Addressing the ice nucleating abilities of marine aerosol: A combination of deposition mode laboratory and field measurements

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Abstract

This study addresses, through two types of experiments, the potential for the oceans to act as a source of atmospheric ice-nucleating particles (INPs). The INP concentration via deposition mode nucleation was measured in situ at a coastal site in British Columbia in August 2013. The INP concentration at conditions relevant to cirrus clouds (i.e., -40°C and relative humidity with respect to ice, $RH_{ice}=139\%$) ranged from 0.2 L^{-1} to 3.3 L^{-1} . Correlations of the INP concentrations with levels of anthropogenic tracers (i.e., CO, SO₂, NO_x, and black carbon) and numbers of fluorescent particles do not indicate a significant influence from anthropogenic sources or submicron bioaerosols, respectively. Additionally, the INPs measured in the deposition mode showed a poor correlation with the concentration of particles with sizes larger than 500 nm, which is in contrast with observations made in the immersion freezing mode. To investigate the nature of particles that could have acted as deposition INP, laboratory experiments with potential marine aerosol particles were conducted under the ice-nucleating conditions used in the field. At -40°C, no deposition activity was observed with salt aerosol particles (sodium chloride and two forms of commercial sea salt: Sigma-Aldrich and Instant Ocean), particles composed of a commercial source of natural organic matter (Suwannee River humic material), or particle mixtures of sea salt and humic material. In contrast, exudates from three phytoplankton (*Thalassiosira pseudonana*, *Nanochloris atomus*, and *Emiliania huxleyi*) and one marine bacterium (*Vibrio harveyi*) exhibited INP activity at low RH_{ice} values, down to below 110%. This suggests that the INPs measured at the field site were of marine biological origins, although we cannot rule out other sources, including mineral dust.

Key words: Ice nucleating particles, Cirrus clouds, Marine aerosol, Biological particles, Exudates

1 Introduction

Aerosol particles emitted by oceans can act as cloud condensation nuclei to form water clouds (Matrai et al., 2008; Orellana et al., 2011; and Karl et al., 2013); however, large uncertainties remain related to the role that the oceans play in ice cloud formation through ice-nucleating particle (INP) production. Ice clouds (mixed-phase and cirrus) can form via heterogeneous nucleation through different processes, such as immersion/condensation freezing, deposition nucleation, and contact freezing (Vali, 1985). The formation of mixed-phase and cirrus clouds at temperatures above -38°C or below water saturation requires the presence of INPs, with immersion freezing and deposition nucleation being the most likely ice nucleation pathways, respectively (Hoose and Mohler, 2012; and Murray et al., 2012). Even though ice clouds have been recognized to play a key role in the global radiative balance and hydrological cycle (Lohmann and Feichter, 2005; and IPCC, 2013), a better understanding of the ice nucleation mechanisms and the sources of INPs is needed to reduce uncertainties in regional and global climate model predictions.

Although many studies have observed INPs above the oceans (Bigg, 1973; Schnell, 1974; Schnell and Vali, 1975; Schnell and Vali, 1976; Schnell, 1982; Rosinski et al., 1987; Saxena and Weintraub, 1988; Rogers et al., 2001; Prenni et al., 2007; Prenni et al., 2009b; and Mason et al., 2015), the ubiquity of oceanic sources of biological INPs was not clear until recently (DeMott et al., 2010b; Wilson et al., 2015; DeMott et al., 2015). Such INP measurements are mostly relevant only to mixed-phase clouds as the sampling temperatures have been above -30°C and nucleation is typically at water saturation (Burrows et al., 2013). Even so, the INP concentration in marine environments at temperatures relevant to mixed-phase clouds is very poorly constrained, with estimates ranging over many orders of magnitude, from 0.001 to 1000 L^{-1} (Burrows et al., 2013). There is also evidence that heterogeneous nucleation can occur in the cirrus cloud regime (Strom et al., 2003; Jensen et al., 2010, 2012; Cziczo et al., 2013; Cziczo and Froyd, 2014), but marine INP concentrations at temperatures relevant to cirrus clouds are unknown.

