OCEANFILMS sea-spray organic aerosol emissions – Part 1: implementation and impacts on clouds

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Abstract. The OCEANFILMS parameterization for sea-spray organic aerosol emissions has been implemented into a global Earth system model, the Energy Exascale Earth System Model (E3SM). OCEANFILMS is a physically-based model that links sea spray chemistry with ocean biogeochemistry using a Langmuir partitioning approach. Here we describe the implementation within E3SM and investigate the impacts of the parameterization on the model's aerosols, clouds and climate. Four sensitivity
5 cases are tested, in which organic emissions either strictly add to or strictly replace sea salt emissions (in mass and number), and are either fully internally or fully externally mixed with sea salt. The simulation with internally-mixed, added organics agrees best with observed seasonal cycles of organic matter in marine aerosol. In this configuration, marine organic aerosols contribute an additional source of cloud condensation nuclei, adding up to 30 cm^{-3} to Southern Ocean boundary-layer CCN concentrations (supersaturation= 0.1%). The addition of this new aerosol source strengthens shortwave radiative cooling by
10 clouds by -0.36 W/m^2 in the global annual mean, and contributes more than -3.5 W/m^2 to summertime zonal mean cloud forcing in the Southern Ocean, with maximum zonal mean impacts of about -4 W/m^2 around 50°S–60°S. This is consistent with a previous top-down, satellite-based empirical estimate of the radiative forcing by marine organic aerosol over the Southern Ocean.

1 Introduction

15 It has long been noted that organic matter can constitute a substantial portion of submicron marine aerosol mass (Hoffman and Duce, 1974, 1976, 1977; Duce et al., 1983; Oppo et al., 1999). However, only in more recent years has it been widely appreciated that water-insoluble organic matter (WIOM) contributes substantially to submicron marine aerosol downwind of strong seasonal phytoplankton blooms (O'Dowd et al., 2004), and has the potential to impact the number and chemical character of aerosol and cloud condensation nuclei (CCN) in certain marine regions (McCoy et al., 2015). Clouds in remote marine areas
20 are particularly sensitive to changes in aerosol concentrations (Karydis et al., 2012; Moore et al., 2013). These clouds, located in regions where anthropogenic aerosols are scarce, are primarily influenced by natural aerosol sources (Hamilton et al., 2014) and the ability to constrain climate sensitivity using historical climate records is in part limited by quantification of remote aerosol concentrations (Karydis et al., 2012; Carslaw et al., 2013). Recent research also suggests that marine organic aerosol

particles can serve as nuclei for freezing of cloud droplets (Knopf et al., 2011; Wilson et al., 2015; DeMott et al., 2016) and may play an important role as atmospheric ice nuclei in remote marine regions (Schnell and Vali, 1975, 1976; Burrows et al., 2013; Wilson et al., 2015; J. V. Temprado and Wilson., 2016).

Several previous studies have proposed and implemented representations of marine organic aerosol (MOA) emissions within a global climate model, with variations in the emissions representation and the assumed aerosol microphysical properties. Most of these studies were based on aerosol chemistry observations taken primarily from two sites, at Mace Head, Ireland and at Amsterdam Island, in the Southern Ocean (Sciare et al., 2009a; Rinaldi et al., 2013). O'Dowd et al. (2008a) proposed an early parameterization for MOA emissions, which was later modified by Langmann et al. (2008) for inclusion in a global model, and further updated and evaluated by Vignati et al. (2010) (which also corrects a typographical error in the formulation as printed in Langmann et al. (2008)). In this approach, the organic mass fraction (OMF), defined as the ratio of MOA mass to the total of and sea salt aerosol (SSA) mass, depends linearly on Chlorophyll-a [Chl-a], with an imposed upper bound corresponding to the highest observed values of OMF. Rinaldi et al. (2013) further updated this parameterization by adding a linear dependence of OMF on wind speed. This study also showed that the correlation between upwind [Chl-a] and OMF was improved when a time lag of 8-10 days was introduced.

Gantt et al. (2011) proposed an emission parameterization in which OMF depends on wind speed and [Chl-a], by fitting a non-linear equation form to observed OMF at Mace Head, Ireland and Point Reyes, California. Meskhidze et al. (2011) further evaluated this parameterization and compared it to Vignati et al. (2010), concluding that both parameterizations captured the magnitude of marine organic aerosol concentrations, with Gantt et al. (2011) attaining better seasonality.

Long et al. (2011) proposed another alternative approach in which OMF depends non-linearly on [Chl-a], using the functional form of the Langmuir isotherm to drive the relationship, and using a fit to observed [Chl-a] and OMF from two sea spray generation experiments to constrain the model parameters. The parameterization also takes particle diameter into consideration.

Additional model studies of marine organic aerosol have largely built upon these initial proposed parameterizations, and further explored their uncertainties, their sensitivities to certain aspects of the model implementation, and the resulting implications for climate. These studies have emphasized uncertainties in the choice to either add to or replace existing sea salt (Westervelt et al., 2012), to assume that aerosols are internally versus externally mixed (Meskhidze et al., 2011), and in the sea spray fine mode particle size (Tsigaridis et al., 2013). Some of these differing assumptions have been implemented and are the subject of sensitivity tests in this study, as will be described in Section 3. The calculation of underlying ina spray emission fluxes also contributes a significant source of uncertainty, with parameterizations differing by as much as a factor of two (De Leeuw et al., 2011), which further amplifies uncertainties in MOA emissions (Tsigaridis et al., 2013).

Other studies have aimed to constrain the magnitude of the global sea-spray organic aerosol source required to produce the best agreement with observed concentrations. Lapina et al. (2011) found that adding a MOA source of about 9 TgC y^{-1} to simulations in a global atmospheric chemistry model improved agreement with remote ship-based observations of marine organic aerosol concentrations from multiple field campaigns. Spracklen et al. (2008) used observed OC, back-trajectories, and remotely-sensed [Chl-a] from Mace Head, Amsterdam Island and the Azores to derive an empirical relationship between [Chl-a] and total (primary and secondary) oceanic organic aerosol concentrations. This study found that including an oceanic

organic carbon (OC) source of ca. 8 Tg/yr improved the modelled seasonal cycle at Mace Head and Amsterdam Island, and increased the global burden of OC by 20%, and by up to a factor of 20 or more in parts of the Southern Ocean.

Ito and Kawamiya (2010) implemented the [Chl-a]-based parameterization of O'Dowd et al. (2008b) and Langmann et al. (2008) into a global Earth system model, using an ocean biogeochemistry model to calculate [Chl-a] concentrations. An

5 estimate of marine isoprene emissions and subsequent SOA formation was also implemented. Marine organic aerosol sources were found to contribute to improved organic aerosol concentrations at remote marine locations, and led to a large increase in simulated organic aerosol concentrations in the future ice-free Arctic.

While empirical, [Chl-a]-based parameterizations have been successful in capturing some major observed features of the organic fraction of sea spray aerosol and its seasonal cycle, particularly at locations like Mace Head, Ireland, and Amsterdam

10 Island, these approaches do not offer a path towards explaining or testing hypotheses to explain the seasonal and geographic variability in the emissions or organic matter in sea spray. In particular, without understanding the mechanisms driving these emissions, we cannot have confidence that empirical parameterizations derived from mid-latitude observations will be an accurate guide to the behavior of tropical or polar ocean ecosystems, or that present-day observations will be an accurate guide to the behavior of future ocean ecosystems. In an effort to provide a path forward, Elliott et al. (2014) proposed the prospect of

15 an approach based on understanding of ocean surface films, and Burrows et al. (2014) introduced a new framework for modeling the functional relationships between ocean biogeochemical variables and the composition of emitted sea spray particles, called OCEANFILMS (**O**rganic **C**ompounds from **E**cosystems to **A**erosols: **N**atural **F**ilms and **I**nterfaces via **L**angmuir **M**olecular **S**urfactants). OCEANFILMS describes the organic mass fraction of emitted sea spray aerosol as a function of several classes of marine organic matter, each of which is assigned several chemical characteristics: adsorptivity at the air-water interface,

20 molecular weight, area occupied at the air-water interface, organic matter to organic carbon mass ratio (OM:OC). The value of each of these parameters is derived from laboratory studies of selected surrogate molecules, as described in detail in Burrows et al. (2014); the ocean distributions of surfactants are described further in Ogunro et al. (2015).

