



Ice nuclei in marine air: biogenic particles or dust?

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Abstract. Ice nuclei impact clouds, but their sources and distribution in the atmosphere are still not well known. Particularly little attention has been paid to IN sources in marine environments, although evidence from field studies suggests that IN populations in remote marine regions may be dominated by primary biogenic particles associated with sea spray. In this exploratory model study, we aim to bring attention to this long-neglected topic and identify promising target regions for future field campaigns. We assess the likely global distribution of marine biogenic ice nuclei using a combination of historical observations, satellite data and model output. By comparing simulated marine biogenic immersion IN distributions and dust immersion IN distributions, we predict strong regional differences in the importance of marine biogenic IN relative to dust IN. Our analysis suggests that marine biogenic IN are most likely to play a dominant role in determining IN concentrations in near-surface-air over the Southern Ocean, so future field campaigns aimed at investigating marine biogenic IN should target that region. Climate-related changes in the abundance and emission of biogenic marine IN could affect marine cloud properties, thereby introducing previously unconsidered feedbacks that influence the hydrological cycle and the Earth's energy balance. Furthermore, marine biogenic IN may be an important aspect to consider in proposals for marine cloud brightening by artificial sea spray production.

1 Introduction

The formation of ice is a crucial process in cloud development, with most precipitation globally originating in clouds containing ice. Because pure water droplets cannot freeze at temperatures above about -40°C , ice formation in warmer clouds is initiated by airborne particles that serve as ice nuclei (IN). Particles that are effective IN are rare, often fewer than one out of one million airborne particles (Rosinski et al., 1988). Current approaches to understanding global IN distributions consider only desert dust and other continental sources (DeMott et al., 2010). However, certain biological particles are also known to nucleate ice efficiently and have been hypothesized to influence cloud development (Möhler et al., 2007). Evidence from a limited number of field studies suggests that a marine source of biogenic particles determines IN abundance in air over remote, biologically active regions of the ocean.

1.1 Evidence for a possible marine biogenic IN source

There are two distinct lines of evidence for the existence of marine biogenic atmospheric ice nuclei, evidence coming from IN counts in the atmosphere and from laboratory testing of source material.

1. *IN counts in the atmosphere:* evidence from in situ observations reported in a number of studies scattered over four decades suggests that in remote, biologically active areas of the ocean, the background atmospheric IN concentrations measured on ships are highly influenced by local marine biological activity and sea spray production. Early evidence was provided by Bigg in 1973 (hereafter B73), who

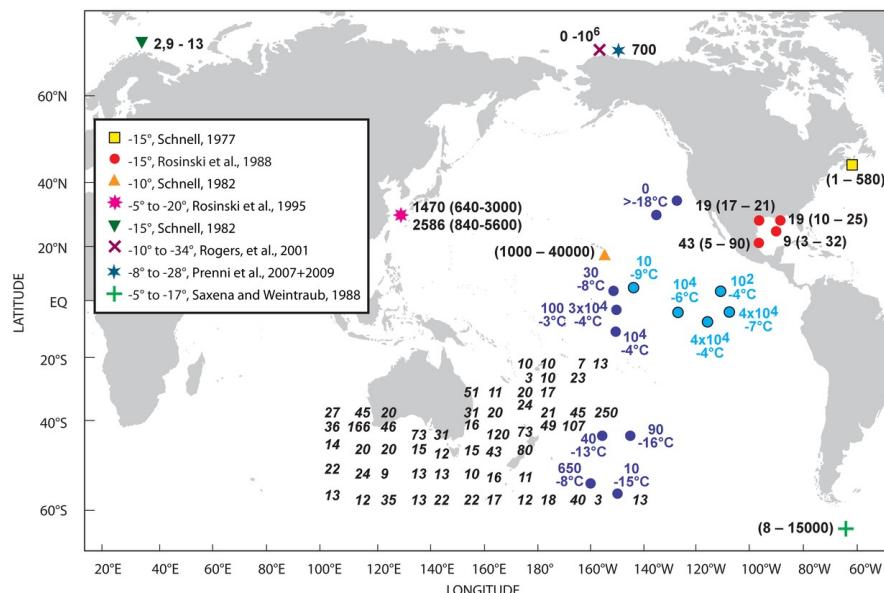


Fig. 1. Number densities of atmospheric ice nuclei (m^{-3}) in the marine boundary layer. Measurements by condensation-followed-by-freezing, ship-based and coastal: Australia (italic text): -15°C and water saturation (Bigg, 1973). Pacific Ocean: 29 May–16 June 1985: Rosinski et al. (1987). 17 February–29 March 1984: Rosinski et al. (1987). Gulf of Mexico: Rosinski et al. (1988). East China Sea: Rosinski et al. (1995). Arctic: Bigg (1996). Antarctica: Saxena (1983). Nova Scotia: Schnell (1977). Airborne measurements by drop freezing: Hawaii: Schnell (1982). Airborne measurements by continuous flow diffusion chamber: Arctic: Rogers et al. (2001); Prenni et al. (2009b).

presented long-term measurements of IN concentrations in the marine boundary layer south of and around Australia and New Zealand (Bigg, 1973). Since that time, only a handful of further observations of marine IN concentrations have been published (Fig. 1). In the B73 observations, mean concentrations of IN were generally highest around 40°S , a region in which rough seas are common, marine biological activity is strong, and large amounts of sea spray containing organic matter are produced. It was later suggested that the source of IN might be associated with the plankton growing in this nutrient-rich upwelling region of the ocean (Schnell and Vali, 1976). Further evidence for a connection between marine biological activity and marine IN concentrations was uncovered in later studies: ship-based measurements in remote marine regions found that atmospheric IN concentrations were higher in ocean upwelling regions, or were associated with high concentrations of biogenic materials in samples of ocean water. Physical and chemical analyses of IN collected in the remote marine boundary layer of the equatorial Pacific Ocean showed that they were submicron-sized, probably carbonaceous particles (Rosinski et al., 1987). It should be noted that these historical measurements suffer from several limitations. Most importantly, the filter membrane method used at the time of those observations had significant systematic errors; these are discussed in Sect. 3.6. Also, the link to biological activity is inferred primarily from temporal or spatial correlations with biological activity in the ocean, rather than directly.

2. *Laboratory testing of source material:* samples of possible source material can be tested for ice nucleation activity under controlled conditions in the laboratory. Results of such studies for marine biogenic particles are discussed in more detail in Sect. 1.2. Such studies can characterize the IN activity of particular species or types of particles in detail over the full temperature range of interest, however, they provide no information on which particles are present in the atmosphere, their concentrations, distribution, or IN activity under atmospheric conditions.

Another open question is how marine biogenic IN might be affected by condensation of volatile gases in the marine boundary layer environment. Little is known about the effects of such coating on biogenic particles, but it may differ from the effects of coating on mineral dust IN activity: in one laboratory study, Chernoff and Bertram (2010) found that sulfate coatings reduced the ice nucleation activity of several types of mineral dust particles, but did not reduce the IN activity of SNOMAX, a well-known biological IN.

1.2 Candidates for marine biogenic IN

For the purposes of this study, we hypothesize a marine source of IN from “biogenic particles”. This class of particles includes “primary biological aerosol particles” (primarily cellular matter such as microorganisms and fungal spores, Després et al., 2012). In addition, it also includes other, non-cellular particles consisting primarily of complex biological

macromolecules related to marine biological activity, which may be waste products or exudates of marine organisms.

The chemistry of the marine aerosol is correlated with the chemistry of the underlying water (Gaston et al., 2011; Moore et al., 2011; Ovadnevaite et al., 2011). Marine microorganisms make up only a small fraction of the particulate mass associated with marine microbiological activity; the largest portion of this mass is made up of waste products and exudates. Dissolved organic matter accumulates in the sea surface microlayer (Reinthalter et al., 2008), a thin layer on the ocean surface that directly impacts the composition of the atmospheric aerosol. Many studies have shown that the presence of microorganisms in seawater significantly influences the chemical composition of the marine aerosol (Moore et al., 2011; Ovadnevaite et al., 2011), and there is evidence of a biogenic marine organic source of aerosol from the Austral Ocean (Sciare et al., 2009). Organic submicron particles in the marine aerosol have been identified as insoluble organic colloids and aggregates similar to those found in marine surface waters (Facchini et al., 2008), samples from air over the North Atlantic and Arctic Oceans contained a large fraction of organic hydroxyl groups characteristic of saccharides, and of likely marine origin (Russell et al., 2010). Near Edge X-Ray Absorption Fine Structure (NEXAFS) single particle spectromicroscopy has been used to identify the following distinct groups among marine aerosol particles: calcareous phytoplankton, submicron spherical particles with spectral similarity to marine sediments, and supermicron amide and alkane-containing particles, which were inferred to likely consist of marine proteinaceous material (Hawkins and Russell, 2010). Some of these particles are believed to originate from exopolymer secretions (EPS), a gel-like combination of compounds emitted by marine microorganisms either as a waste product or to perform a function for the organism, the presence of these compounds has been observed in the atmospheric aerosol (Bigg and Leck, 2001; Leck and Bigg, 2005b,a). Microorganisms make up only a few percent of the particulate mass in marine waters, with marine gels and colloids accounting for up to 7×10^{16} g C, 10–50 times larger than the total biomass of marine microorganisms (Chin et al., 1998; Verdugo et al., 2004, 2008).

Types of marine biogenic particles that are found in the atmosphere and could potentially act as IN include:

1. *Marine microorganisms*: marine waters host a great variety of marine microorganisms, including cyanobacteria and eukaryotic phytoplankton such as some species of diatoms, dinoflagellates and coccolithophorids; heterotrophic bacteria; archaea; protists; and in far lesser concentrations, fungi and yeasts. Consistent with this, observations show that only a minor fraction of organic particles in the marine aerosol (up to a few percent on average by number) are marine microorganisms (Leck and Bigg, 2005b). However, because of the known high IN efficiency of certain microorganisms of mostly continental origin, it has been suggested that IN-active marine microorganism species might be identified.

