Atmos. Chem. Phys. Discuss., 12, 21779–21813, 2012
www.atmos-chem-phys-discuss.net/12/21779/2012/
doi:10.5194/acpd-12-21779-2012

Atmospheric Chemistry and Physics Discussions

The physical and chemical characteristics of marine organic aerosols: a review

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Received: 19 July 2012 – Accepted: 12 August 2012 – Published: 23 August 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Knowledge of the physical characteristics and chemical composition of marine organic aerosols is needed for the quantification of their effects on solar radiation transfer and cloud processes. Global emission estimates of marine organic aerosol are in a range of 2 to 70 $\mathrm{Tg\,yr^{-1}}$ and occur over regions most susceptible to aerosol perturbations. This review examines research pertinent to the chemical composition, size distribution, mixing state, emission mechanism, and climatic impact of marine primary organic aerosols associated with sea spray. Numerous measurements have shown that both the ambient mass concentration of marine organic aerosol and size-resolved organic mass fraction of sea spray aerosol are related to surface ocean biological activity. Recent studies have also indicated that fine mode (smaller than 200 nm in diameter) marine organic aerosols can have a size distribution independent from sea-salt, while coarse mode aerosols (larger than 1000 nm in diameter) are more likely to be internally-mixed with sea-salt. Climate studies have found that marine organic aerosols can cause large local increases in the cloud condensation nuclei concentration, with the potential to have a non-negligible influence on the anthropogenic aerosol indirect forcing. Despite these signs of climate-relevance for marine organic aerosols, the source strength, chemical composition, mixing state, hygroscopicity, cloud droplet activation potential, atmospheric aging, and removal of marine organic aerosols remain poorly quantified. Additional laboratory, field, and modeling studies focused on the chemistry, size distribution, and mixing state of sea spray aerosols are needed to better understand and quantify their importance.

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 the remote oceans where cloud condensation nuclei (CCN) concentrations are very low ranging from few tens per cm^3 to few hundred per cm^3 (Andreae and Rosenfeld, 2008). Overcast stratocumulus/stratus, scattered shallow cumulus, or transitional mixtures of cloud types frequently present within the marine boundary layer (MBL) can have a significant impact on the underlying surface energy budget and are among the most susceptible to aerosol perturbations (Platnick and Twomey, 1994). Therefore, the lower bounds (from 0 to 40 cm^{-3}) of background marine aerosol number concentration often prescribed in global climate models (GCMs) can vary the simulated indirect effect of anthropogenic aerosols by as much as 80 % (Hoose et al., 2009). Despite recognizing their crucial role for marine boundary layer CCN budget, the size-dependent chemical composition and physical properties of marine aerosols remain 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 ∼2000–10 000 Tg yr^{-1} when limited to diameters $< 20\,\mu$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; Bates et al., 2005). 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. 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 (SSA) production (de Leeuw et al., 2011), the definition of SSA has been expanded to include both sea-salt and organics. While the sources and general chemical composition of marine organic aerosols are briefly described in these studies, they also point to many open questions involving the climate-relevant characteristics of marine organic aerosol.

It has been known for quite some time that large amounts of organic substances can be incorporated in submicron SSA (Blanchard, 1964), although the mixing state of sea-salt and organics in the marine atmosphere is still not well characterized. There have been numerous measurements of the organic aerosol concentration in the remote marine areas, with an average surface concentration of $\sim 0.5 \pm 0.4\,\mu g\,C\,m^{-3}$ (Duce, 1978; Penner, 1995). As these concentrations levels are well below that of rural continental and urban regions, relatively little attention has been devoted to the formation processes, chemical composition, and physical properties of marine organic aerosols. There are two well established marine sources of organic aerosols: (1) bubbles produced by breaking waves which scavenge surface active organic matter from the water column and through bursting inject it to the atmosphere as primary organic aerosols (POA) (Blanchard and Woodcock, 1957; Blanchard, 1964; Barger and Garrett, 1970), and (2) oxidation of phytoplankton-emitted volatile organic compounds (VOCs) such as DMS, aliphatic amines, isoprene, and monoterpenes which can form secondary organic aerosols (SOA) (Bates et al., 1992; Bonsang et al., 1992; Yassaa et al., 2008; Facchini et al., 2008a; Myriokefalitakis et al., 2010). The focus of this review is on marine POA, which have been shown to have emissions/surface concentrations that are typically higher than that of marine SOA (Arnold et al., 2009; Gantt et al., 2009, 2010; Myriokefalitakis et al., 2010). Some of the open questions concerning marine POA that are addressed in this review include:

1. What is the current understanding of the size-resolved organic composition of SSA?
2. Are SSAs external or internal mixtures of organics and sea-salt?