To further investigate the potential impacts of sea-spray organic aerosol on aerosol concentrations and chemistry, CCN and clouds, we implemented the OCEANFILMS parameterization into an early development version of global Earth system model,

25 the Energy Exascale Earth System Model (E3SM). A companion paper (in preparation) will provide a more detailed evaluation of the simulated aerosol number and mass concentrations, and chemistry, with respect to in situ observations (Burrows et al., 2017). Here we examine the climate implications of marine organic aerosol and its sensitivity to assumptions about its mixing state with sea salt, and about whether it adds to or replaces existing sea salt emissions. Section 2 describes in detail the implementation of the MOA tracers into the atmospheric model.

30 ## 2 Implementation of OCEANFILMS in E3SM

2.1 Model description

E3SM, formerly known as Accelerated Climate Modeling for Energy (ACME), is a global Earth system model developed by the U.S. Department of Energy (DOE) for high-resolution modeling on leadership supercomputing facilities. The model is a

Table 1. MAM4 modes, their size parameters and tracers carried, including number (N) and species mass M_{species}.

	Size range	σ_g	Nominal D_{gn} [m]	Low bound D_{gn} [m]	High bound D_{gn} [m]	Species
Aitken	20 – 80 nm	1.6	2.6e-8	8.70e-9	5.20e-8	$N, M_{SO_4}, M_{SOA}, M_{NCL}, M_{MOA}$
Accumulation	80 nm – 1 μm	1.8	1.1e-7	5.35e-8	4.40e-7	$N, M_{SO_4}, M_{SOA}, M_{POA}, M_{BC},$ $M_{DST}, M_{NCL}, M_{MOA}$
Coarse	1 – 10 μm	1.8	2.0e-6	1.00e-6	4.00e-6	$N, M_{SO_4}{}^1, M_{SOA}{}^1, M_{POA}{}^1, M_{BC}{}^1,$ $M_{DST}, M_{NCL}, M_{MOA}$
Primary carbon	80 nm – 1 μm	1.6	5.0e-8	1.00e-8	1.00e-7	$N, M_{POA}, M_{BC}, M_{MOA}$

[a]The original formulation of MAM4 did not contain M_{SO_4} M_{BC}, M_{SOA}, and M_{POA} in the coarse mode (Liu et al., 2016). These species were added to the coarse mode as part of the resuspension treatment discussed in this paper, as mass from any species can be transferred to the coarse mode during resuspension.

descendant of the Community Earth System Model version 1 (CESM1; Hurrell et al., 2013). The present paper focuses on the atmosphere component (E3SM Atmosphere model, or EAM), which is a descendant of the CAM5 (Community Atmosphere Model 5) model (Neale et al., 2010), and the version of the model used here closely resembles CESM1.3_beta10, except for some minor bug fixes and retuning that have small impact on the simulated climate, and the modifications described

5   herein. In the simulations discussed here, aerosol concentrations and microphysics are represented using the Modal Aerosol Module (MAM). Specifically, the implementation of OCEANFILMS builds on the 4-mode version of MAM (MAM4, Liu et al., 2016), which is an aerosol microphysics module that represents the aerosol size distribution by means of four lognormal modes. MAM4 extends an earlier 3-mode aerosol treatment (MAM3; Liu et al., 2012) by adding a fourth, insoluble submicron aerosol mode (the primary carbon mode), which carries primary organic and black carbon aerosol, and significantly improves

10 their concentrations relative to MAM3 simulations, at a lower computational cost than the more detailed 7-mode treatment implemented in MAM7 (Liu et al., 2016). The model version used in this study also includes a number of improvements to representations of aerosol-cloud interactions, which especially improve the simulated aerosol transport and removal, and concentrations of aerosols at high latitudes and in the upper troposphere (Wang et al., 2013).

2.2   Introduction of marine organic aerosol tracers

15 The unmodified MAM4 model carries the following chemical species: sea salt, dust, sulfate, secondary organic aerosol (SOA), black carbon (BC) and all non-MOA primary organic aerosol (POA), e.g., from terrestrial combustion sources and ship emissions (Table 1). POA is also referred to as primary organic matter (POM). The chemical species carried in each mode of the original MAM4 are identified in Liu et al. (2016). In the model version used here, the coarse mode also contains BC, SOA, and POA. Each mode's lognormal size distribution is defined by its prognostic aerosol number and mass mixing ratios and

20 a fixed geometric standard deviation (σ_g) (Table 1), and the mode's number-median diameter (D_{gn}) is a diagnostic variable.

Each species is characterized by physical properties describing its optical properties, density and hygroscopicity, summarized in Table 2.

In order to fully represent primary marine organic aerosol in the model and allow for the specification of chemical properties particular to this class of particles, we introduced an additional aerosol chemical species into the model, which we term "marine
5 organic aerosol" (MOA). MOA tracers were introduced into the model in each of the MAM4 aerosol modes.

2.3 Sea spray emissions

Sea spray aerosol in MAM is emitted according to the parameterization of Martensson et al. (2003) for particle diameters from 20 nm – 2.5 μm, and Monahan (1986) from 2.5 – 10 μm. The Martensson et al. parameterization is based upon laboratory simulations of particle production, using a sintered glass filter to generate a bubble plume leading to bubble bursting and
10 emissions. These experiments used synthetic seawater, i.e., pure Milli-Q water with the addition of synthetic sea salt and so the resulting parameterization is presumed not to include any contributions from organic matter. The Monahan (1986) parameterization, by contrast, was derived from whitecap simulation experiments in a tank filled with natural seawater collected from open coastal waters. However, since this parameterization is used only for sea spray particles of diameters greater than 2.5 μm, which have consistently been observed to contain minimal organic matter (e.g., O'Dowd et al., 2004; Facchini et al.,
15 2008; Prather et al., 2013; Quinn et al., 2014), these two sea spray emission parameterizations can be taken to include only salt emissions and not organics.

2.4 Emissions of marine organic aerosol according to OCEANFILMS

The OCEANFILMS parameterization, introduced and described in detail in Burrows et al. (2014), proposes a mechanistic approach for connecting emissions of sea-spray organic aerosol to models of ocean biogeochemistry. Monthly-mean concen-
20 trations of five broad classes of macromolecules in ocean surface waters are derived from distributions of phytoplankton, zooplankton, and semi-labile dissolved organic carbon, as simulated by an ocean biogeochemistry model. Chemical and physical properties are assigned to each of these macromolecular classes, based on representative proxy molecules for which laboratory measurements are available. Using a Langmuir isotherm-based approach, OCEANFILMS then predicts the surface coverage of ocean bubble films with each of these model macromolecules. This surface film coverage, together with a prescribed bubble
25 film thickness, determines the OMF of the emitted sea spray aerosol.

