GANTT, BRETT DANIEL. Marine Organic Aerosols and Their Implication to Climate. (Under the direction of Nicholas Meskhidze.)

Despite the fact that marine organic aerosols have been hypothesized to affect climate through their impact on cloud microphysical properties, emission parameterizations have only recently been available and have not undergone extensive model evaluation. In a literature review of the chemical and physical characteristics of marine organic aerosols, recent trends indicate that these aerosols are externally-mixed with sea-salt and can influence the size distribution towards larger and more numerous particles. Simulations of the emission of secondary and primary marine organic aerosols are performed using the Community Multiscale Air Quality (CMAQ) version 4.7 model, with primary organic aerosols (POA) having a much larger effect on surface aerosol mass concentrations. To develop an improved marine primary organic aerosol emission parameterization, observations of organic mass fraction of sea spray aerosol (OMSSA), chlorophyll-a concentration ([Chl-a]), and 10 meter wind speed (U_{10}) at two coastal sites are used to multi-variable size-resolved parameterization that has global emissions of 2.8 to 5.6 Tg C yr^−1 whose seasonality is more consistent with observations. These emissions, as well as several previously published marine POA emission parameterizations, are evaluated within the GEOS-Chem modeling framework. From this evaluation, marine POA emissions directly related to [Chl-a] best predicted the seasonality of surface concentrations while no parameterization performed well predicting episodic events.

The climate impact of marine organic aerosols is determined by implementation of their emissions into the Community Atmosphere Model version 5 (CAM5) with aerosol microphysics. The combination of marine secondary organic aerosols, methane sulfonate, and primary organic aerosol contribute up to 400 ng m^−3 in annual average submicron organic aerosol mass concentration. Compared to the simulations without marine organic aerosols, the simulations with externally-mixed marine POA emissions have a 20% increase in the surface cloud condensation nuclei (CCN) concentration near biologically productive ocean
regions. The simulations only including secondary marine organic aerosol sources or internally-mixed marine POA emissions did not have large differences in the surface CCN concentration relative to the simulations with marine organic aerosols. Model simulations with and without marine organic aerosol and anthropogenic emissions are compared to determine the impact of marine organic aerosols on the current and preindustrial climate. Marine organic aerosols increase the model-predicted aerosol indirect forcing estimate by ~0.1 W m\(^{-2}\) mainly due to changes in cloud microphysical properties in the pristine preindustrial climate.
Marine Organic Aerosols and Their Implication to Climate

by
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BIOGRAPHY

Brett Gantt was born and raised in Asheville, NC in heart of the beautiful Blue Ridge Mountains. It was from his frequent trips to Mount Mitchell via the Blue Ridge Parkway that he gained an interest in environmental protection and air quality issues. He graduated from T.C. Roberson High School in the spring of 2003 and started college at the University of North Carolina at Chapel Hill in the fall of 2003. While at Carolina, Brett initially began his studies in the geography department later expanded his focus to environmental science with the Carolina Environmental Program, now known as the UNC Institute for the Environment. He graduated in May, 2007 with a B.A. in Geography and a B.S. in Environmental Science. Brett began graduate school at the rival North Carolina State University in the Department of Marine, Earth, and Atmospheric Science under the advisement of Dr. Nicholas Meskhidze in the fall of 2007. He graduated with a Master of Science in Atmosphere Science in the spring of 2009.
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CHAPTER 1. THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF MARINE ORGANIC AEROSOLS: A LITERATURE REVIEW

*This chapter has been submitted to Atmospheric Chemistry and Physics Discussions.

1.1 Introduction

According to the Fourth Assessment Report from the IPCC (2007), the largest source of uncertainty for climate projections is the indirect effect of anthropogenic aerosols. To characterize the effects of anthropogenic aerosol, the impact of all aerosols (anthropogenic plus natural) on the system including the role of “aerosol before pollution” (Andreae, 2007) must be understood. One of the largest uncertainties of the aerosol-cloud system is the background concentration of natural aerosols, especially over marine areas where cloud concentration nuclei (CCN) over the remote oceans are very low ranging from few tens per cm$^3$ to few hundred per cm$^3$ (Andreae and Rosenfeld, 2008). The lower bounds (from 0 to 40 cm$^3$) of background aerosol concentration often prescribed in global climate models (GCMs) for remote marine areas can vary the simulated indirect effect of anthropogenic aerosols by 80% (Hoose et al., 2009) due to widespread coverage of stratocumulus/stratus in the marine boundary layer (MBL) and sensitivity of these clouds to additional particles (Platnick and Twomey, 1994). Despite recognizing their crucial role in serving as CCN for aerosol-sensitive, climate-relevant clouds, the size-dependent physical and chemical composition of marine aerosols remains poorly quantified (O’Dowd and de Leeuw, 2007).

Aerosols over the remote oceans consist of a mixture of sea-salt, sulfates, and organics, with frequent contributions from continental emissions (e.g., mineral dust and biomass burning) (Andreae, 2007). Of the aerosols with a marine source, sea-salt and dimethyl sulfide (DMS)-derived sulfate have been the most studied. Sea-salt aerosol, whose global emissions are estimated to be \(\sim 2,000-10,000 \text{ Tg yr}^{-1}\) when limited to diameters < 20 \(\mu\text{m}\) (de Leeuw et al., 2011), have been proposed to be a major component of marine aerosol mass over the regions where wind speeds are high and/or other aerosol sources are weak (O’Dowd et al., 1997; Murphy et al., 1998; Quinn et al., 1998). DMS, whose global
emissions are estimated to be 17.6-34.4 Tg S yr^{-1} (Lana et al., 2011), have been proposed to be the precursor to sulfate aerosol which is a major component of marine aerosol over biologically-productive regions. Both aerosol sources are thought to affect climate; the estimated indirect forcing of sea-salt is a high as -2.9 W m^{-2} (Ma et al., 2008) while the radiative forcing due to DMS is estimated to be -2.0 W m^{-2} (Thomas et al., 2010).

It has been known for quite some time that the MBL contains organic aerosols, beginning with the documentation of surface active material in sea spray aerosols (Blanchard, 1964). There have been numerous measurements of the organic aerosol surface concentration in the remote marine areas, with an average concentration of ~0.5 ± 0.4 µg C m^{-3} (Duce, 1978; Penner, 1995). As these concentrations levels are well below that of rural continental and urban regions, relatively little attention has been focused on the formation, chemistry, and physics of marine organic aerosols. There are two well established sources of marine organic aerosols; 1) bursting of bubbles produced by breaking waves which scavenge surface active organic matter from the water column and inject it to the atmosphere as primary organic aerosols (Blanchard and Woodcock, 1957; Blanchard, 1964; Barger and Garrett, 1970) and 2) oxidation of phytoplankton-emitted volatile organic compounds (VOCs) such as isoprene and monoterpenes which form secondary organic aerosols (SOA).

In this review, we assume that marine organic aerosols are mostly primary organic aerosols (POA) associated with the organic fraction of sea spray aerosol as opposed to secondary organic aerosol (SOA) formed from marine source VOCs. This assumption is based on modeling results showing that emissions/surface concentrations of marine POA are far higher than that of marine SOA (Arnold et al., 2009; Gantt et al., 2009; Gantt et al., 2010). It should be noted that not including marine SOA would constitute a lower limit of the climate impacts of marine organic aerosols as VOCs/SOA have been shown to influence climate-relevant processes such as nucleation and particle growth (Vaattovaara et al., 2006; Modini et al., 2009). For a comprehensive review of the seawater concentration, emission rates, and
marine boundary layer concentration of marine isoprene and monoterpenes, see Shaw et al. (2010).

In recent reviews of cloud-active aerosols (Andreae and Rosenfeld, 2008), natural aerosols (Carslaw et al. 2010), marine aerosols (O’Dowd and de Leeuw, 2007), and sea spray aerosol production (de Leeuw et al., 2011), the sources and general chemical composition of marine organic aerosols are briefly described. However, these studies point to many open questions involving the climate-relevant characteristics of marine organic aerosol. Some of these open questions addressed in this review include:

1) What is the current understanding of the size-resolved chemical composition of marine organic aerosols?

2) Are marine organic aerosols externally- or internally-mixed with sea-salt?

3) Do marine organic aerosols influence aerosol size distribution, CCN concentrations, and cloud microphysical properties?

1.2 Chemistry

1.2.1 Bulk aerosol

1.2.1.1 Concentrations

With improvements and increased abundance of aerosol instrumentation, a more comprehensive understanding of the spatial distribution and temporal changes in marine organic aerosol concentrations has emerged. The first detection of organic material in sea spray aerosols used surface active nature of organics to separate them from sea-salt (Blanchard, 1964). Barger and Garrett (1970) collected sea spray aerosols from the Hawaiian coast on glass fiber filters and determined the concentration of chloroform extractable organic (lipoid) material to be between 0.6 and 5.7 µg m⁻³, values far higher than most subsequent observations. Hoffman and Duce (1974) used the hot persulfate-induced
organic material oxidation method of Menzel and Vaccaro (1964) to measure an organic aerosol concentration in Bermuda ranging from 0.15 to 0.47 µg m\(^{-3}\). This was the first of many measurements of the organic aerosol concentration in the remote marine boundary layer averaging \(~0.5\) µg m\(^{-3}\) (Duce, 1976). While the concentration of organic aerosols in remote marine regions is typically far lower than that of continental areas, Ovadnevaite et al. (2011) reported concentrations of up to 3.8 µg m\(^{-3}\) in a marine organic aerosol plume in the N.E. Atlantic. A summary of several measurements of marine organic aerosol concentrations can be found in Table 1.1 and Figure 1.1. Long-term measurements have found that the concentration of organic aerosols follow a strong seasonal component, with the highest concentrations at Mace Head, Ireland and Amsterdam Island occurring in the spring-summer and lowest in the winter (Yoon et al., 2007; Sciare et al., 2009). Sciare et al. (2009) hypothesized that the seasonality of marine organic aerosol concentrations was due to changes in surface chlorophyll-\(a\) concentration ([Chl-\(a\)]) which was shown to have a similar seasonal cycle. Yoon et al. (2007) further described this result as an “apparent paradox” because the periods of high [Chl-\(a\)] tend to have lower winds resulting in lower sea spray emissions. Two explanations for this paradox were proposed by Yoon et al. (2007); 1) the forced bursting of surfactant-stabilized bubbles resulting in an increased flux of larger droplets and 2) the presence of surfactants that replaced water in the marine aerosol leading to greater residual aerosol mass as the droplet evaporates.

In addition to solely organic aerosol concentration measurements, several studies have reported an organic carbon (OC) to sea-salt mass ratio (OC/SS) which can be used to scale POA emission from the ocean with sea-salt fluxes. The first measurements capable of finding a value equivalent to OC/SS took place on the east coast of Hawaii; Blanchard (1968) found a surface active film/salt mass ratio varied from 0.3 to 0.7 on sea spray particles while Barger and Garrett (1970) found a lipoid/salt ratio of 0.07-0.14. In Barger and Garrett (1970), the OC/SS ratio was observed to increase with increasing wind speed and thought to be associated with increasing bubble bursting with wind speed which transports adsorbed
surface active material from the sea surface to the atmosphere. Hoffman and Duce (1974) reported an OC/SS of 0.01 to 0.19 in Bermuda, with the ratio increasing with salt concentration. Long-term measurements of sea-salt and organic aerosols at two coastal sites show that the OC/SS ratio has a seasonal cycle, with the highest values occurring in the spring-summer and the lowest in the winter (Yoon et al. 2007; Sciare et al. 2000, 2009). Recent work quantifying the emission of marine organic aerosols using an organic-inorganic sea spray function which calculates the organic mass fraction of sea spray aerosol (OMSSA) (O’Dowd et al., 2008) is described Sec. 1.4. Generally, these studies show that the average organic aerosol concentrations and OC/SS in remote marine environments is 0.5 µg m$^{-3}$ and 0.1, respectively, with some spatiotemporal differences related to ocean biological productivity that may result in concentrations and OC/SS that are nearly an order of magnitude higher or lower.

1.2.1.2 Composition

As the ocean surface is proposed to be the major source of marine POA, measurements of the chemical composition of bulk seawater and the sea surface microlayer waters have been useful in characterizing the composition of marine organic aerosols. Organic matter in the subsurface seawater and the sea surface microlayer has been shown to have a chemical composition that varies between phytoplankton communities with carbohydrates typically comprising the major fraction and proteins, lipids, and humic substances having minor fractions (Myklestad, 1995; Penna et al., 1999; Wurl et al., 2009). Russell et al. (2009) describes how these organic compounds have progressively higher concentrations (relative to sea-salt) as you go from the subsurface water to atmospheric aerosols. This transition in relative concentrations between the subsurface seawater and aerosol can be large, with the organic carbon/sodium ratio increasing from $10^{-4}$ in the subsurface water, $10^{-3}$ in the sea surface microlayer, and 1 in the aerosol (Russell et al., 2009). Analysis of stable carbon isotopes in seawater organic compounds is one such tool used to identify marine organic aerosols. Several studies (Williams and Gordon, 1970; Eadie et al., 1978; Fontugne and
Duplessy, 1978, 1981; Loh et al., 2004) have found a δ¹³C (¹³C/¹²C ratio relative to that of a standard) value of -20±2‰ for protein-like fraction, carbohydrates, and dissolved organic carbon in ocean water and -27±2‰ for organic carbon derived from terrestrial plants due to their differences in the supply of inorganic carbon in water during peak biological activity. Identification of unique chemical signatures of organic compounds in the bulk seawater and sea surface microlayer such as carbohydrates and δ¹³C values has enabled improved identification of the sources and formation mechanisms of marine organic aerosols.

Analysis of the composition of airborne marine organic particles has been consistent with that of the sea surface microlayer, with evidence of carbohydrates (Leck and Bigg, 2005; Facchini et al, 2008; Russell et al., 2010), amino acids (Leck and Bigg, 1999), and marine microorganisms (Leck and Bigg, 2005). Using a Scanning Transmission X-ray Microscopy with Near-Edge X-ray Absorption Fine Structure (STXM-NEXAFS), Hawkins and Russell (2010) classified marine organic aerosols into four chemically distinct types: 1) carboxylic acid-containing polysaccharides, 2) low-solubility polysaccharides, 3) calcareous phytoplankton fragments, and 4) proteinaceous. These types are spatially inconsistent, with organic aerosols in the Arctic and Southeastern Pacific having distinct distributions of the different types (Hawkins and Russell, 2010). Beginning with Chesselet (1981), several studies have used the δ¹³C of marine aerosols to differentiate the influence of marine and terrestrial sources of organic aerosol in different locations and seasons (Chesselet et al., 1981; Cachier, 1989; Turekian et al., 2003; Narukawa et al., 2008; Miyazaki et al., 2010). Ceburnis et al. (2011) used a combination of δ¹³C and Δ¹⁴C (¹⁴C/¹²C ratio relative to that of a standard and whose values are depleted in fossil fuels) isotopic analysis to find that 80% of the organic aerosol measured during clean marine conditions at Mace Head, Ireland could be linked to plankton emissions as opposed to terrestrial or fossil fuel emissions. Using an aerosol time-of-flight mass spectrometer, Gaston et al. (2011) detected unique magnesium (Mg)-type particles containing Mg²⁺, Ca²⁺, K⁺, and organic carbon that were suggested to be a proxy for marine organic aerosols due to their temporal correlation with DMS and [Chl-a].
These spectroscopic and isotopic analyses of organic aerosols can be used to identify a marine source in addition to/instead of terrestrial and anthropogenic proxies such as black carbon and radon.

1.2.2 Size-resolved

1.2.2.1 Concentrations

As an aerosols’ size is an important characteristic of its potential to act as a cloud condensation nuclei, size-resolved concentrations of specific aerosol types gives valuable information in determining the climate impact. Despite having low bulk concentrations described in Sec. 2.1.1, marine organic aerosols have a high potential climate impact due their relatively large abundance in the accumulation size range (diameters between ~50 and 300 nm) compared to sea-salt. Beginning with the Barker and Zeitlin (1972) and Hoffman and Duce (1977) use of cascade impactors to determine size-resolved sea spray aerosol chemistry, most study have found that marine organic aerosols make up a progressively larger mass fraction of sea spray aerosol as the particle size decreases. Oppo et al. (1999) developed a spray drop adsorption model to describe these observations by quantifying the volume of an organic film surrounding a marine aerosol relative to the total aerosol volume. Ellison et al. (1999) explained this model by describing the organic film as hydrophobic inverted micelles surrounding a sea-salt-water core, and used a geometric argument to show that the organic film/total aerosol mass ratio is an inverse function of aerosol diameter. O’Dowd et al. (2004) described how the organic contribution to total marine aerosol mass in the accumulation mode is related to ocean biological productivity, with high and low biological activity (HBA and LBA) periods having a much different (> 60% and < 20% for HBA and LBA periods, respectively). Subsequent measurements by Rinaldi et al. (2010) and Miyazaki et al. (2010) also reveal progressively larger contributions of organic aerosol to total aerosol mass with decreasing particle size and increasing marine biological activity.
These measurements are summarized in Figure 1.2 with the high and low biological activity measurement periods denoted with red and blue lines, respectively.

In bubble bursting experiments replicating nascent sea spray aerosol emission, Keene et al. (2007) and Facchini et al. (2008) found that the organic fraction of sea spray aerosol can be up to ~80% at the smallest aerosol sizes. Facchini et al. (2008) further compared their observations with concurrent ambient measurements which showed a similar size distribution of marine organic aerosol mass relative to that of sea-salt. These very high organic mass fractions in accumulation model aerosols have not been found in all bubble-bursting experiments. Using the hygroscopic growth of sea spray aerosol (SSA) to determine the presence of organics (see Sect. 2.2.3), Sellegrigi et al. (2008), Modini et al. (2010a,b), and Fuentes et al., 2010, 2011) all found organic mass fractions < 40%. Specifically, Modini et al. (2010a), using a Volatility Hygroscopicity-Tandem Differential Mobility Analyzer (HTDMA), found that the organic volume fraction of aerosols produced from bubble-bursting of seawater off the Australian coast was 8±6% for aerosols between 71–77 nm in diameter and less than 20% (with up to 40 %) for 40 nm particles. Fuentes et al. (2011) estimated a submicron aerosol organic volume fraction of 8–37% (with higher organic volume fractions for 20 to 70 nm size particles) from laboratory grown phytoplankton cultures via HTDMA measurements. It is unclear whether the inconsistent results from bubble bursting experiments are due to differences in measurement technique or sea water composition; this suggests the need for aerosol measurements to be made under the same sea water and environmental conditions.

1.2.2.2 Composition

Recent improvements in single particle measurement techniques such as Near-Edge Absorption X-ray Fine Structure (NEXAFS) spectromicroscopy and transmission electron microscopy (TEM) have shown that aerosol size can have large effect on the chemical composition of marine organic aerosol. Leck and Bigg (2010) report that aerosols less than
50 nm in diameter sized particles, previously thought to be formed only through nucleation, display characteristics of fragmented aggregates of microcolloids. TEM images of marine aerosols from multiple locations in the size range between 50 and 200 nm in diameter led Leck and Bigg (2008) to two conclusions: 1) aggregates of microcolloids and exopolymer secretions are the dominant organic aerosol type and 2) sea-salt aerosols are nearly absent. In the size range between 200 and 1000 nm in diameter, Hawkins and Russell (2010) using NEXAFS analysis showed that marine organic aerosols with diameters between 200-700 nm 700-1000 nm were mostly calcareous phytoplankton fragments and low-solubility polysaccharides, respectively. In the supermicron sized particles, Hawkins and Russell (2010) found that marine organic aerosols were mostly composed of carboxylic acid-containing polysaccharides associated with sea-salt aerosol (Hawkins and Russell, 2010). For northern Pacific sea spray aerosols in the size range from 500 to 2000 µm in diameter, Gaston et al. (2011) reported a normalized number concentration of Mg-type particles (proxy for marine organic aerosols) which rapidly decreased with particle size and was higher than that of sea-salt aerosol in the size range between 500 and 700 nm in diameter. These different measurement techniques focused on different aerosol sizes show marine organic aerosols more abundant relative to sea-salt at smaller aerosol sizes and that their chemical composition changes with size, potentially due to different formation mechanisms.

1.2.2.3 Hygroscopicity and Volatility

For marine aerosols, the growth factor (GF, defined as the ratio of wet and dry particle mobility diameters) has been used alongside volatility measurements to give the relative contribution of sea-salt, sulfate, and organic aerosols. In the marine environment, the common GF values include ammonium sulfate (1.7), ammonium bisulfate (1.8), sea-salt (2.0), water soluble organic matter (WSOM) (1.2) and water insoluble organic matter (WIOM) (1.0). In a review of GF measurements in multiple environments, Swietlicki et al. (2008) reported that marine environments have a nearly ubiquitous occurrence of aerosols within the more-hygroscopic group whose GF is ~1.5, likely corresponding to a volume ratio
of 85% ammonium bisulfate and 15% organic compounds (Swietlicki et al., 2008). The frequency of the highly-hygroscopic (sea-salt) group was much less frequently measured in marine environments. During HBA periods in the North Atlantic Ocean, Cavalli et al. (2004) measured a GF of 1.2 for aerosols with 50% equivalent aerodynamic cutoff diameters < 0.125 µm. Recently, Ovadnevaite et al. (2011) described a HBA period in the North Atlantic which had a concurrence of low GF (~1.25), high organic mass fraction of submicron aerosols, and high particle mean diameter (~150 nm in diameter) relative to periods of high sulfate mass fraction (~100 nm in diameter). In addition to the biological activity, the wind speed also plays a role in the observed growth factor with Nilsson et al. (2001) reporting a GF of 2.0 (sea-salt) during high wind speeds (> 12 m s⁻¹) and a GF of 1.5 (mixture of sulfate and organics) during low winds (< 3 m s⁻¹). The volatility of an aerosol can also be used for chemical characterization, with the semi-volatile organic compounds typically evaporating at temperatures < 300°C and low volatility sea-salt and some organic compounds remaining at temperatures up to 600°C. Hultin et al. (2010) found that the fraction of HBA North Atlantic sea spray aerosols that are semi-volatile varied by aerosol size, with the highest semi-volatile fraction (~35%) occurring with particles 140-150 nm in diameter. In bubble bursting experiments of the Australian coast representing nascent sea spray emissions, Modini et al. (2010) observed a low semi-volatile fraction (10%) and little difference with aerosol size in the range of 38 to 173 nm in diameter. These GF and volatility measurements have been successfully used to determine the aerosol chemistry at sizes difficult to measure using mass-based methods, and show that the biological activity and environmental conditions can affect the relative amounts of organic and sea-salt in sea spray aerosol.
1.3 Physics

1.3.1 Size distribution

Concurrent measurements of marine aerosol size distribution and chemical composition have shown that the marine organic aerosol number size distribution is distinct from that of sea-salt. Historically, the number size distribution of marine organic aerosols could only be estimated because typical aerosol sizing techniques did not include chemistry. Novakov and Penner (1993) made one of the first estimations of the number size distribution through the application of the Twomey inversion algorithm (Twomey, 1975) to cascade impactor mass concentrations at a site in Puerto Rico. Through this analysis, Novakov and Penner (1993) found that organic aerosols later described as having a marine source (Novakov et al., 1997) made up a major part of the aerosol number concentration and CCN fraction due to their high numbers in the size range between 50 and 200 nm in diameter. Comprehensive characterization of the size-resolved mass concentrations of marine aerosols at Mace Head, Ireland (Cavalli et al., 2004) showed that the mass concentration of WSOM in the size range of aerosols with diameters < 200 nm was the highest of any chemical species measured. The aerosol number size distribution over the North Atlantic changed between the LBA and HBA periods, with the increase in accumulation mode mean diameter and number concentration during the HBA period attributed to the additional marine organic aerosol (O’Dowd et al. 2004). de Leeuw et al. (2007) used eddy covariance with an optical particle counter with heated inlet to find that sea spray aerosol number emission flux size distributions for the total aerosol is substantially larger than that of the heated aerosol. This difference, which was as large as two orders of magnitude for aerosol sizes between 200 and 500 nm in diameter, was attributed to drying of the aerosol and volatilization of sulfate and organic aerosols. Yoon et al. (2007) reported an increase in aerosol modal diameter and number during periods of HBA relative to periods of LBA for the North Atlantic. This result was summarized as “aerosols with the large organic fraction appear to be physically larger than the aerosols without” (Yoon et al., 2007). Russell et al. (2009) found a positive linear relationship between the
number mean diameter of CCN (aerosols > 80 nm in diameter) and organic aerosol mass concentration for both the north Atlantic and Arctic, a result consistent with that of Yoon et al. (2007). Ovadnevaite et al. (2011) reported similar results in an AMS study at Mace Head, finding that periods with high organic fractions and low growth factors also had a higher weighted average particle size. The aerosol size distribution during this period shifted to larger and more numerous particles in the 100 to 300 nm diameter range, suggesting that marine organic aerosols play an important role in CCN concentrations in the marine boundary layer.

The tendency of marine organic aerosols to increase the number concentration and modal diameter of accumulation mode aerosols in ambient samples is not consistently reproduced in laboratory measurements of bubble bursting experiments representing nascent sea spray emissions. Sellegri et al. (2006) described how the sea spray size distribution is affected by the presence of the surfactant sodium dodecyl sulphate (SDS, described as a proxy for surfactants found in natural seawater) in the bubble bursting tank. When SDS was added to a tank of synthetic seawater simulating calm conditions, the surfactant caused aerosol number concentrations in the Aitken mode (~45 nm in diameter) to increase. In another set of experiments in which SDS was added to the tank simulating low wind speeds, the number concentration of an aerosol size mode centered at 300 nm in diameter was enhanced relative to experiments without the surfactant. Fuentes et al. (2010) observed a similar increase to the calm conditions experiments of Sellegri et al. (2006) when the Aitken mode aerosol number concentration increased from the addition of phytoplankton exudates (especially that of Diatomaceous phytoplankton) to artificial seawater. Bubble bursting of unfiltered seawater representing nascent sea spray emissions from the tropical Atlantic Ocean resulted in higher Aitken mode number concentration in HBA waters relative to LBA waters (Fuentes et al., 2010). Tyree et al. (2007) did not observe any change in aerosol size distribution during the addition of oleic acid to artificial seawater, although the particle number flux increased by a factor of 1.5 compared to the artificial seawater. Overall, these
laboratory studies suggest that presence of marine compounds increases the particle flux from seawater and it is other environmental conditions such as wind speed that affect the number size distribution of the resulting sea spray aerosols.

1.3.2 Mixing State

The mixing state of marine organic aerosols with other aerosol types present in the marine boundary layer (e.g., sea-salt, organics, ammonium sulfate, methyl sulfonate) has been suggested to impact the cloud droplet number concentration over the ocean during HBA periods (O’Dowd et al., 2004). The general understanding of the mixing state of marine organic aerosols has changed with time as more recent studies have taken advantage of advanced analytical techniques involving spectrometers and electron microscopes. Middlebrook et al. (1998) used a particle analysis by laser mass spectrometry (PALMS) to find that Southern Ocean marine organic aerosols greater than 160 nm in diameter were nearly always found internally mixed in individual sea-salt particles. This finding was consistent with the hypothesis prevalent in earlier studies of an internal mixture of sea-salt and organic aerosols (Pueschel and Van Valin, 1974; Hoffman and Duce, 1976; Gershey, 1983; Tseng et al., 1992). However, more recent analyses suggest that marine organic aerosols and sea-salt may be externally-mixed. Using an aerosol time-of-flight mass spectrometer (ATOFMS) determined that the marine source magnesium-type particles were externally-mixed with sea-salt in Indian Ocean aerosols between 500 and 2000 nm in diameter (Gaston et al., 2011). The volatility measurements of Hultin et al. (2010) in the HBA North Atlantic showing decreases in sea spray particle number using a 300°C heated inlet relative to an unheated inlet led the investigators to sea-salt and organics were externally-mixed up in sea spray aerosols up to 230 nm in diameter. Transmission electron microscopy has been used in marine environments to detect both single particles composed of organic material and bacteria in the absence of sea-salt as well as sea-salt particles associated with surface active EPS (Bigg and Leck, 2001, 2008; Leck and Bigg, 2005a, 2005b, 2008; Leck et al., 2002; Pósfai et al., 2003). There is a size-dependence to the
expected mixing state of sea-salt and organics derived from TEM analysis, as presence of sea-salt is typically reduced in aerosols < 200 nm in diameter (Bigg and Leck, 2008). Hawkins and Russell (2010) found that 3 out of the 4 types of marine organic aerosols identified using STXM-NEXAFS were externally-mixed, with only the supermicron sized carboxylic acid-containing polysaccharides type observed to be internally-mixed with sea-salt.

1.4 Emissions

Until recently, the only estimate of the emissions of marine organic aerosols came from Duce (1978) who estimated global emissions of 1.4 Tg C yr\(^{-1}\) based on a uniform OC/sea-salt ratio of 14 × 10\(^{-3}\) and sea-salt emissions of 1000 Tg yr\(^{-1}\) (Eriksson, 1959). Two top-down model estimates of global marine organic aerosol emissions have had very different results. Spracklen et al. (2008) used a comparison of observed seasonal concentrations of organic aerosol at several coastal sites and based on the remotely sensed [Chl-\(\alpha\)] in surface waters predicted concentrations from the chemical transport model GEOS-Chem (http://acmg.seas.harvard.edu/geos/) to estimate total (primary + secondary) marine organic aerosol emissions of 8 Tg C yr\(^{-1}\), of which 5.5 Tg C yr\(^{-1}\) were predicted to be in the submicron mode. Roelofs (2008) found that ECHAM5-HAM modeled and satellite-derived liquid cloud effective radius in the North Atlantic was most similar with submicron marine organic aerosol emissions of 50 Tg C yr\(^{-1}\). O’Dowd et al. (2008) introduced concept of a combined inorganic-organic sea spray function, with the organic mass fraction of submicron sea spray aerosol (OM\(_{SSA}\)) having a linear dependence to [Chl-\(\alpha\)] based on measurements from Mace Head, Ireland. O’Dowd et al. (2008) also included a change in the size dependence of the SSA production flux as function of the time of year. Recent work has expanded upon the relationship between marine organic aerosol emissions and [Chl-\(\alpha\)], including revisions to the linear dependence of OM\(_{SSA}\) (Langmann et al, 2008; Vignati et al.,
size-dependence of the OM_{SSA} (Long et al., 2011; Gantt et al., 2011), number distribution of the SSA production flux (Fuentes et al., 2010), and wind speed dependence of OM_{SSA} (Gantt et al., 2011). These different studies estimate global marine organic aerosol emissions that vary in magnitude (~2-20 Tg yr$^{-1}$) and spatiotemporal distribution (lower emission rate gradient between low and high [Chl-a] in Gantt et al. (2011) relative to Vignati et al. (2010), for example). Albert et al. (2012) explored some of the uncertainties related to estimates of the global submicron marine POA emission rate, finding that the choice of sea spray source function and OM_{SSA} calculation in low [Chl-a] regions were the major factors affecting the global estimates. In a modeling study of five marine POA emission schemes, Gantt et al. (2012) highlighted the high level of uncertainty in the emissions by showing their large differences in magnitude and seasonality and inability to predict surface concentrations from hourly to month time scales.

