

1 We once again thank the reviewers for their careful consideration of our paper. We have taken their recommendations into  
2 account and have altered the manuscript accordingly. The main concern cited by the reviewers was the use of surface area  
3 normalized INP<sub>SSA</sub> concentrations. We have thus changed the main text to show INP<sub>SSA</sub> normalized by SSA particle count,  
4 rather than surface area. We have added the following explanation to line 284:

5 *“Comparison of the total CPC-based SSA number concentration to the SSA number concentration derived from the DMPS*  
6 *revealed near unity, indicating nearly all of the particles number concentrations were captured by the DMPS. While studies*  
7 *typically present INP concentrations normalized by total SSA surface area, this was not possible in our experiment as the size*  
8 *distribution of supermicron particles was not monitored. However, in the supporting information, we do present a theoretical*  
9 *surface area normalized INP<sub>SSA</sub> calculation for comparison with other studies. The theoretical distribution was based on in-*  
10 *situ particle number concentration measurements at Mace Head and open-ocean eddy correlation flux measurements from the*  
11 *Eastern Atlantic (Table S1) (Ovadnevaite et al., 2014), with the resulting surface area distribution shown in Figure S1.”*

12 We have thus altered Figure 1, the correlations in Tables 2 and 3 and their associated scatter plots, to show INP<sub>SSA</sub> normalized  
13 by SSA particles number concentrations. Furthermore, we altered the single component model in section 4 to account for the  
14 INP<sub>SSA</sub> normalized by particles number concentrations. Conclusions remain unchanged.

15 Since we still believe the theoretical calculation of surface area normalized INP<sub>SSA</sub> concentrations is useful, we have moved  
16 the comparison of concentrations with literature values in Figure 3 as well as comparison with MC18 model in Section 4 to  
17 the Supplementary Information.

18 The other concern by reviewer 2 related to DFPC processing volume:

19 *‘With regard to the DFPC, I didn’t notice any mention of volumes processed, which given the need to limit particle loading*  
20 *with the DFPC, and the low concentrations of IN in seawater, is needed.’*

21 We have thus added the following text to the manuscript on line 171 of the main text:

22 *‘The volume sampled on each filter averaged  $8.95 \times 10^3 \pm 2.26 \text{ m}^3$  of air.’*

23  
24  
25

# 26 A Two-Component Parameterization of Marine Ice Nucleating 27 Particles Based on Seawater Biology and Sea Spray Aerosol 28 Measurements in the Mediterranean Sea

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41 **Abstract.** Ice nucleating particles (INP) have a large impact on the climate-relevant properties of clouds over the oceans.  
42 Studies have shown that sea spray aerosols (SSA), produced upon bursting of bubbles at the ocean surface, can be an important  
43 source of marine INP, particularly during periods of enhanced biological productivity. Recent mesocosm experiments using  
44 natural seawater spiked with nutrients have revealed that marine INP are derived from two separate classes of organic matter  
45 in SSA. Despite this finding, existing parameterizations for marine INP abundance are based solely on single variables such  
46 as SSA organic carbon (OC) or SSA surface area, which may mask specific trends in the separate classes of INP. The goal of  
47 this paper is to improve the understanding of the connection between ocean biology and marine INP abundance by reporting  
48 results from a field study and proposing a new parameterization of marine INP that accounts for the two associated classes of  
49 organic matter. The PEACETIME cruise took place from May 10 to June 10, 2017 in the Mediterranean Sea. Throughout the  
50 cruise, INP concentrations in the surface microlayer (INP<sub>SML</sub>) and in SSA (INP<sub>SSA</sub>) produced using a plunging aquarium  
51 apparatus were continuously monitored while surface seawater (SSW) and SML biological properties were measured in  
52 parallel. The organic content of artificially generated SSA was also evaluated. **INP<sub>SML</sub> concentrations were found to be lower**  
53 **than those reported in the literature**, presumably due to the oligotrophic nature of the Mediterranean Sea. A dust wet deposition  
54 event that occurred during the cruise increased the INP concentrations measured in the SML by an order of magnitude, in line  
55 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  
56 days compared to increases in the SML, and are likely a result of a strong influence of bulk SSW INP for the temperatures  
57 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  
58 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  
59 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  
60 correlated with SSA water-insoluble organic carbon (WIOC), and SML dissolved organic carbon (DOC) concentrations. A  
61 relationship was also found between cold INP<sub>SSA</sub> and SSW nano- and micro-phytoplankton cell abundances, indicating that  
62 these species might be a source of water insoluble organic matter with surfactant properties and specific IN activities. **Guided**  
63 **by these results, we formulated and tested multiple parameterizations for the abundance of INP in marine SSA, including a**  
64 **single component model based on POC<sub>SSW</sub> and a two-component model based on SSA WIOC and OC. We also altered a**  
65 **previous model based on OC<sub>SSA</sub> content to account for oligotrophy of the Mediterranean Sea. We then compared this**  
66 **formulation with the previous models. This new parameterization should improve attempts to incorporate marine INP**  
67 **emissions into numerical models.**

## 68 1 Introduction

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

75 While the ice nucleating (IN) ability of marine SSA particles is less efficient than their terrestrial counterparts (DeMott et  
76 al., 2016), modelling studies have shown that marine INP are of particular importance in part due to the lack of other INP  
77 sources in such remote regions (Burrows et al., 2013; Vergara-Temprado et al., 2017). For this reason, recent studies have  
78 been conducted to better understand which SSA particles contribute to the marine INP population as well as the relationship  
79 between SSA emission and ecosystem productivity. Results from these studies suggest that the IN ability of SSA is linked to  
80 the biological productivity of source waters, with higher productivity leading to greater IN activity (DeMott et al., 2016; Bigg,  
81 1973; Schnell and Vali, 1976). For example, it has been shown that both the cell surface and organic exudate of the marine  
82 diatom *Thalassiosira pseudonana* can promote freezing at conditions relevant to mixed-phase clouds (Knopf et al., 2011;  
83 Wilson et al., 2015). More recently, mesocosm studies on phytoplankton blooms using two separate in-lab SSA-generation  
84 techniques have furthered the understanding of the connection between ocean biology and the IN activity of SSA (McCluskey  
85 et al., 2017). In-depth chemical analysis of the artificially generated SSA during this set of experiments has revealed marine  
86 INP may be related to two classes of organic matter: a regularly occurring surface-active molecule type related to DOC and  
87 long-chain fatty acids, and an episodic heat-labile microbially-derived type (McCluskey et al., 2018a).

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

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

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

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

## 115 **2 Methods**

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

### 122 **2.1 Surface Seawater (SSW)**

123 SSW properties presented here were obtained from sampling at depths of 20 cm and 5 m. First, 21 parameters including  
124 various chemical properties, microbial assemblages, hydrological properties, and optical properties were monitored using the  
125 ship’s underway system that continuously collected seawater at 5 m under the ship using a large peristaltic pump (Verder VF40  
126 with EPDM hose). These measurements included counts of specific microbial classes (e.g., *Synechococcus*, *Prochlorococcus*,  
127 picoeukaryotes, nanoeukaryotes, microphytoplankton, high phycoerythrin containing cells, coccolithophores, cryptophytes), as  
128 well as seawater biovolume, chlorophyll-*a* (chl-*a*), and POC concentrations. Chl-*a* was determined from the particulate  
129 absorption spectrum line-height at 676 nm after adjusting to PEACETIME chl-*a* from high performance liquid chromatography  
130 (HPLC). POC was estimated from the particulate attenuation at 660 nm using an empirical relationship specific to  
131 PEACETIME ( $POC = 1405.1 \times c_p(660) - 52.4$ ). For enumeration of phytoplankton cells, an automated Cytosense flow  
132 cytometer (Cytobuoy, NL) operating at a time resolution of one-hour was connected to the continuous underway seawater  
133 system. Particles were carried in a laminar flow filtered seawater sheath fluid and subsequently detected with forward scatter  
134 and sideward scatter as well as fluorescence in the red (FLR > 652 nm) and orange (FLO 552-652 nm). Distinction between  
135 highly concentrated picophytoplankton and cyanobacteria groups and lower concentrated nano- and microphytoplankton was  
136 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  
137 trigger level FLR 14.87 mV at a speed of  $8 \text{ mm}^3 \text{ s}^{-1}$  analysing  $3.57 \pm 0.97 \text{ cm}^3$ ).