2.5 Participation of MOA in transport, aerosol and cloud microphysical processes, and loss processes

Aerosol particles evolve through a large number of processes including transport (by resolved winds, turbulent mixing, convective cloud updrafts and downdrafts, gravitational sedimentation, dry deposition), emissions, microphysical processes (condensation/evaporation of trace gases including water vapor, homogeneous nucleation, coagulation, renaming, aging), and
30 cloud/precipitation processes (aqueous chemistry in cloud droplets, activation, resuspension from evaporating cloud droplets and rain, in-cloud and below-cloud wet removal by both stratiform and convective clouds/precipitation). Marine organic
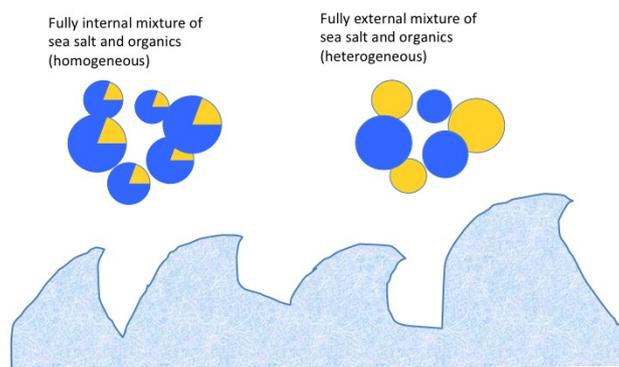
Figure 1. Illustration of internal versus external mixing states of sea spray aerosol upon emission. The emitted aerosol contains both sea salt (blue) and organic matter (yellow).

aerosols participate in almost all of these processes. MAM assumes that within each mode, particles are internally mixed, so at a given time and location, all particles in a mode have identical fractional composition (as illustrated in Figure 1). As a result, most processes affect all aerosol species within a mode in an identical manner. E.g., if 5% (on a mass basis) of the Aitken mode particles coagulate with accumulation mode particles during a model time step, then 5% of the mass of each

5   Aitken mode species is transferred to the corresponding accumulation mode species. Thus extending MAM to treat the new MOA species involved little or no changes to processes modules, and nearly all process modules automatically treat the new MOA species. The exception was emissions, where MOA specific coding was added. Also, many processes utilize physical properties that are averaged or summed over all species in a mode (e.g., total mass mixing ratio used in many processes, or the dry-volume weighted hygroscopicity used in activation and water uptake processes), and the MOA species contribute to these.

10   MOA is initially emitted into either the accumulation or primary carbon mode (depending on initial mixing state assumptions, see below) and the Aitken mode. Aitken mode particles and their MOA are transferred to the accumulation mode by growth processes (condensation of H_2SO_4 and organic vapors and aqueous sulfate production) and coagulation. The transfer by growth processes is termed renaming, wherein particles that grow larger than a size cut of ca. 80 nm diameter are transferred. Primary carbon mode particles and their MOA are also transferred to the accumulation mode by condensational growth

15   and coagulation. The transfer due to condensation is termed aging, and particles that acquire a specified number of sulfate monolayers, or a hygroscopically equivalent amount of SOA, are transferred (Liu et al., 2012, 2016). The aging criterion used was 3 monolayers, which resulted in an effective aging lifetime of approximately 2 days. The sensitivity of the model's aerosol lifetime to the aging criterion is discussed in Liu et al. (2016).

Table 2. Aerosol species and material properties in model simulations

Abbreviation	Name	Density [kg m^{-3}]	Hygroscopicity (κ)
MOA	Marine organic aerosol	1601	0.1
NCL	Sea salt	1900	1.16
POA	Primary organic matter	1000	1.0×10^{-10}
SOA	Secondary organic matter	1000	0.14
SO4	Sulfate aerosol	1000	0.507
DST	Dust	2600	0.068
BC	Black carbon	1700	1.0×10^{-10}

MOA and other aerosol species are also transferred to the coarse mode through evaporation of rain. When a rain drop completely evaporates, the aerosol material it contains (from in and below cloud scavenging that occurred at higher levels) is resuspended as a coarse mode particle. Because each rain drop is generally formed from thousands of cloud droplets, and the CCN on which each cloud droplet formed, the resuspended particle is generally of coarse mode size. This differs from the earlier MAM treatment (Liu et al., 2012) in which particles resuspended from evaporating rain are returned to their original mode. This change mainly affects aerosol number concentrations (the number of particles resuspended is much smaller in the new treatment) and has a minor impact on aerosol mass concentrations.

2.6 Optical and cloud-forming properties of marine organic aerosol

Particle CCN activation is determined by the Abdul-Razzak and Ghan scheme (Abdul-Razzak et al., 1998; Abdul-Razzak and Ghan, 2000; Ghan et al., 2011). The prescribed hygroscopicity for MOA is $\kappa_{\mathrm{MOA}} = 0.1$ (which is the hygroscopicity of, for example, xanthan gum, sometimes used as a proxy for marine organic matter (Dawson et al., 2016)), compared with a sea salt hygroscopicity of $\kappa_{\mathrm{NCl}} = 1.16$, and the prescribed density of MOA is 1601 kg/m^3, compared with a sea salt density of 1900 kg/m^3 (Table 2). The optical properties of marine organic aerosol are prescribed to be identical to those of sea salt aerosol, and are parameterized according to Ghan and Zaveri (2007). The marine organic aerosol does not contribute to ice nucleation in the current model configuration, but recent research indicates that marine organic particles can act as ice nucleating particles (INP), and may be an important source of INP to remote marine regions (Knopf et al., 2011; Burrows et al., 2013; Wilson et al., 2015; DeMott et al., 2016), so this may be a fruitful avenue for future studies. Additionally, surfactant effects on aerosol activation (due to alteration of surface tension) are not treated, but evidence suggests that the organic matter in marine aerosol is highly surface active (Blanchard, 1963; Barger and Garrett, 1970; Blanchard, 1975; Loglio et al., 1985; Giovannelli et al., 1988; Oppo et al., 1999; Mochida et al., 2002; Tervahattu et al., 2002; Cavalli et al., 2004; Facchini et al., 2008), and that particle activation rates can be significantly modified for aerosol particles that contain salts mixed with substantial amounts of surfactants (e.g., 70% or more by mass) (Sorjamaa et al., 2004; McFiggans et al., 2006), suggesting a possible role for surface

Table 3. Simulation sensitivity cases

Short name	Description
CNTL	Default model
	(no marine organics)
EXT_REPLACE	External mixing, replace sea salt
EXT_ADD	External mixing, add to sea salt
INT_REPLACE	Internal mixing, replace sea salt
INT_ADD	Internal mixing, add to sea salt

activity of marine organic matter in altering the water uptake and growth of marine aerosol particles (Abdul-Razzak and Ghan, 2004; Ovadnevaite et al., 2011; Petters and Kreidenweis, 2013; Ruehl and Wilson, 2014; Ruehl et al., 2016; Dawson et al., 2016). It has been suggested organic matter in submicron sea spray, by suppressing aerosol hygroscopic growth, may reduce the climate cooling associated with the scattering of sunlight by sea spray particles (direct aerosol effect) (Randles et al., 2004).

3   Model simulations and analysis methods

Several sensitivity simulations were performed, which were identical in their configurations, except for the changes in model physical assumptions described in Section 3.1. All simulations were performed as free-running atmosphere-only climate simulations with year 2000 boundary conditions and fixed sea surface temperature. Ocean macromolecular concentrations, which drive the calculation of OMF in emitted aerosol, are provided to the model as climatological monthly mean values, and are the same in each year of the model simulation. The model was allowed to spin up for a full year in order to allow MOA concentrations (initialized at zero throughout the atmosphere) to fully equilibrate in the atmosphere. After the first year, ten additional years were simulated and all further analysis was performed using the climatological monthly means of the ten years. The evaluation of these simulations by comparison with observations of marine aerosol number, mass, and chemistry is described in detail in a companion paper (Burrows et al., 2017).

3.1   Description of sensitivity cases

In implementing the emissions of marine organic aerosol, decisions must be made about a number of factors, in particular (1) the mixing state of the aerosol, especially with respect to sea salt, with which it is co-emitted, and (2) the impact on the total number and mass of particles emitted. Experiments and observations currently do not provide precise constraints on how the mixing state and amount of emitted particles respond to different ocean biology and chemistry conditions. Therefore, we conducted sensitivity experiments with four sets of assumptions that bracket the extremes of possible responses.

An overview of the sensitivity cases tested is shown in Table 3. In the control simulation, no marine organic aerosols are emitted. In the four sensitivity cases, marine organic aerosols are emitted using different assumptions in each case. In the "externally mixed" cases, emitted MOA is fully externally mixed with sea salt, meaning that it is emitted to the primary carbon mode. In the "internally mixed" cases, MOA is emitted to the soluble accumulation mode, together with sea salt (See Fig. 1

5   for schematic overview). Because MAM4 has only one Aitken mode, MOA emissions in the Aitken mode are internally mixed with all other aerosol species in both cases.

