# Effects of Marine Organic Aerosols as Sources of Immersion-Mode Ice Nucleating Particles on High Latitude Mixed-Phase Clouds

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12 Abstract. Mixed-phase clouds are frequently observed in high latitude regions, and have important impacts on the surface energy budget and regional climate. Marine organic 13 14 aerosol (MOA), a natural source of aerosol emitted over  $\sim$ 70% of Earth's surface, may 15significantly modify the properties and radiative forcing of mixed-phase clouds. However, 16 the relative importance of MOA as a source of ice nucleating particles (INPs) in 17 comparison to mineral dust, and its effects as cloud condensation nuclei (CCN) and INPs 18 on mixed-phase clouds are still open questions. In this study, we implement MOA as a 19 new aerosol species into the Community Atmosphere Model version 6 (CAM6), the 20 atmosphere component of the Community Earth System Model version 2 (CESM2), and 21 allow the treatments of aerosol-cloud interactions of MOA via droplet activation and ice 22 nucleation. CAM6 reproduces observed seasonal cycles of marine organic matter at Mace 23 Head and Amsterdam Island when the MOA fraction of sea spray aerosol in the model is 24 assumed to depend on sea spray biology, but fails when this fraction is assumed to be 25 constant. Model results indicate that marine INPs dominate primary ice nucleation below 26 400 hPa over the Southern Ocean and Arctic boundary layer, while dust INPs are more 27 abundant elsewhere. By acting as CCN, MOA exerts a shortwave cloud forcing change of -2.78 W m<sup>-2</sup> over the Southern Ocean in the austral summer. By acting as INPs, MOA 28 enhances the longwave cloud forcing by 0.35 W m<sup>-2</sup> over the Southern Ocean in the 29 30 austral winter. The annual global mean net cloud forcing changes due to CCN and INPs of 31 MOA are -0.35 and 0.016 W m<sup>-2</sup>, respectively. These findings highlight the vital 32 importance of Earth System Models to consider the MOA as an important aerosol species 33 for the interactions of biogeochemistry, hydrological cycle, and climate change.

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## 37 **1 Introduction**

38 Ice crystals in clouds play a critical role in determining cloud phase, lifetime, 39 electrification, and radiative properties. As a result, cloud ice influences precipitation and 40 cloud radiative forcing. To quantify the impact of ice crystals on the hydrologic cycle and 41 energy budget of the Earth system, it is important to advance the process-based 42 understanding of initiation and evolution of ice particles. Ice particles can be initialized 43 by homogeneous freezing or by heterogeneous nucleation. Homogeneous freezing of 44 cloud droplets and aerosol solution droplets happens when air temperature is below 45 approximately -38° C. In mixed-phase clouds in which air temperature is between -38° C 46 and  $0^{\circ}$  C, ice is initialized only by heterogeneous nucleation on ice nucleating particles 47 (INPs) (Vali et al., 2015).

48 INPs have different characteristics depending on their composition and origin. 49 Previous studies (Hoose and Möhler, 2012; Murray et al., 2012; Kanji et al., 2017) have 50 shown that mineral dust, primary bioaerosols (e.g., fungal spores, bacteria, and pollen), 51 and volcanic ash can be effective INPs. However, large uncertainties exist surrounding 52 the ice nucleating properties of black carbon (Schill et al., 2020; Vergara-Temprado et al., 53 2018) and organic carbon from biomass burning and fossil fuel combustion. A majority 54 of INPs are of terrestrial origin. Due to their large emission quantities and high efficiency 55 at forming ice, mineral dust may play a dominant role in ice formation over continents. 56 However, in remote oceanic regions where terrestrial INPs are rare, the aerosol species 57 contributing to INPs and the mechanisms for ice initialization remain poorly understood. 58 Recent observational and modelling studies have shown that marine organic aerosol 59 (MOA) is potentially an important source of INPs over remote oceanic regions (Wilson et 60 al., 2015; DeMott et al., 2016; Vergara-Temprado et al., 2017; Huang et al., 2018; 61 McCluskey et al., 2019).

MOA can be generated from both primary and secondary processes during ocean
biological activities, producing either water-soluble or insoluble organic aerosols.
Previous studies have inferred that water-insoluble marine organic matter is mainly
derived from the primary emissions of sea spray aerosols (SSAs) (Ceburnis et al., 2008).
In this production process, SSAs and associated organic matter are injected into the marine
boundary layer when bubbles burst at the air-sea interface. Long-term measurements of

68 seasonal variability in SSAs (O'Dowd et al., 2004; Yoon et al., 2007; Rinaldi et al., 2013) 69 and organic matter in remote marine air (Sciare et al., 2009) are consistent with the 70 hypothesis that the amount of organic matter is associated with ocean biological activity. 71 Laboratory experiments have also demonstrated that the presence of phytoplankton blooms 72 can be associated with significant changes in the number flux and size distribution of 73 emitted SSAs (Ault et al., 2013, Alpert et al., 2015; Rastelli et al., 2017; Forestieri et al., 74 2018; Christiansen et al., 2019), as well as the SSA organic content (Facchini et al., 2008; 75 Ault et al., 2013).

76 Parameterizations for the primary emission of MOA have been developed with the 77 intention to be used in models. Most of these parameterizations relate MOA emission flux 78 to ocean chlorophyll a concentration [Chl-a]. An advantage of this approach is that [Chl-a] 79 is globally available from satellite-based measurements, especially over the remote oceans 80 where ground-based observations are difficult to conduct. Although [Chl-a] makes up only 81 a minor fraction of the organic matter in the ocean (Gardner et al., 2006), it has a long 82 history as a widely-used proxy for the biomass of phytoplankton in ocean surface waters 83 (Steele et al., 1962; Cullen et al., 1982), and has been used to derive empirical relationships 84 between satellite-observed [Chl-a] and the observed MOA contribution to submicron SSAs. 85 Several studies have also found that measured organic matter in SSA correlates more 86 strongly with ocean [Chl-a] than with other satellite-retrieved ocean chemistry variables, 87 such as particulate organic carbon, dissolved organic carbon, and colored dissolved and 88 detrital organic matter (O'Dowd et al., 2004; Sciare et al., 2009; Gantt et al., 2011; Rinaldi 89 et al., 2013).

90 O'Dowd et al. (2008) proposed a MOA emission parameterization, which was further 91 modified by Langmann et al. (2008) and Vignati et al. (2010). In this parameterization, the 92 fraction of emitted organic matter in SSA has a linear relationship with ocean [Chl-a] and is 93 not dependent on surface wind speed. Gantt et al. (2011) took a step further, and developed 94 an emission parameterization in which the organic matter fraction is an empirical function 95 of ocean [Chl-a], 10 m wind speed, and aerosol size. Both parameterizations from Gantt et 96 al.(2011) and Vignati et al. (2010) were found to capture the magnitude of MOA 97 concentrations compared to observations, but the parameterization from Gantt et al. (2011) 98 had a better representation of seasonal variability of MOA concentrations at Amsterdam

99 Island and Mace Head, Ireland (Meskhidze et al., 2011). Rinaldi et al. (2013) also

100 developed a MOA emission parameterization which depends on surface wind speed and

101 [Chl-a], and by assuming an 8–10 day time lag between upwind ocean [Chl-a] and

102 enhanced production of MOA the correlation between enriched MOA and [Chl-a] was

103 improved. Burrows et al. (2014) proposed a physically-based approach to represent MOA

104 emission process (i.e., OCEANFILMS) instead of using the empirical [Chl-a]. This

105 method was implemented in the DOE Energy Exascale Earth System Model version 1

(E3SMv1) (Golaz et al., 2019; Rasch et al., 2019), and the CCN effect of MOA on cloud
droplet activation was investigated (Burrows et al., 2018).

108 Recent observational evidence continuously shows the importance of MOA as INPs 109 in natural clouds (Wilson et al., 2015; DeMott et al., 2016; McCluskey et al., 2018a, b). 110 However, there have been very limited modeling studies to quantify the effects of MOA 111 INPs on clouds. Yun and Penner (2013) conducted the first global study of MOA on ice 112 formation and radiative forcing using the CAM3 model. Their study indicated that MOA 113 INPs are the dominant INPs for mixed-phase clouds over the Southern Hemisphere (SH), 114 and after including MOA INPs, the model generated a more reasonable ice water path 115 (IWP) compared with the International Satellite Cloud Climatology Project (ISCCP) 116 observation data. In their study, the model simulated frozen fraction of MOA at  $-15^{\circ}$ C is 117 3.75% for their lowest size bin ( $0.05 - 0.63 \mu m$ ) and 100% for their larger size bins. These 118 values may be too high compared with both historical and recent measurements of the ice 119 nucleation efficiency of sea surface material (Schnell and Vali, 1975; Wilson et al., 2015) 120 and SSAs (DeMott et al., 2016; McCluskey et al., 2018b).

121 With more measurements of MOA and sea spray INPs becoming available, recent 122 modeling studies have been able to improve upon past MOA INP parameterizations. 123 Huang et al. (2018) used the ECHAM6-HAM2 model to study the MOA influence on ice 124 formation and climate. They followed the [Chl-a]-based method of Rinaldi et al. (2013) to 125represent the MOA emission and compared two empirical methods for calculating the 126 MOA INP efficiency (Wilson et al., 2015; DeMott et al., 2016). They found that MOA 127 influenced the cloud ice number concentration and effective radius only slightly, and MOA 128 did not exert a significant influence on the global radiative balance due to compensating

129 cloud responses. However, these conclusions also depend on the sensitivity of their model130 to the change in INP number concentration.

