Geophysical Research Letters

RESEARCH LETTER
10.1029/2018GL079981

Observations of Ice Nucleating Particles Over Southern Ocean Waters

C. S. McCluskey[1,2], T. C. J. Hill[1], R. S. Humphries[3], A. M. Rauker[1], S. Moreau[4,5], P. G. Strutton[4,6], S. D. Chambers[7], A. G. Williams[7], I. McRobert[8], J. Ward[3,9], M. D. Keywood[3], J. Harnwell[3], W. Ponsonby[8], Z. M. Loh[3], P. B. Krummel[3], A. Protat[10], S. M. Kreidenweis[1], and P. J. DeMott[1]

[1]Department of Atmospheric Science, Colorado State University, Fort Collins, CO, USA, [2]Now at Advanced Study Program, National Center for Atmospheric Research, Boulder, CO, USA, [3]Climate Science Centre, CSIRO Oceans and Atmosphere, Aspendale, Victoria, Australia, [4]Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Tasmania, Australia, [5]Now at Norwegian Polar Institute, Fram Centre, Tromsø, Norway, [6]Australian Research Council Centre of Excellence for Climate Extremes, University of Tasmania, Sydney, New South Wales, Australia, [7]Environmental Research, ANSTO, Lucas Heights, New South Wales, Australia, [8]Engineering and Technology Program, CSIRO Oceans and Atmosphere, Hobart, Tasmania, Australia, [9]Now at School of Public and Environmental Affairs, Indiana University, Bloomington, Bloomington, IN, USA, [10]Australian Bureau of Meteorology, Melbourne, Victoria, Australia

Key Points:
- Number concentrations of ice nucleating particles over the Southern Ocean in March 2016 were a factor of 100 lower than historical surveys
- The ice nucleating particle source strength of Southern Ocean seawater was lower than previous measurements in northern hemisphere seawater
- Ice nucleation site densities were lower over the Southern Ocean compared to measurements of pristine air masses from other ocean basins

Supporting Information:
- Supporting Information S1

Correspondence to:
C. S. McCluskey,
cmcclus@ucar.edu

Citation:
McCluskey, C. S., Hill, T. C. J., Humphries, R. S., Rauker, A. M., Moreau, S., Strutton, P. G., et al. (2018). Observations of ice nucleating particles over Southern Ocean waters. *Geophysical Research Letters*, *45*, 11,989–11,997. https://doi.org/10.1029/2018GL079981

Received 9 AUG 2018
Accepted 15 OCT 2018
Accepted article online 17 OCT 2018
Published online 5 NOV 2018

Abstract A likely important feature of the poorly understood aerosol-cloud interactions over the Southern Ocean (SO) is the dominant role of sea spray aerosol, versus terrestrial aerosol. Ice nucleating particles (INPs), or particles required for heterogeneous ice nucleation, present over the SO have not been studied in several decades. In this study, boundary layer aerosol properties and immersion freezing INP number concentrations (n_{INPs}) were measured during a ship campaign that occurred south of Australia (down to 53°S) in March–April 2016. Ocean surface chlorophyll *a* concentrations ranged from 0.11 to 1.77 mg/m^3, and n_{INPs} were a factor of 100 lower than historical surveys, ranging from 0.38 to 4.6 m^{-3} at −20 °C. The INP population included organic heat-stable material, with contributions from heat-labile material. Lower INP source potentials of SO seawater samples compared to Arctic seawater were consistent with lower ice nucleating site densities in this study compared to north Atlantic air masses.

Plain Language Summary The Southern Ocean is known for a prevalence of clouds that contain both liquid and ice, which are one of the most poorly understood cloud regimes in the climate system. A large gap in understanding important processes in these clouds is a lack of knowledge regarding particles (e.g., sea spray) required for forming ice crystals, termed ice nucleating particles. In a ship-based monthlong field study, several instruments were deployed in efforts to characterize the ice nucleating particles present over the Southern Ocean for the first time in over four decades. Abundances of ice nucleating particles throughout the voyage were extremely low compared to other ocean regions, and concentrations were 2 orders of magnitude lower than the most recent survey conducted in the 1970s. We report that the ocean-derived ice nucleating particles observed in this study were organic in nature, supporting a hypothesized link between ice nucleating particles and organic particles associated with phytoplankton blooms. The data from this study provide a desperately needed benchmark for constraining the number of ice crystals that may form in the remote and poorly understood clouds occurring over the Southern Ocean.

1. Introduction

Southern Ocean (SO) cloud phase partitioning likely contributes to large shortwave radiative biases that impact climate sensitivity estimates in global climate models. (Tan et al., 2016). With a high prevalence of supercooled liquid clouds (Huang et al., 2015) and a lack of terrestrial aerosol sources, aerosol-cloud interactions are likely unique over the SO. Ice nucleating particles (INPs), particles required for heterogeneous ice formation, are a likely important and uncertain component for estimating cloud phase, lifetime, and radiative properties (Vergara-Temprado et al., 2018). Here the immersion freezing mode of ice nucleation is considered unless otherwise stated. Modeled estimates indicate that the organic component, associated with ocean biological activity, of sea spray aerosol (SSA) produced at the ocean surface via bubble bursting dominate the INP population over the SO (Burrows et al., 2013; Vergara-Temprado et al., 2017). This study

advances recent research regarding marine INPs by providing the first reported observations of INP composition and abundance over the SO in over four decades.