1.5 Climate Impacts

With observations of the chemical and physical characteristics of marine organic aerosols and development of size-resolved aerosol emission parameterizations linked to sea spray number and/or mass fluxes, it is possible to estimate their climate impact. Novakov and Penner (1993) and Novakov et al. (1997) first hypothesized that organic aerosols with a marine source play an important role in determining CCN concentrations using a combination of size-resolved chemistry condensation nuclei (CN) measurements. O’Dowd et al. (2004) used size-resolved chemistry and number distribution measurements from Mace Head to estimate the potential impact of marine organic aerosols on cloud droplet number concentration (CDNC), finding that the CDNC increases between 15 and 100% depending on the mixing state. During clean marine air masses at Mace Head, Ovadnevaite et al. (2011) found that periods which had aerosols with high organic fractions also had high CCN
concentrations and CDNC. Two recent studies in which marine organic aerosols were implemented into global climate models are consistent with these estimates. Roelofs (2008) reported ECHAM5-HAM model results in which marine organic aerosols with global emissions of 50 Tg C yr\(^{-1}\) distributed between the Aitken and accumulation modes and externally-mixed with sea-salt increased North Atlantic CDNC by a factor of 3-4 (~35 to 120 cm\(^{-3}\)) and decreased cloud effective radii from 15-20 µm to 10-14 µm in diameter. These increases in CDNC and decreases in cloud effective radii brought the model closer to satellite-derived values for the North Atlantic. Meskhidze et al. (2011) and Gantt et al. (2012), after implementation of marine organic aerosols in the Community Atmosphere Model version 5.0 (CAM5) with a 7-mode Modal Aerosol Model (MAM7), describe how the mixing state determines the climate impact. In the model, externally-mixed marine organic aerosols were added as additional aerosol number and mass while the internally-mixed marine organic aerosols were only added mass. The global CCN surface concentration increased by 1.4% and the model predicted aerosol indirect forcing decreased by 8% due to externally-mixed marine organic aerosol. In the simulations with internally-mixed marine organic, the CCN surface concentration and aerosol indirect forcing were not substantially different than the simulation without marine organic aerosols (Meskhidze et al., 2011; Gantt et al., 2012). This importance of the mixing state of marine organic aerosols and sea-salt within sea spray was also observed by Westervelt et al. (2012) using the GISS II-prime climate model. When Westervelt et al. (2012) replaced highly hygroscopic sea-salt with lower hygroscopicity organics in sea spray aerosols, surface CCN concentrations decreased of 5% regionally and < 0.5% globally. However, a sensitivity simulation in which marine organic aerosols were implemented as additional number emissions experienced increases in surface CCN concentration approaching 50% regionally and 4% globally (Westervelt et al., 2012).

Despite several studies showing increases in CCN due to marine organic aerosols, hygroscopic and CCN activity measurements of laboratory bubble bursting experiments from
Fuentes et al. (2010) and Moore et al. (2011) suggest a different climate impact: the higher hydrophobicity and lower CCN activity of organic compounds in sea spray aerosol imply small changes in CCN concentration associated with marine organic aerosols and negligible impact on cloud formation. As the understanding of mixing state of marine organic aerosol emissions is evolving, future climate studies would be well served to assume both external and internal mixtures in order to place upper and lower bounds on the climate impact.

1.6 Discussion

As marine organic aerosols have received considerable research interest in the last decade, improvements in instrumentation and computer modeling tools have enabled a more comprehensive and quantitative view of the chemistry, physics, and potential climatic impact of these aerosols. Although certain locations near biologically productive waters can have episodic concentrations much higher (> 3.0 µg m\(^{-3}\)), the average mass concentration of marine organic aerosols is typically less than 0.5 µg m\(^{-3}\). Due to their low concentrations and number distribution mainly in the accumulation model, marine organic aerosols present some measurement challenges including having concentrations below the detection limit and the majority of aerosol number below the minimum size cutoff. However, despite having such low mass concentrations, the number concentration of marine organic aerosols has been suggested to be greater than sea-salt aerosols in the climatically relevant size range between 100 and 500 nm in diameter. The organic mass fraction of sea spray aerosol (OM\(_{SSA}\)) has been consistently shown to be inversely related to the aerosol size, with the magnitude of organic mass fraction for a given aerosol size dependent on oceanic factors such as [Chl-\(a\)] and meteorological factors such as wind speed. There is general agreement that the composition of marine organic aerosols is similar to that of the sea surface microlayer, with polysaccharides, phytoplankton fragments/secretions, and proteinaceous aerosols all contributing to the total mass. Chemical indicators that can be used to determine a marine
source of organic aerosols include hygroscopic growth factors, volatility, aerosol mass spectrometer-derived magnesium typing, and carbon isotopes. Global emissions of submicron marine organic aerosols have averaged ~10 Tg yr\(^{-1}\) but vary by an order of magnitude.

By taking a historical perspective on marine organic aerosol research, certain trends seem to have emerged since the initial research began in the 1960-1980’s that help answer the questions presented in Sect. 1. These trends include the existence of external mixtures of marine organic aerosols and sea-salt, changes in the aerosol number distribution due to marine organic aerosols, and the dominance of marine organic aerosol (relative to sea-salt aerosol) for sizes 100-200 nm in diameter that are particularly important for their ability to serve as cloud condensation nuclei (CCN). Combined, these three trends suggest an increased potential climatic impact associated with marine organic aerosols. The increasing complexity of climate and air quality models has enabled the ability to implement emissions of marine organic aerosols, although quantification of their impact on cloud microphysics is uncertain due to the limited knowledge of the chemical and physical characteristics of marine organic aerosol. The few modeling studies that have been performed show regionally substantial changes in CCN concentration, cloud droplet number concentration (CDNC), liquid cloud microphysical properties, and shortwave cloud forcing resulting from marine organic aerosols. The change in aerosol indirect forcing due to marine organic aerosols has been estimated to be ~0.1 W m\(^{-2}\) (8%). Refinement of this estimate will require improvements both in the emission mechanisms and model treatment of the microphysical, atmospheric transformations, and hygroscopic properties of marine organic aerosols.

1.7 Objectives

Due to the limited observational dataset and recent emergence of the topic, the magnitude and mechanism of emissions and associated impact of these aerosols on clouds is currently
undergoing scientific debate. In this work, the two objectives are to 1) review, evaluate, and develop emission parameterizations for marine isoprene, monoterpenes, and primary organic aerosols and 2) model the impact of marine organic aerosols on background aerosol concentration and cloud microphysical properties.

In a review of the chemical and physical characteristics of marine organic aerosols, measurements of the concentration, composition, size distribution, and mixing state among other characteristics are review and the modeling of the climatic impacts are described. Quantification of the relative impact of secondary and primary sources of marine organic aerosols is performed using a regional air quality model. An evaluation of marine VOC emissions employs both emission and concentration observations to compare to predictions from a laboratory-based emission parameterization. Additionally, coincident observations of organic aerosol concentration, chlorophyll-\(a\) concentration, and 10 meter wind speed are used to develop an emission parameterization for marine primary organic aerosols. These emissions, as well as several previously published marine primary organic aerosol emission parameterizations, are evaluated within the same modeling framework to determine which can replicate concentrations at multiple sites with temporal resolutions ranging from hourly to monthly.

Finally, the climate impact of these emissions is determined by implementation into a global climate model (GCM) with aerosol microphysics. Specifically, emissions of marine isoprene, monoterpenes, methane sulfonate, and primary organic aerosols are implemented into the National Centers for Atmospheric Research (NCAR) Community Atmosphere Model (CAM5). Model simulations with and without marine and anthropogenic emission are compared to determine the impact on the current and preindustrial climate. Ultimately, a parameterization of marine organic aerosol emissions that recreate the magnitude and seasonality of surface concentration observations would be useful in improving the representation of remote marine aerosol concentration and cloud microphysics in climate models.
References


Rinaldi, M., Decesari, S., Finessi, E., Giulianielli, L., Carbone, C., Fuzzi, S., O’Dowd, C. D., Ceburnis, D., and Facchini, M. C.: Primary and secondary organic marine aerosol and


Table 1.1. Summary of observed remote marine organic aerosol concentrations

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<th>Conc.</th>
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*Submicron values with EC < 0.1 ug m⁻³
Figure 1.1. Climatological chlorophyll-\(a\) concentration (mg m\(^{-3}\)) from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) superimposed with organic aerosol concentration measurements (\(\mu\)g C m\(^{-3}\)) in remote marine locations. See Table 1 for measurement details and references.
Figure 1.2. Size-resolved organic mass fraction of sea spray aerosol in remote marine locations. The blue lines represent low-productivity periods and red lines represent high productivity periods.
CHAPTER 2. MODELING THE AIR QUALITY IMPACT OF MARINE ORGANIC AEROSOLS

Preface:

Despite evidence of marine organic aerosols in remote marine areas as described in Chapter 1, no regional air quality modeling of the different emissions sources had been performed to determine which emission source is most significant. Furthermore, the relative importance of primary and secondary sources of marine organic aerosols had not been well established at the time of this study. A regional air quality modeling simulation has previously been performed in which the inclusion of marine isoprene emissions had a minor effect on the ozone and aerosol mass concentration near coastal areas of the United States. In this article published in ACP in 2010, marine emissions of isoprene, monoterpenes, and primary organic aerosol have been implemented in the Community Multiscale Air Quality (CMAQv4.7) modeling system. Specifically, offline emissions of marine isoprene and monoterpenes and online emissions of marine primary organic aerosols were derived using MODIS/Aqua chlorophyll-concentrations and in the case of primary organic aerosols scaled to the CMAQ sea-salt emissions. Using the western United States during the June to August time period as a case study for the impact of marine organic aerosols on coastal air quality, we found that these emissions resulted in up to a 0.3 µg m$^{-3}$ (10%) increase in the mass concentration of aerosols less than 2.5 µm in diameter. These small concentration increases are mainly important in improving the model-predicted background organic aerosol concentration near the coast during periods of onshore flow as compared to observations. This concentration of marine organic aerosols is consistent with previous measurements described in Chapter 1 showing organic aerosol concentrations of ~0.5 µg m$^{-3}$ in remote marine areas. The important findings from this work for the remaining chapters include 1) identification of marine primary organic aerosols as the dominant contributor total marine organic aerosol mass concentrations and 2) confirming that existing marine primary organic aerosol emission parameterizations can accurately predict background marine organic aerosols concentrations.
The contribution of marine organics to the air quality of the western United States

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Abstract

The contribution of marine organic emissions to the air quality in coastal areas of the western United States is studied using the latest version of the U.S. Environmental Protection Agency (EPA) regional-scale Community Multiscale Air Quality (CMAQv4.7) modeling system. Emissions of marine isoprene, monoterpenes, and primary organic matter (POM) from the ocean are implemented into the model to provide a comprehensive view of the connection between ocean biology and atmospheric chemistry and air pollution. Model simulations show that marine organics can increase the concentration of PM₂.₅ by 0.1-0.3 µg m⁻³ (up to 5%) in some coastal cities such as San Francisco, CA. This increase in the PM₂.₅ concentration is primarily attributed to the POM emissions, with small contributions from the marine isoprene and monoterpenes. When marine organic emissions are included, organic carbon (OC) concentrations over the remote ocean are increased by up to 50% (25% in coastal areas), values consistent with recent observational findings. This study is the first to quantify the air quality impacts from marine POM and monoterpenes for the United States, and highlights the need for inclusion of marine organic emissions in air quality models.
2.1 Introduction

Several studies have shown that marine emissions of biogenic volatile organic compounds (BVOCs) and primary organic aerosols have the potential to affect coastal air quality (O’Dowd et al., 2004, Liakakou et al., 2007, Gantt et al., 2010). Observations of aerosol composition show that these emissions, which include both biogenic trace gases and particles, are strongly tied to the seasonal cycles in ocean biology (O’Dowd et al., 2004). Organic aerosols in the marine boundary layer are proposed to have different sources that can be broadly classified as primary, e.g., derived from the mechanical process of bubble bursting, and secondary, derived through ocean emission of BVOCs followed by chemical reaction and subsequent condensation of products into the aerosol phase (Ceburnis et al., 2008; Sellegrí et al., 2008). Starting with several contributions of Blanchard and Woodcock in the 1950s (e.g. Blanchard and Woodcock, 1957 and references therein), the bursting of bubbles entrained in ocean waters has been understood to present a significant source of primary organic matter (POM). Since then a large body of work, recently reviewed in great detail by Lewis and Schwartz (2004), has contributed to our understanding of the microphysical aerosol production mechanisms, aerosol mass and number fluxes, aerosol size distributions, aerosol chemical composition and the relationship of these with respect to wind speed, seawater temperature, ambient relative humidity and seawater composition in the bulk and at the surface. Many organic compounds accumulate at the seawater/air interface, either due to their low solubility or active transport by sub-millimeter size bubbles to the surface. Bubbles that burst in the presence of the microlayer can become considerably enriched with organic compounds in the aerosol relative to bulk seawater concentrations (Hoffman and Duce, 1976; Donaldson and Vaida, 2006) which is often observed over the productive waters of the ocean (O’Dowd et al., 2004; Facchini et al., 2008a). The observed chemical compositions of marine-derived organic compounds are diverse, containing exopolymer secretions (Bigg, 2007; Bigg and Leck, 2008; Leck and Bigg, 2008), oxygenated carbohydrate-like molecules (Hawkins et al., 2010; Russell et al., 2010), and alkylammonium
salts (Facchini et al., 2008b) that are water insoluble in some (O'Dowd et al., 2004; Sciare et al., 2009) but not all cases reported so far (Facchini et al., 2008; Rinaldi et al., 2010). Since organic carbon enrichment of marine aerosols generally increases with decreases in aerosol size (Keene et al., 2007; Facchini et al., 2008a), such aerosols can be easily transported to the coastal areas, contributing to the organic aerosol load.

Production of secondary organic aerosols (SOA) from phytoplankton-generated reactive trace gases is a topic of considerable debates in the recent literature. Formation of SOA with a marine source begins with the oxidation of BVOCs emitted by phytoplankton. After oxidation through gas and aqueous-phase reactions, the lower volatility products can condense on pre-existing particles or form new particles over marine areas (O’Dowd et al., 2007 and references therein). Several VOCs with the potential to form aerosols have been measured in the marine boundary layer, including dimethyl sulfide (DMS), iodine species, isoprene, monoterpenes, and amines (Shaw et al., 1983; O’Dowd et al., 2002; Bonsang et al., 1992; Yassaa et al., 2008; Facchini et al., 2008b). Currently, “bottom-up” and “top-down” global estimates of oceanic emissions of isoprene and α-pinene differ by over a factor of 30 and 2000, respectively (Luo and Yu, 2010). Simulations suggest that the oceanic α-pinene emission based on the bottom-up value has little effect on OC aerosol formation; however, emissions derived from the top-down approach can enhance the zonally-averaged total condensable secondary organic matter by more than 100 ng C m$^{-3}$ in the lower troposphere of the Southern Hemisphere (40° S - 60° S) (Luo and Yu, 2010). Due to such large uncertainty, the contribution of marine isoprene and monoterpenes to OC aerosol concentrations are examined in this study.

Several recent studies have implemented emission of marine isoprene and primary organic aerosols into 3-dimensional photochemical models to determine the air quality impacts. O’Dowd et al. (2008) implemented North Atlantic primary emissions into the REMOTE climate model by using a relationship between the organic fraction of sub-micron sea spray and [Chl-a]. The model-predicted aerosol concentration of between 0.2 - 0.3 µg m$^{-3}$
were similar to observations at Mace Head, Ireland, for both the summer and winter months. Marine isoprene emissions were implemented in the Community Multiscale Air Quality (CMAQ) model to determine the impacts on air quality in the United States (Gantt et al., 2010). They show that marine isoprene can add up to 0.004 µg m\(^{-3}\) to the SOA concentration in coastal areas, a minor contribution (< 0.5%) when compared to the terrestrial sources (Gantt et al., 2010). The effect of marine isoprene on ozone (O\(_3\)) formation in urban coastal areas was also small, with enhancement of maximum 8-hour average O\(_3\) only by 0.2 ppb. In this study, we expand upon Gantt et al. (2010) by examining the impact of both POM and SOA from marine sources on the air quality of the western US.

2.2 Method

2.2.1 CMAQ model description

We have conducted three summertime (June - August) simulations with CMAQ model (Version 4.7) using a 12 × 12 km\(^2\) spatial resolution in a domain comprising the western US and parts of the Pacific Ocean. The model simulations are conducted using meteorological data generated offline by the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Modeling System Generation 5 (MM5) version 3.7.4 (Grell et al., 1994). Simulations start on June 1\(^{st}\), 2005 using the initial conditions from the May 31\(^{st}\) output from year-long CMAQ simulations performed by the EPA. The boundary conditions are set every hour from a global chemical transport model, the Goddard Earth Observing System (GEOS)-Chem (Park et al., 2004). Emissions of anthropogenic gaseous and aerosol species are based on the 2005 National Emissions Inventory (NEI) version 1, while biogenic emissions are based on the Biogenic Emissions Inventory System (BEIS) version 3.13. Gas-phase chemistry is computed using the Carbon-Bond Mechanism version 5 (CB05) reactions, with SOA formation simulated using an advanced module including processes such as acid catalyzation, oligomerization, and in-cloud processing (Carlton et al., 2010).
Using this model configuration, three different summertime simulations were performed. The first is a baseline simulation in which no marine emissions are added. The second, referred hereto as the bottom-up simulation, includes emissions of marine isoprene based on laboratory measurements of Gantt et al. (2009) and marine POM based on O’Dowd et al. (2008). Marine monoterpenes were not included in bottom-up simulations due to the lack of well established and constrained laboratory-based emission rates (Yassaa et al., 2008; Luo and Yu, 2010). The third simulation, referred as the top-down, is similar to the bottom-up approach except both marine isoprene and monoterpane emissions are calculated based on marine boundary layer (MBL) concentration measurements reported for the Southern Ocean (Colomb et al., 2009). Marine monoterpenes are included in the top-down approach due to reported ambient concentrations comparable to phytoplankton-produced isoprene (Yassaa et al., 2008; Colomb et al., 2009). A detailed description of the method used to create these emissions is found in Sections 2.2 and 2.3. The summertime period of this model simulation was chosen due to the high solar radiation which potentially results in the highest emissions of marine BVOCs and rapid photochemistry.

The selected model domain includes nearly the entire coastal upwelling region; therefore it is well suited to study the impact of marine organic emissions on air quality in the western United States. However, outside this area, boundary conditions that are derived from outputs of global models did not include marine OC aerosol and trace gas emissions. Due to relatively close (~150 km) proximity of some parts of the coast to the model boundary, we have carefully examined the effects of boundary conditions on marine primary and secondary aerosol concentration. Over the western portion of our model domain which is downwind of the boundary conditions, it was found that average surface concentrations of marine aerosols in grid cells directly adjacent to the domain boundary were up to ~80% of the maximum concentration in the entire model domain. Furthermore, the sharp concentration gradients of marine aerosols (between ocean and terrestrial areas, for example) were much smaller (~2-3 grid cells) than the distance from the domain boundary to the coast (≥ 12 grid cells).
Qualitatively, these observations lead us to believe that the boundary conditions had a minor effect on surface concentrations of aerosols and ozone.

2.2.2 Marine VOC emissions

In both the bottom-up and top-down simulations, marine VOC emissions were added offline to the existing terrestrial emissions files. For the bottom-up simulations, marine isoprene emissions were created based on laboratory measurements of isoprene production from diatoms under a range of light conditions from Gantt et al. (2009). Diatoms were chosen in this study because they are one of the dominant summer phytoplankton classes for Pacific coast of the U.S. (Chavez et al., 1991), despite considerable variation in species dominance with latitude and seasonality. The creation and implementation of marine isoprene emissions followed the same method of Gantt et al. (2010), with the main difference being the use of monthly-averaged Level 3 MODIS/Aqua-derived [Chl-a] and $k_{490}$ coefficient at ~4 km resolution for the three months of simulations. These data were regridded to the 12 × 12 km$^2$ spatial resolution and projected into the Lambert Conformal Conic coordinates of the model domain. The ambient solar radiation, 10 meter winds, and skin temperature (a proxy for sea surface temperature (SST)) were obtained from the MM5 meteorological fields to calculate the emission rates. Detailed description of the bottom-up marine isoprene emission calculations and implementation into the CMAQ model are given in Gantt et al. (2009) and Gantt et al. (2010), respectively.

Marine isoprene and monoterpenes emissions in our top-down approach are based on average surface concentration measurements of Colomb et al. (2009) in the remote MBL of the Southern Indian Ocean using a method similar to Luo and Yu (2010). In this approach, surface VOC concentration measurements from a region of maximum biological activity and little influence from terrestrial emissions are used to estimate the surface fluxes. The averaged VOC emissions over the Southern Indian Ocean (normalized by chlorophyll abundance, surface wind speed and SST) are then used to calculate marine isoprene and
monoterpene emissions over the model domain. The emissions of marine isoprene and monoterpene emissions are estimated using the following equation of Guenther et al. (1996), suggested for terrestrial isoprene emissions calculations: \( E_{SIO} = C \cdot H \cdot \tau^{-1} \). In this formulation, \( E_{SIO} \) is the emission rate (molecules cm\(^{-2}\) s\(^{-1}\)) at the Southern Indian Ocean site, \( C \) is the average MBL concentration (molecules cm\(^{-3}\)), \( H \) is the MBL height (cm), and \( \tau \) is the lifetime of the gas (sec). We assume a \( \tau \) of 2 hr (7200 sec) for isoprene and 3.75 hours (13500 sec) for monoterpene emissions, values adapted from Atkinson and Arey (1998) and Galbally et al. (2007). The lifetime of monoterpene emissions is based on the lifetime of \( \alpha \)-pinene, the most common monoterpene measured in the MBL (Yassaa et al., 2008). Because Colomb et al. (2009) report the surface VOC concentrations and meteorological/ocean measurements as \( \sim \)12-hour averages over the surface ocean waters of variable biological productivity, the flux footprint is very complex and hard to interpret. Parameters affecting VOC emission rates/ambient concentrations such as phytoplankton abundance and speciation, surface solar radiation, and wind speed/direction are not well constrained. The very short atmospheric lifetime of isoprene also leads to strongly decaying vertical mixing ratios that further complicate emission rate calculations. As a result of these uncertainties, to convert the reported surface concentrations to \( C \) values used in the above equation, we employ MBL vertical profiles of isoprene predicted by the bottom-up CMAQ simulation in remote ocean regions off the coast of Baja California, northern California, and Washington. Isoprene and monoterpene emissions derived for the Southern Indian Ocean are then normalized by gas exchange coefficients and \([\text{Chl-a}]/\) values and applied to the CMAQ domain. The emission rate in CMAQ \((E_{CMAQ})\) can be calculated using the following equation:

\[
E_{CMAQ} = \frac{k_{CMAQ}}{k_{SIO}} \cdot E_{SIO} \cdot \frac{[\text{Chl-a}]_{CMAQ}}{[\text{Chl-a}]_{SIO}} \cdot SA
\]

where \( E_{CMAQ} \) is in units of moles s\(^{-1}\), \( SA \) denotes 12 \( \times \) 12 km\(^2\) CMAQ grid, \( k_{SIO}, k_{CMAQ} \) and \([\text{Chl-a}]_{SIO}, [\text{Chl-a}]_{CMAQ} \) are the gas exchange coefficients (m s\(^{-1}\)) and surface chlorophyll concentration (mg m\(^{-3}\)) at the Southern Indian Ocean measurement site and CMAQ domain,
respectively. The gas exchange coefficient is given by the equation: 

$$k = 0.31 U_{10}^2 \cdot \left( \frac{6600}{Sc} \right)^{0.5}$$

(Wanninkhof, 1992), with $U_{10}$ taken from the measurements of Colomb et al. (2009) and the MM5 hourly 10 meter wind speed for Southern Indian Ocean and CMAQ domain, respectively. Schmidt number ($Sc$) is calculated using De Bruyn and Saltzman (1997) formulation.

2.2.3 Marine Primary Organic Emissions

Emissions of marine primary organic aerosols were added to the model online in both the bottom-up and top-down simulations. The emission rate of marine primary organic aerosols was determined using the relationship between [Chl-$a$] and the sub-micron organic mass fraction of sea spray mass concentration from O’Dowd et al. (2008). The marine primary organic aerosol emissions in CMAQ are added to the existing Aitken (0.01% by mass) and accumulation mode (99.9% by mass) primary organic carbon emissions, which were previously restricted exclusively to terrestrial regions. Using the sub-micron sea spray function to calculate the organic fraction of the CMAQ accumulation mode sea spray mass is justified, as the majority of the CMAQ accumulation mode particle mass is less than 1 μm in diameter. The [Chl-$a$] for each model grid is determined from the monthly-averaged Level 3 MODIS/Aqua-derived [Chl-$a$], and the sea spray mass emissions are calculated from the existing accumulation mode CMAQ sea salt emissions. The CMAQ sea salt fluxes are driven by the MM5 meteorological variables using the Gong-Monahan (Gong, 2003) and the deLeeuw (deLeeuw et al., 2000) emission functions for the open ocean and the surf zone, respectively. A complete description of the sea salt emission model in this version of CMAQ, including relative humidity and white cap coverage dependence, is found in Kelly et al. (2009). The sea salt emissions were converted into sea spray emissions by calculating the apparent density of the sea spray aerosol as a function of organic fraction. In the model results, the sum of the Aitken and accumulation mode constitutes particles with an aerodynamic diameter less than 2.5 μm. For model-predicted changes in OC$_{2.5}$
concentrations due to marine organics, an OM/OC mass ratio of 1.4 is used for marine primary organic aerosols (Decesari et al., 2007).

2.3 Results

2.3.1 Comparison with observations

To test the effect of the marine emissions on model-predicted atmospheric concentrations of OC, the simulated values were compared to ambient measurements at several different monitoring stations on the coast of California. OC concentration observations were obtained from Point Reyes National Seashore (38.12°N, 122.91°W) and Redwood National Park (41.56°N, 124.09°W) as part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (http://vista.cira.colostate.edu/improve/). Both IMPROVE stations, whose locations are shown in Fig. 2.1, are less than 5 km distance from the ocean, and typically experience onshore winds. The IMPROVE stations sample organic carbon particles < 2.5 µm in aerodynamic diameter (OC$_{2.5}$) on filters for 24 hours every 3 days to give the average daily concentration in µg m$^{-3}$. In the model, OC$_{2.5}$ is the sum of the accumulation mode secondary organic carbon from biogenic and anthropogenic VOCs and the Aitken/accumulation mode primary OC. Table 1 shows that for the entire simulation period (1 June to 31 August 2005) the model tends to overpredict surface OC$_{2.5}$ concentration for the two coastal sites, and the addition of marine OC$_{2.5}$ aerosol brings the simulated mean further from the observations. However, careful examination of time series revealed considerable differences between roughly two halves of the simulation period where the first half (1 June to 15 July) was characterized by greater contribution of marine OC$_{2.5}$ to total OC$_{2.5}$ (Fig. 2.2). Table 1 shows that during this period with less anthropogenic influence, the inclusion of marine organic emissions improves magnitude and correlation (Redwood only) of the model-predicted OC$_{2.5}$ concentration for the Point Reyes and Redwood sites. Additional analysis of OC$_{2.5}$ observations at these sites showed little seasonal variation.
which when combined with the relatively steady emission source of marine primary organic aerosol off the Pacific coast indicates that the model improvements from the inclusion of marine organic emissions may occur throughout the year. Our model-predicted marine OC$_{2.5}$ values over the ocean agree relatively well with summertime OC measurements in areas influenced by open ocean air masses such as Amsterdam Island (Sciare et al. 2009), Mace Head, Ireland (Yoon et al., 2007), the Azores (Pio et al., 2007), and the Northern Atlantic (Russell et al., 2010) which have reported average concentrations of ~0.2, 0.4, 0.5, and 0.25 µg m$^{-3}$, respectively.

To assess the accuracy of marine isoprene emissions, the model-predicted ambient isoprene concentrations were compared to observations taken from Photochemical Assessment Monitoring Stations (PAMS) network (http://www.epa.gov/air/oaqps/pams/index.html) located in Ventura, CA (34.28°N, 119.31°W) and Oceanside, CA (33.22°N, 117.40°W) on the southern California coast (see Fig. 2.1). The PAMS stations use gas chromatography-flame ionization detector (GC-FID) to measure the instantaneous isoprene concentrations in units of ppb every 6 days several times during the day. The two PAMS stations used for comparison are within 1 km of the Pacific Ocean. The bottom-up and top-down approaches slightly improve the dramatic underprediction of isoprene concentrations in the baseline simulation at both sites shown in Table 2. However, the addition of marine isoprene emissions does not improve correlations between model predicted and observed concentrations. This is likely due to the uncertainty in the magnitude and mechanisms of marine isoprene emissions and the high detection limit (0.05 ppbC) of isoprene with the GC-FID. Additional uncertainties and potential differences between stations arise from inability to isolate the relatively small marine isoprene emissions from the much larger terrestrial background (Palmer and Shaw, 2005) in the observations, and from the previously-documented consistent disagreement between CMAQ predictions and the PAMS network measurements (Carlton and Reff, 2009).
2.3.2 Changes in $OC_{2.5}$ and $PM_{2.5}$

The most substantial air quality effect of marine organic emissions was the increase in $OC_{2.5}$ concentration. Fig. 2.3 shows that over the remote ocean up to 50% of the $OC_{2.5}$ concentration can be attributed to the marine sources. This value is consistent with the findings of Russell et al. (2010) who show that 50% of the Northern Atlantic MBL OM$_1$ mass has a marine origin. Fig. 2.3 also demonstrates that at the coastal areas a considerable fraction (up to 25% in certain locations) of $OC_{2.5}$ aerosol mass can have marine origin. There are also episodic periods where marine sources contribute nearly the entire model-predicted $OC_{2.5}$ at the coastal IMPROVE sites (Fig. 2.2). This is important because the age and chemical evolution of organic aerosols affects their reactivity, hygroscopicity, volatility, and optical properties which can influence both climate forcing and human health (Andreae et al., 2009; Jimenez et al., 2009). The periods of highest marine contribution to model-predicted OC typically occur when concentrations are low, which means that marine organics mainly impact the background aerosol concentration. However, even with such large contribution to MBL $OC_{2.5}$ aerosol mass, marine organic emissions seem to have modest influence on model-predicted marine $PM_{2.5}$ which is mostly composed of sea salt. Fig. 2.4a shows that the greatest increase in $PM_{2.5}$ (over 0.3 µg m$^{-3}$) occurs over the ocean near the northern California coast where both 10 meter wind speed (not shown) and ocean biological productivity (see Fig. 2.1) are high. The spatial distribution of the percentage contribution of marine organic aerosols to average surface $PM_{2.5}$ concentration (Fig. 2.4b) is similar to that of the total change in $PM_{2.5}$ (Fig. 2.4a), with values up to 10% near the northern California coast where concentration increases were the highest. The model-predicted increases and percentage contribution of marine OC to $PM_{2.5}$ rapidly decrease with distance from the coast to near zero within ~100 km. The gradient of marine contribution to $PM_{2.5}$ is especially sharp in areas with steep topography. Despite lesser (up to 5%) percentage contribution to $PM_{2.5}$ in terrestrial areas with higher concentrations of anthropogenic and biogenic aerosols, marine organic aerosol emissions may still be important for regulatory purposes for the
coastal cities like San Francisco, CA that are in nonattainment for the 2006 PM$_{2.5}$ National Ambient Air Quality Standard (NAAQS) (http://www.epa.gov/air/oaqps/greenbk/pm25_2006_designations_20091113.pdf).

