https://doi.org/10.5194/acp-2020-487
Preprint. Discussion started: 23 June 2020

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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 total organic carbon (TOC) or SSA surface area, which may mask specific trends in the separate classes of INPs. 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 (SML) and in SSA 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. 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 INPs in marine SSA (INP_{SSA}) were not observed before 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°C for SSA, T=-16°C for SSW). Results confirmed that INP_{SSA} are divided into two classes depending on their associated organic matter. Here we find that warm (T ≥ -22C) INP_{SSA} concentrations are correlated with water soluble organic matter in the SSA, but also to SSW parameters (POC_{SSW} $INP_{SSW,-16C}$) while cold INP_{SSA} (T < -22C) are correlated with SSA water-insoluble organic carbon (WIOC) and SML dissolved organic carbon (DOC) concentration. A relationship was also found between cold INP_{SSA} and SSW microphytoplankton cell abundances, indicating that these species might be at the origin of water insoluble organic matter with surfactant properties and specific IN properties. Using these results, we propose a two-component parameterization for the abundance of INP in marine SSA and compare it with previous single-component models based on SSA surface area and TOC content. This new, two-component parameterization should improve attempts to incorporate marine INP emissions into numerical models. Future studies will be conducted to confirm if our parameterization can be extended to regions of higher biological productivity, such as the Southern Ocean.

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1 Introduction

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

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

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

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

This paper addresses the current gaps in the knowledge of marine INP by 1) testing existing parameterizations of INP on a new set of field measurements by extending the current inventory of field measurements beyond eutrophic waters to more

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oligotrophic regions for the first time 2) improving the understanding of how INPs in the SML and SSA are linked to both seawater biological and SSA organic properties and 3) proposing a new parameterization based on the two-component nature of INPs. Here we present results from the research cruise entitled the ProcEss studies at the Air-sEa Interface after dust deposition in the Mediterranean Sea (PEACETIME) study. The cruise took place in the central and western Mediterranean Sea from May 10-June 10, 2017. Observations of INP concentrations both in the SML and SSA were compared with a suite of surface seawater, surface microlayer, and SSA properties to better determine how INP concentrations were related to biology.

2 Methods

In the frame of the PEACETIME project (http://peacetime-project.org/), an oceanographic campaign took place aboard the French R/V 'Pourquoi Pas?' between May 10-June 10, 2017. The purpose of the voyage was to investigate the processes that occur at the air-sea interface in the Mediterranean Sea. Figure 1 shows the transect of the cruise, which started in La Seyne, France and travelled in a clockwise fashion from 35˚ to 42˚ latitude and 0˚ to 20˚ longitude. The observations and process studies performed on board both in the whole water column and the atmosphere are described elsewhere (Guieu et al., 2020). Here, we focus on the measurements conducted to describe the SML, SSW, and aerosol properties.

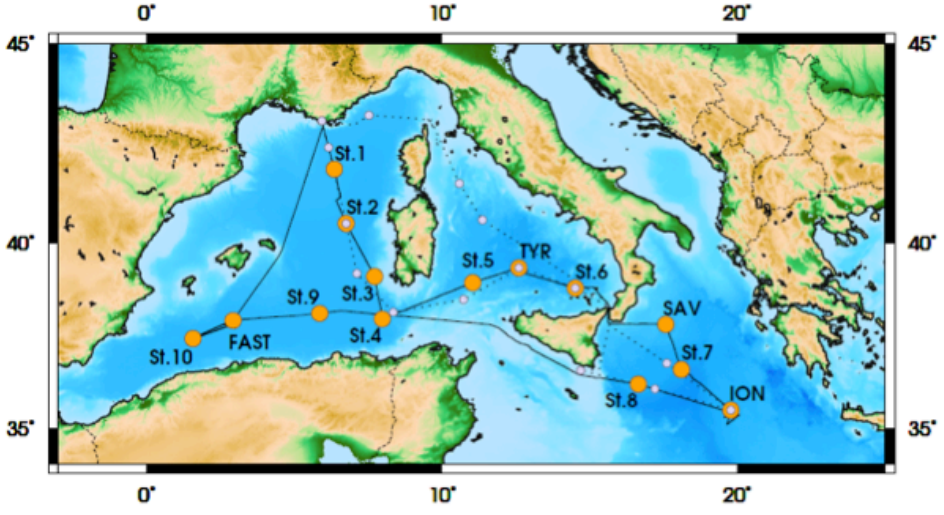

Figure 1. Transect of the PEACETIME cruise (May 10 – June 10, 2017).

2.1 Surface Seawater (SSW)

SSW properties presented here were obtained from sampling at depth of 20 cm and 5 m. First, 21 parameters including various chemical properties, microbial assemblages, hydrological properties, and optical properties were monitored using the ship's underway system that continuously collected seawater at 5 m under the ship using a large peristaltic pump (Verder VF40 with EPDM hose). These measurements included counts of specific microbial classes (e.g., *Synechococcus*, *Prochlorococcus*, picoeukaryotes, nanoeukaryotes, microphytoplankton, high phycoerythin containing cells, coccolithophores, cryptophytes), as well as seawater biovolume, chlorophyll-*a* (chl-*a*), and POC concentrations. Chl-*a* was determined from the particulate absorption spectrum line-height at 676 nm after adjusting to PEACETIME chl-*a* from HPLC. POC was estimated from the particulate attenuation at 660 nm using an empirical relationship specific to PEACETIME (POC = 1405.1 x $c_p(660)$ – 52.4). For enumeration of phytoplankton cells, an automated Cytosense flow

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cytometer (Cytobuoy, NL) operating at a time resolution of one-hour was connected to the continuous underway seawater system. Particles were carried in a laminar flow filtered seawater sheath fluid and subsequently detected with forward scatter (FWS) and sideward scatter (SWS) as well as fluorescence in the red (FLR > 652 nm) and orange (FLO 552-652 nm). Distinction between highly concentrated picophytoplankton and cyanobacteria groups and lower concentrated nano- and microphytoplankton was accomplished using two trigger levels (trigger level FLR 7.34 mV, sampling speed of 4 mm^3 s^{-1} analysing 0.65 ± 0.18 cm^3 and trigger level FLR 14.87 mV at a speed of 8 mm^3 s^{-1} analysing 3.57 ± 0.97 cm^3).

