

Wind speed dependent size-resolved parameterization for the organic mass fraction of sea spray aerosol

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Abstract. For oceans to be a significant source of primary organic aerosol (POA), sea spray aerosol (SSA) 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 (OM_{SSA}). 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-*a*, dissolved organic carbon, and particulate organic carbon. Of all the parameters examined, a multi-variable logistic regression revealed that the combination of 10 m wind speed and surface chlorophyll-*a* concentration ($[Chl-a]$) are the most consistent predictors of OM_{SSA} . This relationship, combined with the published aerosol size dependence of OM_{SSA} , resulted in a new parameterization for the organic mass fraction of SSA. Global emissions of marine POA are investigated here by applying this newly-developed relationship to existing sea spray emission functions, satellite-derived $[Chl-a]$, and modeled 10 m winds. Analysis of model simulations shows that global annual sub-micron 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.

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) (Lohmann et al., 1999, 2007; Takemura et al., 2005; Wang and Penner, 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% (Kirkevåg et al., 2008; Hoose et al., 2009). Changes of this magnitude can have profound effects on the model-predicted extent of human-induced climate change and highlight the need for improved quantification of marine aerosol number size distribution and chemical composition over remote marine regions.

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 sub-micron aerosol mass concentration near biologically productive waters (O'Dowd et al., 2004). Marine boundary layer organic aerosol concentrations, while typically averaging between 0.2 and 0.5 $\mu\text{g m}^{-3}$ (Russell et al., 2010), have been shown to be up to 3.8 $\mu\text{g m}^{-3}$ on the Atlantic coast of Ireland 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.,



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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 (Bonsang et al., 1992) or from the chemical transformation of primary or secondary components present in the condensed phase (Rinaldi et al., 2010). 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). 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 chlorophyll-*a* ([Chl-*a*]), dissolved organic carbon ([DOC]), and particulate organic carbon ([POC]) can be used as a proxy for the organic mass fraction of sea spray aerosol (OM_{SSA}) (Gershey, 1983a, b; Hoffman and Duce, 1976; O'Dowd et al., 2004, 2008; Russell et al., 2010). Most of the recent parameterizations of marine POA emissions use [Chl-*a*] as a proxy for deriving the organic mass fraction of sea spray aerosols (O'Dowd et al., 2008; Vignati et al., 2010) or for determining the total magnitude of the emissions (Spracklen et al., 2008). 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 should 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 SSA). Here, we examine the factors that affect the emission of marine primary organic aerosols (POA).

Laboratory and ambient measurements have revealed that the ratios of organic carbon (OC) to sodium (Na) in subsurface waters range from 10^{-4} to 10^{-3} , whereas submicron aerosol-phase ratios of OC/Na range from 10^{-1} to 1 (Blan-

chard, 1964; Gershey, 1983a; Hoffman and Duce, 1974, 1976; Oppo et al., 1999; Keene et al., 2007; Facchini et al., 2008; Russell et al., 2010). The exact mechanism for such large organic mass fraction (and roughly by 2 to 3 orders of magnitude organic enrichment relative to subsurface waters) of submicron SSA is not well defined. It is thought that when ocean bubbles generated by the entrainment of air due to wave action rise to the surface, the surface active material in the bulk water aggregates to the walls of the bubbles. When these bubbles reach the water surface after having been enriched in organics relative to the bulk sea water, they burst and eject the organics absorbed on their surface into the atmosphere along with dissolved inorganic constituents of seawater (Blanchard, 1964). The amount of organics absorbed on the bubble surface is thought to be mainly controlled by the abundance of dissolved and particulate organic matter of the subsurface water (broadly characterized as lipids, amino and fatty acids, mono- and poly-saccharides, humic substances, and phytoplankton cell fragments) (Benner et al., 1992; Millero, 2006). However, not all the organic material brought to the surface gets aerosolized. A significant amount of biogenic organic matter can accumulate at the air-sea interface, forming an organic film (the "sea surface microlayer", SML) (Blanchard, 1964; Gershey et al., 1983b; Liss and Duce, 1997). Bubble-mediated processes also are not the only mechanism for forming SML. Transparent copolymer particles (TEP) formed from dissolved exudates released by phytoplankton and bacteria are positively buoyant and able to ascend the water column (Alldredge et al., 1993; Azetsu-Scott and Passow, 2004). These gel-like clumps are mostly polysaccharide, negatively charged, very sticky particles ranging in size from ~ 2 to $\sim 200 \mu\text{m}$ and present in high concentrations in most sea and freshwaters (Azetsu-Scott and Passow, 2004). The ascending TEP can initiate the formation of natural biofilms on surfaces even under calm conditions. Overall, a number of water column processes (convection, mobile biota, biota attached to buoyant particles, bursting bubbles, buoyant TEPs, diffusion and wave motion) can regulate the accumulation and reduction of material in SML (Wurl and Obbard, 2004; Cunliffe et al., 2011). Past studies have shown that the SML can have a strong influence on the bubble-bursting process at the air-sea interface and submicron marine aerosol production and chemical composition (e.g., Ellison et al., 1999; O'Dowd et al., 2004).