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

## 149 2.2 Surface Microlayer

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

$$157 \quad EF = \frac{SML}{SSW}$$

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

$$165 \quad \frac{INP}{volume} = \frac{\ln(N_{total}) - \ln(N_{unfrozen})}{V_{tube}}$$

166 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  
167 each tube. The number of unfrozen tubes is calculated by first blank correcting the number of frozen tubes, and then subtracting  
168 that value from the total number of tubes. We calculated uncertainty as the binomial proportion confidence interval (95%)  
169 using the Wilson score interval. Samples were not corrected for salinity in this study.

## 170 2.3 Artificially Generated Sea Spray Aerosol

171 Sea spray aerosols were generated using a sea spray generation apparatus which has been described previously (Schwier  
172 et al., 2015; Schwier et al., 2017). The characteristics of the setup were selected to mimic Fuentes et al. (2010). These  
173 parameters (water flow rates, plunging water depth, etc.) have been shown to mimic well nascent SSA. The apparatus consists  
174 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  
175 seawater circulating system (described above) was supplied to the apparatus. Particle free air was passed perpendicular to the  
176 water surface at a height of 1 cm to send a constant airflow across the surface of the water. Aerosols were then either dried  
177 with a 1 m long silica dryer for online instrumentation (see Section 2.3.3), with a 30 cm silica gel dryer cascade impactor  
178 sampling with subsequent chemical analysis, or were sampled directly from the sea spray generator onto filters for INP  
179 analysis.

### 180 2.3.1 Offline PM1 Filter Analysis

181 Aerosol particles were also sampled onto PM1 quartz fiber filters mounted on a 4-stage cascade impactor (10 LPM)  
182 on a daily basis (24-hour duration). Samples were then extracted in Milli-Q water by sonication for 30 minutes for the analysis  
183 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  
184 via ion chromatography. An IonPac CS16 3x 250 mm Dionex separation column with gradient methanesulfonic acid elution  
185 was used for cations, while an IonPac AS11 2 x 250 mm Dionex column with gradient potassium hydroxide elution was used  
186 for anions. Water soluble organic carbon (WSOC) and water insoluble organic carbon (WIOC) were also determined. WSOC  
187 was measured after water extraction using a high-temperature catalytic oxidation instrument (Shimadzu; TOC 5000 A). Total

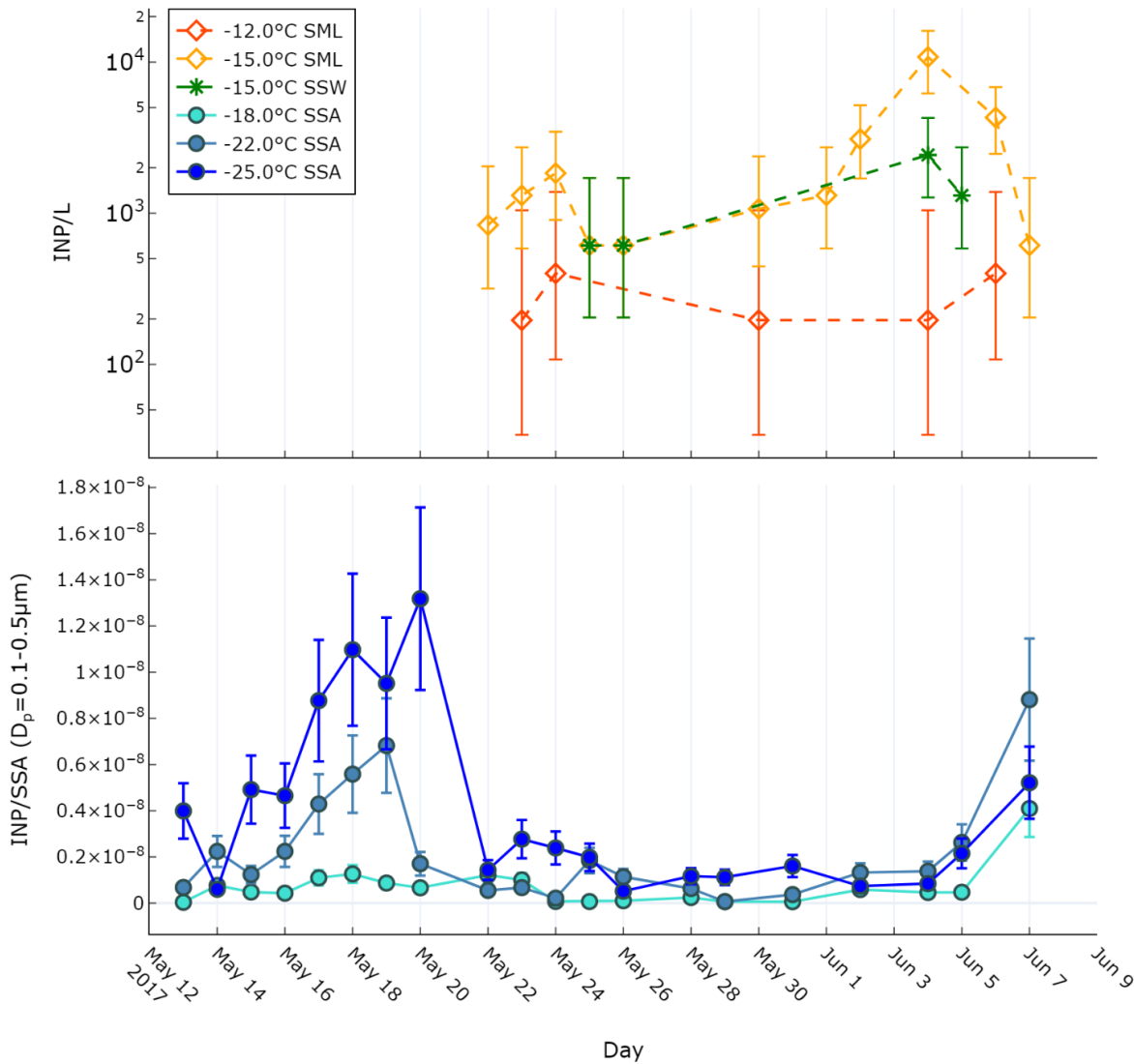
188 organic carbon (which we now refer to as OC), was measured using a Multi N/C 2100 elemental analyzer (Analytik Jena,  
189 Germany) with a furnace solids module. The analysis was performed on an 8 mm diameter filter punch, pre-treated with 40  
190  $\mu\text{L}$  of  $\text{H}_3\text{PO}_4$  (20% v/v) to remove contributions from inorganic carbon. WIOC was determined as the difference between OC  
191 and WSOC. Finally, we calculated organic mass fraction of SSA (OMSS) by taking the ratio of  $\text{OM}/(\text{OM}+\text{SeaSalt})$ , where  
192 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  
193 of inorganic ion abundance as determined above.

### 194 2.3.2 INP

195 INP concentrations were determined from filter-based samples of total suspended particles over a 24-hour duration daily  
196 or from the average of two filters (day and night). The volume sampled on each filter averaged  $8.95 \times 10^3 \pm 2.26 \text{ m}^3$  of air. The  
197 concentration of INP in the SSA was determined for the condensation freezing mode using a Dynamic Filter Processing  
198 Chamber (DFPC), which has been used in multiple previous studies and found to agree well with other INP monitoring  
199 instruments (DeMott et al., 2018; Hiranuma et al., 2019; McCluskey et al., 2018b). A full description of the instrument can be  
200 found in the literature (DeMott et al., 2018). Briefly, bulk SSA formed using the plunging apparatus were impacted  
201 onto 47 mm nitrocellulose filters which were then placed on a metal plate coated with a smooth surface of Vaseline. Air entered  
202 the chamber and was sent through a cooling coil allowing it to become saturated with respect to water. Different  
203 supersaturations with respect to ice and liquid water can be obtained by controlling the temperatures of the filter and the air  
204 flowing across the filter. Filter air temperature combinations were set three different ways, all resulting in a supersaturation  
205 with respect to liquid water of 1.02. The filter temperatures were -18, -22, and -25°C (-15.9, -19.6, and -22.3°C for air  
206 temperature). Under these conditions, condensation freezing is expected to be the dominant freezing mode for INP. It has been  
207 reported (Vali et al., 2015) that condensation freezing and immersion freezing are not distinguishable from one another. Filters  
208 were processed inside the DFPC for 15 minutes and monitored for formation of ice crystals upon activation of INPs. Based on  
209 sampling time and flow rate, the number of INP/volume were calculated. We report an uncertainty of  $\pm 30\%$  based on previous  
210 reports of the DFPC (DeMott et al., 2018).