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

2.2 Surface Microlayer

At the same time SSW samples were manually collected on the pneumatic boat, SML samples were also collected using a glass plate sampling method which has been previously described in the literature (Tovar-Sanchez et al., 2019). The glass plate was cleaned overnight with acid and rinsed with ultrapure MQ water. Roughly 100 dips of the glass were conducted to collect 500 mL of SML water into 0.5L acid cleaned low-density polyethylene plastic bottles. The samples were then acidified on board to pH<2 with ultrapure-grade HCL in a class-100 HEPA laminar flow hood. The same measurements done for the SSW samples (see above) were then made on the SML samples.

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

2.3 Artificially Generated Sea Spray Aerosol

Sea spray aerosols were generated using a sea spray generation apparatus which has been described previously (Schwier et al., 2015). The apparatus consisted 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 seawater circulating system (described above) was supplied to the apparatus. Particle free air was passed perpendicular to the water surface at a height of 1 cm to send a constant airflow across the surface of the water. Aerosols were then either dried with a 1 meter long silica dryer for online instrumentation (DMPS, CPC, and ACSM), with a 30 cm silica gel dryer cascade impactor sampling with subsequent chemical analysis, or were sampled directly from the sea spray generator onto filters for INP analysis.

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149 **2.3.1 Size Distribution Measurements**

150 Particle size distribution and number concentrations of aerosols generated with the plunging apparatus were
151 monitored using a custom-made differential mobility particle sizer (DMPS) preceded by a 1 micron size-cut impactor and X-
152 ray neutralizer (TSI inc.). Total counts from the DMPS system were checked using a condensation particle counter (CPC,
153 TSI3010). Using the DMPS, a total of 25 size bins ranging between 10-500nm were scanned over a 10-minute time period.
154 For the purpose of the present study, surface area of SSA particles were calculated from the number size distributions.

155 **2.3.2 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 MilliQ water by sonication for 30 minutes for the
158 analysis 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
159 analysed via ion chromatography. An IonPac CS16 3x 250 mm Dionex separation column with gradient MSA elution was
160 used for cations, while an IonPac AS11 2 x 250 mm Dionex column with gradient KOH elution was used for anions.
161 Organic content (WSOC and WIOC) were also determined. WSOC was determined using a TOC thermal combustion
162 analyser (Shimadzu TOC-5000A). Total carbon (TC) content was measured on filter punches which were cut prior to water
163 extraction using a thermal combustion analyser equipped with a furnace for solid samples (Analytik Jena, Multi NC2100S).
164 Prior to analysis, the filter punches were acidified to remove inorganic carbon from TC to obtain TOC.

165 **2.3.3 INPs**

166 INP concentrations were determined from filter-based samples of total suspended particles over a 24h duration daily or
167 from the average of two filters (day and night). The concentration of INPs in the SSA was determined for the condensation
168 freezing mode using a Dynamic Filter Processing Chamber (DFPC). Briefly, SSA formed using the aquarium apparatus were
169 impacted onto 47mm nitrocellulose filters which were then placed on a metal plate coated with a smooth surface of Vaseline.
170 Air entered the chamber and was sent through a cooling coil allowing it to become saturated with respect to ice. Different
171 supersaturations with respect to ice and water were obtained by controlling the temperatures of the filter and the air flowing
172 across the filter. Filter air temperature combinations were set three different ways, all set to a supersaturation with respect to
173 water of 1.02. The filter temperatures were -18, -22, and -25C (-15.9, -19.6, and -22.3 C for air temperature). Filters were
174 placed inside the DFPC for 15 minutes and monitored for formation of ice crystals upon activation of INPs. Based on
175 sampling time and flow rate, the number of INP/volume were calculated.

176 **3 Results**

177 **3.1 INP in SML and SSA**

178 Ice nucleating particle concentrations were determined for the SSW, SML and SSA. Figure 2a shows the concentration
179 of INP in the SML (INP_{SML}) at three different temperatures and in the SSW (INP_{SSW}) at -15.0C as monitored using the
180 LINDA instrument. In the SML, the trends between the three temperatures are similar, although with decreasing abundances
181 at warmer temperatures to the point that INP at T=-10C were rarely observed. An initial increase occurred on May 24
182 ($1.8x10^3$ INP/L at T=-15C) followed by a much larger peak around June 4th ($1.1x10^4$ INP/L at T=-15C). SSW concentrations
183 were similar to SML concentrations, with the exception of June 4 when SML INP became enriched relative to the SSW.

