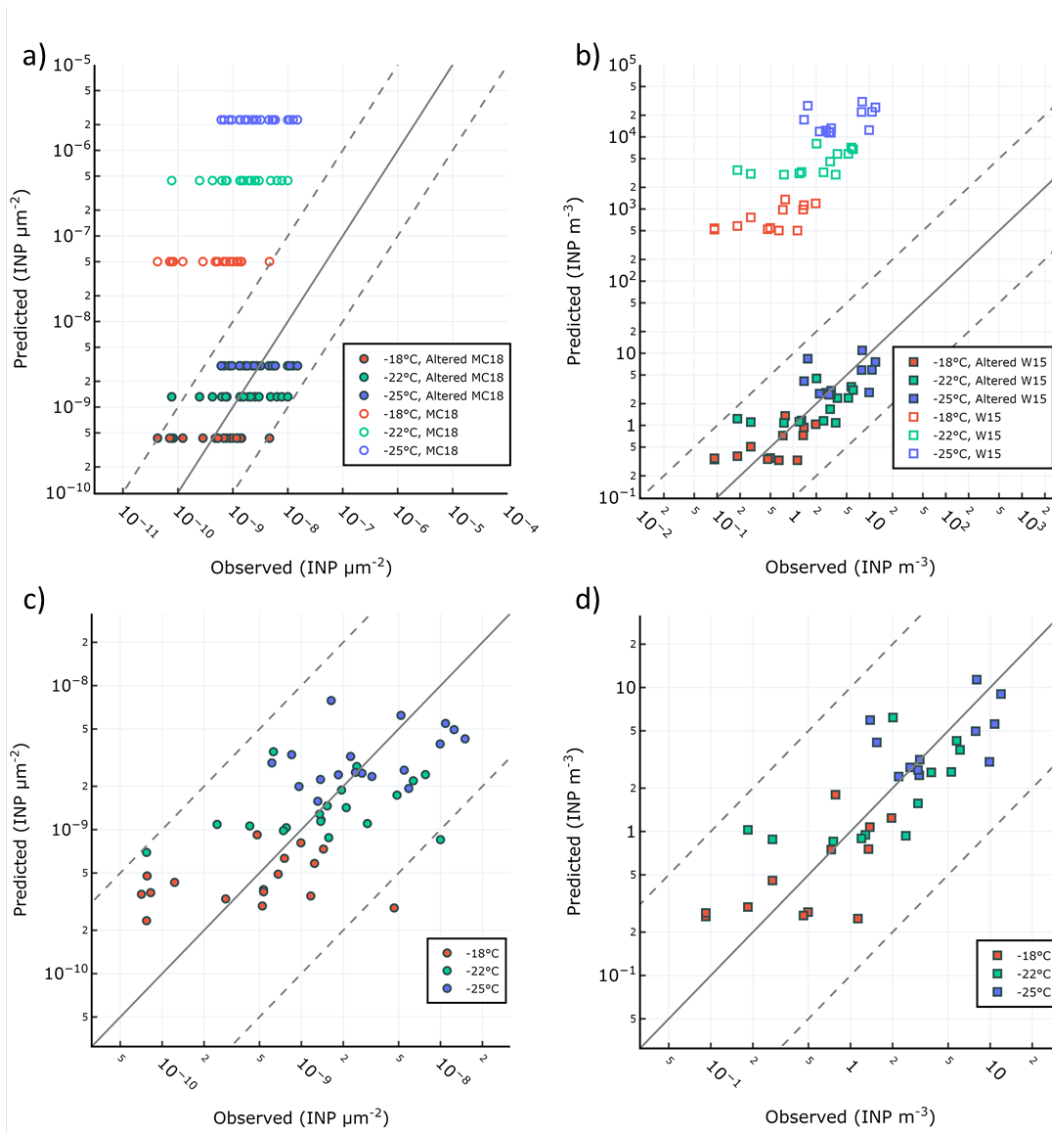
457 Figure 10a shows observed vs predicted  $INP_{SSA}$  for the W15 model, while Figure 10b shows the same but using the  
 458 MC18 parameterization. Similar to our results for seawater INP (Figure 6), a large overprediction is found relative to our  
 459 observations when using W15. Figure 10b shows that while MC18 is a slight improvement over the W15 approach, it still  
 460 overpredicts INP by two orders of magnitude. We also present re-calculated best-fit-lines to data using the same features as in  
 461 W15 and MC18 (i.e., OC and SSA surface area) in order to account for possible changes due to the oligotrophic nature of the  
 462 Mediterranean Sea. We term these two parameterizations the altered Wilson fit for oligotrophy, which is given by:

$$\frac{INP}{m^3} = \exp(-7.332 - (0.2989 * T) + (0.3792 * OC_{SSA}))$$

463 and the altered McCluskey fit for oligotrophy, given as:

$$\frac{INP}{\mu m^2} = \exp(-26.57 - (0.2782 * T))$$

464 The results for these fits are shown in Figure 10a,b alongside the results of the original W15 and MC18 parameterizations.  
 465 Both altered models offer improvements over the original parameterizations. The adjusted  $R^2$  of the altered Wilson fit for  
 466 oligotrophy on log-transformed INP abundance was  $R_{adj}^2=0.59$  and was  $R_{adj}^2=0.32$  for the altered McCluskey fit for  
 467 oligotrophy. Interestingly, the adjusted Wilson fit for oligotrophy performs better than the adjust McCluskey fit for  
 468 oligotrophy, which is the opposite of what was found when comparing the original models.



469 **Figure 10. Different parameterizations for prediction of INP in SSA. a) W15 and refit of same method using PEACETIME**  
 470 **observations b) MK18 and refit of same method using PEACETIME observations c) single-component parameterization for**  
 471 **INP/ $\mu\text{m}^2$  SSA surface area where INP at all temperatures are related to  $\text{POC}_{\text{SSW}}$  d) two-component parameterization for INP/ $\text{m}^3$**   
 472 **where  $\text{INP}_{\geq -22^\circ\text{C}}$  are related to OC and  $\text{INP}_{< -22^\circ\text{C}}$  are related to WIOC.**

473 We also tried a range of novel parameterizations based on the observed correlations between  $\text{INP}_{\text{SSA}}$  with seawater  
 474 and SSA properties. Below we describe two parameterizations which offered good fits to the data. The single-component  
 475 parameterization assumes the abundance of INP per unit surface area of total SSA at each temperature can be predicted from  
 476  $\text{POC}_{\text{SSW}}$  concentrations:

$$\frac{\text{INP}}{\mu\text{m}^2} = \exp(-28.5324 - (0.2729 * T) + (0.0361 * \text{POC}_{\text{SSW}}))$$

477 The second parameterization separates INP into warm and cold classes, where warm INP ( $\geq -22^\circ\text{C}$ ) are related to SSA  
 478 OC and cold INP ( $< -22^\circ\text{C}$ ) are related to the concentration of SSA WIOC. This two-component parameterization predicts the  
 479 concentration of  $\text{INP}/\text{m}^3$  through the following equations:

$$\frac{\text{INP}_{T \geq -22^\circ\text{C}}}{\text{m}^3} = \exp(-7.9857 - (0.3178 * T) + (0.4643 * \text{OC}_{\text{SSA}}))$$

$$\frac{\text{INP}_{T < -22^\circ\text{C}}}{\text{m}^3} = \exp(-6.6606 - (0.2712 * T) + (0.5755 * \text{WIOC}_{\text{SSA}}))$$

480 Figure 10c,d shows the results of our single-component model using  $\text{POC}_{\text{SSW}}$  and the two-part model which uses SSA  
 481 WIOC and OC and considers the separate temperature classes of INP. The adjusted  $R^2$  for each model on the log-transformed  
 482 INP abundance were  $R_{\text{adj}}^2=0.404$  for the single component model using  $\text{POC}_{\text{SSW}}$  and  $R_{\text{adj}}^2=0.60$  for the two-component model  
 483 using OC and WIOC. This result reveals that they both fit the observations better than the altered McCluskey parameterization