2.3.3 Comparison of bottom-up and top-down simulations

The primary difference between the bottom-up and top-down simulation is the introduction of marine monoterpenes into the model and increased emissions of marine isoprene. These additional emissions result in noticeable changes in the O$_3$ concentration when compared to the bottom-up simulation. Fig. 2.5a shows that for the top-down approach model simulations predict moderate enhancement (0.5%) of average surface O$_3$ concentration in coastal urban areas and slight decrease (-0.1%) in concentration over the remote ocean. The differences between top-down and bottom-up simulations shown on Figs. 2.5a and 2.5b can be viewed as the high and low estimates of the potential role that marine isoprene and monoterpenes can play in O$_3$ formation near coastal areas. Figs. 2.5c and 2.5d display surface SOA concentration changes due to emissions of marine isoprene and monoterpenes for the top-down and bottom-up simulations, respectively with the maximum increases of <0.04 µg m$^{-3}$ occurring along the northern California coast where emissions are high. Compared to marine primary organic aerosols, there is a larger inland extent of the marine SOA into areas like the San Joaquin Valley in central California due to the time required for gas-to-particle conversion. These figures show that while the simulated SOA change in top-down approach is considerably higher than that of the bottom-up simulation, the contribution of marine sources of SOA to the total PM$_{2.5}$ concentrations is an order of magnitude lower compared to the POM marine biogenic sources. The time series of source-resolved OC$_{2.5}$ at the IMPROVE sites in Fig. 2.2 confirms that only at times of very low marine primary OC concentrations are secondary OC concentrations similar in magnitude. Therefore, our model simulations suggest that marine isoprene and monoterpenes contribute a minor fraction of marine OC aerosol mass concentration in near coastal regions. This result is consistent with the modeling and observational studies of Arnold et al. (2009) and Claeys et al. (2009) who
show that marine isoprene-SOA makes up a minor portion of fine mode marine OC aerosol mass. It is worth noting that oceanic sources of sulfur (principally DMS) and marine sources of ammonia and amines are not treated by the version of CMAQ model used in the simulations. As marine sources of sulfur, ammonia and alkyamines were shown to be potentially significant contributors to sub-micrometer sized marine aerosol (Charlson et al., 1987; Facchini et al., 2008b; Smith and Mueller, 2010), the reported SOA from marine isoprene and monoterpenes likely represent a low estimate of the total marine secondary OC aerosol.

2.4 Conclusion

This is the first study to quantify the combined contribution of marine primary organic aerosol, isoprene, and monoterpane emissions to the air quality of a coastal region. Building on a previous modeling study examining the air quality effect of marine isoprene (Gantt et al. 2010), emissions of marine isoprene, monoterpenes, and primary organic aerosols were implemented in the U.S. EPA’s CMAQ model with a domain over the Pacific Ocean and western US. The terrestrial impact of marine organic emissions is strongest at the coast, with average surface PM$_{2.5}$ and O$_3$ concentrations increasing by up to 5% and 0.5%, respectively. Further inland, the contribution of marine organic emissions quickly diminishes within ~100 km of the coast. Over the remote ocean, marine organics contributed over 50% of the surface OC$_{2.5}$ and resulted in a 10% change in PM$_{2.5}$ concentrations. The source of additional PM$_{2.5}$ in the simulations is dominated by POM, with the SOA source from isoprene and monoterpenes making up a much smaller portion of the PM$_{2.5}$ mass. Model calculations indicate that during periods of high marine organic aerosol contribution, the inclusion of marine organic emissions can yield improved model predictions of surface OC$_{2.5}$ concentration at the California coast. The addition of isoprene and monoterpenes from marine sources did not have considerable effect on O$_3$ or SOA surface concentration in
coastal areas. For surface isoprene concentrations measured at the southern California coast, the large underprediction by the model is slightly improved by the additional marine isoprene emissions. This study suggests that marine organic aerosols account for a considerable portion of the aerosol mass over the remote ocean and some near-coastal regions and, therefore needs to be considered in future air quality models. The subsequent health impacts of marine organics may be underestimated by these results, as studies have shown that the organic mass fraction of marine aerosols is particularly large for particles < 0.125 µm in diameter (O’Dowd et al., 2004). Furthermore, organic vapors from marine sources of VOC have been implicated to aid nucleation events and growth of ultrafine particles in coastal environments, potentially producing large numbers of particles at sizes problematic for human health (Vaattovaara et al., 2006; Modini et al., 2009). While this modeling study shows a small contribution of marine isoprene and monoterpene-SOA to total OC aerosol mass over the ocean, a number of important sources of marine-SOA from biogenic amines and methanesulfonate were not included in the current CMAQ simulations. Additional field measurements and model simulations with improved aerosol size/chemical characterization and emission source functions may be necessary to fully explore the significance of marine organic aerosol and biogenic trace gas emissions on coastal air quality and human health.

ACKNOWLEDGEMENTS

This research was supported by the Office of Science (BER), U.S. Department of Energy, Grant No. DE-FG02-08ER64508. Thanks to Kirk Baker of the U.S. EPA/OAQPS for providing the meteorological fields, emission inventories, initial and boundary conditions for the baseline simulations.
DISCLAIMER

Although this paper has been reviewed by EPA and approved for publication, it does not necessarily reflect EPA’s policies or views.
References


Table 2.1. Comparison between simulated and observed organic carbon aerosol concentrations for two coastal IMPROVE stations during the simulation period and the period from 1 June to 15 July, 2005.

<table>
<thead>
<tr>
<th>Station</th>
<th>Mean Obs. (µg m⁻³)</th>
<th>Simulation</th>
<th>Mean Sim. (µg m⁻³)</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 June to 31 Aug.</td>
<td>1 June to 15 July</td>
<td>1 June to 31 Aug.</td>
<td>1 June to 15 July</td>
</tr>
<tr>
<td>Point Reyes, CA</td>
<td>0.57</td>
<td>0.38</td>
<td>Baseline</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bottom-up</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Top-down</td>
<td>0.80</td>
</tr>
<tr>
<td>Redwood NP, CA</td>
<td>0.44</td>
<td>0.37</td>
<td>Baseline</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bottom-up</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Top-down</td>
<td>1.69</td>
</tr>
<tr>
<td>Station</td>
<td>Mean Obs. (ppb)</td>
<td>Simulation</td>
<td>Mean Sim. (ppb)</td>
<td>Correlation Coefficient</td>
</tr>
<tr>
<td>---------------</td>
<td>----------------</td>
<td>------------</td>
<td>----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Ventura, CA</td>
<td>0.41</td>
<td>Baseline</td>
<td>0.05</td>
<td>-0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom-up</td>
<td>0.05</td>
<td>-0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Top-down</td>
<td>0.08</td>
<td>-0.24</td>
</tr>
<tr>
<td>Oceanside, CA</td>
<td>0.06</td>
<td>Baseline</td>
<td>0.02</td>
<td>-0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom-up</td>
<td>0.03</td>
<td>-0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Top-down</td>
<td>0.03</td>
<td>-0.14</td>
</tr>
</tbody>
</table>

Table 2.2. Comparison of isoprene observations and simulations for two coastal PAMS stations from 1 June to 31 August, 2005.
Fig. 2.1. Locations of the IMPROVE and PAMS stations used in this study and the seasonally-averaged chlorophyll-\textit{a} concentrations for the summer of 2005.
Fig. 2.2. Time series of hourly top-down model-predicted surface OC$_{2.5}$, marine primary and secondary OC$_{2.5}$ and 24-h average observed OC$_{2.5}$ for the (a) Point Reyes and (b) Redwood IMPROVE sites. The concentration values above 5 µg m$^{-3}$ are not shown.
Fig. 2.3. Average percentage contribution of marine organics to surface OC$_{2.5}$ concentration for the bottom-up simulation from 1 June to 31 August, 2005.
Fig. 2.4. Average increase (a) and percentage change (b) in surface PM$_{2.5}$ concentration from marine organics for the bottom-up simulation from 1 June to 31 August, 2005.
Fig. 2.5. Average percentage change in surface O$_3$ for the top-down (a) and bottom-up (b) simulations and average increase in surface SOA$_{2.5}$ concentrations concentration for the top-down (c) and bottom-up (d) simulations due to marine emissions from 1 June to 31 August, 2005.
CHAPTER 3. IMPROVING THE EMISSIONS OF MARINE PRIMARY ORGANIC AEROSOLS

Preface:

In addition to chlorophyll-\(a\) concentration ([Chl-\(a\)]), it has been shown that other factors such as meteorological conditions and aerosol size can affect the organic mass fraction of sea spray aerosols and are not included in current emission parameterizations. Neglecting these factors in previous studies has resulted in the prediction of marine primary organic aerosol emissions/concentrations that do not replicate the observed seasonality. In this article published in ACP in 2011, a new parameterization for the organic mass fraction of sea spray aerosol is developed by including dependences with wind speed and aerosol size. This was achieved by comparing the observed organic mass fraction of sea spray aerosol at two sites, Mace Head, Ireland, and Point Reyes, CA, with satellite-derived [Chl-\(a\)], dissolved organic carbon (DOC), particulate organic carbon (POC), and 10 meter wind speed (\(U_{10}\)). Of the oceanic and meteorological variables, a multi-variable logistic relationship between [Chl-\(a\)], \(U_{10}\), and OM\(_{SSA}\) was found to have the strongest correlations and global submicron marine primary organic aerosol (POA) emission of 2.8 to 5.6 Tg C yr\(^{-1}\). Compared to previous parameterizations in which the organic mass fraction of sea spray aerosol is a linear function of [Chl-\(a\)], this new parameterization predicts lower emission rates over high wind areas such as the Southern Ocean in which the linear function is a poor predictor of concentration seasonality. Additionally, the size dependence of the parameterization allows for the submicron emissions to be explicitly divided into Aitken, accumulation, and fine modes in order for their size distribution to be estimated in climate models. This marine POA emission scheme is among the parameterizations that have been implemented into the GEOS-Chem for evaluation (Chapter 4) and the CAM5 model for quantification of their climate impacts (Chapters 5 and 6).

Many of the uncertainties of this parameterization are described within the text, including lower observed organic fractions than at Mace Head and Point Reyes, coastal vs.
open ocean measurements, and the potential SOA contribution to organic aerosol concentrations. One source of uncertainty not discussed is the use of satellite [Chl-$a$] in the analysis. For this study, the Sea Wide Field-of-view Sensor (SeaWiFS) OC4v4 chlorophyll-$a$ product was used to determine the 24-hour upwind average [Chl-$a$] that was compared to OM$_{SSA}$ in the derivation of the multi-variable logistic relationship in the article. Evaluation of this satellite [Chl-$a$] dataset with in-situ measurements has shown a global RMS around 0.2 mg m$^{-3}$ (~30%). This uncertainty, while significant, is likely lower than the other sources of uncertainty because of the low bias (< 8%), high correlation (0.9), and large uncertainties chronicled in Section 3.4 (Section 4 of the published version of the article).
Wind speed dependent size-resolved parameterization for the organic enrichment of sea spray

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Abstract

For oceans to become a significant source of primary organic aerosol (POA), sea spray must be highly enriched with organics relative to the bulk seawater. We propose that organic enrichment at the air-sea interface, chemical composition of seawater, and the aerosol size are three main parameters controlling the organic mass fraction of sea spray aerosol (OMSSA). To test this hypothesis, we developed a new marine POA emission function based on a conceptual relationship between the organic enrichment at the air-sea interface and surface wind speed. The resulting parameterization is explored using aerosol chemical composition and surface wind speed from Atlantic and Pacific coastal stations, and satellite-derived ocean concentrations of chlorophyll-α, dissolved organic carbon, and particulate organic carbon. Of all the parameters examined, a multi-variable logistic regression revealed that the combination of 10 meter wind speed and surface chlorophyll-α concentration ([Chl-α]) are the most consistent predictors of OMSSA. This relationship, combined the published aerosol size dependence of OMSSA, resulted in a new parameterization for the organic carbon fraction of sea spray. Global marine primary organic emission is investigated here by applying this
newly-developed relationship to existing sea spray emission functions, satellite-derived [Chl-
$a$, and modeled 10 meter winds. Analysis of model simulations show that global annual
submicron marine organic emission associated with sea spray is estimated to be from 2.8 to
5.6 Tg C yr$^{-1}$. This study provides additional evidence that marine primary organic aerosols
are a globally significant source of organics in the atmosphere.

3.1 Introduction

Indirect radiative forcing of anthropogenic aerosols is the major source of uncertainty in
climate projections today (IPCC, 2007). A large fraction of this uncertainty may be related
to the number concentration and size distribution of marine aerosol that are prescribed or
diagnosed in global climate models (GCMs) (Hoose et al., 2009), and the uncertainties
associated with forcings and feedbacks involving marine clouds and precipitation (Bony and
Dufresne, 2005; Clement et al., 2009). Marine aerosols are particularly important as they
contribute considerably to the global aerosol load and are emitted from a large area of the
Earth’s surface underlying an atmosphere with low aerosol concentration. The lower bounds
(typically from 10 to 40 cm$^{-3}$) of background aerosol concentration often prescribed in GCMs
can vary the simulated aerosol indirect effect by over 80%, from -1.8 W m$^{-2}$ to -0.2 W m$^{-2}$
(Hoose et al., 2009).

Although sea-salt typically dominates total marine aerosol mass burden and emission
rates, organic aerosols of marine origin can contribute a considerable fraction of the
submicron aerosol mass concentration near biologically productive waters (O’Dowd et al.,
2004). Organic aerosol concentrations of up to 3.8 µg m$^{-3}$ have been observed at Mace Head
during periods of onshore flow (Ovadnevaite et al., 2011) where on average ~80% of the
carbonaceous material has been directly linked to plankton emissions (Ceburnis et al., 2011).
Cloud condensation nuclei (CCN) over the remote oceans typically range from a few tens per
cm$^{3}$ over biologically inactive regions (seasons) to a few hundred per cm$^{3}$ under biologically
active conditions (Andreae, 2007). Since cloud properties are most sensitive to the addition of particles when the background concentration is low (Platnick and Twomey, 1994), ambient measurements, remote sensing, and modeling studies indicate that ocean biology could influence marine cloud microphysical properties (Shaw et al., 1983; Charlson et al., 1987; Middlebrook et al., 1998; O’Dowd et al., 2004; Meskhidze and Nenes, 2006; 2010; Bigg and Leck, 2008; Sorooshian et al., 2009; 2010; Thomas et al., 2010).

Organic aerosols in the marine boundary layer are proposed to have different sources that can be broadly classified as primary, produced from the mechanical process of bubble bursting, and secondary (SOA), derived from precursor biogenic volatile organic compounds (BVOCs) emitted by phytoplankton and macroalgae or by photolysis of chromophoric dissolved organic matter (CDOM) in the water column (Zhou and Mopper, 1997; O’Dowd and de Leeuw, 2007; Sellegri et al., 2008). In addition, SOA can also be derived from the chemical transformation of primary or secondary components present in the condensed phase. Such complex transformations could take place at the particle surface or in the aqueous phase, and may also involve a further step through the gas phase in which semivolatile aerosol components can be oxidized to form new condensable products (Rinaldi et al., 2010). Due to the potentially important contribution of marine organic aerosol to the CCN budget over the remote ocean, improvement of the fundamental process-level understanding of marine primary and secondary aerosol production mechanisms is needed to develop more reliable parameterizations that can be confidently applied in GCMs. These new parameterizations must capture the total mass of marine organic aerosol emission as well as their cloud nucleating properties (i.e., number concentration and size dependent chemical composition of submicron sea spray). Here, we examine the factors that affect the emission of marine primary organic aerosols (POA).

Laboratory and ambient measurements have revealed that the organic fraction of submicron sea spray aerosols can be enriched (relative to the underlying seawater) by as much as 2 to 3 orders of magnitude (Blanchard, 1964; Gershey, 1983a; Hoffman and Duce,
The organic enrichment of sea spray is thought to be controlled by the accumulation of insoluble organic matter at the air-sea interface (Hoffman and Duce, 1976; Gershey et al., 1983b). This natural enrichment of the ocean surface layer by organics has been shown to be a function of both meteorological factors, such as surface wind speed, and oceanic parameters including the concentration of dissolved organic carbon ([DOC]), particulate organic carbon ([POC]), chlorophyll-a ([Chl-a]), and type of organic carbon (OC) in the air-sea interface and underlying water (Hoffman and Duce, 1976; Gershey, 1983a; 1983b; O’Dowd et al., 2004; 2008; Russell et al., 2010).

The air-sea interface can roughly be thought of as being in three regimes where 1) very high organic enrichment leads to visible biogenic surface slicks thicker than 50 μm, 2) moderate organic enrichment leads to a non-slick microlayer ~50 μm thick, and 3) no enrichment is present. Figure 3.1 shows the conceptual relationship between the organic enrichment of the air-sea interface (given as an OC/Na ratio based on values summarized by Russell et al., 2010) and surface wind speed based on a review of previous works. This figure shows that for given chemical composition of seawater, the highest enrichments are expected during calm winds. An increase in wind speed above 3-4 m s\(^{-1}\) will cause a rapid decrease in the enrichment (the Langmuir circulations starts breaking up the slicks), and its effective removal for wind speeds in exceed 8 m s\(^{-1}\) (when the wave breaking thoroughly mixes the microlayer with the underlying water). Although there is significant spread in observational data, most of the studies agree that slicks in the open ocean are only observed for surface wind speed < 5 m s\(^{-1}\) (Romano, 1996). When winds increase from 2 to 5 m s\(^{-1}\), there is an increase in the formation of gaps and a decrease in the satellite-derived areal extent of ocean slicks (Marmorino et al., 2008). This increase of gaps and subsequent decrease in slick coverage is consistent with the Dysthe (2006) model describing the tearing of a surface film in a region of positive surface straining from Langmuir circulations (Langmuir, 1938; Leibovich, 1983). Many studies also report a decrease in microlayer (non-
slick organic layer of moderate enrichment) concentration relative to the underlying seawater for surface wind speeds in excess of ~ 4 m s\(^{-1}\) (Obernosterer et al., 2008), except for Wurl et al. (2010) who report constant microlayer surfactant enrichment for winds up to 5.5 m s\(^{-1}\), with enrichment persisting for winds up to 10 m s\(^{-1}\). When surface winds exceed 8 m s\(^{-1}\), the initiation of wave breaking is expected to cause the destruction of the microlayer by mixing it into the underlying seawater (Carlson, 1983). Extrapolation of the linear decrease in microlayer thickness with wind speed observed by Liu and Dickhut (1998) predicts a microlayer thickness of 0 µm at a wind speed of ~ 8.5 m s\(^{-1}\), consistent with this picture. At wind speeds in excess of ~11 ms\(^{-1}\), the mechanism for sea spray generation is via mechanical disruption of wave crests (e.g., Andreas, 1998 and references therein). The spume drops torn from the wave crests consequently have composition of bulk seawater with little enrichment. Overall, review of published studies indicates that surface wind speed can play a crucial role in determining the physical and chemical characteristics of the air-sea interface and thus the organic enrichment of sea spray.

In addition to the potential impact from wind speed, the organic enrichment of sea spray has been shown to be affected by the chemical composition of seawater. Past studies have consistently found that the marine aerosol OC concentration is higher over regions of high biological activity (O’Dowd et al., 2004; Sciare et al., 2009; Miyazaki et al., 2010). The results of multiple ambient and laboratory studies indicated that the upwind concentrations of [Chl-\(\alpha\)], [POC], and [DOC] can be used as a proxy for the organic enrichment of sea spray (Gershe, 1983a; 1983b; Hoffman and Duce, 1976; O’Dowd et al., 2004; 2008; Russell et al., 2010).

Several attempts to quantify and characterize size-dependent chemical composition of sea spray aerosols have recently been carried out. These measurements consistently have shown that the organic mass fraction of submicron sea spray increases with decreasing particle size (Oppo et al., 1999; Keene et al., 2007; Facchini et al., 2008), with a small and relatively constant organic fraction for supermicron particles with aerodynamic diameter <
10 μm (Oppo et al., 1999; Keene et al., 2007; Facchini et al., 2008). Keene et al. (2007) reported that the water soluble organic carbon of artificially generated aerosols within a chamber was highly enriched in all aerosol size fractions, with greatest enrichments in size fraction with geometric mean diameter of 0.13 μm. In this smallest size fraction sampled, organic carbon comprised up to 80 % of aerosol mass and dominated the mass of most individual particles (Keene et al., 2007). Facchini et al. (2008) similarly reported a high contribution of organic matter in submicron sea spray particles (up to 77 ± 5% in the 0.125–0.25 μm size range). However, their analysis discriminated between water soluble and insoluble organic carbon (WSOC and WIOC, respectively), finding a dominant contribution (up to 94 ± 4%) from the water insoluble fraction.

Despite the likely impact of both meteorological factors and chemical composition of seawater on sea spray chemistry, most of the recent parameterizations of marine POA emissions use only [Chl-a] as a proxy for deriving the organic mass fraction of sea spray aerosols (O’Dowd et al., 2008) or for determining the total magnitude of the emissions (Spracklen et al., 2008). In this paper, we develop a new parameterization for organic fraction of sea spray aerosol based on the conceptual picture of Fig. 3.1, and constrain it using ambient data from two different oceanic regions.

3.2 Data and methods

3.2.1 Aerosol chemistry

Two coastal stations with long-term measurements of aerosol chemistry were selected for this study; the Mace Head Atmospheric Research Station (53.33°N, 9.90°W) on the Atlantic coast of Ireland and a site at the Point Reyes National Seashore (38.12°N, 122.91°W) on the Pacific coast of California. Measurements of the ~50-100 hour average chemical composition of aerosols with an aerodynamic diameter < 1.5 μm from Mace Head (Cavalli et al., 2004; Yoon et al., 2007) have been supplemented with measurements of the chemical
composition of aerosols with diameters < 2.5 µm at Point Reyes near San Francisco, CA taken as part of the United States’ Interagency Monitoring of Protected Visual Environments (IMPROVE) network (http://vista.cira.colostate.edu/improve/). At Point Reyes, aerosols are captured on filters for 24 hours (midnight to midnight local time) every 3 days and analyzed for chemical composition. Point Reyes was selected from the large (170 stations) IMPROVE monitoring network because it is located very close to the coast (~4 km) and has the highest frequency of aerosols exhibiting marine characteristics (White, 2008).

Several compounds are included in the analysis of aerosol chemical composition, including elemental carbon (EC), OC, and sodium (Na). To avoid potential problems with Na measurements (White, 2008), the data at Point Reyes were analyzed for the years 2000-2001 and 2005-2007. For Mace Head, the aerosol concentrations measurements conducted only during periods of “clean sector” conditions (wind direction from 180° to 300°, particle concentration < 700 cm⁻³, EC < 0.05 µg m⁻³) for the years 2002 to 2006 are included in the analysis. The OC measurements from Mace Head are further separated into WSOC and WIOC following Cavalli et al. (2004). Unlike Mace Head, OC measurements obtained from the IMPROVE network do not segregate WSOC and WIOC. To be consistent with the Mace Head data, it was assumed that 70% of the OC measured at Point Reyes is insoluble. This WIOC/OC fraction was similar to that observed at Mace Head (Cavalli et al., 2004; O’Dowd et al., 2004) and Amsterdam Island (37.80°S, 77.57°E) (Sciare et al. 2009) during the summer when OC concentrations were highest. The organic mass fraction of sea spray (OM_{SSA}) can then be determined by converting the OC measurements to organic matter (OM) using a 1.4 OM/OC ratio (Descari et al., 2007; Facchini et al., 2008) and using the equation OM_{SSA} = WIOM/(WIOM+sea-salt) first employed in O’Dowd et al. (2008), where sea-salt is estimated as Na/0.3061 corresponding to the mass fraction of sodium in dry sea-salt (Seinfeld and Pandis, 2006). OM_{SSA} is used here as the primary variable of the analysis because it is independent of the sea spray concentration (considering that POA of marine...
origin and sea-salt have similar production mechanisms and sinks) and can be easily applied to published sea spray emission parameterizations.

3.2.2 Meteorology

Wind speed and direction data used in the analysis is different for the two stations. At Mace Head, 10 meter wind speed and direction was measured at the same location as the aerosol measurements, with the speed recorded only during periods when aerosols were being measured. At Point Reyes, hourly wind speed and direction at 5 meters was measured at the Bodega Bay buoy #46013 (38.24°N 123.30°W) as part of the United States’ National Data Buoy Center network (http://www.ndbc.noaa.gov/). This buoy is located ~37 km west of Point Reyes in the Pacific Ocean. The 5 meter wind speed was converted to 10 meters using the power-law wind-profile as follows: $U_{10} = U_5\left(\frac{10}{5}\right)^{0.11}$ (Hsu et al., 1994). In order to make the aerosol measurements between the two sites more comparable, a wind direction filter was used on the Point Reyes data including only days with all 24 hours having onshore wind directions (between 180° and 315°). Such rigorous filtering reduced the number of qualifying days from 365 to 36. Further filtering of the Point Reyes aerosol measurements included only days with EC < 0.05 µg m$^{-3}$ in order to avoid potential influence of OM from anthropogenic sources (Clarke, 1989) and to make them consistent with the Mace Head clean sector data.

3.2.3 Ocean chemistry

The oceanic parameters derived from satellite data include 8-day average Level 3 surface [Chl-$a$], [POC], and [DOC] from the Sea Wide Field-of-view Sensor (SeaWiFS) for the years 2000-2007. [Chl-$a$] is determined using the OC4v4 algorithm (O'Reilly et al., 1998, 2000), and [POC] was calculated from normalized water-leaving radiances at 443, 490, and 555 nm using the method of Stramska et al. (2009). In order to estimate the ocean [DOC] distribution, a sea surface temperature (SST)-based approach (Siegel et al., 2002) and a colored dissolved organic matter (CDOM)-based approach (Mannino et al., 2008) were
combined to generate the estimates of surface layer [DOC] for the years 2000-2007. The 8-day average SST data was obtained from Moderate Resolution Imaging Spectroradiometer (MODIS), and the 8-day average normalized water leaving radiance data at 490 and 555nm (required for the CDOM-based approach) were retrieved from SeaWiFS. As each method is designed to estimate the [DOC] in different parts of the ocean, the SST-based approach was used for the open ocean and the CDOM-based approach was used for coastal waters (Siegel et al., 2002; Mannino et al., 2008). All of the satellite-derived data was regridded to 1° × 1° spatial resolution. The reported global root mean squared error of the [Chl-a], [POC], and [DOC] were ~0.2 mg m⁻³, 20 mg m⁻³, and 2.6 - 8.6 µmol L⁻¹, respectively (Siegel et al., 2005; Stramska et al., 2009; Mannino et al., 2008; Siegel et al., 2002). For each aerosol measurement, a non-weighted upwind average of the temporally-collocated [Chl-a], [DOC] and [POC] was calculated using 24-hour back-trajectories based on the observed wind speed and direction (grouped into 45° vectors).

3.3 Results and discussion

3.3.1 Factors affecting organics in sea spray

3.3.1.1 Wind speed

A plot of organic carbon fraction against surface wind speed in Fig. 3.2a shows that for both the Mace Head and Point Reyes measurement stations, the OMₘₙₐ decreases with increasing 10 meter wind speed in a manner consistent with our conceptual picture given on Fig. 3.1. For wind speeds above 10 m s⁻¹, sea spray aerosols are largely composed of sea-salt with very little contribution from organics. As wind speeds decrease to 5 m s⁻¹, a strong increase in the organic fraction of sea spray was observed. This trend can be explained by the presence of a surface microlayer described by our conceptual wind speed-organic enrichment relationship. No data exists for surface winds of less than 4 m s⁻¹ due to longer averaging time at the two stations (Mace Head data was typically averaged over 50-100 hours and Point
Reyes over 24 hours). However, considering that wind speed of $\geq 4 \text{ m s}^{-1}$ is typically associated with the onset of bubble formation (Monahan and O'Muircheartaigh, 1986), enrichment at wind speed values lower than that may not be environmentally relevant. Nevertheless, our conceptual picture on Fig. 3.1 predicts that $\text{OM}_{\text{SSA}}$ should plateau at a wind speed value of $\sim 3 \text{ m s}^{-1}$. Using the MATLAB curve fitting tool and the proposed conceptual relationship, we have developed a logistic function that is a good fit ($R^2 = 0.38-0.47$) for the existing ambient measurements and requires no artificial cutoff. The general relationship between sea spray organic enrichment and wind speed shown on Fig. 3.2a suggests that winds (through their effect on air-sea interface) may play a considerable role in the enrichment of sea spray aerosol.

3.3.1.2 Ocean chemistry

Analysis of ambient marine aerosol chemical composition suggests that there is a maximum enrichment of sea spray aerosols by organics that, although usually occurring at low wind speed, can be vastly different for different measurement locations. Figs. 3.2b-d show that each ocean chemistry parameter examined ([POC], [DOC], and [Chl-$a$]) had a positive relationship with $\text{OM}_{\text{SSA}}$. It is worth noting that the relationship between $\text{OM}_{\text{SSA}}$ and [POC] (Fig. 3.2c) was stronger than [DOC] (Fig. 3.2d) for Mace Head, consistent with the hypothesis of Russell et al. (2010) that [POC] influences organic enrichment of Northern Atlantic sea spray aerosols. Overall, out of the three ocean parameters examined, the strongest and most consistent relationship was found between $\text{OM}_{\text{SSA}}$ and [Chl-$a$] (Fig. 3.2b). Therefore, in our new parameterization of the organic carbon fraction of sea spray, [Chl-$a$] was chosen as a proxy for the ocean chemistry. Using the MATLAB surface fitting tool and a general multi-variable logistic equation, the combined relationships of $\text{OM}_{\text{SSA}}$ vs. $U_{10}$ and $\text{OM}_{\text{SSA}}$ vs. [Chl-$a$] were found to be very similar for both stations. The corresponding coefficients in each equation were averaged to yield:

$$\text{OM}_{\text{SSA}}(\text{Chl}-a,U_{10}) = \frac{\text{OM}_{\text{SSA}}^{\max}}{1 + \exp(-2.65[\text{Chl}-a]+0.18U_{10})}$$

(1)
where [Chl-α] is in units of mg m\(^{-3}\) and \(U_{10}\) is in units of m s\(^{-1}\). The magnitude-determining numerator of the equation, \(OM^{\text{max}}_{\text{SSA}}\), is the maximum \(OM_{\text{SSA}}\) observed at the two sites during the entire measurement period (0.24 for Point Reyes and 0.78 for Mace Head). When compared to measurement data, the \(R^2\) value for Eq. (1) is \(~0.52\) and 0.56 at Point Reyes and Mace Head, respectively (see Fig S1 for scatterplot). A 3D visualization of Eq. (2) in Fig. 3.3 shows the interdependence of [Chl-α] and \(U_{10}\) in determining \(OM_{\text{SSA}}\), where the steepest slope corresponding to highest sensitivity occurs in the intermediate [Chl-α] and \(U_{10}\) values and the shallowest slopes (constant \(OM_{\text{SSA}}\)) occur at the extreme values where [Chl-α] > 1 mg m\(^{-3}\) and \(U_{10}\) > 1.5 m s\(^{-1}\). Despite the relationship between [Chl-α] and wind speed that exists because of seasonal effects (high [Chl-α] and low winds in summer, low [Chl-α] and high winds in winter), the inverse relationship between \(OM_{\text{SSA}}\) and \(U_{10}\) remains even when the measurements are binned into “low”, “moderate” and “high” [Chl-α] regimes (see Fig. 3.S2). Comparison of Eq. (1) with the high organic aerosol concentration episode at Mace Head described in Ovadnevaite et al. (2011) reveals remarkably good agreement, with an observed and predicted \(OM_{\text{SSA}}\) of 0.57 and 0.54, respectively (assuming \(U_{10} = 10\) m s\(^{-1}\) and [Chl-α] = 1 mg m\(^{-3}\) based on Table 3.1 and Fig. 3.1 from Ovadnevaite et al., 2011).

The differences between the relationship in Eq. (1) and those of previous parameterizations are greatest at high and low wind speeds. For a given [Chl-α], our equivalent submicron \(OM_{\text{SSA}}\) will typically be lower than that of O’Dowd et al. (2008) and Viganti et al. (2010) for strong winds and higher for low wind conditions. Figure 3.S3 shows that \(OM_{\text{SSA}}\) surface wind speed relationships derived in different studies can yield considerably different values for the organic mass fraction of sea spray aerosol.