The composition of primary marine INPs, that is, the specific types of aerosol from which they form, remains unclear. Past studies, both field observations and laboratory studies, have found evidence that INPs can form from both inorganic and organic materials, including biological cells and their components (see references within Hoose and Mohler, 2012). In addition, secondary particles can be formed by gas-to-particle conversion and gases can condense onto primary particles having the potential to act as INPs as well. Cziczo et al. (2013) and Cziczo and Froyd (2014) found that sodium chloride constituents were present in ice crystal residues sampled from cirrus clouds over the open ocean, and DeLeon-Rodriguez et al. (2013) showed that oceanic bacteria can be transported to the upper troposphere by convective activity, suggesting a role of particles of marine origin throughout the troposphere. Indeed, through laboratory experiments, Wise et al. (2012) and Wagner and Mohler (2013) found that NaCl particles are able to nucleate ice via deposition nucleation at temperatures relevant to cirrus clouds. Schill and Tolbert (2014) also found that commercially available sea salt (Instant Ocean Aquarium Sea Salt, ISS) and ISS mixed with sucrose are able to nucleate ice in the cirrus regime. The addition of sucrose to ISS attempted to mimic the composition of the sea-spray aerosol particles thought to be composed of both sea salt and organic matter (Blanchard, 1964; O'Dowd et al., 2004; Yoon et al., 2007; Russell et al., 2010; Vignati et al., 2010; Prather et al., 2013). As summarized by Burrows et al. (2013), marine microorganisms, exopolymer secretion (EPS)

aggregates, and dissolved organics are possible constituents of the primary oceanic particles formed by bubble bursting and wave activity (primary particles). Studies by the Knopf group showed that cells (or their fragments) of the phytoplankton species *Thalassiosira pseudonana*, *Nannochloris atomus*, and *Emiliania huxleyi* nucleate ice via deposition nucleation and immersion freezing over a wide range of temperatures (Knopf et al., 2011; Alpert et al., 2011a,b). More recently, Wilson et al. (2015) found that sea surface microlayer (SML) samples collected at three different ocean locations contained INPs which were able to nucleate ice via immersion freezing and deposition nucleation. Additionally, they found that the SML was enriched in INPs compared to sub-surface waters, and suggested that the SML INPs have biogenic origins.

A number of modelling studies (Burrows et al., 2013; Yun and Penner, 2013; and Wilson et al., 2015), have demonstrated that marine aerosol could contribute significantly to INP concentrations in remote regions, including the Southern Ocean, the North Pacific Ocean, and the North Atlantic Ocean. As well, those studies also modelled the cloud and climate impacts, identifying a lack of experimental data in ocean regions, especially under cirrus cloud conditions, and a need for more field studies in marine environments, as well as laboratory studies using aerosol particles from marine origins.

In this study, we address the INPs that may exist in marine settings both by measuring ambient deposition INPs at a coastal location and by studying in the laboratory the ice-nucleating properties of particles that are possible constituents of a marine atmospheric environment. This work was conducted under the NETCARE project, i.e. the Network for Climate and Aerosols: Addressing Uncertainties in Remote Canadian Environments. Specifically, the ice-nucleating activity of the different aerosol types was studied under cirrus cloud conditions using the University of Toronto continuous flow diffusion chamber (UT-CFDC). Our results are relevant to particles transported from the ocean into cold atmospheric environments, such as the upper troposphere or the winter/spring polar boundary layer.

2 Methods

2.1 Field measurements

The ambient INP concentration was measured at a coastal location between August 5 and 13, 2013, about 100 m from the ocean. The sampling trailer shown in Figure S1 was situated about 2 km from the center of Ucluelet, British Columbia (population 1600) which is on the west coast of Vancouver Island (48.92°N, 125.54°W, Figure 1). More details on the sampling site are given in Yakobi-Hancock et al. (2014) and Mason et al. (2015), as both studies were conducted in parallel to the present study. The INP concentrations were measured using the UT-CFDC (Kanji and Abbatt, 2009) at $RH_{ice}=139\pm3\%$ and $-40.0\pm1.0^{\circ}\text{C}$. The absolute uncertainty in the relative humidity in the UT-CFDC originates from the comparison of the supersaturation measured by thermocouples in the plates and the conditions observed for homogeneous freezing. Particles that grew to at least $5.0\text{ }\mu\text{m}$ were classified as INPs, as measured by the signal from the large channel of the optical particle counter (OPC, CI-20) used in the UT-CFDC.