484 for oligotrophy, while the two-component method performs as well as the altered Wilson parameterization. Each  
485 parameterization's fit to the data is improved when considering pre-dust days only ( $R_{adj}^2=0.63$  for the two-component  
486 parameterization and  $R_{adj}^2=0.57$  for the single-component parameterization). The improvement is more pronounced for the  
487 single-component parameterization using  $POC_{SSW}$ , further pointing to the fact that such dust deposition events can alter the  
488 INP properties of surface waters and the subsequent SSA, either through introduction of terrestrial OC or by triggering changes  
489 to the trophic status of the surface waters, resulting in a different class of biologically produced OC. We note that the ratio of  
490  $INP_{SSA,-18C}/OC_{SSA}$  is on average  $2.08 \times 10^5 \pm 1.4 \times 10^5$  INP/gC while the ratio of  $INP_{SML,-15C}/TOC_{SML}$  as reported in Section 3.2.1  
491 is  $3.2 \times 10^6 \pm 3.5 \times 10^6$  INP/gC. This points to a depletion in the abundance of INP active material by a factor 16 as it transfers  
492 from the seawater to the SSA, which is typically assumed to be negligible in modelling studies. However, when available,  
493 using a ratio of  $INP_{SSW}/TOC_{SSW}$  to predict sea spray originating INP in the atmosphere seems a better approach than using the  
494 ratio  $INP_{SSW}/NaCl_{SSW}$ . Finally, we remind the readers that the two-component parameterization uses results of SSA chemistry  
495 for submicron particles only. As previous studies have shown that the overwhelming majority of SSA OC is found in the  
496 submicron phase (Gantt and Meskhidze, 2013), we argue that our analysis of WIOC, WSOC, and OC concentrations in  
497 submicron SSA is representative of the whole size range of SSA.

498

## 499 **5 Conclusions**

500 In this paper we have presented results from the month-long PEACETIME cruise which took place in the Mediterranean  
501 Sea during the spring of 2017, which was characterized with a dust wet deposition event that occurred towards the end of the  
502 cruise. First, we find that the INP concentrations measured in the seawater are in agreement with previous studies on  
503 oligotrophic waters (Gong et al., 2020). Observed INP cm<sup>2</sup> of SSA are below those reported in the literature, likely due to  
504 differences in biological activity of source waters. We next investigated the relationship between seawater INP concentrations  
505 and seawater biogeochemical properties. In the SML, the increase of  $INP_{SML,-15C}$  concentrations during the dust deposition  
506 event followed the SML microbial cell counts (e.g., NCBL, CBL and heterotrophic bacteria),  $Fe_{SML}$  and  $DOC_{EF}$ . Excluding  
507 this dust event,  $INP_{SML,-15C}$  were still correlated to Fe and bacteria (although not significantly) in the SML. Overall  $INP_{SML,-15C}$   
508 were not correlated with TOC nor DOC in the SML and compared to previous studies, the INP/TOC in the SML observed  
509 during the PEACETIME cruise was low. We surmise that these low INP/TOC is a result of TOC from the oligotrophic  
510 Mediterranean being less IN active.

511 The impact of dust deposition on  $INP_{SML,-15C}$  is fairly large, as we observe an increase of  $INP_{SML,-15C}$  by almost an order  
512 of magnitude during this event. This impact of dust deposition could have climate implications if  $INP_{SML,-15C}$  were efficiently  
513 transferred to the sea spray emitted to the atmosphere. However, we find that  $INP_{SSA}$  does not evolve in the same manner as  
514 the  $INP_{SML}$  does, as an increase of  $INP_{SSA}$  is observed with at least a three day delay after the dust wet deposition event. This  
515 difference could be attributed to the fact that  $INP_{SSA}$  measured at  $-18^\circ C$  are more influenced by the INP concentration in the  
516 bulk surface seawater (as shown by the correlation between  $INP_{SSA,-18C}$  and  $INP_{SSW,-16C}$ ). It is possible that IN active species  
517 deposited during the rain event, either dust- related or biology-related, take a few days before entering the bulk surface layer.

518 We also investigated the relationship between  $INP_{SSA}$  and various biogeochemical values in the SML, SSW, and SSA. In  
519 general, we observed the existence of two classes of  $INP_{SSA}$ , each linked to different classes of organic matter. Our results  
520 indicate each class is active at separate temperatures. Warm INP ( $INP_{SSA,-18C}$ ) are linked to water soluble organic matter in the  
521 SSA, but also to SSW parameters ( $POC_{SSW}$   $INP_{SSW,-16C}$ ). This indicates that INP at this temperature come from the bulk water  
522 rather than the SML. Colder INP ( $INP_{SSA,-25C}$ ) are rather correlated with SSA water-insoluble organic carbon, and SML  
523 properties (DOC). As the cold INP are also correlated to the SSW nano- and micro-NCBL cell abundance as well, we  
524 hypothesize that these classes of phytoplankton produce surface-active water-insoluble organic matter that is active as IN at  
525 these temperatures and are transferred to the atmosphere via the SML. Unfortunately, we do not have measurements of the  
526 "colder" temperatures INP in the SML to check this hypothesis.