131 In contrast to the findings of Huang et al. (2018), Vergara-Temprado et al. (2017) and 132 McCluskey et al. (2019) found that MOA was the dominant source of INPs over the 133 Southern Ocean. Vergara-Temprado et al. (2017) used the Global Model of Aerosol Processes (GLOMAP) to investigate the relative importance of feldspar and MOA for ice 134 135 nucleation. Ice nucleation by MOA follows the Wilson et al. (2015) parameterization. This 136 study also found that on 10–30 % of days in the study period there were more MOA INPs 137 than feldspar INPs over the Northern Hemisphere (NH) Ocean. McCluskey et al. (2019) 138 used the aerosol concentrations calculated offline from the Community Atmosphere Model 139 version 5 (CAM5) to show that MOA is the dominant INPs over the Southern Ocean. Ice 140 nucleation by MOA follows the McCluskey et al. (2018b) parameterization.

141 Isolating the INP effect of MOA on clouds and radiative forcing has rarely been 142 examined directly, which motivates our study to address MOA ice nucleation process and 143 to better understand the climate influence of MOA INPs. Our approach is different from 144 previous studies. For example, we use a more physically-based approach (Burrows et al., 145 2014) to represent MOA emission instead of the empirical [Chl-a] based method used in 146 Huang et al. (2018). Instead of the offline evaluation of INP parameterizations in CAM5 147 (McCluskey et al., 2019), this study implements the MOA emission and other process 148 representations in the Community Atmosphere Model version 6 (CAM6), the latest 149 atmosphere component of Community Earth System Model version 2 (CESM2), and 150 allows for the impacts of MOA on modeled clouds and radiative forcing interactively. 151 Lastly, we isolate the INP effect from the CCN effect of MOA in order to better understand 152 the MOA influence on clouds via these two mechanisms. 153 This paper is organized as follows. Section 2 presents the model, parameterizations of

MOA as well as model experiments. Section 3 describes the model results and comparison with observations. Section 4 discusses the remaining questions. Section 5 summarizes and draws the conclusions of this study.

# 157 **2 Methods**

## 158 **2.1 Model and parameterizations**

159 CAM6 with the Finite-Volume (FV) dynamical core (Lin and Rood, 1997) is used 160 in this study. CAM6 treats important physical processes in the atmosphere, including 161 radiative transfer, deep convection, cloud macrophysics, cloud microphysics, shallow 162 convection, and planetary boundary layer turbulence. Cloud and aerosol interactions with 163 longwave and shortwave radiation transfer are treated by the Rapid Radiative Transfer 164 Model for GCMs (RRTMG) scheme (Iacono et al., 2008; Mlawer et al., 1997). A 165double-moment scheme (Gettelman et al., 2015) is used to describe the microphysical 166 processes of cloud and precipitation hydrometeors in large-scale stratiform clouds, while 167 the deep convection is represented by the Zhang and McFarlane (1995) scheme. CAM6 168 uses the Cloud Layers Unified By Binormals (CLUBB) scheme (Golaz et al., 2002; 169 Larson et al., 2002) to unify the representations of cloud macrophysics, turbulence, and 170 shallow convection.

171 The four-mode version of the Modal Aerosol Module (MAM4), which is an 172extension of the three-mode version of MAM (Liu et al., 2012), is used to describe the 173aerosol properties and processes in CAM6 (Liu et al., 2016). MAM4 uses the modal 174 method to represent the size distributions of four aerosol modes: Aitken, accumulation, 175 coarse, and primary carbon. The original MAM4 encompasses six aerosol species: black 176 carbon, dust, primary organic aerosol, sea salt, secondary organic aerosol, and sulfate 177(Table 1). The primary organic aerosol here refers to non-marine sources of organic 178 matter, usually from terrestrial biomass burning, fossil fuel, and biofuel burning. Aerosol 179 species are internally-mixed within a mode and externally-mixed between modes. Then 180 the log-normal size distribution can be determined for each mode based on a prescribed 181 geometric standard deviation (Table 1). Different aerosol species are characterized by a 182 variety of properties such as hygroscopicity, density, and optical properties (Table 2).

183 MAM in CAM6 adopts the modal approach, where aerosol species are assumed to 184 be internally mixed within a mode, and externally mixed between modes. MOA is 185 emitted into the fine aerosol modes with different assumptions of mixing state with 186 inorganic sea salt: (1) MOA is emitted into the Aitken and accumulation modes together

187 with sea salt in the case of internally mixed with sea salt; or (2) MOA is emitted into the 188 Aitken and primary carbon mode separately from sea salt in the case of externally mixed 189 with sea salt. In addition, there is another assumption of whether the experimentally 190 derived parameterizations of SSA mass emission flux represent the total emission of 191 MOA and sea salt or only account for the emission of sea salt. In the former case, MOA 192 will replace the mass and number emission fluxes of sea salt. In the latter case, MOA will 193 add onto the sea salt mass and number emission fluxes. Burrows et al. (2018) tested 194 different combinations of the two assumptions and found that the "internally-mixed" and 195 "added" MOA approach provides the most physically realistic configuration compared to 196 the observations. Thus, in our study we use this configuration but acknowledge that 197 current observations do not provide precise constrains on the mixing state.

198 While anthropogenic aerosol and precursor gas emissions are prescribed for 199 model simulations, emissions of natural aerosols (e.g., SSA, dust) are calculated 200 interactively in the model. SSA in MAM is emitted following the parameterization of 201 Mårtensson et al. (2003) for dry particle diameters from 0.020 to 2.8  $\mu$ m, and Monahan et 202 al. (1986) from 2.8 to 10 µm. The Mårtensson et al. parameterization is derived from 203 laboratory experiments in which particles were produced by bubble bursting using a 204 sintered glass filter in synthetic seawater. The emission rate depends linearly on the sea 205 surface temperature and is proportional to 10-m wind speed, raised to the power of 3.41 206 (Monahan et al., 1986; Gong et al., 1997). 207

# 208 **2.2 MOA in CAM6**

In this study, several modifications are implemented in CAM6 in order to explicitly quantify the influence of marine organic matter on aerosols, clouds, and radiation. These modifications are comprised of (1) emission schemes of MOA, as introduced in section 2.2.1, and (2) ice nucleation parameterizations for MOA, as introduced in section 2.2.2.

## **214 2.2.1 Emission of MOA**

Three different methods for online MOA emissions are implemented in CAM6.

These methods parameterize the organic mass fraction of sea spray and use the fraction to compute MOA emissions based on the emission rate of SSA.

218 The mass fraction of MOA in total SSA,  $F_{MOA/SSA}$  is defined as the following:

219 
$$F_{MOA/SSA} = \frac{M_{MOA}}{M_{sea \, spray}} = \frac{M_{MOA}}{M_{MOA} + M_{sea \, salt}}$$
(1)

in which  $M_{MOA}$  is the mass mixing ratio of MOA, and  $M_{sea \ salt}$  is the mass mixing ratio of sea salt. Thus, the emitted MOA mass mixing ratio can be computed as:

222 
$$M_{MOA} = \frac{F_{MOA/SSA} \times M_{sea \, salt}}{1 - F_{MOA/SSA}}$$
(2)

The MOA number emission flux is calculated based on the MOA mass emission flux for a given particle diameter within the emission size range (from 0.020 to 2.8  $\mu$ m for the Mårtensson et al. parameterization) and particle density of MOA, the latter of which is set to be 1601 kg m<sup>-3</sup> (Liu et al., 2012), as given in Table 2.

227 Differences between the three emission methods lie in how to determine the 228 organic mass fraction  $F_{MOA/SSA}$ . These methods are compared in this study: the first is 229 the Langmuir isotherm-based parameterization by Burrows et al. (2014) (B14), the 230 second is based on wind speed and [Chl-a] by Gantt et al. (2011) (G11), and the third, 231 which represents a null hypothesis, assumes a fixed mass fraction between organic matter 232 and sea salt (NULL).

## 233 a. G11 emission scheme

A chlorophyll-based emission scheme of MOA was derived based on the [Chl-a] and the 10-m wind speed (Gantt et al. (2011), hereafter referred to as G11). In this method, the organic mass fraction of sea spray is parameterized as:

237 
$$F_{MOA/SSA} = \frac{\frac{1}{1+0.03 \times e^{6.81 \times D_p} + 0.03}}{\frac{1}{1+e^{-2.63 \times (Chl-a)+0.18U_{10}}}$$
(3)

238 where  $D_p$  is the dry diameter of particles.

## 239 **b. B14 emission scheme**

- 240 Different from the earlier empirical chlorophyll-based scheme, a physically-based 241 scheme, named OCEANFILMS was proposed for modeling the relationship between 242 emitted SSA chemistry and ocean biogeochemistry (Burrows et al. (2014), hereafter 243 referred to as B14). The Langmuir isotherm-based mechanism is adopted to describe the 244 organic enrichment on the bubble film. When the bubble film bursts, the film breaks up 245 into film drops, which are suspended in the air. After evaporation of water from these 246 droplets, the remaining suspending materials form MOA and sea salt aerosol particles. In 247 this method, the organic matter on one side of the bubble film (per area) is determined 248 by:
- 249

$$M_{S MOA} = S_m \times \theta \tag{4}$$

where  $S_m$  is the organic mass per area at saturation (Table 3), and  $\theta$  is the surface coverage fraction of organics calculated based on the Langmuir adsorption equilibrium assumption:

253

$$\theta = \frac{\alpha \times C_M}{1 + \alpha \times C_M} \tag{5}$$

where  $\alpha$  is the Langmuir parameter as prescribed in Table 3, and  $C_M$  is the mass concentration of organic matters in the ocean.  $C_M$  is prescribed from the monthly mean surface distribution of macromolecule concentrations, which is generated by ocean biogeochemical simulations (Burrows et al., 2014). In this method, three different organic classes are considered with molecular weights and mass per area at saturation as prescribed in Table 3.