### 211 2.3.3 Size Distribution Measurements

212 Particle size distribution and number concentrations of aerosols generated with the plunging apparatus were  
213 monitored using a custom-made differential mobility particle sizer (DMPS) preceded by a 1-micron size-cut impactor and X-  
214 ray neutralizer (TSI Inc.). Total counts from the DMPS system were checked using a condensation particle counter (CPC,  
215 TSI3010). Using the DMPS, a total of 25 size bins ranging between 10-500 nm (dry particle electrical mobility diameter) were  
216 scanned over a 10-minute time period. We then averaged the size distributions across each DFPC sampling period. Comparison  
217 of the total CPC-based SSA number concentration to the SSA number concentration derived from the DMPS revealed near  
218 unity, indicating nearly all of the particle number concentrations were captured by the DMPS. While studies typically  
219 present INP concentrations normalized by total SSA surface area, this was not possible in our experiment as the size  
220 distribution of supermicron particles was not monitored. However, in the supporting information, we do present a theoretical  
221 surface area normalized  $\text{INP}_{\text{SSA}}$  calculation for comparison with other studies. The theoretical distribution was based on in-  
222 situ particle number concentration measurements at Mace Head and open-ocean eddy correlation flux measurements from the  
223 Eastern Atlantic (Table S1) (Ovadnevaite et al., 2014), with the resulting surface area distribution shown in Figure S1.

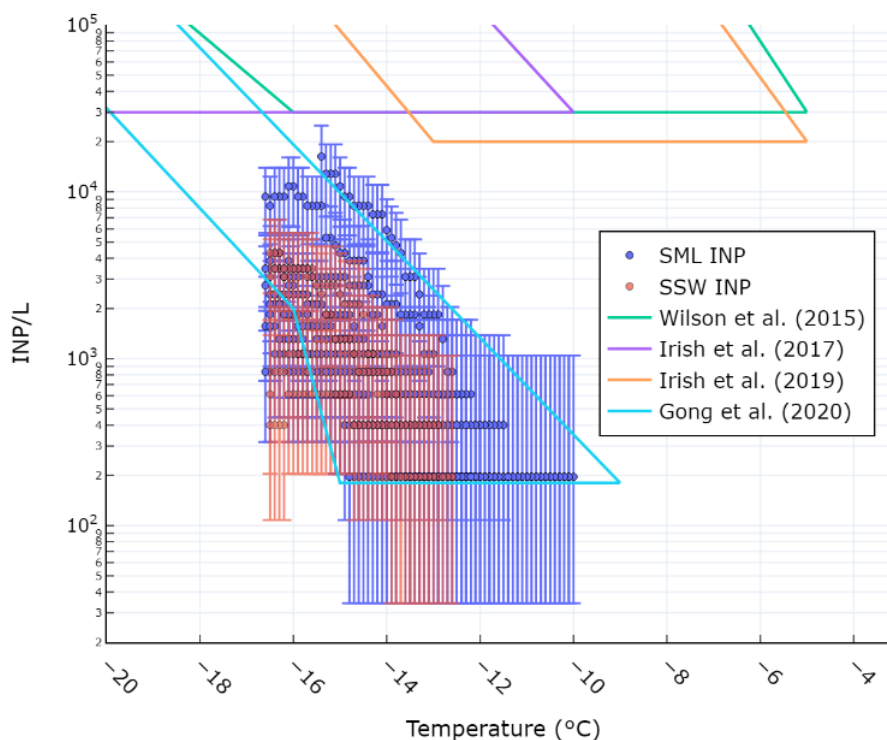


226 **Figure 1. a) INP concentrations observed during the PEACETIME cruise in the SML and SSW as measured using the LINDA**  
 227 **instrument. Error bars represent the binomial proportion confidence interval (95%) using the Wilson score interval. b) INP<sub>SSA</sub>**  
 228 **concentrations as observed by the DFPC normalized by SSA particle number concentration. Error bars represent ±30% uncertainty**  
 229 **of the DFPC instrument, as cited previously (DeMott et al., 2018).**

230 Ice nucleating particle characteristics were determined for the SSW, SML, and SSA. Figure 1a shows the concentration  
 231 of INP in the SML (INP<sub>SML</sub>) at two different temperatures (-12°C, -15°C) and in the SSW (INP<sub>SSW</sub>) at -15°C as determined  
 232 using the LINDA instrument. An initial increase of INP<sub>SML</sub> occurred on May 24 (1.8 × 10<sup>3</sup> INP/L at T=-15°C) relative to May  
 233 22 which was then followed by a further increase on June 4 (1.1 × 10<sup>4</sup> INP/L at T=-15°C). The enhancement on June 4 occurred  
 234 on the same day as a dust deposition event which led to an enrichment of iron in the SML relative to the underlying water (see  
 235 Section 3.2). While only four SSW samples were analysed for INP concentrations, they exhibited similar concentrations and  
 236 trends to those seen in the SML, with an observed maximum on June 4 (2.4 × 10<sup>3</sup> INP/L at T=-15.0°C). Based on these four  
 237 samples, no significant enrichment of INP was observed in the SML compared to SSW, except during the dust deposition  
 238 event when the SML concentration was enriched by a factor 4.5.

239 Figure 1b shows the concentration of ice nucleating particles in SSA (INP<sub>SSA</sub>) normalized by SSA particle concentration  
 240 for particles with diameters between 0.1 and 0.5 μm at three different temperatures as observed by the DFPC. It should be  
 241 noted that INP<sub>SSA</sub> measurements were conducted at colder temperatures than for the INP<sub>SML</sub> measurements due to differences  
 242 between the LINDA and DFPC instruments. In general, the highest concentrations of INP<sub>SSA</sub> were observed at the beginning

243 of the voyage, with an initial value of  $4.0 \times 10^{-9}$   $\text{INP}_{\text{SSA},-25\text{C}}/\text{SSA}$  observed on May 13, increasing to a maximum observed value  
 244 of  $1.3 \times 10^{-8}$   $\text{INP}_{\text{SSA},-25\text{C}}/\text{SSA}$  on May 20. After May 20, a considerable drop in  $\text{INP}_{\text{SSA},-25\text{C}}$  concentrations was observed.  
 245 Concentrations remained low, albeit with slight fluctuations, before increasing again to  $5.2 \times 10^{-9}$   $\text{INP}_{\text{SSA},-25\text{C}}/\text{SSA}$  on June 7. It  
 246 is also worth noting that the highest concentrations of INP active at  $-18^\circ\text{C}$  ( $\text{INP}_{\text{SSA},-18\text{C}}/\text{SSA}$ ) were observed on this day. The  
 247 increase of INP concentrations around the time of the dust deposition event in early June is similar to the trend observed for  
 248 seawater INP, albeit with a lag of at least one day (no observations of  $\text{INP}_{\text{SSA}}$  were made on June 6).



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

251 Figure 2 shows the comparison of observed INP concentrations at various temperatures in the SML and SSW with  
 252 those reported in previous studies. The concentrations we report here are lower than those from Arctic seawater samples  
 253 reported by Irish et al. (2017; 2019) and from Arctic and North Atlantic seawater samples reported in Wilson et al. (2015).  
 254 The difference can likely be attributed to the fact that eutrophic Arctic and North Atlantic seawater is more biologically active  
 255 than the oligotrophic Mediterranean Sea. Our values agree well with those reported by Gong et al. (2020) who calculated INP  
 256 concentrations in mid-latitude seawater off the coast of Cabo Verde. The authors of that study also posited that the low INP  
 257 concentrations relative to Irish et al. (2017; 2019) and Wilson et al. (2015) was due to the lower biological activity of the  
 258 oligotrophic seawater near Cabo Verde. As we did not measure the size distribution of particles larger than 500 nm, we cannot  
 259 directly compare our  $\text{INP}_{\text{SSA}}$  abundance to values cited in previous studies, where concentrations are typically normalized by  
 260 SSA surface area which is dominated by supermicron particles. However, we were able to calculate a theoretical surface area  
 261 distribution for particles between 0.5-10  $\mu\text{m}$  based on previous studies. The resulting surface area normalized INP  
 262 concentrations and comparison with literature values is shown in the supporting information (Figure S2).