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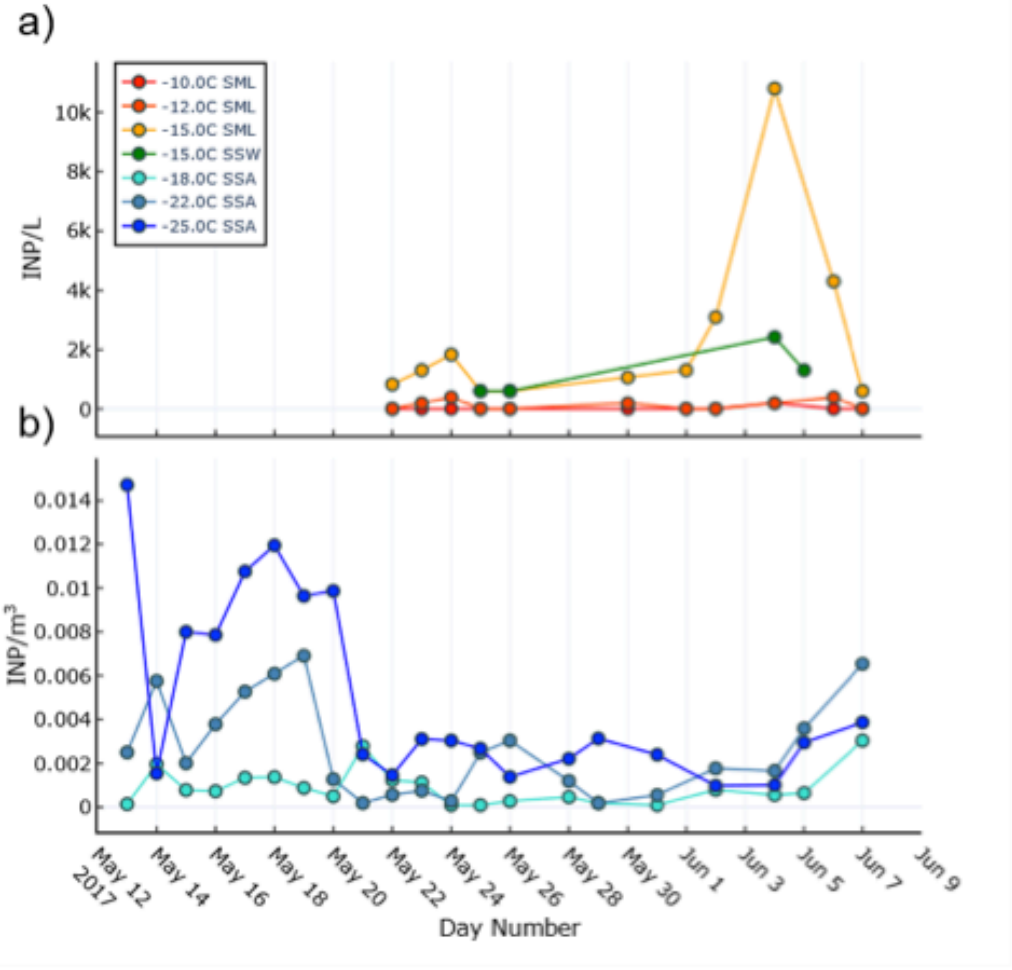

Figure 2. INP concentrations observed during the PEACETIME cruise. a) INP_{SML} and INP_{SSW} concentration as measured using the LINDA instrument and b) INP_{SSA} concentrations observed by the DFPC.

Figure 2b shows the concentration of ice nucleating particles in SSA (INP_{SSA}) at three different temperatures as observed by the DFPC. It should be noted that INP_{SSA} measurements were conducted at colder temperatures than for the INP_{SML} measurements due to differences between the LINDA and DFPC instruments. In general, the largest concentrations of INP_{SSA} were observed at the beginning of the voyage between May 12-May 20. For example, $INP_{SSA,-25C}$ peaked on May 12 (14.7×10^{-3} INP/m^3) and again on May 18 (11.9×10^{-3} INP/m^3). After May 20, a considerable drop in $INP_{SSA,-25C}$ concentrations was observed. Concentrations remained at this level, albeit with slight fluctuations, before increasing again between June 5-7 to a second peak of 3.9×10^{-3} INP/m^3 on June 7. Both INP_{SML} and INP_{SSA} showed increases during June after a rain event during which iron became highly enriched in the SML as a result of dust deposition (see next section). Interestingly, the peak in INP_{SSA} during this time occurred one day after the increase observed for INP_{SML}.

3.2 Correlations between INP and Biogeochemical Conditions

As described in the methods section, various seawater biogeochemical properties were monitored throughout the voyage for the SSW and SML. Plots of selected continuous measurements from the R/V's underway sampling system and discrete measurements from the pneumatic boat of relevant biogeochemical values are found in the supporting information (SI) (Figure S1 and Figure S2, respectively). Biogeochemical properties are described in more detail in our companion papers

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(Guieu et al., 2020; Tovar-Sanchez et al., 2019) and gel properties will be discussed in an upcoming paper. Here, we present a broad summary. In general, surface waters were characterized by oligotrophic conditions as expected for the season. Bacteria concentrations ranged between $2x10^5$ and $7x10^5$ cells/mL in the SSW and were greatest at the start and end periods of the voyage. NCBL abundance followed a similar trend and ranged between 400-4000 cells/mL. DOC and POC values were within the range of expected values for the oligotrophic Mediterranean (Pujo-Pay et al., 2011), with DOC ranging between 700-900 µgC/L and POC between 42-80 µgC/L. SSW TEP concentrations ranged between $1.2x10^6$ and $1.1x10^7$ particles/L, with CSP between $5.6x10^6$ and $9.3x10^6$ particles/L, and will be discussed in a future paper.

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

3.2.1 Correlations Between INP_{SML} Abundance and Seawater Properties

Table 1. Correlations between $INP_{SML,-15C}$ and seawater properties.

Variable	p	R (R^2)	n
	SSW		
DOC	0.045	-0.76 (0.59)	7
$CSP_{abundance}$	0.005	0.87 (0.75)	8
Nanoeukaryotes <10µm	0.04	-0.63 (0.40)	11
	SML		
Dissolved Iron	$2.0x10^{-6}$	0.99 (0.98)	8
TEP EF	0.0003	0.95 (0.90)	8
Total Bacteria EF	0.0007	0.93 (0.87)	8
$CSP_{abundance}$	0.005	0.87 (0.76)	8
Total NCBL	0.005	0.87 (0.75)	8
pico NCBL	0.009	0.84 (0.71)	8
Total bacteria	0.02	0.81 (0.65)	8
Phytoplankton (NCBL+CBL)	0.02	0.78 (0.61)	8
NCBL EF	0.78	0.78 (0.61)	8
DOC EF	0.04	0.78 (0.60)	7
nano NCBL	0.03	0.77 (0.59)	8