Figure 2a shows the field experimental setup. Most of the instrumentation in Figure 2a was in the main trailer situated 100 m away from the shore (Figure S1), with the exception of the gas analyzers (SO_2 : Teledyne API T100U, NO_x : Thermo Fisher Scientific 42i, CO : Thermo Fisher Scientific 48i-TL, and O_3 : Thermo Fisher Scientific 49i), the aerosol chemical speciation monitor (ACSM, Aerodyne; Ng et al. 2011), and the multi-angle absorption photometer (MAAP; Thermo Scientific, 5012), which were in a separate trailer 10 m closer to the shore (the “Environment

Canada" trailer in Figure S1). The UT-CFDC and the wideband integrated bioaerosol sensor (WIBS-4A, DMT) had dedicated sampling lines, whereas the cloud condensation nuclei counter (CCNC, DMT 100), and the scanning mobility particle sizer (SMPS, TSI 3080) shared the same line. As described in Yakobi-Hancock et al. (2014), the UT-CFDC sampling inlet consisted of two meters of vertical 1/2" OD stainless steel tubing installed on the trailer's roof with an intake about 25 m above sea level. Aerosol particles larger than 1 μm were removed by an impactor (TSI 1035900) prior to the diffusion dryers. The tubing after the impactor was 1/4" OD stainless steel. In a few cases, short lengths (ca. 20 cm) of 1/4" ID conductive black tubing were used. Water on the aerosol particles was removed by two silica gel dryers, which were dried every 24 hours. The flow through the inlet was 0.3 L min⁻¹.

Fifteen-minute background measurements for the CFDC were collected every 30 minutes by placing a filter at the sampling inlet outside the trailer (i.e., 15 minutes of background measurements alternated with 15 minutes of sampling). The particle counts for the 15-minute sampling intervals were averaged and the average background from the previous 15 minutes was subtracted. The size of the background signals varied between 0.01 and 1.4 L⁻¹. Only those data points with background values equal to or smaller than 1/3 of the sampling counts were taken into account. The corresponding standard deviations are represented by the error bars. Particle growth calculations for a deliquesced 2.0 μm aerosol particle (assuming the efficiency of the PM1 impactor is not 100%) indicate that it will grow to a size less than 3.0 μm at water saturation (Rogers and Yau, 1989), which is below the lower detection limit of the OPC large channel. Thus, ambient particles that grow in the chamber and do not nucleate ice do not interfere with ice particle identification. Particle losses at the sampling inlet were estimated to be smaller than 5% and 2% for 1.0 μm and 0.5 μm particles, respectively.

The sea surface temperature (SST) was measured by Fisheries and Oceans Canada, at two different locations: Amphitrite Point (48.55°N 125.32°W) and the C46206 buoy (48.83°N 126.00°W). At Amphitrite Point surface water was collected with a bucket within 1 hour of the daytime high tide, and the temperature was measured using a thermometer with a scale division of 0.1°C. At the buoy, the SST was measured continuously and averaged on an hourly basis. The water salinity was measured in parallel with the SST at Amphitrite Point. As described in Mason et al. (2015), the relative humidity, temperature, wind direction, and wind speed were measured at the Amphitrite Lighthouse situated ca. 50 m from the trailer. The wind direction and the wind speed were measured with a wind monitor (Model 05305L) manufactured by RM Young (Traverse City, MI), and the relative humidity and temperature were measured using a Vaisala Inc. probe (HMP45C). For more details about the sampling site and related instrumentation, refer to Yakobi-Hancock et al. (2014) and Mason et al. (2015).

2.2 Laboratory experiments

Deposition ice nucleation experiments with sodium chloride (NaCl), sea salt (SS, Sigma-Aldrich, purity level >99.5%), Instant Ocean Aquarium Sea Salt (ISS, Instant Ocean), and natural organic matter (NOM, Suwannee River Humic Material from the International Humic Substances Society) particles were largely conducted at -40°C in the UT-CFDC. See Kanji and Abbatt (2009) for details on the instrument. A few experiments were conducted down to -52°C. The Suwannee River NOM was used as a proxy of organic material as it is a standard reference material used for humic acids, fulvic acids, and natural organic matter (Serkiz and Perdue, 1990). Its similarity to genuine oceanic organic matter is not established. Typically, 5 mg of NaCl, SS, ISS, or NOM were dissolved in 50 mL of 18.2 M Ω cm ultrapure water. Equal amounts of SS or ISS were mixed with NOM and dissolved in 50 mL of 18.2 M Ω cm ultrapure water.