### 263 3.2 Correlations between INP and Biogeochemical Conditions

264 As described in the methods section, various seawater biogeochemical properties were monitored throughout the voyage  
 265 for the SSW and SML. Plots of selected continuous measurements from the R/V's underway sampling system and discrete  
 266 measurements from the pneumatic boat of relevant biogeochemical values are found in the supporting information (Figure S3  
 267 and Figure S4, respectively). Biogeochemical properties are described in more detail in our companion papers (Freney et al.,



268 2020; Tovar-Sanchez et al., 2019) and seawater gel properties will be discussed in an upcoming paper. Here, we present a  
 269 broad summary of observed conditions.

270 In general, surface waters were characterized by oligotrophic conditions as expected for the season. Bacteria  
 271 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  
 272 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  
 273 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  
 274 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  
 275 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  
 276 be discussed in a future paper.

277 Enrichment factors (EF) in the SML relative to the SSW remained low with an average of 1.10 for DOC, 1.07 for bacteria,  
 278 and 1.17 for NCBL. As POC was not measured in the SML, we cannot report its EF. TEP was typically enriched relative to  
 279 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  
 280 on June 4 lead to a drastic increase in SML dissolved iron relative to the SSW (EF ~800). This deposition event had important  
 281 impacts on the biology of the surface seawaters, which is the focus of another paper (Freney et al., 2020). As a result, TEP EF  
 282 increased to 17, bacteria EF increased to 1.5, and NBCL to 2.4. We next discuss the correlations between INP abundances and  
 283 biogeochemical properties in the following sections.

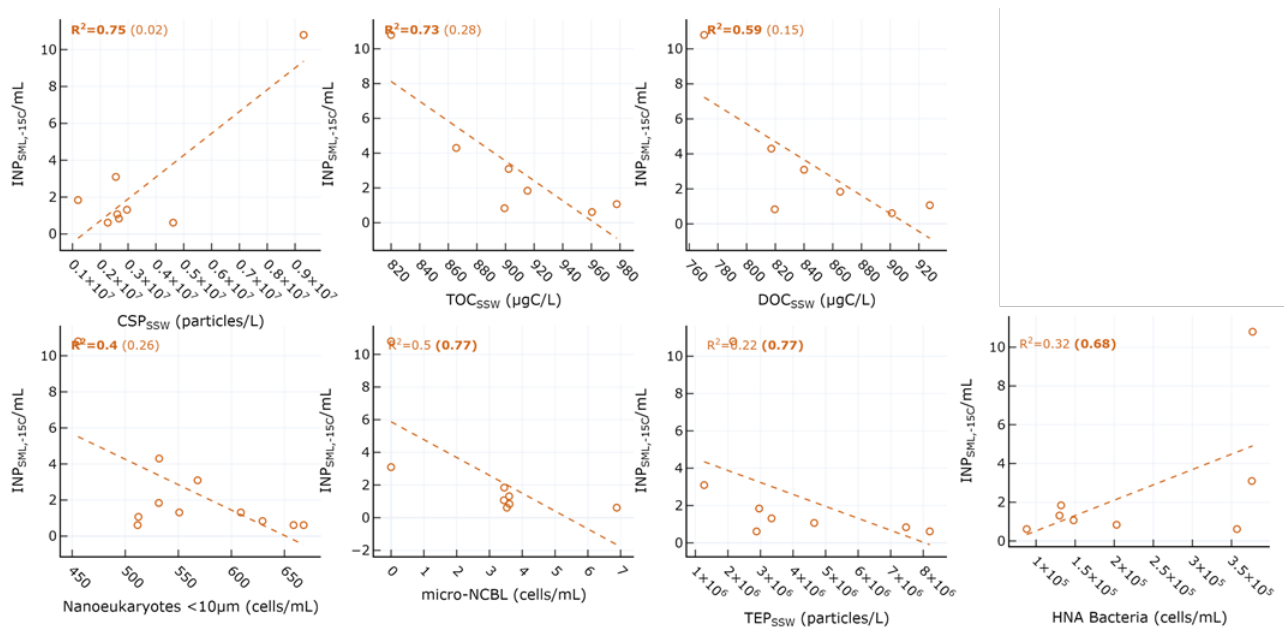
### 284 3.2.1 Correlations Between $\text{INP}_{\text{SML}}$ Abundance and Seawater Properties

285 **Table 1. Correlation statistics between  $\text{INP}_{\text{SML},-15\text{C}}$  and seawater properties in the SML and SSW, where p is the p-value test for  
 286 significance and r is the Pearson correlation coefficient. Values in parentheses are calculated for days before the dust deposition  
 287 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)
$\text{TOC}_{\text{SSW}}$	0.015 (0.36)	-0.85 (-0.53)
$\text{DOC}_{\text{SSW}}$	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)
$\text{TOC}_{\text{SML}}$	0.50 (0.020)	0.31 (-0.93)

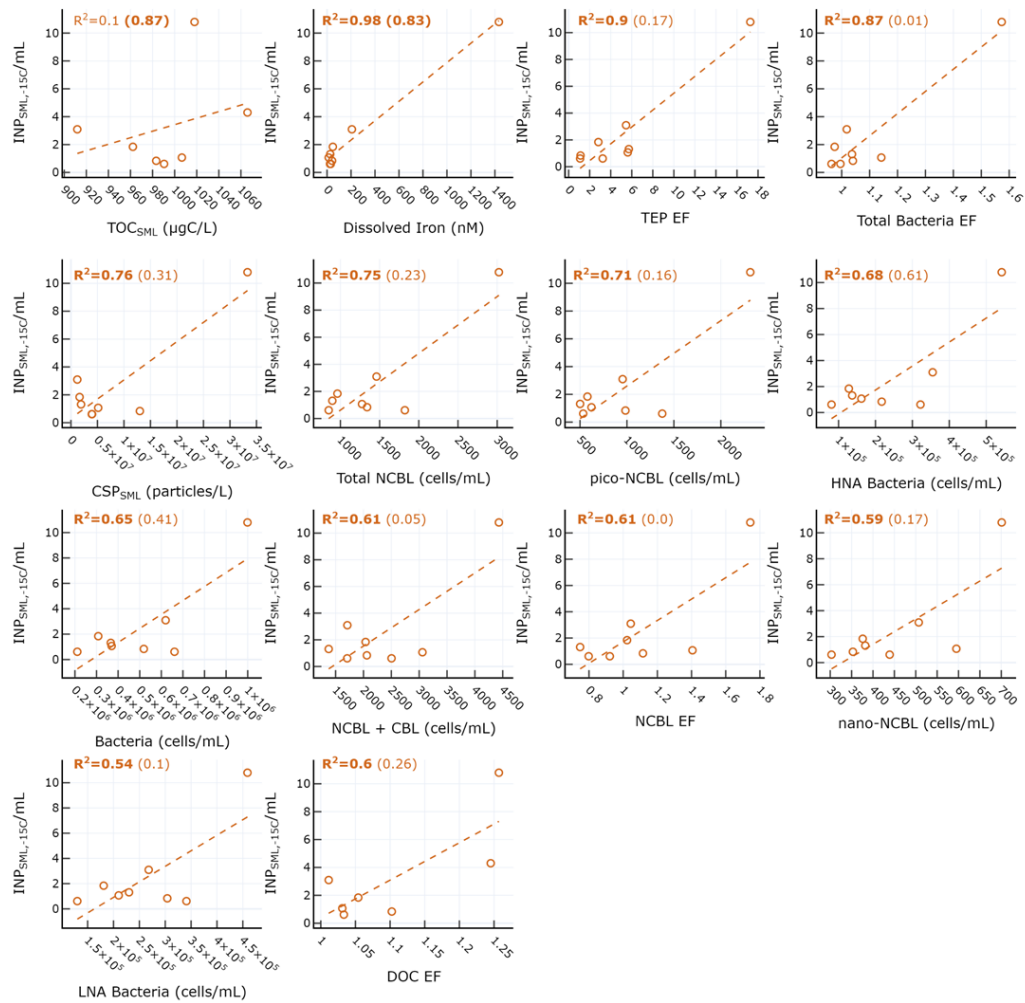
288  
 289 Table 1 shows the correlation statistics between  $\text{INP}_{\text{SML},-15\text{C}}$  and selected observed seawater properties (SSW and  
 290 SML), calculated either for all days of the PEACETIME experiment or only for days before the dust deposition event (i.e.,