Table 1 shows the statistically significant correlations ($p < 0.05$) between $INP_{SML,-15C}$ and observed seawater properties. We note the only statistically significant correlations between $INP_{SML,-15C}$ and SSW parameters were with DOC (R=-0.76, n=7), CSP (R=0.87, n=8), and nanoeukaryote cell abundance <10µm (R=-0.63 n=11) as measured from the underway system. Nanoeukaryote cell abundances in the SSW were identified in a companion paper (Freney et al., this issue) as related to a fraction of organic matter that has a signature of fatty acids and amino acids (MOA), likely enriched in the SML and having surface active properties. Figure 3 shows scatterplots of relationships with significant correlations. In the SML, $INP_{SML,-15C}$ were most strongly positively correlated with dissolved iron. However, this relationship as well as others, may be skewed by an outlier due to the dramatic increase in iron observed on June 4 (Figure S2a) as described previously. Indeed, when days after June 3 are removed, only the relation to Fe_{SML} (R=0.91, p=0.01 n=6) and bacteria HnA (high nucleic acid) in the SSW (R=0.83, p=0.04, n=6) remain as significant positive correlations. This suggests that the dust deposition event observed during June had a significant impact on the $INP_{SML,-15C}$ concentration. The strong correlation with Fe_{SML} indicates that the presence of dust in the SML, of which Fe_{SML} is a tracer, may increase the $INP_{SML,-15C}$ concentrations,

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as dust is known to have good INP properties. The correlations with biological populations found in the SML of all types (NCBL (R=0.77), pico NCBL (R=0.84), nano NCBL (R=0.77), total heterotrophic bacteria (R=0.81), and total phytoplankton (NCBL and CBL combined) (R=0.78) cell counts) suggests that some of the biological species found in these groups and developed over the dust particles also have good INP properties. It is difficult from this data set to segregate between the dust and biological impact on the $INP_{SML,-15C}$.

Previous reports examining the correlation between INP and microbial abundance have yielded mixed results. For example, a report of INP in Arctic SML and SSW found no statistically significant relationship between the temperature at which 10% of droplets had frozen and bacteria or phytoplankton abundances in bulk SSW and SML samples (Irish et al., 2017). However, recent mesocosm studies using nutrient-enriched seawater found that INP abundances between -15C and -25C in the aerosol phase were positively correlated with aerosolized bacterial abundance (McCluskey et al., 2017).

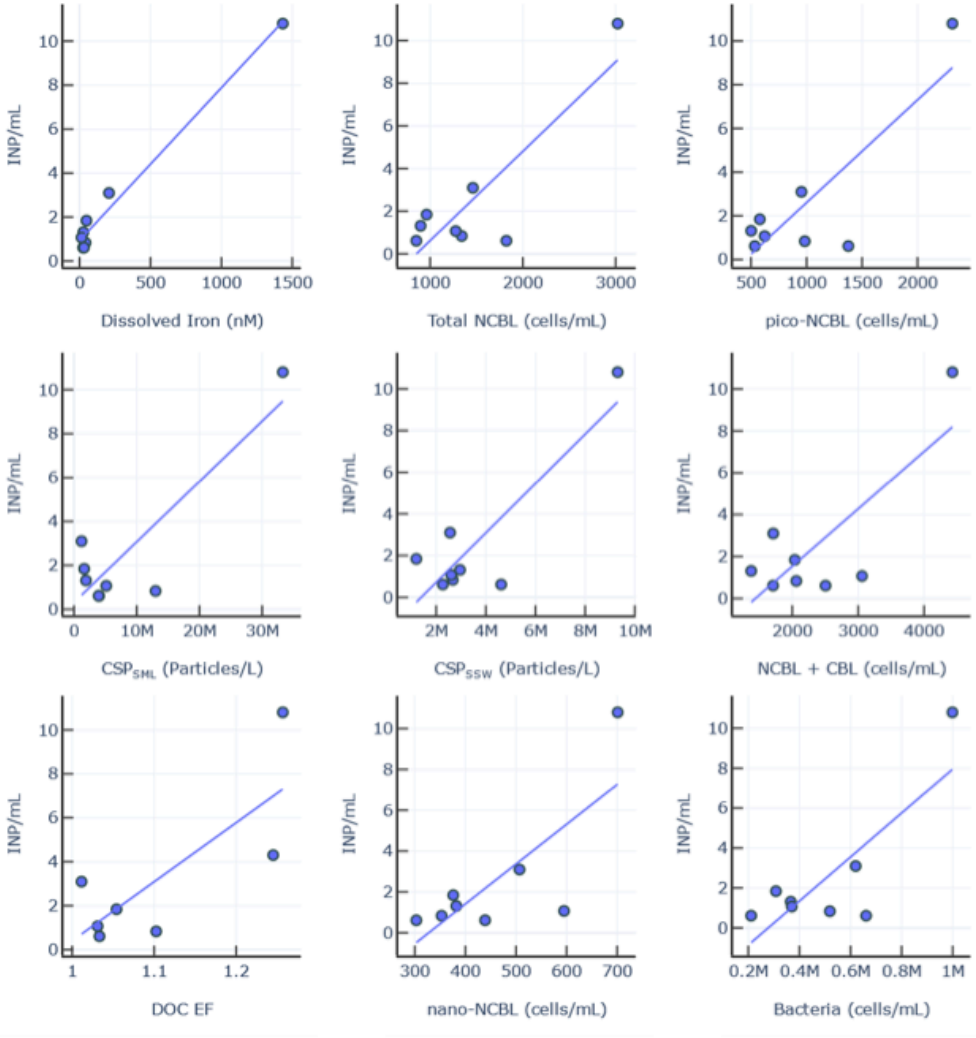

Figure 3. Correlation matrix of INP in the SML ($INP_{SML,-15C}$) and various biogeochemical parameters.