3.3.1.3 Aerosol size

The different aerosol sizes (< 1.5 µm from Mace Head and < 2.5 µm at Point Reyes) measured at each site were likely to contribute to the differences in \(OM^{\text{max}}_{\text{SSA}}\). Since neither the Mace Head nor Point Reyes datasets we used had size-resolved aerosol composition, to better
constrain OMSSA as a function of aerosol size we used published measurements of the size-resolved organic mass fraction of aerosols generated from bubble-bursting of seawater over the biologically-active Northern Atlantic (Facchini et al., 2008). Fig. 3.4 shows the OMSSA measurements from Facchini et al. (2008) fitted by the following equation:

$$\text{OMSSA}(D_p) = \frac{\text{OM}^{\text{max}}_{\text{SSA}}(D_p)}{1 + 0.03 \exp(6.81 D_p)} + \text{OM}^{\text{min}}_{\text{SSA}}(D_p)$$ (2)

where $D_p$ is the ambient (RH = 80 ± 8%) aerosol aerodynamic diameter in micrometers, and OM$^{\text{max}}_{\text{SSA}}(D_p)$ and OM$^{\text{min}}_{\text{SSA}}(D_p)$ are size-dependent maximum and minimum organic carbon fraction of sea spray with values of 0.82 and 0.03, respectively.

Our size-dependent organic enrichment is consistent with other measurements/parameterizations. Size-resolved measurements from Keene et al. (2007) give similar results for the organic fraction of sea spray, but the reported OC as only water soluble is potentially incompatible with the data from Mace Head. Both Oppo et al. (1999) and Long et al. (2011) describe similar size-dependent organic enrichment of sea spray through adsorption models.

3.3.1.4 Combination of wind speed, [Chl-a], and aerosol size

To create an OMSSA equation as a function of [Chl-a], $U_{10}$, and sea spray size, we have combined Eqs. (1) and (2) in a way that retains the size dependence of OMSSA from Eq. (2) but scales with [Chl-a] and $U_{10}$ as described in Eq. (1). Specifically, the OM$^{\text{max}}_{\text{SSA}}(D_p)$ and OM$^{\text{min}}_{\text{SSA}}(D_p)$ values from Eq. (2) were scaled with the OMSSA from Eq. (1) after setting OM$^{\text{max}}_{\text{SSA}}$ to 1 reflecting the highest potential enrichment in the organic fraction (Bigg and Leck, 2008). This allows the size dependence from biologically-active Northern Atlantic (Facchini et al., 2008) region to be globally applicable to areas with vastly different winds and [Chl-a]. The resulting final OMSSA parameterization is:

$$\text{OMSSA(Chl-a, U}_{10}\text{, }D_p) = \frac{1}{1 + 0.03 \exp(6.81 D_p)} + \frac{0.03}{1 + \exp(-2.63 [\text{Chl-a} + 0.18 U_{10}])}$$ (3)
There are two main advantages of Eq. (3): i) it does not require any artificial cutoffs of wind speed or [Chl-a] and ii) it can give the size-resolved organic carbon fraction of sea spray aerosols from globally-available U_{10} and [Chl-a] data. Fig. 3.5 examines the dependence of OM_{SSA} on three parameters: sea spray size (D_p), chemical composition of ocean seawater ([Chl-a]) and physical mechanism of aerosol emission (U_{10}) described by Eq. (3). To make the dependence of OM_{SSA} on all three parameters easily visible, we have selected three different aerosol diameters roughly corresponding to typical marine aerosol Aitken, accumulation, and coarse mode diameters (Yoon et al., 2007). According to Fig. 3.5, OM_{SSA} increases for higher ocean biological productivity and lower wind speed and shows very strong dependence on aerosol size. These general trends are non-linear; changes in OM_{SSA} occur rapidly at moderate wind speed and [Chl-a] and more slowly at the extremes due to the plateaus found in the logistic curve. Our calculations suggest that there is little difference between the maximum organic fraction of the Aitken and accumulation mode aerosols (~0.8-0.9), while the coarse mode maximum organic fraction is substantially lower (< 0.02) due to the increasing dominance of sea-salt in these particles.

3.3.2 Estimated emission rate

To estimate marine POA fluxes in different parts of the oceans, we have used Mårtensson et al. (2003) and Gong (2003) sea spray functions with hourly averaged U_{10} calculated by the Community Atmosphere Model (CAM5) (Collins et al., 2006) and monthly-averaged climatological [Chl-a] retrieved by SeaWiFS. The Mårtensson et al. (2003) function was used for dry particle diameters ranging from ~0.02 to 2.8 µm and the Gong (2003) function for diameters from ~2.8 to 20 µm. Both the Mårtensson et al. (2003) and Gong et al. (2003) functions are assumed to represent sea spray aerosols whose effective densities are determined by the fractional contribution of sea-salt and organics. Since the magnitude of OM_{SSA} can potentially influence the hygroscopicity of the aerosol, a conversion between dry and ambient aerosol diameters was achieved by changing the OM_{SSA} from Eq. (3) to an organic volume fraction ($\rho_{organic} = 1$ g cm$^{-3}$ and $\rho_{NaCl} = 2.165$ g cm$^{-3}$) and using it to estimate
the resulting hygroscopicity (kappa - κ) values. The growth factor (GF) was derived at ambient RH = 80% for the combined organic-inorganic particle by assuming κ_{organic} = 0 and κ_{NaCl} = 1.12 (Petters and Kreidenweis, 2007). Fig. 3.6 shows the global annual submicron (dry aerosol diameter < 1 μm) marine primary organic aerosol emission rate, with the highest emissions occurring over the mid latitude waters (30-60°N and 30-60°S) where strong winds and high [Chl-a] are common throughout the year. Despite having a low OM_{SSA}, areas with strong winds and low [Chl-a] still have moderate marine POA emissions due to the exponential wind speed dependence of sea spray emissions. The predicted emission rates in tropical oceanic regions, however, are larger than those from previous studies (Vignati et al., 2010; Langmann et al., 2008; Gantt et al., 2009). As there have been relatively few aerosol measurements from tropical oceanic regions, the predicted organic emission rates are difficult to verify. The global magnitude of submicron marine POA emissions in this study is 2.8 Tg C yr⁻¹, with emissions up to 5.6 Tg C yr⁻¹ when using a growth factor of aerosols composed of 100% organic (GF = 1). In this later formation, a GF of 1 effectively assumes that the aerosol diameter measurements of Facchini et al. (2008) thus the D_p in Eq. (2) represents the dry aerosol diameter. This assumption is not unreasonable due to some drying from the pressure drop going down the stages of the Berner impactor used in Facchini et al. (2008). The measurements of Facchini et al. (2008) did not extend as far into the coarse mode as the model, so our estimated total global marine POA emission rate of 15.9 Tg C yr⁻¹ (up to 18.7 Tg C yr⁻¹ when using a growth factor of 1) is highly uncertain. The considerable organic enrichment in the largest aerosol size fraction (up to 40% of aerosol mass) reported in size-dependent measurements of Keene et al. (2007) suggests that this value could be a low estimate.
3.4 Caveats and uncertainty

One of the main caveats in our study arises from the use of observed or estimated WIOC at a few coastal sites as a proxy for global marine POA. To derive chemical composition of the organic fraction of sea spray, we have used values reported by Facchini et al. (2008) which reported a high contribution (up to $77 \pm 5\%$) of organic matter in small diameter sea spray particles. Although this large organic contribution was also observed by Keene et al. (2007), such high fractions of organics have not been found in all locations (Modini et al., 2010). Additionally, the WIOC/OC ratio used for the Point Reyes data is also uncertain as not all sites have observed this ratio (Miyazaki et al., 2010). At Mace Head, long term measurements have revealed that this ratio is not consistently observed (Rinaldi et al., 2010).

Coastal sites also suffer from uncertainties related to the influence of the surf zone and continental aerosols. Even though sea spray aerosol production by surf-zone wave breaking were shown to be 1-2 orders of magnitude higher than that of the open ocean (de Leeuw et al., 2000; Vignati et al., 2001), previous studies have suggested that aerosol chemical composition and flux parameterizations derived from coastal measurements can provide a suitable proxy for open ocean conditions and therefore can been successfully used for global emissions assessments (Clarke, 2006; Rinaldi et al., 2009). The use of wind speed measurements near the aerosol sampling location for both the Point Reyes and Mace Head sites also leads to some uncertainty due to the size of the concentration footprint from which the sea spray is emitted. Ceburnis et al. (2008) describes that while the flux footprint of the Mace Head station is typically within 5 km, the concentration footprint can be 10-100 times further upwind. We feel as though this uncertainty does not result in large errors in the magnitude and direction of our wind speed dependence because of the similarity between Mace Head nearshore and offshore wind speeds derived from NASA's Quick Scatterometer (QuikSCAT) (see Fig. 3.S4) when averaged over the 50-100 h sampling period. Continental sources can also potentially contribute to OM_{SSA} measurements at marine sites (Turekian et al., 2003), though it is expected such sources to be minor in this study due to the very long...
(thousands of kilometers) upwind fetch of open ocean at both sites and evidence from a recent study that 80% of the onshore flow organic aerosols at Mace Head had a marine source (Ceburnis et al., 2011). These inconsistencies and uncertainties highlight the difficulty in confidently applying our organic sea spray parameterization (derived using limited spatiotemporal measurements) to the global scale.

Moreover, when we compared our conceptual model to measurement data from Mace Head and Point Reyes, we assumed consistency between measured or estimated WIOM and POA. Such an assumption may lead to additional uncertainty in marine POA emissions, as it disregards the fraction marine SOA that may be water insoluble or POA that is water soluble (even though these contributions are expected to be minimal). The well recognized SOA component of marine aerosol derived from ocean-emitted BVOCs is methanesulfonate (MS⁻) from dimethyl sulfide (Saltzman et al., 1983), but other SOA precursor gases such as biogenic isoprene and monoterpenes emitted from phytoplankton have also been postulated to affect marine organic aerosols (Meskhidze and Nenes, 2006; Gantt et al., 2009; Luo and Yu, 2010). Additionally, oxidation of marine primary OM has been suggested to lead to the formation of WSOM which has typically been considered to have secondary sources (Ceburnis et al., 2008; Claeys et al., 2009; Rinaldi et al., 2010; Ovadnevaite et al., 2011). Such uncertainty regarding the origin of marine-source primary and secondary organic aerosols and inadequate understanding of marine organic aerosol formation processes adds to the difficulty in estimating marine POA emissions.

3.5 Conclusion

A conceptual relationship between wind speed and sea spray organic mass fraction (OM_{SSA}) has been developed and used to calculate marine primary organic aerosol (POA) emissions in different parts of the global oceans. Our analysis predicts the highest enrichments of marine aerosol with organics during calm winds, when large amounts of organic material can
accumulate at the sea-surface often forming visible slicks. An increase in wind speed (above 3-4 m s\(^{-1}\)) will initiate Langmuir circulations causing a breakup of the slicks and a rapid decrease in OM\(_{SSA}\). Wave breaking (caused by wind speeds in excess of 8 m s\(^{-1}\)) will thoroughly mix the microlayer with the underlying water, effectively reducing organic enrichment at the air-sea interface and thus in sea spray aerosols. Derived relationships between observed 10 meter wind speed (\(U_{10}\)) and remotely-sensed upwind oceanic concentrations of chlorophyll-\(a\) ([Chl-\(a\)]), particulate organic carbon ([POC]), and dissolved organic carbon ([DOC]) were compared to aerosol chemical composition from the Mace Head (Atlantic) and Point Reyes (Pacific) coastal sites. Our results indicate that wind speed, [Chl-\(a\)], and aerosol size are likely to be the three most important parameters regulating OM\(_{SSA}\).

The new empirical parameterization using a logistic fit for the relationship between OM\(_{SSA}\) and [Chl-\(a\)], \(U_{10}\), and aerosol diameter was then used to calculate size-resolved global marine POA emissions using established sea spray functions. Although our model-predicted submicron marine organic carbon emission rate ranging from 2.8 to 5.6 Tg C yr\(^{-1}\) is comparable to several recent studies (Spracklen et al., 2008; Vignati et al., 2010), the wind speed dependence of our parameterization gives a distinct spatial distribution. The exponential wind speed dependence of the sea spray function leads to the highest marine POA emissions in areas with strong winds; however, we also predict moderate emissions widespread throughout the global oceans due to the inverse relationship between wind speed and OM\(_{SSA}\). Our parameterization suggests that oceanic regions with high biological productivity are more likely to have higher marine POA emissions than areas with low productivity. Additional comparative modeling analysis of different marine POA emission schemes, combined with long-term measurements of marine aerosol concentration in previously under-sampled areas (i.e., tropical oceans), is needed to determine the accuracy of this marine organic aerosol emission parameterization.
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References


Fig. 3.1. Conceptual relationship between the organic mass fraction of sea spray aerosol ($OM_{SSA}$) and surface wind speed. Different colors depict potential regimes of the physical and chemical characteristics of the sea surface microlayer (SML) and the gray shading representing uncertainty in the $OM_{SSA}$ due other environment factors other than wind speed. These values represent global averages and may not be applicable for any given location.
Fig. 3.2. Organic mass fraction of sea spray aerosol as a function of (a) observed 10m wind speed ($U_{10}$) and upwind averaged ocean concentrations of 8-day averaged (b) [Chl-$\alpha$], (c) [POC], and (d) [DOC] for Mace Head and Point Reyes. In Fig. 3.2b, four outlier data points for Mace Head with [Chl-$\alpha$] > 1.25 mg m$^{-3}$ have been excluded due to their occurrence during anomalously high chlorophyll-$\alpha$ concentrations in the region. The aerosol sizes measured at Mace Head and Point Reyes were PM$_{1.5}$ and PM$_{2.5}$, respectively, the solid lines show regression relationships for each station, and the dotted lines show an extrapolation of the regression relationship.
Fig. 3.3. Organic mass fraction of sea spray aerosol as a function of both 10 meter wind speed and [Chl-a] for Mace Head (red) and Point Reyes (black) with the surface regression based on Eq. (1) in the same color scheme for each site.
Fig. 3.4. Observed organic mass fraction of sea spray (solid circles) as a function of ambient aerosol aerodynamic diameter from Facchini et al. (2008). The solid curve shows a logistic fit to the geometric mean of the diameter range, with the dashed curves corresponding to the logistic fit of the high and low end of the measured aerodynamic size ranges. Vertical bars show one standard deviation from the mean as described in Facchini et al. (2008).
Fig. 3.5. Contour plots of the organic mass fraction of sea spray as a function of [Chl-a] and 10 meter wind speed ($U_{10}$) for sea spray aerosols with ambient aerodynamic diameters of a) 0.05, b) 0.2, and c) 2 $\mu$m.
Fig. 3.6. Annual average submicron marine POA emission rate in units of ng C m$^{-2}$ s$^{-1}$ using the Mårtensson et al. (2003) sea spray function, monthly average climatological [Chl-$a$] from SeaWiFS, and modeled $U_{10}$ when global submicron marine POA emissions are 2.8 Tg C yr$^{-1}$.
Fig 3.S1. Scatterplot of predicted vs. observed organic mass fraction of sea spray for the Mace Head (red) and Point Reyes (black) sites with the 1:1 line in blue.
Fig. 3.S2. Organic mass fraction of sea spray as a function of observed 10 meter wind speed ($U_{10}$) for Mace Head as shown in Fig. 3.2a but with the colors representing the corresponding chlorophyll-$a$ concentrations binned into “low” ($[\text{Chl-}a] < 0.25 \text{ mg m}^{-3}$ in black), “moderate” ($0.25 < [\text{Chl-}a] < 0.5 \text{ mg m}^{-3}$ in blue), and “high” ($[\text{Chl-}a] > 0.5 \text{ mg m}^{-3}$ in green) concentrations. The color of the linear trendlines correspond to the $[\text{Chl-}a]$ bin.
Figure 3.S3. Organic mass fraction of sea spray aerosol as a function of 18 meter wind speed and [Chl-a] for Eq. (3) from Vignati et al. (2010) based on Mace Head data (blue) and Russell et al. (2010) for the Northern Atlantic Ocean (green).
Fig. 3.S4. Scatterplot of average nearshore (nearest 1° × 1° grid to Mace Head) and offshore (1° × 1° grid 24 hours upwind of Mace Head) wind speeds derived by NASA’s Quick Scatterometer (QuikSCAT) during the Mace Head aerosol sampling periods with linear trendline in black and 1:1 line in blue.
CHAPTER 4. EVALUATING MARINE PRIMARY ORGANIC AEROSOLS EMISSIONS

Preface:

Despite the publication of several marine primary organic aerosol emission schemes and interest in implementing these emissions into air quality and climate models, there has been no comprehensive evaluation of the different schemes. Several previous studies have shown that the existing marine primary organic aerosol emission schemes can replicate the magnitude of concentrations, but few show an accurate representation of the seasonality. As the seasonality of the emissions can strongly influence the impact of marine organic aerosols on clouds and radiative forcing, it is essential that climate models use the most realistic emissions. In this article submitted to ACPD, five existing marine primary organic aerosol emission schemes are implemented into the GEOS-Chem model under the same modeling framework. This allows for two types of evaluation; 1) comparing the schemes against each other and 2) comparing their predicted concentrations against observations. The emission schemes can be divided into two groups, with one group based directly on chlorophyll-a concentrations and the other group having their emissions related to the organic mass fraction of sea spray aerosol. Seasonal concentrations were best predicted by the chlorophyll-a-based emission scheme and the parameterization described in Chapter 3. Comparison of the predicted concentrations with hourly observations of clean marine conditions at Mace Head, Ireland showed that none of the parameterizations can accurately simulate episodic events. Top-down optimization of the emission parameterizations gives a global emission rate of 6.3 Tg yr\(^{-1}\). Despite the fact that this optimized emission parameterization can accurately predict seasonal concentrations, episodic concentrations could still not be reproduced. The inability of any existing marine POA emission parameterizations to replicate episodic to seasonal concentrations suggest that new emission parameterizations need to be developed that are grounded in the physical processes unique to the organic fraction of sea spray aerosol.
Model evaluation of marine primary organic aerosol emission schemes

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Abstract:

In this study, several marine primary organic aerosol (POA) emission schemes have been evaluated using the GEOS-Chem chemical transport model in order to provide guidance for their implementation in air quality and climate models. These emission schemes, based on varying dependences of chlorophyll a concentration ([chl a]) and 10 meter wind speed (U₁₀), have large differences in their magnitude, spatial distribution, and seasonality. Model comparison with weekly and monthly mean values of the organic aerosol mass concentration at two coastal sites shows that the source function exclusively related to [chl a] does a better job replicating surface observations. Sensitivity simulations in which the negative U₁₀ and positive [chl a] dependence of the organic mass fraction of sea spray aerosol are enhanced show improved prediction of the seasonality of the marine POA concentrations. A top-down estimate of submicron marine POA emissions based on the parameterization that compares best to the observed weekly and monthly mean values of marine organic aerosol surface concentrations has a global average emission rate of 6.3 Tg yr⁻¹. Evaluation of existing marine POA source functions against a case study during which marine POA contributed the major fraction of submicron aerosol mass shows that none of the existing parameterizations are able to reproduce the hourly-averaged observations. Our calculations suggest that in
order to capture episodic events and short-term variability in submicron marine POA concentration over the ocean, new source functions need to be developed that are grounded in the physical processes unique to the organic fraction of sea spray aerosol.

4.1 Introduction

Recently, there have been several studies attempting to parameterize the emissions of marine primary organic aerosols (POA) (O’Dowd et al., 2008), estimate their concentrations in the marine boundary layer (Vignati et al., 2010), and evaluate their impact on cloud condensation nuclei (Roelofs, 2008; Fuentes et al., 2011; Meskhidze et al., 2011; Westervelt et al., 2012) and indirect forcing (Gantt et al., 2012). A few of these emission schemes have been evaluated against satellite-based aerosol optical depth (AOD) and ship-based concentration observations (Lapina et al., 2011), but the majority have not been compared to measurements from hourly to monthly temporal resolutions to enable a process-based evaluation. As the emissions of marine POA have been described as globally significant (Spracklen et al., 2008; Gantt et al., 2009) and shown to contribute to an increase in model-predicted surface CCN concentrations by over 20% (Meskhidze et al., 2011; Westervelt et al., 2012), there is a need for a process-based, comprehensive evaluation of the parameterizations before their widespread implementation into climate and air quality models.

Marine POA emission parameterizations fall into two main groups: 1) emission rates exclusively related to chlorophyll $a$ concentration ([chl $a$]) and 2) emission rates linked to sea spray emissions through the calculation of the organic mass fraction of sea spray aerosol ($OM_{SSA}$). A brief summary of the emission schemes, shorthand notations adopted in the paper, and the parameters that determine the emission rates for different parameterizations are given in Table 1. In the first group, Spracklen et al. (2008) used a top-down modeling approach to fit coastal concentrations to emissions linearly related to [chl $a$]. In the second group linking marine POA emissions with that of sea spray, several studies compared coastal
measurements of organic and sea-salt aerosol with parameters such as [chl \(a\)], 10 meter wind speed (\(U_{10}\)), and aerosol diameter (\(D_p\)) to determine the OM\(_{SSA}\). It was first reported (O’Dowd et al., 2008) and later adjusted (Langmann et al., 2008; Vignati et al., 2010) that the submicron OM\(_{SSA}\) is linearly related to [chl \(a\)]. Gantt et al. (2011) expanded upon this relationship by adding a negative wind speed relationship and size-dependence to the OM\(_{SSA}\) calculation. Long et al. (2011) developed a Langmuir relationship between [chl \(a\)] and OM\(_{SSA}\) and included a size-dependence. Fuentes et al. (2010) showed higher sea spray number emission when phytoplankton exudates are present during laboratory-based bubble bursting experiments. Assuming that the additional emissions are organic in nature and phytoplankton exudates are related to [chl \(a\)], the Fuentes et al. (2010) parameterization is similar to Long et al. (2011) and Gantt et al. (2011) in that the organic mass fraction of sea spray is related to [chl \(a\)] and aerosol size. The resulting submicron emission rates and seasonality predicted by these parameterizations are affected by \(U_{10}\) and/or [chl \(a\)] at varying degrees. In this work, we use all the available marine POA emissions parameterizations and implement them under the same modeling framework to calculate the submicron marine POA source and compare the resulting surface concentrations with aerosol composition measurements from hourly to monthly averaged timescales.

4.2 Model and measurements description

4.2.1 GEOS-Chem

We use version v8-01-01 of the GEOS-Chem (http://geos-chem.org/) global chemical transport model with 2° × 2.5° horizontal resolution and 47 vertical levels, driven by GEOS-5 assimilated meteorology from the NASA Global Modeling Assimilation Office (GMAO). The model is run with a full chemistry configuration, which includes H\(_2\)SO\(_4\)-HNO\(_3\)-NH\(_3\) aerosol thermodynamics coupled to an O\(_3\)-NO\(_x\)-hydrocarbon-aerosol chemical mechanism (Bey et al., 2001; Park et al., 2004). Terrestrial emissions in our simulations include
carbonaceous aerosols and sulfur compounds (Park et al., 2004; Heald et al., 2004). Secondary organic aerosol formation from both terrestrial and marine sources is not included in our simulations; therefore primary organic aerosols are the only organic aerosol source. Sea-salt in the model is emitted in two size bins (fine mode ranging from 0.02 to 1.0 µm in diameter and coarse mode ranging from 1.0 to 20.0 µm in diameter) as a function of a power relationship with $U_{10}$ following the formulation of Gong (2003) and includes the 3rd order polynomial dependence on sea surface temperature (SST) as described by Jaeglé et al. (2011). Implementation of this SST dependence to sea-salt emissions resulted in improved model prediction of both surface concentrations and aerosol optical depth (Jaeglé et al. 2011). Within this model setup, we introduce a hydrophilic and hydrophobic tracer for each marine POA emission scheme. A detailed description of the various marine POA emission schemes and model treatment of the marine POA tracers is given in Sec. 2.2. With this configuration, year-long GEOS-Chem simulations for the years 2006 and 2009 are performed. In addition to the daily global output of concentrations from the model, we also retain hourly concentrations of the marine POA tracers for the entire 2009 simulation period in the North Atlantic Ocean (model grid centered at 54°N, 10°W) near Mace Head, Ireland.

4.2.2 Marine POA Emissions

Beginning with O’Dowd et al. (2008), all marine POA emission schemes have scaled their emissions to [chl $a$] based on the observed correlation with organic aerosol mass concentrations (O’Dowd et al., 2004; Sciare et al., 2009). The differences between the parameterizations, however, is the extent to which other factors besides [chl $a$] affect the emission rates. One such factor is the sea spray emission rate, which can vary by several orders of magnitude (de Leeuw et al., 2011). Such variability in sea spray source functions influences the magnitude of marine POA emissions predicted by the individual parameterizations. In order to explicitly compare the different marine POA emission schemes, all the emission parameterizations in this study are implemented under the same GEOS-Chem modeling framework. For the sea spray-based marine POA emissions, the
Gong (2003) function that calculates sea-salt emissions in the default version of GEOS-Chem is altered to represent sea spray aerosol containing both sea-salt and organic compounds by accounting for the densities of each constituent. The OM$_{SSA}$ calculated for each of the emission parameterizations is applied to the submicron fraction of this combined organic-inorganic sea spray aerosol source function following the method first introduced by O’Dowd et al. (2008). While we acknowledge that some of the marine POA emission parameterizations (Fuentes et al., 2010; Long et al., 2011) were presented in conjunction with the development of novel sea spray source functions and that the magnitude of marine POA emissions is sensitive to the selection of sea spray function, the objective of this study is to describe the spatiotemporal distribution and magnitude of the various marine POA emissions parameterizations relative to each other.

The Spracklen et al. (2008) emissions, whose rates are a linear function of [Chl-$a$], are adjusted to be in the submicron mode by using the suggested submicron/total mass ratio of 0.7 (Spracklen et al., 2008). The Gantt et al. (2011) and Vignati et al. (2010) emissions, which are based on the calculation of OM$_{SSA}$, are implemented into GEOS-Chem using Eq. (1) and (2) from Meskhidze et al. (2011). For the Fuentes et al. (2010) and Long et al. (2011) parameterizations, an OM$_{SSA}$ value was not directly given but had to be calculated. For the Long et al. (2011) emissions, OM$_{SSA}$ is calculated using a conversion from the given organic and sea-salt volume ratio (assuming a density of 1 g cm$^{-3}$ for organics and 2.2 g cm$^{-3}$ for sea-salt (O’Dowd et al., 2008)). In the Fuentes et al. (2010) emissions, OM$_{SSA}$ is derived by assuming that the difference in the size-resolved particle number concentration from the sea spray experiments using artificial sea water with and without phytoplankton exudates can be attributed exclusively to marine organic aerosols. The phytoplankton exudate concentration, which controls the difference in the particle number concentration in Fuentes et al. (2010), is calculated by assuming that the [chl $a$] is associated with diatoms that are in a low phytoplankton grazing regime (see Fig. 16 from Fuentes et al., 2010 for details).
For all the emissions schemes, submicron marine POA emission rates are determined using monthly averages of the [chl $a$] values from the Moderate Resolution Imaging Spectroradiometer (MODIS) aboard the Aqua satellite after regridding (by averaging) from the original $\frac{1}{12}^\circ \times \frac{1}{12}^\circ$ to the $2 \times 2.5^\circ$ horizontal grid used in GEOS-Chem. During this regridding, satellite grids that are over land are given a [chl $a$] value of 0 while cloud-covered grids are considered as missing values. An OM to OC ratio of 1.4 is applied to simulated marine POA to account for the noncarbon component of the organic mass (Desecari et al., 2007; Facchini et al., 2008), and the apparent density of the sea spray is calculated as a function of OM$_{SSA}$ according to Gantt et al. (2009). Similar to terrestrial primary organic aerosols in GEOS-Chem, marine POA are emitted as hydrophobic and converted to hydrophilic in the atmosphere with an e-folding time of 1.2 days (Cooke et al., 1999). This is consistent with the observation that freshly emitted submicron marine primary organic aerosols are almost entirely water insoluble consisting of colloids and aggregates (Facchini et al., 2008) but can become more water soluble through atmospheric aging (Rinaldi et al., 2010).

4.2.3 Observations

Despite recent interest in the modeling of marine organic aerosol, there are very few observational datasets focusing on marine aerosols (relative to that of terrestrial aerosols) with which to evaluate model performance. Of these, we use datasets that represent very different geographical regions and temporal resolutions. Two datasets (Yoon et al., 2007; Rinaldi et al., 2010) are from Mace Head, Ireland ($53.33^\circ$N, $9.90^\circ$W), whose aerosol composition is influenced by the biologically productive waters of the North Atlantic Ocean (O'Dowd et al., 2004). Another dataset (Sciare et al., 2009) is from Amsterdam Island ($37.80^\circ$S, $77.57^\circ$E) in the remote south Indian Ocean, whose aerosol composition is affected by transport from the windy and biologically active Southern Ocean. The surface organic aerosol concentration measurements at Mace Head were taken using a Sierra-Andersen high-
volume cascade impactor that divided the aerosols into a fine ($D_{50} < 1.5$ µm) and coarse ($D_{50} > 1.5$ µm) modes during clean marine conditions ($BC < 50$ ng m$^{-3}$ and wind direction between 180° and 300°) (Yoon et al., 2007; Rinaldi et al., 2010). At Amsterdam Island organic aerosol surface concentration was not separated between sub- and supermicron sizes. An estimate of the submicron fraction of the organic aerosol concentration is derived from Claeys et al. (2009) who found that the $PM_{2.5}$ to $PM_{10}$ ratio was ~0.41 at Amsterdam Island. At both Mace Head and Amsterdam Island, the organic aerosols are differentiated as water soluble and water insoluble organic matter (WSOM, WIOM). For the Yoon et al. (2007) and the Sciare et al. (2009) measurements, the WIOM concentrations are compared to surface concentrations of marine POA from GEOS-Chem to minimize the influence of secondary organic aerosols (SOA) which can be classified as WSOM (Ceburnis et al., 2008). For Rinaldi et al. (2010) measurements, in addition to differentiating between WSOM and WIOM, proton nuclear magnetic resonance ($^1$HNMR) spectroscopy and anion-exchange high performance liquid chromatography (HPLC-TOC) were used for organic chemical characterization. Due to this additional analysis, GEOS-Chem marine POA concentrations are compared to the sum of WIOM and WSOM uncharacterized by the $^1$HNMR and HPLC-TOC analysis. This criterion is based on the discussion in Rinaldi et al. (2010) that these uncharacterized water soluble organic aerosols may be formed by the atmospheric aging of POA to more soluble oxidized organic aerosols.