3. Does the organic fraction of SSA influence aerosol size distribution, CCN concentrations, and cloud microphysical properties?

2 Chemistry

2.1 Bulk aerosol concentrations

With improvements and increased abundance of aerosol measuring instrumentation, a more comprehensive understanding of the spatial distribution and temporal variation in marine organic aerosol concentrations has emerged. The first detectors of organic material in SSA used surface active nature of organics to separate them from sea-salt (Blanchard, 1964). Barger and Garrett (1970) collected SSA 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 $\mu g\,m^{-3}$, 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 $\mu g\,m^{-3}$. This was the first of many measurements of the organic aerosol concentration in the remote marine boundary layer averaging $\sim 0.5\,\mu g\,m^{-3}$ (Duce, 1978). Recently, the upper range of observed organic aerosol concentrations in the remote marine boundary layer has been increased with aerosol mass spectrometer-derived concentrations of up to 3.8 $\mu g\,m^{-3}$ in the North Atlantic Ocean (Ovadnevaite et al., 2011a). A summary of selected measurements of marine organic aerosol concentrations can be found in Table 1 and Fig. 1. Long-term measurements at Mace Head, Ireland in the North Atlantic Ocean and Amsterdam Island in the Southern Indian Ocean have found that the concentration of organic aerosols of marine origin follow a strong seasonal cycle, with the highest concentrations 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.

In addition to measurements reporting only organic aerosol concentration values, several studies have reported an organic carbon (OC) to sea-salt mass ratio (OC/SS). The OC/SS can be a useful parameter for modeling studies as the marine POA emission rates can be scaled to the model-derived sea-salt emission rate. 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 that varied from 0.3 to 0.7 on sea spray particles while Barger and Garrett (1970) found a lipoid/salt ratio from 0.07 to 0.14. In Barger and Garrett (1970), the OC/SS was observed to increase with increasing wind speed; this was thought to be associated with increased transport of adsorbed surface active material from the sea surface to the atmosphere with higher winds. Hoffman and Duce (1974) reported an OC/SS of 0.01 to 0.19 in Bermuda, with the ratio decreasing with increasing salt concentration. Long-term measurements of sea-salt and organic aerosols at two coastal sites (Mace Head and Amsterdam Island) show that like the organic aerosol concentration, the OC/SS 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). This seasonality is consistent with that of the marine-source low molecular weight fatty acid/sea-salt ratio in the North Pacific Ocean (Mochida et al., 2002). Recent work quantifying organic mass fraction of sea spray aerosol (OM_{SSA}) using an organic-inorganic sea spray function (O'Dowd et al., 2008) is described Sect. 4. Generally, past studies show that the average organic aerosol bulk concentration and OC/SS in remote marine environments is $0.5\,\mu g\,m^{-3}$ and 0.1, respectively, with 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.

2.2 Bulk aerosol composition

As the ocean surface is proposed to be the major source of marine POA, measurements of the chemical composition of subsurface seawater and the sea surface microlayer 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 being minor components (Myklestad, 1995; Penna et al., 1999; Wurl et al., 2009). Relative to sea-salt, organic concentration in the subsurface seawater, sea surface microlayer, and sea spray aerosols can be very different, with the OC/SS ratio increasing from $\sim 10^{-4}$ in the subsurface water to $\sim 10^{-3}$ in the sea surface microlayer and ~ 1 in the aerosol (Russell et al., 2010).

Stable carbon isotopic analysis in seawater organic compounds is one tool that can be used to identify marine organic aerosols. Due to their differences in the supply of inorganic carbon, several studies (Williams and Gordon, 1970; Eadie et al., 1978; Fontugne and Duplessy, 1978, 1981; Loh et al., 2004) have found a δ^{13}C (^{13}C/^{12}C ratio relative to that of the Pee Dee Belemnite standard) value of approximately -20 ± 2 ‰ for protein-like fraction, carbohydrates, and dissolved organic carbon in ocean water and approximately -27 ± 2 ‰ for organic carbon derived from terrestrial plants. Identification of unique chemical signatures of organic compounds in the subsurface seawater and sea surface microlayer such as carbohydrates and δ^{13}C values has enabled improved documentation of the sources and formation mechanisms of marine organic aerosols.