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Neither POC in the SSW (POC_{SSW}) nor DOC in the SML (DOC_{SML}) was significantly correlated with $INP_{SML,-15C}$ (R=-0.35, p=0.29, n=11, and R=0.37, p=0.42, n=7 respectively). Interestingly, DOC EF was significantly correlated with $INP_{SML,-15C}$ (R=0.78, p=0.04, n=7), again due to the dust event. This indicates that the fraction of DOC which is enriched in the SML during the dust event has specific IN properties. This DOC type enriched in the SML is likely connected to the CSP abundance, albeit not to the TEP.

A previous study by Wilson and co-authors presented an INP parameterization (hereafter termed W15) based on a positive relationship between seawater TOC and INP abundance in Arctic, North Pacific, and Atlantic SML and SSW waters (Wilson et al., 2015). Total organic carbon (TOC µgC/l), derived here as the sum of particulate organic carbon in the SSW (POC_{SSW}) and dissolved organic carbon in the SML (DOC_{SML}), was weakly correlated with $INP_{SML,-15C}$ (R=0.31, p=0.49, n=7). Figure 6 shows the observed $INP_{SML,-15C}$/TOC ratio (INP per gram of OC) in the SML for various temperatures and days of the experiment compared with the W15 parameterization (grey line). Our results show observed INP_{SML}/TOC ratios below those expected by the model proposed by W15, indicating the TOC in Mediterranean waters is less IN active at these temperatures than predicted by the W15 parameterization.

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

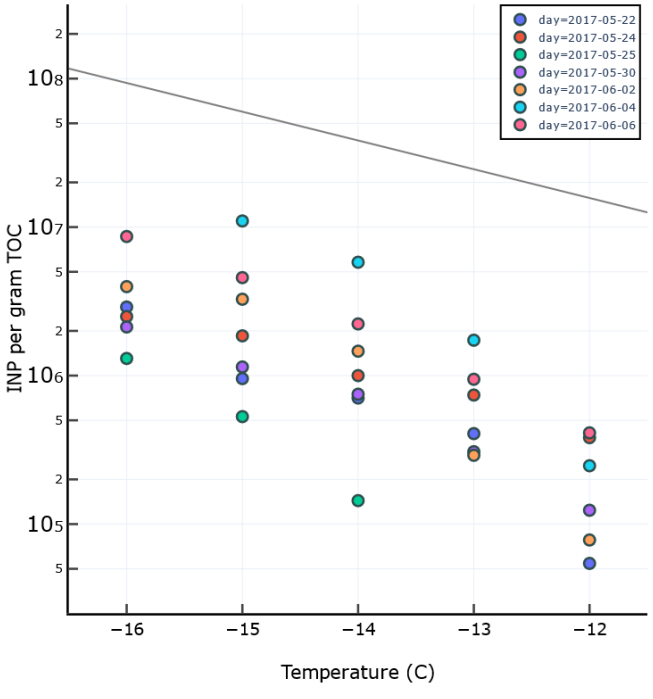

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Figure 4. Observed INP/TOC ratio during PEACETIME experiment for different temperatures. The gray line is a model fit from Wilson et al., 2015.

Another possible explanation for the discrepancy between our results and those from W15 is that the oligotrophic nature of Mediterranean waters results in a TOC of a different chemical composition than what is observed in more biologically productive waters such as the Arctic and Atlantic. For example, the pool of TOC during this study was dominated by DOC and featured low POC content, presumably due to low biological productivity.

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

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

In the following section, we compare INP_{SSA} at various temperatures with seawater and SSA properties. For comparison with seawater properties, INP_{SSA} was first normalized by SSA particle surface area (SSA_{diam}=10-500nm)(Figure S3). As total particle counts matched quite well with SSA counts between 10-500 nm diameter, and as most of the surface area of sea spray is comprised between this size range, this value is a reasonable estimate of total SSA particle surface area. Submicron particle concentrations ranged between 1000-3000 particles/cm^3 (Figure S4) and its dependence of seawater biology is further explored in a separate manuscript. Interestingly, despite the fluctuations, no statistically significant correlations were seen between total submicron particle counts or total SSA surface area and INP_{SSA} at all three temperatures (Figure S5a,b).

Figure 5 shows the scatter plots between $INP_{SSA,-18C}$ normalized by SSA particle surface area (SSA_{diam} 10-500nm) and conditions in the SSW as well as scatter plots between non-normalized $INP_{SSA,-18C}$ and non-normalized SSA properties, for relationships that were found significant. Corresponding correlation parameters are reported Table 2. Correlations did not differ significantly when performed over the whole data set or when performed over a smaller data set that excludes the dust wet deposition event. Surprisingly, there was no significant correlation between $INP_{SSA,-18C}$ and conditions in the SML, including TEP and CSP abundance and enrichment factors, bacteria abundance and enrichment factors, nor with INP_{SML} as measured by the LINDA instrument. This is somewhat unexpected considering INP in the SML at -15C was correlated with SML bacteria counts, which are expected to transfer efficiently from the SML to the aerosol phase, an assumption widely used in the modelling community. Table 2 does however show that $INP_{SSA,-18C}$ are significantly correlated with POC_{SSW} (R=0.71, p=.002, n=16) and $INP_{SSW,-16C}$. This could indicate that INP at this temperature come from the bulk water rather than the SML. We also note that while a correlation exists with $INP_{SSW,-16}$, with a sample size of n=4 this result requires further validation.

Table 2. Correlations for $INP_{SSA,-18C}$ and observed conditions.