Based on Equations (1), (4), and (5), the organic mass fraction of sea spray is expressed as:

262 
$$F_{MOA/SSA} = \frac{S_m \times \frac{\alpha \times C_M}{1 + \alpha \times C_M}}{S_m \times \frac{\alpha \times C_M}{1 + \alpha \times C_M} + M_{s\_sea \ salt}}$$
(6)

263  $M_{s\_sea \ salt}$  is the sea salt mass per area of bubble surface, which is set to be 0.0035875 g 264 m<sup>-2</sup>.

265

## 266 c. NULL emission hypothesis

Null hypothesis assumes that the organic mass fraction of SSA is constant, and
does not vary geographically or seasonally. If we are to adopt a parameterization for the

269 seasonal dependence of MOA, it is desirable to demonstrate that the agreement with 270 observations of MOA is improved by such a parameterization, compared with the null 271hypothesis that no such relationship exists. The choice of the "null" hypothesis is 272 motivated in part by Quinn et al. (2014) and Bates et al. (2020), who measured roughly 273 constant values of F<sub>MOA/SSA</sub> in SSAs generated at sea by using a floating device to 274 generate and sample spray, during five sea-going ship campaigns. These studies 275 measured F<sub>MOA/SSA</sub> values of roughly 0.7–0.9 in sub-0.180 µm particles, and roughly 276 0.05-0.3 in sub-1.1 µm particles.

277 Loosely following the results of Quinn et al. (2014) and Bates et al. (2020), we set 278  $F_{MOA/SSA}$  to 0.8 in the Aitken mode, and to 0.05 in the accumulation mode (see Table 1 279 for the size ranges of Aitken and accumulation modes). For comparison, Facchini et al. 280 (2008) measured SSA generated from oceanic water for its organic and salt content, and 281 found that organic matter comprised roughly 75% of particles in the size range 282  $0.125-0.250 \,\mu\text{m}$ , and that this fraction decreased with increasing particle size to about 5% 283 of 1 µm particles. Similarly, Prather et al. (2013) analyzed sea spray generated in a wave 284 tank during a mesocosm bloom experiment and reported that about 80% of 0.080  $\mu$ m 285 particles were classified as organic carbon by transmission electron microscopy (TEM) 286 with energy-dispersive X-ray (EDX), while a few percents of 1 µm particles were 287 classified as either organic carbon or biological species by the aerosol TOF mass 288 spectrometry (ATOFMS).

289

# 290 2.2.2 Effects of MOA on clouds as CCN and INPs

291 MOA is emitted into different aerosol modes depending on mixing state of MOA 292 and sea salt (Burrows et al., 2014, 2018). In the internally-mixed emission approach, 293 MOA is emitted into the accumulation and Aitken modes along with sea salt, as shown in 294 Table 1. In contrast, MOA is emitted into the Aitken and primary carbon modes in the 295 externally-mixed emission approach. Furthermore, the emission of MOA can replace or 296 be added to sea salt emission in terms of mass and number in the model. Burrows et al. 297 (2018) found that simulated MOA amounts, seasonal cycles, and impacts on CCN over 298 the Southern Ocean show better agreement with observations under the assumption that 299 emitted MOA is added to, and internally mixed with sea salt. Thus, we used the

300 "internally-mixed" and "added" approach for MOA emission in this study. As shown in Table 2, the hygroscopicity of MOA is set to be 0.1 following Burrows et al. (2014, 301 302 2018), compared to 1.16 for sea salt. The mode hygroscopicity is calculated as the 303 volume-weighted average of hygroscopicities of all species in a mode, which is then used 304 in the Abdul-Razzak and Ghan (2000) droplet activation parameterization in CAM6. The 305 mode hygroscopicity is reduced due to lower hygroscopicity of MOA. However, based 306 on the method to calculate sea salt emission (Liu et al., 2012) for a given aerosol mode, 307 the "added" MOA mass increases the number concentrations of particles in the Aitken 308 and accumulation modes, which overcomes the reduction in mode hygroscopicity to 309 activate more CCN.

In this study, in addition to the CCN effect of MOA, we also include its effect on clouds as INPs. For this purpose, two different ice nucleation parameterizations for MOA are implemented in CAM6. Additionally, we examine the relative importance of MOA to dust INPs with different ice nucleation parameterizations.

314

## a. W15 ice nucleation scheme of MOA

315 An INP parameterization for MOA was proposed based on immersion-freezing 316 measurements of materials aerosolized from sea surface microlayer (SML) water samples 317 collected in the North Atlantic and Arctic Oceans (Wilson et al., 2015). In this 318 parameterization (hereafter as W15), the number concentration of MOA INPs is a 319 function of temperature (T) and the total organic carbon (TOC) mass concentration, given 320 as:

321

322

$$N_{IN,T} = TOC \times e^{(11.2186 - (0.4459 \times T))}$$
(7)

In which, TOC is calculated as  $M_{MOA} \times \frac{oc}{oM}$ , where the  $\frac{oc}{oM} = 0.5$  following McCluskey et al., 2018a.

W15 is developed based on the TOC in the sea surface microlayer samples, which may not be representative of ambient MOA. W15 assumes that relationship between TOC and INPs in airborne sea spray is the same as that in SML samples due to limited measurement data in the early stage. However, recent research suggests that INPs may be transferred differently from TOC during the sea spray production (Wang et al., 2017),

330 calling this assumption into question. The quantitative importance of this selective

- 331 transfer of INPs from SML to the SSAs is a topic requiring further research beyond the
- 332 scope of the current study and is not accounted for here. Additionally, this approach did
- 333 not attempt to correct for the possible entrainment of multiple ice-nucleating entities into
- 334 a single sea spray particle.

#### 335 M18 ice nucleation scheme of MOA b.

- 336 Another empirical INP parameterization of MOA was derived based on the correlation between ambient aerosols and INPs measured during the "clean scenario" at 337 338 Mace Head Station in August 2015 (McCluskey et al., 2018a, hereafter as M18). 339 Therefore, M18 includes the effect of physiochemical selective emission and aerosol 340 chemistry in the air which is missed in W15. This parameterization follows the same 341 functional form as the surface-active site density  $(n_s)$  parameterization of Niemand et al. 342 (2012) for dust, but with different coefficients for MOA, as given below:
- 343

$$n_s(T) = e^{(-0.545(T - 273.15) + 1.0125)}$$
(8)

MOA INP number concentration is then calculated by:  $N_{INP}(T) = N_{tot}S_{ae}n_s(T)$ , where 344  $S_{ae}$  and  $N_{tot}$  are the total surface area and number mixing ratio of SSA, calculated for 345 346 the Aitken and accumulation modes, respectively.

347

#### N12 ice nucleation scheme of dust c.

348 A surface-active site density-based ice nucleation scheme for immersion freezing 349 on dust was derived by Niemand et al. (2012) (hereafter referred to as N12) based on 350 measurements of the AIDA cloud chamber. N12 relates the number concentration of dust 351 INPs to the dust aerosol number concentration  $(N_{tot})$ , dust particle surface area  $(S_{ae})$ , 352 calculated based on dry diameter of particles), and the density of ice-active surface sites 353  $(n_s(T))$  at a given temperature T, shown as:

354

355

$$N_{INP}(T) = N_{tot} S_{ae} n_s(T) \tag{9}$$

356 in which  $n_s(T)$  is given as:

357 
$$n_s(T) = e^{(-0.517(T - 273.15) + 8.934)}$$
(10)

358 N12 is valid in the temperature range from -36 to -12 °C.

360

#### D15 ice nucleation scheme of dust d.

361 As the N12 scheme relates INPs to all sizes of dust aerosol, it may overestimate 362 INPs, since smaller dust aerosol (<0.5 µm) may not be effective as INPs. An empirical 363 ice nucleation scheme for the immersion freezing on dust aerosol with sizes larger than 364 0.5 µm was derived based on field and laboratory measurements (DeMott et al., 2015) 365 (hereafter referred to as D15). The dust INP number concentration is calculated as 366

- $N_{INP}(T) = a(n_{0.5})^b e^{c(T-273.15)-d}$ (11)
- 368

367

369 where a = 3, b = 1.25, c = -0.46, d = 11.6, and  $n_{0.5}$  is the number concentration of dust 370 particles with diameters larger than 0.5 µm.

371 We note that the above ice nucleation parameterizations (W15, M18, N12, and 372 D15) are based on empirical formulations. The default heterogeneous ice nucleation 373 parameterization in CAM6 follows the classical nucleation theory (CNT) (Wang et al., 374 2014). CNT is a stochastic scheme that links the freezing rate to the number 375 concentrations of dust and black carbon aerosols through different heterogeneous ice 376 nucleation mechanisms (deposition, contact, and immersion). Due to large uncertainties 377 in heterogeneous nucleation parameterizations, we conducted several ice nucleation 378 sensitivity experiments in CAM6 as will be discussed in section 2.3.

379

# 2.3 Model configurations and experiments

380 In this study, we carried out several numerical experiments to investigate the 381 influence of MOA on aerosols as well as CCN and INP activities (Table 4). All 382 simulations were performed for 10 years with prescribed climatological sea surface 383 temperatures and sea ice. The first year of simulations was treated as model spin-up, and 384 last nine years of simulations were used in analyses. The simulations were driven by the 385 present-day (year 2000) aerosol and precursor gas emissions with given greenhouse gas 386 concentrations. The model was run for 32 vertical levels from surface up to 3 hPa with a 387 horizontal resolution of 0.9° (latitudes) by 1.25° (longitude). We conducted two sets of

388 experiments. The first set of experiments, as listed in Table 4, are used to test the model 389 sensitivity to different MOA emission schemes. The baseline experiment (BASE) uses 390 the default CAM6 model which does not account for MOA emission and related physical 391 processes. In addition to the BASE experiment, the B14 experiment addresses emission, 392 advection, dry/wet deposition, and CCN effect of MOA using the Burrows et al. (2014) 393 emission scheme. We also designed two additional experiments (G11 and NULL) to 394 address the model sensitivity to emission methods. These simulations (B14 and G11) 395 were conducted with the added and internally-mixed MOA approach, following Burrows 396 et al. (2018). The INP effect of MOA is not considered in this set of experiments.