Three phytoplankton species (*Thalassiosira pseudonana*, *Nanochloris atomus*, *Emiliania huxleyi*) were cultured in growth media prepared with ISS at a 36 g L⁻¹ concentration (similar to seawater salinity). *T. pseudonana* and *N. atomus* were grown in f/2 medium and *E. huxleyi* in f/50 medium (Guillard and Ryther, 1962). One bacterial species (*Vibrio harveyi*) was grown in a modified marine broth (TY/100) prepared with 5 mg tryptone and 1 mg peptone in 100 mL ISS and filtered through a 0.1 µm filter to sterilize and remove precipitates. The exudates from the phytoplankton and bacteria (likely mostly exopolymer secretions, but also possibly some cellular debris) were separated from cells and size fractionated using 0.8, 0.2, and 0.1 µm Whatman Nuclepore Track Etched Membrane Filters. The exudates were kept at -80°C to prevent enzymatic degradation. Control experiments were also conducted with uninoculated growth media. Additional controls with filtered air were conducted for the experiments with salts, NOM, and exudates.

The experimental setup is the same as that used by Yakobi-Hancock et al. (2013). Briefly, as shown in Figure 2b, aerosol particles were generated with an atomizer (TSI 3076) and the relative humidity was lowered with two silica gel dryers to below 2%. Dry aerosol particles were size selected with a differential mobility analyzer (DMA, TSI 3081). Although 200 nm particles were size-selected for the NaCl, NOM, SS, ISS, SS/NOM, and ISS/NOM experiments, 500 nm particles were size selected for the exudate experiments, because the particle concentration at lower sizes was higher than the upper detection limit of the condensation particle counter (CPC, TSI 3010). The particle concentration could have been further reduced by diluting the sample with water; however, as this may have modified the ice-nucleating properties of the particles, 500 nm sizes were used. The large particle channel in the CFDC OPC (>5 µm) was used to detect ice formation to avoid interference from water uptake and deliquesced particles. Similar to the 2.0 µm deliquesced ambient particles, a deliquesced, triply-charged, 500 nm aerosol particle will grow to a size below 2.0 µm at water saturation. A dilution system similar to that used in Wilson et al. (2015) was added during the exudate experiments (Figure 2b) to keep the total particle number concentration sufficiently low. Typical concentrations of particles entering the CFDC ranged between 100 and 200 cm⁻³.

3 Results and Discussion

3.1 Ice-Nucleating Particle Field Measurements

The ambient INP concentration was measured at Ucluelet for nine days at times ranging from 11:43 to 20:36 Pacific standard time (PST) at -40°C and RH_{ice}=139%. As shown in Figure 3, the INP concentration varied from 0.2 L⁻¹ to 3.3 L⁻¹.

To assess the source of the sampled air, back trajectories were calculated for 72 h transit times using HYSPLIT (the National Oceanographic and Atmospheric Administration, Stein et al., 2015). The nine back trajectories (see Figure 4) indicate that the air masses at Ucluelet during the sampling period were largely from the northwest and of coastal origin, with no significant continental influence. The area to the north of Ucluelet is largely unpopulated, although there are isolated logging operations, small communities, recreational sites, and some shipping in the region. The altitude dependence of the trajectories (see Figure S2) illustrates that all air masses had been in the boundary layer for three days prior to arrival at the sampling site. We grouped the trajectories into two sub-groups (high INP, with a daily average INP concentration > 1.0 L⁻¹, and low INP, with a daily average < 1.0 L⁻¹). Figure S2 shows that the back trajectories for the high INP concentration period (August 5-6 and August 12-13) were all at very low altitudes, close to the sea surface, whereas the back trajectories for the low INP period (August 7-11) had a tendency towards higher altitudes. This is consistent with a surface source of INPs, but the correlation is not robust given questions about the ability of HYSPLIT to resolve trajectory

altitudes with the required precision. Additionally, the land-sea breeze close to the sampling site has the potential to influence the back trajectory calculations.

The wind direction and the wind speed time series, alongside the INP concentrations, are shown in Figure S3. The corresponding r^2 values for correlations with INP concentration are low, i.e., 0.20 and 0.054 for wind speed and wind direction, respectively. Most of the time the sampled air was coming from the northwest (i.e., from the coastal Pacific Ocean), corroborating the data from the back-trajectories (Figure 4). The INP concentrations also do not closely follow the submicron aerosol particle concentrations measured with the SMPS (Figure S4), with r^2 values of only 0.031, 0.024, and 0.019 for correlations with total particle number, particle numbers larger than 300 nm, and particle numbers larger than 500 nm, respectively. By contrast, DeMott et al. (2010) showed that INP concentrations in the immersion mode correlated with particles larger than 500 nm. This relationship between particle and INP concentrations deserves further attention, given that information on INPs from the deposition mode at temperatures below -36°C is limited.