Analysis of the composition of airborne marine organic particles over the remote MBL has been consistent with that of the sea surface microlayer, with evidence of carbohydrates (Leck and Bigg, 2005; Facchini et al., 2008b; Russell et al., 2010), amino acids (Leck and Bigg, 1999), lipids (Mochida et al., 2002), 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. Beginning with Chesselet (1981), several studies have used the δ^{13}C 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 δ^{13}C and ^{14}C (whose values in fossil fuel derived aerosols are depleted due to radioactive decay) isotopic analysis to differentiate terrestrial, anthropogenic, and marine organic aerosol sources; 80 % of the organic aerosol mass concentration measured during clean marine conditions at the Mace Head experimental station was found to have a marine source likely associated with plankton emissions. Using an aerosol time-of-flight mass spectrometer, Gaston et al. (2011) detected unique magnesium (Mg)-type particles containing Mg^{2+}, Ca^{2+}, 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*]. In the Arctic, Orellana et al. (2011) found that marine-source organic microgels stabilized by Ca^{2+} ionic bonds and identifiable by staining with chlortetracycline were a major contributor to CCN concentrations. Independent of terrestrial and anthropogenic proxies such as black carbon and radon, spectroscopic, isotopic, and microscopic analyses of organic aerosols can be used to identify a marine source.

2.3 Size-resolved aerosol concentrations

Sea spray chemical composition has been repeatedly shown to vary considerably with aerosol size. As the size of an aerosol is important for its CCN activity, size-resolved concentrations of specific aerosol types give valuable information in determining their climatic impact. Despite having low bulk concentrations as described in Sect. 2.1, marine organic aerosols can have a high climatic impact due their relatively large mass (and number depending on the mixing state) concentration in the accumulation mode (diameters between ∼ 50 and 300 nm) compared to other aerosols present in remote MBL. Beginning with the Barker and Zeitlin (1972) and Hoffman and Duce (1977) use of cascade impactors to determine size-resolved SSA chemistry, most studies have found that with a decrease in aerosol diameter marine organics make up a progressively larger mass fraction of SSA. 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 fraction of accumulation mode aerosol mass concentration over the North Atlantic Ocean is related to ocean biological productivity, with organics making up $>60\,\%$ of aerosol mass during high biological activity (HBA) periods and $<20\,\%$ during low biological activity (LBA) periods. Subsequent measurements by Rinaldi et al. (2010) and Miyazaki et al. (2010) also revealed progressively larger contributions of organic aerosol to total aerosol mass with decreasing particle size and increasing surface ocean biological activity. These measurements are summarized in Fig. 2 with the high and low biological activity measurement periods denoted with red and blue lines, respectively.

In bubble bursting experiments replicating nascent SSA emission, Keene et al. (2007) and Facchini et al. (2008b) found that the $\mathrm{OM_{SSA}}$ can be up to ∼ 80 % at the smallest aerosol sizes. Such high organic mass fractions in accumulation mode sea spray aerosols have not been found in all bubble-bursting experiments. Using the hygroscopic growth of SSA to determine the presence of organics (see Sect. 2.5), Sellegri 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 $8\pm6\,\%$ for aerosols between 71 and 77 nm in diameter with little variability in the organic volume fraction for aerosol with diameters between 38 and 173 nm. Using laboratory grown phytoplankton cultures, Fuentes et al. (2011) estimated (through HTDMA measurements) a submicron aerosol organic volume fraction ranging from 8 to 37 %. Currently, 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 by different research groups to be conducted under the same environmental conditions and using the same seawater.