3.1.1 Experimental evidence on sea spray mixing state response to ocean biology

Experiments in which sea spray aerosol is generated by breaking waves in the presence of induced phytoplankton blooms provide the most realistic physical model of the sea spray aerosol production process (Ault et al., 2013; Collins et al., 2013;

10   Prather et al., 2013). These experiments, combined with single-particle mass spectrometry and electron microscopy, have shown that the smallest emitted particles are primarily organic, and marine organic matter is typically mixed internally with sea salt upon emission for intermediate sizes. The vast majority of the largest particles are composed almost entirely of inorganic salts.

3.1.2 Experimental evidence on sea spray number flux response to ocean biology

15   Experiments that illuminate the impacts of phytoplankton activity on the total number and mass of particles emitted are fewer and can be less straightforward to interpret. Perhaps the clearest experiment published to date that addresses this question may be Alpert et al. (2015), which reported results from sea spray aerosol production in a phytoplankton mesocosm experiment using a plunging jet system for aerosol generation. They report an increase of sea spray aerosol (SSA) particle number concentrations in the tank by a factor of about three when phytoplankton and bacteria were present in the tank, with the in-

20   crease occurring mainly for particles less than 200 nm in diameter. While bubble generation was turned off, particle counts were the same with lights on and off, and the lamps used in the experiments put out photosynthetically active radiation with wavelengths of 400 to 700 nm (Alpert et al., 2015). Thus it is unlikely that the results are due to either SOA formation or the recently-recognized mechanism of UV-initiated (wavelengths from 300-400 nm) photosensitized reaction pathways at the air-water interface (Rossignol et al., 2016; Fu et al., 2015; Tinel et al., 2016; Bernard et al., 2016). A similar observation was made

25   in an earlier study by Fuentes et al. (2011), where sea spray aerosol was artificially generated by a plunging multijet system, and aerosol emissions ($d < 200$ nm) increased substantially in the presence of phytoplankton exudates, with the magnitude of the increase varying depending on the phytoplankton species from which the exudate was derived.

Similarly, Long et al. (2014) also reported an increase in aerosol production in the presence of active biological production and light, in aerosol generation experiments using a plunging jet system to generate aerosol from natural seawater, onboard a

30   ship. Increased aerosol production was observed only during daytime, and only in the biologically-active waters of George's Bank (a coastal ecosystem); an increase was not observed in the oligotrophic waters of the Sargasso Sea. It is unclear, however, what the source of the increased aerosol production in these experiments was: this observation might be explained by photochemical oxidation of volatile precursors in the presence of light, leading to secondary organic aerosol formation, or
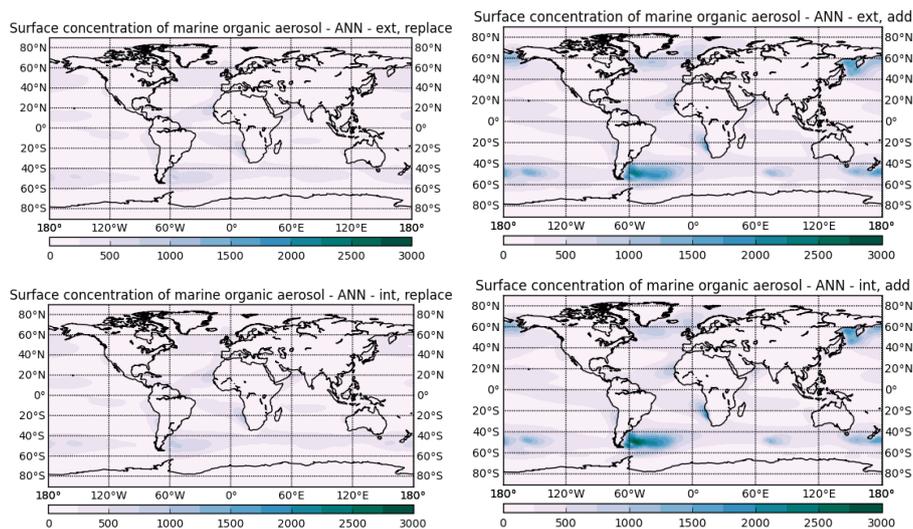
Figure 2. Simulated annual mean mass concentration [ng m^{-3}] of marine organic aerosol (atmospheric boundary layer), for four sensitivity cases described in Table 3.

alternatively might be the result of photosensitized reactions at the water surface, or of a response of biological systems to the availability of light for photosynthesis.

3.2 Significance testing

The statistical significance of differences induced by the introduction of marine organic aerosol emissions is presented for
5   some key model fields in this paper. In each case, statistical significance of changes in a monthly or seasonal mean field was calculated by Welch's unequal variances t-test, treating the monthly or seasonal mean from each year of the ten-year simulation as an independent sample. The t-statistic was calculated in either each grid box of a 2-D field, or at each latitude after zonal averaging of a 2-D field.

4   Results and discussion

10   ### 4.1   Sensitivity of simulated organic aerosol concentrations to model assumptions