A few studies have observed IN activity associated with cultures of certain marine plankton species. Schnell (1975) measured IN activity in cultures of the phytoplankton species *Ca-chonina niei*, *Ochromonas danica* and *Porphyridium aeruginosum*. However, Schnell (1975) was unable to determine whether the observed ice nucleation activity was caused by the cells of the cultured plankton species, excretion products, marine bacteria associated with the plankton, or other associated particles. Fall and Schnell (1985) identified an efficiently ice nucleating bacteria species associated with the *Heterocapsa niei* culture, however, they could not determine whether this bacterium was of terrestrial or of marine origin. Parker et al. (1985) detected IN activity in a sample of sea ice that was rich in biological material, but the nature of the nuclei was not determined. Parker et al. (1985) also screened eleven strains of psychrophilic or psychrotrophic Antarctic marine bacteria, which were primarily isolated from sea ice. Of these, one unidentified psychrotrophic strain was IN-active at temperatures between -2.0 and -3.5 °C, while the ten other strains showed no IN activity at temperatures higher than -30 °C. In addition, Parker et al. (1985) also tested several laboratory cultures of Antarctic marine diatoms (*Syndra* sp., *Chaetoceros dichaeta* Ehrenberg, *Chaetoceros flexuosum* Fryxell, *Porosira glacialis* (Grunow) Jorgensen, and *Pososira pseudodenticulata* (Hustedt) Jouse, which showed no significant IN activity at temperatures higher than -12 °C, but at least one of these, *C. flexuosum*, was IN-active at temperatures between -14 °C and -18 °C.

More recently, IN activity was unambiguously identified in the cosmopolitan marine diatom species *Thalassiosira pseudonana* (Knopf et al., 2011; Alpert et al., 2011a), as well as the marine phytoplankton species *Nannochloris atomus* (Alpert et al., 2011b).

Tests of heterogeneous ice nucleation have been reported for a number of other marine microorganism species, for which IN activity was found to be much more limited. Schnell (1975) tested 21 species, one of which was highly IN-active, with a median ice nucleation temperature of -11.5 °C, while the remaining species nucleated ice at -19.5 °C and colder. Junge and Swanson (2008) report high-resolution ice-nucleation spectra for 15 Arctic and Antarctic sea-ice bacteria isolates and one polar *Colwellia* phage virus. All of these species were found to raise the temperature of freezing in the immersion mode only by a few degrees Celsius above the homogeneous freezing temperature, from -42.2 °C for artificial seawater to a maximum of -40.4 °C for seawater containing one of the sampled species. A possible explanation for this very low IN activity is that these cold-adapted strains may employ freezing-avoidance strategies as an adaptation to their environment (Raymond and Knight, 2003; Raymond and Janech, 2003; Raymond et al., 2007; Junge and Swanson, 2008).

A further observation that weighs against microorganisms as a source of marine IN is the report by Rosinski et al. (1987) on IN collected over the remote Pacific Ocean, which were

found to evaporate completely in a vacuum, from which it was concluded that the IN were likely neither bacteria nor proteins, although a biogenic origin of the IN could not be excluded.

2. *Exopolymer secretions/colloidal aggregates:* another candidate for marine biogenic IN is aggregates of microcolloids and their components or building blocks, which likely originate from exopolymer secretions (EPS) of marine microbiota (Chin et al., 1998; Verdugo et al., 2004, 2008). Analysis of TEM photographs of hundreds of particles collected at each of five observation sites has shown that these have equivalent spherical radii that are usually in the range of about 10–40 nm, and can supply as many as 20 % of the particles in that size range (Bigg and Leck, 2008).

3. *Glassy organic aerosols:* recently, evidence has emerged that under some conditions, certain organic aerosol particles can transition into a glassy state under atmospheric conditions (Zobrist et al., 2006; Murray, 2008; Zobrist et al., 2008; Mikhailov et al., 2009; Virtanen et al., 2010; Wagner et al., 2010; Koop et al., 2011; Shiraiwa et al., 2011; Wagner et al., 2011; Murray et al., 2012), which may either inhibit homogeneous ice formation (Murray, 2008) or stimulate heterogeneous ice nucleation (Baustian et al., 2010; Murray et al., 2010; Wilson et al., 2012).

4. *Crystalline hydrated NaCl:* another potential source of sea-spray-related IN at colder temperatures is the salt that makes up the bulk of the supermicron sea spray particles. Recent evidence has emerged that hydrated NaCl may serve as depositional IN at temperatures from -52.1°C to -35.15°C (Wise et al., 2012).

5. *Frost flowers:* where sea ice is present, another proposed source of marine particles, of which the potential IN activity is unknown, is the aerosolization of particles from frost flowers forming on the surface of sea ice (Russell et al., 2010).

Further experiments with modern methods would be needed to characterize the IN activity of various particles in marine organic matter. A recent series of papers reports results from such experiments (Knopf et al., 2011; Alpert et al., 2011b,a). These show that biogenic particles with different biogenic surfaces can have both comparable and contrasting effects on ice nucleation behavior, depending on the temperature, water vapor supersaturation and mode of freezing (deposition or immersion).

1.3 Enrichment of marine organic matter in sea spray

Laboratory experiments have shown that organic matter can be strongly enriched during sea spray aerosol formation by bubble bursting. Due to their surface-active properties, organic substances are preferentially collected on the surface of rising bubbles and subsequently transferred to the aerosol with concentrations that are commonly a factor of 10–100 or more higher than in the bulk seawater. The ratio of the concentration of a substance in the aerosol phase to its con-

centration in the bulk is termed the “enrichment factor” (EF) (see tabulated values in Table B1).

Bubble bursting experiments with ocean water sampled during a phytoplankton bloom show a dominant contribution of water-insoluble organic compounds to the submicron fraction of the marine aerosol, consistent with results from ship and coastal station measurements during bloom periods (O’Dowd et al., 2004; Facchini et al., 2008). In ship-based measurements in the North Atlantic and Arctic Oceans, the observed ratio of organic mass to Na in the submicron aerosol was enriched by a factor of 10^2 – 10^3 relative to reported sea surface concentration ratios (Russell et al., 2010). This ratio is higher than many other reported enrichment factors, at least in part because the enrichment is greatest in the submicron aerosol. The global marine emissions of submicron primary organic aerosol particles by sea spray have been estimated to be 8.2 Tg yr^{-1} (Vignati et al., 2010).

Comparison of IN concentrations with ship emissions and chlorophyll

The strong correspondence between the B73 boundary-layer IN counts and chlorophyll spatial distributions led Schnell and Vali (1976) to propose a marine biogenic source of ice nuclei. This geographic correspondence is illustrated in Fig. 2.

In contrast to this, we also show a comparison to ship emissions, another significant source of particulate matter in remote marine regions. Ship emissions are unlikely to explain the observed IN distribution, because: (1) observations by (Rosinski et al., 1987) found no IN while on the shipping lane from California to Hawaii, but high concentrations of IN in the Equatorial Pacific, far from major shipping lanes (Fig. 1). (2) The spatial pattern of ship emissions does not match the spatial pattern of IN concentrations; inspection of the horizontal distribution confirms that the B73 IN concentrations are very high in several regions where there is no ship traffic (Fig. 2).

1.4 Aims and approach

The aims of this study are (1) to use published observational data to estimate the global emissions of ice nuclei resulting from a hypothesized marine biogenic source, (2) to compare the boundary-layer concentration of simulated marine biogenic IN to the simulated concentration of dust IN at the same temperature, and thereby (3) to identify regions in which marine biogenic IN are most likely to play a role in driving boundary-layer IN concentrations, relative to dust.

The hypothesized source is estimated using the following assumptions:

1. there is a primary source of ice nucleating particles to the atmosphere from sea spray,

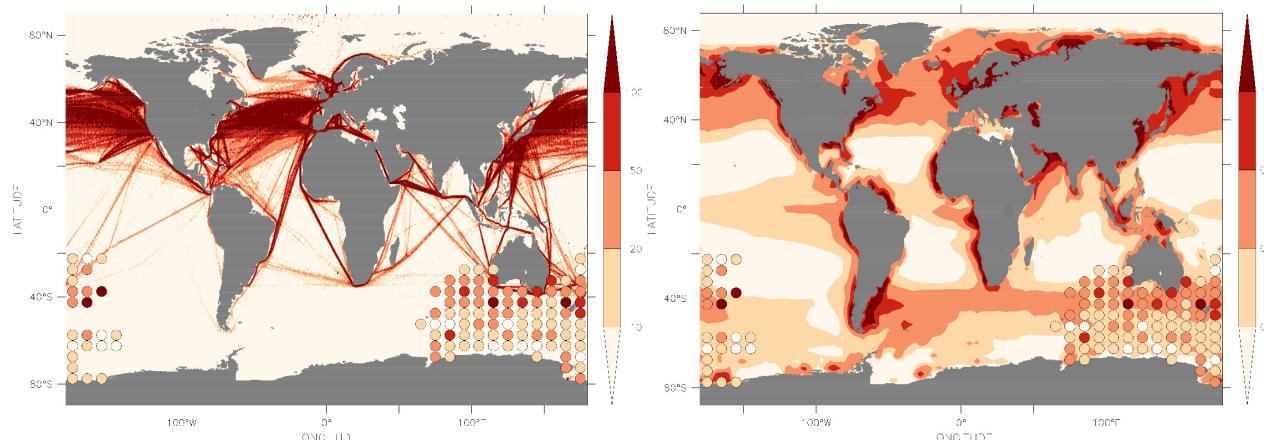


Fig. 2. Geographic distribution of IN concentrations observed by B73, compared to ship emissions and chlorophyll. Top: natural logarithm of estimated particulates emitted from ships, assuming an 800-m boundary layer height and 5-day residence time in the boundary layer ($\mu\text{g m}^{-3}$), calculated from estimated year 1970 emissions (Endresen et al., 2003; Eyring et al., 2005, 2010; Wang et al., 2007; Lamarque et al., 2010), with the natural logarithm of B73 IN mean number density (m^{-3}) superimposed as coloured dots (different colour scale). Bottom: mean ocean chlorophyll *a* concentrations from MODIS-Aqua (mg m^{-3} , July 2002–June 2008), with IN number densities (IN active at -15°C per m^3 , $\times 10$) observed by B73.

2. this source is associated with biologically-derived material,
3. the concentration of marine biogenic IN in sea spray is proportional to the mass of marine biogenic particulates in sea spray.