Bigg (1973, hereafter B73) reported a 3-year survey of SO INPs (20–75°S and 60–40°W) and found annual average number concentrations of INPs (n_{INPs}) active at −15 °C ranging over 3 orders of magnitude (3 to 250 m^{-3}). B73 speculated that aerosol transported from distant continents contributed to n_{INPs} variability, but source regions were never identified. Subsequently, Schnell and Vali (1976) showed that higher n_{INPs} reported by B73 were colocated with ocean regions preferential to enhanced biological activity (i.e., phytoplankton blooms) and reported higher ice nucleation activity in phytoplankton-rich seawater compared to seawater containing low phytoplankton concentrations, ultimately hypothesizing that biogenic INPs are emitted from biologically active ocean waters. Additional SO n_{INPs} measurements by Bigg (1990) revealed lower average n_{INPs} (0.20 ± 0.02 m^{-3}, 60–65°S) compared to the B73 survey, and Bigg (1990) suggested that SO n_{INPs} were decreasing, potentially due to changes in climate, weather systems, and transport. SO biology is diverse, and long-term changes are unknown due to limited historical chlorophyll *a* concentration (Chl *a*) data. Satellite observations since 1997 indicate that phytoplankton blooms start between October and February with annual mean Chl *a* up to 1 mg/m^3 (Ardyna et al., 2017). While dust concentrations are low over the SO (Jickells et al., 2005), the ice nucleation site density of mineral dust is several orders of magnitude greater than pristine marine aerosol (Niemand et al., 2012, McCluskey, Ovadnevaite, et al., 2018) and thus minimal amounts of transported dust may influence the INP population in this region. Modeling studies informed by historical measurements found that marine organic aerosol was likely the dominant INP source over the SO (e.g., Burrows et al., 2013). However, Burrows et al. (2013) also discussed uncertainties associated with the membrane filter INP measurement technique used in B73 and Bigg (1990) and the lack of modern knowledge regarding their abundance in the region, constituting a major limitation for evaluating the role of INPs (and their variability) in SO clouds.

Marine INPs linked to biological activity have been observed in laboratory and field measurements of SSA-impacted air masses (e.g., DeMott et al., 2016) and the sea surface microlayer (SML; Irish et al., 2017; Wilson et al., 2015). Rosinski et al. (1987) suggested that marine INPs were smaller than 0.5 μm and were not proteins or bacteria, while Schnell and Vali (1976) found marine INPs to be approximately 1 μm and from microbial source. Both the cell surface (Knopf et al., 2011) and exudates (Wilson et al., 2015) of a marine diatom species, *Thalassiosira pseudonana*, have been shown to be ice nucleation active. Wilson et al. (2015) also reported that ice nucleating entities (INEs, Vali et al., 2015) in North Atlantic and Arctic SML samples were smaller than 0.2 μm and positively correlated with total organic carbon. Irish et al. (2017) found that INEs in Canadian Arctic SML samples were smaller than 0.2 μm and heat labile. From laboratory mesocosm experiments, McCluskey, Hill et al. (2018) proposed that marine INPs comprised two types: (1) particulate organic carbon INPs (POC INPs) that are heat labile and larger than 0.2 μm and (2) dissolved organic carbon INPs (DOC INPs) that are refractory (i.e., heat stable) and smaller than 0.2 μm. Our understanding of the biological processes that control the production of INEs in seawater and the physicochemical processes that govern their release in SSA remains extremely limited. Applying marine INP parameterizations developed from specific ocean basins and seasons (McCluskey, Ovadnevaite et al., 2018Wilson et al., 2015) to global marine INP emissions remains a necessary, but uncertain, assumption due to a lack of direct observations, particularly over the SO. In this study, INP observations made over the SO, south of Australia, will be used to (1) provide observational constraints for numerical predictions of n_{INPs} and (2) investigate the composition of marine INPs in the SO region.

2. Methods

2.1. Project Overview

The Clouds, Aerosols, Precipitation, Radiation, and atmospherIc Composition Over the southeRN ocean (CAPRICORN) campaign was conducted from 13 March to 15 April in 2016 onboard the RV *Investigator* (voyage IN2016_V02), an Australian Government research platform operated by the Commonwealth Science and Industrial Research Organisation. The research voyage occurred south of Australia during the late Austral summer and early autumn seasons, shown in Figure 1. Chl *a* ranged from 0.11 to 1.77 mg/m^3 during CAPRICORN (Figure 1), representative of this region (Ardyna et al., 2017).

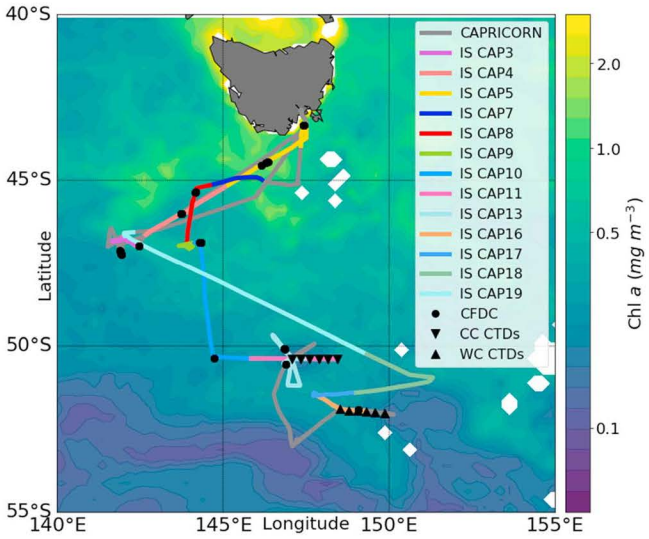

Figure 1. Map of the RV *Investigator* track south of Tasmania, Australia, during Clouds, Aerosols, Precipitation, Radiation, and atmospherIc Composition Over the southeRN ocean (CAPRICORN). Colors represent aerosol filter collection periods. Also shown are the location of Continuous Flow Diffusion Chamber (CFDC) measurements (filled circles) seawater collections from the nascent warm-core eddy (WC, upright triangles) and cold-core eddy (CC, upside down triangles). Contoured colors show the average ocean surface chlorophyll a concentrations from 13 March to 13 April 2016 (Moderate Resolution Imaging Spectroradiomete, https://oceandata.sci.gsfc.nasa.gov/MODIS-Aqua).