2.4 Size-resolved aerosol 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 particles less than 50 nm in diameter, previously thought to be formed only through nucleation, display characteristics of fragmented aggregates of microcolloids. TEM images of marine aerosols from multiple locations led Leck and Bigg (2008) to conclude that in the size range from 50 to 200 nm in diameter sea-salt aerosols are nearly absent and the aggregates of microcolloids and exopolymer secretions are the dominant organic aerosol type. In the size range from 200 to 1000 nm in diameter, Hawkins and Russell (2010) using NEXAFS analysis showed that marine organic aerosols were mostly calcareous phytoplankton fragments and low-solubility polysaccharides. In the supermicron sized particles, Hawkins and Russell (2010) found that marine organic aerosols were mostly composed of carboxylic acid-containing polysaccharides mixed with sea-salt aerosol. For Northern Pacific sea spray aerosols in the size range from 500 to ~2500 nm in diameter, Gaston et al. (2011) reported a number concentration of Mg-type particles (proxy for marine organic aerosols) which peaked at the smallest measured diameter (500 nm) and decreased with size. This was in contrast to sea-salt, whose number concentration increased as the aerosol diameter increased from 500 to 1000 nm before decreasing with size for aerosols > 1000 nm in diameter (Gaston et al., 2011). The marine-source organic microgels identified by Orellana et al. (2011) as being a major CCN contributor in the Arctic had a number concentration whose two modes (a major Aitken mode and very minor accumulation mode) peaked at ∼ 10 nm and ∼ 175 nm in diameter. These different measurement techniques focused on different aerosol sizes show that marine organic aerosols typically are more abundant than sea-salt at smaller aerosol sizes and that their chemical composition changes with size.

2.5 Aerosol hygroscopicity and volatility

For marine aerosols, the growth factor (GF, defined as the ratio of wet and dry particle mobility diameters) and volatility have been used to give the relative contribution of sea-salt, sulfate, and organic aerosols. The reference GFs of various marine aerosol chemical components 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 terms of reference volatilities, semi-volatile organic compounds typically volatilize at temperatures < 100 °C, sulfate at 160 °C, and very low volatility organics and sea-salt remaining at 600 °C (Qian and Mopper, 1996; Spyres et al., 2000; de Leeuw et al., 2007). 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). Relative to the more-hygroscopic (GF ∼ 1.5) group, the highly-hygroscopic (sea-salt) group was less frequently present in the marine environments (Swietlicki et al., 2008). During HBA periods in the North Atlantic Ocean, Cavalli et al. (2004) measured a GF of 1.2 for aerosols with diameters < 125 nm. Recently, Ovadnevaite et al. (2011b) 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 ($> 12\,\mathrm{m\,s^{-1}}$ at a height of 35 m) and a GF of 1.5 during low winds ($< 3\,\mathrm{m\,s^{-1}}$ at 35 m). Hultin et al. (2010) found that the fraction of HBA North Atlantic sea spray aerosols that are semi-volatile (evaporated at 300 °C) varied by aerosol size, with the highest semi-volatile fraction (~ 35 %) occurring with particles 140–150 nm in diameter. In bubble bursting experiments of seawater off the Australian coast representing nascent sea spray emissions, Modini et al. (2010a) observed a low semi-volatile (evaporated at temperatures between 200 and 500 °C) 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 infer the aerosol chemistry at sizes difficult to measure using mass-based methods. The measurements indicate that the biological activity and environmental conditions can affect the relative amounts of organic and sea-salt in sea spray aerosol.

3 Physics

3.1 Aerosol size distribution

Concurrent measurements of marine aerosol size distribution and chemical composition have shown that the marine organic aerosol number size distribution can be distinct from that of sea-salt. Historically, the number size distribution of marine organic aerosols could only be approximated because typical aerosol sizing techniques did not include chemistry. Novakov and Penner (1993) made one of the first estimates of the number size distribution through the application of the Twomey inversion algorithm (Twomey, 1975) to aerosol mass concentrations measured by cascade impactor at a site in Puerto Rico. Novakov and Penner (1993) found that due to their high numbers in the size range between 50 and 200 nm in diameter, organic aerosols that were later described as having a marine source (Novakov et al., 1997) made up a major part of the aerosol number concentration and CCN fraction. 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 WIOM for aerosols with diameters < 200 nm was the highest of any chemical species (i.e., sea-salt, sulfate, ammonium, nitrate, WSOM, and black carbon) 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; Yoon et al., 2007). de Leeuw et al. (2007) found that the size distribution of marine aerosol number concentration in the 200 to 500 nm aerosol diameter range was affected by the inlet temperature, with the heated inlet (which at 300 °C measured mostly sea-salt and very low volatility organics) having a number concentration two orders of magnitude lower than that of the non-heated inlet. The same setup of de Leeuw et al. (2007) showed less than an order of magnitude difference between heated and non-heated inlets when aerosols larger than 1000 nm in diameter were examined. Russell et al. (2010) found a positive linear relationship between the number mean diameter of CCN 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. (2011b) reported similar results in an AMS study at Mace Head, finding that periods with high organic mass fractions and low growth factors also had a higher weighted average particle size and increased number concentration in the 100 to 500 nm diameter range.