We deal here with the concentrations of IN in near-surface air. However, we note that particles emitted from the surface are removed more rapidly from the atmosphere than particles transported from distant sources at higher altitudes (Fig. 6). As a result, at cloud altitude the relative contribution of marine biogenic particles to the total particle population and the IN population will be reduced. An evaluation of cloud impacts is beyond the scope of this paper, but a potentially interesting topic for future study.

Our estimation is explained in detail in the following section.

2 Methods

For the purposes of comparing the geographic distribution with observations and with dust, we chose to estimate the distribution of marine biogenic IN at a single temperature. We chose -15°C , the temperature at which the geographic distribution of IN concentrations from B73 is presented. The efficiency of ice nucleation by various particles is a strong function of temperature, therefore, the relative importance of different types of ice nuclei will be different at different temperatures. However, the source of marine IN has not yet been unambiguously identified and the relationship between temperature and IN activity in marine surface water samples is not yet clear from currently available data (Table A1 and

Fig. A1). Given the limited data, we did not feel justified in assuming a temperature dependence of the ice-active fraction, although we note that B73 observed IN concentrations at -10°C to be about one order of magnitude lower than at -15°C , which is roughly consistent with the experiments of Schnell and Vali (1975); dust IN activity also is observed to decrease by approximately an order of magnitude over the same temperature range (Niemand et al., 2012). Similarly, the dependence of IN counts on atmospheric relative humidity is beyond the scope of this work.

For this study, we consider only the immersion freezing mode. The filter method used in B73 captures only (immersion) freezing following condensation, and deposition freezing (only relevant at lower temperatures), but not the contact freezing mode. Drop freezing measurements, such as those of IN concentrations in samples of particulates from a plankton bloom (Schnell and Vali, 1975) that we use in developing our emissions estimate, measure only the immersion mode of freezing. However, we expect that since marine biogenic particles are predominantly hygroscopic, they will typically be coated with water or contained in water droplets, and the immersion mode will be the dominant mode of freezing in many areas of interest.

2.1 General equation for marine IN emissions estimate

In order to simulate the spatial and temporal distribution of the marine organic contribution to the atmospheric IN, we parameterized emissions to be consistent with knowledge of biologically-associated sea spray and observed IN concentrations in planktonic matter (Schnell and Vali, 1975). The emissions of biogenic IN are assumed to be proportional to the wind-speed-dependent emissions of accumulation mode

sea spray (with dry radius range $0.05 < r_{\text{dry}} < 0.5 \mu\text{m}$), calculated using the LSCE sea spray parameterization (Guille et al., 2001; Kerkweg et al., 2006b). Sea spray emissions are then multiplied by an ocean biological variable, either chlorophyll or particulate organic carbon (POC), and by a scaling factor α , i.e.:

$$\begin{aligned} \alpha & [(\text{kg sea spray})^{-1} (\text{mg POC or Chl } a \times \text{m}^{-3})^{-1}] \\ & \times \text{POC or Chl } a \text{ in seawater } [\text{mg m}^{-3}] \\ & \times \text{Accumulation mode sea spray emissions } [\text{kg m}^{-2} \text{ s}^{-1}] \\ & = \text{Emissions of biogenic IN active at } -15^\circ\text{C } [\text{m}^{-2} \text{ s}^{-1}] \quad (1) \end{aligned}$$

The value of α is chosen to be consistent with observations that provide information about the relationship between POC and chlorophyll *a* concentrations and the concentration of IN in ocean water: $\alpha_{\text{POC}} = (75\text{--}900) \times 10^6$ $[(\text{kg sea spray})^{-1} (\text{mg POC m}^{-3})^{-1}]$ and $\alpha_{\text{CHL}} = (15\text{--}250) \times 10^9$ $[(\text{kg sea spray})^{-1} (\text{mg Chl } a \text{ m}^{-3})^{-1}]$. Details about the derivation of these factors follow (also see Table 1, as well as Tables A1 and 2). The values of α are each calculated as the product of five factors that can be estimated based on field or laboratory studies. However, each of these factors has a large uncertainty range, and any errors in the same direction will combine multiplicatively, so the uncertainty in α is at least a factor of 10 in each direction. We choose three sets of values for these factors: a “low” value using the low end of the range for each parameter, a “best” value using the center of the range for each parameter, and a “high” value using the upper end of the range for each parameter, which leads to a value of α_{CHL} or α_{POC} that is 10.5 or 13.2 times greater than the “best” value, respectively, and in better agreement with IN concentrations as reported by B73. As discussed further below, we emphasize that new observations will be needed to constrain the uncertainties.

2.2 Estimate of scaling factor α

The value of α is chosen to be consistent with observations that provide information about the relationship between POC and chlorophyll *a* concentrations and the concentration of IN in ocean water. For POC-based emissions, it is given by:

$$\begin{aligned} \alpha_{\text{POC}} &= \\ & \times \frac{\text{POM}}{\text{POC}} (= 1.8) \\ & \times \frac{\text{IN}}{\text{POM}} (= 10\text{--}20 \times 10^4 \text{ mg}^{-1}) \\ & \times \text{Enrichment Factor (EF)} (= 500\text{--}1000) \\ & \times \text{Particle size correction} (= 30\text{--}90) \\ & / \text{Sea salt in water} (= 36 \text{ kg m}^{-3}) \\ & = 75 \times 10^6 \text{--} 900 \times 10^6 \quad [(\text{kg sea spray})^{-1} (\text{mg POC m}^{-3})^{-1}] \quad (2) \end{aligned}$$

and for chlorophyll *a*-based emissions, it is given by:

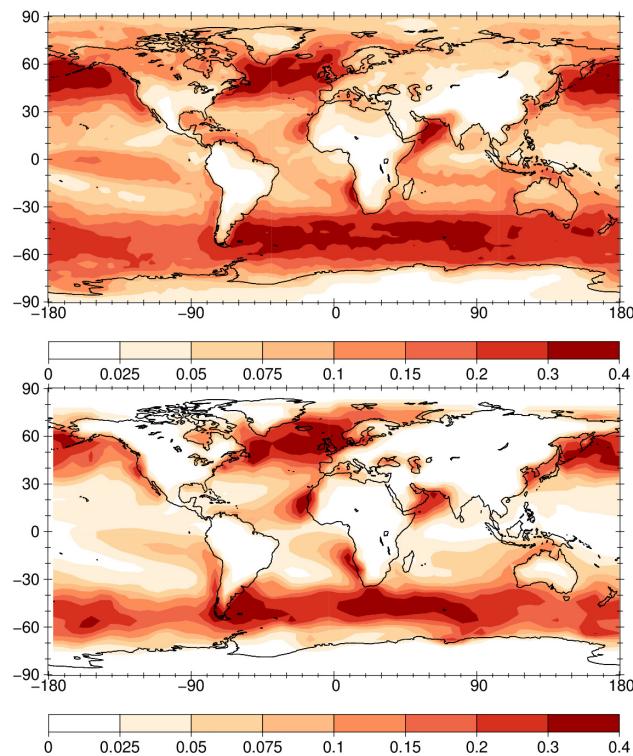


Fig. 3. Annual mean mass density of accumulation mode sea spray particulate organic mass ($\text{POM} = 1.8 \cdot \text{POC}$, $\mu\text{g m}^{-3}$) in the model surface layer. **(A)** Simulation based on MODIS-Aqua POC seasonal climatology (this work). **(B)** Modelled water-insoluble organic mass from primary sea spray emissions in the TM5 model (Vignati et al., 2010). Differences in the distributions result from differences in emissions, but also in loss processes and other model components.

$$\alpha_{\text{CHL}} =$$

$$\begin{aligned} & \times \text{Bacterial cells per mg Chl } a (= 4\text{--}7 \times 10^{12} \text{ mg}^{-1}) \\ & \times \text{Mass of bacterial cell} (= 75\text{--}100 \times 10^{-12} \text{ mg}) \\ & \times \frac{\text{POM}}{\text{bacterial mass}} (= 35\text{--}64) \\ & \times \frac{\text{IN}}{\text{POM}} (= 10\text{--}20 \times 10^4 \text{ mg}^{-1}) \\ & \times \text{Enrichment Factor (EF)} (= 500\text{--}1000) \\ & / \text{Sea salt in water} (= 36 \text{ kg m}^{-3}) \\ & = 15 \times 10^9 \text{--} 250 \times 10^9 \quad [(\text{kg sea spray})^{-1} (\text{mg Chl } a \text{ m}^{-3})^{-1}] \quad (3) \end{aligned}$$

The use of a constant enrichment factor presupposes a linear relationship between the concentration of a substance in marine water and its concentration in the atmospheric aerosol. Here we have assumed a linear relationship between marine chlorophyll or POM and the fractional contribution of marine particulate organic matter to sea spray emissions. This assumption is consistent with most recent initial attempts to develop parameterizations of marine organic sea

Table 1. Scaling factors applied in estimation of sea spray IN concentrations

Factor	Range from literature	Low value	Best value	High value	References
Scaling of POC-driven emissions					
POM/POC	1.2–2.6	1.2	1.9	2.6	Facchini et al. (2008); Russell et al. (2010); Hahn (1980)
IN ¹ per mg marine POM	(.1–2) × 10 ³	.1 × 10 ³	1 × 10 ³	2 × 10 ³	Schnell and Vali (1975)
Mean ratio of total sea spray POM to sub-micron sea spray POM ²	1.4–2.5	1.4	2.0	2.5	Cavalli et al. (2004); Keene et al. (2007); Facchini et al. (2008); Rinaldi et al. (2009)
Correction for size of submicron POM ³	ca. 2–16	2	9	16	Facchini et al. (2008)
IN per mg POC in water (product of above factors)		5.0 × 10³	3.9 × 10⁶	21 × 10⁶	
Enrichment factor	ca. 10–1000	10	500	1000	Hoffman and Duce (1976); Russell et al. (2010), Table B1
IN per mg emitted POC (product with enrichment factor)		50 × 10³	2.0 × 10⁹	21 × 10⁹	
Maximum POM emissions as percent of sea spray ⁴			76 %		Vignati et al. (2010)
Scaling of chlorophyll-driven emissions (microorganism assumption)					
Bacterial cells per mg Chl <i>a</i>	1 × 10 ¹² –7 × 10 ¹²	1 × 10¹²	4 × 10¹²	7 × 10¹²	Li et al. (2004)
Mass of marine bacterial cell (mg)	50–100 × 10 ⁻¹²	50 × 10⁻¹²	75 × 10⁻¹²	100 × 10⁻¹²	Ducklow (2000), Table 2
Ratio of POM to bacteria mass in accumulation mode aerosol	at least ca. 20–50	20	35	50	Bigg (2007)
IN ¹ per mg marine POM	(.1–2) × 10 ³	.1 × 10 ³	1 × 10 ³	2 × 10 ³	Schnell and Vali (1975)
IN per mg Chl <i>a</i> in water (product of above factors)		1 × 10⁶	1.1 × 10⁹	7.0 × 10⁹	
Enrichment factor	ca. 10–1000	10	500	1000	Blanchard and Syzdek (1982); Aller et al. (2005); Kuznetsova et al. (2005), Table B1
IN per mg emitted Chl <i>a</i> (product with enrichment factor)		10 × 10⁶	0.53 × 10¹²	7.0 × 10¹²	
Maximum bacteria emissions as percent of sea spray ⁴			10 %		

¹ IN active at -15°C . Low value represents drop freezing measurements with concentrated plankton seivings in seawater; high value represents the same using distilled water. Tests with seawater result in lower IN number counts due to freezing point depression from the salts in the seawater. In marine aerosol samples, certain biogenic particles such as bacteria are found to be separate from salt particles, while other marine particles contain a mixture of salt and organic matter (Bigg, 2007).