2.2. INP Observations

The Colorado State University (CSU) ice spectrometer (IS, Hiranuma et al., 2015) was used to determine INP number concentrations (n_{INPs}) active in the immersion freezing mode from particles collected onto filters onboard the RV *Investigator*. Aerosol particles were collected onto polycarbonate membrane filters in open-faced filter holders that were located approximately 23 m above the ocean surface. In efforts to avoid ship exhaust contamination, the IS pump was powered with a sector-specific sampler, where power was supplied to the pump when ship-relative wind direction was coming from the fore of the ship, that is relative wind directions larger than 270° and less than 90° (through 360). Additional analyses and consideration of exhaust influences are discussed in section 2.5. Blank filters were collected throughout the voyage and processed to account for instrument background. Sample collection periods ranged from 21 to 63 hr, corresponding to 19 to 55 m^3 (mean of 33 m^3, Table S1 in the supporting information) of sampled air. Samples were frozen (−20 °C) and kept frozen during shipping and before measurement at CSU. Impacts of prefreezing on marine samples have not been extensively studied, but previous studies have indicated limited effect of prefreezing samples (Hill et al., 2014; Polen et al., 2016). Following the methods of McCluskey et al. (2017), n_{INPs} were determined as a function of temperature based on Vali (1971). IS measurements uncertainties were described by binomial sampling confidence intervals (95%), according to Agresti and Coull (1998, formula 2). More details on IS measurements are provided in Text S1. Ice nucleation site density (n_s) was calculated using aerosol surface area estimated from a nephelometer (see Text S4 and Figure S3).

In situ INP measurements under conditions emphasizing immersion freezing were made using the CSU Continuous Flow Diffusion Chamber (CFDC), an online thermal diffusion chamber technique. During CAPRICORN, the CFDC operation conditions were such that the supersaturation with respect to water was 3–7.5% and temperature was <-25 °C in the sample lamina, calculated using the analytical equations given in Rogers (1988). Before entering the CFDC, sampled aerosol was dried using silica gel diffusion driers, and particles larger than 1.5 μm were removed via impaction, similar to McCluskey et al. (2017). Details regarding the design of the CFDC can be found in previous publications (Rogers, 1988; Schill et al., 2016). The n_{INPs} were determined following recent studies (Schill et al., 2016), and details are provided in Text S2. Briefly, instrument background (frost) was monitored regularly and subtracted from n_{INPs} measurements of sample air. Measurement standard deviations were calculated according to Poisson counting statistics (Taylor, 1997), and sample and background errors were propagated in quadrature. Data were considered statistically significant if n_{INPs} was greater than 1.64 times their error (i.e., Z statistic at 95% confidence interval for one-tailed distribution). An aerosol concentrator (MSP Corporation, Model 4240, Romay et al., 2002) was used upstream of the CFDC, as described by Tobo et al. (2013) and McCluskey et al. (2017), to increase the detection limit of the CFDC by enhancing concentrations of larger particles (those larger than 0.5 μm). Details regarding the aerosol concentrator, including the corrections and assumption involved, are provided in Text S2.

During CAPRICORN, CFDC measurements were made from the RV *Investigator*'s custom-designed air sampling inlet and a dedicated sampling line for the aerosol concentrator (both located approximately 18.4 m above sea level at the front of the ship). Details of the sampling inlets are provided in Text S2. We note here that particle transmission efficiencies associated with the sampling manifolds, and the dependences on wind conditions and ship motion, have not yet been fully characterized (Texts S1 and S2). Regardless, offline INP methods (IS) indicate agreement with CFDC data during CAPRICORN (Figure 2a), consistent with previous SSA measurements (DeMott et al., 2016).

2.3. INP Source Strength of SO

Conductivity temperature depth profiles were used to collect seawater (SW) samples for analyses; near-surface SW samples (collection depths of <15 m) were used for detection of INEs and Chl *a*. INEs were

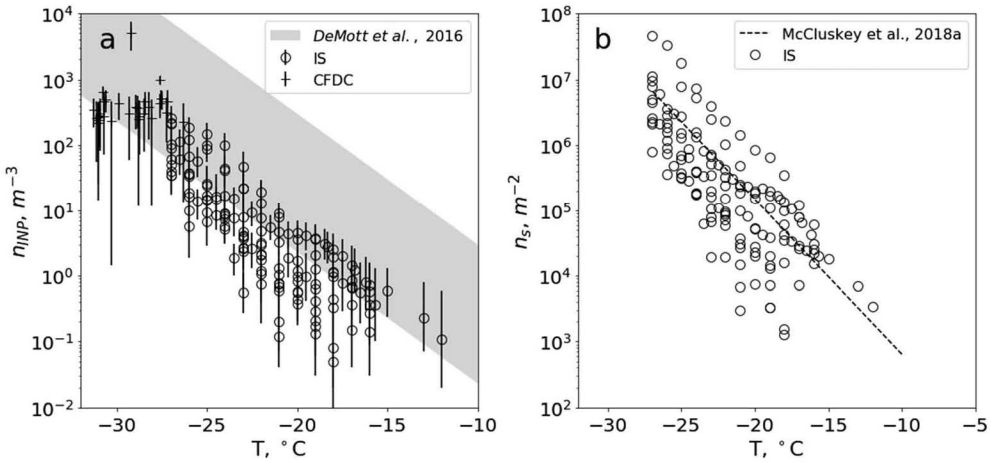

Figure 2. a) Ice nucleating particle (INP) temperature spectra from the Continuous Flow Diffusion Chamber (CFDC; crosses) and the ice spectrometer (IS) (circles) during CAPRICORN and from observations attributed to sea spray aerosol by DeMott et al. (2016; gray shaded area). (b) Ice nucleation site densities (n_s) for IS measurements during CAPRICORN (circles) and a parameterization for pristine North Atlantic air masses (dashed line; McCluskey, Ovadnevaite, et al., 2018). CAPRICORN = Clouds, Aerosols, Precipitation, Radiation, and atmospheric Composition Over the southeRN ocean.

determined using immersion freezing of aliquots of SW samples (stored frozen) and the IS. Chl *a* were measured using standard techniques (filtering and acetone extraction, Holm-Hansen et al., 1965; Lorenzen, 1966) with a Turner Trilogy fluorometer (Moreau et al., 2017). Satellite-derived ocean color (Moderate Resolution Imaging Spectroradiomete, https://oceandata.sci.gsfc.nasa.gov/MODIS-Aqua) was used to estimate ocean surface Chl *a* during CAPRICORN.

2.4. Offline Treatments of Aerosol and Seawater Ice Nucleating Material

Following the methodology from McCluskey, Ovadnevaite, et al. (2018) and McCluskey, Hill, et al., (2018), INP and INE identities were characterized by applying offline treatments to aerosol and SW samples. Heating (95 °C for 20 min) was used to determine contributions from heat-labile material. Contributions of organic INPs or INEs were determined using a hydrogen peroxide digestion (see McCluskey, Ovadnevaite, et al., 2018; McCluskey, Hill, et al., 2018). Finally, the sizes of INEs were investigated by filtering seawater with syringe filters (pore size 0.2 μm). These processed samples were reanalyzed in the IS to determine the difference in n_{INPs} or n_{INEs} due to the treatments, revealing size and composition information. More details can be found in Text S3.