291 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  
 292 days. Figure 3 shows the corresponding scatterplots of  $INP_{SML,-15C}$  abundance and SSW properties. We note a statistically  
 293 significant correlation between  $INP_{SML,-15C}$  and CSP ( $r=0.87$ ) as measured from the underway system. When considering only  
 294 days before the dust deposition event,  $INP_{SML,-15C}$  were significantly correlated with HNA bacteria ( $r=0.83$ ) while the  
 295 correlation with CSP is no longer statistically significant.  $INP_{SML,-15C}$  are actually negatively correlated with most of the  
 296 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  
 297 TOC<sub>SSW</sub>, DOC<sub>SSW</sub> and nanoeukaryotes cell abundances). **This points to a non-proportional transfer of each species from the**  
 298 **bulk seawater to the SML relative to one another. Given the high p-values and weak correlation coefficients, it is likely that**  
 299  **$INP_{SML}$  are not strongly driven by the properties of the underlying SSW. Rather, we posit that INP in the SML are dictated by**  
 300 **SML properties, as shown in the following paragraph.**



301 **Figure 3. Scatter plot of INP in the SML and various biogeochemical parameters in the SSW.  $R^2$  for all days are shown in each plot,**  
 302 **with  $R^2$  calculated for only days before the dust event shown in parentheses. Statistically significant relationships are shown in bold.**

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

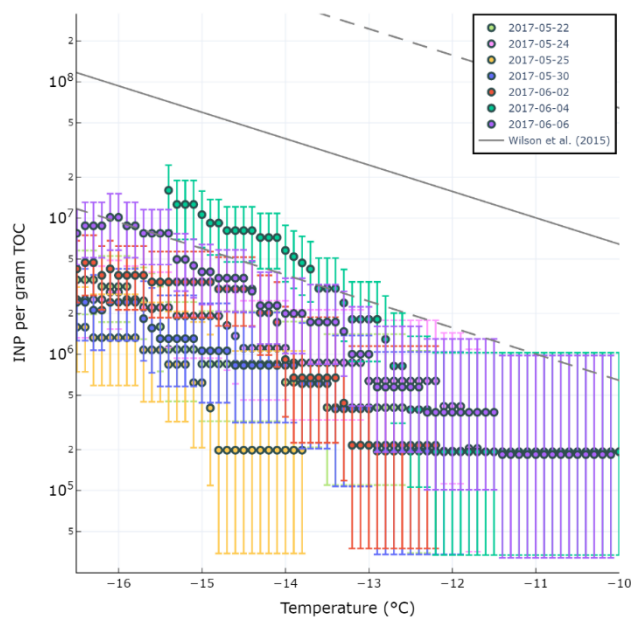


318 **Figure 4. Scatter plot of INP in the SML and various biogeochemical properties in the SML.  $R^2$  for all days are shown in each plot,**  
 319 **with  $R^2$  calculated for only days before the dust event shown in parentheses. Statistically significant  $R^2$  values are shown in bold.**

320 A previous study by Wilson and co-authors presented an INP parameterization (hereafter termed W15) based on a  
 321 positive relationship between seawater TOC and INP abundance in Arctic, North Pacific, and Atlantic SML and SSW (Wilson  
 322 et al., 2015). Total organic carbon in the SML ( $\text{TOC}_{\text{SML}}$   $\mu\text{gC/L}$ ), derived here as the sum of POC in the SSW ( $\text{POC}_{\text{SSW}}$ ) and  
 323 DOC in the SML ( $\text{DOC}_{\text{SML}}$ ), was poorly correlated with  $\text{INP}_{\text{SML},-15\text{C}}$  ( $r=0.31$ ,  $p=0.50$ ). Figure 5 shows the observed  $\text{INP}_{\text{SML},-15\text{C}}/$   
 324  $\text{TOC}_{\text{SML}}$  ratio (INP per gram of TOC) for various temperatures and days of the experiment compared with the W15  
 325 parameterization (grey line). Our results show observed  $\text{INP}_{\text{SML}}/\text{TOC}_{\text{SML}}$  ratios below those expected by the model proposed  
 326 by W15, indicating the  $\text{TOC}_{\text{SML}}$  in Mediterranean waters is less IN active at these temperatures than predicted by the W15  
 327 parameterization.

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

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



342 **Figure 5. Observed INP/TOC ratio in the SML during PEACETIME experiment for different temperatures. The gray line is the fit**  
 343 **from Wilson et al., 2015.**

344 In summary,  $INP_{SML,-15C}$  increased with SML microbial cell counts (e.g., NCBL and heterotrophic bacteria),  $F_{SML}$   
 345 and  $DOC_{EF}$  during a dust deposition event, but were overall not correlated with TOC nor DOC in the SML. Compared to  
 346 previous studies, the INP/TOC ratio observed in the Mediterranean is low. We surmise that the overprediction of INP/TOC by  
 347 the model may either be caused by a different relationship between INP and TOC at warmer temperatures, or possibly be due  
 348 to the chemical characteristics of TOC in the oligotrophic Mediterranean. This complicated relationship between seawater  
 349 TOC and  $INP_{SML}$  highlights the need for further studies focused on the chemical composition of DOC and POC in bulk SSW  
 350 and SML. Further experiments during low and high biological productivity are needed in controlled environments to better  
 351 determine under what conditions (oligotrophic and eutrophic) and location in the water column (i.e., bulk SSW vs SML) TOC,  
 352 bacteria, and phytoplankton are linked to INP across a range of temperatures. Finally, regardless of the exact mechanism, the  
 353 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  
 354 magnitude during the dust event. This impact may have climate implications if  $INP_{SML,-15C}$  were efficiently transferred to the  
 355 sea spray.

### 356 3.2.2 Correlations Between $INP_{SSA}$ Abundance and Observed SSA and Seawater Conditions

357 In the following section, we compare  $INP_{SSA}$  at various temperatures with seawater and SSA properties. Submicron  
 358 particle concentrations ranged between 1000-3000 particles/cm<sup>3</sup> (Figure S5) and its dependence of seawater biology is further  
 359 explored in a separate manuscript (Sellegrri et al. under revision). **For comparison with seawater properties,  $INP_{SSA}$  was first**  
 360 **normalized by SSA particle concentration ( $0.1 < D_p < 0.5 \mu m$ ).**

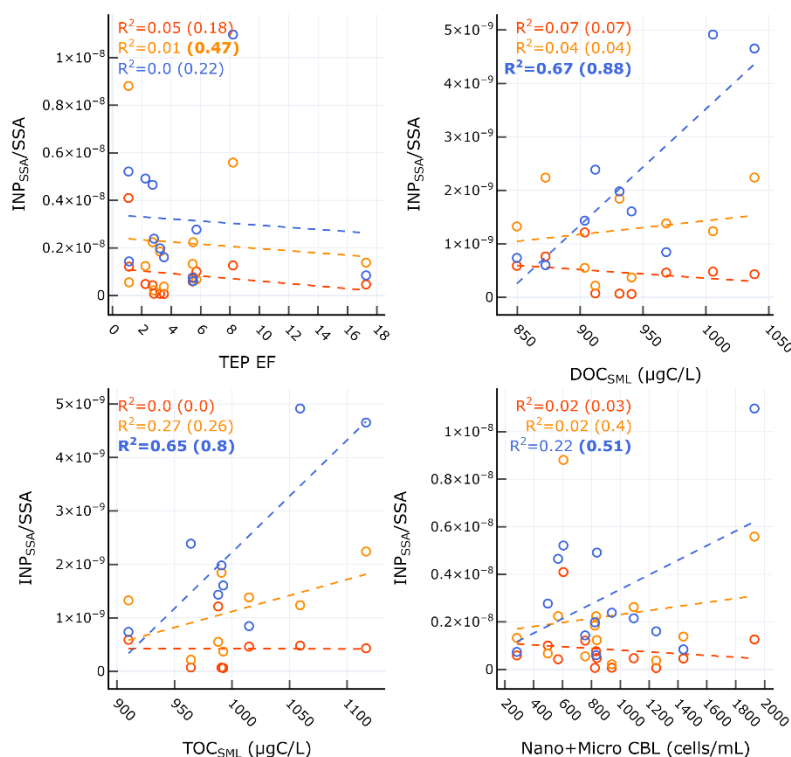
361 Table 2 shows the correlation statistics between  $INP_{SSA}$  normalized by SSA particle **number concentration** and select  
 362 conditions in the SML for relationships that were statistically significant. Figure 6 shows the corresponding scatter plots for  
 363 these relationships. We also tested for correlations on days not affected by the dust event (i.e., days before June 4), and their  
 364 statistics are shown in parentheses in Table 2 and Figure 6. Surprisingly, there were no significant correlations between  $INP_{SSA,-}$   
 365  $18C$  and conditions in the SML, including TEP and CSP abundance and enrichment factors, bacteria abundance and enrichment