² Mass of OM in sea spray is dominated by coarse mode, however, few studies have quantified the partitioning of OM between the submicron and supermicron mode, due to the larger uncertainties associated with super-micron flux measurements (Vignati et al., 2010). It is also possible that a significant fraction of the coarse mode OM results from condensation (O'Dowd and de Leeuw, 2007; Vignati et al., 2010). Keene et al. (2007) measured values of 2.45 ± 0.15 . Rinaldi et al. (2009) measured 2.4 and 1.5 for Mace Head and over open ocean, respectively.

³ Particles were modelled with assumed radius of $0.1 \mu\text{m}$ for accumulation mode, but mass-weighted mean radius for submicron mode is likely in the range $r = 0.125\text{--}0.25 \mu\text{m}$, this must be corrected for in calculating the mass density of particles from their number density.

⁴ Maximum percent of sea spray mass in accumulation mode.

spray emissions (Spracklen et al., 2008; Vignati et al., 2010; O'Dowd et al., 2008). The enrichment factor may, however, also depend on conditions such as wind speed and the dissolved organic compounds in the sea surface microlayer (Kuznetsova et al., 2004; Russell et al., 2010; Gantt et al., 2011). In particular, under high-wind conditions, turbulent mixing reduces the enrichment of organics in the sea-surface microlayer, and as a consequence, organic enrichment in the aerosol may also be reduced (Kuznetsova et al., 2004; Gantt et al., 2011). Furthermore, enrichment factors may be higher when dissolved organic concentrations are lower

(Gantt et al., 2011), and the presence of dissolved organics can affect emitted particle number concentrations and size distributions (Fuentes et al., 2010b). In addition, it should be noted that enrichment factors for organic carbon vary substantially with particle size, for instance Keene et al. (2007) bubbled air through natural seawater and obtained enrichment factors for organic carbon of $> 10^5$ for particles around $1 \mu\text{m}$. Enrichment factors decreased with increasing particle size, with values between 10^3 and 10^4 for $1\text{-}\mu\text{m}$ particles, to a minimum of about 100 at sizes near $10 \mu\text{m}$, and increased again to about 10^4 for $30\text{-}\mu\text{m}$ particles.

The ranges of values supported by the observations for the scaling factors relating biological proxies to IN concentrations are provided in Table 1. While a range of values are possible, the “high” values chosen here for the scaling factors result in approximate agreement between simulated mean IN concentrations and the three-year mean concentrations reported by B73, while the “best” values chosen for the scaling factors represent approximately the middles of the ranges of possible values found in the literature. Where not otherwise stated, results shown here use the higher estimate. A further constraint is applied that POM mass emissions not exceed 76 % of accumulation mode sea spray emissions, and bacterial mass emissions (an intermediate result in the chl-a scaling) not exceed 10 % of accumulation mode sea spray emissions. The emitted particles are assumed to be spherical, with a radius of 0.1 μm for POC-driven emissions and 0.2 μm for chlorophyll-driven emissions. Note that the mass ratio of POC to Chl varies greatly in ocean water, with highest values in chlorophyll-poor regions: one analysis of satellite data found this ratio ranged from 33 to 1736, averaging 575 for $\text{Chl} < 0.1 \text{ mg m}^{-3}$ and 79 for $\text{Chl} > 1 \text{ mg m}^{-3}$ (Stramski et al., 1998).

The greatest uncertainty in the scaling parameters α_{POC} and α_{CHL} is the enrichment factor, observed values of which vary over more than two orders of magnitude under different experimental conditions (Table B1). However, it has been consistently observed that enrichment of organics is greatest in accumulation mode sea spray aerosol, justifying our choice of a value at the upper end of this range for our estimate, which is derived from simulation of accumulation mode sea spray.

The second greatest uncertainty is in the fraction of marine organic particles that act as IN. We express this in terms of the number of IN per unit of particulate organic mass (POM). Experiments that measured the concentration of IN in particulate matter sieved from a plankton bloom (Schnell and Vali, 1975) are assumed to be approximately representative of this value, observed concentrations of IN in marine surface waters and marine particulates are shown in Table A1 and Fig. A1. In addition, scaling IN emissions with POM mass allows us to cross-check our simulation results with independent observations and models of marine POM concentrations and emissions (Fig. 3).

The overall scaling factor was chosen to obtain approximate agreement between simulated mean IN concentrations and the three-year mean concentrations reported by B73. For each parameter, we list the range of values allowed by observations together with the value chosen for the analysis presented here in Table 1 (supporting information in Table B1 and Table 2).

We use satellite-derived proxies to scale the biogenic fraction of sea spray with ocean biological activity. For ocean surface particulate organic carbon (POC) and chlorophyll *a* concentrations, we use seasonal climatologies from MODIS-Aqua (July 2002 to June 2010, Esaias et al., 2002).

Finally, the size distribution of the organic sea spray is not well known. The impact this may have on our analysis is discussed Sect. 2.6.

2.3 Enrichment factors in sea-to-air-transfer of organic aerosols

Gas bubbles bursting at the water surface eject two types of drops: jet drops and film drops. The jet drops emerge from the bottom of the collapsing bubble cavity, and each drop produces up to ten jet drops, the size of which is on the order of some tenths of a millimetre. Jet drops probably dominate the sea spray aerosol mass. In addition, each bubble produces a large number of film drops, up to about 75 per bubble, which arise from the thin film of water that separates the air in the bubble from the atmosphere. Most of the aerosols smaller than 1–20 μm are believed to be film drops, and film drops dominate the sea spray aerosol production in terms of total number (Blanchard, 1989).

The studies summarised in Table B1 show that measured enrichment factors can be affected by a variety of variables, including bubble size, bubble rise distance, and chemical properties of the substance in question. For bacteria, increased cell surface hydrophobicity is believed to enhance the attachment to bubbles and therefore the transfer to aerosol. Cell surface hydrophobicity can be affected by cell pigmentation among other variables, this is hypothesised to explain the higher enrichment factors measured for pigmented as compared to non-pigmented strains of *S. marcescens* (Burger and Bennett, 1985).

The measurement of enrichment factors is not entirely standardised, but two general approaches can be distinguished. The first approach is to artificially generate bubbles to form aerosol from an aqueous solution or marine water sample. This approach has the advantage of allowing controlled, reproducible experiments on the process level. The disadvantage is that the results can depend strongly on the method used to generate the aerosol, and this method may not precisely mimic the natural sea spray formation mechanism. Enrichment factors measured with bubble-bursting experiments refer to the ratio of the concentration of a substance in the aerosol droplets upon production to its concentration in the bulk water. A recent brief review of methods of bubble generation can be found in (Keene et al., 2007).

The second approach is to measure the concentration of a substance in the naturally occurring marine aerosol and the surface sea waters. Often, the submicron surface layer is distinguished from the bulk seawater near the surface. However, because freshly emitted aerosol mixes with a preexisting aerosol population and is rapidly chemically modified after entering the atmosphere, the interpretation of field measurements is ambiguous. To negate the concentrating effect of evaporation, enrichment factors are typically determined relative to the salt content of the aerosol, since sea salt shows little or no enrichment during sea-to-air transfer.

In Table B1, we present enrichment factors for various organic compounds, derived using both of the general approaches described above, and with other variations in methodology, which we summarise in the table. Some recent results on primary and secondary organic marine aerosol are reviewed in (Rinaldi et al., 2010).

2.4 Sea spray parameterization and model simulations to estimate biogenic IN emissions

The emission parameterization for biogenic ice nuclei was implemented in a slightly modified version of the global chemistry-climate model ECHAM5/MESSy-Atmospheric Chemistry (EMAC) (Jöckel et al., 2006), version 1.9. The following MESSy submodels were utilised for simulation of aerosol emission and deposition processes: online emissions via ONLEM (Kerkweg et al., 2006b), wet deposition (impaction and nucleation scavenging) via SCAV (Tost et al., 2006), and sedimentation and dry deposition via SEDI and DRYDEP, respectively (Kerkweg et al., 2006a). Modifications to the model comprised the addition of emission functions for marine organic particles as described in the main text of this paper, and updates to the SCAV submodel (Tost et al., 2010). EMAC satisfactorily reproduces atmospheric aerosol transport for passive tracers and dust (Lelieveld et al., 2012; Gläser et al., 2012; Kunkel et al., 2012).

All simulations were conducted in T42L90 resolution, corresponding to a horizontal grid spacing of about 2.8° latitude and longitude, and 90 vertical levels. Simulations were conducted for four simulated years (plus one year of start-up) with climatological sea surface temperatures and online simulation of atmospheric dynamics. For ocean surface particulate organic carbon (POC) and chlorophyll *a* concentrations, we use seasonal climatologies from MODIS-Aqua (July 2002 to June 2010; Esaias et al., 2002). We emit a monodisperse, passively transported aerosol with a prescribed aerodynamic diameter of $0.1\text{ }\mu\text{m}$ for POC-driven emissions, or $0.26\text{ }\mu\text{m}$ for Chl *a*-driven emissions, which gave similar results. This is consistent with observations showing marine IN to have diameters between $0.1\text{--}0.3\text{ }\mu\text{m}$ (Rosinski et al., 1987, Sect. 2.6). Regions covered by sea ice were excluded, and points where satellite data were not available were set to zero (these largely overlap with sea ice regions).