2.5. Accounting for Ship Exhaust and Terrestrial Influences

Diesel-electric engines provided power and propulsion to the ship, and waste was incinerated while at sea. These activities emitted combustion products, including black carbon and other POC. While the IS pump was powered using a sector sampling strategy based on wind direction (section 2.2), ship exhaust was also characterized based on atmospheric composition measurements. Aerosol number concentrations (CN, condensation particle counter, CPC Model 3776, TSI), and mass concentrations of black carbon (BC, Multiangle Absorption Photometer, MAAP Model 5012, Thermo Fisher Scientific) were used to estimate possible contamination from ship exhaust.

Atmospheric radon (^{222}Rn) concentrations were measured using a 700-L dual flow loop two-filter detector (Chambers et al., 2014; Griffiths et al., 2016), built by the Australian Nuclear Science and Technology Organization and installed as part of the permanent suite of atmospheric instrumentation onboard the RV *Investigator*. With its predominately terrestrial source, unreactive nature, and 3.82-day radioactive half-life, radon is used as an unambiguous tracer of terrestrial influences on sampled air masses. For IS filter measurements, the contribution from exhaust and terrestrial sources was estimated by determining the average CN, BC, and ^{222}Rn concentration measured during the IS sampling periods.

3. Results and Discussions

3.1. INPs Measured During CAPRICORN

Temperature spectra from CFDC and IS measurements during CAPRICORN are shown in Figure 2a. The n_{INPs} ranged from 0.38 to 4.6 m^{-3} for INPs active at −20 °C, with an average concentration of 1.5 ± 1.4 m^{-3}. The ice nucleation activity of combustion particles is an active area of research (e.g., Schill et al., 2016; Thomson et al., 2018), and it is possible that these particles influenced measurements in this remote region (i.e., extremely low n_{INPs}). Thus, linear regression analyses between n_{INPs} and sample-averaged BC and CN concentrations (Figures S5 and S6) were conducted to investigate the influence of ship exhaust on measured n_{INPs}. While sample number is limited, the statistically insignificant relationship between n_{INPs} and BC and CN suggests that there was no influence of exhaust in these measurements. Observed n_{INPs} varied by over a factor of 10 across all temperatures, with a maximum observed variability at −23 °C (Figure 2a). As best could be discerned considering the modest overlap of sampling temperatures, n_{INPs} measured by the CFDC and IS were in good agreement, similar to previous studies (e.g., McCluskey et al., 2017). This agreement suggests that the aerosol sizes containing the majority of INPs were successfully transferred to the CFDC via the sampling inlet and concentrator inlet.

The CAPRICORN n_{INPs} are at the lower range of n_{INPs} reported for several Northern Hemisphere ocean regions during summertime (Chl *a* ranging from 0.1 to 3 mg/m^3; DeMott et al., 2016), also shown in Figure 2a. However, observed n_{INPs} from CAPRICORN were a factor of 100 lower (maximum n_{INPs} = 4.6 m^{-3} at −20 °C) than those reported by B73 (> 200 m^{-3} at −20 °C for −40°S to −55°S) and reasons for this discrepancy are discussed here. First, we note that the ability to detect extremely low levels of n_{INPs} is a result of an advanced understanding of materials that nucleate ice and advances in making artifact-free measurements of low concentrations of INPs. However, an assessment of contamination in the B73 survey was conducted (Text S5) and, while it is a possible contributor to the discrepancies between these studies, its influence appears to be modest. B73 reported gridded annual means of n_{INPs} based on 3 years of data, and thus, it is possible that a seasonal maximum may be missing from data reported here. In fact, B73 observed a maximum in n_{INPs} during Austral winter months; by contrast, modeling studies indicate a seasonal maximum of dust transport over the SO during Austral summer (Ito & Kok, 2017). Finally, barring any influences of the above-mentioned concerns regarding possible measurement artifacts, data from this study are consistent with a long-term decadal decline in n_{INPs}, proposed by Bigg (1990). Changes occurring in the SO have been explored from the point of view of oceanographers, revealing a statistically significant 10% decrease in iron (i.e., dust) deposition and a corresponding reduction in ocean biological activity between years 1997–2002 and 1979–1986 (Gregg et al., 2003), which may also induce a perturbation to INP sources. Dust INPs (e.g., Niemand et al., 2012) are 3–4 orders of magnitude more ice nucleation active than pristine marine aerosol (McCluskey, Ovadnevaite, et al., 2018), and, thus a 10% decrease in dust transport may be significant for SO INP populations. Additionally, INPs associated with organic aerosol arising from phytoplankton blooms (e.g., DeMott et al., 2016) may be lower in recent decades due to reduced iron fertilization. Regardless, evidence for such a decline in INPs is limited.

Normalizing the data by aerosol surface area to obtain the ice nucleation active site densities (n_s) indicates that n_s observed during CAPRICORN were similar to the n_s measured in Northeast Atlantic pristine marine air masses (Mace Head Research Station, MHD, McCluskey, Ovadnevaite, et al., 2018), shown in Figure 2b. Lower n_s observed during CAPRICORN compared to MHD may be due to persistently higher wind speeds present over the SO. While maximum annual wind speeds are similar over high latitudes in both hemispheres (~15 m/s in winter), the seasonal variability in the Northern Hemisphere high latitudes is much greater compared to the Southern Hemisphere high latitudes (summer minimum of 10 and 7.9 m/s in Southern Hemisphere and Northern Hemisphere, respectively, Young, 1999). Lower organic mass fractions (Gantt et al., 2011) and coarse mode SSA (Lewis & Schwartz, 2004) have been observed in association with higher wind speeds, suggesting an increase in the total aerosol surface area without increasing the organic component of SSA (i.e., ice nucleating material), resulting in a lower n_s. Laboratory and field measurements also indicate that INP production changes depending on biological state. The time of year and the small change in Chl *a* over during CAPRICORN (Figure S7) suggest that the phytoplankton community was in a *plateau-like* period after a bloom. The composition of the community was likely shifting from larger to smaller phytoplankton species, while bacteria and virus numbers may have been higher, as typically observed during