Variable	p	R (R^2)	n
	SSW		

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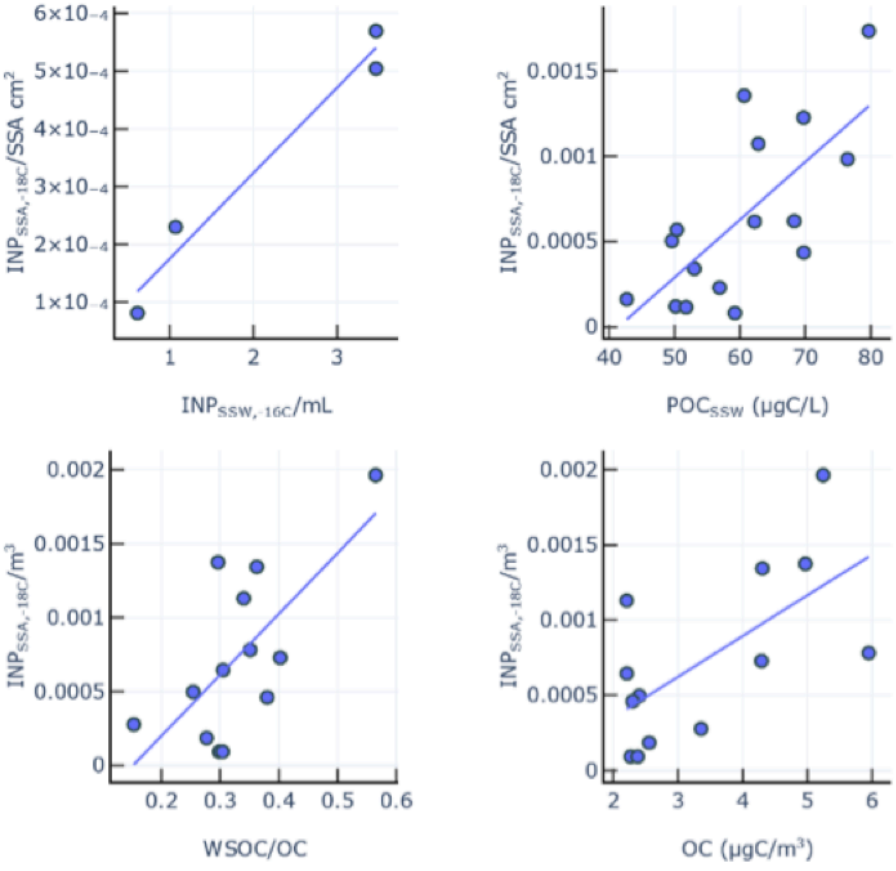
$INP_{SSW,-16}$	0.01	0.99 (0.98)	4
POC	0.002	0.71 (0.50)	16
	SSA		
OC	0.02	0.64 (0.41)	13
WSOC/OC	0.01	0.68 (0.47)	13

311

312 Table 2 also shows the significant correlations between $INP_{SSA,-18C}$ and SSA properties. A positive correlation exists
313 between $INP_{SSA,-18C}$ and SSA organic carbon (OC) as well as the ratio of SSA water-soluble organic carbon to organic carbon
314 (WSOC/OC). The correlation between WSOC/OC and $INP_{SSA,-18C}$ makes sense given the finding that $INP_{SSA,-18C}$ was
315 correlated with POC_{SSW}, as a higher WSOC/OC value would suggest a higher fraction of soluble organics which would be
316 expected to transfer to the atmosphere from the bulk SSW rather than the SML due to their high solubility.



319 **Figure 5. Correlation matrix of INP in SSA at -18C and various biogeochemical parameters.**

320 Figure 6 shows the organic content of artificially generated SSA using the plunging aquarium system continuously
321 filled with seawater from the boat's underway system. SSA organic carbon concentration (OC) was greatest during the first
322 part of the cruise, decreasing from ~6 µgC/m^3 (May 15), down to ~2.5 at FAST (June 5), except for a brief increase on May
323 26 (3.6 µgC/m^3). The highest concentration of OC was concomitant with a bacteria abundance peak in SSW and SML
324 bacteria and DOC (Figure S2). Interestingly, OC was not enhanced on June 5th despite the enhanced seawater bacteria and

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DOC concentration around the same time (Figure S2). WIOC peaked on May 15 (3.9 µgC/m^3), May 18 (3.5 µgC/m^3), and May 26 (2.8 µgC/m^3). A separate manuscript discusses the trend and controls on SSA chemical composition (Freney et al., 2020).

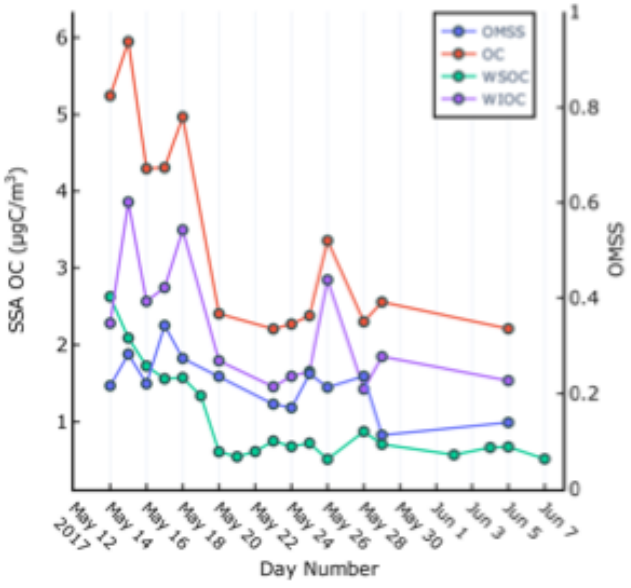

Figure 6. Organic carbon content of SSA.

