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Interactive comment on "Ice nuclei in marine air: bioparticles or dust?" *by* S. M. Burrows et al.

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We thank Gabor Vali for his careful review of our manuscript. Our responses to his specific comments are given below.

As a general comment, we would like to reemphasize our central aim in this manuscript. Our aim was to make best possible use of the available published observations in order to derive an estimate of the likely global distribution of marine biologically-derived ice

nuclei concentrations in the marine boundary layer, and to compare this with estimates of dust IN concentrations. In doing so, we made a number of assumptions, among these, we assumed that there is indeed a source of biological IN from sea spray emissions to the marine boundary layer, which can be described by using marine Chl-a or POC as a proxy for their concentration in sea spray emissions. We take this hypothesis as a starting point and assess the consequences that would follow.

In this manuscript, we do not attempt to assess climate impacts of marine biological IN, and indeed to do so would be premature. Instead, we have the more limited goal of attempting to assess their likely distribution, in comparison to the distributions of other possible marine IN, which could be an important step towards a future assessment of their climate impact.

We have taken care to point out the associated uncertainties, which are quite large. However, we would like to point out that in global chemistry-climate models, uncertainties in the modeled concentrations of even relatively well-studied naturally-occurring aerosol species, particularly sea salt and dust, are commonly about an order of magnitude in each direction. Nonetheless, model estimates of their emissions and concentrations have proved to be a useful tool in advancing understanding of their impact on the climate system.

Our goal is that this exploratory analysis will help motivate further experiments with modern methods that will test our conclusions and further advance knowledge of this topic.

In the revised manuscript, we will add the following introductory section:

"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 biological source, 2. to compare the near-surface-air concentration of marine biological IN to the simulated concentration of dust IN at the same temperature, and thereby 3. to identify regions in which marine biological 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,

2. this source is associated with biologically-derived material,

3. the concentration of marine biological IN in sea spray is proportional to the mass of marine biological particulates in sea spray."

Comment 1

Of the three main components of this paper - global chemistry/climate model, aerosol emission rates and ice nucleating activity - these comments address only the last. That is probably the major source of uncertainty in this work due to the paucity of data. The first difficulty when discussing heterogeneous ice nucleation is that the term covers a phenomenon that may take place, as is well known, over a wide range of temperatures (and to a lesser extent supersaturations). The number of potential sources of ice nuclei is significantly greater at lower temperatures than close to the melting point. Therefore, it leads to a great lack of clarity when ice nucleation is described and various substances or aerosols are compared without regard to that fact. The review of ice nucleating activity in this paper suffers from this. Only in one place (page 4378, line 15) is the temperature specified for the activity that is being modeled.

Accepting the choice of -15°C (to be re-examined later) as the target for assessing IN populations from marine sources filters the potential sources that are considered. This in turn requires that the results and the methods of measurement in earlier work be examined in more detail than has been done here. Several of the biogenic sources considered in the paper do not show significant levels of activity at -15°C. The diatom and phytoplankton samples of Knopf (2011) and Alpert et al. (2011) yielded measurable activity only at temperatures lower than that. Leaving those sources aside, the only identified sources are those reported by Schnell and Vali(1975), Schnell (1975) and Fall and Schnell (1985). It is also significant that Fall and Schnell found little IN acitivity in several sea water samples and that the they considered it uncertain whether the one species of bacteria found to be highly active was truly marine or terrestrial origin. Parker et al. (1985 Antarctic J. 126-128) found one bacterial species active above -10°C. In all, the evidence is very sketchy for what marine microorganisms produce IN activity. Other data come from measurements of ice nuclei in the air; with inferences about possible connection to biological activity or chemical analyses of similar aerosol. On the other hand, the impacts of IN on precipitation and climate also depend strongly on the temperature at which their activity becomes appreciable. This is where some of the biogenic sources are unique and differ from dusts in general. Therefore, the potential climate impacts of these IN should be considered with their regime of activity taken into account. This paper oversimplifies the issue by focusing on one temperature of activity only, and one that is lower than the domain of greatest potential impact of the biogenic IN. Consequently, this paper misses the main point.

Response 1

We would again like to emphasize that our manuscript does not attempt to assess the potential climate impacts of marine biogenic IN, but has the more limited goal of making a first step towards estimates of their global distribution and determining whether, and in which geographic regions, they might be expected to contribute significantly to

atmospheric ice nucleation, relative to dust.

We agree with Dr. Vali that the variation of IN activity with temperature is an essential parameter to be considered in evaluating their climate impact. However, as Dr. Vali also points out, it is not known in general which marine particles produce IN activity, nor how this activity varies with temperature. We did include an overview of some relevant measurements of the IN activity of marine particulate matter (collected from the source by filtration) as a function of temperature (Figure A1). This is a reprinting of data that is scattered over several plots in Rosinski et al (1988) and Schnell and Vali (1975), here we have simply collected these data on a single plot for the purpose of comparison. The differences between the various observations are large.