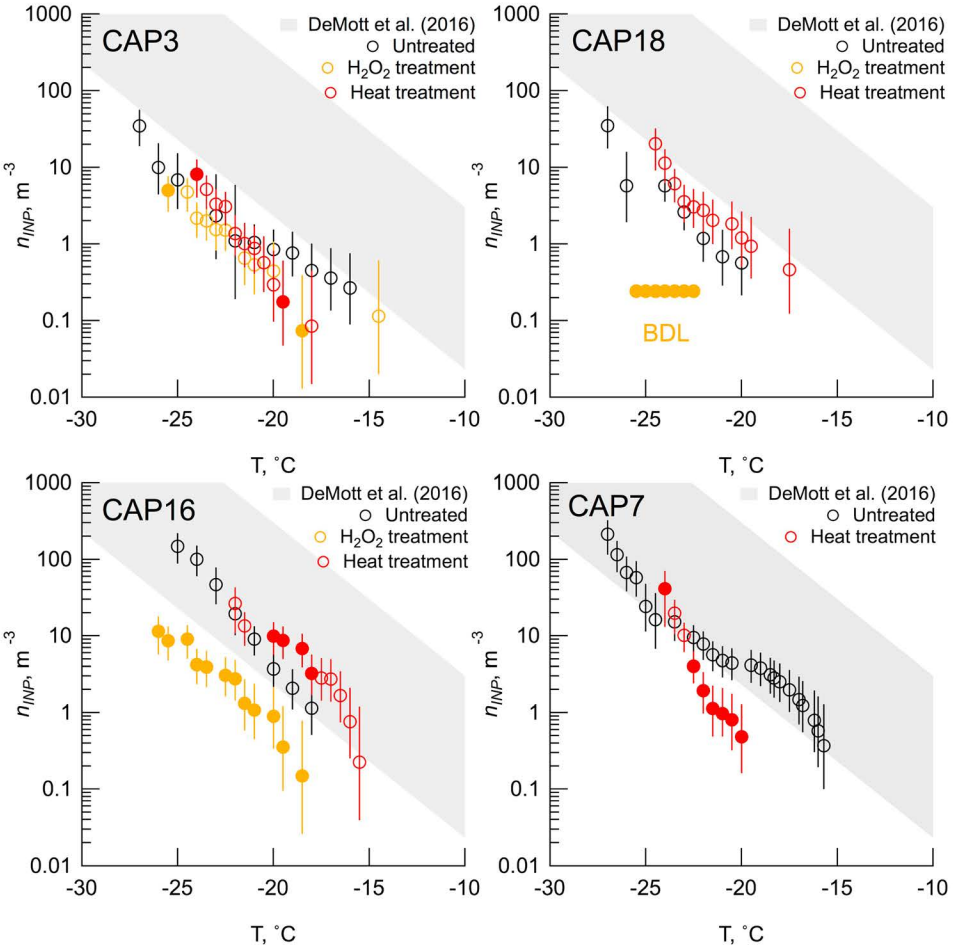

Figure 3. Ice nucleating particle (INP) spectra for untreated (black), heated (red), and H_2O_2-treated (gold) samples and from observations attributed to sea spray aerosol by DeMott et al. (2016; gray shaded area). Results from the H_2O_2 treatment on CAP18 resulted in values below detection limit. H_2O_2 treatment was not performed on CAP7. Treated values that are statistically significantly different ($p < 0.05$) from untreated values are indicated by filled circles. Vertical bars are the 95% confidence intervals.

that phase of the biological succession (e.g., Moreau et al., 2014). Differences in the biological state of the ocean during this campaign and that during the MHD measurement add complexity to a comparison of n_s.

3.2. Characteristics of INPs Observed During CAPRICORN

The contribution of terrestrial masses to the INPs observed during CAPRICORN was evaluated using ambient radon (^{222}Rn) concentrations, shown in Figure S8. Chambers et al. (2014) reported average ^{222}Rn concentrations up to 150 mBq/m^3 in Antarctica and found that high ^{222}Rn events (greater than 400 mBq/m^3) originated from distant landmasses (South America). Linear regression analyses of n_{INPs} and ^{222}Rn for a range of temperatures (Figure S9) revealed no statistically significant correlation. However, the warmest temperature with measurable IN activity (−12 °C) corresponded to a sample with highest ^{222}Rn concentrations (150 mBq/m^3) that was collected near land (CAP5, Figure 1), suggesting a possible influence of terrestrial aerosol (Figure S10) in this sample. For all other samples, ^{222}Rn concentrations less than 100 mBq/m^3 were observed. We conclude that the measured aerosol and n_{INPs} reported here are representative of oceanic sources.

Offline treatments for testing heat lability and organic composition were performed on four SSA samples, shown in Figure 3. The n_{INPs} detected during CAP3 were some of the lowest observed during CAPRICORN, over a region with moderate Chl *a* (0.34 to 0.61 mg/m^3, Figure S11); INPs detected on CAP3 were heat stable and not organic (on the basis of H_2O_2 digestion). In contrast, CAP18 was collected over a region with similar

Chl *a* (0.20 to 0.38 mg/m^3) and, while INPs were heat stable, they were comprised entirely of organic material (no freezing detected for H_2O_2 treated sample). CAP16 was collected over the nascent warm-core eddy region (section 3.3) with Chl *a* of 0.19 to 0.35 mg/m^3. As with CAP18, INPs were heat stable and largely comprised of organic material, although some IN activity remained following carbon digestion, similar to levels of n_{INPs} observed from CAP3. Finally, CAP7 was collected over ocean regions with higher Chl *a* (0.42 to 1.32 mg/m^3) and INPs appear to be largely comprised of heat-labile INPs at −22 °C and warmer (the contribution from organic matter was not tested for CAP7). These treatments collectively reveal wide variability in the contributions of organic matter and heat-labile material to the INP population measured during CAPRICORN.