527 We finally proposed a single-component model linking INP/m<sup>3</sup> to POC<sub>SSW</sub> and a two-component model linking warm  
528 INP to SSA OC and cold INP to SSA WIOC. Both models utilize features that are readily approximated either from satellite  
529 data, biogeochemical models, or from existing parameterizations and observations (Aumont et al., 2015; Rasse et al., 2017;  
530 Albert et al., 2010). We then showed these parameterizations fit the data much better than previous single component models  
531 based solely on SSA surface area (MC18) or OC content (W15), developed from studies of more biologically active waters.  
532 We also re-calculated parameterizations based on SSA surface area and SSA OC content but for the oligotrophic Mediterranean  
533 Sea. The parameterization using SSA OC content fits almost as well as the two-component model using SSA OC and WIOC.  
534 However, given the results of correlation analysis with SSA properties as well as results from previous studies indicating a  
535 dual composition of INP, we believe the two-component model should help improve attempts to incorporate marine INP  
536 emissions into numerical models.

537

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546

## 547 **References**

- 548 Albert, M. F. M. A., Schaap, M., de Leeuw, G., and Buitjes, P. J. H.: Progress in the determination of the sea spray  
549 source function using satellite data, *Journal of Integrative Environmental Sciences*, 7, 159-166,  
550 [10.1080/19438151003621466](https://doi.org/10.1080/19438151003621466), 2010.
- 551 Aumont, O., Ethé, C., Tagliabue, A., Bopp, L., and Gehlen, M.: PISCES-v2: an ocean biogeochemical model for  
552 carbon and ecosystem studies, *Geosci. Model Dev.*, 8, 2465-2513, [10.5194/gmd-8-2465-2015](https://doi.org/10.5194/gmd-8-2465-2015), 2015.
- 553 Bigg, E. K.: Ice Nucleus Concentrations in Remote Areas, *J. Atmos. Sci.*, 30, 1153-1157,  
554 [https://doi.org/10.1175/1520-0469\(1973\)030%3C1153:INCIRA%3E2.0.CO;2](https://doi.org/10.1175/1520-0469(1973)030%3C1153:INCIRA%3E2.0.CO;2), 1973.
- 555 Burrows, S. M., Hoose, C., Pöschl, U., and Lawrence, M. G.: Ice Nuclei in Marine Air: Biogenic Particles or Dust?,  
556 *ACP*, 13, 245-267, <https://doi.org/10.5194/acp-13-245-2013>, 2013.
- 557 Burrows, S. M., Ogunro, O., Frossard, A. A., Russell, L. M., Rasch, P. J., and Elliott, S. M.: A Physically Based  
558 Framework for Modeling the Organic Fractionation of Sea Spray Aerosol from Bubble Film Langmuir Equilibria,  
559 *ACP*, 14, 13601-13629, <https://doi.org/10.5194/acp-14-13601-2014>, 2014.
- 560 Cochran, R. E., Laskina, O., Trueblood, J. V., Estillore, A. D., Morris, H. S., Jayarathne, T., Sultana, C. M., Lee, C., Lin,  
561 P., Laskin, J., Laskin, A., Dowling, J. A., Qin, Z., Cappa, C. D., Bertram, T. H., Tivanski, A. V., Stone, E. A., Prather, K.  
562 A., and Grassian, V. H.: Molecular Diversity of Sea Spray Aerosol Particles: Impact of Ocean Biology on Particle  
563 Composition and Hygroscopicity, *Chem*, 2, 655-667, [10.1016/j.chempr.2017.03.007](https://doi.org/10.1016/j.chempr.2017.03.007), 2017.
- 564 DeMott, P. J., Hill, T. C. J., McCluskey, C. S., Prather, K. A., Collins, D. B., Sullivan, R. C., Ruppel, M. J., Mason, R. H.,  
565 Irish, V. E., Lee, T., Hwang, C. Y., Rhee, T. S., Snider, J. R., McMeeking, G. R., Dhaniyala, S., Lewis, E. R., Wentzell, J.  
566 J. B., Abbatt, J., Lee, C., Sultana, C. M., Ault, A. P., Axson, J. L., Martinez, M. D., Venero, I., Santos-Figueroa, G.,  
567 Stokes, D. M., Deane, G. B., Mayol-Bracero, O. L., Grassian, V. H., Bertram, T. H., Bertram, A. K., Moffett, B. F., and  
568 Franc, G. D.: Sea Spray Aerosol as a Unique Source of ice Nucleating Particles, *PNAS*, 113, 5797-5803,  
569 <https://doi.org/10.1073/pnas.1514034112>, 2016.
- 570 DeMott, P. J., Möhler, O., Cziczo, D. J., Hiranuma, N., Petters, M. D., Petters, S. S., Belosi, F., Bingemer, H. G.,  
571 Brooks, S. D., Budke, C., Burkert-Kohn, M., Collier, K. N., Danielczok, A., Eppers, O., Felgitsch, L., Garimella, S.,  
572 Grothe, H., Herenz, P., Hill, T. C. J., Höhler, K., Kanji, Z. A., Kiselev, A., Koop, T., Kristensen, T. B., Krüger, K., Kulkarni,