To assess whether there was an anthropogenic source for the deposition INPs we observed, we compared the INP concentrations with the CO , SO_2 , NO_x , and O_3 mixing ratios. The r^2 values of those correlations were all below 0.16, with weak negative correlations with SO_2 and NO_x (Figure S5). Similarly, the correlation with black carbon (BC) aerosol mass concentrations was very low (Figure S6). Therefore, it is unlikely that the measured INPs arose from local ship traffic emissions.

The poor correlation between the fluorescent particle concentrations measured by the WIBS and the INP concentrations (see Figure S7) indicates there may not be a strong influence of biological aerosols to the sub-micron INP population measured. This is in contrast with the results shown by Mason et al. (2015), who found a good correlation between super-micron fluorescent bioaerosol concentrations and INPs (ranging from 200 nm to 10 μm) measured in the immersion freezing mode. However, note that the WIBS collection efficiency is poor at particle sizes smaller than 800 nm (Healy et al., 2012), and the use of a PM1 impactor upstream of the CFDC limits the overlap of particle size. Thus, most of the fluorescent particles detected by the WIBS will not be detected by the CFDC. A direct comparison between the INPs reported in Mason et al. (2015) and the INPs from the present study is not possible given that the Mason et al. (2015) study focused on immersion freezing at temperatures ranging from -15°C to -30°C . This is in contrast with our measurements that were conducted under deposition nucleation conditions at -40°C .

The ambient INP concentrations were also not correlated with other variables, such as seawater salinity, precipitation, sea surface temperature, and cloud condensation nuclei concentration (see Yakobi-Hancock et al. (2014) for the CCN measurements). Correlations between all these variables and INP concentrations had low r^2 values (Table S1) aside from the value for sea surface temperature at the shore.

3.2 Ice Nucleation Ability of Phytoplankton and Bacterial Exudates

A set of laboratory experiments was conducted to investigate the ice-nucleating abilities of particles likely to be present in a marine environment, using the same operating conditions for the UT-CFDC as those employed in Ucluelet. Knopf et al. (2011) and Alpert et al. (2011a) showed that diatom cells can nucleate ice. Following this, Wilson et al. (2015) demonstrated that the ice-nucleating abilities of *T. pseudonana* cells and their exudates are very similar in the immersion mode. Furthermore, Alpert et al. 2011b showed that *N. atomus* cells induced immersion freezing and deposition ice nucleation and that *E. huxleyi* cells were less efficient

inducing immersion freezing than deposition ice nucleation for temperatures covering cirrus and mixed-phase cloud conditions. Additionally, examining aerosol from mesocosm experiments, Prather et al. (2013), Wang et al. (2015), and Schill et al. (2015) also identified ice-nucleating particles which could potentially be important in cloud formation. The exudates of marine species (e.g., phytoplankton and bacteria) likely have a greater potential to influence ice cloud formation at high altitudes since the intact cells from which they came have larger sizes, which may not be transported as efficiently to higher altitudes. For this reason, the ice-nucleating abilities of exudates from three different phytoplankton species (*T. pseudonana*, *N. atomus*, *E. huxleyi*) and a marine bacterium (*V. harveyi*) were investigated in the deposition mode.

The four exudates were found to nucleate ice at -40°C at RH_{ice} values well below the homogeneous freezing line. In general, ice was detected at RH_{ice} values as low as 105%, but with very low activated fractions, between 10^{-5} and 10^{-4} . The average activation scans from four to eight experiments are shown in Figure 5 and indicate that the *T. pseudonana* and *N. atomus* exudates are slightly better at nucleating ice, compared to the other two exudates (*E. huxleyi* and *V. harveyi*). The activation curves varied from one run to another, but in all cases were significantly higher than the activation curves for the control of growth media mixed with ISS. Thus, we are confident that neither the sea salts nor the organic matter present in the growth media are responsible for the ice nucleation. Although ice was observed at very low RH_{ice} in the biological samples, the fraction of the ice active material is very low compared to other INPs such as mineral dust. This can be seen in the shape of the activation scans shown in Figure 5. The variability in the nucleation from scan to scan is likely due to varying fractions of the ice-nucleating material in the particles generated from the atomizer.