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 geometric mean 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 result similar to that of the calm conditions experiments of Sellegri et al. (2006), with 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 from the tropical Atlantic Ocean resulted in higher Aitken mode number concentration from HBA waters relative to LBA waters (Fuentes et al., 2010). Compared to the bubble bursting experiments of artificial seawater, Tyree et al. (2007) did not observe any change in accumulation mode geometric mean diameter (~ 90 nm) during the addition of oleic acid but did find that the total number concentration increased by 50 %. Overall, these laboratory studies suggest that presence of marine organic matter increases the aerosol flux from seawater and it could be other environmental conditions such as wind speed (and its influence on bubble bursting dynamics) that affect the modal diameters of the resulting sea spray aerosol size distribution.

3.2 Aerosol 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, methane sulfonate) has been suggested to impact the cloud droplet number concentration over the ocean (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 with individual sea-salt particles. This finding was consistent with the hypothesis of an internal mixture of sea-salt and organic aerosols prevalent in earlier studies (Pueschel and Van Valin, 1974; Hoffman and Duce, 1976; Gershey, 1983; Tseng et al., 1992). However, more recent analyses suggest that some marine organic aerosols and sea-salt may be externally-mixed. Using an aerosol time-of-flight mass spectrometer 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). Volatility measurements of sea spray aerosols up to 230 nm in diameter produced by bubble bursting experiments with seawater from the biologically-active North Atlantic Ocean showed a decrease in sea spray particle number when a 300 °C heated inlet was used relative to an unheated inlet, indicating an external mixture of sea-salt and organics (Hultin et al., 2010). TEM analysis 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 material (Bigg and Leck, 2001, 2008; Leck and Bigg, 2005, 2008; Leck et al., 2002; Pósfai et al., 2003). The reduction (to near absence) in the frequency of sea-salt visible in aerosols < 200 nm in diameter from TEM analysis suggests that SSA is an external mixture of sea-salt and organics (with the majority of aerosols being organic) in this size range (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. The overall consensus of available studies is that marine organic aerosols seem to be both internally- and externally-mixed with sea-salt, with smaller aerosols (< 200 nm in diameter) more likely to be externally-mixed and larger aerosols (> 1000 nm in diameter) more likely to be internally-mixed.

4 Marine organic aerosol emissions

Historically, the only estimate for the emissions of marine organic aerosols came from Duce (1978) who estimated a global rate of $14\,\mathrm{Tg\,C\,yr^{-1}}$ ($20\,\mathrm{Tg\,yr^{-1}}$ assuming an OM/OC ratio of 1.4) based on a uniform OC/SS ratio of 14×10^{-3} and sea-salt emissions of $1000\,\mathrm{Tg\,yr^{-1}}$ (Eriksson, 1959). Two recent 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 *a*] 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 11 $\mathrm{Tg\,yr^{-1}}$, of which 8 $\mathrm{Tg\,yr^{-1}}$ 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 70 $\mathrm{Tg\,yr^{-1}}$. Based on the measurements from Mace Head, Ireland, O'Dowd et al. (2008) introduced concept of a combined inorganic-organic sea spray function, with $\mathrm{OM_{SSA}}$ having a linear dependence with [chl *a*]. 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 *a*], including revisions to the linear dependence of $\mathrm{OM_{SSA}}$ (Langmann et al., 2008; Vignati et al., 2010; Long et al., 2011), size-dependence of the SSA production flux (Vignati et al., 2010), size-dependence of the $\mathrm{OM_{SSA}}$ (Long et al., 2011; Gantt et al., 2011), number distribution of the SSA production flux (Fuentes et al., 2010), and wind speed dependence of $\mathrm{OM_{SSA}}$ (Gantt et al., 2011). These different studies using $\mathrm{OM_{SSA}}$ as an emission parameter have global marine organic aerosol emission rates that vary in magnitude ($\sim$ 2–20 $\mathrm{Tg\,yr^{-1}}$) and spatiotemporal distribution (higher emission rates over high [chl *a*] regions). 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 aerosol source function and $\mathrm{OM_{SSA}}$ 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 monthly time scales.