397 We conducted another set of experiments to investigate both CCN and INP effects 398 of MOA, as listed in Table 4. The control experiment (CTL) is the same as BASE except 399 that the D15 dust ice nucleation scheme was used to replace the CNT scheme in BASE, 400 because D15 gave a better model performance compared with observations in our 401 previous study (Shi and Liu, 2019). The B14 D15, which is based on CTL, considers the 402 MOA emission from B14 and the CCN effect of MOA. The B14 D15 M18 experiment, 403 which is based on B14 D15, additionally considers the INP effect of MOA based on 404 M18. The comparison between CTL and B14 D15 shows the CCN effect of MOA, while 405 the comparison between B14 D15 and B14 D15 M18 shows its INP effect. 406 We further conducted three experiments to examine the model sensitivity to a 407 different MOA ice nucleation parameterization (i.e., W15) in B14 D15 W15, and to two 408 different dust ice nucleation parameterizations (i.e., N12 and CNT) in B14 N12 M18 409 and B14 CNT M18 by comparing them with the B14 D15 M18 experiment,

410 respectively.

## 411 **3 Results**

## 412 **3.1 Evaluation of modeled MOA**

Given that a realistic representation of MOA emissions is a prerequisite for
models to quantify its influence on ice nucleation, we evaluate three different MOA
emission parameterizations in this section. We also analyze the processes contributing to
MOA burden such as emission, transport, and removal, because the burden pattern

417 largely determines the INP distribution pattern. Comparisons with available observations418 are made to examine the performance of different MOA emission schemes.

419 Table 5 lists the annual global mean emissions and burdens of MOA and sea salt 420 from different simulations. Overall, the G11 method generates the largest global MOA 421 emission (27.1 Tg yr<sup>-1</sup>) followed by the B14 method (24.5 Tg yr<sup>-1</sup>). The magnitudes of 422 MOA emissions are within the range of previous studies (Huang et al., 2018; Meskhidze 423 et al., 2011; Langmann et al., 2008). The ratios of MOA emission to sea salt emission are 424 0.67% and 0.74% for the B14 and G11 experiments, respectively, which are also 425 comparable to previous studies ranging from 0.3% to 3.2% (Huang et al., 2018; 426 Meskhidze et al., 2011). The NULL approach only gives an annual global MOA emission of 4.6 Tg yr<sup>-1</sup>, with the ratio of MOA emission to sea salt emission of 0.13%. These 427 428 values are much lower than those of B14 and G11 approaches. We note that emissions 429 and burdens of sea salt include the contribution from the coarse mode, which dominates 430 the total sea salt emissions and burdens. We further evaluate aerosol mass mixing ratios 431 and number concentrations in each aerosol mode in the B14 experiment, where MOA is 432 added and internally mixed with sea salt. In B14, the ratio of MOA to sea salt mass 433 burdens reaches up to 2.3 and 1.0 for the Aitken and accumulation modes, respectively. 434 Number concentrations of accumulation mode aerosols near the surface are increased by 435 up to 50% over some regions of the Southern Ocean and Arctic.

Despite the fact that there are differences in the global annual mean value, B14 and G11 generate similar spatial patterns of MOA emission rates (Fig. 1), while G11 tends to give higher emission rates than B14. Large emission rates are located in the mid-latitude storm tracks, equatorial upwelling, and coastal regions as shown in Fig. 1. These locations largely reflect the geographic distribution of primary ocean productivity as indicated by [Chl-a] (in G11) or organic matter concentrations (in B14).

Here we illustrate the influence of surface wind speeds (supplemental Fig. S1) on the emission of MOA. Although high MOA emissions are mostly co-located with vigorous oceanic biological activities, the oceanic area with smaller/larger wind speed tends to have a decreased/elevated emission rate relative to their biological activities. For instance, due to weak wind speeds (~5 m s<sup>-1</sup>), a strong signal of oceanic organic matter concentration does not correspond to a large emission rate in the west coast of South

America. On the contrary, because of strong wind speeds ( $\sim 10 \text{ m s}^{-1}$ ), moderate emission 448 449 rates are noticed over the subtropical North Pacific Ocean and subtropical South Indian 450 Ocean despite relatively small [Chl-a] or organic matter concentrations. This wind speed 451 dependent pattern is more clearly shown in the B14 results than in the G11 results, because in the B14 emission scheme,  $F_{MOA/SSA}$  is not related to the wind speed while 452 453 SSA emission is proportional to the surface wind speed, as described in section 2.2.1. 454 Conversely,  $F_{MOA/SSA}$  is inversely related to the wind speed in G11, results in a more 455 complicated relationship between wind speed and MOA emission rate in G11.

456 The global mean MOA burden is 0.097 Tg in B14, which is in close agreement 457 with previous studies which suggested a range of 0.031 to 0.131 Tg (Huang et al., 2018; 458 Burrows et al., 2018). The global distribution of MOA column burden shares the similar patterns between G11 and B14, with the peak burden around 1 mg m<sup>-2</sup> over the mid-to 459 460 high latitude Southern Ocean (Fig. 1). Despite the fact that large burdens are usually 461 related to locations of high emissions, they are also influenced by advection (dependent 462 on 3-D wind), dry deposition (dependent on particle size), and wet deposition (dependent 463 on precipitation). The oceanic regions with small annual precipitation rates (supplemental 464 Fig. S1) lead to considerable accumulations of MOA in G11 and B14. For instance, the peak burdens with maximum values of 0.4 to 0.6 mg  $m^{-2}$ , on either side of the Pacific 465 tropical convection zone correspond to the subsidence induced dry zone (i.e., subsiding 466 467 branch of Walker and Hadley circulations).

468 Zonally-averaged vertical distributions of MOA mass mixing ratio illustrate the 469 vertical transport of MOA (Fig. 1). Simulations from G11 and B14 exhibit a maximum value of 0.35  $\mu$ g kg<sup>-1</sup> within the boundary layer, located in 40°–50°S of the Southern 470 Ocean, while the maximum value is only 0.05  $\mu$ g kg<sup>-1</sup> in NULL. Globally, G11 shows 471 472 slightly higher MOA mass mixing ratios over all latitudes compared with B14, and 473 transports more MOA to high altitudes over the tropical regions. It is clear that MOA is 474 accumulated in the lower troposphere, i.e. below 600 hPa in G11 and B14, and below 800 475 hPa in NULL. The reason is that MOA is generated over the oceans, especially over the 476 storm track regions with high precipitation, limiting MOA mainly to the lower 477 troposphere.

478 We further evaluate model simulated MOA concentrations with measurements at 479 Mace Head (Ireland) and Amsterdam Island (Fig. 2). The B14 and G11 methods do well 480 in capturing the observed seasonal variation of MOA concentrations at Amsterdam Island 481 (Fig. 2a), although the model produces slightly higher MOA concentrations. At Mace 482 Head, the two methods produce delayed concentration peaks by about one month 483 compared with observations (Fig. 2b). The mass fraction of MOA in SSA (Fig. 2c) shows 484 a better agreement between the model and observation. Both the simulated and observed 485 organic mass fraction increase from March and reaches a peak in July, although the 486 observed peak is broader. The sea ice extent prescribed in the model as a boundary 487 condition has a strong seasonal variation over the Southern Ocean, as shown in 488 supplementary Figure S2. This can greatly impact the emission of MOA there (e.g., low 489 emission during the austral winter and early spring). The NULL approach does not 490 reproduce observed seasonal cycles of MOA and significantly underestimates observed 491 MOA concentrations due to the prescribed mass fraction (0.05) in the accumulation 492 mode.

Based on our analyses and comparisons with observations, we show that B14
implementation of MOA emission into CAM6 reasonably captures the concentrations and
seasonal variations of MOA. Next we will study the MOA effects on clouds via acting as
CCN (section 3.2) and INPs (section 3.3), based on model experiments with the B14
emission (Table 4).

# 498 **3.2 Impact of MOA on CCN**

After introducing MOA in the model, we notice an obvious increase in oceanic 499 500 surface CCN concentrations at high latitudes. Figure 3 shows the spatial distribution of 501 annual mean percentage changes in surface CCN concentrations at a supersaturation of 502 0.1% due to MOA, derived from the two experiments (CTL and B14 D15). From Fig. 3, 503 the annual mean CCN concentration increases by 15%-35% over much of the oceans 504 from 30°S to 70°S, with a maximum increase of 45% located over the Southern Ocean 505 (60°S, 55°E). Other regions showing significant increases of CCN are over the pristine high latitudes, with increases of 25–35% from 60°S to Antarctica in the SH and from 506 507 60°N to 80°N in the NH. These results are comparable with previous results with an

508 average increase by 12% and up to 20% of CCN over the Southern Ocean (Meskhidze et 509 al., 2011). Over low- and mid-latitude oceans, CCN changes due to MOA are smaller. 510 Generally, the distribution of CCN change is consistent with the MOA emission pattern. 511 The vertical profiles of CCN concentrations from the two model experiments and 512 observations during the eight field campaigns are shown in Fig. 3. Clear increases of 513 CCN concentrations in the boundary layer due to MOA are evident for campaigns over 514 the ocean or coastal regions (SOCEX1, SOCEX2, ACE1, FIRE1, and ASTEX), with a 515 maximum increase (26%) in ACE1. Observed CCN from FIRE1 shows a strong 516 inversion of CCN below 800 hPa, and this inversion is challenging for the model due to 517 its coarse vertical resolution. An obvious underestimation of CCN in the model is noticed 518 at FIRE3 over the Arctic Ocean in Spring, which is attributed to the underestimated 519 transport of air pollution caused by too strong wet scavenging in the model (Liu et al., 520 2012).