366 factors, nor with  $INP_{SML}$  as measured by the LINDA instrument. This is somewhat unexpected considering INP in the SML at  
 367  $-15^{\circ}C$  was correlated with SML phytoplankton and bacteria counts, which are all expected to transfer efficiently from the SML  
 368 to the aerosol phase, an assumption widely used in the modelling community. Similarly,  $-22^{\circ}C$   $INP_{SSA}$  had no significant  
 369 correlations with SML variables, except for TEP EF which was positively correlated ( $r=0.69$ ) when only considering days  
 370 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  
 371 days ( $r=0.82$  and  $r=0.80$  for DOC and TOC, respectively). When examining only pre-dust event days, the significant  
 372 correlations included DOC enrichment as well as nano- and micro-CBL.

373 **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**  
 374 **Pearson correlation coefficient. Values in parentheses are calculated for days before the dust deposition event (i.e., days before June**  
 375 **4). Values that are not statistically significant ( $p > .05$ ) are italicized.**

Variable	All days ( $p_{pre-dust}$ )	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	<b>0.80 (0.028)</b>	<b>-0.081 (0.69)</b>
<b><math>-25^{\circ}C</math></b>		
$DOC_{SML}$	<b>0.0071 (0.00055)</b>	<b>0.82 (0.94)</b>
$TOC_{SML}$	<b>0.016 (0.0066)</b>	<b>0.80 (0.89)</b>
DOC EF	<b>0.45 (0.014)</b>	<b>0.29 (0.81)</b>
Nano+Micro CBL	<b>0.10 (0.021)</b>	<b>0.47 (0.71)</b>

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377 **Figure 6. Scatter plots of  $INP_{SSA}$  normalized by SSA particle surface area at three temperatures and select conditions in the SML**  
 378 **for relationships that were statistically significant. Corresponding correlation parameters are reported Table 2.  $R^2$  values for all**  
 379 **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.**  
 380  **$R^2$  for statistically significant relationships are shown in bold.**

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382 **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**  
 383 **Pearson correlation coefficient. Values in parentheses are calculated for days before the dust deposition event (i.e., days before June**  
 384 **4). Values that are not statistically significant ( $p > .05$ ) are italicized.**

Variable	All days (P <sub>pre-dust</sub> )	All days (r <sub>pre-dust</sub> )
<b>-18°C</b>		
POC <sub>SSW</sub>	0.95 (0.010)	0.017 (0.64)
DOC <sub>SSW</sub>	0.16 (0.023)	-0.51 (-0.78)
<b>-22°C</b>		
Nanoeukaryotes <10µm	0.021 (0.050)	-0.51 (-0.48)
Prochlorococcus	0.23 (0.000014)	0.31 (0.90)
POC <sub>SSW</sub>	0.44 (0.036)	0.20 (0.54)
Coccolithophores	0.67 (0.033)	0.10 (0.52)
Micro-NCBL	0.14 (0.0085)	0.43 (0.77)
<b>-25°C</b>		
Nanoeukaryotes <10µm	0.0065 (0.0042)	-0.59 (-0.65)
Prochlorococcus	0.00033 (0.00014)	0.77 (0.84)
Coccolithophores	0.033 (0.039)	0.48 (0.50)
Cryptophytes	0.034 (0.052)	0.48 (0.48)
Micro-NCBL	0.0013 (0.0053)	0.79 (0.80)
Nano-NCBL	0.049 (0.059)	0.56 (0.61)

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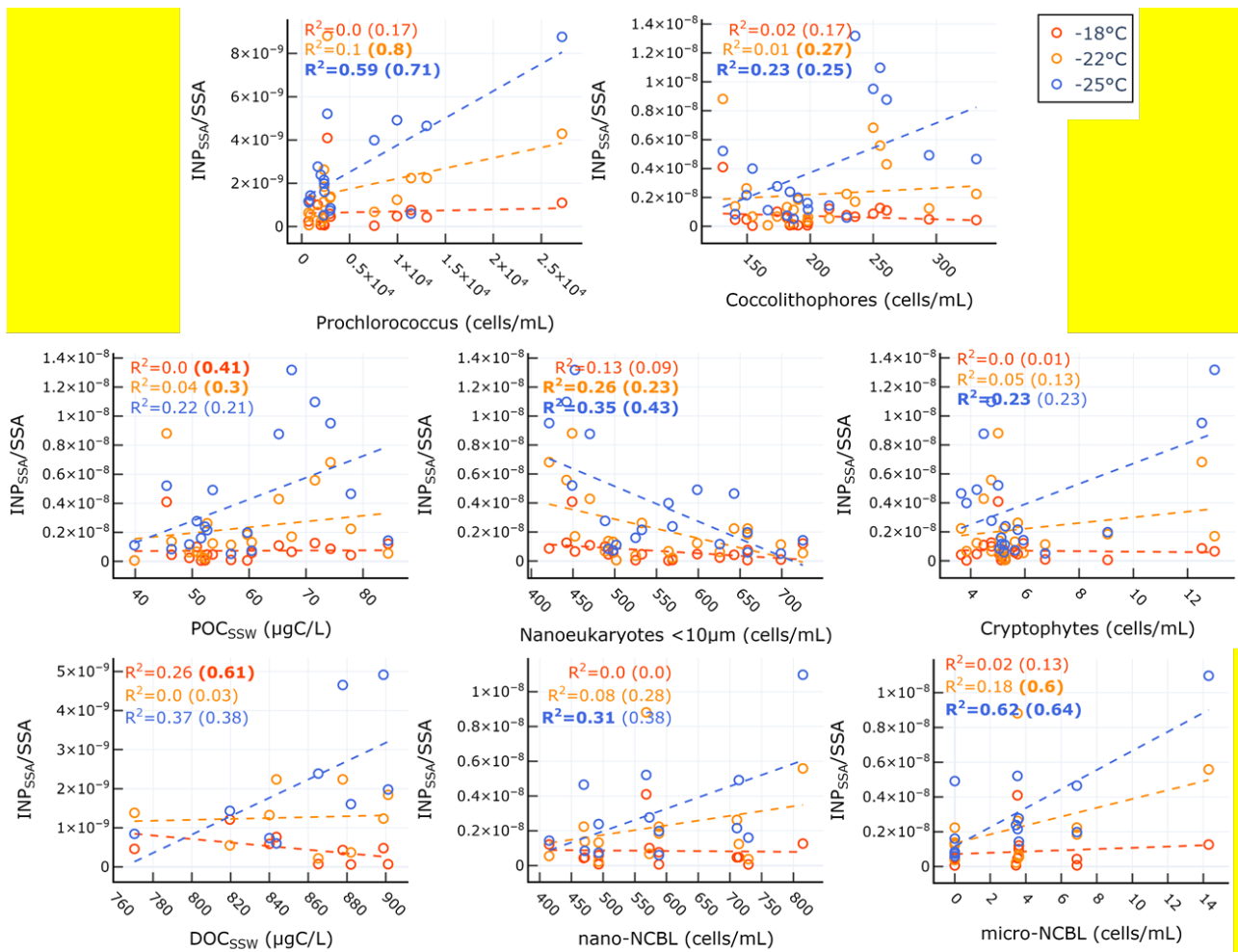
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Table 3 and the corresponding scatter plots in Figure 7 show that a weak correlation exists between INP<sub>SSA</sub> active at -18°C and POC<sub>SSW</sub> for all days, but becomes significant and strong for days not including the dust event. This 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<sub>SSA,-18C</sub> are also significantly correlated INP<sub>SSW,-16C</sub>, (results not shown) but with a sample size of n=4 this finding requires further validation. Nonetheless, this result could indicate that INP<sub>SSA</sub> at this temperature come from the bulk water rather than the SML. INP<sub>SSA</sub> at -22°C show a slightly weaker, yet still significant correlation with POC<sub>SSW</sub> than INP<sub>SSA</sub> 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<sub>SSA</sub> at -25°C were correlated with similar variables as INP<sub>SSA</sub> at -22°C, with the exception POC<sub>SSW</sub>. Furthermore, the correlations with the various microbial categories was stronger for INP<sub>SSA</sub> at -25°C than at warmer temperatures, indicating these parameters are more associated with cold INP. Interestingly, INP<sub>SSA,-25C</sub> 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.