2.5 Estimation of dust IN concentrations

State-of-the-art dust treatments in global atmospheric models can simulate dust deposition, surface mass concentrations and satellite-observable indicators of dust concentrations to within approximately a factor of ten. The largest errors generally appear in remote areas; in particular, many models underestimate surface mass concentrations at Antarctic coastal sites, and simulate more accurate surface concentrations at measurement stations affected by Saharan dust than those affected by Asian dust (Huneeus et al., 2011). Unfortunately,

no comprehensive evaluation of model dust distributions has yet been published for dust number concentrations. Observations of surface dust concentrations typically report only the mass density of dust in the air, however, for ice nucleation either the number density or surface concentration density is more relevant. The relationship between these variables depends on the size distribution of dust particles, adding an additional source of model uncertainty.

The dust IN concentration at -15°C is calculated from the dust surface area simulated in CAM-Oslo (Hoose et al., 2010a) and a temperature-dependent active site density (Niemand et al., 2012). This parameterization is obtained from a large number of immersion freezing experiments in the AIDA cloud chamber with natural dust samples, extending the study by Connolly et al. (2009). The uncertainty in the dust IN surface site density is estimated to be about a factor of 10 in each direction; furthermore, global models currently can predict observed dust concentrations only to within about a factor of ten, adding additional uncertainty to the simulated dust IN concentrations (Huneeus et al., 2011).

2.6 Considerations with regard to particle size

Field campaigns in the equatorial Pacific and the Gulf of Mexico found that marine IN were submicron particles with equivalent radii in the range $50\text{--}250\text{ nm}$ (Rosinski et al., 1986, 1987, 1988).

If IN are microorganisms, then we can examine typical sizes of marine microorganisms to determine an approximate size. Numerous studies have estimated the mean size of marine bacteria. The results of some of these studies are presented in Table 2. Bacteria grow larger in the presence of greater nutrient availability, and bacteria in coastal waters are on average larger than bacteria in open ocean. We take a cell volume of $0.075\text{ }\mu\text{m}^3$, or a spherical equivalent radius of 260 nm , as representative of typical marine bacteria sizes. The marine diatoms identified by Knopf et al. (2011) as ice nucleation active were an order of magnitude larger, with a typical diameter of ca. $5\text{ }\mu\text{m}$ (corresponding to a geometric mean surface area of $1.2 \times 10^{-6}\text{ cm}^2$), however, there are no field measurements available indicating the that such large ice nuclei are present in marine air in significant numbers. We further assume that the bacteria are externally mixed (not coated or attached to other particles), which is supported by single-particle observations (Pósfai et al., 2003; Bigg and Leck, 2001; Leck and Bigg, 2005a,b, 2008). We neglect any possible aerodynamic effects of microorganism shape, i.e. we assume the aerodynamic diameter of the microorganism is equal to its spherical equivalent diameter.

Turning to studies of organic sea spray, these suggest that the organic fraction of the sea spray aerosol is largest for particle radii smaller than about $r = 100\text{ nm}$ (maximum relative OM mass contribution and corresponding size fraction: 80 %, $r = 65\text{ nm}$ (Keene et al., 2007); $77 \pm 5\text{ %}$, $r = 62.5\text{--}125\text{ nm}$ (Facchini et al., 2008); 4 %, $35\text{--}38\text{ nm}$ (Modini et al., 2010)).

Table 2. Size of bacterial cells from natural marine populations, and other aquatic bacteria samples. Unless otherwise stated, values are reported as mean \pm standard deviation and/or as range. Published values are printed in upright font; values derived from the published values are printed in italics.

Where	Cell volume (μm^3) ¹	Total mass (fg cell $^{-1}$)	Carbon mass (fg cell $^{-1}$) ¹	Spherical equivalent radius (μm)	Method/notes	Reference
Natural marine bacteria						
Crane Neck, Long Island	0.05	50	20	0.23 (0.20– 0.26)	Microscopic volume estimates of cultured cells from natural assemblages	Lee and Fuhrman (1987)
Open ocean			12.4 \pm 6.3		High temperature catalytic oxidation, used natural assemblages	Fukuda et al. (1998)
Coastal waters			30.2 \pm 12.3			
Hawaii			10		Solved a multiple linear regression using Chl <i>a</i> and ATP data	Christian and Karl (1994)
Open ocean south of Bermuda	0.08 ³	80	15	0.27	Constrained by ancillary measurements, e.g. of PC, Chl, C:Chl ratios etc.	Caron et al. (1995)
Arctic	0.100 \pm 0.04	100 \pm 40		0.29	Protein + DAPI staining, automated microscopic counting	
Antarctica	0.106 \pm 0.04	106 \pm 40		0.29		Straza et al. (2009)
Delaware Bay	0.087 \pm 0.06	87 \pm 60		0.27		
Ross Sea, Antarctica	0.06–0.09	60–90	7–13	0.24–0.28	Mass balance approach using high-precision analyses of DOC and TCO ₂	Carlson et al. (1999), as cited in Ducklow (2000)
Freshwater, estuarine, and cultured bacteria						
Two lakes and one estuary in Denmark	(0.036–0.077)			0.27–0.43	Automated analysis of epifluorescent microscopic images	Bjørnsen (1986), as cited in Christian and Karl (1994)
80 lakes in the Pyrenees	0.16 ⁴ (0.09–0.45)	160 (90–450)		0.34 (0.28–0.48)	Epifluorescence microscopy	Felip et al. (2007)
Exponential growth	1.78 \pm 0.17	1780 \pm 170	149 \pm 8	0.75	Marine bacteria isolated and grown in cultures until nutrient-limited. X-ray microanalysis.	
C-limited	0.45 \pm 0.06	450 \pm 60	39 \pm 3	0.48		Vrede et al. (2002)
N-limited	1.40 \pm 0.12	1400 \pm 120	92 \pm 5	0.69		
P-limited	2.38 \pm 0.38	2380 \pm 380	106 \pm 23	0.83		

¹ Calculated values in italics are spherical equivalent volumes, except as noted.

² Calculated masses are based on the assumption that bacterial cell density equals 1 g per cm^3 .

³ Calculated using the authors' conversion factor of 183 fg C per μm^3 .

⁴ Median.

During biologically active periods (algal bloom episodes), observations have found the aerosol mass below 200 nm diameter to be dominated by organic matter (O'Dowd et al., 2004). However, note that the particle size ranges with the greatest organic contribution represent the lower detection limits of the impactor samples in those studies (Facchini et al., 2008; Keene et al., 2007), so they do not rule out a large organic contribution to even smaller particle size ranges.

In artificially-generated sea spray, Facchini et al. (2008) measured a mass-weighted mean radius for the submicron water-insoluble organic aerosol in the range 0.125–0.25. To test the effect of particle size on our analysis, we simulated

the emissions and transport of particles with the following equivalent spherical radii: 50 nm, 100 nm and 260 nm. The particles size affects two aspects of our estimation: the rate of removal from the atmosphere, which determines resulting number concentrations, and the average particle mass, which we use in converting simulated particle number concentrations to mass concentrations. Relative changes in the simulated particle number concentrations were less than 5 %. Differences in particle mass, however, are large. Relative to the 100 nm particles used in our initial calculations, particles in this size range have volumes ca. 2–16 times greater, and thus would contain 2–16 times more mass. This must

be accounted for in converting between model-simulated aerosol number mixing ratios and aerosol mass densities, as reflected in Table 1.

3 Results and discussion

3.1 Simulated POM distribution

Simulated distributions of primary organic mass (POM) are broadly comparable with the results of a recent, state-of-the-art model study of marine primary organic aerosol that used chlorophyll maps to partition sea spray production into organic and inorganic parts (Vignati et al., 2010). The results of the simulation are qualitatively consistent with the climatological mean IN concentrations measured by B73, particularly in terms of the zonal distribution (Fig. 7; comparisons of results using different satellite data and the zonal profile of emissions can be found in Fig. S1 and Fig. S2, respectively). The simulated IN source and concentrations are largest in the mid-latitudes, especially the “roaring forties” of the Southern Hemisphere, where high wind speeds combine with seasonally strong biological activity to produce a strong emission to the atmosphere.

Both the simulated and observed IN concentrations are highly uncertain. However, by using scaling parameters within the range of available observations, we show that the B73 measurements may be broadly consistent with a postulated marine biogenic sea spray source of IN, the strength of which is estimated using current knowledge of the concentrations of ice-nucleating particles in the biologically active surface waters of the oceans (Table A1 and Fig. A1), together with an estimate of the injection of water-insoluble organic matter from the ocean surface into the sea spray aerosol. For the latitude band 20–70° S, maximum zonal mean concentrations of simulated IN are obtained near 60° S latitude for the marine biogenic source, and near 45° S for the sum of marine biogenic and dust IN; dust IN concentrations reach a local maximum around 20° S (Fig. 7, top). The zonal mean IN counts from B73 reach a maximum near 40° S. In the latitude band 50–70° S, IN concentrations from a marine biogenic source may exceed those from dust IN (Fig. 7, bottom).

In other words, there is a distinct possibility that the marine biogenic source is a significant, and perhaps the main, contributor to IN counts (at -15°C) in remote marine boundary layer air. Further research is needed to better constrain their contribution.