# 521 **3.3 Impact of MOA on INPs**

522 In order to examine the importance of MOA INPs, we compare modeled INPs 523 from MOA versus dust as well as compare them with observations from several field 524 campaigns in high latitudes (Fig. 4). Modeled INP concentrations from MOA are 525 calculated online using M18 and W15 parameterizations (from B14 D15 M18 and 526 B14 D15 W15 experiments, respectively), while dust INP concentrations are calculated 527 online using D15, CNT, and N12 parameterizations (from B14 D15 M18, 528 B14 CNT M18, and B14 N12 M18 experiments, respectively). Modeled INP 529 concentrations are computed based on aerosol concentrations at different temperatures 530 and are selected at the same altitudes and locations as the observations. The measured 531 INP data were obtained from Mace Head, the CAPRICORN campaign (Clouds, Aerosols, 532 Precipitation, Radiation, and Atmospheric Composition over the Southern Ocean), 533 Oliktok Point, Zeppelin, and the SOCRATES campaign (Southern Ocean Clouds, 534 Radiation, Aerosol Transport Experimental Study) (McCluskey et al., 2018a; McCluskey 535 et al., 2018b; Creamean et al., 2018; Tobo et al., 2019). 536 As illustrated in Fig. 4, the M18 parameterization tends to underestimate observed

537 INP concentrations except at temperatures colder than -25°C. On the other hand, the W15

parameterization overestimates observed INP concentrations except at temperatures
warmer than -20°C. Under the same MOA scenario, the W15 parameterization is more
efficient in producing INPs than M18. This is because the M18 parameterization was
derived from MOA in the atmosphere which accounts for the effect of physiochemical
selective emission and aerosol chemistry in the air. In contrast, the W15 parameterization
was derived based on the total organic carbon in sea surface microlayer samples, which
contain higher organic mass concentrations compared with ambient MOA.

545 The dust INP concentration calculated with CNT shows an underestimation when 546 temperature is warmer than  $-20^{\circ}$ C and an overestimation when temperature is between 547  $-30^{\circ}$ C and  $-20^{\circ}$ C. This is consistent with previous work by Wang et al. (2014). The D15 548 parameterization indicates a clear underestimation. The N12 scheme has the better 549 performance than D15 in Figure 4. However, the field campaigns used in Figure 4 are 550 marine aerosol dominant/contained scenario campaigns. MOA is identified as an 551 important INP source during these campaigns from measurements (McCluskey, 552Ovadnevaite, Rinaldi, et al., 2018b; McCluskey, Hill, Humphries, et al., 2018a). Thus, 553 dust should not be expected to be the dominant INPs as indicated by the N12 scheme 554 which only considers dust INPs. This suggests that N12 may overestimate dust INPs, 555 which is consistent with our earlier study (Shi and Liu, 2019). These results suggest that the N12 parameterization is more efficient in producing dust INPs than the D15 556 557 parameterization under the same dust loading. INP concentrations from N12 are 558 calculated based on the coarse, accumulation, and Aitken mode dust aerosol, which 559 account for fine dust particles, while INP concentrations from D15 are calculated based 560 on the number concentration of dust particles with diameters larger than 0.5  $\mu$ m (DeMott 561 et al., 2015). Simulated total INPs, the sum of dust and MOA INPs from D15 and M18, 562 gives a better agreement with observations than D15 and M18 alone, although 563 underestimations still exist at warmer temperatures.

Fig. 5 shows the comparison between simulated and measured INPs from five parameterization schemes as a function of temperature for the same field campaigns as in Fig. 4. Generally, an inverse linear relationship is revealed between log<sub>10</sub>(INPs) and temperature in the measurements. This relationship is also shown in simulated INP number concentrations from the empirical parameterizations (N12, D15, W15, M18). However, for

569 CNT, nearly constant INP number concentrations are presented at temperatures from

570

 $-35^{\circ}$ C to  $-20^{\circ}$ C, and then a rapid decrease with increasing temperature when temperature

- 571 is warmer than  $-20^{\circ}$ C. At temperatures higher than  $-15^{\circ}$ C, nearly no INPs are produced by
- 572 CNT, leading to the underestimation of INPs in the CNT method at these temperatures.
- We notice higher INP number concentrations are produced from M18 compared with W15 at Zeppelin during March 2017. The most distinctive feature of this campaign is its very low aerosol loadings. For example, simulated SSA mass mixing ratio is around 0.6  $\mu$ g kg<sup>-1</sup> with the maximum value at 1.8  $\mu$ g kg<sup>-1</sup> below 850 hPa, and the dust mass mixing ratio is around 0.3  $\mu$ g kg<sup>-1</sup>. We note that simulated dust INP number concentrations from N12 are always higher than those from D15, and both N12 and D15 are more efficient in producing INPs than CNT when temperature is warmer than –20°C.

580 The global distribution pattern of annual mean MOA INP concentrations at 950 581 hPa at temperature of -25°C is similar to that of MOA column burden concentrations, as shown in Fig. 6a. The MOA INPs are spread over the oceans, with peaks ( $\sim 0.1 L^{-1}$ ) over 582 583 40°S to 60°S of the Southern Ocean, the subtropical Southern Indian Ocean, the 584 subtropical Atlantic Ocean, and the subtropical Eastern Pacific Ocean. Meanwhile, dust 585 INP concentrations diagnosed at the same pressure and at the same temperature (Fig. 6b) 586 are dominant over the NH and downwind of dust source regions in the SH (e.g., around 587 Australia and extended to 50°S).

588 Fig. 6c shows the horizontal distribution of ratio of MOA INP concentration to 589 dust INP concentration at 950 hPa. It is clear that MOA INPs are more important than dust INPs in the 40°S south of SH, where MOA INP concentrations can reach up to 1000 590 591 times higher than those of dust INPs. The zonal mean vertical distribution of ratio of 592 MOA INP concentration to dust INP concentration is illustrated in Fig. 6d. The ratio 593 peaks near 65°S, indicating that MOA INPs are more important than dust INPs over the 594 Southern Ocean from surface up to 400 hPa, and extends poleward to 90°S. Above the 595 400 hPa altitude, dust particles are still more important INPs. Because dust particles are 596 emitted over drier deserts (i.e., with lower precipitation and thus less wet scavenging), 597 dust can be subject to long-range transport at high elevations. In contrast, most MOA 598 particles are generated over the storm track regions with high occurrences of precipitation. Taking into account of emission, transport and wet scavenging of MOA and dust particles 599

results in MOA INPs dominating below 400 hPa over the Southern Ocean while dustINPs are generally more important elsewhere.

602 Immersion freezing on MOA in mixed-phase clouds requires that there are cloud 603 droplets at temperatures colder than -4°C. Ice nucleation consumes cloud liquid water, and 604 thus will compete with other processes for cloud liquid water (e.g., autoconversion of 605 cloud water to rain, accretion of cloud water by rain and snow). This competition is 606 expected to result in a reduction of ice nucleation rate of MOA compared with the offline 607 calculation of ice nucleation rate as in McCluskey et al. (2019). Fig. 7 shows the annual 608 zonal mean ice production rates from the immersion freezing of MOA and dust, which are 609 calculated online for the cloud ice production tendency in the B14 D15 M18 experiment. 610 Over the NH, the immersion freezing of dust dominates the primary ice production, giving an averaged ice production rate at 5 kg<sup>-1</sup>s<sup>-1</sup> and up to 20 kg<sup>-1</sup>s<sup>-1</sup> over 40°N at 400 hPa (Fig. 611 7b), while the MOA ice production rate is around 1 kg<sup>-1</sup>s<sup>-1</sup> (Fig. 7a). However, in the 612 613 Arctic boundary layer, the MOA fraction of total ice production rate is around 0.6~0.7 (Fig. 614 7c), indicating that MOA INPs are more important in generating ice crystals than dust INPs 615 there. Over the SH, the immersion freezing rate of MOA dominates the primary ice 616 production below 400 hPa with the MOA fraction close to 1. The zonal average ice 617 nucleation rate of MOA is around 1 kg<sup>-1</sup>s<sup>-1</sup>, and up to 5 kg<sup>-1</sup>s<sup>-1</sup> over the 65°S Southern Ocean at 400–600 hPa. The immersion freezing rate of dust is around 1 kg<sup>-1</sup>s<sup>-1</sup> above 500 618 hPa, and smaller than 0.1 kg<sup>-1</sup>s<sup>-1</sup> below 600 hPa altitude in the SH. Analysis of the seasonal 619 620 variation of ice nucleation rate of MOA indicates that a maximum rate of about 16 kg<sup>-1</sup>s<sup>-1</sup> 621 occurs at 400-600 hPa over 60°S in July (austral winter). In summary, the annual mean 622 immersion freezing of MOA dominates the primary ice production over the SH below 400 623 hPa altitude and in the Arctic boundary layer.