Currently there is a large uncertainty regarding the chemical and biological heterogeneity, depth, and spatiotemporal variability of the SML with no consensus even on the most appropriate strategy for sampling (Agogu e et al., 2004; Cunliffe et al., 2011). As the importance of ambient parameters in the formation and distribution of the SML have not been well established (Carlson, 1982, 1983; Williams et al., 1986; Liu and Dickhut, 1998; Wurl et al., 2009, 2011), in this study we consider the effect of the SML on OM_{SSA} as being in three different regimes based on sea surface wind speed: (1) high OM_{SSA} occurring under the conditions

when biogenic SML covers the majority of the sea surface, (2) moderate OM_{SSA} when SML only covers a portion of the sea surface often appearing as visible slicks or streaks, and (3) low OM_{SSA} when SML coverage is strongly reduced due to wave action. Figure 1 shows our interpretation of the relationships between the organic fraction of sea spray aerosol, SML coverage, and surface wind speed based on a review of previous works described below. This figure suggests that for given chemical composition of seawater, the largest coverage of sea surface by SML is expected during calm winds. An increase in wind speed above $3\text{--}4\text{ m s}^{-1}$ will cause a rapid decrease of the SML coverage (the Langmuir circulations starts breaking up the film and formation of slicks and streaks), and its effective removal for wind speeds in exceed 8 m s^{-1} (when the wave breaking thoroughly mixes the SML with the underlying water resulting in homogeneous water column). Although there is significant spread in observational data, most of the studies agree that SMLs in the open ocean are more typically observed under completely calm conditions when the large fraction of the ocean surface may be covered by the monomolecular layer of the organics (Dietz and Lafond, 1950; Williams et al., 1986; Romano, 1996). As winds increase from $2\text{ to }5\text{ m s}^{-1}$, SML can be collected into visible streaks or slicks (Welander, 1963; Leibovich, 1983; Williams et al., 1986; Liu and Dickhut, 1998; Obernosterer et al., 2008) with the subsequent increase in the formation of gaps and a decrease in the satellite-derived areal extent of SML (Marmorino et al., 2008). This increase of gaps and decrease in SML areal 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). Wurl et al. (2009) also report a decrease in TEP concentrations in the SML with wind speed, although such a reduction in the concentration with wind speed was not consistent for total surface active material (Wurl et al., 2011). When surface winds exceed 8 m s^{-1} , the initiation of wave breaking is expected to cause the destruction of the SML by mixing it into the underlying seawater (Carlson, 1983). Extrapolation of the linear decrease in SML thickness with wind speed observed by Liu and Dickhut (1998) predicts the absence of the SML at a wind speed of $\sim 8.5\text{ m s}^{-1}$, consistent with this picture.

In addition to total organic mass fraction of submicron aerosol, several attempts have recently been carried out to quantify and characterize size-dependent chemical composition of SSA. These measurements consistently have shown that the organic mass fraction of submicron SSA increases with decreasing particle size (Oppo et al., 1999; Keene et al., 2007; Facchini et al., 2008; Fuentes et al., 2010), with a small and relatively constant organic mass fraction for supermicron particles with aerodynamic diameter $<10\text{ }\mu\text{m}$ (Oppo et al., 1999; Keene et al., 2007; Facchini et al., 2008). Keene et al. (2007) reported that the water soluble organic carbon mass fraction of artificially generated aerosols within a chamber was highest in size fraction with geometric mean