3.3. SO INP Source Potential

Number concentrations of INEs (n_{INEs}) in seawater samples collected during CAPRICORN were used to characterize the INP source potential, or the number of INEs in seawater that potentially contribute to the INP population via bubble bursting. Specifically, seawater samples were collected in mesoscale oceanic eddies, which are ocean dynamical features analogous to atmospheric low and high pressure systems and have large spatial (100 km) and time (weeks to months) scales (McGillicuddy, 2016). Oceanic eddies are ubiquitous features in the SO (Frenger et al., 2015) that impact biological productivity by advecting phytoplankton patches or by enhancing or prohibiting upwelling of deep ocean waters containing high nutrients (Gaube et al., 2013). As described by Moreau et al. (2017), the cold-core eddy sampled during CAPRICORN developed from the Sub-Antarctic Front and was identified based on negative sea surface height anomalies, with an eddy diameter of approximately 190 km. This cold-core eddy contained low surface Chl *a* in the eddy center (0.33 mg/m^3) with higher surface Chl *a* at the eddy peripherals (0.74 mg/m^3; Moreau et al., 2017). SW samples were also collected in a nascent warm-core eddy forming from a southward meandering of the Antarctic Circumpolar Current, with positive sea surface height anomalies and fairly homogeneous surface Chl *a* (0.54 to 0.71 mg/m^3). Six conductivity temperature depth profiles were deployed from edge to center in both features, enabling characterization of horizontal changes in n_{INEs} through biologically varying productive water (Figure 1).

During CAPRICORN, n_{INEs} at −20 °C were less than 3 ml^{-1}, corresponding to the baseline of n_{INEs} reported for Arctic (Irish et al., 2017) and Atlantic (Schnell, 1977) seawater. While Chl *a* were lowest at the cold-core eddy center, no clear difference was observed between n_{INEs} measured at the core compared to the eddy edge (Figure S12). This was also true for the SW collected in the nascent warm-core region. Laboratory studies have suggested that SW INEs are generated during the phytoplankton bloom decay phase (McCluskey et al., 2017). Thus, we expect that the lack of observed changes in n_{INEs} found in these SW samples may be due to the bloom phase that was prevalent at the time of sampling. Offline heat and 0.2-μm filtering treatments, shown in Figure S13, suggest that the majority of SW INEs measured in the cold-core core eddy were smaller than 0.2 μm, similar to recent findings (Irish et al., 2017; Wilson et al., 2015), and heat stable, consistent with the DOC INP type (McCluskey, Hill, et al., 2018). Seawater from the nascent warm-core eddy region contained INEs that were removed larger than 0.2 μm and heat labile, similar to the POC INP type (McCluskey, Hill, et al., 2018), but INEs that were smaller than 0.2 μm and heat stable remained after treatments. These results suggest that the INEs observed during CAPRICORN were dominated by the DOC INP type.

4. Conclusions

Measurements made during the monthlong CAPRICORN study provide the first systematic evaluation of INPs in the SO region in over four decades. No correlation was observed between n_{INPs} and radon, a tracer for terrestrial air masses, and thus, we conclude that ambient n_{INPs} originated from local oceanic sources. Observed n_{INPs} were lower than n_{INPs} observed in the marine boundary layer over other oceans (DeMott et al., 2016) and were over two orders of magnitude lower than annual averaged n_{INPs} reported from an extensive 3-year survey by Bigg (1973) for the same region. Reasons for this large discrepancy may include differences in measurement techniques, seasonal variability that was inaccessible in this monthlong campaign, or a decadal decreasing trend in n_{INPs} over the SO (Bigg, 1990). Offline treatments of sampled aerosol and seawater revealed organic heat-stable material was a common contributor to the observed INP populations. Heat-labile INPs were also observed during this study. The INP source strengths of SO seawater from this study

were at the baseline of values reported for Arctic (Irish et al., 2017) and Atlantic (Schnell, 1977) regions. This difference was also reflected in the SSA, where n_{INPs} were lower than those observed in North Atlantic air masses (McCluskey, Ovadnevaite et al., 2018). These observations update the scientific knowledge regarding the number and composition of INPs present over the SO, revealing an incredibly pristine marine boundary layer with extremely low n_{INPs}, consistent with a hypothesis that these low concentrations of INPs that feed ice formation account for the anomalously persistent supercooled liquid clouds found over the SO.

Acknowledgments
This research was supported by the National Science Foundation (AGS-1450760 and AGS-1660486). S. Moreau and P. Strutton were supported by the Australian Research Council's Special Research Initiative for Antarctic Gateway Partnership (Project ID SR140300001) and the Discovery Program and Centres of Excellence program, respectively. The Authors wish to thank the CSIRO Marine National Facility (MNF) for its support in the form of sea time on RV *Investigator*, support personnel, scientific equipment, and data management. All data and samples acquired on the voyage are made publicly available in accordance with MNF policy. The MNF ship underway data (e.g., ship navigation, wind, and sector pump switch) are available for download from the RV *Investigator* Voyage IN2016_V02 Underway Data metadata record at http://www.marlin.csiro.au/geonetwork/srv/eng/search#!2cf37561-1c43-0d22-e053-08114f8c7cd2. All remaining data are listed in the references, tables, and supporting information and are archived in a digital repository at Colorado State University (https://hdl.handle.net/10217/192127).

References

Agresti, A., & Coull, B. A. (1998). Approximate is better than "exact" for interval estimation of binomial proportions. *The American Statistician*, *52*(2), 119–126. https://doi.org/10.1080/00031305.1998.10480550

Ardyna, M., Claustre, H., Sallée, J.-B., D'Ovidio, F., Gentili, B., van Dijken, G., et al. (2017). Delineating environmental control of phytoplankton biomass and phenology in the Southern Ocean: Phytoplankton dynamics in the SO. *Geophysical Research Letters*, *44*, 5016–5024. https://doi.org/10.1002/2016GL072428

Bigg, E. K. (1973). Ice nucleus concentrations in remote areas. *Journal of the Atmospheric Sciences*, *30*, 1153–1157. https://doi.org/10.1175/1520-0469(1973)030<1153:INCIRA>2.0.CO;2

Bigg, E. K. (1990). Long-term trends in ice nucleus concentrations. *Atmospheric Research*, *25*(5), 409–415. https://doi.org/10.1016/0169-8095(90)90025-8