# 624 **3.4 Impact of MOA on clouds and radiative forcing**

Table 6 displays the differences of cloud and precipitation variables between the CTL and B14\_D15\_M18 experiments. With added MOA aerosol, the global annual mean surface concentration of CCN at 0.1% supersaturation changes from 103.3 cm<sup>-3</sup> in CTL to 106.6 cm<sup>-3</sup> in B14\_D15\_M18. This increase of 3.28 cm<sup>-3</sup> is comparable to other model estimates of 3.66 cm<sup>-3</sup> (Burrows et al., 2018), and 2.6–3.0 cm<sup>-3</sup> (Meskhidze et al., 2011).

630 The vertically-integrated cloud droplet number concentration (CDNUMC) increases by

 $631 - 7.5 \times 104 \text{ cm}^{-2}$  (5.25% in percent change) on the global annual mean, and by  $1.1 \times 104 \text{ cm}^{-2}$ 

632 (0.94%) and  $3.2 \times 105 \text{ cm}^{-2}$  (16.89%) over 20–90°S during the austral winter

633 (June-July-August) and summer (December-January-February), respectively, by

634 comparing B14\_D15\_M18 with CTL. This reflects a strong seasonal variation of MOA

635 emissions due to changes in the sea ice extent as well as biological activity. The global

636 annual mean liquid water path (LWP), ice water path (IWP), longwave cloud forcing

637 (LWCF), and total cloud fraction (CLDTOT) do not show obvious changes between CTL

and B14\_D15\_M18. The global annual mean shortwave cloud forcing is stronger by -0.41

639 W m<sup>-2</sup> due to MOA. During the austral summer over 20–90°S, we notice an increase of

640 4.57 g m<sup>-2</sup> (5.10%) in LWP, and a 1.35% (2.52%) increase in low-cloud fraction. As a

641 consequence, SWCF is enhanced by -2.87 W m<sup>-2</sup> (Table 6), which is comparable to -3.5

 $W m^{-2}$  estimated in Burrows et al. (2018). Ice number concentration on  $-15^{\circ}C$  isotherm increases by 9.34% during the austral winter. There does not appear to be a significant change in LWCF, which is consistent with the result of Huang et al. (2018).

645 Strong CCN effect of MOA on clouds (in terms of significant changes in CCN and 646 CDNUMC) tends to occur only in the SH over 40–60°S, while strong INP effect (in terms 647 of significant changes in cloud ice mass and number concentrations) is notable over 50-70° in both Hemispheres (Fig. 8). Over 40–60°S, a significant increase from 70 to 90 cm<sup>-3</sup> in 648 649 the annual zonal mean surface CCN concentration is observed. The CCN concentration 650 there is nearly 30% higher in B14 D15 and B14 D15 M18 than in CTL. As a result, CDNUMC increases from  $2.6 \times 10^{10}$  m<sup>-2</sup> in CTL to  $3.0 \times 10^{10}$  m<sup>-2</sup> in B14 D15 and 651 652 B14 D15 M18 over 40-60°S, leading to an increase in LWP due to the aerosol indirect effect (Fig. 8). Furthermore, we notice a stronger SWCF at 40–60°S by 3 W m<sup>-2</sup> in 653 654 B14 D15 compared with CTL. After considering the INP effect of MOA in the model, we 655 notice that cloud ice number concentration and cloud ice mass mixing ratio increase in 656 mixed-phase clouds which led to a slightly decrease in CDNUMC. As indicated in Fig. 8b,d, cloud ice number concentration increases from 4500 kg<sup>-1</sup> in B14 D15 to 5500 kg<sup>-1</sup> in 657 658 B14 D15 M18 at ~60°S, with cloud ice mass mixing ratio increased by 0.25 mg kg<sup>-1</sup>. Over 60°N, cloud ice number concentration increases from 4200 kg<sup>-1</sup> in B14 D15 to 5200 659

 $660 \text{ kg}^{-1}$  in B14\_D15\_M18, with cloud ice mass mixing ratio increased by 0.1 mg kg<sup>-1</sup>.

- 661 Fig. 9 shows the seasonal variations of cloud properties and cloud radiative forcing 662 averaged over the 20°S-90°S in SH, in response to the introduction of MOA as CCN and 663 INPs. The seasonal variation of surface CCN concentration at 0.1% supersaturation shows the maximum value of 72 cm<sup>-3</sup> in the austral summer and the minimum value of  $\sim$ 50 cm<sup>-3</sup> 664 in the austral winter in CTL. Similar seasonal variation patterns are also noted for 665 666 CDNUMC and LWP. With the inclusion of MOA in the model, B14 D15 and B14 D15 M18 produce more surface CCN, with an increase of up to 14 cm<sup>-3</sup> ( $\sim$ 20%) in 667 January, compared with CTL. Accordingly, CDNUMC increases from 2.1×10<sup>10</sup> m<sup>-2</sup> in 668 CTL to  $2.5 \times 10^{10}$  m<sup>-2</sup> in B14 D15 in January, and LWP increases from 93 g m<sup>-2</sup> in CTL to 669 97 g m<sup>-2</sup> in B14 D15 in January. As a consequence, SWCF is stronger by -3.5 W m<sup>-2</sup> in 670 B14 D15 compared with CTL during the austral summer. We also notice that CCN, 671 672 CDNUMC, and SWCF show smaller changes during the austral winter due to weaker
- 673 oceanic biological activity and larger sea ice extent.
- 674 Different from the warm cloud features above, seasonal variations of ice properties in 675 mixed-phase clouds (i.e., cloud ice mass mixing ratio and number concentration on -15°C 676 isotherm, IWP) clearly show winter maxima. After introducing the INP effect of MOA in 677 the model, ice number concentration on  $-15^{\circ}$ C isotherm increases by comparing B14 D15 678 with B14 D15 M18, with obvious increases of up to 27% in June. Ice mass mixing ratio on  $-15^{\circ}$ C isotherm increases by 0.19 mg kg<sup>-1</sup> (13%) in June. Increases in both cloud ice 679 number and mass contribute to the increase of IWP by 0.5 g  $m^{-2}$  in austral winter. The 680 681 seasonal change of LWCF is not well correlated with changes in ice number concentration 682 and mass mixing ratio in mixed-phase clouds, because LWCF is controlled more by high 683 clouds. Our introduction of MOA INPs mainly occurs in mixed-phased clouds, and 684 therefore has a small influence on LWCF.
- As shown in Table 7, the CCN effect of MOA on SWCF is strongest in the austral summer, with the value of -2.78 W m<sup>-2</sup> over the 20°S–90°S in SH. In contrast, the INP effect of MOA on LWCF is strongest in the austral winter, with the value of 0.35 W m<sup>-2</sup> (Table 8). For the net cloud forcing (SWCF + LWCF), the CCN effect of MOA is 2.65 W m<sup>-2</sup> in the austral summer, and the INP effect is 0.65 W m<sup>-2</sup> in austral spring over the 20°S–90°S. The annual global mean CCN and INP effects of MOA on the net cloud forcing are -0.35 and 0.016 W m<sup>-2</sup>, respectively. From an annual mean perspective, the
  - 24

692  $\,$  CCN effect of MOA on SWCF is –0.84 W  $m^{-2}$  over 20–90°S and is about twice as much as

the global mean value ( $-0.41 \text{ W m}^{-2}$ ), which indicates that the global annual mean SWCF

694 change due to MOA is dominated by SH contributions.

# 695 **4 Discussion**

696 In this study, for the MOA emission process, we only considered the generation 697 of MOA during the film drop breakup in B14, and the generation of MOA from jet drops 698 is not currently included. The film drops form from bubble-cap films bursting, while the 699 jet drops generate from the base of breaking bubbles. Particles from jet drops, with the 700 diameter is around supermicrometer, are considered larger than particles from film drops 701 (Wang et al., 2017). These large aerosol particles from jet drops are more effective as 702 CCN and INPs. Extending the current emission scheme to include MOA emissions 703 through jet drops (Wang et al., 2017) may be possible with more measurements and an 704 improved understanding of physical mechanisms that determine the sea spray organic 705 emission.

706 For the ice nucleation efficiency of MOA, the M18 parameterization only 707 includes the more persistent, heat-stable component observed in ambient sea spray 708 aerosol INP sampling. This neglects the heat-labile organic INPs (McCluskey et al., 709 2018b). Regarding ice nucleation mechanisms, only the immersion mode of ice 710 nucleation is implemented in this study, however, recent laboratory experiments (Wolf et 711 al., 2019) have indicated a potentially important role of MOA in the deposition mode at 712 temperatures below  $-40^{\circ}$ C. Future work will focus on improving the limitations of the 713 current understanding of MOA emission and ice nucleation in the model.

In this study, other potential INP species than dust and MOA, such as ash,
biomass-burning particles, or other land-borne biological particles (Hoose et al., 2010;
Jahn et al., 2020; Schill et al., 2020) are not represented in the model. These INP species
can be regionally important at certain temperature regimes of mixed-phase clouds.
Accounting for these species may increase the INP concentrations predicted in the model
and change the mixed-phase cloud properties, particularly at warmer temperatures >
-15°C. The impacts of these INP species will be quantified in our future studies.

721 Recent studies indicated an underestimation of ice formation in CAM6 722 (D'Alessandro et al., 2019) that results in too much cloud liquid and too little cloud ice in 723 mixed-phase clouds. In addition to ice nucleation undertaken in this study, other factors 724 may contribute to this model bias. For example, the CLUBB scheme used in CAM6 for 725 turbulence and shallow convection treats only liquid phase condensation, lacking ice 726 formation in the model's large-scale cloud macrophysics (Zhang et al., 2020). 727 Furthermore, CAM6 misses the representation of several important mechanisms of 728 secondary ice formation. Observed secondary ice formation processes include rime 729 splintering, ice-ice collision fragmentation, droplet shattering during freezing, and 730 fragmentation during sublimation of ice bridges (Field et al., 2017). Currently, only the 731 rime splintering is considered in CAM6. Lastly, CAM6 with a horizontal resolution of 732 approximately 100 km may not resolve the subgrid cloud processes and heterogeneous 733 distributions of cloud hydrometeors (Tan et al., 2016; Zhang et al., 2019). These issues 734 will be addressed in future studies.