For the model comparison, we use multi-year monthly averaged WIOM observations at Mace Head and Amsterdam Island for January 2002 to June 2004 (Yoon et al., 2007), and May 2003 to November 2007 (Sciare et al., 2009), respectively. GEOS-Chem results are also compared to weekly (4 to 12-days) averaged WIOM surface concentrations from January to December 2006 at Amsterdam Island and weekly averaged WIOM plus uncharacterized WSOM surface concentrations from January to December 2006 at Mace Head (Rinaldi et al., 2010). Comparison of the model output with monthly and weekly averaged OM concentration measurements at two sites with vastly different ocean biological
productivity (i.e., Mace Head and Amsterdam Island) can be used to test the ability of parameterization to capture global patterns of marine POA emission as well as emission seasonality. However, a process-based evaluation of marine organic aerosol emissions requires comparison with marine POA fluxes instead of long-term averaged concentrations. Due to the lack of such data, hourly averaged surface concentrations of marine POA predicted from GEOS-Chem are evaluated against a third dataset of high temporal resolution (10 minute resolution averaged hourly) Aerosol Mass Spectrometer (AMS) measurements of the total submicron OM concentration at Mace Head from the year 2009. A detailed description of these measurements, including analysis of a high concentration marine organic aerosol plume and description of AMS sea-salt detection, can be found in Ovadnevaite et al. (2011a) and Ovadnevaite et al. (submitted). Of note, these AMS data were compared to a SMPS size spectra and a collection efficiency of 0.5 (Matthew et al., 2008) was applied to account for the detection losses mainly due to bounce of particles off the vaporizer. Coincident measurements of wind speed/direction and black carbon (BC) concentration were performed at Mace Head at temporal resolutions of 1 and 5 minutes, respectively. The AMS measurements are averaged hourly after filtering to only include data in which clean marine conditions persisted for the entire hour. This averaging and filtering is done to be consistent with the hourly GEOS-Chem output of marine POA tracers. We have confidence that this comparison is reasonable because 80% of the organic aerosol mass measured in clean marine air masses at Mace Head has been shown to be directly associated with ocean biology (Ceburnis et al., 2011). For all the observations, the GEOS-Chem grid cell nearest to the measurement site spatially and temporally is selected for comparison.

4.2.4 Sensitivity study

A sensitivity study is conducted to explore the OM_{SSA} dependency on [chl a] and U_{10} in the G11 emissions scheme by scaling the emission values to best represent the monthly averaged observations from Mace Head and Amsterdam Island. The aim of such a study is to create a sea spray-based marine POA emission scheme with improved seasonality. The G11
emissions are used in this sensitivity study because of the flexibility in changing the dependencies of $[\text{chl } a]$ and $U_{10}$. The need for adjustment of the dependency of $\text{OM}_{\text{SSA}}$ to $[\text{chl } a]$ and $U_{10}$ has been shown by several modeling studies (Meskhidze et al., 2011; Westervelt et al., 2012) who found that modeled marine POA concentrations using sea spray-based emissions struggled to capture the observed seasonality. As marine organic aerosol concentrations have been shown to be directly related to the seasonal cycle of $[\text{chl } a]$ and inversely related to $U_{10}$ seasonality (Sciare et al., 2000, 2009; O’Dowd et al., 2004), we have tuned the coefficients in Eq. (1) of Gantt et al. (2011) to get better agreement between the model and measurements.

\[
\text{OM}_{\text{SSA}}(\text{chl } a, U_{10}, D_p) = \frac{1}{1+0.03 \exp(6.81D_p)} + \frac{0.03}{1+0.03 \exp(4.18([\text{chl } a]+0.18(U_{10})))}
\]  

In this formulation, an $A$ value greater than 1 increases the positive dependence of $\text{OM}_{\text{SSA}}$ on $[\text{chl } a]$ and negative dependence of $\text{OM}_{\text{SSA}}$ on $U_{10}$.

4.3 Results

4.3.1 Emissions

Multi-year (2006 and 2009) averaged emission rates for submicron sea-salt aerosol (G03) and the five different marine POA emission schemes are shown in Fig. 4.1. The main differences between S08, G11, and the other marine POA emission schemes are in the location of the highest emissions rates and the global magnitude of the emissions. For the S08 scheme, high emission rates occur along the productive coastal and open ocean (equatorial and the high-latitude ocean) upwelling regions. The F10, V10, and L11 schemes predict highest emissions over the windy/productive high-latitude oceans similar to that of sea-salt aerosol, while the G11 scheme predicts high emissions over the both coastal upwelling regions and high-latitude oceans. Comparison of the latitudinal percentage contributions to the marine POA emissions (Table 2) highlights this difference; the S08
(based entirely on [chl a]) and G11 (based on a combination of [chl a] and U_{10}) schemes have a considerable percentage of their emissions from the moderately windy equatorial and northern Atlantic and Pacific Ocean while the F10, V10, and L11 emissions schemes are like sea-salt aerosols in that they have a relatively higher percentage of their emissions occurring in the Southern Ocean where winds are very strong. Table 2 also shows that the magnitude of global marine POA emissions, while substantially lower than sea-salt, is considerably different between the different schemes. On the high end is L08, which at 11.9 Tg yr^{-1} is more than two orders of magnitude higher than the lowest estimate (F10 at 0.1 Tg yr^{-1}). The G11, V10, and S08 emission schemes fall within the range of 3 to 8 Tg yr^{-1}. Although these rates (with the exception of S08) are sensitive to the choice of sea spray function, all but the F10 emissions fall within the ~2-70 Tg yr^{-1} range of previous global marine POA emission estimates (Langmann et al., 2008; Roelofs, 2008).

4.3.2 Global concentrations

The different emission schemes lead to a large spatiotemporal variation in surface concentrations of marine POA. Figure 4.2 shows the January and July (2006 and 2009 average) surface concentrations from the simulations using the S08, V10, and G11 emissions schemes. These time periods are shown because they represent the most intense periods for marine biological activities in the Southern Ocean (January) and North Atlantic and North Pacific Oceans (July). The three emission schemes are selected because they have comparable global rates and represent emission schemes dominated by [chl a] (S08), U_{10} (V10), and a mixture of [chl a] and U_{10} (G11) (see Table 1). Figure 4.2 shows that the S08 emissions yield very large seasonal changes in surface POA concentrations over the high productivity oceanic regions (Southern Ocean, northern Atlantic, and northern Pacific Oceans) with high/low concentrations in the summer/winter in high latitude oceanic regions. By comparison, both V10 and G11 emissions schemes show limited seasonal variability in the surface POA concentrations over the high latitudinal oceanic regions with G11 having a somewhat larger seasonal range. Such differences in the model predicted surface POA
concentrations are primarily due to the opposing seasonal cycles of $U_{10}$ and $[chl a]$ produced in V10 and G11 schemes (notice in Fig. 4.S1 that the seasons with the high chlorophyll concentrations are typically associated with low wind speed and vice versa), while emissions from S08 are exclusively dependent on $[chl a]$. Figure 4.2 also shows large differences between the three emission schemes over the coastal and equatorial Pacific upwelling regions, where S08 predicts much higher concentrations throughout the year compared to V10 and G11.

4.3.3 Comparison with measurements

4.3.3.1 Monthly and weekly mean values

Observations of monthly averaged WIOM surface concentrations reveal distinct seasonal cycles for both Mace Head and Amsterdam Island (charts on left column of Fig. 4.3), with the highest values in the summer and lowest in the winter. When comparing these observations to the predicted concentrations, this figure shows the mixed ability of the five emissions schemes to replicate the seasonality in marine POA surface concentrations. According to Table 3, the S08 simulation best captures the seasonal cycle with a linear correlation coefficient of 0.81 and 0.50 at Mace Head and Amsterdam Island, respectively. S08 also reproduces the magnitude of the observed concentrations at Mace Head, with a normalized mean bias (NMB) of <1%. However, it overpredicts the concentrations at Amsterdam Island with a NMB of 142%. For completeness, it should be noted that the $[chl a]$ coefficient used in S08 was specifically designed for GEOS-Chem by matching modeled and observed organic aerosol concentrations at Mace Head and Amsterdam Island among other sites and therefore is expected to yield good agreement with the observations. Table 3 shows that the sea spray-based emission schemes underestimate summertime marine POA concentrations at the Mace Head station and overestimate wintertime concentrations (except F10) at Amsterdam Island. At the extremes of the global emission rates, the F10 simulation strongly underpredicts the surface POA concentrations at both sites while L11 strongly
overpredicts the concentrations at Amsterdam Island. The linear regression relationship for measured and model-predicted (using different sea spray-based parameterizations) submicron WIOM concentrations also shows poor correlation. Table 3 shows that out of all sea spray-based source functions G11 (correlation of 0.74 at Mace Head and 0.34 at Amsterdam Island) best captures the seasonal variation in surface POA concentrations. Figure 4.3 shows that in all sea spray-based parameterizations, the large negative bias in marine POA predicted at Mace Head is largely due to the underpredictions in summertime concentrations. During the summertime, Mace Head is exposed to marine air masses originating over surface oceans with high [chl a] but with relatively low wind speeds. It appears that the strong effect of such high levels of [chl a] on organic aerosol concentrations first described by O’Dowd et al. (2004) is not sufficiently well captured in any of the sea spray-based parameterizations due to the strong influence of \( U_{10} \). The overestimation of marine POA concentrations in sea-spray-based parameterizations at Amsterdam Island during the austral winter is likely due to the strong winds that have an inordinate influence on the predicted marine POA emission rates. This inability of the sea spray-based emission parameterizations to result in surface concentrations with the correct seasonal cycle indicates that the main processes responsible for POA production over the oceans may not be well reproduced by the existing marine POA source functions.

Similar to the multi-year monthly averages, comparison of the weekly averages (WIOM from Amsterdam Island and total OM from Mace Head) from 2006 for the two sites reveals that the S08 and G11 emissions best predict the surface concentrations (charts on right column of Fig. 4.3). While the S08 emissions consistently overpredict the weekly concentrations at both sites (NMB of 132.7 and 108.5% at Mace Head and Amsterdam Island), the correlations between the observations and predicted concentrations are high relative to the other parameterizations. Table 4.3 shows that of the sea spray-based emissions, only the G11 emissions lead to predicted concentrations whose correlations with observations are positive for both sites.
4.3.3.2 Hourly averaged data

Hourly-averaged total OM concentration measurements from Mace Head reveals considerable hourly variability (see Fig. 4.4). The correlation between the model-predicted concentrations and measurements are poor, with S08 having the highest correlation (0.19). In terms of magnitude, there is reasonable agreement between the measurements and the predicted concentrations in the summertime (with the exception of F10) while wintertime predictions (with the exception of L11) are underpredicted. It should be noted that the sea spray source function does not seem to be the only cause of the poor model performance as the surface sea-salt concentrations predicted by G03 and measured by the AMS (Ovadnevaite et al., submitted) have a higher correlation (0.40) compared to marine POA.

A case study of marine organic aerosol plume event from biologically-rich North Atlantic waters when organic mass comprised a major fraction of the total submicron non-refractory aerosol mass allows us to examine how different emissions parameterizations are able to capture an isolated event. This plume, shown as an inset in Fig. 4.4, occurred between 14 and 18 August 2009 and experienced organic aerosol concentrations of up to 3.8 μg m$^{-3}$ (Ovadnevaite et al., 2011a). Figure 4.4 and Table 4.4 show that none of the parameterizations for marine POA emissions were able to capture the magnitude of organic aerosol concentrations or have positive correlations with measurements for this event. The S08 simulation, which has the highest positive correlation with the year-long time series, exhibits the largest negative correlation (-0.40). The inability of the various parameterizations to capture this plume could be due to multiple reasons which are difficult to confirm with a global model. One such factor may be the time lag between offshore [chl $a$] and OM$_{SSA}$ at Mace Head thought to be related to biological processes responsible for the production of organic material transferable to the atmosphere (Rinaldi et al., submitted).

Scatterplots of the 2009 hourly observed and predicted S08 and G11 concentrations color-coded by wind speed (Figs. 4.5a and 4.5b) give us some insights for the potential
weaknesses of the two schemes. This figure shows that each emission scheme suffers from a systematic bias, placing the data outside the 1:2 and 2:1 lines. While not universal, many of the predicted S08 hourly concentrations that are too low occur during high winds and those that are too high occur during low winds. This suggests that marine POA emissions are affected by the surface wind speed (likely due to their association with sea spray) and that the [chl a]-based source function may not be able to capture the actual emission rates during periods of strong winds. The G11 (and the other sea spray-based marine POA source functions not shown) concentration predictions that are too low compared to observations typically occur during periods of low wind speed and the few that are too high typically occur during very high winds. This finding suggests that sea spray-based source functions may have too strong of a wind speed dependence.

4.4 Sensitivity study

In a sensitivity study, the OMSSA dependence on [Chl-a] and U10 is explored by adjusting A coefficients in Eq. (1) to improve the seasonality and magnitude of the model-predicted concentrations. As previous studies have shown that seasonality is a major weakness of existing marine POA emission schemes, we compare the modeled concentrations to the multi-year monthly averages at Mace Head and Amsterdam Island for the top-down estimate of the A value. Through varying the A coefficient until the best match between modeled and observed concentrations was obtained, it was found that the best correlation (0.82 at Mace Head and 0.56 at Amsterdam Island) and a reasonable prediction of seasonality (see Fig. 4.3) occurs with a A value of 3 in Eq. (1) (see Table 3). The updated OMSSA calculation is given in Eq. (2)

\[
\text{OMSSA(chl a, U}_{10}\text{, D}_p) = \left(\frac{1}{1+0.03\exp(6.81D_p)}\right) + \frac{0.03}{1+\exp(3(-2.63[chl a] + 3(0.18(U_{10}))))}
\]
Due to a decrease in the magnitude of marine POA emissions associated with the change in the $A$ value for Eq. (1) to 3, the NMB at the two sites (-18.5 and 17.5% for Mace Head and Amsterdam Island) were minimized when the marine POA emissions were increased by a factor of 6. The top-down estimate of the marine POA emission rate ($E_{POA}$) derived for GEOS-Chem in the sensitivity study is given in Eq. (3)

$$E_{POA}(chl, U_{10}, D_p) = 6E_{SSA}OM_{SSA}$$

where $E_{SSA}$ is the mass emissions of sea spray aerosol according to Gong et al. (2003) source function with SST dependence of Jaeglé et al. (2011) and an apparent density of the sea spray aerosol calculated as a function of $OM_{SSA}$ according to Gantt et al. (2009) and $OM_{SSA}$ given by Eq. (2).

Global submicron marine POA emissions simulated using Eq. (3) total 6.3 Tg yr$^{-1}$, with a predicted multi-year annual average surface concentration distribution shown in the map in Fig. 4.3 that are highest in the biologically productive regions of the northern and southern Atlantic Ocean. Because Eq. (3) is based on model comparison with measurements, factor of 6 increase in the emission rate is model-dependent and would likely be lower with a slower atmospheric conversion of marine POA from hydrophobic to hydrophilic or with the selection of sea spray source function with a higher submicron flux such as Mårtensson et al. (2003).

Because Eq. (3) was developed using multi-year monthly averaged measurements, it is possible to do an evaluation of the emissions using the 2006 weekly observations at Mace Head and Amsterdam Island and the 2009 hourly observations from Mace Head. For the 2006 weekly observations, the Eq. (3)-derived concentrations had a higher correlation and lower NMB than the G11 concentrations at both sites, with the highest correlation and lowest NMB of all the emission parameterizations for Amsterdam Island. Comparison of surface marine POA concentrations produced from Eq. (3)-based emissions with the hourly observations (shown in Table 4) reveals slightly improved correlation (0.20) relative to the
G11 simulations (0.16) and S08 (0.19) for the entire 2009 period. However, Table 4 also shows a negative correlation for the plume event, suggesting that tuning coefficients, while improving the agreement with seasonally and monthly averaged observations of marine organic aerosol, cannot improve the emission mechanism for the existing parameterizations. The scatterplot (see Fig. 4.5c) of the observed and predicted hourly concentrations from Eq. (3) shows that the majority of data is still outside the 1:2 and 2:1 lines, although when compared to Fig. 4.5b some improvement with the low wind speed bias can be noticed.

4.5 Summary and conclusions

Five marine primary organic aerosol (POA) emissions parameterizations were implemented into the GEOS-Chem chemical transport model and evaluated with observations at different locations and temporal resolutions to examine which processes driving the emissions result in better predictions of surface concentrations. To enable comparison amongst the different emission schemes, the same sea spray source function, surface chlorophyll-$a$ concentration ([chl $a$]) and meteorological data were used to drive the emissions. Prognostic model simulations were conducted to identify spatiotemporal differences in emissions and surface concentrations of marine POA for all available emissions parameterizations. Our calculations suggest that marine POA emissions parameterizations exclusively related to [chl $a$] (i.e., Spracklen et al., 2008) result in predicted concentrations whose seasonality was most similar to that of the observations. However, it should be noted that the [chl $a$] coefficient used in S08 was specifically designed for GEOS-Chem by matching modeled and observed organic aerosol concentrations at Mace Head and Amsterdam Island. Marine POA emissions schemes which calculate the organic mass fraction of sea spray ($\text{OM}_{\text{SSA}}$) (Vignati et al., 2010; Fuentes et al., 2010; Long et al., 2011; and Gantt et al., 2011) typically overpredict monthly and weekly average concentrations in the wintertime and underpredict summertime concentrations due to the strong influence of the 10 meter wind speed ($U_{10}$) on the emission
rates. Hourly observations at Mace Head, Ireland reveal that the surface concentrations predicted by the various emissions schemes have poor correlations with measurements and have difficulty capturing the magnitude of the observed concentrations. This difficulty of the model to replicate the magnitude of concentrations was particularly evident during a marine organic aerosol plume event described by Ovadnevaite et al. (2011a), where observed concentrations of > 3.0 µg m$^{-3}$ are well above the predicted concentrations. As this marine organic aerosol plume event was associated with high cloud condensation nuclei (CCN) and cloud droplet number concentrations (CDNC) (Ovadnevaite et al., 2011b), the inability of the marine POA emission schemes to capture episodic events suggests that current source functions may have difficulties reproducing the effects of marine biology on cloud microphysical properties. New parameterizations need to be derived that are grounded in physical processes unique to the organic fraction of sea spray aerosol, rather than being constrained by the processes that affect sea spray more generally.

The sensitivity study revealed that enhancing the positive dependency of the OM$_{SSA}$ on [chl $a$] and negative dependency on $U_{10}$ improves the modeled monthly and weekly average concentrations. A top-down emission scheme developed in this study estimates global marine POA emissions at 6.3 Tg yr$^{-1}$ and reproduces the observations of marine organic aerosol concentrations at all temporal scale with minimal biases. However, comparison of model-simulated concentrations to marine organic aerosol plume event data showed, that mere tuning of coefficients, without fundamental understanding of the processes controlling marine organic aerosol production did not lead to considerable improvements. To fully assess air quality and climate importance of marine organic aerosol, these new physically-based marine POA source functions need to be evaluated against measurements of marine organic aerosol number and size distribution, CCN properties, and mixing state.
Acknowledgements

This research was supported by the Office of Science (BER), US Department of Energy Grant No. DE-FG02-08ER64508 and by the National Science Foundation through the grant ATM-0826117. BG is also supported by the NASA Earth and Space Science Fellowship (NESSF) Program. EPA Ireland is acknowledged for Research Support at Mace Head.
References


Fuentes, E., Coe, H., Green, D., and McFiggans, G.: On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol – Part 2:


Rinaldi, M., Decesari, S., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., O’Dowd, C. D., Ceburnis, D., and Facchini, M. C.: Primary and secondary organic marine aerosol and


Table 4.1. Summary of marine POA emission schemes used in GEOS-Chem

<table>
<thead>
<tr>
<th>Parameterization</th>
<th>Determining factors</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>G03 (sea-salt)</td>
<td>$U_{10}^{3.41}$, $D_p$, SST</td>
<td>Gong (2003), Jaeglé et al. (2011)</td>
</tr>
<tr>
<td>S08</td>
<td>[chl $a$]</td>
<td>Spracklen et al. (2008)</td>
</tr>
<tr>
<td>V10</td>
<td>$U_{10}^{3.41}$, $D_p^{a}$, SST, [chl $a$]</td>
<td>Vignati et al. (2010), Meskhidze et al. (2011)</td>
</tr>
<tr>
<td>F10</td>
<td>$U_{10}^{3.41}$, $D_p$, SST, [chl $a$]</td>
<td>Fuentes et al. (2010)</td>
</tr>
<tr>
<td>L11</td>
<td>$U_{10}^{3.41}$, $D_p$, SST, [chl $a$]</td>
<td>Long et al. (2011)</td>
</tr>
<tr>
<td>G11</td>
<td>$U_{10}^{3.41}$, $D_p$, SST, [chl $a$], $U_{10}$</td>
<td>Gantt et al. (2011)</td>
</tr>
</tbody>
</table>

Sensitivity Study

| Eq. (3) | $U_{10}^{3.41}$, $D_p$, SST, [chl $a$], $U_{10}$ | This work |

$^{a}$Aerosol size dependency added by Meskhidze et al. (2011)
<table>
<thead>
<tr>
<th>Parameterization</th>
<th>Global mass (Tg)</th>
<th>Percentage Contribution to Global Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>90°S-31°S</td>
</tr>
<tr>
<td>G03 (sea-salt)</td>
<td>73.6</td>
<td>38.8</td>
</tr>
<tr>
<td>S08</td>
<td>8.3</td>
<td>25.5</td>
</tr>
<tr>
<td>V10</td>
<td>2.9</td>
<td>39.0</td>
</tr>
<tr>
<td>F10</td>
<td>0.1</td>
<td>38.9</td>
</tr>
<tr>
<td>L11</td>
<td>11.9</td>
<td>38.9</td>
</tr>
<tr>
<td>G11</td>
<td>2.9</td>
<td>29.2</td>
</tr>
<tr>
<td>Eq. (3)</td>
<td>6.3</td>
<td>22.9</td>
</tr>
</tbody>
</table>
Table 4.3. Comparison of GEOS-Chem marine POA surface concentrations with monthly and weekly average submicron WIOM concentration observations from Mace Head and Amsterdam Island

<table>
<thead>
<tr>
<th>Multi-year monthly average</th>
<th>Mace Head&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Amsterdam Island&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB (%)</td>
<td>Correlation</td>
</tr>
<tr>
<td>S08</td>
<td>-0.7</td>
<td>0.81</td>
</tr>
<tr>
<td>V10</td>
<td>-82.4</td>
<td>0.59</td>
</tr>
<tr>
<td>F10</td>
<td>-99.3</td>
<td>0.66</td>
</tr>
<tr>
<td>L11</td>
<td>-50.2</td>
<td>-0.07</td>
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<tr>
<td>G11</td>
<td>-82.1</td>
<td>0.74</td>
</tr>
<tr>
<td>Eq. (3)</td>
<td>-18.5</td>
<td>0.82</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2006 weekly average</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB (%)</td>
<td>Correlation</td>
<td>NMB (%)</td>
<td>Correlation</td>
</tr>
<tr>
<td>S08</td>
<td>132.7</td>
<td>0.81</td>
<td>108.5</td>
<td>0.21</td>
</tr>
<tr>
<td>V10</td>
<td>-44.5</td>
<td>-0.21</td>
<td>-4.6</td>
<td>-0.00</td>
</tr>
<tr>
<td>F10</td>
<td>-97.9</td>
<td>0.18</td>
<td>-96.2</td>
<td>-0.01</td>
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<tr>
<td>L11</td>
<td>75.2</td>
<td>-0.64</td>
<td>327.3</td>
<td>-0.00</td>
</tr>
<tr>
<td>G11</td>
<td>-49.9</td>
<td>0.37</td>
<td>-15.7</td>
<td>0.23</td>
</tr>
<tr>
<td>Eq. (3)</td>
<td>94.6</td>
<td>0.58</td>
<td>0.3</td>
<td>0.24</td>
</tr>
</tbody>
</table>

<sup>a</sup>2006 Mace Head concentrations (lower half of table) are WIOM + uncharacterized WSOM

<sup>b</sup>PM<sub>1</sub>:PM<sub>bulk</sub> ratio of 0.41 taken from Claeys et al. (2009) WIOM PM<sub>2.5</sub>:PM<sub>10</sub>
Table 4.4. Comparison of 2009 hourly GEOS-Chem marine POA surface concentrations and submicron OM observations from Mace Head

<table>
<thead>
<tr>
<th>Parameterization</th>
<th>2009 Hourly Mace Head</th>
<th>Ovadnevaite et al. (2011a) period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB (%)</td>
<td>Correlation</td>
</tr>
<tr>
<td>S08</td>
<td>28.2</td>
<td>0.19</td>
</tr>
<tr>
<td>V10</td>
<td>-59.2</td>
<td>0.08</td>
</tr>
<tr>
<td>F10</td>
<td>-98.3</td>
<td>0.11</td>
</tr>
<tr>
<td>L11</td>
<td>13.0</td>
<td>0.03</td>
</tr>
<tr>
<td>G11</td>
<td>-61.9</td>
<td>0.16</td>
</tr>
<tr>
<td>Eq. (3)</td>
<td>68.3</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Fig. 4.1. Annual average submicron emissions in units of ng m$^{-2}$ s$^{-1}$ of sea-salt (Gong, 2003) and marine POA from the five emission schemes.
Fig. 4.2. Average submicron surface concentrations of marine POA in units of ng m$^{-3}$ for January (top row) and July (bottom row) from the Spracklen et al. (2008), Vignati et al. (2010), and Gantt et al. (2011) emission schemes.
Fig. 4.3. Multi-year average submicron surface concentration of marine POA using the Eq. (3) emissions with the top and bottom charts comparing the multi-year monthly average (left column) and 2006 weekly average (right column) observations of WIOM concentrations with the modeled POA at Mace Head, Ireland and Amsterdam Island, respectively.
Fig. 4.4. Comparison of hourly submicron OM concentrations from Mace Head for 2009 during clean marine conditions as measured by an Aerosol Mass Spectrometer (AMS) with hourly modeled marine POA concentrations. The inset shows the comparison for the marine organic aerosol plume event described by Ovadnevaite et al. (2011a). White areas indicate missing data.
Fig. 4.5. Scatterplots of the 2009 hourly observed submicron OM concentration and predicted marine POA concentration from the a) S08, b) G11, and c) Eq. (3) emissions at Mace Head. Data is color-coded by the hourly observed wind speed. 23 (~1% of clean marine periods) observational datapoints with concentrations in excess of 1500 ng m$^{-3}$ were removed.
Fig. 4.S1. Multi-year (2006 and 2009) average January (top row) and July (bottom row) $U_{10}$ (right column in units of m s$^{-1}$) and [chl $a$] (left column in units of mg m$^{-3}$) values used in GEOS-Chem.
Preface:

In Chapter 1, recent evidence has shown the marine organic aerosols can be externally-mixed with sea-salt and shift the number size distribution to larger and more numerous particles. Both of these effects would have the impact of increasing the cloud condensation nuclei (CCN) concentration and likely the cloud droplet number concentration (CDNC) in areas of high biological productivity. Despite evidence of marine organic aerosols having the ability to affect CCN concentrations, few modeling studies have been performed which quantify these impacts on a global scale. In this article published in ACP in 2011, marine primary and secondary organic aerosols are implemented in the global climate model Community Atmosphere Model version 5 (CAM5) with aerosol microphysics. Specifically, marine isoprene/monoterpenes, methane sulfonate, and two primary organic aerosol (POA) emission schemes with different mixing states are implemented into CAM5 for 5-year simulations with current climate and anthropogenic emissions. In the simulations in which marine POA emissions are externally-mixed with sea salt, marine organic aerosol contribute to a regional increase of up to 400 ng m$^{-3}$ in surface aerosol mass concentration and a 20% increase in surface CCN concentration. The areas with the largest changes in aerosol mass and CCN concentrations were in the biologically-productive oceanic regions where emission rates are the highest. The mixing state played an important role in the ability of marine organic aerosols to affect CCN concentrations, with the external mixture simulations having large CCN changes while the internal mixture simulations showing little change in CCN. Global analysis of the aerosol number concentration in the three submicron aerosol modes revealed that an increase in the accumulation mode (80-300 nm diameters) number was the cause of the increase in CCN concentrations. Chapter 6 expands upon this modeling study by
describing changes in the cloud microphysical properties and radiative forcing associated with marine organic aerosols.
Global distribution and climate forcing of marine organic aerosol: 1. Model improvements and evaluation

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**BG ran the simulations, wrote the paper, and designed the figures.

Abstract

Marine organic aerosol emissions have been implemented and evaluated within the National Center of Atmospheric Research (NCAR)’s Community Atmosphere Model (CAM5) with the Pacific Northwest National Laboratory’s 7-mode Modal Aerosol Module (MAM-7). Emissions of marine primary organic aerosols (POA), phytoplankton-produced isoprene- and monoterpenes-derived secondary organic aerosols (SOA) and methane sulfonate (MS⁻) are shown to affect surface concentrations of organic aerosols in remote marine regions. Global emissions of submicron marine POA is estimated to be 7.9 and 9.4 Tg yr⁻¹, for the Gantt et al. (2011) and Vignati et al. (2010) emission parameterizations, respectively. Marine sources of SOA and particulate MS⁻ (containing both sulfur and carbon atoms) contribute an additional
0.2 and 5.1 Tg yr\(^{-1}\), respectively. Widespread areas over productive waters of the Northern Atlantic, Northern Pacific, and the Southern ocean show marine-source submicron organic aerosol surface concentrations of 100 ng m\(^{-3}\), with values up to 400 ng m\(^{-3}\) over biologically productive areas. Comparison of long-term surface observations of water insoluble organic matter (WIOM) with POA concentrations from the two emission parameterizations shows that despite revealed discrepancies (often more than a factor of 2), both Gantt et al. (2011) and Vignati et al. (2010) formulations are able to capture the magnitude of marine organic aerosol concentrations, with the Gantt et al. (2011) parameterization attaining better seasonality. Model simulations show that the mixing state of the marine POA can impact the surface number concentration of cloud condensation nuclei (CCN). The largest increases (up to 20%) in CCN (at a supersaturation \((S)\) of 0.2%) number concentration are obtained over biologically productive ocean waters when marine organic aerosol is assumed to be externally mixed with sea-salt. Assuming marine organics are internally-mixed with sea-salt provides diverse results with increases and decreases in the concentration of CCN over different parts of the ocean. The sign of the CCN change due to the addition of marine organics to sea-salt aerosol is determined by the relative significance of the increase in mean modal diameter due to addition of mass, and the decrease in particle hygroscopicity due to compositional changes in marine aerosol. Based on emerging evidence for increased CCN concentration over biologically active surface ocean areas/periods, our study suggests that treatment of sea spray in global climate models (GCMs) as an internal mixture of marine organic aerosols and sea-salt will likely lead to an underestimation in CCN number concentration.

5.1 Introduction

The indirect effect of anthropogenic aerosols remains as the largest source of uncertainty for climate projections (IPCC, 2007). To characterize the effects of anthropogenic aerosol, the
impact of all aerosols (anthropogenic and natural) on the earth system, and the role of “aerosols before pollution” (Andreae, 2007) must be understood. One of the largest uncertainties of the aerosol-cloud system is the emission rate of natural aerosols, especially over marine areas. Marine aerosols are important for the global cloud condensation nuclei (CCN) budget, as they contribute considerably to the overall aerosol load, are emitted from a large surface area, and can strongly affect radiative properties and the lifetime of marine stratiform clouds (Klein and Hartmann, 1993). Marine aerosols could be particularly important for understanding the cloud-mediated effects of aerosols on climate, because cloud properties respond nonlinearly to aerosols and are most sensitive to CCN changes when their background concentration is low (Platnick and Twomey, 1994). This sensitivity is evident in measured cloud droplet number concentration (CDNC) over the remote oceans, which ranges from tens per cm$^3$ in biologically inactive regions to hundreds per cm$^3$ under biologically active conditions (Andreae, 2007). Thus, factors that regulate the concentration of marine aerosols and the resulting reflectivity of low-level marine clouds can critically affect the climate system as a whole (e.g., Randall et al., 1984; Stevens et al., 2005). Despite their importance, the source strength and chemical composition of marine aerosols remain poorly quantified (O'Dowd and de Leeuw, 2007; Andreae and Rosenfeld, 2008). Therefore, most modeling studies that have attempted to simulate the atmosphere before the advent of humans do not represent natural marine aerosols realistically. Instead, to compensate for missing natural marine aerosol sources, global aerosol-climate models impose lower bounds on CDNC or aerosol number concentration over remote marine areas (Lohmann et al., 1999; 2007; Takemura et al., 2005; Wang and Penner, 2009). When these possibly unphysical constraints are removed, the simulated aerosol indirect effect can change by up to 80% (Hoose et al., 2009; Kirkevåg et al., 2008). Changes of this magnitude can have profound effects on the model-predicted extent of human-induced climate change and highlight the need for improved modeling of marine aerosol number size distribution and chemical composition over pristine marine regions.
Natural aerosols over remote oceanic regions consist mainly of a mixture of sea-salt particles, organics, and sulfates from the oxidation of biogenic dimethyl sulfide (DMS) with contributions from mineral dust and smoke from wildfires in some regions (Andreae, 2007). Sea-salt has been proposed to be a major component of marine aerosol over the regions where wind speeds are high and/or other aerosol sources are weak (O'Dowd et al., 1997; Murphy et al., 1998; Quinn et al., 1998). At typical wind speeds encountered during the cruises, sea-salt have been shown to be present in aerosol from 10 nm to several micrometers in diameter with a total number concentration above 100 cm$^{-3}$ (Geever et al., 2005; Clarke et al., 2006; Smith, 2007). Using a coupled global aerosol-climate model with a size-resolved sea-salt aerosol parameterization, Ma et al. (2008) estimated that global direct and first indirect radiative forcings associated with sea-salt aerosol were -0.60 W m$^{-2}$ and -1.34 W m$^{-2}$, respectively.