Here we discuss the simulated organic aerosol concentrations in the four sensitivity cases, and their realism in comparison to observed seasonal cycles. Figure 2 shows the annual mean surface mass concentration [ng m^{-3}] of MOA in all sensitivity cases. Annual mean mass concentrations are < 250 ng m^{-3} over much of the globe in all sensitivity cases. However, in the ADD cases, much higher annual mean concentrations are produced, which can exceed 2.5 μg m^{-3} locally. These higher concentrations are
15   the result of higher emissions in the ADD cases; since OMF of emitted aerosol is approximately the same in both cases, the
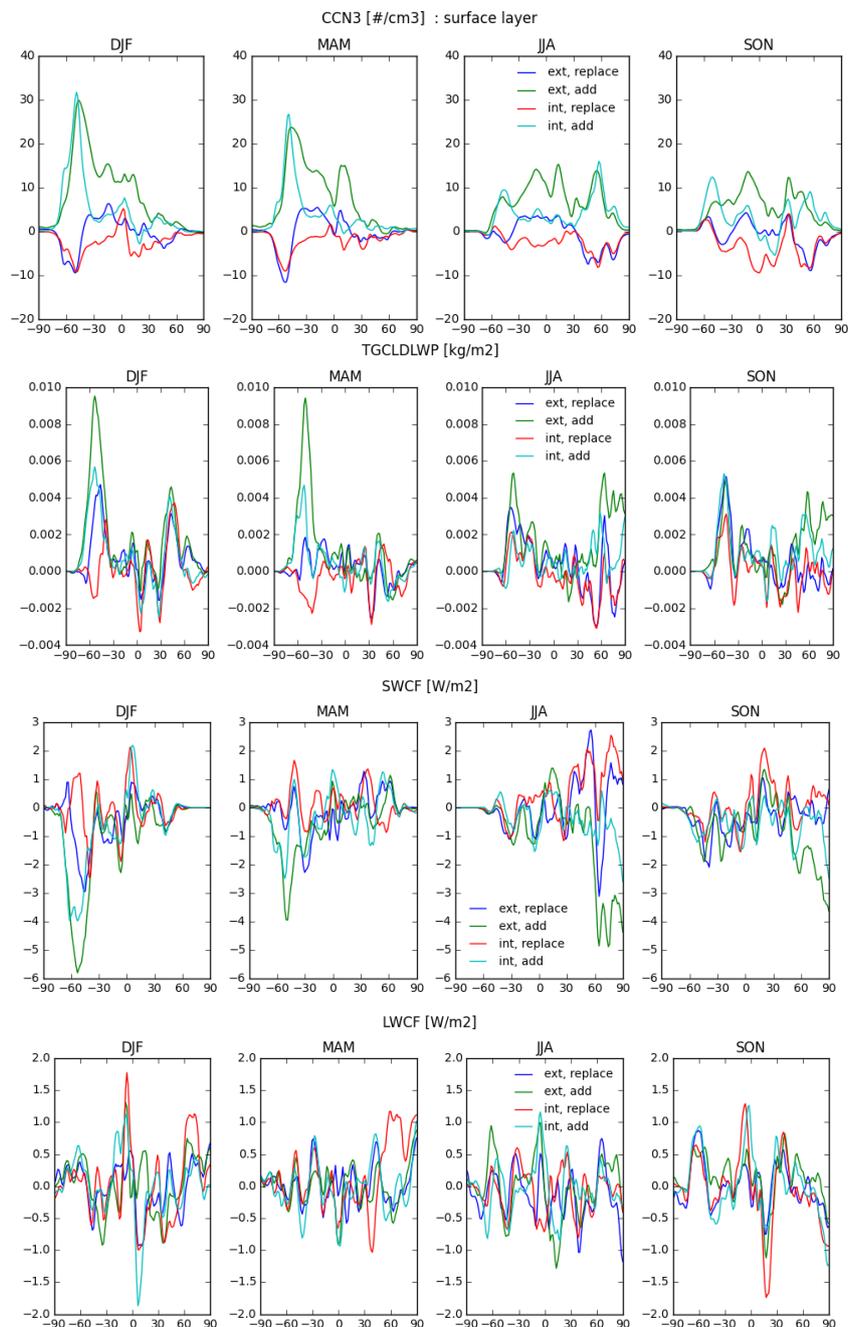
Figure 3. Difference in zonal mean for marine organics cases, relative to control simulation, by season. Top: CCN at S=0.1% in lowest model layer [cm^{-3}]. Second row: Total grid-box average cloud liquid water path [kg m^{-2}]. Third row: Short-wave cloud forcing [W m^{-2}]. Fourth row: Long-wave cloud forcing [W m^{-2}].
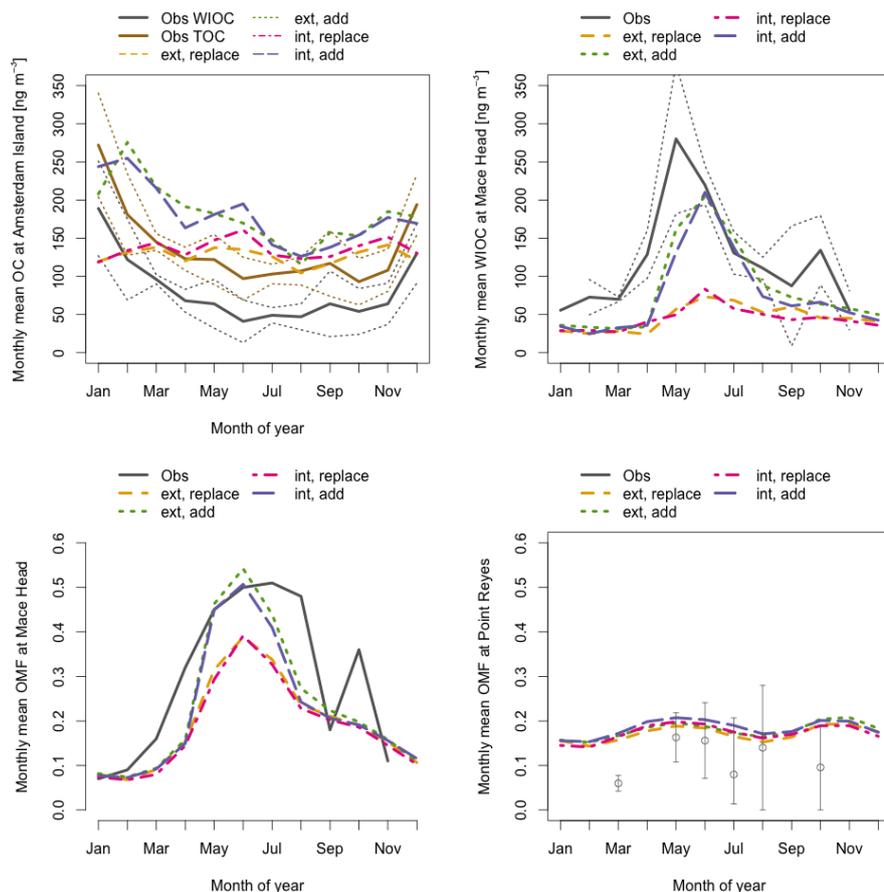
Figure 4. Top: Observed and simulated seasonal cycle, observed water-insoluble organic carbon (WIOC) and total organic carbon (TOC) in aerosol versus modelled marine organic carbon (MOC; converted from marine OM using OM:OC=1.9), at Amsterdam Island (left; d < 1.0 μm, Sciare et al. (2009b)) and Mace Head, Ireland (right; d < 1.5 μm, Rinaldi et al. (2013)). Note that the Mace Head samples were selected for "clean marine" conditions as described in Rinaldi et al. (2013), and that pristine conditions typically prevail at Amsterdam Island. Dashed lines represent the standard deviation of measurements from the same month, where more than one observation was available for a given month. Bottom: Observed and simulated seasonal cycle, organic mass fraction of aerosol as reported under clean marine sampling conditions, Mace Head, Ireland (d < 1.5 μm; (Rinaldi et al., 2013)), and Point Reyes, California (d < 2.5 μm; (Gantt et al., 2011)).

emissions of MOA required to achieve a given value of OMF are much higher in the ADD case than in the REPLACE case. Global mean concentrations are slightly higher in the externally-mixed cases, a reflection of the longer atmospheric residence time of aerosol emitted into the externally-mixed primary carbon mode, until it is aged into the accumulation mode.

Figure 3 shows the seasonal zonal mean changes in several relevant model fields, for all four sensitivity cases. As the number 5 of total aerosol particles increases in the ADD cases, this leads directly to increases in boundary-layer CCN concentrations (at

Table 4. Global atmospheric residence times for marine organic aerosol in the Aitken mode, and the combined accumulation and Primary carbon modes, for each sensitivity case. Residence times are calculated as the global annual mean burden divided by total global annual losses due to wet and dry deposition.

| | Marine organic aerosol global metrics | | | |
| | | external | | internal | |
		replace	add	replace	add
Aitken	Global annual mean burden (Gg)	0.05	0.09	0.05	0.09
	Global annual source (Gg/yr)	63.5	96.3	64.2	95.7
	Global annual mean residence time (d)	0.30	0.33	0.29	0.33
Accumulation + Primary carbon	Global annual mean burden (Gg)	31.3	44.3	34.3	47.8
	Global annual source (Gg/yr)	7.71×10^3	11.3×10^3	10.6×10^3	14.6×10^3
	Global annual mean residence time (d)	1.1	1.1	1.2	1.2

supersaturation S=0.1%; Figure 3, top row). This is particularly true in the austral summertime (DJF) over the Southern Ocean, where boundary-layer CCN (S=0.1%) number increases by up to 30 cm^{-3}, and by 5–10 cm^{-3} in winter, thus adding about $20 - 25$ cm^{-3} to the seasonal cycle in CCN number. For context, Ayers and Gras (1991) reported a summer-winter difference of 50 cm^{-3} in CCN (S= 0.23%) in a nine-year observational record at Amsterdam Island. McCoy et al. (2015) reported an average summer-winter difference of 10 cm^{-3} in satellite-observed cloud-top cloud droplet number concentrations over oceans from 35 S to 55 S, and attributed the seasonal cycle primarily to sulfate aerosol and secondarily to organic matter in sea spray aerosol. In the REPLACE cases, by contrast, CCN numbers are depressed over the Southern Ocean and Arctic in summertime, which is inconsistent with observational evidence. This is an expected feature of the simulation in the REPLACE cases, since salt emissions are reduced and replaced by less-hygroscopic organic matter.

In response to the changes in CCN number, there are also changes in simulated cloud liquid water path (Figure 3, second row). In particular, grid-box average liquid water path increases over the summertime Southern Ocean in the ADD and EXT cases. Liquid water path also increases in the summertime Arctic in the EXT_ADD case, but decreases in the REPLACE cases.