We did not observe a clear difference in the behavior of the exudate samples filtered through different pore-size membranes, as shown in Figure 6 for *T. pseudonana* and *N. atomus*. Presumably this is because the nucleating substances are less than $0.1\text{ }\mu\text{m}$ in size. This is also in agreement with Wilson et al. (2015), who found that the ice-nucleating activity of SML samples in the immersion mode was significantly suppressed only when filtered through a $0.01\text{ }\mu\text{m}$ pore size, with significant activity remaining for larger pore sizes.

3.3 Ice Nucleation Ability of other Relevant Marine Aerosol Types

The -40°C activation onsets (0.01% activation threshold, 200 nm particles) of NaCl, Sigma-Aldrich sea salt (SS), Instant Ocean sea salt (ISS), natural organic matter (NOM), and mixtures (SS/NOM and ISS/NOM) were 142.4%, 142.6%, 140.8%, 143.0%, 144.6%, and 142.1% respectively (See Figure 7). The corresponding value for homogeneous freezing of 200 nm particles is 145.5% (Koop et al., 2000). Because all species showed very abrupt activation curves, within a few percent of the homogeneous freezing line, allows us to conclude that each of these samples froze homogeneously under these conditions. Indeed, the fact that these species all froze under such similar conditions indicates that the RH's reported in this work, calculated from observed temperatures in the CFDC plates, are likely to be biased by approximately 3%.

The high RH_{ice} onsets for particles composed of marine salts, natural organic matter and mixtures of salts with NOM indicate that they are all unlikely to have acted as INPs in the Ucluelet field measurements. However, the exudates could be the source of the measured INPs, given that they exhibited ice-nucleating activity much lower than the homogeneous freezing value. To examine consistency with the field measurements, we perform a back-of-the-envelope calculation to compare the sub-micron organic aerosol loading measured at Ucluelet to the ice nucleating properties measured in the lab for the exudates. In particular, the ACSM was operating for just one day, August 13, coincident with the INP measurements. If we assume

that the organics measured on that day (average concentration of $1.0 \mu\text{g m}^{-3}$) arose from biological exudates with ice-nucleating properties similar to the exudates studied in the laboratory, we predict that an INP concentration of 1.5 L^{-1} would have been measured, very close to the measured value of between 1.0 to 1.6 L^{-1} . Thus, this calculation is consistent with exudates as the source of the measured INPs. We note that there are many assumptions in this simple calculation that limit what can be concluded, i.e., that the organics in the field particles are all primary and that the laboratory particles contain only exudate material (and no sea salt or growth media).

Although our focus was on the ice nucleation properties of marine aerosol particles at -40°C , we also performed experiments with the same aerosol types at lower temperatures, for comparison to previous studies. Figure 7 summarizes the RH_{ice} onsets at temperatures ranging from -38°C to -54°C . At low temperatures, NaCl and ISS were found to nucleate ice below the homogeneous threshold, because they do not deliquesce before ice nucleation occurs. The onsets reported in this work are higher than those reported by Schill and Tolbert (2014) and Wise et al. (2012), using deposited particles, likely because of the definition of onset for the different experimental techniques used. Our results are closer to those of Wagner and Mohler (2013), who used suspended particles in the AIDA chamber (with an ice active fraction of 1.0% when using an ultrasonic nebulizer for particle generation).

The ice-nucleating properties of these salt particles are lower than other particle types that have been measured using the same UT-CFDC approach, such as some mineral dusts, including feldspars (see Yakobi-Hancock et al. 2013). In contrast, the heterogeneous ice-nucleating abilities of SS and NOM, and the ISS/NOM and SS/NOM mixtures were low, with RH_{ice} onsets close to the homogeneous freezing line. The suppression of the heterogeneous nucleation of ISS by mixing it with NOM is consistent with organics generally being poor INP (Prenni et al., 2009a; Cziczo et al., 2013; and Ladino et al., 2014), as they have previously been shown to suppress the ice-nucleating abilities of mineral dust and ammonium sulfate (Mohler et al., 2008; Ladino et al., 2014; and Schill et al., 2014).