In addition to sea-salt and DMS products, significant concentrations of submicron organic carbon (OC) aerosols have been identified in marine environments (Novakov et al., 1997; Ellison et al., 1999; Putaud et al., 2000; O’Dowd et al., 2004; Cavalli et al., 2004; Yoon et al., 2007; Pio et al., 2007, Sciare et al., 2009; Russell et al., 2010; Hultin et al., 2010). Abundance of marine-source OC aerosols are particularly high over regions of enhanced oceanic biological activity, where they make up to 63% of the accumulation mode mass (O'Dowd et al., 2004) with concentrations up to 3.8 µg m$^{-3}$ (Ovadnevaite et al., 2011). These organic aerosols have been broadly classified as primary or secondary based on chemical composition (Ceburnis et al., 2008), although this classification has recently been subjected to criticism (Rinaldi et al., 2010). Bubble bursting processes that emit sea-salt aerosols into the marine boundary layer also lead to the emission of marine primary organic aerosols (POA) composed of biogenic secretions and bacterial/viral debris (Blanchard, 1957; Middlebrook et al., 1998; O’Dowd et al., 2004; Leck and Bigg, 2005). Owing to their enhanced fine-mode concentration and surface active nature, these small insoluble organic particles have been proposed to influence both concentration and CCN activity of remote
marine aerosols (O’Dowd et al., 2004; Leck and Bigg, 2007; Moore et al., 2008). However, to date laboratory and modeling studies have reported widely inconsistent results, suggesting increase, decrease or no effect of marine POA on CCN number concentration (Blanchard, 1963; Sellegrbi et al., 2006; Tyree et al., 2007; Fuentes et al., 2010; Westervelt et al., 2011).

Phytoplankton can also emit several types of biogenic volatile organic compounds (BVOCs), such as isoprene, monoterpenes, and amines that have the potential to form secondary organic aerosols (SOA) (Bonsang et al., 1992; Shaw et al., 2003, 2010; Yassaa et al., 2008; Facchini et al., 2008a; Sabolis, 2010). Marine isoprene emissions and their impact on SOA formation have been the subject of several recent studies (Arnold et al., 2009; Gantt et al., 2009; Luo and Yu, 2010; Myriokefalitakis et al., 2010). While the magnitude of SOA-forming potential from marine isoprene has been estimated to be small on the global scale (Arnold et al., 2009), size-resolved local/regional contributions are still not well understood (Gantt et al., 2009). It has been proposed that SOA produced from plankton-emitted isoprene can act synergistically with the established mechanisms of DMS-derived sulfate and sea-salt aerosols to change the chemical composition and number concentration of marine CCN (Meskhidze and Nenes, 2006).

In this work, we use the National Center of Atmospheric Research (NCAR)’s Community Atmosphere Model (CAM5), which includes the Pacific Northwest National Laboratory’s 7-mode Modal Aerosol Model (MAM-7), to examine the potential effects of marine organic aerosols on climate assessments. Our model simulations consider three main effects of marine-induced organic aerosols on marine clouds: 1) CCN number concentration; 2) cloud microphysical and radiative properties; and 3) the range in the assessments of shortwave cloud forcing. Calculations are conducted using different mixing states and emission mechanisms of marine organic aerosols, and different cloud droplet activation parameterizations. This study is the first of a two-part sequence and focuses on the impacts of marine organic emissions on aerosol abundance, chemical composition, and CCN activity.
The second part (Meskhidze et al., 2011) will focus on the impact of these emissions on cloud microphysical properties and shortwave radiative forcing.

5.2 Model and Methods

5.2.1 Model description

CAM5 is a general circulation model (GCM) with a complete representation of the aerosol lifecycle, a physically-based treatment of aerosol activation, double-moment cloud microphysics, and interactive cloud radiative properties. The model simulations are conducted at 1.9° × 2.5° horizontal grid resolution with a vertical resolution of 30 layers from the surface to 2.19 hPa. CAM5/MAM-7 (hereinafter referred to as CAM5) treats aerosols as internal mixtures of all major species within each of seven externally-mixed modes whose properties are given in Table 1. A detailed description of CAM5 can be found at http://www.cesm.ucar.edu/models/cesm1.0/cam and Neale et al. (2010). Of particular importance to this study is the treatment of aerosol water uptake and activation. Water uptake is determined using Köhler theory (Ghan and Zaveri, 2007) with a parameterized treatment of aerosol hygroscopicity values equivalent to the κ-Köhler theory approach of Petters and Kreidenweis (2007). Aerosol activation to form cloud droplets is calculated by the scheme of Abdul-Razzak and Ghan (2000) (hereinafter referred to as AR-G), which is based on all modes of the aerosol size distribution and the volume-weighted hygroscopicity in each mode. Treating the competition between modes during droplet formation is important when the surface area of the accumulation and coarse modes of the aerosol are comparable (Ghan et al., 1998).

Anthropogenic emissions, including sulfur dioxide (SO₂), POA, and black carbon (BC) are from the Lamarque et al. (2010) Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5) emission data set, updated by Bond et al. (2007) and Junker and Liousse (2008). Injection heights and size distributions of primary emitted particles and precursor gases follow the Aerosol Comparisons between Observations and
Models (AEROCOM) protocols (Dentener et al., 2006). SOA production from five (lumped) biogenic and anthropogenic hydrocarbon emissions is prescribed using monthly-averaged VOC emissions from the MOZART-2 dataset (Horowitz et al., 2003) for the year 1997 and assumed SOA yields for each different VOC species to form a single lumped semi-volatile gas that then condenses onto each aerosol mode using gas-to-particle mass transfer expressions (Seinfeld and Pandis, 2006) that are integrated over the size distribution of each mode (Binkowski and Shankar, 1995). Sea-salt emissions are calculated online using Mårtensson et al. (2003) for particles < 2.8 μm in dry diameter and Monahan et al. (1986) for particles > 2.8 μm in dry diameter, and assumed upper cut off diameters of 0.08, 0.3, 1.0 and 10 μm to determine the sea-salt number and mass emissions into the Aitken, accumulation, and fine/coarse sea-salt modes. Dust emissions are also calculated online using the Dust Entrainment and Deposition (DEAD) scheme of Zender et al. (2003). Primary aerosol emissions specify both mass and number emissions. With the exception of sea-salt (which is emitted as a number and then converted to mass), the aerosol number emission is calculated based on the size distribution of each aerosol type. Aerosol wet removal is calculated using the wet removal routine of Rasch et al. (2000) and Barth et al. (2000) with modifications for the consistency with cloud macro- and microphysics. The routine treats in-cloud scavenging (the removal of cloud-borne aerosol particles) and below cloud scavenging (the removal of interstitial aerosol particles by precipitation particles through impaction and Brownian diffusion). Aerosol dry deposition velocities are calculated using the (Zhang et al., 2001) parameterization with the CAM5 land-use and surface layer information. Gravitational settling velocities are calculated at layers above the surface (Seinfeld and Pandis, 1998). Dry deposition velocities depend on particle wet size and are different for mass and number and between modes (Neale et al., 2010).

5.2.2 Model improvement

In this work, several updates have been developed and implemented into the CAM5 model to allow for improved quantification of marine organics and aerosol radiative effects. These
model updates, which are described in the following sections, include parameterizations for marine primary organics and BVOC emissions, modifications to marine SOA production pathways, extension of the AR-G aerosol activation parameterization to allow treatment of the influence of organic surfactants on the activation process, and implementation of an alternate aerosol activation parameterization.

5.2.2.1 Marine primary organic aerosol

The two distinct online emission mechanisms for marine POA that have been implemented in CAM5 in this work are described in detail by Vignati et al. (2010) and Gantt et al. (2011). Both parameterizations compute organic mass fraction of sea spray (OM$_{SSA}$), and use it to estimate the emissions of marine POA based on the default sea spray emission rates. The major difference between the two OM$_{SSA}$ emissions schemes is the mechanism that determines the organic enrichment of sea spray. In the Vignati et al. (2010) scheme which updates O’Dowd et al. (2008), the organic fraction of sea spray is determined using a positive linear relationship with ocean surface chlorophyll-a concentration ([Chl-a]) obtained from the Sea Wide Field-of-view Sensor (SeaWiFS) using the OC4v4 algorithm (O’Reilly et al., 1998) for the years 2000 - 2007. In addition to [Chl-a], the Gantt et al. (2011) scheme considers wind speed and aerosol diameter ($D_p$) in determining the OM$_{SSA}$. The wind speed dependence of the Gantt et al. (2011) parameterization is based on a conceptual relationship between the organic enrichment at the air-sea interface and surface wind speed, while the aerosol size dependence is based on measurements of Facchini et al. (2008b). The multi-variable logistic regression between OM$_{SSA}$ and [Chl-a], 10-meter wind speed ($U_{10}$), and aerosol diameter in Gantt et al. (2011) is given as:

\[
OM_{SSA}(\text{Chl-a}, U_{10}, D_p) = \frac{\frac{1}{1+\exp(-2.63[\text{Chl-a}]+0.18U_{10})}}{1+0.03\exp(6.81D_p)} + \frac{0.03}{1+\exp(-2.63[\text{Chl-a}]-0.18U_{10})}
\]  

(1)
The resulting OM$_{SSA}$ parameterization is applicable to areas with vastly different winds and [Chl-$a$] and can give the size-resolved organic carbon fraction of sea spray aerosols globally, using model-predicted $U_{10}$ and remotely-sensed [Chl-$a$] data.

The Vignati et al. (2010) parameterization is derived for the bulk of submicron aerosols and does not include information on size distribution. To make it consistent with the Gantt et al. (2011) parameterization, the same Facchini et al. (2008b) size distribution is applied to the Vignati et al. (2010) parameterization as follows:

$$\text{OM}_{SSA} (\text{Chl}-a, D_p) = 0.435 \left[ \frac{0.138 \text{Chl}-a + 0.138}{1 + 0.03 \exp(6.81D_p)} \right] + 0.03 \times (0.435 \text{Chl}-a + 0.138) \quad (2)$$

The marine primary organic emission parameterizations implemented in CAM5 also incorporate the change in density when transitioning between sea-salt and organics as described in Gantt et al. (2009). The magnitude of OM$_{SSA}$ can influence the hygroscopicity and thus the growth factor of the aerosol as described in Gantt et al. (2011). For marine POA emissions described by Eq. (2) to be consistent with the rates from Vignati et al. (2010), no growth factor effects were considered ($GF = 1$) and the $D_p$ in Eqs. (1) and (2) is assumed to represent a dry diameter. Since marine POA and sea-salt are thought to have similar emission mechanisms (i.e., bubble bursting), the modeled marine primary organics are emitted into the same aerosol modes that contain sea-salt (i.e., Aitken, accumulation, and fine/coarse sea-salt). As the Mårtensson et al. (2003) parameterization was developed for a synthetic sea-water (without organics) and in light of observational and laboratory evidence for the external mixtures of sea-salt and marine POA (Leck and Bigg, 2007; Hawkins et al., 2010; Hultin et al., 2010) and changes in number and size distribution of marine aerosol during high biological productivity (Andreae et al., 2007; Yoon et al., 2007; Fuentes et al., 2010), two different approaches are used for modeling marine POA: externally-mixed and internally-mixed (with sea-salt) emissions. In both approaches, the organic mass fraction of sea spray in Aitken, accumulation, and fine/coarse sea-salt modes (see Table 1) is calculated using Eqs. (1) and (2). In the externally-mixed emission approach, the added marine POA
mass emissions are accompanied by corresponding increases to sea spray number emissions into 4 model modes, based on the assumed size distribution for sea spray emissions (from Mårtensson et al., 2003, and Monahan et al., 1986). The externally-mixed approach increases the aerosol number emission within the aerosol modes and slightly decreases the mean modal diameter of the emissions (by ~4% when OM$_{SSA} = 0.5$) due to the lower density of marine POA relative to sea-salt. In the internally-mixed approach, only the sea spray aerosol mass is enhanced by addition of organics. Sea-spray number emissions into the 4 model modes are unchanged; the additional marine POA alters the chemical composition and increases the mean modal diameter of the emissions (by ~10% when OM$_{SSA} = 0.5$). As the number concentration of organic aerosols in marine environments is relatively unconstrained, addition of marine POA emissions as both external and internal mixtures to CAM5 using the OM$_{SSA}$ from Eqs. (1) and (2) is believed to cover the range of possible scenarios by which marine carbonations aerosols can influence the CCN activity of aerosols over the ocean.

For both the internally- and externally-mixed emission approaches, the aerosols in each mode are assumed to be internally-mixed and the hygroscopicity is calculated as a mixture of a volume-weighted average of the hygroscopicity values of individual components (Petters and Kreidenweis, 2007). Few observational data are available for the physical and chemical properties of marine POA; so, the chemical properties of sub- and super-micron marine POA are assumed to be that of terrestrial POA, i.e., a hygroscopicity value ($\kappa$) of $10^{-10}$ and a density of 1000 kg m$^{-3}$ (Neale et al., 2010). However, in light of higher hygroscopicity values of marine POA inferred by Cavalli et al. (2004) and Moore et al. (2008) and the sensitivity of aerosol indirect forcing to the hygroscopicity of terrestrial POA (Liu and Wang, 2010), calculations documenting the sensitivity of our results to an increased marine POA hygroscopicity will be presented in the second part of this study.
5.2.2.2 Marine SOA

It has been well established that marine photosynthetic organisms emit a suite of BVOCs. In this study we consider DMS, isoprene, and monoterpenes (e.g., α- and β-pinene, and d-limonene). DMS fluxes in CAM5 are from Dentener et al. (2006), where the oceanic DMS emissions are from simulations by the Laboratoire de Météorologie Dynamique-Zoom (LMDZ) general circulation model (Boucher et al., 2003), using Kettle et al. (1999) seawater DMS concentrations and the Nightingale (2000) air-ocean exchange parameterization. Previous modeling studies (e.g., Chin et al., 2000; Boucher et al., 2003; Easter et al., 2004; Myriokefalitakis et al., 2010) have found that over 90% of atmospheric DMS is converted to SO$_2$, but 1 - 2 Tg S yr$^{-1}$ are converted to gaseous methanesulfonic acid which condenses to particulate methane sulfonate (MS$^-$$^{-}$). To account for the contribution of MS$^-$$^{-}$ to both sulfur and SOA budgets (notice that particulate MS$^-$$^{-}$ contains both sulfur and carbon atoms) in CAM5, we have implemented a temperature-dependent empirical equation for the MS$^-$$^{-}$/nss-SO$_4^{2-}$ molar ratio proposed by Bates et al. (1992). This formulation compares well with both the observational data (Bates et al., 1992) and the results of complex multiphase chemical models of DMS oxidation (Campolongo et al., 1999). In the model, advection as well as dry and wet deposition of MS$^-$$^{-}$ is treated in a way similar to SO$_4^{2-}$.

The marine emissions of isoprene and monoterpenes are calculated using the Gantt et al. (2009) scheme. This emission module accounts for phytoplankton abundance in the surface ocean column, their speciation, $U_{10}$, sea surface temperature (SST), and the incoming solar radiation at a specific water depth based on diffuse attenuation of sunlight throughout the ocean column. Isoprene production rates as a function of light intensity for various phytoplankton groups are taken from Gantt et al. (2009). Production rates for marine α- and β-pinene, and d-limonene are scaled to isoprene emissions based on the measurements of Sabolis (2010). Both isoprene and monoterpene emission rates used in this study are based on laboratory measurements from different phytoplankton functional groups (i.e., diatoms,
coccolithophores, dinoflagellates) under variable environmental conditions (i.e., light and temperature). For the irreversible conversion of marine BVOC to SOA, a 28.6% mass yield is assumed for isoprene (Surratt et al., 2010), 30% for α- and β-pinene, and 60% for d-limonene (Lee et al., 2006). Unlike marine POA emissions that are added to CAM5 as an additional mass and number, the SOA and MS⁻ are condensed to pre-existing particles in different aerosol modes (based on their surface areas) and therefore can only influence total mass and chemical composition of individual aerosol modes. Since the properties of marine SOA are not well characterized, they are set to the same values as that of the terrestrial SOA in CAM5, i.e., a κ = 0.14 and a density of 1000 kg m⁻³ (Neale et al., 2010).

5.2.2.3 Surfactant effect

Models of cloud droplet formation based on laboratory studies with idealized composition of CCN suggest that organic solutes can lower surface tension (σ), one of the factors that control the vapor pressure of small droplets. Chemical effects on cloud droplet number concentration could be particularly pronounced for shallow marine clouds that are characterized by low droplet number concentrations and weak updraft velocities (compared to continental clouds) (Rissman et al., 2004). Here we carry out an extension of AR-G parameterization in CAM5 to include explicit treatment of surface-active species by implementing the modified multi-mode parameterization of Rissman et al. (2004). Recent surface tension measurements for marine dissolved organic matter have shown that surface tension depression for marine organics can be represented by Szyskowski-Langmuir adsorption isotherm (Langmuir, 1917) as a function of carbon concentration, C:

\[ \sigma = \sigma_w - \alpha T \ln(1 + \beta C) \]

where σₔ is surface tension of water (i.e., an “infinitely diluted” sample), T is the absolute temperature, and α and β are empirical constants. Surfactant effects of marine organics are explored using two different sets of constants: \( \alpha = 1.7 \times 10^{-4} \text{ N m}^{-1} \text{ K}^{-1} \) and \( \beta = 11.86 \text{ L mol}^{-1} \) from Cavalli et al. (2004) and \( \alpha = 2.952 \times 10^{-3} \text{ N m}^{-1} \text{ K}^{-1} \) and \( \beta = 2.4 \times 10^{2} \text{ L mol}^{-1} \) from
Moore et al. (2008). The organic mass fraction of marine aerosols in different modes is calculated by dividing marine POA by the total mass of dry aerosol components within each mode. Due to the overwhelming contribution of sea-salt, surfactant effects of supermicron marine POA aerosols are not considered in the simulations. Previous studies have revealed that Eq. (3) does not account for the possible partitioning of surface-active compounds between droplet surface and the bulk phase (Sorjamaa et al., 2004; Li et al., 2010). As neglecting such partitioning effects can potentially overestimate the surface tension depression, surfactant effects of marine organics treated this way should be viewed as a maximum effect on CCN number concentration.

5.2.2.4 Aerosol activation parameterization

A prognostic aerosol activation/droplet nucleation parameterization developed by Nenes and Seinfeld (2003) and updated by Fountoukis and Nenes (2005) (hereafter referred to as FN) and Barahona et al. (2010) has been implemented in CAM5. The FN parameterization is one of the most comprehensive cloud droplet activation mechanisms developed to date (Fountoukis and Nenes, 2005). In addition to treating the competition among all modes, the FN parameterization can also include the presence of surfactants and slightly soluble species (Shulman et al., 1996; Laaksonen et al., 1998). The FN parameterization includes a size-dependent mass transfer coefficient for the growth of water droplets to accommodate the effect of size (and potentially organic films) on the droplet growth rate. The FN parameterization gives similar results to a detailed numerical cloud parcel model with a substantially lower simulation time, and has been shown to accurately predict cloud droplet activation for a wide range of observational conditions for non-precipitating warm clouds of variable microphysics, aerosol composition, and size distribution (Nenes and Seinfeld, 2003; Meskheidze et al., 2005; Fountoukis et al., 2007; Ghan et al., 2011). The combination of accuracy and speed makes this parameterization appropriate for the calculation of the aerosol activation processes in GCMs. The FN parameterization can employ both sectional (binned) and modal (lognormal) representations of the aerosol size distribution and chemical
composition. The modal version has been implemented in CAM5. As both the mass and number fractions activated for each mode are needed to determine the nucleation scavenging rate of aerosols in the model, the FN parameterization was modified by adding activated mass fraction calculation following Abdul-Razzak et al. (1998). Although, the FN parameterization enables variable accommodation coefficients, to be consistent with the rest of CAM5 model results employing AR-G, a mass accommodation coefficient of 1 is used in the simulations with the FN parameterization. Using two different state-of-the-art aerosol activation parameterizations gives a robust assessment of the extent to which ocean ecosystems can influence regional aerosol and cloud radiative properties.

5.3 Simulation setup

Table 2 lists the simulations carried out to study the effects of marine OC emissions on ambient aerosol concentration and CCN activity. All simulations are conducted for 5 years with a 3 month spin-up. The CAM5 runs are carried out for three emissions schemes: “Default”, “V10”, and “G11”. The Default simulation uses all the original options of CAM5, including the AR-G aerosol activation scheme and the baseline terrestrial and marine emissions. The baseline marine emissions in the model include sea-salt and DMS (with only yield of $\text{SO}_4^{2-}$). The V10 simulation uses all the same options as the Default, with the addition of marine POA emissions following Vignati et al. (2010) and marine SOA/MS$^-$ production as described above. The G11 simulation is similar to the V10 but employs the Ganttt et al. (2011) marine POA emissions. Therefore, the differences among the Default, V10, and G11 simulations can be attributed exclusively to the effects of marine POA and SOA (including MS$^-$). Differences between V10 and G11 are due to differences in marine POA emission parameterizations. A number of sensitivity studies are also carried out to examine how reasonable variations in the key parameters for marine organic aerosol affect the model-predicted CCN and cloud microphysics properties. The “V10-Internal” and “G11-Internal” simulations are intended to test the effects of mixing state of the marine POA emissions. In these two simulations, marine POA emissions are added to the aerosol modes
as internally-mixed with sea-salt and marine SOA and MS\textsuperscript{-} production are not considered. In “SOA/MS\textsuperscript{-}” simulations, only marine SOA and MS\textsuperscript{-} production (no marine POA emissions) are added to the Default scheme to study the contribution of these marine secondary aerosols to model-predicted effects of marine organic aerosols.

5.4 Results

5.4.1 Marine emissions

Table 3 lists simulated global annual emissions of compounds with marine sources. For both V10 and G11 simulations, the emission amounts of POA increase with larger aerosol sizes like that of sea-salt; however, relative to sea-salt the emissions of marine POA in the coarse mode are modest due to the progressively smaller organic enrichment of sea spray with size. The emission amounts of submicron marine POA estimated using the two parameterizations in this study are 9.4 Tg yr\textsuperscript{-1} in the V10 simulation and 7.9 Tg yr\textsuperscript{-1} in the G11 simulation. Note that the size dependent scheme of OM\textsubscript{SSA} supplemented to the Vignati et al. (2010) parameterization had an overall minor effect on the absolute amount of submicron marine organic aerosol emissions (c.f., 8.2 and 7 - 8 Tg yr\textsuperscript{-1} reported by Vignati et al. (2010) and Myriokefalitakis et al. (2010), respectively). This is somewhat unexpected, as the Mårtensson et al. (2003) emission function (used in CAM5) predicts a factor of five higher emission of submicron sea-salt mass, as compared to the Gong et al. (2003) function (used in Vignati et al., 2010). The lower than expected emissions of POA in the V10 simulations can be explained by the size-dependent OM\textsubscript{SSA} enrichment mechanism (with lower organic enrichments for larger sized submicron mode particles) applied to the Vignati et al. (2010) formulation. As the submicron sea spray mass is typically weighted toward the larger sizes (O’Dowd et al., 1997), the reduction of OM\textsubscript{SSA} with aerosol size yields lower marine POA mass emissions. The coarse mode contributes \sim 70\% of the total marine POA mass for both
V10 and G11, but it is expected to have little climatic impact as it represents < 1% of coarse mode sea-salt mass emissions.

Although relatively similar in the magnitude of global emissions, the V10 and G11 parameterizations predict considerably different spatial distributions. Figures 5.1a-b show that over the mid- and high-latitude oceans (30-90°N and 30-90°S), the annual average global emissions of submicron marine POA from the G11 simulation are lower than those of V10, while over the most of the tropical oceans (30°N to 30°S) G11 predicts higher emissions as compared to V10. The distributions of SOA and MS\(^{-}\), shown in Figs. 5.1c-d, are different compared to that of POA in both magnitude and spatial distribution. For SOA, the magnitude of emissions is much lower than that of POA and the emissions are concentrated over the coastal upwelling regions characterized by high productivity. The magnitude of the MS\(^{-}\) emissions is comparable to that of POA but is more focused in the high latitude oceans due to the high DMS flux and negative temperature dependence of the MS\(^{-}\) yields (e.g., Bates et al., 1994; Kettle et al., 1999; Barnes et al., 2006).

5.4.2 Marine organic aerosol mass concentrations

The differences in the POA emission rates for the G11 and V10 simulations (Figs. 5.1a and 5.1b) lead to differences in the surface POA concentrations as shown in Figs. 5.2a and 5.2b. The largest differences in surface concentrations of marine organic aerosols for G11 and V10 simulations occur over the Southern Ocean, where G11 predicts substantially lower concentrations (up to 100 ng m\(^{-3}\)) compared to V10 (up to 200 ng m\(^{-3}\)) due to the stronger wind speed dependence of the V10 emission scheme and high wind speeds throughout the region. In the tropical Pacific, where wind speeds are much lower, G11 shows elevated concentrations relative to that of V10 due to its higher emissions rate there. Overall, the G11 simulation produces relatively uniform surface concentrations with values greater than 50 ng m\(^{-3}\) of marine organic aerosols over most of the oceanic regions. In addition to the emissions, surface layer POA concentrations are also influenced by the differences in
transport and deposition patterns. Comparison of Figs. 5.1a and 5.2a shows that although the high concentrations are typically co-located with the regions of high emissions, the oceanic areas with low annual precipitation (e.g., tropical oceans on both sides of the Intertropical Convergence Zone) tend to have elevated concentrations relative to their emission rates. Figs. 5.2a and 5.2b show that over most of the oceanic regions, surface concentrations of submicron marine POA are between 50 - 200 ng m$^{-3}$ (with maximum of 250 ng m$^{-3}$), which are slightly lower than the values of 100 - 500 ng m$^{-3}$ reported in previous observational and modeling studies (Sciare et al., 2009; Russell et al., 2010, 2011; Gantt et al., 2010). Potential reasons for the model underestimation include the climatological surface ocean [Chl-a] used in both V10 and G11 emission parameterizations, the annual averaging of the emissions, and the coarse horizontal resolution of the model that may not capture local point observations. The assumption of a single value of 1.4 for the organic aerosol to OC mass ratio (Decesari et al., 2007; Facchini et al., 2008b) is also likely to be a source of uncertainty. In terms of total marine-source submicron OM (OM = POA+SOA+MS$^-$) concentrations, Fig. 5.2c shows that widespread areas over productive waters of the Northern Atlantic, Northern Pacific, and the Southern Ocean have marine-source submicron OM surface concentrations of 100 ng m$^{-3}$ with values over 400 ng m$^{-3}$ in the most productive areas.

Global climate models like CAM5 give an average realization of the atmospheric state and therefore should not be directly compared to the measurements conducted for a short period of time at specific locations. This puts a strict constraint on observational data suitable for model validation. On Fig. 5.2c the model components of OM (POA, SOA, and MS$^-$) are compared to long-term monthly-average observations of water insoluble organic matter (WIOM), water soluble organic matter (WSOM), and MS$^-$ at two coastal sites: Mace Head and Amsterdam Island (Sciare et al., 2009). It is commonly assumed that WIOM over the marine environment is predominantly associated with primary emissions from the sea surface, while WSOM is of secondary origin (Ceburnis et al., 2008; Facchini et al. 2008). However, recent studies revealed that oxidation of marine primary OM could also lead to the
formation of WSOM (Rinaldi et al., 2010; Ovadnevaite et al., 2011). Long-term observations of marine organic aerosols available from these two sites smooth out day-to-day variations and therefore are suitable for judging the accuracy of the CAM5 predicted organic aerosol concentrations over the remote marine regions. Fig. 5.2c shows that at the Mace Head station located on the Atlantic coast of Ireland (Yoon et al., 2007) both the V10 and G11 simulations are roughly able to replicate the magnitude of ocean-derived WIOM for the periods of low biological activity (November through March). Fig. 5.2c also highlights a significant underestimation of ocean-derived POA, particularly during the periods of high biological activity at Mace Head. Possible reasons for the model underestimation include the climatological monthly mean surface ocean [Chl-a], coarse model grid averaging of wind speed and [Chl-a] over highly productive surface regions off the coast of Mace Head, small but non-negligible (~20%) contribution of fossil fuel to OM classified as “marine” at Mace Head (Ceburnis et al., 2011), and uncertainties related to the surf zone impact on aerosol emissions (de Leeuw et al., 2000; Vignati et al., 2001).

According to Fig. 5.2c, seasonal differences between the V10 and G11 schemes are predicted at Amsterdam Island, over the Southern Ocean. This figure shows that at Amsterdam Island the G11 scheme captures the seasonal variation of POA (more productive summer and less productive winter periods) slightly better than V10, although neither simulation accurately predicts the range of concentrations observed during the different seasons. Neglecting any potential non-emission related inadequacies in the model, the most likely reason for this problem is the strong wind speed dependence of the sea spray function employed by the two emission schemes. Although aerosol chemical composition over Amsterdam Island can be considered to be representative for marine background (Sciare et al., 2009), given an extreme paucity of ground-based long-term measurements of marine organic aerosols, it is difficult to assess the accuracy of either V10 or G11 emission mechanism on a global scale. More detailed studies using global 3-D chemical transport models (CTMs) may be needed for improved evaluation of different emission mechanisms.
against larger suite of observational data. Nevertheless, Fig. 5.2c indicates that compared to simulations when only terrestrial emissions of POA are accounted for, the implementation of marine POA in CAM5 (either through V10 or G11 schemes) leads to an improvement (Default: mean bias of -106 ng m\(^{-3}\) and correlation of -0.51 and G11: mean bias of 69 ng m\(^{-3}\) and correlation of -0.17) in the predicted organic aerosol concentrations at Amsterdam Island. Figure 5.3 shows that in general, both G11 and V10 simulations display distinct seasonalities in OM mass concentrations over the wider Southern Ocean waters (roughly between 40° S to 70° S) caused by variability in [Chl-a] (large biological productivity during austral summer and low in winter). However, despite such similarities, Fig. 5.3 shows that due to stronger wind speed dependence, V10 is consistently predicting higher OM mass concentrations and less seasonal variability compared to G11.

Also shown in Fig. 5.2c is the observed monthly-average surface WSOM concentration at both sites which are well in excess of the modeled SOA concentrations. The underestimation of WSOM in CAM5 may be caused by several factors including an underestimation of phytoplankton emissions of isoprene and monoterpenes with the ratio of “top-down” to “bottom-up” estimates on the order of 30 and 2000, respectively (Luo and Yu, 2010), a lack of accounting for aged POA from marine sources that exhibit increased solubility (Rinaldi et al., 2010), or condensation of semi-volatile POA (Robinson et al., 2007) of possible marine origin. These model results are consistent with several recent studies suggesting that SOA produced from marine BVOCs may not be enough to explain the observed WSOM concentrations, especially over the Southern Ocean (Arnold et al., 2009; Claeys et al., 2009).