Burrows, S. M., Hoose, C., Pöschl, U., & Lawrence, M. G. (2013). Ice nuclei in marine air: Biogenic particles or dust? *Atmospheric Chemistry and Physics*, *13*(1), 245–267. https://doi.org/10.5194/acp-13-245-2013

Chambers, S. D., Hong, S.-B., Williams, A. G., Crawford, J., Griffiths, A. D., & Park, S.-J. (2014). Characterising terrestrial influences on Antarctic air masses using Radon-222 measurements at King George Island. *Atmospheric Chemistry and Physics*, *14*(18), 9903–9916. https://doi.org/10.5194/acp-14-9903-2014

DeMott, P. J., Hill, T. C. J., McCluskey, C. S., Prather, K. A., Collins, D. B., Sullivan, R. C., et al. (2016). Sea spray aerosol as a unique source of ice nucleating particles. *Proceedings of the National Academy of Sciences*, *113*(21), 5797–5803. https://doi.org/10.1073/pnas.1514034112

Frenger, I., Münnich, M., Gruber, N., & Knutti, R. (2015). Southern Ocean eddy phenomenology. *Journal of Geophysical Research: Oceans*, *120*, 7413–7449. https://doi.org/10.1002/2015JC011047

Gantt, B., meskhidze, N., Facchini, M. C., Rinaldi, M., Ceburnis, D., & O'Dowd, C. D. (2011). Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol. *Atmospheric Chemistry and Physics*, *11*(16), 8777–8790. https://doi.org/10.5194/acp-11-8777-2011

Gaube, P., Chelton, D. B., Strutton, P. G., & Behrenfeld, M. J. (2013). Satellite observations of chlorophyll, phytoplankton biomass, and Ekman pumping in nonlinear mesoscale eddies. *Journal of Geophysical Research: Oceans*, *118*, 6349–6370. https://doi.org/10.1002/2013JC009027

Gregg, W. W., Conkright, M. E., Ginoux, P., O'Reilly, J. E., & Casey, N. W. (2003). Ocean primary production and climate: Global decadal changes. *Geophysical Research Letters*, *30*(15), 1809. https://doi.org/10.1029/2003GL016889

Griffiths, A. D., Chambers, S. D., Williams, A. G., & Werczynski, S. (2016). Increasing the accuracy and temporal resolution of two-filter radon–222 measurements by correcting for the instrument response. *Atmospheric Measurement Techniques*, *9*(6), 2689–2707. https://doi.org/10.5194/amt-9-2689-2016

Hill, C. J., Moffet, B. F., DeMott, P. J., Georgakopoulos, D. G., Stump, W. L., & Franc, G. D. (2014). Measurement of ice nucleation-active bacteria on plants and in precipitation by quantitative PCR. *Applied and Environmental Microbiology*, *80*(4), 1256–1267. https://doi.org/10.1128/AEM.02967-13

Hiranuma, N., Augustin-Bauditz, S., Bingemer, H., Budke, C., Curtius, J., Danielczok, A., et al. (2015). A comprehensive laboratory study on the immersion freezing behavior of illite NX particles: A comparison of 17 ice nucleation measurement techniques. *Atmospheric Chemistry and Physics*, *15*(5), 2489–2518. https://doi.org/10.5194/acp-15-2489-2015

Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., & Strickland, J. D. H. (1965). Fluorometric determination of chlorophyll. *Journal du Conseil*, *30*(1), 3–15. https://doi.org/10.1093/icesjms/30.1.3

Huang, Y., Protat, A., Siems, S. T., & Manton, M. J. (2015). A-train observations of maritime Midlatitude storm-track cloud systems: Comparing the Southern Ocean against the North Atlantic. *Journal of Climate*, *28*(5), 1920–1939. https://doi.org/10.1175/JCLI-D-14-00169.1

Irish, V. E., Elizondo, P., Chen, J., Chou, C., Charette, J., Lizotte, M., et al. (2017). Ice-nucleating particles in Canadian Arctic Sea-surface microlayer and bulk seawater. *Atmospheric Chemistry and Physics*, *17*(17), 10,583–10,595. https://doi.org/10.5194/acp-17-10583-2017

Ito, A., & Kok, J. F. (2017). Do dust emissions from sparsely vegetated regions dominate atmospheric iron supply to the Southern Ocean? *Journal of Geophysical Research: Atmospheres*, *122*, 3987–4002. https://doi.org/10.1002/2016JD025939

Jickells, T. D., An, Z. S., Anderson, K. K., Baker, A. R., Bergametti, G., Brooks, N., et al. (2005). Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science*, *308*(5718), 67–71. https://doi.org/10.1126/science.1105959

Knopf, D. A., Alpert, P. A., Wang, B., & Aller, J. Y. (2011). Stimulation of ice nucleation by marine diatoms. *Nature Geoscience*, *4*, 88–90.

Lewis, E. R., & Schwartz, S. E. (2004). *Sea salt aerosol production mechanisms, methods, measurements, and models*. Washington, DC: American Geophysical Union.

Lorenzen, C. J. (1966). A method for the continuous measurement of in vivo chlorophyll concentration. *Deep Sea Research and Oceanographic Abstracts*, *13*(2), 223–227. https://doi.org/10.1016/0011-7471(66)91102-8

McCluskey, C. S., Hill, T. C. J., Malfatti, F., Sultana, C. M., Lee, C., Santander, M. V., et al. (2017). A dynamic link between ice nucleating particles released in nascent sea spray aerosol and oceanic biological activity during two mesocosm experiments. *Journal of the Atmospheric Sciences*, *74*(1), 151–166. https://doi.org/10.1175/JAS-D-16-0087.1

McCluskey, C. S., Hill, T. C. J., Sultana, C. M., Laskina, O., Trueblood, J., Santander, M. V., et al. (2018). A mesocosm double feature: Insights into the chemical makeup of marine ice nucleating particles. *Journal of the Atmospheric Sciences*, *75*(7), 2405–2423. https://doi.org/10.1175/JAS-D-17-0155.1

McCluskey, C. S., Ovadnevaite, J., Rinaldi, M., Atkinson, J., Belosi, F., Ceburnis, D., et al. (2018). Marine and terrestrial organic ice-nucleating particles in pristine marine to continentally influenced Northeast Atlantic air masses. *Journal of Geophysical Research: Atmospheres*, *123*, 6196–6212. https://doi.org/10.1029/2017JD028033