# 735 **5 Summary and Conclusions**

This study introduces MOA into CAM6 as a new aerosol species and treats the chemistry, advection, and wet/dry deposition of MOA in the model. This paper also considers the MOA influences on droplet activation and ice nucleation, particularly focusing on quantifying the INP effect of MOA on cloud properties and radiation. Here we summarize our main findings:

741 (1) Three different emission schemes (B14, G11, and NULL) of MOA were 742 implemented in the model and simulated MOA concentrations were evaluated with 743 available observations. The global simulation indicates that high MOA burden centers are 744 mostly co-located with regions of vigorous oceanic biological activities and high wind 745 speeds such as in mid-latitude storm tracks, the equatorial upwelling, and coastal regions. 746 The global MOA emission is 24.5 Tg yr<sup>-1</sup> in B14, 27.1 Tg yr<sup>-1</sup> in G11, and 4.6 Tg yr<sup>-1</sup> in 747 the NULL emission approach. On the global scale, the MOA mass emission is 0.67%, 748 0.74%, and 0.13% of the sea salt mass emission from B14, G11, and NULL, respectively. 749 We show that observed seasonal cycles of marine organic matter at Mace Head and 750 Amsterdam Island are reproduced when the MOA fraction of SSA is assumed to depend

on sea spray biology (B14, G11), but are not reproduced when this fraction is assumed to
be constant (NULL). Our study does not support the constant organic mass fraction of
SSA emissions (Quinn et al., 2014; Saliba et al., 2019; Bates et al., 2020).

754 (2) After introducing MOA in the model, annual mean CCN concentrations (at 755 supersaturation of 0.1%) are increased by 15%-30% over the oceans ranging from  $30^{\circ}$ S 756 to 70°S. Two different ice nucleation schemes of MOA (M18 and W15) are implemented 757 and compared with available measurements. The INPs from MOA by the M18 758 parameterization show a reasonable agreement with observations at NH and SH high 759 latitudes, while simulated total INPs, the sum of MOA INPs from M18 and dust INPs 760 from D15, give a better agreement with observations. W15 for MOA alone overestimates 761 the observed INP concentrations across all temperatures. At -25°C, MOA INP 762 concentrations can be 1000 times higher than those of dust INPs over 40-60°S in the SH 763 boundary layer while dust INP concentrations are higher above 400 hPa altitude over SH 764 and NH.

765 (3) We notice a strong CCN effect of MOA over 40-60°S only in SH, while a 766 strong INP effect of MOA is identified over 50–70° in both Hemispheres. For seasonal 767 variations, CCN effect is stronger during the austral summer than winter, while INP 768 effect is stronger in the austral winter than summer. The CCN effect of MOA on SWCF is strongest in the austral summer over SH with a value of -2.78 W m<sup>-2</sup>, while the INP 769 770 effect on LWCF is strongest in the austral winter over SH with a value of 0.35 W m<sup>-2</sup>. 771 The annual global mean CCN and INP effect of MOA on the net cloud forcing is -0.35 and 0.016 W m<sup>-2</sup>, respectively. This work is a stepping stone towards better climate models 772 773 because the important role of MOA in biogeochemistry, hydrological cycle, and climate 774 change.

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- 776
- 777 **Competing interests:** The authors declare that they have no conflict of interest.
- 778

- 779 **Data availability:** The model code is available at
- 780 https://github.com/CESM-Development. The observed INP data is available at
- 781 https://data.eol.ucar.edu/master\_lists/generated/socrates/.
- 782
- 783 Author contributions: XZ and XL conceptualized the analysis and wrote the manuscript
- with input from the co-authors. XZ modified the code, carried out the simulations, and
- performed the analysis. SB provided scientific suggestions to the manuscript and
- provided the model code for the emission of marine organic aerosol. YS provided help in
- setting up the global climate model, designing the model runs, and created Figures. XL
- 788 was involved with obtaining the project grant, supervised the study. All authors were
- involved in helpful discussions and contributed to the manuscript.
- 790

791 Acknowledgment: This research was supported by the DOE Atmospheric System

- Research (ASR) Program (grant DE-SC0020510). S. M. Burrows was also funded by the
- U.S. DOE Early Career Research Program. We thank Christina McCluskey for providing
- the INP data from the SOCRATES campaign.

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Table 1. Aerosol species in MAM4 modes

	Accumulation	Aitken	Coarse	Primary Carbon	
	num_a1, so4_a1,	num_a2, so4_a2,	num_a3, dst_a3,	num_a4, pom_a4,	
Second	pom_a1, soa_a1,	soa_a2, ncl_a2,	ncl_a3, so4_a3	bc_a4, (moa_a4 if	
Species	bc_a1, dst_a1, ncl_a1,	dst_a2, moa_a2		externally added)	
	moa_a1				
Size range	$0.08-1 \ \mu m$	$0.02-0.08\;\mu m$	1–10 µm	0.08 <b>-</b> 1 μm	
Standard Deviation $\sigma g$	1.6	1.6	1.2	1.6	
Number-median	1.1	$2 < 10^{-8}$	2010-6	F 0 10-8	
diameter Dgn	1.1 × 10 '	2.6 × 10 °	2.0 × 10 °	$5.0 \times 10^{-6}$	
Low bound Dgn	$5.35 \times 10^{-8}$	$8.7 \times 10^{-9}$	$4.0 \times 10^{-7}$	$1.0 \times 10^{-8}$	
High bound Dgn	$4.8 \times 10^{-7}$	$5.2 \times 10^{-8}$	$4.0 \times 10^{-5}$	$1.0 \times 10^{-7}$	

<sup>1</sup>so4\_aX: sulfate mass mixing ratio in mode X; pom\_aX: particulate organic matter (POM) mass mixing ratio in mode X; soa\_aX: secondary organic aerosol (SOA) mass mixing ratio in mode X; bc\_aX: black carbon (BC) mass mixing ratio in mode X; dst\_aX: dust mass mixing ratio in mode X; ncl\_aX: sea salt mass mixing ratio in mode X; moa\_aX: marine organic aerosol (MOA) mass mixing ratio in mode X; and num\_aX: number mixing ratio of mode X. \*\_a1: accumulation mode; \*\_a2: Aitken mode; \*\_a3: coarse mode; and \*\_a4: coarse mode.

Species	Name	Density (kg m <sup>-3</sup> )	Hygroscopicity	
BC	Black carbon	1700	$1.0 \times 10^{-10}$	
SO4	Sulfate	1770	0.507	
SOA	Secondary organic	1000	0.14	
POA	Primary organic	1000	$1.0 \times 10^{-10}$	
DST	Dust	2600	0.068	
NCL	Sea salt	1900	1.16	
MOA	Marine organic aerosol	1601	0.1	

Table 2. Aerosol species and physical properties

Species	polysaccharides	proteins	Lipids
Molecular weight	250000	66463	284
$[g mol^{-1}]$			
mass per area at saturation	0.1376	0.00219	0.002593
$[g m^{-2}]$			
Langmuir parameter	90.58	25175	18205
$[m^3 mol^{-1}]$			

Table 3. Molecular weights, mass at saturation, Langmuir parameters of the three ocean macromolecules

Name	Emission of MOA	DUST ice nucleation	MOA ice nucleation	Notes
BASE	_	CNT	—	Base line simulation
B14	Burrows et al. [2014]	CNT	_	Sensitivity test of emission scheme
G11	Gantt et al. [2011]	CNT	—	Sensitivity test of emission scheme
NULL	NULL	CNT	_	Sensitivity test of emission scheme
CTL		DeMott et al. [2015]		Control simulation
B14_D15	Burrows et al. [2014]	DeMott et al. [2015]		CCN effect
B14_D15_M18	Burrows et al. [2014]	DeMott et al. [2015]	McCluskey et al. [2018]	INP effect
B14_D15_W15	Burrows et al. [2014]	DeMott et al. [2015]	Wilson et al. [2015]	Sensitivity test of MOA INP parameterization
B14_N12_M18	Burrows et al. [2014]	Niemand et al. [2012]	McCluskey et al. [2018]	Sensitivity test of dust INP parameterization
B14_CNT_M18	Burrows et al. [2014]	CNT	McCluskey et al. [2018]	Sensitivity test of dust INP parameterization

Table 4. List of experiments to test model sensitivity to different emission and ice nucleation schemes

Name	Sea salt	MOA emission	Sea salt burden	MOA burden	MOA/Sea salt emission
	emission	$(Tg yr^{-1})$	(Tg)	(Tg)	(%)
	$(Tg yr^{-1})$				
BASE	3651		8.83		_
B14	3656	24.5	8.88	0.097	0.67
G11	3666	27.1	8.86	0.120	0.74
NULL	3648	4.6	8.85	0.018	0.13

Table 5. Annual global mean emissions and burdens of MOA and sea salt

 $\begin{array}{c}1\\2\\3\\4\\5\\6\\7\\8\end{array}$ 

Table 6. Mean changes and relative changes (%) between CTL and B14\_D15\_M18 experiments. Included in the table are surface CCN concentrations at 0.1% (CCN), ice particle number concentration at -15°C thermal level (Ni\_15), vertically-integrated cloud droplet number concentration (CDNUMC), total grid-box cloud liquid water path (LWP), total grid-box cloud ice water path (IWP), shortwave and longwave cloud forcings (SWCF, LWCF), total cloud fraction (CLDTOT), high/mid-level/low-level clouds (CLDHGH, CLDMED, CLDLOW), and total surface precipitation rate (PRECT), with bold fond indicating relative changes larger than 3%.