For precisely this reason, we refrain from assuming that marine IN activity is associated with any particular marine microorganism, and from making assumptions about the variation of the IN activity with temperature. The development of a parameterization for the dependence of marine IN activity on temperature is a challenging and potentially fruitful topic for future study, but goes beyond the scope of this manuscript.

By choosing a single temperature for comparison, we are able to make use of available observations to focus on an estimate of the geographic distribution and number concentrations of marine biological IN, and to compare this to observed average IN concentrations, and to a simulated geographic distribution of dust IN. Our choice of -15°C was guided primarily by the use of -15°C as a reference temperature for presentation of observations by Bigg (1973).

It is certainly possible that marine biological IN are far more active relative to dust at higher temperatures. If this were the case, it would mean a potentially greater influence of marine biological IN on cloud development, particularly if freezing at high temper-

ature were enhanced by ice multiplication processes. However, we show that marine biological IN could still drive IN counts in the remote marine boundary layer, even if their concentrations are quite low, in those regions that are less affected by dust.

The existing data indicate that marine biological IN concentrations might be reduced by about an order of magnitude at -10°C, relative to their concentrations at -15°C (Schnell and Vali, 1975); and IN concentrations observed by Bigg (1973) at -10°C were about an order of magnitude lower than at -15°C. Measurements from the AIDA chamber indicate a similar relationship for dust (however, this requires extrapolating slightly, since the warmest measurements were conducted at about -12°C) (Niemand et al., 2012).

In a revised version of the manuscript, we will add the following text at the beginning of the methods section to clarify our approach:

"For the purposes of comparing the geographic distribution with observations and with dust, we chose to estimate the distribution of marine biological IN at a single temperature. We chose -15°C, the temperature at which the geographic distribution of IN concentrations from B73 is presented. 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 Figure 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)."

Following Dr. Vali's suggestion, we will add a summary of the results of Parker et al. (1985):

"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 psycrophilic 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 (*Synedra* 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."

Comment 2

The results of Junge and Swanson (2008) do not show inhibition, as this paper states. Junge and Swanson found little activity for the several strains of bacteria and one virus isolated from Arctic ice-core and Antarctic ice samples raised nucleation temperatures above that of homogeneous nucleation but by only a few degrees Celsius. These results prove that the species tested do not make a significant contribution to atmospheric IN, and the discussion provided in their paper assesses the importance of these findings very well. The paper deserves to be considered more carefully in the work here reported if only to better bound the range of possible sources of IN.

Response 2

We will correct our statement with regard to the results of Junge and Swanson (2008), thanks for pointing this out.

The results of Junge and Swanson (2008), Knopf et al. (2011), Alpert et al. (2011), and other similar studies describe the IN activity of particular microorganism species grown in laboratory cultures, but do not tell us anything about the concentration of those species in marine air, nor indeed necessarily about their ice nucleating properties after aerosolization in sea spray, which may differ from laboratory conditions. We may conclude from these studies that certain marine microorganisms act very weakly as IN, and that some samples of marine water and biological particulates contain strong IN, while others contain very few or very weak IN. It is impossible to extrapolate from those studies to any conclusion about marine biological particles as IN in general. There could easily be any number of other, highly IN-active strains of marine microorganisms that have simply not yet been tested (as is also pointed out, for example, by Junge and Swanson, 2008). Our analysis suggests that there may be on the order of 1 IN per 1000 marine bacteria based on the scaling factors presented in Table 1. Alternately, one may compare observed IN concentrations in seawater ($\leq$.2 to about 350 per cm^3 at -15°C ; Figure A1, Rosinski et al., 1988; Schnell and Vali, 1977), with median bacteria concentrations in seawater (about 4×10^6 per cm^3 ; Li et al., 2004), this would suggest 1 IN per $> 10^4$ marine bacteria. Therefore, if they are indeed marine microorganisms, the IN could very easily be a very minor component of the marine microflora that has not yet been specifically tested. Junge and Swanson (2008) "considered marine psychrophiles to be good candidates for high-temperature INA, since they are abundant in polar waters and sea-ice" (INA=ice-nucleation active [particles]), but the rarity of marine IN would seem to suggest that any marine bacterial species that makes up a significant fraction of the microbiota is unlikely to be highly IN active, since IN concentrations in seawater would then exceed those observed. We will add a sentence to the revised manuscript pointing this out.

Furthermore, while laboratory studies have generally focused on marine microorganisms as potential IN, it seems a very plausible hypothesis that biologically-associated particles other than microorganisms (e.g. waste products, exopolymer secretions) may

act as ice nuclei. The association of IN counts in the atmosphere with biological activity in the ocean seems to point to some biological marine IN source, but it is not necessarily due to microorganisms, which indeed make up only a very small fraction of the organic particulate matter in ocean surface waters.

For these reasons, we did not attempt to use the results of laboratory measurements of the IN activity of individual species to derive our estimate of marine biological IN emissions. Because we did not make direct use of them, we also do not discuss them in detail in our manuscript, which focuses on source estimation.