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Interactive Discussion

5 Impact on climate

With observations of the chemical and physical characteristics and development of size-resolved aerosol emission parameterizations linked to sea spray number and/or mass fluxes, it is possible to estimate climatic impact of marine organic aerosols. By using the derived number size distribution of different aerosol types (estimated by applying the Twomey inversion algorithm (Twomey, 1975) to aerosol mass concentrations) and measured condensation nuclei (CN) concentration, 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. O'Dowd et al. (2004) used the chemical composition of size-resolved mass concentrations and number size 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. (2011b) found that periods which had aerosols with high organic fractions also had high observed 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 $\mathrm{Tg\,C\,yr^{-1}}$ distributed between the Aitken and accumulation modes and externally-mixed with sea-salt increased North Atlantic CDNC by a factor of 3–4 ($\sim$ 35 to 120 $\mathrm{cm^{-3}}$) 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), described how the SSA mixing state determines the climatic impact. In the model, marine organic aerosols externally-mixed with sea-salt were added as additional aerosol number and mass while the internally-mixed marine organic aerosols were only added as mass. Calculations show that addition of externally-mixed marine organic aerosol caused increases in the regional and global CCN surface concentrations by 20 % and 1.3 %, respectively and produced a 7 % reduction in model-predicted aerosol indirect forcing. In the simulations with internally-mixed marine organic aerosol, the CCN surface concentration and aerosol indirect forcing were not substantially different than the simulation without the inclusion of 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 SSA 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 internally-mixed SSA, surface CCN concentrations decreased by 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 climatic impact: the higher hydrophobicity and lower CCN activity of organic matter in sea spray aerosol results in small changes in CCN concentration associated with marine organic aerosols and negligible impact on cloud formation. However, extrapolation of the laboratory measurements of nascent sea spray aerosol production to the cloud and climate scales should be done with caution as marine organic aerosols could be of considerable importance to marine CCN concentrations even if they are emitted at a size below the critical diameter for aerosol activation. Such organic aerosols could serve as growth nuclei for CCN through condensational growth by deposition of sulfate derived from DMS oxidation (Leck and Bigg, 2005). As the understanding of mixing state and CCN impact of marine organic aerosol emissions is evolving, future climate studies would be well served to assume both external and internal mixtures of organics and sea-salt in

SSA and incorporate detailed aerosol microphysics in order to place upper and lower bounds on the climatic impact of marine organic aerosol.

6 Discussion and future directions

As marine organic aerosols have received considerable research interest in the last decade, improvements in instrumentation and computer modeling have enabled a more comprehensive and quantitative view of their chemistry, physics, and potential climatic impact. Although certain locations near biologically productive waters can have episodic high concentrations ($> 3.0\,\mu\mathrm{g\,m^{-3}}$), the average mass concentration of marine organic aerosols is typically less than $0.5\,\mu\mathrm{g\,m^{-3}}$. Due to their low concentrations and number distribution mainly in the accumulation mode, marine organic aerosols present some measurement challenges including having concentrations below the detection limit and the majority of aerosol number concentration below the minimum size cut-off of some instruments like the cascade impactor. 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 climate-relevant size range between ~ 50 and 150 nm in diameter. The organic mass fraction of sea spray aerosol 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 seawater chemical and biological composition and meteorological fields 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 emission estimates of submicron marine organic aerosol have averaged $\sim 10\,\mathrm{Tg\,yr^{-1}}$ but vary by nearly an order of magnitude in different studies.

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 hypotheses of the existence of external mixtures of marine organic aerosols and sea-salt, changes in the aerosol number distribution due to marine organics, and the dominance of marine organic aerosol (relative to sea-salt aerosol) for diameters between 50 and 150 nm that are particularly important for their ability to serve as cloud condensation nuclei (CCN). Combined, these hypotheses 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, 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 $\sim 0.1\,\mathrm{W\,m^{-2}}$ (7 %). Future development of marine organic aerosol emission parameterizations will likely proceed in two distinct directions: (1) a size-dependent marine organic aerosol source function (likely a function of chlorophyll *a* concentration, 10 m wind speed, dissolved organic carbon, phytoplankton senescence, and/or bacterial abundance) that calculates the number and mass emission rates independent of sea-salt or (2) an updated sea spray source function whose whitecap fraction and number size distribution are a function of several oceanic biological/chemical factors ([chl *a*], phytoplankton senescence, bacterial abundance, dissolved organic carbon) in addition to the existing power relationship with 10 m wind speed. Modeling efforts attempting to further quantify the climatic impact of marine organic aerosols need to be explicit in their treatment of the size distribution, mixing state, hygroscopicity, atmospheric transformations, and removal of marine organic aerosols.