These changes in cloud droplet number concentrations and liquid water path lead to changes in cloud radiative forcing. Zonal mean short-wave cloud forcing changes (Figure 3, third row) are strong, and significantly different from the natural variability ($p < 0.1\%$), over the summertime Southern Ocean in the INT_ADD and EXT_ADD cases, and over the summertime Arctic in the EXT_ADD case. Changes in long-wave cloud forcing (LWCF), by contrast, are smaller (Figure 3, fourth row) and do not differ significantly from natural variability (t-test calculations for significance not shown).

Table 4 shows the global atmospheric residence times, with respect to all removal processes, for marine organic aerosol in the Aitken, accumulation and primary carbon modes, in each sensitivity case. The mean global residence time ranges from

0.29 — 0.33 days for the Aitken mode, and 1.1 — 1.2 days for the accumulation and primary carbon modes, with small variations across sensitivity cases.

4.1.1 Comparison of marine OC and OMF seasonal cycles in four sensitivity cases

Here we evaluate which of the four sensitivity cases produces the most realistic seasonal cycles of observed organic aerosol
5 mass and organic mass fraction, at several coastal sites where long-term observations are available. The seasonal cycle of organic aerosol concentrations at marine sites is compared with simulated seasonal cycles from all four model configurations in Figure 4. In the upper left panel, observed $d < 1.0\mu$m total organic carbon (TOC) and water-insoluble organic carbon (WIOC) at Amsterdam Island, a remote marine location where pristine marine conditions predominate, is compared with simulated Aitken and accumulation mode marine organic carbon (MOC), converted using an OM:OC ratio of 1.9. Overall, the model's
10 annual mean matches well with observed TOC in the `REPLACE` configurations (annual mean bias: -3%, `EXT_REPLACE`; 4%, `INT_REPLACE`) and is biased high in the `ADD` configurations (annual mean bias: 39%, `EXT_ADD`; 37%, `INT_ADD`). However, the best correlations of seasonal cycle are achieved in the `ADD` configurations ($\rho = 0.55$, `EXT_ADD`; 0.68, `INT_ADD`), while the `REPLACE` configurations are weakly anti-correlated ($\rho = $ -0.19, `EXT_REPLACE`; -0.47, `INT_REPLACE`).

The upper right panel of Figure 4 compares the seasonal cycle of WIOC at Mace Head, Ireland. Observations at this site
15 have been filtered for "clean marine" conditions as described in Rinaldi et al. (2013), so we assume that these samples are relatively unaffected by continental OC sources, and compare with the simulated marine OC mass only. At Mace Head, the "add" cases clearly match the observed seasonal cycle far better than the "replace" cases, with both a lower annual bias in the annual mean (-62%, `EXT_REPLACE`; -64%, `INT_REPLACE`; -33%, `EXT_ADD`; -38%, `INT_ADD`) and a higher correlation ($\rho = 0.56$, `EXT_REPLACE`; $\rho = 0.67$, `INT_REPLACE`; $\rho = 0.81$, `EXT_ADD`; $\rho = 0.77$, `INT_ADD`). Again, the best correlation
20 is achieved in the `INT_ADD` case.

The lower panels of Figure 4 compare the modeled and observed OMF at Mace Head (left) and at Point Reyes, California (right), where observations have also been screened for "clean marine conditions" in a similar fashion to those from Mace Head. Although the OMF of emissions is fixed, the `ADD` cases simulate higher OMF in boundary-layer aerosol at Mace Head; such a discrepancy can occur if aerosol from lower-OMF and higher-OMF regions mixes, due to the fact that the total aerosol
25 number and mass will be increased disproportionately more in the high-OMF regions for `ADD` cases. Once again, the `ADD` cases produce a better agreement with the Mace Head observations; at Point Reyes, all four configurations of the model give nearly identical results. Notably, the model reproduces the observed difference between a strong seasonal cycle at Mace Head and a weak or non-existant seasonal cycle at Point Reyes. Gantt and Meskhidze (2013) accounted for this difference by introducing a dependence of the OMF of emitted aerosol on wind speed, however, Figure 4 shows that this different seasonal behavior can be
30 simulated without resorting to a wind speed dependence. In the companion paper (Burrows et al., 2017), we will show that the correlations of OMF and wind speed in observations may be explained by correlations in seasonal cycles rather than a causal effect of wind speed on emitted OMF.

We have shown that the `ADD` cases produce better agreement with observed seasonal cycles of marine organic aerosol, and in Section 3.1 we discussed laboratory experiments by Fuentes et al. (2011) and Alpert et al. (2015) showing an increase in

Table 5. Annual and DJF mean changes in aerosols, clouds, and radiative fluxes, globally and over the Southern Ocean (`INT_ADD` case).

Study	Gantt et al. (2012)	This study			
Mean change (%) from control simulation, `INT_ADD` simulation					
Variable	Annual global	Annual global	DJF global	Annual 20–90 S	DJF 20–90 S
CCN, boundary layer (S=0.1%)		3.66	4.66	13.01	22.93
Cloud LWP (g m^{-2}) (Grid average)	0.21	7.0	6.0	2.1	2.4
SWCF (W m^{-2})	-0.12	-0.36	-0.45	-0.74	-1.64
LWCF (W m^{-2})		-0.01	-0.08	-0.20	-0.27

aerosol number emitted ($d < 200$ nm) in the presence of artificially-induced phytoplankton blooms. Furthermore, McCoy et al. (2015) showed from top-down satellite constraints that cloud drop number concentrations are elevated above phytoplankton blooms, suggesting an increased number of CCN in those regions that could not be explained by modelled sulfate or sea salt aerosol. Taken together, we believe these three strands of evidence support the hypothesis that the number and mass of emitted aerosol increase in the presence of phytoplankton blooms, and that the `ADD` cases are more physically realistic. Experimental evidence also suggests that particles in the accumulation mode are largely internally mixed (e.g., Prather et al., 2013), so this will be the more realistic assumption for the size range that primarily impacts CCN. Based on this analysis, we conclude that the `INT_ADD` case is the most physically-realistic of the four sensitivity cases, and our remaining analysis focusses on this configuration of the model.

4.2   Changes in aerosol emissions, chemistry, and amount between `INT_ADD` and `CNTL`

Introducing the marine organic aerosol representation (`INT_ADD` configuration) directly impacts aerosol chemistry, aerosol number emissions and concentration, and CCN number, particularly over biologically-active marine regions. The top panels of Figure 5 show the annual mean organic mass fraction in the boundary layer and at 850 hPa. Over emission "hot spots" such as southeast of South America, OMF is slightly lower at 850 hPa, relative to the boundary layer, likely due to mixing with lower-OMF aerosol from non-local sources. However, overall the OMF at 850 hPa is quite similar to OMF in the model's surface layer, indicating that sea spray organic matter is transported with sea salt to altitudes relevant for cloud formation.