3.2 Comparison with latitudinal distribution of other aerosol types

In Fig. 4, we show the zonal distribution measured by B73 together with modern data sources describing the year 2000 latitudinal distributions of various types of natural and man-made aerosols in the marine boundary layer, and our simulated distribution of biogenic sea spray IN. We note that

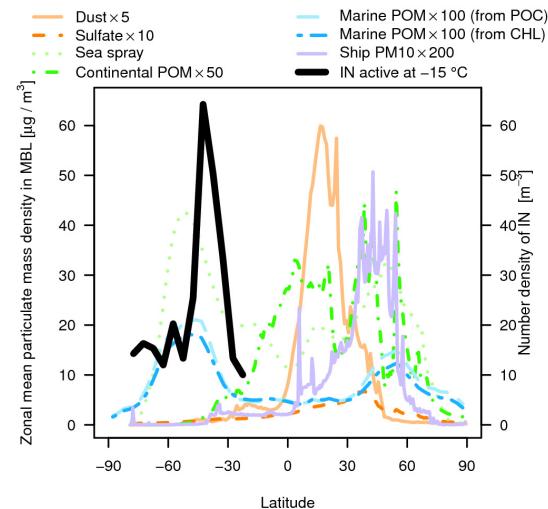


Fig. 4. Latitudinal dependence of aerosol surface concentrations over oceans. Left axis: mean surface mass densities, latitudinal average over oceans. Shown here are dust, sulfate, sea spray, and (continental) POM from the AEROCOM median model (year 2000) (Texier et al., 2006; Kinne et al., 2006; Schulz et al., 2006), simulated marine POM (this work) and estimated particulate matter from ship emissions (year 1970, PM₁₀, assuming 5-day residence time in 800-m boundary layer) (Lamarque et al., 2010). Right axis: Observed number densities of IN active at $T = -15^{\circ}\text{C}$, as reported by B73, latitudinal average over sampled region.

a continental biological source is unlikely to contribute significantly to simulated biogenic IN abundance in marine air, except in continental outflow regions, where continental IN may outnumber marine IN (Fig. 8), but are in turn far outnumbered by dust IN.

3.3 Comparison of simulated marine biogenic IN and dust IN

Globally, desert dust is the primary and best-understood source of atmospheric ice nuclei, and has been shown to contribute to ice nuclei populations at great distances from the source regions (DeMott et al., 2003), although the uncertainty in both modelled concentrations of desert dust and the ice nucleating fraction remains large. Comparing our simulated distribution of marine biogenic IN to simulated distributions of dust IN (Hoose et al., 2010a), we show (Fig. 5 and Fig. 4) that marine biogenic IN are most likely to play an important role in driving ice nuclei concentrations in remote marine regions that are less affected by the long-distance transport of continental dust and more affected by sea spray generation due to strong surface winds, especially in the Southern Ocean, where rough seas are common and the biological content of seawater is high. The simulated vertical distribution at 60° S shows a decrease in the relative contribution of marine biogenic IN with altitude (Fig. 6). This

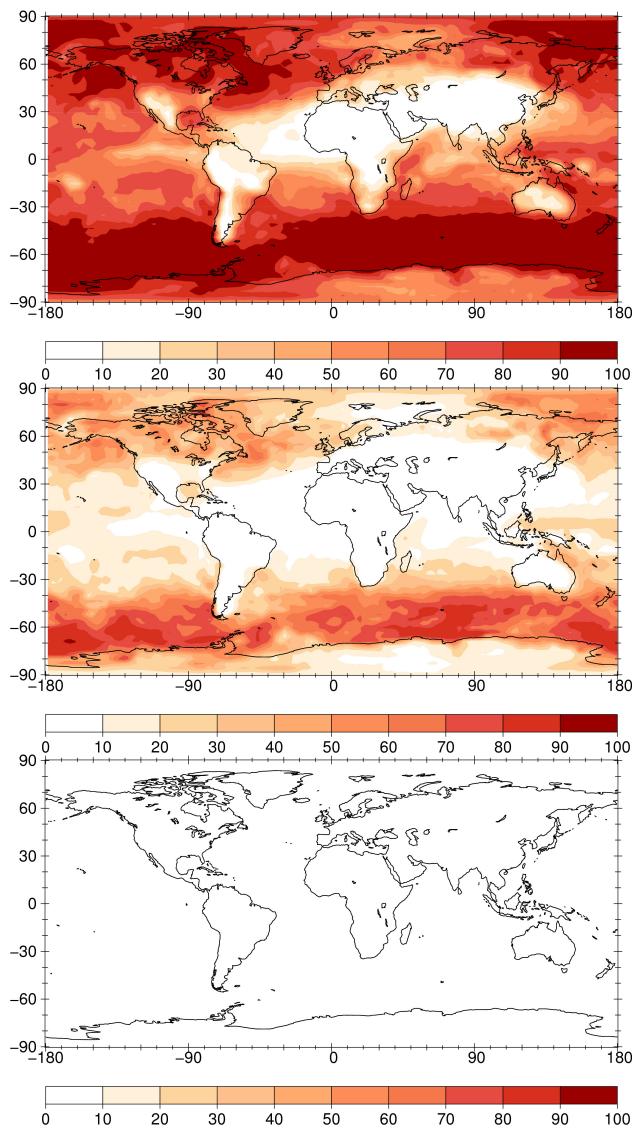


Fig. 5. Simulated relative contribution of marine biogenic IN to marine boundary layer IN concentrations at -15°C , as a percent of annual mean dust IN and marine biogenic IN. Middle: estimate using “control” dust IN concentrations and “best” biogenic IN concentrations; Top: with “high” biogenic IN concentrations; Bottom: with “low” biogenic IN concentrations. For zonal mean comparison of simulated marine IN and dust IN, see Fig. 7.

is because marine biogenic IN, emitted from a local source, are present in highest concentrations in the boundary layer, and decrease in concentration with increasing altitude. Dust IN, by contrast, originate from a distant source, and are thus more well-mixed in the remote marine troposphere. For comparison, CLOUDSAT satellite data show that the majority of Southern Ocean clouds have cloud tops below 3 km (Mace et al., 2007), so biogenic particles do not have to reach very high altitudes in order to potentially impact clouds. While we consider average concentrations here, since the variability

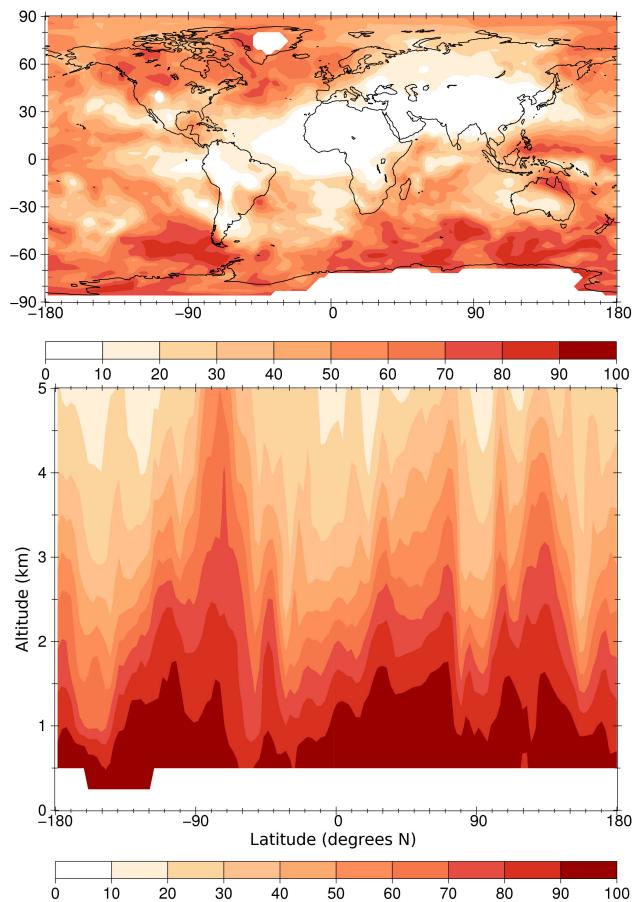


Fig. 6. Simulated relative contribution of marine biogenic IN at -15°C , as a percent of annual mean dust IN and marine biogenic IN (“control” dust IN and “high” biogenic IN concentrations). Top: horizontal cross-section at 2 km altitude. Bottom: vertical cross-section at 60°S latitude.

in both marine emissions and long-distance transported dust concentrations is very high, local marine emissions could dominate the cloud-height IN population at certain times, while long-distance transport dominates at other times (in analogy to the observations over the Amazon rainforest by Prenni et al., 2009a).

The impact of marine IN emissions on clouds would be expected to be significant only during the Austral winter, when the temperature is low enough to render significant ice nucleation in the marine boundary layer. Furthermore, IN activity may change as particles age: exposure to UV radiation may cause certain particles to break down; and coating with sulfate may make marine particles good CCN, but may limit their effect as IN by deactivating IN active sites on particle surfaces.

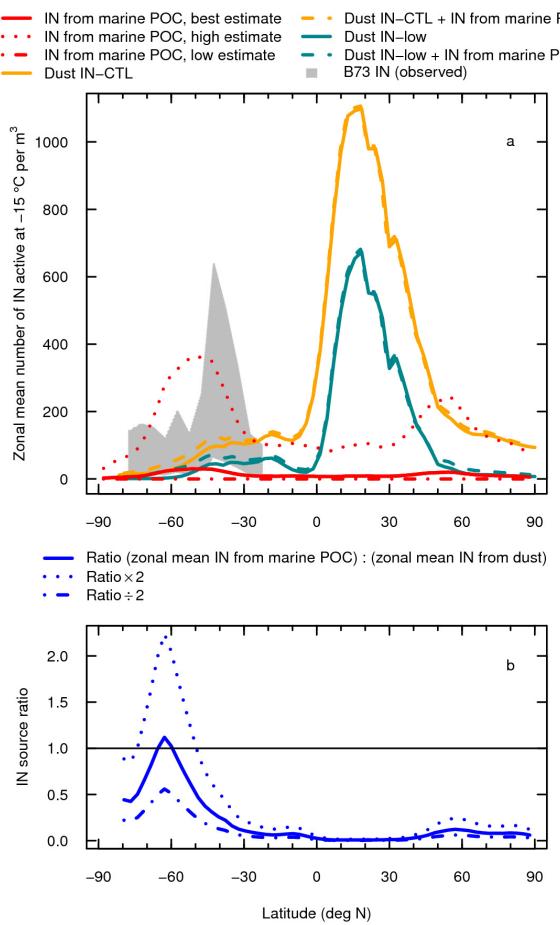


Fig. 7. (a) Latitudinal dependence over oceans of observed IN, and simulated marine biogenic IN and estimated dust IN concentrations. Red lines: results of simulations performed on the basis of POC climatological distribution from MODIS-Aqua (alternative results using chlorophyll climatology are shown in the Supplement). Observed zonal mean IN number densities are from B73; the values as reported in B73 form the lower boundary of the shaded region, the “true” IN values are expected to be about a factor of 10 higher, indicated by the upper boundary of the shaded region. Dust IN concentrations are estimated from two cases of simulated dust number concentrations, a control simulation (CTL; orange solid line) and a simulation with lower dust concentrations (low; turquoise solid line) (Hoose et al., 2010a). The sum of predicted dust IN and marine biogenic IN is shown for the control dust and low dust cases by dashed lines. (b) Ratio of zonal mean marine biogenic IN to zonal mean dust IN, over oceans.