Figure 7 shows the correlations between $INP_{SSA,-25C}$ and properties of SSW, SML and SSA for parameters they were found to be significant. In Table 3 we report the corresponding correlation parameters. At this temperature, INP_{SSA} were significantly correlated with DOC_{SML}, a result not seen for the warmer INP at -18C. We also note that $INP_{SSA,-25C}$ was not correlated with DOC_{SSW}, potentially indicating an important step in the process of transfer of IN active DOC material to the atmosphere is its enrichment at the SML. $INP_{SSA,-25C}$ was also correlated with SSW concentrations of micro NCBL (R=.84, p=0.0006) and cryptophytes. $INP_{SSA,-25C}$ were also correlated to POC_{SSW} (R=0.53, p=0.04) although with less statistical significance than the correlation between POC_{SSW} and $INP_{SSA,-18C}$. Phytoplankton are known for their ability to produce extracellular polymeric substances (Thornton, 2014). A previous mesocosm experiment showed microbially-derived fatty acids were efficiently ejected from the seawater as SSA, increasing the fraction of highly-aliphatic OC (Cochran et al., 2017). Seemingly in agreement with this, our results show that $INP_{SSA,-25C}$ was correlated with SSA WIOC and organic mass fraction of sea spray (OMSS). To summarize, $INP_{SSA,-25C}$ was correlated with DOC_{SML}, larger species of phytoplankton in the SSW, and water insoluble organic carbon in the SSA.

Table 3. Correlations between $INP_{SSA,-25C}$ and observed conditions.

Variable	p	R (R^2)	n
	SML		
DOC	0.03	0.70 (0.50)	9
	SSW		
micro-NCBL	0.0006	0.84 (0.71)	12
Cryptophytes	0.000017	0.82 (0.67)	19
POC	0.04	0.53 (0.28)	16
	SSA		
OMSS	0.02	0.65 (0.42)	13
WIOC	0.04	0.58 (0.34)	13

The results presented thus far point towards the existence of two classes of INP with separate sources: 1) a class of INP related to POC in the bulk SSW and SSA water soluble organic carbon and 2) a class of INP related to large phytoplankton and POC in the SSW, DOC in the SML, and WIOC in SSA. These findings of a two-component marine INP population agree with a recent study which also reported on the existence of dual classes of INP emitted as SSA during two

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mesocosm experiments, described as: 1) particulate organic carbon INPs coming from intact cells or IN-active microbe fragments and 2) dissolved organic carbon INPs composed of IN-active molecules enhanced during periods when the SML is enriched with exudates and cellular detritus (McCluskey et al., 2018a). However, in contrast to that study, we report here the existence of separate temperature regimes at which each INP class is active. Here, the first class of INP consists of INP that are more active at warmer temperatures (T = -18C). The second class of INP are active at colder temperatures (T = -25C). Interestingly, INP at T=-22C correlates with items from both warm and cold (Table S1).

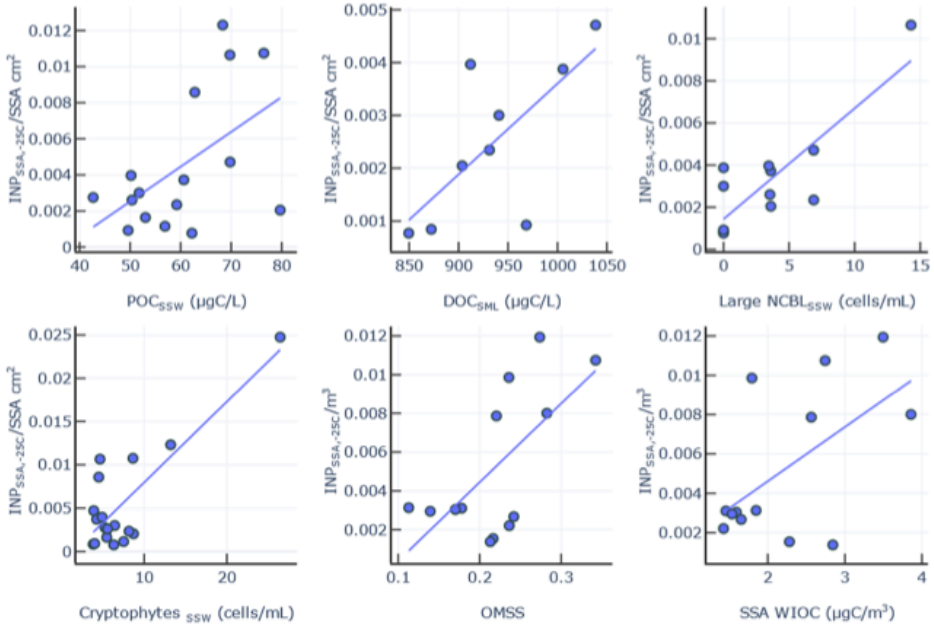

Figure 7. Correlation matrix of INP in SSA at -25C and various biogeochemical parameters.

4 Proposal of New INP Parameterization and Comparison with Previous Models

To date, parameterizations for the estimation of INPs in SSA have not incorporated the knowledge of a two-component INP population. Rather, they have predicted INP based on TOC or SSA surface area (W15 and MC18, respectively). Here we propose a new, two-component temperature-dependent parameterization that accounts for the two classes of organic matter that contribute to the total INP population, as discussed in the previous section, to calculate INP per m^3 per unit SSA surface area. In our model, warm INP (≥-24C) are linked to POC_{SSW} (µgC/L) as shown in Eq. 1, while cold

$$\frac{INP_{T\geq -22}}{\mu m^2} = \exp\big(-35.01 - (.304 * T) + (.056 * POC)\big) \quad (1)$$

$$\frac{INP_{T<-22}}{\mu m^2} = \exp\big(-29.31 - (.1805 * T) + (.113 * NCBL_{large})\big) \quad (2)$$

INP (<-24C) are linked to the abundance of large NCBL (cells/mL) as shown in Eq. 2:

NCBL large were chosen for equation 2 rather than DOC_{SML} due to the difficulty in determining such a variable remotely. We justify this by noting that the DOC here is likely related to the NCBL as large phytoplankton are known for their ability to secrete large amounts of extracellular material which become enriched at the SML. We further note that the link between large NCBL and the class of DOC in the SML that is IN active may change depending on a number of factors (e.g., trophic status) and thus needs to be verified in future studies.