573 G., Levin, E. J. T., Murray, B. J., Nicosia, A., O'Sullivan, D., Peckhaus, A., Polen, M. J., Price, H. C., Reicher, N.,  
574 Rothenberg, D. A., Rudich, Y., Santachiara, G., Schiebel, T., Schrod, J., Seifried, T. M., Stratmann, F., Sullivan, R. C.,  
575 Suski, K. J., Szakáll, M., Taylor, H. P., Ullrich, R., Vergara-Temprado, J., Wagner, R., Whale, T. F., Weber, D., Welti,  
576 A., Wilson, T. W., Wolf, M. J., and Zenker, J.: The Fifth International Workshop on Ice Nucleation phase 2 (FIN-02):  
577 laboratory intercomparison of ice nucleation measurements, *Atmospheric Measurement Techniques*, 11, 6231-  
578 6257, [10.5194/amt-11-6231-2018](https://doi.org/10.5194/amt-11-6231-2018), 2018.

579 Engel, A.: Determination of Marine Gel Particles, in: *Practical Guidelines for the Analysis of Seawater*, edited by:  
580 Wurl, O., (CRC Press Taylor & Francis Group), Boca Raton, FL, 125-142, 2009.

581 Franklin, C. N., Z. Sun, D. B., Yan, M. D. H., and Bodas-Salcedo, A.: Evaluation of Clouds in ACCESS Using the Satellite  
582 Simulator Package COSP: Global, Seasonal, and Regional Cloud Properties, *J. Geophys. Res. Atmos.*, 118, 732-748,  
583 <https://doi.org/10.1029/2012JD018469>, 2013.

584 Freney, E., Sellegri, K., Nicosia, A., Trueblood, J. V., Bloss, M., Rinaldi, M., Prevot, A., Slowik, J. G., Thyssen, M.,  
585 Gregori, G., Engel, A., Zanker, B., Desboeufs, K., Asmi, E., Lefevre, D., and Guieu, C.: High Time Resolution of  
586 Organic Content and Biological Origin of Mediterranean Sea Spray Aerosol, *ACP*, 2020.

587 Fuentes, E., Coe, H., Green, D., de Leeuw, G., and McFiggans, G.: Laboratory-generated primary marine aerosol  
588 via bubble-bursting and atomization, *Atmos. Meas. Tech.*, 3, 141-162, [10.5194/amt-3-141-2010](https://doi.org/10.5194/amt-3-141-2010), 2010.

589 Gantt, B., and Meskhidze, N.: The physical and chemical characteristics of marine primary organic aerosol: a  
590 review, *Atmospheric Chemistry and Physics*, 13, 3979-3996, [10.5194/acp-13-3979-2013](https://doi.org/10.5194/acp-13-3979-2013), 2013.

591 Gong, X., Wex, H., van Pinxteren, M., Triesch, N., Fomba, K. W., Lubitz, J., Stolle, C., Robinson, T.-B., Müller, T.,  
592 Herrmann, H., and Stratmann, F.: Characterization of aerosol particles at Cabo Verde close to sea level and at the  
593 cloud level – Part 2: Ice-nucleating particles in air, cloud and seawater, *Atmospheric Chemistry and Physics*, 20,  
594 1451-1468, [10.5194/acp-20-1451-2020](https://doi.org/10.5194/acp-20-1451-2020), 2020.