	Global ANN	20S–90S ANN	20S–90S JJA	20S–90S DJF
CCN (cm <sup>-3</sup> )	3.28 (3.17)	4.85 (8.45)	1.37 (2.84)	9.26 (13.47)
Ni_15 (m <sup>-3</sup> )	39.39 (2.25)	102.0 (5.21)	275.93 (9.34)	-3.05 (-0.510)
CDNUMC (cm <sup>-2</sup> )	$7.53 \times 10^4$ (5.25)	$1.27 \times 10^5$ (8.65)	$1.10 \times 10^4 \ (0.94)$	$3.22 \times 10^5$ (16.89)
LWP (g m <sup>-2</sup> )	0.69 (1.02)	0.66 (0.77)	-1.86 (-2.32)	4.57 (5.10)
IWP (g m <sup>-2</sup> )	0.05 (0.37)	0.10 (0.99)	0.42 (3.69)	0.13 (1.48)
SWCF (W m <sup>-2</sup> )	-0.41 (0.86)	-0.63 (1.17)	0.400 (-1.48)	-2.87 (3.47)
LWCF (W m <sup>-2</sup> )	0.08 (0.35)	0.031 (0.15)	0.13 (0.57)	0.11 (0.52)
CLDTOT (%)	0.12 (0.17)	0.17 (0.22)	0.011 (0.014)	1.05 (1.45)
CLDHGH (%)	0.016 (0.039)	-0.0082 (-0.021)	-0.027 (-0.071)	-0.18 (-0.47)
CLDMED (%)	0.078 (0.26)	0.19 (0.55)	0.20 (0.54)	0.017 (0.054)
CLDLOW (%)	0.13 (0.33)	0.14 (0.24)	-0.43 (-0.69)	1.35 (2.52)
PRECT (mm day <sup>-1</sup> )	-0.0011 (-0.038)	0.0042 (0.17)	0.019 (0.71)	0.040 (1.66)

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Table 7. CCN and INP effects of MOA on SWCF, and the values in the table are the mean change and

relative change (%). The CCN effect is calculated between CTL and B14\_D15 experiments, and the INP

 $\begin{array}{c} 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \end{array}$ effect is calculated between B14\_D15 and B14D15\_M18 experiments, with the bold font indicated the maximum change.

	ANN	MAM	JJA	SON	DJF
20–90S CCN	-0.84 (1.58)	-0.47 (1.16)	0.48 (-1.78)	-0.59 (0.95)	-2.78 (3.36)
INP	0.22 (-0.50)	0.084 (-0.20)	-0.080 (0.30)	0.94 (-1.51)	-0.088 (0.10)
global CCN	-0.41 (0.85)	-0.21 (0.48)	-0.43 (0.89)	0.027 (-0.056)	-1.01 (1.96)
INP	-0.0037 (0.0077)	0.047 (-0.11)	0.27 (-0.54)	-0.16 (0.33)	-0.17 (0.33)

21Table 8. CCN and INP effect of MOA on LWCF, and the values in the table are the mean change and22relative change (%). The CCN effect is calculated between CTL and B14\_D15 experiments, and the INP

<u> </u>	relative change (%). The CCN effect is calculated between CTL and B14_D15 experiments, and the INP
23	effect is calculated between B14 D15 and B14D15 M18 experiments, with the bold fond indicated the
24	maximum change.

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	ANN	MAM	JJA	SON	DJF
20–90S CCN	0.064 (0.30)	0.033 (0.15)	-0.21 (-0.93)	0.29 (1.39)	0.15 (0.73)
INP	-0.033 (-0.15)	-0.15 (-0.68)	0.35 (1.5)	-0.29 (-1.35)	-0.042 (-0.20)
global CCN	0.064 (0.27)	-0.0097 (-0.040)	-0.032 (-0.13)	0.0890 (0.38)	0.21 (0.91)
INP	0.020 (0.085)	-0.12 (-0.50)	0.21 (0.85)	0.035 (0.15)	-0.039 (-0.17)

## Figures





Figure 1. Spatial distributions of annual mean surface flux (first column, in unit of  $\mu g m^{-2} s^{-1}$ ) and vertically-integrated (column) burden of MOA (second column, in unit of mg m<sup>-2</sup>), and latitude-pressure

31 32 33 34 35 36 37 38 cross-sections of annual mean MOA mixing ratio (third column, in unit of µg kg<sup>-1</sup>) from the B14 (first row), G11 (second row), and NULL (third row) experiments. The right black cross in the second row indicates

- the position of Mace Head, and the left black cross indicates the position of Amsterdam Island.



 $39 \\ 40 \\ 41 \\ 42 \\ 43 \\ 44 \\ 45$ 

Figure 2. Monthly averaged concentrations of MOA at (a) Amsterdam Island and (b) Mace Head Ireland;

and (c) monthly averaged mass fraction of MOA in SSA at Mace Head Ireland. The locations of

Amsterdam Island and Mace Head Ireland are shown in Figure 1.





46 47 48 Figure 3. Spatial distribution of annual mean percentage changes of surface CCN concentrations at 0.1% supersaturation due to MOA (by comparing B14 D15 and BASE), and vertical distribution of CCN 49 concentrations at 0.1% supersaturation from eight measurements (solid gray lines), BASE (solid orange 50 line) and B14 D15 (solid green line). Dashed lines outline a range of 10th and 90th percentiles for 51 measurements in different field campaigns: FIRE1 (the First International Satellite Cloud Climatology 52 Project Reginal Experiment) locates at 33° N and 238° E in California coast, the data is collected during 53 June to July, 1987; the FIRE3 locates at 72° N and 210° E in Arctic Ocean, the data is collected during May, 54 1998; the ASTEX (Atlantic Stratocumulus Transition Experiment) locates at 38° N and 332° E in Azores, the 55 data is collected during June, 1992; the SOCEX1 (Southern Ocean Cloud Experiment) is located as -42 ° S 56 and 142° E in Tasmania, the data is collected during July 1993; the data of SOCEX2 is collected during

- 57 58 59 January to February 1995; the ACE1 (Aerosol Characterization Experiment) locates at  $-45 \circ S$ ,  $145^{\circ} E$  in Tasmania, the data is collected during November to December, 1995; and the ENA\_JJA(Eastern North
- Atlantic) locates at 39° N and 332° E in Eastern North Atlantic, the data is collected during June to August,
- 60 61 while ENA\_DJF is collected during December, January, and February, 2006 to 2020.



 $\begin{array}{c} 63 \\ 64 \end{array}$ Figure 4. Comparison of simulated vs. observed INP number concentrations for different simulations: (a) 65 MOA INPs from M18 [McCluskey et al., 2018], (b) MOA INPs from W15 [Wilson et al., 2015], (c) dust 66 INPs from CNT [Wang et al., 2014], (d) dust INPs from D15 [DeMott et al., 2015], (e) dust INPs from N12 67 [Niemand et al., 2012], and (f) sum of dust and MOA INPs from D15 and M18. Simulated INPs data are 68 sampled at the same pressures, longitudes and latitudes as the field measurements. Dashed lines outline a 69 factor of 10 about the 1:1 line (solid) in all the panels. Color bar shows the observed temperature in °C, 70 while different markers represent different field campaigns. Zeppelin site locates at 78.9081° N, 11.8814° E, 71475 m above mean sea level in NyÅlesund, Svalbard, the INP data is collected during July 2016 and March 72 2017 [Tobo et al., 2019]; Oliktok Point site locates at 70.50° N 149.89°W, the INP data is collected during 73 March-May 2017 [Creamean et al., 2018)]; CAPRICORN (Clouds, Aerosols, Precipitation, Radiation, and 74Atmospheric Composition over the Southern Ocean) INP data is collected on ships during 13 March to 15 75 April in 2016 over the Southern Ocean [McCluskey, Hill, Humphries, et al., 2018a]; Mace Head site 76 locates at 53.32°N, 9.90°W, the INP data is collected during August 2015 [McCluskey, Ovadnevaite, 77 Rinaldi, et al., 2018b]; SOCRATES (Southern Ocean Clouds, Radiation, Aerosol Transport Experimental 78 Study) INP data is collected on flights during January-February 2018 over the Southern Ocean by Paul 79 DeMott (https://data.eol.ucar.edu/master lists/generated/socrates/). 80





87 88 89 90 91 92 Figure 6. Spatial distribution of annual mean concentrations of (a) MOA INPs, (b) dust INPs, and (c) ratio of MOA INP concentration to dust INP concentration at 950 hPa, and (d) vertical cross sections of ratio of MOA INP concentration to dust INP concentration. INP concentrations are diagnosed at temperature of −25°C.



- Figure 7. Annual zonal mean pressure-latitude cross sections of ice nucleation rates from (a) MOA, (b) dust,
- and (c) MOA fraction of total ice production rate.



97 98

Figure 8. Annual zonal-mean distributions of (a) surface CCN concentration at S=0.1%, (b) cloud ice 99 number concentration on T = -15 °C isotherm, (c) vertically-integrated cloud droplet number concentration, 100 (d) cloud ice mass mixing ratio on  $T = -15^{\circ}C$  isotherm, (e) liquid water path over ocean, (f) ice water path, 101 (g) shortwave cloud forcing, and (h) longwave cloud forcing for CTL (black), B14\_D15 (orange), and 102 B14 D15 M18 (green), along with available observations (gray dashed lines) as references. The -15°C 103 isotherm level was selected in (b) and (d) to better represent the mixed-phase cloud feature. 104