McGillicuddy, D. J. (2016). Mechanisms of physical-biological-biogeochemical interaction at the oceanic mesoscale. *Annual Review of Marine Science*, *8*(1), 125–159. https://doi.org/10.1146/annurev-marine-010814-015606

Moreau, S., Mostajir, B., Almandoz, G., Demers, S., Hernando, M., Lemarchand, K., et al. (2014). Effects of enhanced temperature and ultraviolet B radiation on a natural plankton community of the Beagle Channel (southern Argentina): A mesocosm study. *Aquatic Microbial Ecology*, *72*(2), 155–173. https://doi.org/10.3354/ame01694

Moreau, S., Penna, A. D., Llort, J., Patel, R., Langlais, C., Boyd, P. W., et al. (2017). Eddy-induced carbon transport across the Antarctic circumpolar current. *Global Biogeochemical Cycles*, *31*, 1368–1386. https://doi.org/10.1002/2017GB005669

Niemand, M., Möhler, O., Vogel, B., Vogel, H., Hoose, C., Connolly, P., et al. (2012). A particle-surface-area-based parameterization of immersion freezing on desert dust particles. *Journal of Atmospheric Science*, *69*(10), 3077–3092. https://doi.org/10.1175/JAS-D-11-0249.1

Polen, M., Lawlis, E., & Sullivan, R. C. (2016). The unstable ice nucleation properties of Snomax® bacterial particles. *Journal of Geophysical Research: Atmospheres*, *121*, 11,666–11,678. https://doi.org/10.1002/2016JD025251

Rogers, D. C. (1988). Development of a continuous flow thermal gradient diffusion chamber for ice nucleation studies. *Atmospheric Research*, *22*(2), 149–181. https://doi.org/10.1016/0169-8095(88)90005-1

Romay, F. J., Roberts, D. L., Marple, V. A., Liu, B. Y. H., & Olson, B. A. (2002). A high-performance aerosol concentrator for biological agent detection. *Aerosol Science and Technology*, *36*(2), 217–226. https://doi.org/10.1080/027868202753504074

Rosinski, J., Haagenson, P. L., Nagamoto, C. T., & Parungo, F. (1987). Nature of ice-forming nuclei in marine air masses. *Journal of Aerosol Science*, *18*(3), 291–309. https://doi.org/10.1016/0021-8502(87)90024-3

Schill, G. P., Jathar, S. H., Kodros, J. K., Levin, E. J. T., Galang, A. M., Friedman, B., et al. (2016). Ice-nucleating particle emissions from photochemically aged diesel and biodiesel exhaust. *Geophysical Research Letters*, *43*, 5524–5531. https://doi.org/10.1002/2016GL069529

Schnell, R. (1977). Ice nuclei in seawater, fog water and marine air off the coast of Nova Scotia summer 1975. *Journal of the Atmospheric Sciences*, *34*(8), 1299–1305. https://doi.org/10.1175/1520-0469(1977)034<1299:INISFW>2.0.CO;2

Schnell, R. C., & Vali, G. (1976). Biogenic ice nuclei: Part I. Terrestrial and marine sources. *Journal of the Atmospheric Sciences*, *33*(8), 1554–1564. https://doi.org/10.1175/1520-0469(1976)033<1554:BINPIT>2.0.CO;2

Tan, I., Storelvmo, T., & Zelinka, M. D. (2016). Observational constraints on mixed-phase clouds imply higher climate sensitivity. *Science*, *352*(6282), 224–227. https://doi.org/10.1126/science.aad5300

Taylor, J. R. (1997). *An introduction to error analysis: The study of uncertainty in physical measurements*. Sausalito, CA: University Science Books.

Thomson, E. S., Weber, D., Bingemer, H. G., Tuomi, J., Ebert, M., & Pettersson, J. B. C. (2018). Intensification of ice nucleation observed in ocean ship emissions. *Scientific Reports*, *8*(1). https://doi.org/10.1038/s41598-018-19297-y

Tobo, Y., Prenni, A. J., DeMott, P. J., Huffman, J. A., McCluskey, C. S., Tian, G., et al. (2013). Biological aerosol particles as a key determinant of ice nuclei populations in a forest ecosystem. *Journal of Geophysical Research: Atmospheres*, *118*, 10,100–10,110. https://doi.org/10.1002/jgrd.50801

Vali, G. (1971). Quantitative evaluation of experimental results on the heterogeneous freezing nucleation of supercooled liquids. *Journal of the Atmospheric Sciences*, *28*(3), 402–409. https://doi.org/10.1175/1520-0469(1971)028,0402:QEOERA.2.0.CO;2

Vali, G., DeMott, P. J., Möhler, O., & Whale, T. F. (2015). Technical note: A proposal for ice nucleation terminology. *Atmospheric Chemistry and Physics*, *15*(18), 10,263–10,270. https://doi.org/10.5194/acp-15-10263-2015

Vergara-Temprado, J., Miltenberger, A. K., Furtado, K., Grosvenor, D. P., Shipway, B. J., Hill, A. A., et al. (2018). Strong control of Southern Ocean cloud reflectivity by ice-nucleating particles. *Proceedings of the National Academy of Sciences*, *115*(11), 2687–2692. https://doi.org/10.1073/pnas.1721627115

Vergara-Temprado, J., Murray, B. J., Wilson, T. W., O'Sullivan, D., Browse, J., et al. (2017). Contribution of feldspar and marine organic aerosols to global ice nucleating particle concentrations. *Atmospheric Chemistry and Physics*, *17*(5), 3637–3658. https://doi.org/10.5194/acp-17-3637-2017

Wilson, T. W., Ladino, L. A., Alpert, P. A., Breckels, M. N., Brooks, I. M., Browse, J., et al. (2015). A marine biogenic source of atmospheric ice-nucleating particles. *Nature*, *525*(7568), 234–238. https://doi.org/10.1038/nature14986

Young, I. R. (1999). Seasonal variability of the global ocean wind and wave climate. *International Journal of Climatology*, *19*(9), 931–950. https://doi.org/10.1002/(SICI)1097-0088(199907)19:9<931::AID-JOC412>3.0.CO;2-O