595 Hiranuma, N., Adachi, K., Bell, D. M., Belosi, F., Beydoun, H., Bhaduri, B., Bingemer, H., Budke, C., Clemen, H.-C.,  
596 Conen, F., Cory, K. M., Curtius, J., DeMott, P. J., Eppers, O., Grawe, S., Hartmann, S., Hoffmann, N., Höhler, K.,  
597 Jantsch, E., Kiselev, A., Koop, T., Kulkarni, G., Mayer, A., Murakami, M., Murray, B. J., Nicosia, A., Petters, M. D.,  
598 Piazza, M., Polen, M., Reicher, N., Rudich, Y., Saito, A., Santachiara, G., Schiebel, T., Schill, G. P., Schneider, J.,  
599 Segev, L., Stopelli, E., Sullivan, R. C., Suski, K., Szakáll, M., Tajiri, T., Taylor, H., Tobo, Y., Ullrich, R., Weber, D., Wex,  
600 H., Whale, T. F., Whiteside, C. L., Yamashita, K., Zelenyuk, A., and Möhler, O.: A comprehensive characterization  
601 of ice nucleation by three different types of cellulose particles immersed in water, *Atmospheric Chemistry and  
602 Physics*, 19, 4823-4849, [10.5194/acp-19-4823-2019](https://doi.org/10.5194/acp-19-4823-2019), 2019.

603 Irish, V. E., Elizondo, P., Chen, J., Chou, C., Charette, J., Lizotte, M., Ladino, L. A., Wilson, T. W., Gosselin, M.,  
604 Murray, B. J., Polishchuk, E., Abbatt, J. P. D., Miller, L. A., and Bertram, A. K.: Ice-Nucleating Particles in Canadian  
605 Arctic Sea-Surface Microlayer and Bulk Seawater, *Atmos. Chem. Phys.*, 17, 10583-10595,  
606 <https://doi.org/10.5194/acp-17-10583-2017>, 2017.

607 Irish, V. E., Hanna, S. J., Xi, Y., Boyer, M., Polishchuk, E., Ahmed, M., Chen, J., Abbatt, J. P. D., Gosselin, M., Chang,  
608 R., Miller, L. A., and Bertram, A. K.: Revisiting properties and concentrations of ice-nucleating particles in the sea  
609 surface microlayer and bulk seawater in the Canadian Arctic during summer, *Atmospheric Chemistry and Physics*,  
610 19, 7775-7787, [10.5194/acp-19-7775-2019](https://doi.org/10.5194/acp-19-7775-2019), 2019.

611 Knopf, D. A., Alpert, P. A., Wang, B., and Aller, J. Y.: Stimulation of Ice Nucleation by Marine Diatoms, *Nat. Geosci.*,  
612 4, 88-90, <https://doi.org/10.1038/ngeo1037>, 2011.

613 McCluskey, C. S., Hill, T. C. J., Malfatti, F., Sultana, C. M., Lee, C., Santander, M. V., Beall, C. M., Moore, K. A.,  
614 Cornwell, G. C., Collins, D. B., Prather, K. A., Jayarathne, T., Stone, E. A., Azam, F., Kreidenweis, S. M., and DeMott,  
615 P. J.: A Dynamic Link between Ice Nucleating Particles Released in Nascent Sea Spray Aerosol and Oceanic  
616 Biological Activity during Two Mesocosm Experiments, *J. Atmos. Sci.*, 74, 151-166, <https://doi.org/10.1175/JAS-D-16-0087.1>, 2017.

617 McCluskey, C. S., Hill, T. C. J., Humphries, R. S., Rauker, A. M., Moreau, S., Stratton, P. G., Chambers, S. D., Williams,  
618 A. G., McRobert, I., Ward, J., Keywood, M. D., Harnwell, J., Ponsonby, W., Loh, Z. M., Krummel, P. B., Protat, A.,  
619 Kreidenweis, S. M., and DeMott, P. J.: Observations of Ice Nucleating Particles Over Southern Ocean Waters,  
620 *Geophysical Research Letters*, 45, 11,989-911,997, [10.1029/2018gl079981](https://doi.org/10.1029/2018gl079981), 2018a.

621 McCluskey, C. S., Hill, T. C. J., Sultana, C. M., Laksina, O., Trueblood, J. V., Santander, M. V., Beall, C. M., Michaud,  
622 J. M., Kreidenweis, S. M., Prather, K. A., Grassian, V. H., and DeMott, P. J.: A Mesocosm Double Feature: Insights  
623 into the Chemical Makeup of Marine Ice Nucleating Particles, *J. Atmos. Sci.*, 75, 2405-2423,  
624 <https://doi.org/10.1175/JAS-D-17-0155.1>, 2018b.