The spatial distribution of marine-source OM surface concentration for each of the three components (POA, SOA, and MS\(^{-}\)) shown in Fig. 5.4 reveal distinct patterns over the global oceans: POA and to a lesser degree SOA are comprising the majority of tropical ocean OM mass while a combination of POA and MS\(^{-}\) is making up the mid-latitude OM, with MS\(^{-}\) dominating at high-latitudes. These results are similar to that of Myriokefalitakis et al. (2010), although POA contributes more to tropical OM in the G11 simulation due to the
higher emissions/concentrations. Not shown is the contribution of each of the three components to submicron marine OC mass, which would be somewhat different owing to the distinct OM/OC ratios intrinsic to each type of OM. Marine POA, for example, would contribute substantially to global marine OC because of the assumed 1.4 OM/OC ratio (Decesari et al., 2007; Facchini et al., 2008b) as compared to an OM/OC ratio of ~8 for MS.

5.4.3 Changes in CCN concentration

A number of studies (e.g., Lohmann et al., 1999, 2007; Takemura et al., 2005; Wang and Penner, 2009; Hoose et al., 2009) highlight the challenges for GCMs to accurately represent the seeds of cloud droplets over pristine remote oceanic regions. To evaluate the representativeness of the model-predicted marine organic aerosols to serve as CCN over remote marine regions, we compare CAM5 simulated surface CCN concentration ($S = 0.2\%$) with observations from several field campaigns. A supersaturation of 0.2% is selected to be representative of an average effective supersaturation in marine boundary-layer stratocumulus clouds, while the choice of the first model layer allows our results to be consistent with the above discussion of marine organic aerosol distribution over the ocean. Fig. 5.5a shows that when marine organic aerosols are assumed to be externally-mixed with sea-salt (the G11 simulation), the greatest percentage changes (~20%) in the surface CCN occur in the vicinity of biologically productive ocean waters. The results of the paired t-test ($P <0.05$) between marine-source submicron OM concentration and CCN number changes show that the regional increases in CCN in the vicinity of biologically active regions are statistically significant (see Fig. S1 in Supplement). A similar spatial distribution and sign of these changes, albeit at different magnitudes, is predicted for CCN concentration at supersaturations of 0.01% and 1% (see Supplemental Fig. 5.S2). Vertical profiles of model-predicted and observed CCN have been compared by selecting the collocated CAM5 grid cell and simulated month(s) closest to that of each campaign. The detailed description of the
location and dates for each of the field experiments can be found elsewhere (e.g., Ghan et al., 2001 and references therein; Wang et al., 2008, 2010). When compared to observed CCN concentrations ($S = 0.2\%$) from various field campaigns (vertical plots on Fig. 5.5a), it can be seen that for the selected measurement locations, marine organic aerosols have a minor effect on model-predicted CCN. Fig. 5.5a shows that all model-predicted vertical profiles of CCN concentration decrease with height, except FIRE3 where simulation profiles are nearly invariant with height. The agreement between simulated and observed profiles is within the range of variability in the observations. Deviations of model-predicted CCN from the observations (e.g., for SOCEX1) were previously attributed to a combination of factors including excessive MS$^-$ and inefficient wet removal in the model (Ghan et al., 2001).

Comparison of Figs. 5.5a and 5.5b shows that the surface CCN concentration changes are similar between the G11 and V10 simulations (with the exception of the Southern Ocean which had a greater increase in the V10 simulation). These figures show that over most of the oceans, marine-source organic aerosols increase surface CCN concentration by less than 10%. Inspection of Fig. 5.5 also reveals reduction of CCN concentration for most of the land regions (sometimes far inland over the Europe and North America). Our data analysis (shown in Table 4) indicates that for all the simulations examined, changes in globally-averaged surface CCN concentration due to marine organic aerosols have different signs over the land and the ocean. The CAM5 is a coupled aerosol/climate model that solves the three dimensional conservation equations for meteorological fields and includes physically-based treatment of aerosols and clouds. Therefore, it is plausible that the reduction in CCN number concentration over the land, thousands of kilometers away from the emission sources, is caused by marine-source organic aerosol-induced changes to meteorology and cloud microphysical processes. This hypothesis will be explored in detail in the second part of this study which examines the spatially heterogeneous climate forcing by marine organic aerosol. Overall, Fig. 5.5 shows that the effects of marine organic aerosol are likely to be global and not merely limited to oceanic regions.
The spatial variations of percentage change in surface CCN number concentration due to marine organics are shown in Fig. 5.6. Despite marked seasonality in submicron marine OM mass concentration over productive waters of the Northern Pacific and Atlantic and the Southern Oceans (see Fig. 5.3), Fig. 5.6 shows modest seasonal modulation in percent change of CCN number. The main reason for this is likely to be the collocation of the strongest sources of marine organic aerosol and DMS, i.e., ocean regions with elevated primary productivity. As DMS is one of the main sources of CCN over the remote marine regions, Fig. 5.6 suggests that the contribution of marine organic aerosol to the CCN budget can be important throughout the whole year. Moreover, according to Eq. (1) the organic mass fraction of sea spray approaches 100% (pure organics) for particles below 100 nm in dry diameter, reflecting the highest potential enrichment in the organic fraction (Sellegri et al., 2006; Bigg and Leck, 2008; Hultin et al., 2010). Several studies using laboratory-generated primary marine aerosol proposed that due to their low CCN activity sub-200 nm diameter organic particles are not expected to enhance the CCN budget over the oceans (Fuentes et al., 2011). However, Fig. 5.6 suggests that these submicron-sized marine POA could be of considerable importance to marine CCN budget even if they are emitted at a size below the critical diameter for droplet activation at supersaturations found in marine stratus clouds. Such organic particles could serve as nuclei for the growth of sulfate particles from the oxidation of DMS, providing an alternative mechanism to homogeneous nucleation of sulfate particles (Andreae and Rosenfeld, 2008). Table 5.5 shows that it is the increase in the accumulation mode aerosol number concentration in the G11 and V10 simulations that has the largest effect on CCN number.

The addition of marine SOA and MS to the model did not make large differences in CCN concentration (see Fig. 5.7a and Table 5.4), except over the polar regions. The low sensitivity of CCN to the marine SOA at low and mid-latitudes indicates the limited influence of marine biogenic trace gases on the size distribution and chemical composition of the climatically-relevant accumulation mode aerosols (see Table 5.5). Overall, Figs. 5.5 and
5.7 suggest that different marine organic aerosol sources may influence CCN concentration in different regions; secondary aerosols increase CCN more in polar regions (primarily due to elevated emissions of DMS), while POA increases CCN concentrations by the greatest percentage in mid-latitude and tropical oceanic regions.

Figs. 5.7b and 5.7c compare the percentage change in CCN concentration between the Default and the G11-Internal and V10-Internal simulations, respectively. These simulations do not include SOA and MS\(^{-}\) production and marine POA emissions are added as internally-mixed with sea-salt. Figs. 5.7b and 5.7c show that for these two simulations the emission of internally-mixed marine POA provides diverse results with enhancement and reduction in surface CCN concentration relative to the Default. These figures show that when sea spray is treated as an internal mixture of marine organics and sea-salt (no change in number), the model predicts slight reduction in CCN concentration, even over the highly productive waters of the southern ocean. The sign of the CCN change due to the addition of marine organics to sea-salt aerosol is determined by the relative significance of the increase in the mean modal diameter due to the addition of mass and the decrease in particle hygroscopicity. According to Table 4, the addition of internally-mixed marine organic aerosol yields a slight reduction in model-predicted global mean surface CCN concentration.

As a supersaturation of 0.2% corresponds to sea-salt particles with dry diameters of \(\sim 72\) nm, i.e., accumulation mode where ambient measurements show the largest increase in CCN number associated with biologically active regions (Bigg, 2007; Yoon et al., 2007; Rinaldi et al., 2010), treatment of marine POA emissions only as internal mixture is likely to underestimate their cloud microphysical and radiative effects. The large discrepancy in yearly-mean surface CCN concentration based on the assumption of mixing state of marine POA, ranging from up to a 20% increase to an anticipated decrease over productive waters, highlights the need for a better characterization of marine organic aerosol emission mechanisms and chemical composition.
5.5 Conclusion

Marine organic emissions are implemented in CAM5 by adding two different online emission parameterizations of marine POA and offline productions of marine SOA and MS−, derived from phytoplankton-emitted BVOCs. The estimated annual total submicron marine POA emissions are 9.4 Tg yr−1 and 7.9 Tg yr−1 using the Vignati et al. (2010) and Gantt et al. (2011) parameterizations, respectively. Over biologically productive surface ocean waters, model-predicted concentrations of submicron marine-source OM are estimated to be up to 400 ng m−3. Marine POA contributes to the major fraction (up to 250 ng m−3) of the submicron organic aerosol mass over the tropical and mid-latitude areas, while MS− is found to dominate in high latitude regions. Marine SOA from phytoplankton-derived isoprene and monoterpenes contributes to a relatively small fraction (up to 20%) of the surface concentration of marine-source OM. Extreme scarcity of ground-based long-term measurements of marine organic aerosols does not allow effective evaluations of marine-source surface OM concentrations predicted by the Vignati et al. (2010) and Gantt et al. (2011) emission mechanisms. Nevertheless, comparisons of model-predicted marine-source POA concentrations with observations of WIOM at the Northern and Southern Hemispheric coastal sites show that the Gantt et al. (2011) emission parameterization yields a more accurate representation for the seasonal cycle of marine organic aerosol mass concentrations. Our model simulations show that, when only the terrestrial emissions of POA are accounted for, CAM5 significantly under-predicts organic aerosol mass concentration over the remote ocean. However, remaining differences (often more than a factor of 2) between measured and model-predicted submicron marine organic aerosol concentrations suggest that additional comparative modeling analysis of different marine POA emission schemes, combined with long-term measurements of size-and composition-dependent production flux of sea spray aerosol and process-based laboratory studies, are needed to improve model simulations of marine organic aerosol.
Although the global model-predicted surface CCN (at a $S = 0.2\%$) concentration is shown to be relatively insensitive to the addition of marine organic aerosols, marine emissions of organics are shown to influence surface CCN concentration over the localized regions of the remote ocean. The largest increases (up to 20%) in yearly-averaged CCN concentration are obtained over biologically productive ocean waters when marine organic aerosol is assumed to be externally mixed with sea-salt. The addition of internally-mixed marine organics provides diverse results, often with reductions of CCN concentration over biologically productive parts of the ocean. Based on the experimental evidence for the increased CCN concentration during the periods of higher [Chl-$a$] levels (e.g., O’Dowd et al., 2004; Yoon et al., 2007; Fuentes et al., 2010), our study suggests that it is unlikely that marine organic aerosols are emitted only as an internal mixture with sea-salt, without changing aerosol number. This study also indicates that externally-mixed marine organic aerosol could be of importance to the marine CCN budget, even if they, as originally produced, are below the critical diameter for droplet activation at the supersaturation of 0.2%. Such particles could serve as nuclei for the growth of sulfate particles from the oxidation of marine biogenic DMS. Neglecting the effects of marine organic aerosols on CCN number concentrations in climate models could, therefore, lead to underestimation in shallow marine cloud droplet number concentration. Changes in cloud microphysics and climate forcing due to marine organic aerosols using multiple aerosol activation parameterizations, surfactant effect calculations, and hygroscopicity values are further explored in the second part of this study.

Acknowledgements

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References


Facchini, M.C., Decesari S., Rinaldi M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D., O’Dowd C. D.: Important source of marine


Wang, J., McGraw, R., Daum, P. H., Sedlacek, A. J., Kleinman, L. I., Senum, G., Lee, Y. N., 
Springston, S.R.: Comparison of aerosol and cloud condensation nuclei (CCN) 
relationship parameterizations with data collected during the 2008 VAMOS Ocean-
Cloud-Atmosphere Land Study (VOCALS) field campaign, Third Quarter FY2010 ASR 
2010.

Wang, M., and Penner, J. E.: Aerosol indirect forcing in a global model with particle 

spray emissions on cloud condensation nuclei concentrations, Atmos. Chem. Phys. 

Yassaa, N., Peeken, I., Zöllner, E., Bluhm, K., Arnold, S., Spracklen, D., and Williams, J.: 
Evidence for marine production of monoterpenes, Environ. Chem., 5, 391-401, 

Yoon, Y. J., Ceburnis, D., Cavalli, F., Jourdan, O., Putaud, J. P., Facchini, M. C., Decesari, 
S., Fuzzi, S., Sellegrini, K., Jennings, S. G., and O’Dowd, C. D.: Seasonal characteristics of 
the physicochemical properties of North Atlantic marine atmospheric aerosols, J. 

Zender, C. S., Bian, H., and Newman, D.: The mineral Dust Entrainment And Deposition 
(DEAD) model: Description and 1990’s dust climatology, J. Geophys. Res., 108 (D14), 
Table 5.1. Size range and chemical components of the seven aerosol modes in CAM5.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Diameter Sizes (µm)</th>
<th>Chemical Constituents Included</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atiken</td>
<td>0.01-0.08</td>
<td>( \text{SO}_4^{2-}, \text{NH}_4^+, \text{SOA}, \text{sea-salt, marine POA} )</td>
</tr>
<tr>
<td>Accumulation</td>
<td>0.08-0.3</td>
<td>( \text{SO}_4^{2-}, \text{NH}_4^+, \text{BC, SOA, POA, sea-salt, marine POA} )</td>
</tr>
<tr>
<td>Fine soil dust</td>
<td>0.1-2.0</td>
<td>( \text{SO}_4^{2-}, \text{NH}_4^+, \text{dust} )</td>
</tr>
<tr>
<td>Fine sea-salt</td>
<td>0.3-1.0</td>
<td>( \text{SO}_4^{2-}, \text{NH}_4^+, \text{sea-salt, marine POA} )</td>
</tr>
<tr>
<td>Primary carbon</td>
<td>0.05-0.3</td>
<td>( \text{BC, POA} )</td>
</tr>
<tr>
<td>Coarse soil dust</td>
<td>2.0-10.0</td>
<td>( \text{SO}_4^{2-}, \text{NH}_4^+, \text{dust} )</td>
</tr>
<tr>
<td>Coarse sea-salt</td>
<td>1.0-10.0</td>
<td>( \text{SO}_4^{2-}, \text{NH}_4^+, \text{sea-salt, marine POA} )</td>
</tr>
</tbody>
</table>

\( ^a \) These size ranges are only approximate, as each mode has a log-normal size distribution with median diameters that vary spatially and temporally.

\( ^b \) Constituents only included in model simulations with marine organic emissions.
Table 5.2. Description of CAM5 sensitivity simulations

<table>
<thead>
<tr>
<th>Name</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default</td>
<td>SO₂, SO₄²⁻, terrestrial POA, terrestrial SOA, BC, NH₃, dust, DMS, sea-salt</td>
</tr>
<tr>
<td>SOA/MS⁻</td>
<td>Same as Default but with marine SOA, MS⁻</td>
</tr>
<tr>
<td>G11</td>
<td>Same as Default but with Gantt et al. (2011) marine POA externally-mixed with sea-salt, marine SOA, MS⁻</td>
</tr>
<tr>
<td>V10</td>
<td>Same as Default but with Vignati et al. (2010) marine POA externally-mixed with sea-salt, marine SOA, MS⁻</td>
</tr>
<tr>
<td>G11-Internal</td>
<td>Same as G11, except marine POA internally-mixed with sea-salt, no marine SOA or MS⁻</td>
</tr>
<tr>
<td>V10-Internal</td>
<td>Same as V10, except marine POA internally-mixed with sea-salt, no marine SOA or MS⁻</td>
</tr>
</tbody>
</table>
Table 5.3. Annual mean global marine-source aerosol emissions and global burdens (units: Tg yr\(^{-1}\) and Tg for emissions and burdens, respectively)

<table>
<thead>
<tr>
<th>Mode</th>
<th>POA (V10)</th>
<th>POA (G11)</th>
<th>MS(^\text{−}) (marine)</th>
<th>Sea-salt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Emissions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accumulation</td>
<td>2.4</td>
<td>1.9</td>
<td></td>
<td>14.8</td>
</tr>
<tr>
<td>Aitken</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>Fine sea-salt</td>
<td>6.9</td>
<td>6.0</td>
<td></td>
<td>100.2</td>
</tr>
<tr>
<td>Submicron</td>
<td>9.4</td>
<td>7.9</td>
<td></td>
<td>115.7</td>
</tr>
<tr>
<td>Coarse sea-salt</td>
<td>23.0</td>
<td>18.6</td>
<td></td>
<td>3427.0</td>
</tr>
<tr>
<td>Total</td>
<td>32.4</td>
<td>26.5</td>
<td>5.1</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Burden</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accumulation</td>
<td>0.012</td>
<td>0.011</td>
<td></td>
<td>0.075</td>
</tr>
<tr>
<td>Aitken</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td>Fine sea-salt</td>
<td>0.036</td>
<td>0.036</td>
<td></td>
<td>0.547</td>
</tr>
<tr>
<td>Submicron</td>
<td>0.047</td>
<td>0.047</td>
<td></td>
<td>0.623</td>
</tr>
<tr>
<td>Coarse sea-salt</td>
<td>0.031</td>
<td>0.032</td>
<td></td>
<td>4.903</td>
</tr>
<tr>
<td>Total</td>
<td>0.078</td>
<td>0.079</td>
<td>0.021</td>
<td>0.002</td>
</tr>
</tbody>
</table>
Table 5.4: Model-predicted annual-mean surface CCN (at 0.2% supersaturation) concentrations (in cm$^{-3}$)

<table>
<thead>
<tr>
<th></th>
<th>Global Average</th>
<th>Difference from Default</th>
<th>Ocean Average</th>
<th>Difference from Default</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default</td>
<td>181.9</td>
<td></td>
<td>107.7</td>
<td></td>
</tr>
<tr>
<td>SOA/MS$^{-}$</td>
<td>182.8</td>
<td>+0.9</td>
<td>108.8</td>
<td>+1.1</td>
</tr>
<tr>
<td>G11</td>
<td>184.5</td>
<td>+2.6</td>
<td>111.7</td>
<td>+4.0</td>
</tr>
<tr>
<td>V10</td>
<td>184.9</td>
<td>+3.0</td>
<td>112.3</td>
<td>+4.6</td>
</tr>
<tr>
<td>G11-Internal</td>
<td>181.6</td>
<td>-0.4</td>
<td>107.4</td>
<td>-0.4</td>
</tr>
<tr>
<td>V10-Internal</td>
<td>181.4</td>
<td>-0.6</td>
<td>107.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 5.5. Model-predicted annual-mean surface aerosol number concentrations (in cm\(^{-3}\)) over the ocean for the four model modes examined in this study.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Accumulation</th>
<th>Aitken</th>
<th>Fine sea-salt</th>
<th>Coarse sea-salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default</td>
<td>122.1</td>
<td>206.5</td>
<td>4.2</td>
<td>0.9</td>
</tr>
<tr>
<td>SOA/MS(^{**})</td>
<td>121.5</td>
<td>200.6</td>
<td>4.2</td>
<td>0.9</td>
</tr>
<tr>
<td>G11</td>
<td>125.1</td>
<td>199.1</td>
<td>4.8</td>
<td>0.9</td>
</tr>
<tr>
<td>V10</td>
<td>125.9</td>
<td>199.3</td>
<td>4.8</td>
<td>0.9</td>
</tr>
<tr>
<td>G11-Internal</td>
<td>121.9</td>
<td>203.6</td>
<td>4.3</td>
<td>0.9</td>
</tr>
<tr>
<td>V10-Internal</td>
<td>122.7</td>
<td>205.4</td>
<td>4.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Fig. 5.1. Annual average global emissions of marine POA for the a) G11 and b) V10 simulations, c) marine SOA, and d) MS− in units of ng m$^{-2}$ s$^{-1}$. 
Figure 5.2. Annual average submicron marine POA concentrations at the surface layer from the (a) G11 and (b) V10 simulations and (c) the total marine OM concentrations in units of ng m$^{-3}$ with the top and bottom charts comparing the monthly average concentrations of WIOM, WSOM, and MS$^-$ concentrations with the modeled POA (error bars are the maximum and minimum monthly averaged values during the 5-yr simulation period), SOA and MS$^-$ at Mace Head, Ireland and Amsterdam Island, respectively. Note that modeled terrestrial POA and SOA are not shown for Mace Head due to the selection of marine air masses for the observations.
Fig 5.3. Average submicron marine-source OM concentrations at the surface in units of ng m$^{-3}$ for a), b) G11 and c), d) V10 for December-February (left column) and June-August (right column).
Fig. 5.4. Relative percentage contribution of a) POA b) SOA, and c) MS\textsuperscript{−} to average surface level marine-source submicron OM mass concentration from the G11 simulation.
Fig. 5.5. Annual average percentage change in surface CCN concentration at 0.2% supersaturation between the Default and a) G11 and b) V10 simulations. The inserts with charts are comparing the observed vertical distribution of CCN (0.2%) from various remote ocean and coastal field campaigns (solid black line represents the mean concentration and dotted lines represent the upper and lower 10 percentile) with the Default, V10, and G11 simulations (solid lines are mean concentrations and error bars are the maximum and minimum monthly averaged values during the 5-year simulation period).
Fig. 5.6. Average percentage change in surface CCN (0.2%) concentration between the Default and G11 for a) December-February and b) June-August.
Fig. 5.7. Annual average percentage change in surface CCN concentration at 0.2% supersaturation between the Default and a) SOA/MS, b) G11-Internal, and c) V10-Internal.
Fig. 5.S1. The results of the paired t-test ($P < 0.05$) between marine-source submicron OM concentration and CCN number changes for a) G11 and b) V10 simulations.
Fig. 5.S2. Annual average percentage change in surface CCN concentration at a) 0.01% and b) 1% supersaturation between the Default and G11 simulations.
Preface:

In addition to increases in cloud condensation nuclei (CCN) concentration associated marine organic aerosols, changes in cloud microphysics and associated radiative forcing have been observed in regions with high levels of ocean productivity. In this article published in ACPD in 2012, results from the modeling study described in Chapter 5 are extended to describing changes in cloud microphysical properties and radiative forcing due to marine organic aerosols. Like CCN concentrations, cloud droplet number concentration (CDNC) increased by up to 20% in biologically active areas of the remote ocean due to marine organic aerosols. Global changes in CDNC, liquid cloud effective radii, liquid water path, and shortwave cloud forcing due to marine organic aerosols range between 0.5 and 2%. In comparing the simulations with and without marine organic aerosols during preindustrial and present day scenarios, marine organic aerosols lead to a 0.1 W m\(^{-2}\) (8%) increase (-1.35 to -1.25 W m\(^{-2}\)) in the model predicted aerosol indirect forcing (AIF). This impact was strongly dependent on the mixing state of marine POA emissions; the internally-mixed marine POA simulation had no change in aerosol indirect forcing due to marine organic aerosols. This change in the AIF due to marine organic aerosols provides a notable link for ocean-ecosystem marine low-level cloud interactions and may be evidence for inclusion of these emissions in future earth system models.
Global distribution and climate forcing of marine organic aerosol - Part 2: Effects on cloud properties and radiative forcing

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Abstract

A series of simulations with the Community Atmosphere Model version 5 (CAM5) with a 7-mode Modal Aerosol Model were conducted to assess the changes in cloud microphysical properties and radiative forcing resulting from marine organic aerosols. Model simulations show that the anthropogenic aerosol indirect forcing (AIF) predicted by CAM5 is decreased in absolute magnitude by up to 0.09 W m\(^{-2}\) (7\%) when marine organic aerosols are included. Changes in the AIF from marine organic aerosols are associated with small global increases in low-level in-cloud droplet number concentration and liquid water path of 1.3 cm\(^{-3}\) (1.5\%) and 0.22 g m\(^{-2}\) (0.5\%), respectively. Areas especially sensitive to changes in cloud properties due to marine organic aerosol include the Southern Ocean, North Pacific Ocean, and North Atlantic Ocean, all of which are characterized by high marine organic emission rates. As
climate models are particularly sensitive to the background aerosol concentration, this small but non-negligible change in the AIF due to marine organic aerosols provides a notable link for ocean-ecosystem marine low-level cloud interactions and may be a candidate for consideration in future earth system models.

6.1 Introduction

Marine organic aerosols, emitted into the atmosphere as primary particles via bursting of bubbles at the ocean surface and secondary particles via oxidation of volatile organic compounds (VOC) such as isoprene, monoterpenes, amines, and dimethyl sulfide (DMS), have been shown to affect the chemistry and number distribution of aerosols in the marine environment (O’Dowd et al., 2004; Meskhidze and Nenes, 2006; Yoon et al., 2007; Facchini et al., 2008). Part 1 of this study (Meskhidze et al., 2011) described the implementation of marine organic aerosols in the Community Atmosphere Model version 5 (CAM5) with a 7-mode Modal Aerosol Module (MAM-7) (Liu et al., 2011). Meskhidze et al. (2011) showed that addition of marine organics led to improved agreement of the model predicted and measured concentrations of organic aerosols in the marine boundary layer, with annual average submicron aerosol mass concentration increased by up to 400 ng m\(^{-3}\) over biologically active oceanic regions. Comparison with long-term observations showed that of the two marine primary organic emission parameterizations implemented into CAM5 (Vignati et al., 2010; Gantt et al., 2011), the Gantt et al. (2011) emissions were slightly better in replicating the seasonal cycle of water insoluble organic aerosol mass concentrations. In the areas with the highest emission rates of marine organic aerosols, the cloud condensation nuclei (CCN) concentrations increased by up to 20% due to an increase in the accumulation mode (80-300 nm in diameter in CAM5) aerosol number concentration.

The potential influence of marine organic aerosols on cloud microphysical properties and radiative forcing was first discussed by Novakov and Penner (1993) and Novakov et al.
(1997), who found that organic aerosols of marine origin contributed to a major fraction of marine boundary layer CCN concentration in the Tropical Atlantic. O’Dowd et al. (2004) described an increase (15-100%) in cloud droplet number concentration (CDNC) at Mace Head with the inclusion of marine organic aerosols derived from size-resolved chemistry and number distribution measurements. Ovadnevaite et al. (2011) reported similar results in an AMS study at Mace Head, finding that periods with high organic fractions and low growth factors also had a higher weighted average particle size, CCN activation efficiency, and estimated CDNC. In a modeling study, Roelofs (2008) reported results from the ECHAM5-HAM model in which marine organic aerosols increased North Atlantic CDNC by a factor of 3-4 (~35 to 120 cm\(^3\)) and decreased cloud effective radius from 15-20 \(\mu m\) to 10-14 \(\mu m\) in diameter. These changes brought the model closer to satellite derived values for the region. However, not all studies examining the potential climate impact of marine organic aerosols have found that they have a large impact. Hygroscopic and CCN activity measurements of laboratory bubble bursting experiments from Fuentes et al. (2011) and Moore et al. (2011) found that despite evidence of organic compounds in sea spray aerosol, their higher hydrophobicity and lower CCN activity lead to a prediction of small changes in CCN concentration associated with marine organic aerosols and negligible impact on cloud formation. Westervelt et al. (2012) suggested that marine organic aerosols have a minor impact on climate due to GISS II-prime modeling results showing a decrease in CCN concentration (due to a decrease in particle solute concentration) in all simulation except when marine organic aerosols and sea-salt were treated as externally-mixed. Here in the second part of the study for climate forcing of marine organic aerosol, we focus on the impact of the marine organic aerosols on cloud microphysical properties and shortwave radiative forcing.
6.2 Model experimental setup

To detect the specific effects of marine organics on aerosol and cloud properties, various sensitivity simulations expanding upon the simulations in Meskhidze et al. (2011) have been performed. We use the National Center of Atmospheric Research (NCAR)'s Community Atmosphere Model (CAM5) with the Pacific Northwest National Laboratory's 7-mode Modal Aerosol Module (MAM-7) for both Part 1 and Part 2 of this study. CAM5 general circulation model with a complete representation of the aerosol lifecycle, a physically-based treatment of aerosol activation, double-moment cloud microphysics, and interactive cloud radiative properties. The model simulations are conducted at 1.9° × 2.5° horizontal grid resolution with a vertical resolution of 30 layers from the surface to 2.19 hPa. CAM5/MAM-7 (hereinafter referred to as CAM5) treats aerosols as internal mixtures of all major species within each of seven externally-mixed modes. A detailed description of CAM5 can be found at http://www.cesm.ucar.edu/models/cesm1.0/cam and Neale et al. (2010). In the Part 1 simulations, the “Default” simulation in which there are no marine organic aerosols was compared to simulations which included production of marine secondary organic aerosol (SOA) and methane sulfonate (MS−) (“SOA/MS−”) and marine POA emissions (Gantt et al., 2011) that were either externally- (“G11”) or internally-mixed (“G11-Internal”). When the marine POA emissions were externally-mixed, they resulted in additional aerosol number and mass in the four model modes (Aitken, accumulation, and fine/coarse sea-salt modes) as opposed to only additional aerosol mass for the internally-mixed marine POA emissions.

The emissions from the G11 simulation in Part 1 are used in the sensitivity simulations for this work because the resulting surface concentrations had a seasonal cycle that was more similar to observations. These sensitivity simulations are carried out to determine the impact of marine organic aerosols on cloud microphysics and radiative forcing for different aerosol activation parameterizations and marine POA hygroscopicity and mixing state. Table 1 gives a summary of the 10- and 5-year long simulations with 3-month spin-up, including those performed in Part 1 on which the simulations in this work are based.
Detailed descriptions of the different aerosol activation schemes, marine POA hygroscopicity and mixing state treatments, and preindustrial and present day anthropogenic emissions can be found in Meskhidze et al. (2011). In addition to simulations using the Abdul-Razzak and Ghan (2000) (hereinafter referred to as AR-G) aerosol activation parameterization from Part 1, the aerosol activation parameterization described by Fountoukis and Nenes (2005) (hereafter referred to as FN) is implemented in simulations with and without the G11 marine organic emissions (“Default-FN” and “G11-FN”, respectively). An additional sensitivity test was conducted for the hygroscopicity parameter (κ) (Petters and Kreidenweis, 2007) of marine POA by increasing it (in the G11 simulation) from the κ = 10\(^{-10}\) value used for terrestrial POA to κ = 0.1 (“G11-κ”) (Liu et al., 2011). This adjusted κ represents the upper end of the potential marine POA hygroscopicity based on the measurements of κ values of 0.006 and 0.04 for estuarine (Moore et al., 2008) and riverine (Svenningsson et al., 2006) organic matter, respectively. In order to estimate the effect of marine organic aerosols on cloud radiative forcing, both the Default and G11 simulations were performed with present-day (PD) (“Default” and “G11”) and pre-industrial (PI) aerosol and precursor emissions (“Default-PI” and “G11-PI”). The anthropogenic aerosol indirect forcing (AIF) is then calculated as the difference in model-predicted short wave cloud forcing (SWCF) between PD and PI conditions. The model simulations with PD and PI emissions used anthropogenic emissions from the IPCC AR5 dataset for the year 2000 and 1850, respectively (Bond et al., 2007; Junker and Liousse, 2008; Lamarque et al., 2010).

6.3 Results

As shown in Meskhidze et al. (2011), treating marine organic aerosols increased the simulated aerosol mass and CCN concentration over much of the ocean. Here we expand upon these results by carrying out a number of sensitivity tests for additional model parameters with the emphasis on the changes in cloud microphysics and radiative forcing
associated with marine organic aerosols. Unless specified otherwise, the reported changes are relative to the Default simulation.