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 chemical/biological 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 climate-relevant aerosols in the 50–150 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 ones. In order to test and expand the 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, dissolved organic carbon, etc.) that may affect the chemical and physical characteristics of sea spray aerosol.

Acknowledgements. This research was supported by the Office of Science (BER), US Department of Energy Grant No. DE-FG02-08ER64508. BG is also supported by the NASA Earth and Space Science Fellowship (NESSF) Program.

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Table 1. Summary of selected measurements of remote marine organic aerosol concentrations.

Location	Lat	Lon	Month	Conc.	Reference
Bermuda	32.2	−64.9	May	0.29	Hoffman and Duce (1974)
North Atlantic	45.0	−20.0	Dec–Feb	0.76	Ketseridis et al. (1976)
Eastern Tropical Pacific	−1.0	−88.0	Feb	0.32	Barger and Garrett (1976)
Eastern Tropical Pacific	4.0	−85.5	Feb	0.49	Barger and Garrett (1976)
Bermuda	32.2	−64.9	Jun	0.25	Hoffman and Duce (1977)
Hawaii	21.4	−147.7	Jul–Oct	0.39	Hoffman and Duce (1977)
Samoa	−14.3	−170.6	Jun–Aug	0.22	Hoffman and Duce (1977)
West coast of Ireland	53.3	−9.9	Jun–Jul	0.57	Eichmann et al. (1979)
Tasmania	−40.7	144.7	Feb	0.53	Eichmann et al. (1980)
Tasmania	−40.7	144.7	Sep	0.23	Andreae (1982)
Tropical Atlantic	−20.0	−40.0	Nov	0.31	Andreae (1983)
North Atlantic	40.0	−10.0	Oct	0.30	Andreae (1983)
Equatorial Pacific	18.0	−140.0	Jul	0.30	Andreae et al. (1984)
Equatorial Pacific	0.0	−115.0	Aug	0.25	Andreae et al. (1984)
Equatorial Pacific	0.0	−140.0	Aug	0.15	Andreae et al. (1984)
Bermuda	32.2	−64.9	Jan–Feb	0.57	Wolff et al. (1986)
Eastern Atlantic	35.7	−22.0	May	0.28	Cachier et al. (1986)
Samoa	−14.3	−170.6	Jul–Aug	0.11	Cachier et al. (1986)
Peruvian coast	−15.0	−80.0	Mar–Apr	0.16	Cachier et al. (1986)
Amsterdam Island	−37.8	77.6	Feb	0.15	Cachier et al. (1986)
New Zealand coast	−34.4	172.7	Jun–Aug	0.13	Cachier et al. (1986)
Puerto Rico	18.3	−65.8	Mar–Apr	0.66	Novakov and Penner (1993)
Puerto Rico	18.4	−65.3	Feb–Jun	0.39	Novakov et al. (1997)
North Pacific	32.9	−165.7	Mar	0.24	Carrico et al. (2003)*
South Atlantic	−44.0	−60.0	Jan–Feb	0.32	Zorn et al. (2008) bloom
South Atlantic	−40.0	0.0	Jan–Feb	0.03	Zorn et al. (2008) clean
South Atlantic	−60.0	−40.0	Jan–Feb	0.02	Zorn et al. (2008) Antarctic
Tropical North Atlantic	17.0	−25.0	May	0.25	Lee et al. (2010)
Tropical North Atlantic	21.0	−22.0	May	0.50	Lee et al. (2010)
North Atlantic	43.7	−58.0	Mar	0.50	Russell et al. (2010)*
North Atlantic	58.5	−22.2	Mar	0.21	Russell et al. (2010)*
North Atlantic	72.0	16.9	Apr	0.42	Russell et al. (2010)*
North Atlantic	78.6	9.1	Apr	0.32	Russell et al. (2010)*
North Atlantic	72.1	−9.1	Apr	0.23	Russell et al. (2010)*
North Pacific	25.0	155.0	Sep	0.76	Miyazaki et al. (2011)
North Pacific	43.0	155.0	Aug	1.11	Miyazaki et al. (2011)
North Pacific	31.0	175.0	Nov	0.16	Fu et al. (2011)
North Pacific	30.0	−160.0	Nov	0.06	Fu et al. (2011)
North Pacific	32.0	−135.0	Nov	0.08	Fu et al. (2011)
North Atlantic	30.0	−60.0	Dec	0.23	Fu et al. (2011)
North Atlantic	30.0	−35.0	Dec	0.18	Fu et al. (2011)

* Submicron values with EC $< 0.1\,\mu g\,m^{-3}$.