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**Figure 7. Scatter plots of  $INP_{SSA}$  normalized by SSA particle surface area at three temperatures and select conditions in the SSW for relationships that were statistically significant. Corresponding correlation parameters are reported Table 3.  $R^2$  values for all 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.  $R^2$  for statistically significant relationships are shown in bold.**

407 Table 4 and Figure 8 show the significant correlations between  $INP_{SSA}$  and SSA properties. A timeseries of SSA chemical  
408 properties is shown in Figure S6. A positive correlation was observed between  $INP_{SSA,-18C}$  and SSA organic carbon (OC) as  
409 well as the ratio of SSA water-soluble organic carbon to organic carbon (WSOC/OC). The correlation between WSOC/OC  
410 and  $INP_{SSA,-18C}$  makes sense given the finding that  $INP_{SSA,-18C}$  was correlated with POC<sub>SSW</sub>. A higher WSOC/OC value would  
411 suggest a higher fraction of soluble organics which would be expected to transfer to the atmosphere from the bulk SSW rather  
412 than the SML due to their high solubility.  
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415 **Table 4. Correlation statistics between  $INP_{SSA}$  and SSA properties, where p is the p-value test for significance and r is the Pearson**  
 416 **correlation coefficient. Values in parentheses are calculated for days before the dust deposition event (i.e., days before June 4).**  
 417 **Values that are not statistically significant ( $p > .05$ ) are italicized.**

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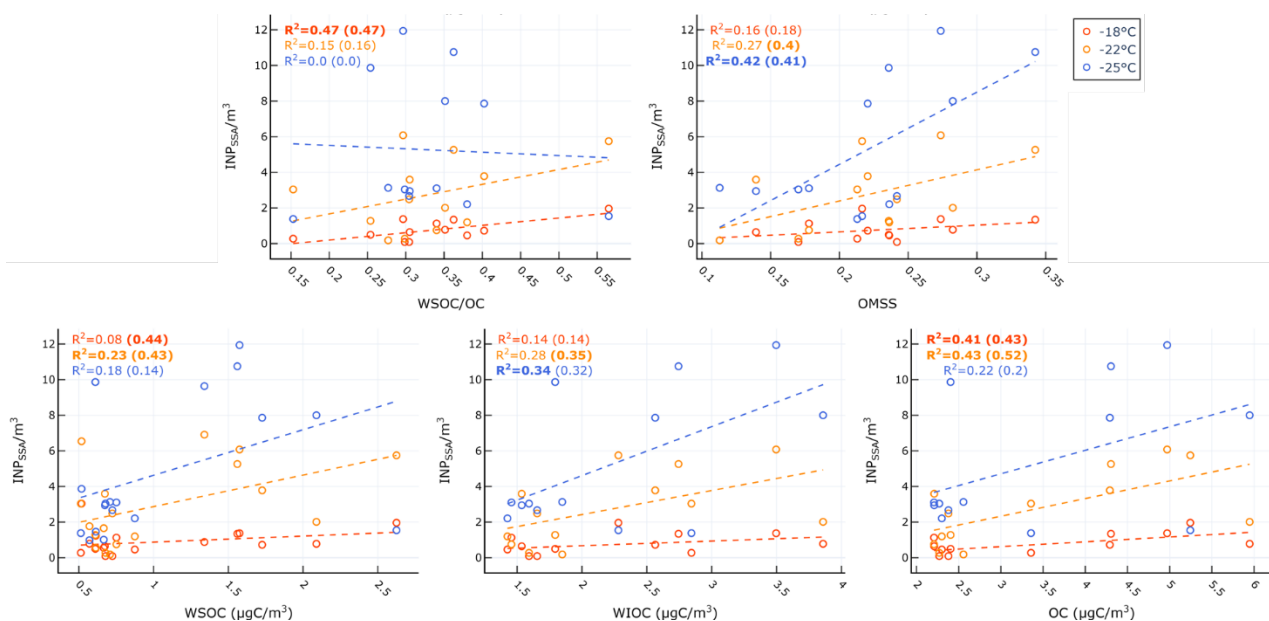
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Variable	$p_{\text{all days}}$ ( $p_{\text{pre-dust}}$ )	$r_{\text{all days}}$ ( $r_{\text{pre-dust}}$ )
<b>-18°C</b>		
WSOC/OC	0.0099 (0.014)	0.68 (0.68)
OC	0.018 (0.021)	0.64 (0.65)
WSOC	<i>0.25</i> (0.0074)	<i>0.29</i> (0.66)
<b>-22°C</b>		
WSOC	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)

Figure 8 and Table 4 also show that  $INP_{SSA,-25°C}$  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,  $INP_{SSA,-25°C}$  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<sub>SSW</sub> and the coccolithophores cell abundance. In light of this and given the correlation of  $INP_{SSA,-25°C}$  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.



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**Figure 8. Scatter plots of  $INP_{SSA}$  at three temperatures and SSA properties for relationships that were statistically significant. Corresponding correlation statistics are reported Table 2.  $R^2$  values for all days are shown in each plot, with values calculated pre-dust event (i.e., days before June 4) in parentheses. Statistically significant values are shown in bold.**



445 To summarize the results thus far, we have found evidence for the existence of two classes of INP in SSA with  
446 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  
447 abundance and POC in the SSW, DOC in the SML, and WIOC in SSA. These findings of a two-component marine INP  
448 population agree with a recent study which also reported on the existence of dual classes of INP emitted as SSA during two  
449 mesocosm experiments, described as: 1) particulate organic carbon INP coming from intact cells or IN-active microbe  
450 fragments and 2) dissolved organic carbon INP composed of IN-active molecules enhanced during periods when the SML is  
451 enriched with exudates and cellular detritus (McCluskey et al., 2018a). However, in contrast to that study, we report here the  
452 existence of separate temperature regimes at which each INP class is active. Here, the first class of INP consists of INP that  
453 are more active at warmer temperatures ( $T=-18^{\circ}\text{C}$ ) while the second class of INP are active at colder temperatures ( $T=-25^{\circ}\text{C}$ ).  
454 INP at  $T=-22^{\circ}\text{C}$  correlates with items from both warm and cold categories.