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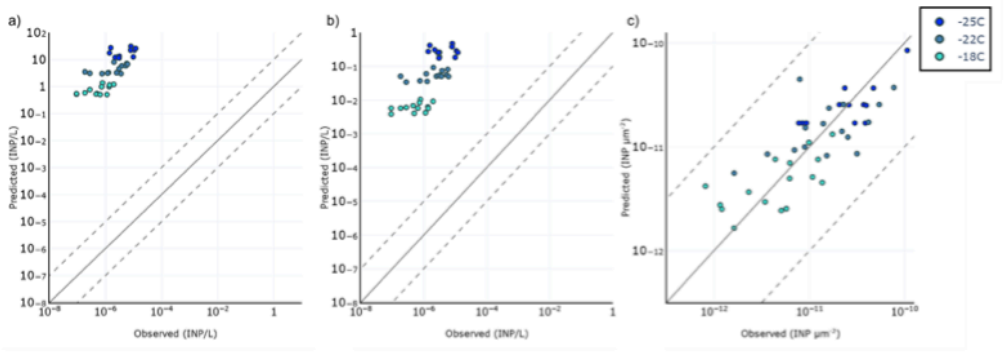
399 Figure 6 shows the comparison of our new model with the W15 (Figure 6a) and MC18 (Figure 6b)
400 parameterizations. Similar to the comparison between W15's parameterization with seawater INP, a large overprediction
401 occurs relative to our observations. Figure 6b shows that while MC18 is a slight improvement, it still overpredicts INP by
402 four orders of magnitude. Figure 6C shows the use of our two-part model which considers the separate classes of INP and
403 shows good agreement between observations and predictions.
404
406



407 **Figure 8. Different models for INP_{SSA} prediction. a) Wilson model, b) McCluskey, c) our model where INP≥-22C are related to**
408 **SSW POC INP <-22C are related to micro NCBL in SSW.**

409 **5 Conclusions**

410 In this paper we have presented results from the month-long PEACETIME cruise which took place in the Mediterranean
411 Sea during the spring of 2017, which was characterized with a dust wet deposition event that occurred towards the end of the
412 cruise.

413 First, we find that the INP concentrations measured in the SSW are in line with the INP measured in the SML, except
414 during the dust wet deposition event when they are significantly enriched in the SML. In the SML, the increase of $INP_{SML,-15C}$
415 concentrations during this dust wet deposition event follow the SML microbial cell counts (e.g., NCBL, CBL and
416 heterotrophic bacteria), Fe_{SML} and DOC_{EF}. Excluding this dust event, $INP_{SML,-15C}$ are still correlated, although more
417 moderately, to bacteria and Fe in the SML. Overall $INP_{SML,-15C}$ were not correlated with TOC nor DOC and compared to
418 previous studies, the INP/TOC observed here is low. We surmise that the overprediction of modelled INP/TOC is a result of
419 TOC from the oligotrophic Mediterranean being less IN active.

420 The impact of dust deposition on $INP_{SML,-15C}$ is fairly large, as we observe an increase of $INP_{SML,-15C}$ by almost an
421 order of magnitude during this event. This impact of dust deposition could have climate implications if $INP_{SML,-15C}$ were
422 efficiently transferred to the sea spray emitted to the atmosphere. However, we find that INP_{SSA} does not evolve as the
423 INP_{SML} does. INP_{SSA} are not increased as $INP_{SML,-15C}$ are during the dust event. An increase of INP_{SSA} is observed at least
424 with a three days delay after the dust wet deposition event. This can be due to INP_{SSA} measured at -18°C, (the closest
425 temperature to the ones at which INPSWL and INPSML are measured) being more influenced by the INP concentration in
426 the bulk surface seawater ($INP_{SSW,-16C}$). It is possible that IN active species deposited during the rain event, either dust-
427 related or biology-related, take a few days before entering the bulk surface layer.

428 In general, we observed the existence of two classes of INP_{SSA}, each linked to different classes of organic matter. Our
429 results indicate each class is active at separate temperatures. Warmer INP ($INP_{SSA,-18C}$) are linked to water soluble organic
430 matter in the SSA, but also to SSW parameters (POC_{SSW} $INP_{SSW,-16C}$). This indicates that INP at this temperature come from
431 the bulk water rather than the SML. Colder INP ($INP_{SSA,-25C}$) are rather correlated with SSA water-insoluble organic carbon,
432 and SML properties (dissolved organic carbon). As the colder INP are correlated to the SSW microphytoplankton cell

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abundance as well, we hypothesize that these classes of phytoplankton produce surface-active water-insoluble organic matter that is active as IN at these temperatures and are transferred to the atmosphere via the SML. Unfortunately, we do not have measurements of the "colder" temperatures INP in the SML to check this hypothesis.

We finally proposed a two-component model for marine INP abundance based on seawater POC and SSW microbial abundance. We then compared this with previous single component models based on SSA surface area and TOC content. Our results should help improve attempts to incorporate marine INP emissions into numerical models. Future studies should be conducted to confirm if our model can be extended to regions of higher biological productivity, such as the Southern Ocean.

Acknowledgements This study is a contribution to the PEACETIME project (http://peacetime-project.org), a joint initiative of the MERMEX and ChArMEx components supported by CNRS-INSU, IFREMER, CEA, and Météo-France as part of the programme MISTRALS coordinated by INSU. PEACETIME was endorsed as a process study by GEOTRACES. PEACETIME cruise https://doi.org/10.17600/17000300. We thank the captain and the crew of the RV *Pourquoi Pas ?* for their professionalism and their work at sea. The underway optical instrumentation was provided by Emmanuel Boss's group funded by Nasa Ocean Biology and Biogeochemistry. This work has also received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Sea2Cloud grant agreement No 771369). Sea2Cloud was endorsed by SOLAS.

https://doi.org/10.5194/acp-2020-487
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