We suggest that the Southern Ocean should be targeted by future field campaigns aiming to investigate the possible role of marine biogenic particles as IN.

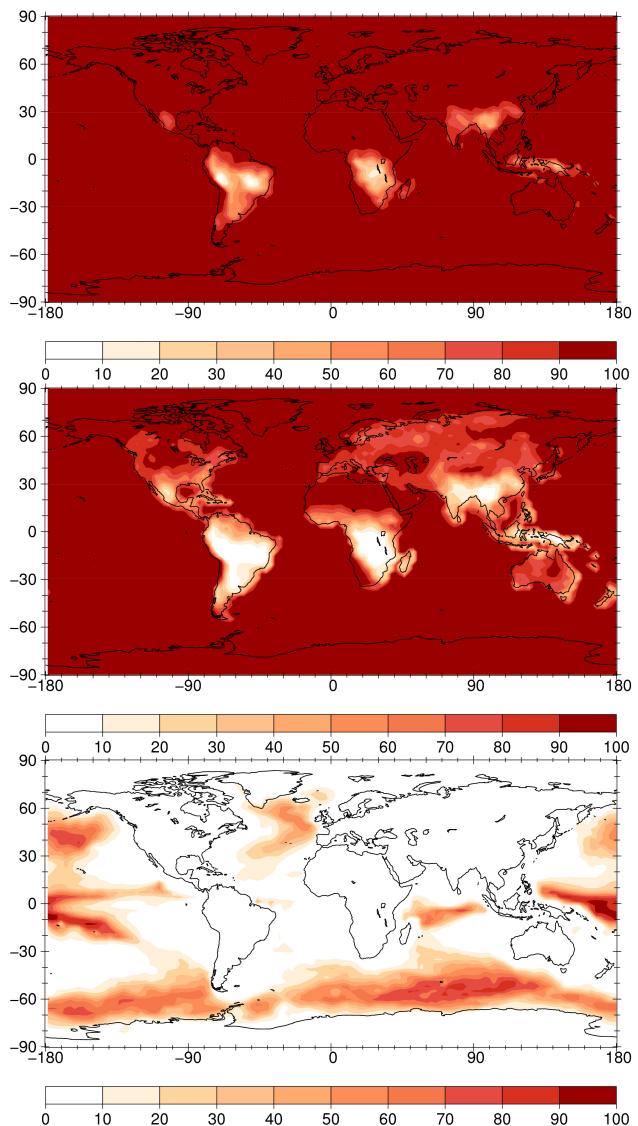


Fig. 8. Estimated percent of biogenic IN, active at -15 °C, from a marine source, relative to the total population of biogenic IN (from continental and marine sources). Top: “high” biogenic IN. Middle: “best” biogenic IN. Bottom: “low” biogenic IN.

3.4 Estimated relative contributions to biogenic IN concentrations from marine and continental sources

To estimate the relative contribution to the biogenic IN population that can be expected from marine sources versus continental sources, we build on work by Hoose et al. (2010b). We use concentrations of bacteria, fungal spores and pollen in CAM-Oslo from that study, and we follow the assumption from that study that all pollen are potentially active as IN, while 1 % of the bacteria and fungal spores carry the gene for IN activity. We further assume that on average 10 % of these potentially IN-active bacteria and fungal spores can be activated at -15 °C, however, the small number of laboratory

studies available indicate that this might range from 0.1 % to 100 % (Després et al., 2012).

The estimated relative contribution of marine biogenic IN is shown in Fig. 8. Because the concentrations of continental biological IN are lower than those of dust IN, their contribution to the global IN distribution is largely masked by dust. Including a continental biological IN source as part of the global total IN would not significantly impact the relative contribution of marine biogenic IN, as shown in Fig. 5. As a result, we do not consider the highly uncertain but very minor contribution of continental biological IN in our main line of analysis. The relative contribution of continental and marine biogenic IN could be constrained by a field campaign in an area where their contributions might be of similar order of magnitude; promising locations for such a campaign can be identified from Fig. 8.

3.5 Potential implications for marine cloud brightening proposals

Marine biogenic IN may also have previously unconsidered consequences for proposals to cool the climate by creating artificial sea spray that would increase the albedo of marine clouds (marine cloud brightening) (Latham et al., 2008), one of the leading proposed schemes for engineering a cooler climate. In one proposed implementation of such a scheme (Salter et al., 2008), a fleet of wind-driven vessels would generate aerosol droplets from surface water at a mean rate of $1.45 \times 10^6 \text{ m}^{-2} \text{ s}^{-1}$ over a targeted ocean area of $7.72 \times 10^{10} \text{ m}^2$. Depending on the technical implementation of spray generation, organic materials might be more or less enriched in concentration during aerosolization (Fuentes et al., 2010a). The system proposed by Salter et al. (2008) would include an ultrafiltration system that presumably would remove all or most biogenic particulates from the generated sea spray. If biogenic particles were present in the generated sea spray, some fraction of generated particles could be biogenic IN.

The hardware design proposed by Salter et al. (2008) aims to generate a monodisperse spray of $0.8 \mu\text{m}$, with a mean spherical volume of $0.27 \mu\text{m}^3$. The mean volume emission flux of the injected spray in the targeted ocean regions would thus be $3.9 \times 10^5 \mu\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$ of surface seawater. The concentrations of biogenic IN in that seawater are roughly $(2.7\text{--}32) \times 10^6$ per mg POC or $(1.1\text{--}8.9) \times 10^9$ per mg Chl *a* (Table 1). The expected IN flux would thus be $(1\text{--}12) \times 10^{-6} \text{ m}^{-2} \text{ s}^{-1}$ per (mg POC m^{-3} in surface water); or $(0.4\text{--}3.5) \times 10^{-3} \text{ m}^{-2} \text{ s}^{-1}$ per (mg Chl *a* m^{-3} in surface water). Assuming a 5-day residence time in an 800-m boundary layer, an enrichment factor of 1000 during the spray production process, this could result in concentrations between about 100 and 500 IN m^{-3} over large areas of the ocean, which could be competitive with naturally occurring concentrations in regions not influenced by mineral dust. This would depend greatly, however, on the engineering of a

spray generating mechanism that allows organic particulates to enter the artificially produced sea spray at highly enriched concentrations.

3.6 Errors in membrane filter measurements and discussion of uncertainties

A complication in interpreting the data reported by B73 arises from the analysis method used in that early study, which relied on collection and analysis of particles on membrane filters. Ice nucleation measurement methods have advanced significantly in the decades since, as flaws in the historical filter measurement methods were discovered and new technologies were developed in response (DeMott et al., 2011). In the measurements reported by B73, particles were collected in the field on a membrane filter, stored, and later analyzed for IN content in the laboratory by cooling the filters and exposing them to air at water saturation. Early membrane filter methods were subsequently shown to underestimate IN concentrations by a factor of about 10–100 compared to a continuous flow diffusion chamber (Hussain and Kayani, 1988). The major known reason for this underestimation is that IN and other hygroscopic particles compete for and rapidly remove the available water vapor, termed the “vapor depletion effect” (Lala and Jiusto, 1972; Huffman and Vali, 1973). However, underestimates are much smaller for low particle concentrations such as those found in remote marine air (Hussain and Kayani, 1988; Bigg, 1990), so we expect the underestimation to be roughly a factor of 10 for this data set, as indicated in Fig. 7 by the grey shaded region.

Another source of undercounting in some measurements of IN counts on filter samples is a layer of Vaseline or oil applied to the filter in order to seal the filter pores and improve the thermal contact of the filter to its underlying cold base. The Vaseline or oil can evaporate if the sample is exposed to a vacuum during analysis, and subsequently coat and deactivate IN (Klein et al., 2010). However, the B73 samples were not exposed to a vacuum during processing, thus they were probably not affected by deactivation due to coating, and later experiments by Bigg did not find evidence for this effect (Bigg, 1990).

In spite of the limitations of the membrane filter measurements, the B73 dataset remains uniquely relevant as one of only a very small number of existing IN climatologies and to our knowledge the only such climatology in a marine region.

Given the likely large underestimate of IN concentrations in the B73 filter measurements, the question presents itself whether “true” concentrations a factor of ten greater than those reported by B73 can be explained at all with current models of dust and marine aerosol, since even the sum of these components would then not reproduce the peak zonal mean values in B73 (Fig. 7). Considering the large uncertainties discussed above, we conclude that the location and magnitude of the peak could be consistently explained either by dust or by a marine biogenic source, or by a combination

of the two. A marine biogenic source is very likely relevant in a latitude band near the Antarctic coast, even if we have overestimated the role of marine biogenic IN relative to dust IN by an order of magnitude (Fig. 5). Only if our estimate of the proportion of biogenic to dust IN were incorrect by two orders of magnitude would we expect either dust or marine biogenic IN to entirely dominate marine IN populations everywhere.

In the absence of better information, we have assumed that marine IN (active at -15°C) are equally distributed in marine biogenic matter around the world. It seems likely that marine IN activity is tied to particular plankton species or their exudates and its geographic distribution would be related to the distribution of that species. Since our analysis suggests that there may be on the order of 1 IN per $10^3\text{--}10^4$ marine bacteria, it is possible that one or more species that make up a very minor component of the marine microflora is responsible for marine IN activity. As a result, the relative IN activity of marine biogenic particulates might depend, for example, on sea surface temperature or light availability. This could be determined by new field experiments characterizing the IN activity of environmental samples of marine particulates from different locations. A challenge in such experiments is that IN testing must be performed rapidly following environmental sampling to avoid any biases arising from changes in biologically active samples during storage. The characterization of individual cultivates in the laboratory might also prove useful, especially if important candidates are previously identified in field experiments.