625 McCluskey, C. S., Ovadnevaite, J., Rinaldi, M., Atkinson, J., Belosi, F., Ceburnis, D., Marullo, S., Hill, T. C. J.,  
626 Lohmann, U., Kanji, Z. A., O'Dowd, C., Kreidenweis, S. M., and DeMott, P. J.: Marine and Terrestrial Organic Ice-

628 Nucleating Particles in Pristine Marine to Continentally Influenced Northeast Atlantic Air Masses, *J. Geophys. Res.*  
629 *Atmos.*, 123, 6196-6212, <https://doi.org/10.1029/2017JD028033>, 2018c.

630 McCluskey, C. S., DeMott, P. J., Ma, P. L., and Burrows, S. M.: Numerical Representations of Marine Ice-Nucleating  
631 Particles in Remote Marine Environments Evaluated Against Observations, *Geophys. Res. Lett.*, 46, 7838-7847,  
632 <https://doi.org/10.1029/2018GL081861>, 2019.

633 McCoy, D. T., Hartmann, D. L., Zelinka, M. D., Ceppi, P., and Grosvenor, D. P.: Mixed-phase Cloud Physics and  
634 Southern Ocean Cloud Feedback in Climate Models, *Journal of Geophysical Research: Atmospheres*, 120, 9539-  
635 95554, <https://doi.org/10.1175/JAS-D-17-0155.1>, 2015.

636 McCoy, D. T., Tan, I., Hartmann, D. L., Zelinka, M. D., and Storelvmo, T.: On the Relationship Among Cloud Cover,  
637 Mixed-phase Partitioning and Planetary Albedo in GCMs, *Journal of Advances in Modeling Earth Systems*, 8, 650-  
638 668, <https://doi.org/10.1002/2015MS000589>, 2016.

639 Ovadnevaite, J., Manders, A., de Leeuw, G., Ceburnis, D., Monahan, C., Partanen, A. I., Korhonen, H., and O'Dowd,  
640 C. D.: A sea spray aerosol flux parameterization encapsulating wave state, *Atmospheric Chemistry and Physics*,  
641 14, 1837-1852, 10.5194/acp-14-1837-2014, 2014.

642 Pujó-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V. C., Falco, C., Ghiglione, J.-F., Goyet, C., Moutin, T., and  
643 Prieur, L.: Integrated Survey of Elemental Stoichiometry (C, N, P) from the Western to Eastern Mediterranean Sea,  
644 *Biogeosciences*, 8, 883-899, <https://doi.org/10.5194/bg-8-883-2011>, 2011.

645 Rasse, R., Dall'Olmo, G., Graff, J., Westberry, T. K., van Dongen-Vogels, V., and Behrenfeld, M. J.: Evaluating Optical  
646 Proxies of Particulate Organic Carbon across the Surface Atlantic Ocean, *Frontiers in Marine Science*, 4, 367, 2017.

647 Rogers, D. C., DeMott, P. J., Kreidenweis, S. M., and Chen, Y.: Measurements of Ice Nucleating Aerosols During  
648 SUCCESS, *Geophys. Res. Lett.*, 25, 1383-1386, <https://doi.org/10.1029%2F97GL03478>, 1998.

649 Schnell, R. C., and Vali, G.: Biogenic ice Nuclei: Part I. Terrestrial and Marine Sources, *J. Atmos. Sci.*, 33, 1554-1564,  
650 [https://doi.org/10.1175/1520-0469\(1976\)033%3C1554:BINPIT%3E2.0.CO;2](https://doi.org/10.1175/1520-0469(1976)033%3C1554:BINPIT%3E2.0.CO;2), 1976.

651 Schwier, A. N., Rose, C., Asmi, E., Ebling, A. M., Landing, W. M., Marro, S., Pedrotti, M.-L., Sallon, A., Iuculano, F.,  
652 Agusti, S., Tsiola, A., Pitta, P., Louis, J., Guieu, C., Gazeau, F., and Sellegri, K.: Primary Marine Aerosol Emissions  
653 from the Mediterranean Sea During Pre-Bloom and Oligotrophic Conditions: Correlations to Seawater  
654 Chlorophyll-a From a Mesocosm Study, *Atmos. Chem. Phys.*, 15, 7961-7976, <https://doi.org/10.5194/acp-15-7961-2015>, 2015.