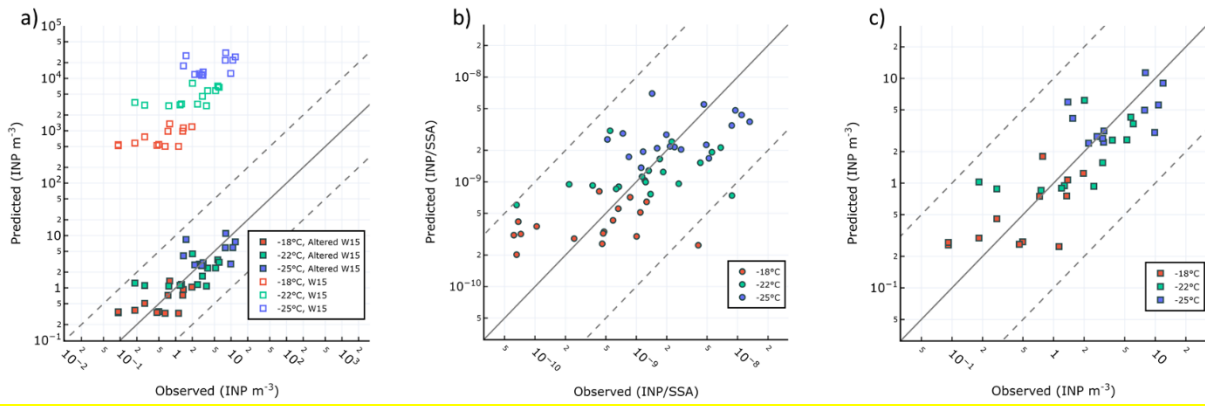
#### 455 **4 Proposal of New INP Parameterization and Comparison with Previous Models**

456 To date, parameterizations for the estimation of INP in SSA have not incorporated the knowledge of a two-component  
457 INP population. Rather, they have predicted INP based on OC or SSA surface area (W15 and MC18, respectively). To improve  
458 upon existing models, we formulated various parameterizations consisting of different time periods, features, and number of  
459 components for temperature ranges. Predictor features were chosen based upon their correlation with INP concentrations as  
460 described in the previous section. Single component parameterizations in which INP across all three temperatures were linked  
461 with the same features were compared with two-component parameterizations in which INP were split into warm and cold  
462 categories, each having their own predictor features. Finally, we developed and compared an altered version of the W15 model  
463 to account for the oligotrophic seawater of the Mediterranean Sea, as the existing model was formulated from observations of  
464 eutrophic waters. An altered version of the MC18 model for oligotrophy is presented in the SI (Figure S7), based on  
465 calculations of INP concentrations normalized by theoretical total SSA surface area. Each parameterization was recalculated  
466 using data across all days of the cruise as well as for only days before the dust deposition event in order to determine the impact  
467 of the dust event on the ability to predict INP. The complete set of parameterizations and their associated fit metrics ( $R^2$  and  
468  $R_{\text{adj.}}^2$ ) are given in Table S2.

469 Figure 10a shows observed vs predicted  $\text{INP}_{\text{SSA}}$  for the W15 model. Similar to our results for seawater INP (Figure  
470 5), a large overprediction is found relative to our observations when using W15. We also present re-calculated best-fit-lines to  
471 data using the same features as in W15 (i.e., OC) in order to account for possible changes due to the oligotrophic nature of the  
472 Mediterranean Sea. We term this parameterization the altered Wilson fit for oligotrophy, which is given by:

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

473  
474 The results for this fit is shown in Figure 9a alongside the results of the original W15 parameterization. The altered model  
475 offers an improvement over the original parameterization, with an adjusted  $R^2$  on log-transformed INP abundance of  
476  $R_{\text{adj.}}^2=0.59$ .



477 **Figure 9. Different parameterizations for prediction of INP in SSA. a) W15 and refit of same method using PEACETIME**  
 478 **observations b) single-component parameterization for INP/SSA where INP at all temperatures are related to  $POC_{SSW}$  c) two-**  
 479 **component parameterization for  $INP/m^3$  where  $INP \geq -22^\circ C$  are related to OC and  $INP < -22^\circ C$  are related to WIOC.**

480 We also tried a range of novel parameterizations based on the observed correlations between  $INP_{SSA}$  with seawater  
 481 and SSA properties. Below we describe two parameterizations which offered good fits to the data. The single-component  
 482 parameterization assumes the abundance of INP per SSA particle at each temperature can be predicted from  $POC_{SSW}$   
 483 concentrations:

$$\frac{INP}{SSA} = \exp(-28.6963 - (0.2729 * T) + (0.0366 * POC_{SSW}))$$

484  
 485 The second parameterization separates INP into warm and cold classes, where warm INP ( $\geq -22^\circ C$ ) are related to SSA  
 486 OC and cold INP ( $< -22^\circ C$ ) are related to the concentration of SSA WIOC. This two-component parameterization predicts the  
 487 concentration of  $INP/m^3$  through the following equations:

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

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

488 Figure 9b,c shows the results of our single-component model using  $POC_{SSW}$  and the two-part model which uses SSA  
 489 WIOC and OC and considers the separate temperature classes of INP. The adjusted  $R^2$  for each model on the log-transformed  
 490 INP abundance were  $R_{adj}^2=0.402$  for the single component model using  $POC_{SSW}$  and  $R_{adj}^2=0.60$  for the two-component model  
 491 using OC and WIOC. This result reveals that the two-component method performs as well as the altered Wilson  
 492 parameterization. Each parameterization's fit to the data is improved when considering pre-dust days only ( $R_{adj}^2=0.63$  for the  
 493 two-component parameterization and  $R_{adj}^2=0.57$  for the single-component parameterization). The improvement is more  
 494 pronounced for the single-component parameterization using  $POC_{SSW}$ , further pointing to the fact that such dust deposition  
 495 events can alter the INP properties of surface waters and the subsequent SSA, either through introduction of terrestrial OC or  
 496 by triggering changes to the trophic status of the surface waters, resulting in a different class of biologically produced OC. We  
 497 note that the ratio of  $INP_{SSA,-18C}/OC_{SSA}$  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  
 498 reported in Section 3.2.1 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  
 499 factor 16 as it transfers from the seawater to the SSA, which is typically assumed to be negligible in modelling studies.  
 500 However, when available, using a ratio of  $INP_{SSW}/TOC_{SSW}$  to predict sea spray originating INP in the atmosphere seems a  
 501 better approach than using the ratio  $INP_{SSW}/NaCl_{SSW}$ . Finally, we remind the readers that the two-component parameterization  
 502 uses results of SSA chemistry for submicron particles only. As previous studies have shown that the overwhelming majority  
 503 of SSA OC is found in the submicron phase (Gantt and Meskhidze, 2013), we argue that our analysis of WIOC, WSOC, and  
 504 OC concentrations in submicron SSA is representative of the whole size range of SSA.

## 507 5 Conclusions

508 In this paper we have presented results from the month-long PEACETIME cruise which took place in the Mediterranean  
509 Sea during the spring of 2017, which was characterized with a dust wet deposition event that occurred towards the end of the  
510 cruise. We find that the INP concentrations measured in the seawater are in agreement with previous studies on oligotrophic  
511 waters (Gong et al., 2020). We next investigated the relationship between seawater INP concentrations and seawater  
512 biogeochemical properties. In the SML, the increase of  $\text{INP}_{\text{SML},-15\text{C}}$  concentrations during the dust deposition event followed  
513 the SML microbial cell counts (e.g., NCBL, CBL and heterotrophic bacteria),  $\text{Fe}_{\text{SML}}$  and  $\text{DOC}_{\text{EF}}$ . Excluding this dust event,  
514  $\text{INP}_{\text{SML},-15\text{C}}$  were still correlated to Fe and bacteria (although not significantly) in the SML. Overall  $\text{INP}_{\text{SML},-15\text{C}}$  were not  
515 correlated with TOC nor DOC in the SML and compared to previous studies, the INP/TOC in the SML observed during the  
516 PEACETIME cruise was low. We surmise that these low INP/TOC is a result of TOC from the oligotrophic Mediterranean  
517 being less IN active.

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

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

534 We finally proposed a single-component model linking INP/SSA to  $\text{POC}_{\text{SSW}}$  and a two-component model linking warm  
535 INP to SSA OC and cold INP to SSA WIOC. Both models utilize features that are readily approximated either from satellite  
536 data, biogeochemical models, or from existing parameterizations and observations (Aumont et al., 2015; Rasse et al., 2017;  
537 Albert et al., 2010). We then showed these parameterizations fit the data much better than previous single component model  
538 based solely on OC content (W15) developed from studies of more biologically active waters. We also re-calculated  
539 parameterizations based on SSA OC content but for the oligotrophic Mediterranean Sea. The parameterization using SSA OC  
540 content fits almost as well as the two-component model using SSA OC and WIOC. However, given the results of correlation  
541 analysis with SSA properties as well as results from previous studies indicating a dual composition of INP, we believe the  
542 two-component model should help improve attempts to incorporate marine INP emissions into numerical models.

543  
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