6.3.1 Effects on cloud physical properties

6.3.1.1 Low-level cloud droplet number

In general it is expected that the addition of CCN may result in an increase in the in-cloud CDNC if the liquid water path (LWP) is held constant (Twomey, 1972, Albrect, 1989). Current simulations show that, when LWP is unconstrained, addition of marine organic aerosols can change both CDNC and LWP of the clouds. The effect is expected to be particularly pronounced for the low-level maritime clouds as marine aerosols are typically found within 1 km above the ocean surface (Kiliyanpilakkil and Meskhidze, 2011). Table 2 shows that compared to the Default simulation, the global annual mean increase in low-level CDNC (between 945 and 980 mb) from marine organics in the G11 simulation is 1.3 cm$^{-3}$ (1.5%) while over the ocean CDNC increases by 1.8 cm$^{-3}$ (2.7%). The spatial distribution of low-level CDNC from the Default and G11 simulations shown in Fig. 6.1a and 6.1b reveals that the increase occurs mostly over the Southern Ocean and Northern Atlantic. Many of these areas also have the greatest percentage changes (up to 20%) in CDNC as shown in Fig. 6.1c and are statistically significant (with a $p$-value < 0.1 according to the paired t-test in Fig. 6.S1). Fig. 6.1c also shows some areas with decreases in low-level CDNC; these changes are typically not statistically significant (see Fig. 6.S1), and are likely due to model noise. The spatial distribution of low-level CDNC percentage changes is similar to the percentage changes in the surface concentration of CCN at 0.2% supersaturation shown in Meskhidze et al. (2011). The magnitude of low-level CDNC changes in our simulations is much lower than the increases of up to ~300% predicted in Roelofs (2008) for the Northern Atlantic Ocean; this difference is likely due to the much higher submicron marine organic aerosol number concentration in Roelofs (2008) resulting from higher emission rates (Roelofs (2008) has up to 25 Tg C yr$^{-1}$ of emissions in both the Aitken and accumulation modes while G11
emits 0.1 and 2.1 Tg C yr\(^{-1}\) in the marine POA Aitken and accumulation modes, respectively).

6.3.1.2 Column cloud properties and radiative forcing

In addition to increases in low-level CDNC, marine organic aerosols in CAM5 lead to changes in the grid-cell averaged column CDNC, LWP, and SWCF. Like the low-level CDNC, the column CDNC (see Fig. 6.2a) experiences statistically significant (Fig. 6.S1) increases of up to 20% over the Southern Ocean where emissions are the highest. Globally, the percentage increases in column droplet number from the Default to the G11 simulation of 1.1% (1.5% over the ocean) is smaller than that of low-level CDNC (see Table 2) as marine organic aerosol typically remain within the boundary layer. For the LWP, Fig 2b shows that despite the seemingly random regions of positive and negative changes between the Default and G11 simulations, there are widespread areas over the Southern Ocean that experience a large (up to 20%) increase in the LWP as a result of marine organic aerosols. The spatial distribution of the changes in SWCF shown in Fig. 6.2c is similar to that of LWP with roughly 10% decreases (~5 W m\(^{-2}\)) in the vicinity of Falkland (52°S, 58°W) and South Georgia Islands (54°S, 36°W) in the South Atlantic Ocean where emissions of marine organic aerosols are very high. Note that the SWCF has a negative value; therefore decrease in SWCF indicates less solar radiation reaching the surface and shows as a positive percentage change in Fig. 6.2c. Like other higher latitude areas, the changes (absolute difference as opposed to percentage difference) in SWCF due to marine OA show a seasonal dependence similar to that of [Chl-\(\alpha\)] (see Fig. 6.S2). The spatial location of this large decrease in SWCF is similar to Meskhidze and Nenes (2006) who reported a satellite-derived 15 W m\(^{-2}\) decrease in TOA short-wave radiation due to changes in the properties of liquid clouds over a summertime phytoplankton bloom near South Georgia Island. The discrepancies in magnitude are likely to be associated with the coarser model grid, annual averaging (summertime SWCF changes of ~5 to -10 W m\(^{-2}\) are predicted throughout the region), selection by Meskhidze and Nenes (2006) of a time period with a particularly large
phytoplankton bloom, and the effect of DMS-derived sulfate aerosols. Since the same DMS emissions are used in the Default and G11 simulations, DMS-derived sulfate aerosols are likely to have a minor influence on the modeled changes in SWCF. Globally, the changes in the LWP and SWCF are much smaller relative to the region near South Georgia Island. Table 2 shows that there is a 0.22 g m$^{-2}$ (0.5%) global average increase in the LWP in the G11 simulation relative to the Default simulation, and a 0.12 W m$^{-2}$ (0.3%) decrease (indicating the increased reflection of shortwave radiation) in the SWCF. Like low-level CDNC, there is a seasonality in the absolute differences of column CDNC, LWP, and SWCF between the G11 and Default simulations at some high latitude areas that is similar to the [Chl-$a$] seasonality.

6.3.2 Sensitivity simulations

6.3.2.1 Aerosol activation parameterizations

Table 2 shows that AR-G and FN aerosol activation parameterizations give considerably different global low-level CDNC, LWP, and SWCF values (Default vs. Default-FN). Ghan et al. (2011) showed that these differences produce a 0.16 W m$^{-2}$ (10%) smaller anthropogenic AIF with the FN scheme (-1.60 W m$^{-2}$ with FN and -1.76 W m$^{-2}$ with AR-G). In current sensitivity simulation, the changes due to marine organic aerosols are relatively consistent between the two schemes (Default vs. G11 and Default-FN vs. G11-FN). The global changes predicted for low-level CDNC, LWP, and SWCF (due to marine organic aerosol emissions) differ slightly between simulations that use FN-scheme (1.2 cm$^{-3}$, 0.21 g m$^{-2}$, and - 0.14 W m$^{-2}$, respectively) and the ones that use AR-G scheme (1.3 cm$^{-3}$, 0.22 g m$^{-2}$, and -0.12 W m$^{-2}$, respectively). Therefore, our simulations indicate that the differences between the AR-G and FN aerosol activation parameterizations appear to be less sensitive to minor changes in CCN concentrations (such as from marine organic aerosols) compared to major changes (such as from anthropogenic aerosols).
6.3.2.2 Marine POA missing state

In Meskhidze et al. (2011), the changes in surface CCN concentration at 0.2% supersaturation were shown to be quite sensitive to the mixing state of marine POA emissions, with an external mixture (added marine POA mass emissions are accompanied by corresponding increases to sea spray number emissions) yielding a much greater effect on CCN number compared to an internal mixture (only the sea spray aerosol mass is enhanced by addition of organics). Table 2 shows that relative to the G11 simulation, which includes an external mixture of marine POA emissions, the simulation with an internal mixture of marine POA emissions (G11-Internal) has consistently lower CDNC and LWP and higher (lower absolute magnitude) SWCF. Meskhidze et al. (2011) showed that when marine organics were added as an internal mixture with sea-salt the model predicted a slight reduction in CCN concentration, even over biologically productive waters of the Southern Ocean. In such a case the increase in CCN number due to the growth of mean modal diameter (caused by the addition of organic mass) is outweighed by the decrease in particle hygroscopicity. As both external and internal mixtures of marine organic aerosols and sea salt have been observed (Hultin et al., 2010), these mixing state differences likely represent upper and lower estimates for the effect of marine organic aerosol on cloud microphysical properties and resulting shortwave radiative forcing.

6.3.2.3 Hygroscopicity

A change in value of $\kappa$ for marine POA from $10^{-10}$ used for G11 to 0.1 (as was used for terrestrial POA in the sensitivity tests of Liu and Wang, 2010) is expected to yield more CCN at relevant supersaturations and hence a greater impact on cloud properties and radiative forcing. However, Table 2 shows that the global and annual mean values from the G11 simulation and the G11-$\kappa$ (the simulation identical to G11 but with marine POA $\kappa$ increased to 0.1) reveal this not to be the case; model predicted low-level CDNC, LWP, and SWCF in the G11-$\kappa$ simulation are nearly equivalent to those of the G11 simulation. This small
change in cloud properties due to changing organic aerosol hygroscopicity is similar to the slight change in global surface CCN at 0.2% supersaturation, which only increased from the 184.5 cm$^{-3}$ reported in Meskhidze et al. (2011) to 185.0 cm$^{-3}$ (0.3%) in G11-$\kappa$. There are two likely reasons for this insensitivity to aerosol hygroscopicity: 1) the aging method of aerosols in CAM5 based on a criterion of 3 mono-layers of sulfate, and 2) the hygroscopicity-dependent wet removal rates in CAM5 (Liu et al., 2011). Non-seasalt sulfate concentrations within the marine boundary layer are relatively high (> 0.2 µg m$^{-3}$) over productive waters where most of the marine POA emissions are coincident with strong DMS emissions; this causes the modeled aerosol aging in these areas to be more rapid than in oceanic areas without strong DMS emissions. As a result, cloud properties and SWCF are not sensitive to the hygroscopicity of the freshly-emitted marine POA, but rather to the $\kappa$ value of aged marine POA which is the same in G11 and G11-$\kappa$. This insensitivity to the POA hygroscopicity due to sufficient aging by sulfate has been observed previously in internally-mixed particles (as are simulated by CAM5), particularly over the industrial regions (Chang et al., 2007; Prenni et al., 2007; Wang et al., 2008; Liu and Wang, 2010; Liu et al., 2011). Furthermore, the atmospheric lifetime and burden of marine POA have an inverse relationship with hygroscopicity because more hygroscopic aerosols experience wet scavenging before those with low hygroscopicity (Liu et al., 2011). As a result, the increase in CCN (at a given supersaturation) due to higher hygroscopicity is offset somewhat by the decrease due to more rapid wet removal.

6.3.2.4 Preindustrial and present day anthropogenic emissions

It has been well documented that increased anthropogenic emissions since the beginning of the industrial revolution have an impact on the present day aerosol burden and associated cloud microphysical properties. Here we examine how the climate forcing due to changes between PI and PD emissions may be influenced by marine organic aerosols. In this set of simulations, all parameters are held constant except for the anthropogenic aerosol and precursor emissions: the Default and G11 simulations use emissions for the year 2000, while
the Default-PI and G11-PI simulations use emissions for the year 1850. Recent studies suggest considerable decline (more than 6%) in ocean primary productivity over the past decade likely attributed to anthropogenic activities and associated climate change (Bopp et al., 2001; Gregg et al., 2003; Behrenfeld et al., 2006). However, the difficulties in separating the natural variability from the global climate change trend has also been proposed (Henson et al., 2010). Due to the absence of reliable ocean productivity data for PI conditions, we use the same monthly chlorophyll-a concentrations (effectively resulting in the same primary and precursor emissions for marine organic aerosols) for both G11 and G11-PI simulations. Table 2 shows that the addition of marine organics has a larger impact on cloud properties for simulations with PI emissions (differences between G11-PI and Default-PI) compared to the simulations with PD emissions (differences between G11 and Default). The global and annual mean differences in PI low-level CDNC, LWP, and SWCF are 1.4 cm$^{-3}$ (2.4%), 0.27 g m$^{-2}$ (0.6%) and -0.21 W m$^{-2}$ (0.5%), respectively, while the mean differences over the ocean are 1.9 cm$^{-3}$ (3.8%), 0.31 g m$^{-2}$ (0.9%) and -0.20 W m$^{-2}$ (0.4%), respectively. The difference in the climatic effect of marine organic aerosol with and without high levels of anthropogenic aerosols is due to the higher susceptibility of preindustrial clouds to additional aerosols (Platnick and Twomey, 1994; Lohmann and Lesins, 2002). Specifically, these simulations show that additional CCN from marine organic aerosol emissions affect the properties of clouds in clean regions more than those in polluted regions. This result is consistent with the study by Hoose et al. (2009) where the slope of the change in SWCF between PI and PD emissions decreases with increases in the prescribed aerosol concentration.

6.4 Aerosol indirect forcing

The effect of marine organic aerosols on anthropogenic AIF is explored for various model configurations. Calculations show that marine organic aerosols reduce the absolute
magnitude of the global average AIF from a default value of -1.38 W m\(^{-2}\) to -1.29 W m\(^{-2}\) (an 7\% change) when comparing the Default/Default-PI and G11/G11-PI differences. Although Wang et al. (2011) have suggested that the sensitivity of SWCF to changes in aerosol loading may be too strong in CAM5, this is not expected to have considerable influence on the relative effect of marine organic aerosols. This change in AIF by the marine OA (+0.09 W m\(^{-2}\)) is similar in magnitude to the SWCF changes between the Default and G11 simulations for both PD (-0.12 W m\(^{-2}\)) and PI (-0.21 W m\(^{-2}\)). In contrast, the SWCF change between the Default and G11-Internal for PD is a factor of 10 smaller, which suggests a much smaller change to AIF by marine OA if the marine POA emissions are considered to be internally mixed with sea salt. As described in Sec. 3.2.4, the reduction of AIF due to marine organic aerosols mainly occurs due to an increase in background low-level CDNC. This result is consistent with Hoose et al. (2009) which showed lower predictions of changes in SWCF with an increase in the minimum CDNC or aerosol concentration. Figs. 6.3a and 6.3b show that oceanic areas like the Southern Ocean and northern Atlantic Ocean, which have high marine organic emissions and low/moderate levels of CDNC, experience the largest decrease in the absolute value of AIF when marine organic aerosols are included. In the more heavily polluted oceanic region downwind of China where the AIF is the greatest, marine organic aerosols have little impact. As concentrations of marine organic aerosols are typically well below those of terrestrial and anthropogenic aerosols in all but “clean” marine air masses, it is not surprising that these areas are the most sensitive to their inclusion. Overall, our calculations suggest that the bi-directional feedbacks between marine organic aerosols, clouds and climate can have a non-trivial impact on the cloud albedo effect predicted by climate models (IPCC, 2007). Therefore, the inclusion of marine organic aerosols has the potential to improve model estimates of CCN, cloud microphysics and model-predicted shortwave radiative forcing especially over remote marine regions.
6.5 Conclusions

A treatment of marine organic aerosols has been implemented into the CAM5 coupled with MAM-7 to examine their effects on cloud properties and radiative forcing. Results show that marine organic aerosols can have large local effects on clouds (up to a 20% annual average increase in low-level in-cloud CDNC in the Southern Ocean, Northern Pacific and Northern Atlantic), especially during the summertime when chlorophyll-a concentration ([Chl-a]) is typically at a maximum. When these aerosols are included in model comparisons of pre-industrial (PI) and present day (PD) anthropogenic emissions, the model-predicted absolute value of anthropogenic aerosol indirect forcing (AIF) can be decreased by up to 0.09 W m\(^{-2}\) (7%). Predicted changes in low-level CDNC and shortwave cloud forcing due to marine organic aerosols are more sensitive to the mixing state of the primary marine organic aerosols (internal vs. external mixtures) than their hygroscopicity (chemistry). As both external and internal mixtures of marine organic aerosols and sea-salt have been observed, this sensitivity to mixing state highlights the need for improved understanding of the emission processes and their implementation in global models. The global changes in cloud microphysical and radiative properties due to marine organic aerosols are higher in the simulations with preindustrial [1.4 cm\(^{-3}\) (2.4%) and -0.21 W m\(^{-2}\) (0.5%) for low level CDNC and SWCF, respectively] than present day emissions [1.3 cm\(^{-3}\) (1.5%) and -0.12 W m\(^{-2}\) (0.3%) for low level CDNC and SWCF, respectively]. This result is consistent with studies showing that pristine clouds have the highest susceptibility to increased aerosol concentrations (Platnick and Twomey, 1994). As climate models are sensitive to the background aerosol concentration and CDNC in remote marine areas (Menon et al., 2002), this study demonstrates the importance of accurate prediction of marine aerosol-cloud-climate interactions for future assessments of model-predicted extent of human-induced climate change.
Acknowledgements

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References


Table 6.1a. Description of the CAM5 simulations\(^a\) in the Part 1 paper that are further analyzed here in this work (i.e., the Part 2 paper)

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default(^b)</td>
<td>sulfur dioxide, sulfate, terrestrial POA, terrestrial SOA, black carbon, ammonia, dust, DMS, sea-salt</td>
</tr>
<tr>
<td>SOA/MS(^\sim)</td>
<td>Same as Default but with marine SOA, MS(^\sim)</td>
</tr>
<tr>
<td>G11(^b)</td>
<td>Same as Default but with Gantt et al. (2011) marine POA emissions externally-mixed with sea-salt, marine SOA, MS(^\sim)</td>
</tr>
<tr>
<td>G11-Internal</td>
<td>Same as G11, except marine POA emissions internally-mixed with sea-salt, no marine SOA or MS(^\sim)</td>
</tr>
</tbody>
</table>

\(^a\)Simulations used the Abdul-Razzak and Ghan (2000) aerosol activation parameterization

\(^b\)Simulations were 10-years long (instead of the typical 5-years) with a 3-month spinup

Table 6.1b. Description of additional CAM5 simulations

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Emissions</th>
<th>Setup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default-PI(^b)</td>
<td>Same as Default but with anthropogenic emissions set to year 1850</td>
<td>Same as Default</td>
</tr>
<tr>
<td>Default-FN</td>
<td>Same as Default</td>
<td>Uses the Fountoukis and Nenes (2005) (FN) aerosol activation parameterization</td>
</tr>
<tr>
<td>G11-FN</td>
<td>Same as G11</td>
<td>Uses the (FN) aerosol activation parameterization</td>
</tr>
<tr>
<td>G11-PI(^b)</td>
<td>Same as G11 but with anthropogenic emissions set to year 1850</td>
<td>Same as G11</td>
</tr>
<tr>
<td>G11-κ</td>
<td>Same as G11</td>
<td>Same as G11 but with hygroscopicity value (κ) for marine POA set to 0.1</td>
</tr>
</tbody>
</table>

\(^b\)Simulations were 10-years long (instead of the typical 5-years) with a 3-month spinup
Table 6.2. CAM5 modeled mean liquid cloud properties

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Low-level CDNC (cm⁻³)ᵃ</th>
<th>Column CDNC (×10⁹ m⁻²)ᵇ</th>
<th>LWP (g m⁻²)ᵇ</th>
<th>SWCF (W m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Global</td>
<td>Ocean</td>
<td>Global</td>
<td>Ocean</td>
</tr>
<tr>
<td>Default</td>
<td>86.86</td>
<td>64.15</td>
<td>12.86</td>
<td>8.85</td>
</tr>
<tr>
<td>SOA/MS</td>
<td>85.34</td>
<td>63.62</td>
<td>12.88</td>
<td>8.80</td>
</tr>
<tr>
<td>G11</td>
<td>88.13</td>
<td>65.91</td>
<td>13.00</td>
<td>8.98</td>
</tr>
<tr>
<td>G11-Internal</td>
<td>84.93</td>
<td>62.80</td>
<td>12.77</td>
<td>8.77</td>
</tr>
<tr>
<td>Default-PI</td>
<td>58.15</td>
<td>48.69</td>
<td>8.46</td>
<td>6.66</td>
</tr>
<tr>
<td>Default-FN</td>
<td>113.51</td>
<td>90.83</td>
<td>17.81</td>
<td>13.51</td>
</tr>
<tr>
<td>G11-FN</td>
<td>114.68</td>
<td>92.27</td>
<td>17.95</td>
<td>13.62</td>
</tr>
<tr>
<td>G11-PI</td>
<td>59.52</td>
<td>50.54</td>
<td>8.60</td>
<td>6.83</td>
</tr>
<tr>
<td>G11-κ</td>
<td>86.11</td>
<td>64.82</td>
<td>12.93</td>
<td>8.94</td>
</tr>
</tbody>
</table>

ᵃAveraged from ~945-980 mb

ᵇCalculated by using the grid-cell mean
Figure 6.1. Model predicted the 10-year average in-cloud droplet number concentration (cm$^{-3}$) from 940-985 mb for the a) Default and b) G11 simulations and the c) percentage (%) change between the two simulations.
Figure 6.2. Model predicted percentage change between the G11 and Default in the 10-year average grid-mean column a) cloud droplet number, b) liquid water path, and c) shortwave cloud forcing by marine emissions.
Figure 6.3. Model predicted difference in the 10-year average shortwave cloud forcing (W m\(^{-2}\)) between the a) Default-PI and Default and between the b) G11-PI and G11 simulations.
Figure 6.S1. Model grids (in red) with significant ($p$-value of paired t-test < 0.1) differences between the G11 and Default simulations over the 10 simulation years for a) in-cloud droplet number concentration from 940-985 mb, and column b) cloud droplet number concentration, c) liquid water path, and d) shortwave cloud forcing.
Figure 6.S2. Model predicted difference in the 10-year average shortwave cloud forcing (W m\(^{-2}\)) between the G11 and Default simulations for a) all months, b) December-February, and c) July-August.
CHAPTER 7. SUMMARY AND FUTURE WORK

7.1 Summary

Ultimately, this dissertation describes the process of developing an emission scheme for primary organic aerosols, evaluating this scheme against other schemes and observations, and finally implementing these emissions into a global climate model to estimate the climatic impacts. With marine primary organic aerosols having a global emission estimate of 5-10 Tg yr\(^{-1}\), affecting regional surface cloud condensation nuclei (CCN) surface concentration changes by 20\%, and causing a 0.1 W m\(^{-2}\) (8\%) change in modeled aerosol indirect forcing, this dissertation provides compelling evidence that these aerosols require more modeling and experimental study.

In Chapter 1, the historical and recent literature of the chemical and physical characteristics of marine organic aerosol is reviewed. The mass concentration of organic aerosols in remote marine locations are typically near or below 0.5 µg m\(^{-3}\), and are derived from phytoplankton in the form of polysaccharides, proteins, and phytoplankton fragments. Recent research has shown that the number concentration of marine aerosols is influenced by marine organic aerosols, with periods dominated by marine organic aerosols having larger and more numerous particles. Furthermore, single particle and microscopy analysis suggest that marine organic aerosols are externally-mixed with sea-salt as opposed to the longstanding view that they are internally-mixed. Together, these number distribution and mixing state characteristics of marine organic aerosols suggest that they may have a potentially significant impact on climate. Studies in which marine organic aerosols have been implemented in climate models suggested that these aerosols could be potentially important for climate because they can affect cloud condensation nuclei concentrations, cloud droplet radii, and cloud droplet number concentrations.

In Chapter 2, a regional air quality modeling study in which marine emissions of isoprene, monoterpane, and primary organic aerosols (POA) is performed. The mass
concentration of organic aerosols off the coast of the Western US is simulated to be ~0.3 µg m⁻³, a value consistent with observations in remote marine areas. The two important findings of this study are that marine primary organic aerosols far outweigh secondary organic aerosols in terms of mass concentration, and that the including of marine organic aerosols improve model predicted coastal concentrations during periods of onshore flow.

In Chapter 3, a comprehensive marine primary organic aerosol emission parameterization that is a function of chlorophyll-\(a\) concentration, \([\text{Chl-a}], 10\text{ meter wind speed} (U_{10}), \text{and aerosol diameter}\) is developed. This parameterization is the first to include the negative wind speed dependence of the organic mass fraction of sea spray aerosol, which has a theoretical basis in the changes in the organic concentration of the sea surface microlayer associated with wind speed. This negative wind speed dependence results in decreased emission rates relative to existing parameterizations during periods of high winds, consistent with the seasonal cycle of marine organic aerosol concentrations. The global marine POA emission rates resulting from this parameterization are 2.8 to 5.6 Tg C yr⁻¹ depending on the treatment of aerosol hygroscopicity in the determination of the organic mass fraction of sea spray aerosol.

In Chapter 4, a global air quality modeling study is performed in which five existing marine primary organic aerosol emission schemes are evaluated against observations. These parameterizations, which have different dependences on chlorophyll-\(a\) concentration, 10 meter wind speed, and aerosol size, result in global emission rates that vary by several orders of magnitude and predict concentrations that have substantially different spatial distribution and seasonality. When evaluating the concentrations predicted by the different emission schemes to observations at time scales ranging from hourly to long-term monthly averages, the scheme with the strongest dependence on chlorophyll-\(a\) concentration had the best performance. Of the emission schemes based on the organic mass fraction of sea spray aerosol, the scheme introduced in Chapter 3 had concentrations that compared most favorably to observations. A top-down emission scheme based on the Chapter 3 scheme and
optimized to the seasonal concentration observations had a global emission rate of 6.3 Tg yr$^{-1}$. None of the emission schemes, however, were able to accurately replicate the hourly concentrations during a marine POA plume in which observed concentrations were in excess of 3.0 µg m$^{-3}$. As this plume was associated with high cloud droplet number concentrations, this inaccuracy suggest that further improvements in the emission schemes are necessary.

In Chapter 5, a global climate modeling study is performed describing the changes in surface aerosol mass concentration and cloud condensation nuclei concentration due to marine organic aerosols. The marine organic aerosol sources in the model, which include secondary organic aerosols, methane sulfonate, and two primary organic aerosol emission schemes, result in submicron aerosol mass concentration increases of 0.4 µg m$^{-3}$ and surface CCN concentration increases of 20% in biologically-productive regions with the highest emissions compared to the simulation with marine organic aerosols. The changes in surface CCN concentration are strongly influenced by the mixing state of the marine POA emissions, with the external mixture simulations having large changes in CCN while the internal mixture simulations showing little change.

Finally, Chapter 6 chronicles the changes in cloud microphysical and radiative properties due to marine organic aerosols from the modeling study described in Chapter 5. Like CCN concentrations, cloud droplet number concentration (CDNC) increased by up to 20% in biologically active areas of the remote ocean due to marine organic aerosols. Global changes in CDNC, liquid cloud effective radii, liquid water path, and shortwave cloud forcing due to marine organic aerosols range between 0.5 and 2%. In comparing the simulations with and without marine organic aerosols during preindustrial and present day scenarios, marine organic aerosols led to a 0.09 W m$^{-2}$ (7%) increase (-1.38 to -1.29 W m$^{-2}$) in the model predicted aerosol indirect forcing (AIF).

Throughout most of these chapters, there are considerable uncertainties in the prediction of surface concentration, CCN concentration, and cloud/radiative effects related to
marine organic aerosols. These uncertainties are enhanced by the scarcity of high quality aerosol observational data over remote marine regions, focus of climate and air quality model development on urban areas at the expense of remote marine regions, and lack of previous modeling studies in which emissions of marine organic aerosols are included. As a result of these uncertainties, the majority of our model analyses has been limited to reporting of the magnitude and seasonality of emissions, concentrations (mass aerosol, CCN, and cloud droplet), and radiative changes associated with marine organic aerosol on a global, long-term basis.

The extensive comparison of modeled and observed aerosol mass concentrations at a variety of temporal scales in Chapter 4, however, necessitates a discussion of the uncertainties that may also exist in the other chapters. One source of uncertainty in all the studies is the use of satellite-derived [Chl-a], which was done out of necessity to have global coverage on a high temporal basis. Chapter 3 describes root mean squared errors of ~0.2 mg m\(^{-3}\) (~30%) in Sea Wide Field-of-view Sensor (SeaWiFS)-derived [Chl-a] globally, and many of the measurement sites used in Chapter 4 are downwind of turbid Case-2 waters which are optically-complex. The monthly averaged satellite-derived [Chl-a] used to scale the marine POA emissions in Chapter 4 also suffer from the lack of data in areas of frequent cloudiness. The averaging of [Chl-a] from the \(\frac{1}{12} \times \frac{1}{12}\) to the \(2 \times 2.5^\circ\) GEOS-Chem grid likely introduces sampling bias by including only clear regions. Monthly averages of [Chl-a], while increasing the likelihood of clear regions relative to 8-day or daily data, lose the temporal variability of phytoplankton blooms which may be reflected in the aerosol measurements. Spatiotemporal averaging of the model grid also makes comparison with point observational data difficult, especially in areas with large meteorological and geographical gradients such as coastal regions. The large GEOS-Chem model grid requires simple parameterizations of the atmospheric aging and sinks of marine POA, whose values are based on that of terrestrial POA despite it having different formation mechanisms and composition. Both the emissions and deposition of marine organic aerosols are dependent on
meteorology, with the emissions driven by 10 meter wind speed and deposition dominated by the precipitation rate. Not only are the GEOS-Chem wind speed and precipitation rates averaged over different time scales (3-hr) from the emission and depositional processes (instantaneous), they are determined from observational data that is sparse over remote oceanic regions. Comparison of modeled concentrations to water soluble and insoluble organic aerosols is not straightforward because the water solubility is an operational definition. In Chapter 4, the aerosol mass spectrometer measurements suffer from a composition-dependent collection factor which requires the measured concentrations to be scaled by as much as a factor of 51 in the case of sea-salt.

When all of these uncertainties are combined, it’s possible that many of the results could be incorrect by many orders of magnitude or have a different sign. However, the comparative nature of the model analyses in this work minimizes the importance of many of these uncertainties. In GEOS-Chem, the five emission parameterizations are compared to each other and observations using the same (albeit uncertain) [Chl-a], meteorology, atmospheric sinks and aging, and spatiotemporal averaging. Because of this consistency, the emission parameterizations are equally advantaged or disadvantaged by these uncertainties and the quantifiable differences in magnitude and seasonality of the emissions/concentrations are significant. Unless the observed concentrations have a seasonal bias, emission parameterizations which have predicted concentrations with similar seasonality are likely the most realistic. The same benefits of consistency in model configuration also exist in the CAM5 studies found in Chapters 5 and 6. Besides the inclusion (or exclusion) of marine organic aerosols, there are no differences in the CAM5 simulations that affect the model outcome. As the model values from the CAM5 studies were mostly reported as changes from the Default simulation, we do not expect the uncertainties in the model to play a major role in the overall results.
7.2 Future Work

In order to expand upon the physical and chemical understanding of marine organic aerosols, more synergistic measurements are need. With any measurement of marine aerosol chemistry, measurements of meteorological and oceanic variables should also be performed. High temporal resolution measurements of these parameters would be of particular value because they would further elucidate the processes affecting the emission, formation, and atmospheric transformations of marine organic aerosols. Optimally, these measurements would be size-resolving with a high spectral resolution for climatically-relevant aerosols in the 50-500 nm in diameter size range. Single particle analysis of marine organic aerosol chemical and physical characteristics is needed alongside these bulk aerosol measurements to determine the frequency of different mixing states, unique chemical signatures, and composition. Such measurements need to be taken in many ocean regions with a diverse set of meteorological, oceanic, and biological parameters. Areas such as the tropical Pacific Ocean that have had relatively few measurements would be good candidates for future field campaigns. As the seasonality of marine organic aerosol concentrations is distinct from that of sea-salt, long-term measurements at additional sites would be helpful in formulating improved emission parameterization and evaluating existing parameterizations. In order to confirm hypotheses derived from field measurements, laboratory measurements of bubble bursting experiments need to both simulate real world conditions and systematically test the individual processes (i.e. surfactants, bubble size, wind speed, phytoplankton abundance/speciation, etc.) that may affect the chemical and physical characteristics of sea spray aerosol.

Development of marine POA sea spray functions will likely proceed in two distinct directions: 1) a size-dependent marine POA sea spray function (likely due to a combination of factors such as [Chl-a], U10, phytoplankton senescence, bacterial abundance) that is independent of sea-salt and 2) a sea spray function whose whitecap fraction is a function of biological factors ([Chl-a], phytoplankton senescence, bacterial abundance) in addition to the
power relationship with $U_{10}$. Modeling efforts attempting to further quantify the climate impact of marine organic aerosols need to be explicit in their treatment of the mixing state and hygroscopicity, and mixing state. Using the properties of terrestrial organic aerosols as a proxy for marine organic aerosols is likely not accurate due to the different sources and transport pathways for the two aerosol types.