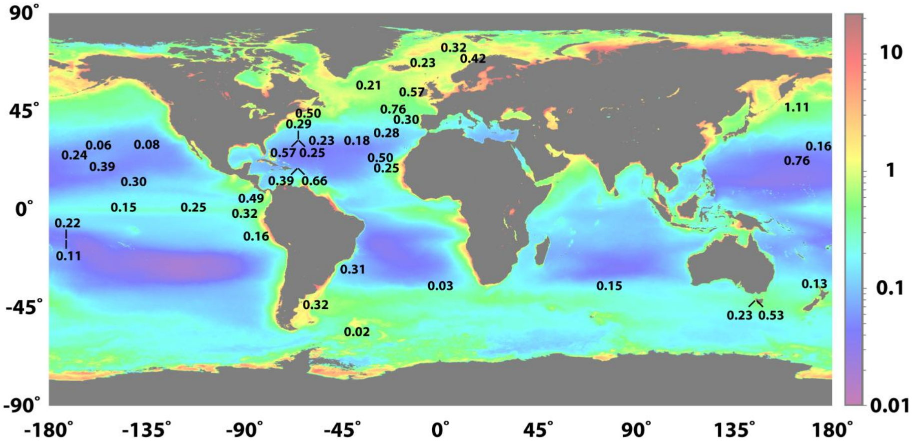

Fig. 1. Climatological chlorophyll *a* concentration (mg m^{-3}) from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) superimposed with selected organic aerosol concentration measurements (µg C m^{-3}) in remote marine locations. See Table 1 for measurement details and references.

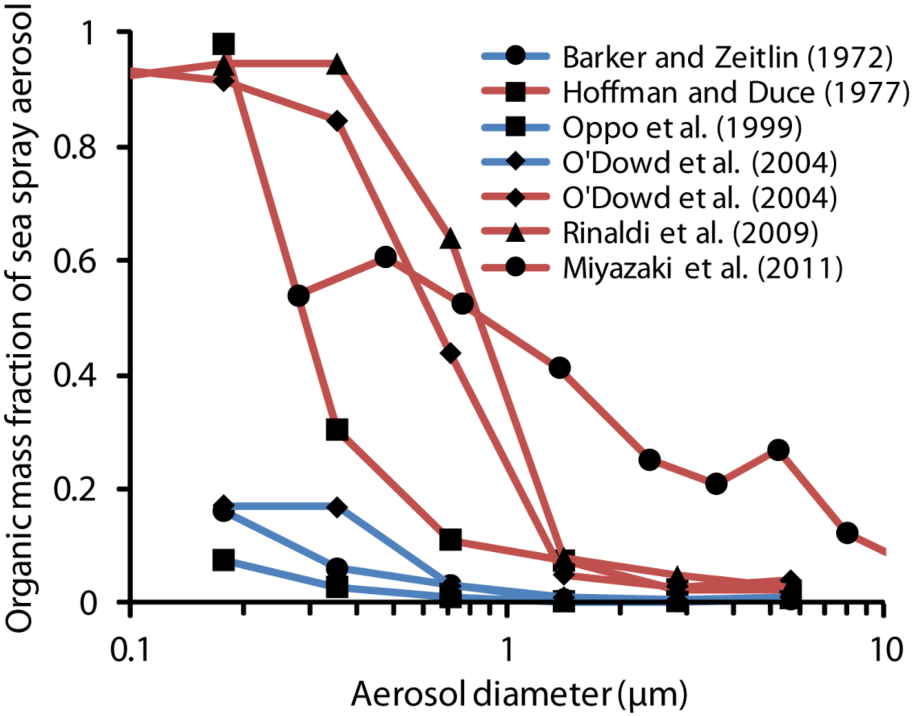

Fig. 2. Size-resolved organic mass fraction of sea spray aerosol measured in remote marine locations. The blue lines represent low biological activity periods and red lines represent high biological activity periods.