For clarity, we will replace the term "biological" with "biogenic" throughout when referring to the hypothesized marine source, and will also add a brief introductory section discussing the types of biological and biogenic particles that are found in the ocean and the marine aerosol:

"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."

Li, W., Head, E., and Glen Harrison, W.: Macroecological limits of heterotrophic bacterial abundance in the ocean, Deep-Sea Res. I, 51, 1529-1540, 2004.

Comment 3

It would be helpful to more emphatically differentiate the two lines of evidence pointing to the possible role of biogenic IN, namely samplings of source material and IN counts in the atmosphere. The latter line of study relies on measurements taken at low temperatures due to limitations of instrumentation, it uses correlations or chemical analyses to examine the biogenic link. Those are important weaknesses, yet these measurements constitute more direct data on what is in the atmosphere than source identifications. The paper would benefit from a discussion of the pro and cons of the two approaches.

Response 3

We will follow Dr. Vali's suggestion and emphasize this distinction more strongly in a revised manuscript.

Comment 4

The limitations of atmospheric IN measurements are widely documented specially when referring to methods used several decades ago. Section 3.6 addresses this issue reasonably well but can hardly do justice to such a complex problem. In any case, it would seem prudent to acknowledge these large uncertainties early on and not allow readers to be misled by the relatively narrow ranges specified in Table 1 for the scaling factors.

Response 4

We do not intend to provide a full discussion of the uncertainties involved in ice nucleation measurements, since these are well-documented elsewhere and beyond the topic of this manuscript, but we will mention these uncertainties earlier in the paper, and refer to the more in-depth discussion in Section 3.6. In addition, to help the reader locate more comprehensive information about IN measurement methods and instru-

mentation, we also will add a reference to the recent review by DeMott et al. (2011, BAMS).

With regard to the uncertainties, we would like to point out that the ranges specified for the scaling factors in Table 1 are unrelated to the range of uncertainty for IN counts from filter measurements. They refer to an independent, "bottom-up" approach to estimating emissions of biological IN under the hypothesized emission model. The results seem to be broadly consistent, within the range of uncertainties, with IN counts from filter measurements, but IN counts were not used to derive the scaling factors.

Comment 5

pg 4374 ln 4 and pg 4375 ln1: While 'anecdotal evidence' appears ever more frequently in the scientific literature, it is basically a self-contradictory expression and is certainly out of place in referring to previous data on marine IN. Those publications present data, not hearsay, and albeit incomplete, they are based on measurements.

Response 5

We will replace the phrase "anecdotal evidence" with "evidence from [a limited number of] field studies" in a revised manuscript.

Comment 6

pg 4376, ln 12: Contrary to what is said in the manuscript, Schnell (1975) states that some of the species tested were specific cultures.

Response 6

We intended to point out that Schnell (1975) tested samples of plankton cultures of

specific species, but could not unambiguously determine whether the plankton species were responsible for the IN activity, or some other particles associated with them. Schnell (1975) states: "It is not presently known whether the ice nucleating property of ODN is derived from intact or fragmented phytoplankton cells, excretion products, or some as-yet-unidentified organism associated with the phytoplankton, such as a marine bacterium, which may correspond to the terrestrial bacteria-derived nuclei (BDN) observed by Maki et al. (1974)." Fall and Schnell (1985) identified a bacterium that acted efficiently as a high-temperature IN in a sample of the marine dinoflagellate *H. niei*, but could not determine whether this bacterium was of terrestrial or of marine origin. Thus neither study was able to attribute efficient IN activity unambiguously to a marine microorganism. In contrast, Knopf et al. (2011) and Alpert et al. (2011) used axenic unialgal cultures, i.e. cultures cloned from a single individual and uncontaminated by other organisms, and cultures were washed and resuspended before testing. The IN activity therefore could unambiguously be attributed to a single marine species.

We will rephrase this statement in a revised version for improved clarity.

Comment 7

pg. 4376, ln 20: While Rosinski et al. (1987) indicate that some of the IN evaporated in vacuum they also say that the this does not exclude the possibility of biogenic origin of some component.

Response 7

Rosinski et al. (1987) states: "Aerosol particles in the 0.1-0.3 μm diameter size range ... were exposed to a vacuum of 10^{-6} mm Hg for 15 h at room temperature. ... The IFN were not detected on filters. This means that the aerosol particles nucleating ice are chemical compounds which evaporated from the surface of filters. Consequently,

they cannot be bacteria or proteins." (p. 303, lns 6 - 11). "... These compounds may, however, be produced by bacteria." (p. 308, ln 5)

On pg. 4376, ln 19-21, we wrote: "IN collected over the remote Pacific Ocean were found to evaporate completely in a vacuum, suggesting that they were not microorganisms (Rosinski et al., 1987)."

We will amend this sentence to point out explicitly that a biogenic origin was not ruled out: "IN collected over the remote Pacific Ocean by Rosinski et al. (1987) 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."

Comment 8

The Rosinski et al. references are mistakenly cited as J. Atmos. Sci. whereas they should be J. Aerosol Sci.

Response 8

Thanks, we have corrected this.