655 Schwier, A. N., Sellegri, K., Mas, S., Charrière, B., Pey, J., Rose, C., Temime-Roussel, B., Jaffrezo, J.-L., Parin, D.,  
656 Picard, D., Ribeiro, M., Roberts, G., Sempéré, R., Marchand, N., and D'Anna, B.: Primary marine aerosol physical  
657 flux and chemical composition during a nutrient enrichment experiment in mesocosms in the Mediterranean Sea,  
658 *Atmospheric Chemistry and Physics*, 17, 14645-14660, 10.5194/acp-17-14645-2017, 2017.

659 Stopelli, E., Conen, F., Zimmermann, L., Alewell, C., and Morris, C. E.: Freezing Nucleation Apparatus puts New  
660 Slant on Study of Biological Ice Nucleators in Precipitation, *Atmos. Meas. Tech.*, 7, 129-134,  
661 <https://doi.org/10.5194/amt-7-129-2014>, 2014.

662 Thornton, D. C. O.: Dissolved organic matter (DOM) release by phytoplankton in the contemporary and future  
663 ocean, *European Journal of Phycology*, 49, 20-46, 10.1080/09670262.2013.875596, 2014.

664 Tovar-Sanchez, A., Arrieta, J. M., Duarte, C. M., and Sanudo-Wilhelmy, S. A.: Spatial Gradients in Trace Metal  
665 Concentrations in the Surface Microlayer of the Mediterranean Sea, *Front. Mar. Sci.*, 1, 1-8,  
666 <https://doi.org/10.3389/fmars.2014.00079>, 2019.

667 Vali, G.: Quantitative Evaluation of Experimental Results on the Heterogeneous Freezing Nucleation of  
668 Supercooled Liquids, *J. Atmos. Sci.*, 28, 402-409, 1971.

669 Vali, G., DeMott, P. J., Möhler, O., and Whale, T. F.: Technical Note: A proposal for ice nucleation terminology,  
670 *Atmospheric Chemistry and Physics*, 15, 10263-10270, 10.5194/acp-15-10263-2015, 2015.

671 Vergara-Temprado, J., Murray, B. J., Wilson, T. W., O'Sullivan, D., Browse, J., Pringle, K. J., O'Sullivan, D., Browse,  
672 J. P., K. J., Ardon-Dryer, K., Bertram, A. K., Burrows, S. M., Ceburnis, D., DeMott, P. J., Mason, R. H., O'Dowd, C. D.,  
673 Rinaldi, M., and Carslaw, K. S.: Contribution of Feldspar and Marine Organic Aerosols to Global Ice Nucleating  
674 Particle Concentrations, *ACP*, 17, 3637-3658, <https://doi.org/10.5194/acp-17-3637-2017>, 2017.

675 Verheggen, B., Cozic, J., Weingartner, E., Bower, K., Mertes, S., Connolly, P., Gallagher, M., Flynn, M., Choulaton,  
676 T., and Baltensperger, U.: Aerosol Partitioning Between the Interstitial and the Condensed Phase in Mixed-phase  
677 Clouds, *J. Geophys. Res.*, 112, <https://doi.org/10.1029/2007JD008714>, 2007.

678 Wilson, T. W., Ladino, L. A., Alpert, P. A., Breckels, M. N., Brooks, I. M., Browse, J., Burrows, S. M., Carslaw, K. S.,  
679 Huffman, J. A., Judd, C., Kilhau, W. P., Mason, R. H., McFiggans, G., Miller, L. A., Nájera, J. J., Polishchuk, E., Rae,  
680 S., Schiller, C. L., Si, M., Vergara Temprado, J., Whale, T. F., Wong, J. P. S., Wurl, O., Yakobi-Hancock, J. D., Abbatt,

682 J. P. D., Aller, J. Y., Bertram, A. K., Knopf, D. A., and Murray, D. J.: A Marine Biogenic Source of Atmospheric Ice-  
683 Nucleating Particles, *Nature*, 525, 234-238, <https://doi.org/10.1038/nature14986>, 2015.  
684 Wolf, M. J., Coe, A., Dove, L. A., Zawadowicz, M. A., Dooley, K., Biller, S. J., Zhang, Y., Chisholm, S. W., and Cziczo,  
685 D. J.: Investigating the Heterogeneous Ice Nucleation of Sea Spray Aerosols Using *Prochlorococcus* as a Model  
686 Source of Marine Organic Matter, *Environ Sci Technol*, 53, 1139-1149, 10.1021/acs.est.8b05150, 2019.  
687