Similar to a CFDC system a controlled vapor cooling-stage microscope system can be used to derive deposition ice nucleation parameters such as active sites or heterogeneous ice nucleation rate coefficients (e.g., Dymarska et al., 2006; Kanji and Abbatt, 2006; Alpert et al., 2011a, b; Knopf et al., 2011; Wang and Knopf, 2011; Wang et al., 2012). However, meaningful comparison between CFDC and cooling-stage derived temperature and RH_{ice} onsets, necessitates similar activated fractions (AFs). If AFs are in the same order of magnitude, agreement between CFDC and cooling stage data has been demonstrated (Wang and Knopf, 2011). Agreement among these instrumentation is also achieved for the case for immersion freezing experiments as discussed in a recent instrument intercomparison study by Hiranuma et al., (2015) and Knopf and Alpert (2013). Keeping the limitation of similar AF in mind, we compare our exudate RH_{ice} onsets with those reported by Knopf et al. (2011) and Alpert et al. (2011b) for phytoplankton cells or their fragments. Alpert et al. (2011b) reported AF values ranging from 5×10^{-4} to 4.4×10^{-3} representing a similar order of magnitude as the AF values reported here. Their RH_{ice} onsets for *T. pseudonana*, *N. atomus*, and *E. huxleyi* cells or their fragments varied between 128% and 149%, with mean values of 131%, 135%, and 130%, at $\sim -38^\circ\text{C}$, respectively. We found that the RH_{ice} onsets for the *T. pseudonana*, *N. atomus*, and *E. huxleyi* exudates varied between 105% and 150%, with mean values of 120%, 123% and 128%, respectively. From this comparison we can conclude that the present results are in agreement with those of Wilson et al. (2015) who showed that the phytoplankton cells (or their fragments) and their exudates hold similar ice-nucleating properties in the immersion freezing mode.

4 Conclusions and Atmospheric Implications

To our knowledge, these are the first measurements of the concentration of ice-nucleating particles under deposition mode in a coastal setting that is influenced by marine air. We observed INP concentrations up to 3.3 L^{-1} at operating conditions of -40°C and $\text{RH}_{\text{ice}}=139\%$. Assigning the source of the INPs is difficult, given their weak correlations with a number of observables (Figures S3-7) and a lack of detailed simultaneous chemical composition measurements. However, there is no indication that anthropogenic sources contributed significantly, given that no strong correlations exist with a number of pollution tracers (NO_x , SO_2 , BC). Instead, the HYSPLIT trajectories indicate a source of marine boundary layer air. We clearly cannot rule out the contribution of efficient terrestrial INPs, such as mineral dust, but an interesting possibility is that primary marine particles are acting as INP, especially given the low altitudes of the back trajectories when INP concentrations were highest.

Following this line of thought, recent experiments have demonstrated that the sea surface microlayer contains particles with high ice-nucleating efficiency that have the potential to become primary marine particles (Wilson et al., 2015). As well, the exudates from phytoplankton have been shown to efficiently nucleate ice in the immersion mode. This observation, along with the field measurements, motivated the laboratory experiments, with the goal of exploring whether marine phytoplankton and bacterial exudates can also efficiently lead to ice nucleation in the deposition mode, and of determining whether non-biological particles of sea salts and natural organic matter could also act as deposition INPs.

The results from the laboratory experiments indicate that marine salt particles and a natural organic matter proxy are inefficient as heterogeneous INP, nucleating ice instead at the homogeneous threshold at -40°C . On the other hand, we show that a fraction of aerosol particles formed from biogenic exudates contain very efficient INPs in the deposition mode. In particular, exudates from representative marine species (*Thalassiosira pseudonana*, *Nanochloris atomus*, *Emiliania huxleyi*) and an exudate from a marine bacterium (*Vibrio harveyi*) nucleate ice via deposition nucleation at -40°C and at RH_{ice} below 110% with an activated threshold of between 10^{-5} and 10^{-4} . With ice active material smaller than $0.1 \mu\text{m}$, it is possible that the ice-nucleating activity is originating from exopolymers. These observations are consistent with those of Wilson et al. (2015), who found that the ice-nucleating activity of Arctic SML samples in the immersion mode remained until filtered through a $0.01 \mu\text{m}$ pore size filter. The small size of the ice active material in the exudate experiments could be the reason of the poor correlation that we found between the ambient deposition INPs and the predicted INPs using DeMott's et al. (2010) parametrization. We also note that whereas our measurements are of deposition INPs that are sub-micron in size, the work performed at the same campaign by Mason et al. (2015) identified biological ice-active particles in the immersion mode, but much larger in sizes in the supermicron range.