The second row of Figure 5 shows the absolute and relative annual mean changes in annual mean accumulation mode aerosol number emissions. Statistically-significant increases occur in accumulation mode number emissions over much of the Southern Ocean and Arctic, with annual mean emissions more than doubling in some regions. The impact of these increased emissions on boundary layer accumulation mode number concentration is shown in the third row of Figure 5. Annual mean number concentrations approximately double over the strong phytoplankton blooms off the southeastern coast of South America, and smaller, but still significant changes occur in the northern Hemisphere around Greenland and the Bering Strait.
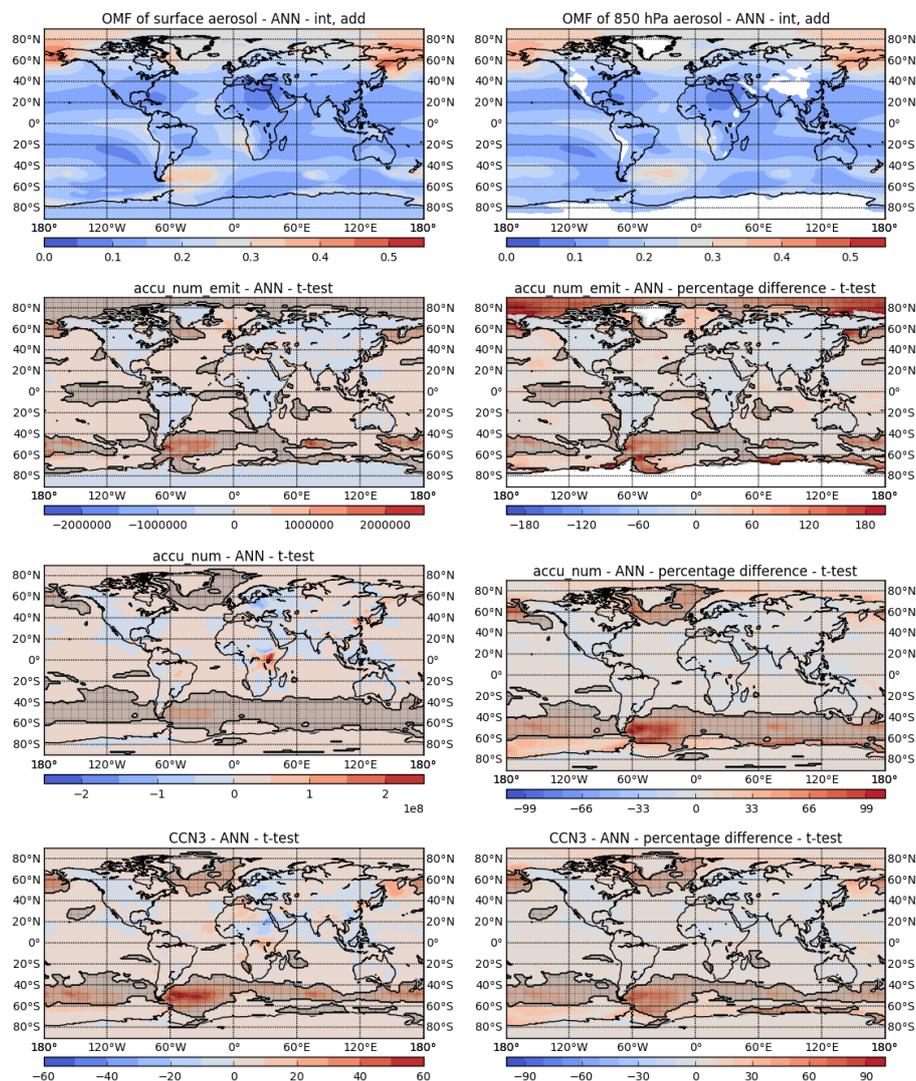
Figure 5. Modelled fields, and changes in modelled fields due to introduction of marine organic aerosol in `INT_ADD` case. Shaded regions outlined with black contours indicate regions where absolute differences are statistically significant by Welch's t-test at the $p < 0.1\%$ level. White space indicates missing values.

Top row: Global annual mean organic mass fraction of accumulation-mode sea spray aerosol at surface (left) and 800 hPa (right). Second row: Global annual mean absolute change (left) and percentage change (right) in accumulation mode number emissions [$\mathrm{m}^{-2}\,\mathrm{s}^{-1}$]. Third row: Global annual mean absolute change (left) and percentage change (right) in accumulation mode number concentration in lowest atmospheric model level [kg^{-1}]. Fourth row: Global annual mean absolute change (left) and percentage change (right) in CCN concentration [cm^{-3}] at S=0.1% in lowest atmospheric model level.
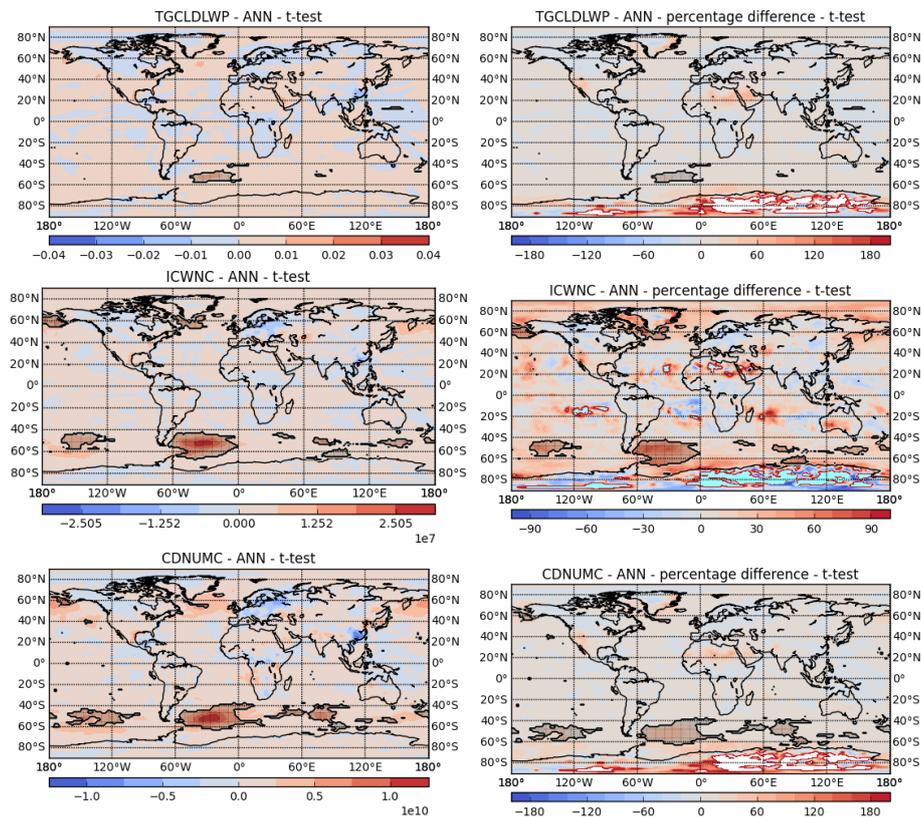
Figure 6. Global mean changes from control simulation in `INT_ADD` case. Top row: Absolute change (left) and percentage change (right) in annual mean cloud liquid water path [kg m^{-2}]. Second row: Absolute change (left) and percentage change (right) in annual mean in-cloud cloud droplet number concentration, lowest model layer [m^{-3}]. Third row: Absolute change (left) and percentage change (right) in annual mean vertically-integrated cloud droplet number concentration [m^{-2}].

4.3 Changes in CCN, cloud properties, and radiative fluxes in `INT_ADD`

4.3.1 Southern Ocean

These increases in aerosol number translate into increases in CCN (S=1%) number concentration (Figure 5, bottom row), with annual mean increases exceeding 50 cm^{-3} regionally. Because the responses of CCN to aerosol number, and of cloud droplet number concentration (Nd) to CCN are approximately logarithmic, it is especially helpful to examine relative changes in aerosol number and CCN (Figure 5, bottom right panel). Relative increases of 20%–50% in annual mean CCN (S=0.1%) concentration occur over much of the ocean from 40°S to 60°S.