4 Conclusions

A commonly held and useful conception of global IN distributions is that IN are more numerous in continental than in marine air (Castro et al., 1998), and the IN population is mostly dominated by large mineral and dust particles (Chen et al., 1998). However, this conception is likely to be refined as new experiments reveal a more nuanced picture of the sources and nature of atmospheric IN. For example, biological particles contribute significantly to the IN concentrations in the clean air over the Amazon rain forest (Pöschl et al., 2010), a “green ocean” regime that shows many characteristics more commonly associated with the marine atmosphere (Williams et al., 2002). As we have shown, there is reason to expect that biogenic IN play a similar role in determining background IN concentrations in remote marine air, but likely with strong regional differences in importance, just as continental IN populations differ between regions dominated by dust and those dominated by biological particles.

The presence of ice in clouds is very important for the formation of precipitation and cloud lifetime, as well as for cloud radiative forcing and thus the Earth’s radiation budget (Choi et al., 2010), which is poorly predicted in the Southern Ocean by current models (Trenberth and Fasullo, 2010). IN

concentrations are especially likely to impact mixed-phase clouds containing both liquid droplets and ice crystals, which are responsible for a large fraction of precipitation globally (Rasmussen et al., 2002). Cloud model simulations of marine mixed-phase boundary-layer clouds in the Arctic indicate that IN concentrations may strongly affect the formation of cloud ice and precipitation, thus affecting cloud lifetime, radiative forcing, and boundary-layer dynamics (Morrison et al., 2005; Prenni et al., 2007; Harrington et al., 1999; Harrington and Olsson, 2001). Model simulations suggest that higher numbers of IN could result in increased freezing of cloud droplets and thus optically thinner ice clouds, and affecting the boundary layer radiation budget (Prenni et al., 2007). Cloud ice plays a crucial role in the formation of precipitation, so a change in biogenic IN concentrations could affect precipitation and cloud cover in remote marine regions, modifying the hydrological cycle and the energy balance of the Earth. It is significant that the region in which biogenic sea spray particles are most likely to play a role in driving IN concentrations is the Southern Ocean. The Southern Ocean has a cloud cover fraction of about 80 %, and Southern Ocean clouds contain an unusually large proportion of supercooled liquid water droplets (Morrison et al., 2011). This likely indicates that droplet freezing is limited by the low availability of IN and these clouds are most likely to be sensitive to the concentrations of ice nuclei. Indeed, one of the few analyses that has found a statistically significant increase in precipitation due to cloud seeding with IN focuses on long-term experiments in Tasmania (Morrison et al., 2009).

Through their influence on the glaciation and micro-physics of marine clouds, biogenic IN may affect climate in multiple ways that are relevant for our understanding of climate change and climate feedback mechanisms. Marine ecosystems are being significantly impacted by human activities and rising ocean temperatures, which could result in a decline in biological productivity and IN concentrations in seawater. On the other hand, in a warming climate wind speeds are expected to increase, resulting in greater emissions of sea spray, including biogenic IN. A targeted field campaign in the Southern Ocean will be necessary to clarify the quantity and role of marine biogenic IN. Such a campaign should combine ship-based and, ideally, airborne measurements of air and water in the Southern Ocean, using recent state-of-the art instruments to measure IN concentrations and composition, as well as the overall dust, biological and organic aerosol concentrations. We suggest and intend to pursue further laboratory, field and model investigations of this challenging and rarely-studied topic.

Appendix A

Concentrations of IN in marine surface waters

Table A1. Concentrations of IN measured in marine surface waters, selected values.

Description	Value	Location	Reference
Active at -7°C			
IN per cm^3 seawater	2–20	San Diego, California, USA	Fall and Schnell (1985)
Active at -10°C			
Number of IN per μg of particulate matter sieved from a phytoplankton bloom	ca. 10–20 for concentrate in distilled water ca. 0.1 for concentrate in seawater	Coastal waters near Bedford, Nova Scotia	Schnell and Vali (1975)
IN per cm^3 of biologically active seawater	ca. 100–200	Bedford, Nova Scotia	Schnell and Vali (1975)
IN per cm^3 seawater	0.1–0.7	Gulf of Mexico	Rosinski et al. (1988)
Active at -15°C			
IN per cm^3 seawater	0.2–2	Gulf of Mexico	Rosinski et al. (1988)
Active at -20°C			
IN per cm^3 seawater	0.3–3	Gulf of Mexico	Rosinski et al. (1988)

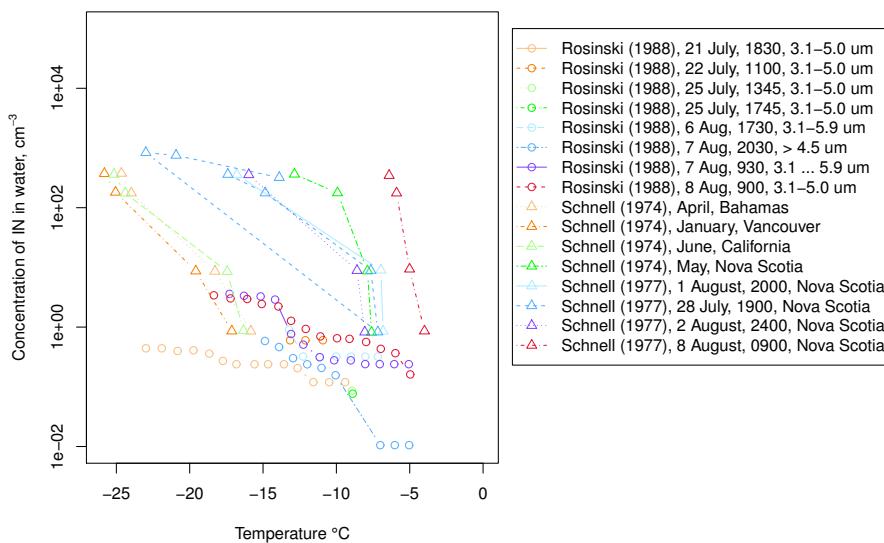


Fig. A1. Ice nucleation spectra of particles separated from sea water by filtration. Rosinski et al. (1988) data (circles) are from the Gulf of Mexico, and IN concentrations were determined by condensation-followed-by-freezing using the dynamic developing chamber of Langer and Rodgers (1975). Results from (Schnell and Vali, 1975) (triangles) are from various locations as indicated, IN concentrations were determined using a drop freezing assay (immersion freezing).

Appendix B

Enrichment factors

Table B1. Enrichment factors reported from field measurements and laboratory experiments for aerosolized marine bacteria and organic compounds.

Enrichment factors for microorganisms			
Enrichment factor	Substance measured	Notes	Reference
1200 8	<i>S. marcescens</i> suspended in distilled water	0.38 mm bubbles, top jet drop Fifth or lowest drop in the jet set	Blanchard and Syzdek (1978)
ca. 10–100		380 µm bubble rising < 1 cm, top jet drop	
ca. 500–600		380 µm bubble rising > 5 cm, top jet drop	
ca. 150–220	<i>S. marcescens</i> suspended in pond water	380 µm bubble rising ca. 100 cm, full jet set	Blanchard et al. (1981)
ca. 70–200		380 µm bubble rising ca. 30 cm, full jet set	
10–20	Suspension of <i>S. marcescens</i> in either pond water or distilled water	1.7 mm bubbles rising 2 cm, film drops	Blanchard and Syzdek (1982)
50–100	Seawater suspension of <i>S. marinorubra</i>	Measured on drops < 10 µm	Cipriano (1979), as cited in Blanchard (1989)
Mean: 10 (max: 22)	DAPI-stained bacteria in aerosol relative to bulk	Ambient samples collected near Long Island, New York, above plankton bloom	Aller et al. (2005)
Mean: 6 (max: 10)	DAPI-stained in sea-surface microlayer relative to bulk		
37–2545 14–585	Culturable mesophile bacteria Culturable psychrophile bacteria	Bubble measurements with coastal seawater samples from the Gulf of Gdansk.	Marks et al. (1996)
ca. 6–140 ca. 4–40 ca. 0.6–6 ca. 1–3 ca. 1–4	<i>S. marinorubra</i> <i>M. euryhalis</i> <i>E. coli</i> <i>P. bathycetes</i> <i>B. subtilis</i>	Bubble-bursting with suspensions of bacterial cultures in 0.85 % or 3 % NaCl at 23 °C. EF is for top jet drop, and is larger for smaller drop diameters. For <i>E. coli</i> , EF also shown to depend on the culture age.	Hejkal et al. (1980)
2–27	DAPI-stained bacteria	Bubble-bursting with samples in NW Mediterranean Sea and Long Island Sound	Kuznetsova et al. (2005)
2–14 0.2–0.6	Pigmented <i>S. marcescens</i> Non-pigmented <i>S. marcescens</i>	Bubble-bursting with suspensions in 0.7 % saline solution, bubble diameter 0.66–0.89 mm, top jet drop	Burger and Bennett (1985)
Enrichment factors for organic compounds			
10 ² –10 ³	Organic mass in submicron aerosol	Enrichment relative to reported Na-to-OM ratios (field measurements).	Russell et al. (2010)
20–40	Organic particles (polysaccharides, proteinaceous particles and amorphous DAPI-stained particles), 3–40 µm	Ambient samples collected near Long Island, New York, above plankton bloom	Aller et al. (2005)
10 (max: 15)	Virus-like particles stained with SYBR gold		
250 ± 145 (130–640); N = 11 74 ± 27 (26–105); N = 7 1460 ± 1350 (320–6080); N = 7	Total organic carbon	Bubble generation, seawater from Narragansett Bay, Rhode Island, USA. Bubble generation, seawater from Sargasso Sea Ambient sampling, Bermuda	Hoffman and Duce (1976)
mean: 6810 median: 387; N = 26	Soluble organic carbon	Bubble generation, seawater from Bermuda.	Turekian et al. (2003) Keene et al. (2007)
2–300	Synthetic silica particles in seawater	Bubble-bursting experiments; EF increased with higher surfactant content	Cloke et al. (1991)
1.2–20	Dissolved free amino acids and dissolved combined amino acids		
5–50	Particulate amino acids	Bubble-bursting with samples in NW Mediterranean Sea and Long Island Sound	Kuznetsova et al. (2005)
57 ± 29	Proteinaceous particles stained by Coomassie Blue		
44 ± 22	Transparent exopolymer particles stained by Alcian Blue		
1–20	Virus-like particles stained with SYBR gold		

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