In summary, this work presents evidence that the metabolic activities of marine microorganisms have the potential to contribute to ice cloud formation. However, their importance is far from being established, especially in the deposition mode. On one hand, Cziczo et al. (2013) found that the contribution of bioaerosols to the formation of cirrus clouds was negligible, as no signs of biogenic particles were observed in the residuals of ice crystals at high altitude. On the other hand, field observations have shown the presence of biological material in ice residuals and precipitation (Christner et al., 2008; Pratt et al., 2009; Creamer et al. 2013). Additionally, modeling suggests that INPs of an oceanic source have the potential to be most important in remote areas (e.g., the remote Southern, the North Pacific, and the North Atlantic Oceans), where the presence of well-known INPs, such as mineral dust, is limited (Burrows et al., 2013; Yun and Penner, 2013; and Wilson et al., 2015). Finally, the source of deposition ice nuclei in

cold polar regions in the springtime, where ice nucleation plays an important role in climate regulation (Girard and Blanchet, 2001a; and Girard and Blanchet, 2001b), needs to be better determined, i.e., in particular the role of long-range particle transport from lower latitude sources, including biologically productive marine regions needs to be established.

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Fig. 1. West coast of Canada map indicating the sampling location (red star). The map was obtained from Googlemaps.

Fig. 2. a) Schematic of the main components of the experimental setup used for the field measurements, which included SO₂, CO, O₃, and NO_x monitors, a multi-angle absorption photometer (MAAP), an aerosol chemical speciation monitor (ACSM), a scanning mobility particle sizer (SMPS), a cloud condensation nuclei counter (CCNC), a wideband integrated bioaerosol sensor (WIBS), the University of Toronto continuous flow diffusion chamber (UT-CFDC), and the optical particle counter (OPC) (modified from Yakobi-Hancock et al., 2014). b) Laboratory experimental setup. DMA refers to the differential mobility analyzer and CPC to the condensation particle counter. The dilution system was only used for the exudate experiments.

Fig. 3. Time series of the ice-nucleating particle (INP) concentration measured outside Ucluelet, British Columbia during August 2013 at -40°C and $\text{RH}_{\text{ice}}=139\%$. The INP values are corrected for background counts (see section 2.1). Each X-axis tick corresponds to midnight (Pacific daylight saving time, PDT). The error bars represent the standard deviations of the INP concentrations over the 15-minute sampling interval, with the corresponding error-propagation when subtracting the backgrounds.

Fig. 4. 72-hour HYSPLIT back trajectories over the sampling period. The numbers in the brackets indicate the ending time (PDT) for the trajectory.

Fig. 5. Average activation scans of the 500 nm size-selected *Thalassiosira pseudonana* (blue), *Nanochloris atomus* (red), *Emiliana huxleyi* (black) and *Vibrio harveyi* (green) exudate particles at -40°C . The activated fraction is defined as the number of ice crystals observed by the $5\text{ }\mu\text{m}$ channel of the OPC connected to UT-CFDC divided by the number of particles entering the CFDC, accounting for dilution. The control experiments conducted with a solution made of Instant Ocean sea salt and the growth media are represented by the orange stars. The error bars represent one standard deviation among replicate experiments, whereas the dotted black line represents the homogeneous freezing line at -40°C (Koop et al., 2000).

Fig. 6. Average activation scans for the a) *Thalassiosira pseudonana* (blue symbols), and b) *Nanochloris atomus* (red symbols) 500 nm phytoplankton exudate particles after filtration through three different pore

sizes (indicated in the legends). The orange stars are the control (see caption for Figure 5). Typically, two to three scans were obtained for each pore size.

Fig. 7. RH_{ice} onsets (activated fraction, AF, of 10^{-4}) of 200 nm sodium chloride (NaCl, green solid squares), Sigma-Aldrich sea salt (SS, black solid diamonds), Instant Ocean sea salt (ISS, blue solid stars), and natural organic matter (NOM, brown solid circles) as a function of temperature. The beige solid diamonds and the light blue solid stars are the onsets for the SS/NOM and ISS/NOM mixtures, respectively. The orange, red, magenta, light purple, and grey bars indicate the range over which the AF is 10^{-4} to 10^{-5} for the control and single exudate experiments which are averaged in Figure 5. The error-bars represent the lowest RH_{ice} values at $AF=10^{-5}$ and the highest RH_{ice} values at $AF=10^{-4}$ among the single scans for each material. Literature data are also plotted with open symbols, for comparison. Note that the Alpert et al. 2011b onsets correspond to the whole cells or their fragments (dotted colored bars), whereas the data from the present study are the onsets from the exudates only. The error bars are the standard deviation for each experiment. The solid black line is the water saturation line, whereas the dotted line is the theoretical homogeneous freezing line for 200 nm solution drops (Koop et al., 2000).