Absolute changes in annual mean areal cloud fraction for low, mid-level, and high clouds do not exceed 6% at any location, and local differences in cloud areal fraction mostly do not pass criteria for statistical significance (not shown). This implies
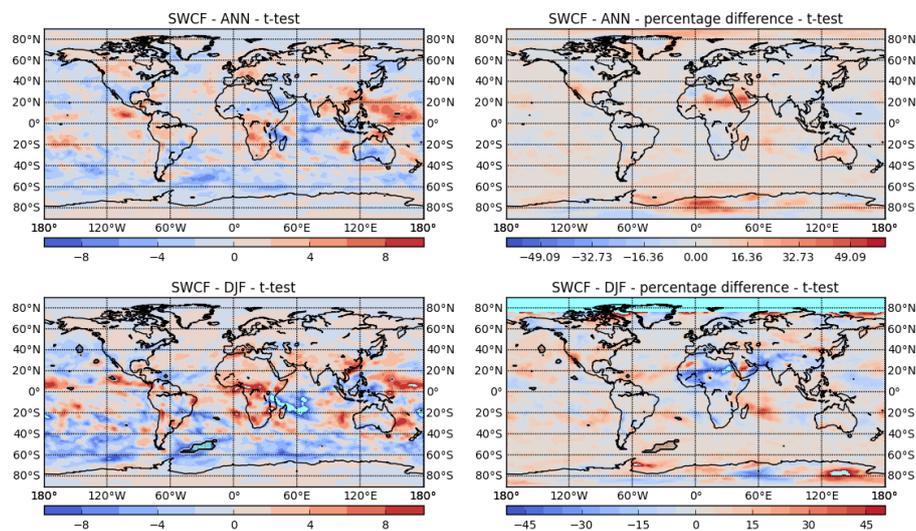
Figure 7. First row: Absolute change (left) and percentage change (right) in annual mean short-wave cloud forcing (W/m^2). Second row: Absolute change (left) and percentage change (right) in DJF mean short-wave cloud forcing (W/m^2).
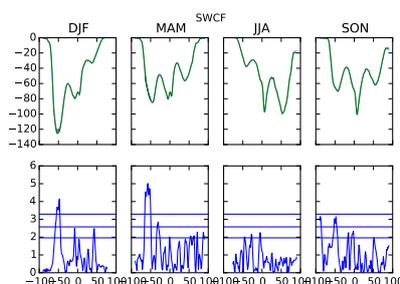
Figure 8. Zonal mean short-wave cloud forcing from control (black) and `INT_ADD` sensitivity case (green) for each season, and Welch's t-test statistic. Shading in top panels highlights regions where differences are significant at the $p < 0.1\%$ level, and horizontal lines on bottom panels indicate levels of significance at $p < 0.1\%$, $p < 1\%$, and $p < 5\%$.

that aerosol impacts on clouds are mostly related to increases in cloud thickness (as indicated by cloud liquid water (Figure 6, top row) and in-cloud cloud droplet number concentration (Figure 6, second row), which combine to produce relative changes in vertically-integrated cloud droplet number concentration exceeding 20% over much of the Southern Ocean (Figure 6, third row).

5   In an earlier study to which some of us contributed (McCoy et al., 2015), we analyzed spatial and regional patterns in satellite-observed cloud-top droplet number concentrations over the Southern Ocean (35° to 55° S) in order to infer the contribution

of CCN from MOA to increases in total cloud droplet number concentration, and hence, to radiative forcing via the cloud albedo effect. That study concluded that increases in cloud albedo due to marine organic aerosol contributed approximately 1–2 W/m^2 additional annual mean radiative cooling over the Southern Ocean, with the cooling occurring primarily during the austral summer months (DJF).

5   In our simulations, zonal annual mean shortwave cloud forcing (SWCF) is strengthened by an average of -1.261 W/m^2 (with the negative sign indicating additional cooling) in this region in the `INT_ADD` case (Table 5; Figure 3). As shown in Table 5, this is about three times the global annual short-wave cloud forcing simulated by Gantt et al. (2012), where the aerosol indirect effect was also estimated to have decreased by up to 0.09 W m^{-2} (7%). Significance testing indicates robust regional impacts on cloud drop number concentration (Figure 6) over the Southern Ocean, leading to statistically significant differences

10   in zonal mean shortwave cloud forcing of about -4 W/m^2 around 50°S in austral summer (Figure 7, Figure 3, Figure 8). This is consistent with top-down constraints inferred by McCoy et al. (2015), lending increased confidence that both the model result and the values inferred from the satellite observations are realistic.

4.3.2   North Atlantic, North Pacific and Arctic

Strong responses to the new marine organic aerosol representation are also observed in the Arctic in some sensitivity cases,
15   with the organic mass fraction exceeding 30% throughout most of the Arctic. While observations of aerosol and clouds from the Arctic are limited due to the difficulty of performing such observations, those observations that do exist suggest that in the central high Arctic, biogenic primary marine aerosol may contribute a large fraction of the aerosol particles and CCN (Bigg and Leck, 2001; Leck et al., 2002; Lohmann and Leck, 2005; Leck and Bigg, 2005; Orellana et al., 2011). The model responds to these emissions of marine organic matter in the Arctic with a strengthening of zonal mean SWCF in the `EXT_ADD` case, and
20   weaker responses in SWCF in the other sensitivity cases (Figure 3).

In contrast with the Southern Ocean, inputs of marine organic aerosol in the North Atlantic and North Pacific do not have appreciable impacts on the clouds there. This is mainly because significant changes in clouds arise where there are large relative changes in CCN number concentrations. Changes in aerosol and CCN concentration in the North Atlantic are statistically significant and of similar absolute magnitude to changes in the Southern Ocean, but in the northern hemisphere, these marine
25   organic aerosol inputs sources are small relative to the continental aerosol sources that dominate the aerosol population in this region. In the Southern Hemisphere, where continental sources are minimal, the impact is much larger.

5   Summary, conclusions and outlook

The parametrization of sea-spary organic aerosol emissions into the atmospheric aerosol described in Burrows et al. (2014) has been implemented into a global atmosphere model, and the responses of the model's clouds and climate to the introduction
30   of this new aerosol source have been characterized in atmosphere-only simulations (with fixed sea surface temperature). Four configurations were tested, which assume full internal or external mixing of sea-spray organic and salt aerosol emissions, and assume that the sea-spray organic emissions partially replace or are added to the sea-spray salt emissions.. Based on a review of

experimental evidence (Fuentes et al., 2010; Alpert et al., 2015), better agreement with observed seasonal cycles (this paper), and indirect evidence from analysis of satellite-observed variability in cloud drop number concentration (McCoy et al., 2015), we conclude that of these four cases, the `INT_ADD` case (organic emissions internally mixed and added) is the most realistic. However, the parameterization could be refined in the future by allowing an intermediate range of assumptions; furthermore,

5   the extent to which aerosol concentration is increased by the presence of phytoplankton is likely a function of the phytoplankton species (Fuentes et al., 2011) and therefore may also differ between ocean biomes.

The primary response of the model's climate is an increase in cloud thickness (as characterized by cloud liquid water path) and in-cloud cloud droplet number concentration, especially over the Southern Ocean. This leads to a strengthening of shortwave radiative cooling by clouds of -0.36 W/m^2 in the global annual mean, and -1.6 W/m^2 in DJF mean over the Southern

10   Ocean.

Additional work is also needed to compare the OCEANFILMS parameterization with [Chl-a]-based parameterizations of the emitted OMF, with the constant OMF hypothesis advanced by Quinn et al. (2014), as well as to intercompare sea-spray organic aerosol simulations between different global chemistry and climate models, which have different native sea spray emission paramaterizations, and different representations of aerosol microphysics and removal processes, to identify whether any of the

15   existing parameterizations can be shown to simulate a more geographic and seasonal distributions of marine organic aerosol.

OCEANFILMS departs from previous parameterizations of sea-spray organic emissions in that it is mechanistically-based rather than empirical. As a result, OCEANFILMS offers a path towards better understanding and representation of the driving mechanisms affecting geographic and seasonal patterns in sea spray organic matter emissions and properties. Additional work is needed to identify how sea-spray organic aerosol emissions may respond to shifts in ocean biology and chemistry in response

20   to ocean acidification, warming, and changes in circulation patterns.

Future work should also explore potential impacts of the effects of the surface activity of marine organics on sea spray aerosol water uptake and activation, and potential interactions of surface tension with sea surface temperature to impact emissions. Extensions of this parameterization could also potentially be applied to investigate impacts of ocean surface tension on sea-air fluxes of trace gases, momentum exchange, and latent and sensible heat flux, due to the suppression of microscale wave

25   breaking by surfactants (Frew et al., 2004; Zappa et al., 2004). Surface-tension reduction by marine biosurfactants in the sea-surface microlayer can also impact aerosol deposition to the ocean surface (del Vento and Dachs, 2007), and the enrichment of surfactants at the sea-surface microlayer can lead to emission of contaminants from water surfaces (Radke and Herrmann, 2003; McMurdo et al., 2008).

Code and data availability. The E3SM model source code is expected be released to the public in early 2018. In the interim, the code

30   modifications and input datasets for adding the OCEANFILMS treatment of sea-spray organic emissions are available from the corresponding author upon request.

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