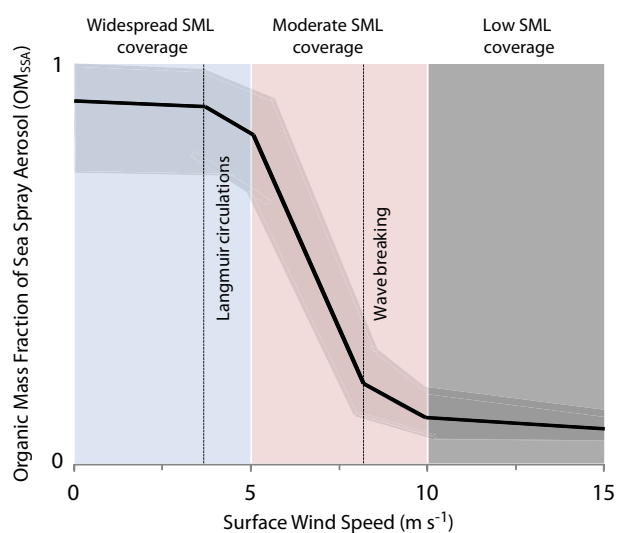


Fig. 1. Conceptual relationship between the organic mass fraction of sea spray aerosol (OM_{SSA}) and surface wind speed. Different colors depict potential regimes of the physical and chemical characteristics of the sea surface microlayer (SML) and the gray shading representing uncertainty in the OM_{SSA} due other environment factors other than wind speed. These values represent global averages and may not be applicable for any given location.

diameter of $0.13\text{ }\mu\text{m}$. 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 mass in submicron SSA (up to $77 \pm 5\%$ in the $0.125\text{--}0.25\text{ }\mu\text{m}$ size range). However, their analysis discriminated between water soluble and insoluble organic carbon (WSOC and WIOC, respectively), finding a dominant contribution (up to $94 \pm 4\%$) from the water insoluble fraction. The high contribution of organics in small SSA sizes ($<0.1\text{ }\mu\text{m}$ in diameter) has not always been observed, as Modini et al. (2010a) and Fuentes et al. (2011) report organic fractions of $8 \pm 6\%$ and $8\text{--}37\%$, respectively.

In this paper, using ambient data from two different oceanic regions we develop a new parameterization for organic fraction of SSA based on the proxies for the chemical composition of sea water, conceptual picture of Fig. 1 for the SML coverage, and laboratory-measured size-dependent chemical composition. The developed parameterization is then used to estimate global emissions of marine primary organic aerosols.

2 Data and methods

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. At Mace Head, measurements of the ~50–100 h average chemical composition of aerosols with an aerodynamic diameter <1.5 μm taken 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 (Cavalli et al., 2004; Yoon et al., 2007) are included in this study (37 total data points). Measurements of the chemical composition of aerosols with diameters <2.5 μm at Point Reyes near San Francisco, CA were 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 h (midnight to midnight local time) every 3 days and chemical composition is determined. Point Reyes was selected from the large (170 stations) IMPROVE monitoring network because it is located very close to the coast (~4 km) in a rocky and grassy plain with little upwind anthropogenic influence and has the highest frequency of aerosols exhibiting marine characteristics (White, 2008). Because Point Reyes aerosol measurements do not have a clean sector filtering at the site, we have adopted a data filter consistent to the one used at Mace Head (described in Sect. 2.2).

Several compounds included in the analysis of aerosol chemical composition are elemental carbon (EC), OC, and Na. To avoid potential problems with Na measurements caused by tube-generated X-ray fluorescence (White, 2008), the data at Point Reyes were analyzed for the years 2000–2001 and 2005–2007. The OC measurements from Mace Head are further separated into WSOC and WIOC following Cavalli et al. (2004). Unlike Mace Head, OC measurements at Point Reyes obtained from the IMPROVE network do not segregate WSOC and WIOC. In order to estimate the WIOC concentrations, 70 % of the OC measured at Point Reyes is assumed to be insoluble. This WIOC/OC fraction, which is a potential source of uncertainty as described in Sect. 4, is 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) and thought to be representative of marine primary organic aerosols. The OM_{SSA} can then be determined by converting the OC measurements to organic matter (OM) using a 1.4 OM/OC ratio (Decesari et al., 2007; Facchini et al., 2008) and using the equation $OM_{SSA} = WIOM / (WIOM + \text{sea-salt})$, where sea-salt is estimated as Na/0.3061 corresponding to the mass fraction of sodium in dry sea-salt (Seinfeld and Pandis, 2006; O’Dowd et al., 2008). OM_{SSA} is used here as the primary variable of the analysis because it is independent of the SSA concentration (considering that POA of marine origin and sea-salt have similar production mechanisms and sinks) and can be easily applied to published SSA emission parameterizations.

2.2 Meteorology

Wind speed and direction data used in this study are different for the two stations. At Mace Head, 10 m 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 m 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 m wind speed was converted to 10 m using the power-law wind-profile as follows: $U_{10} = U_5 \left(\frac{10}{5}\right)^{0.11}$ (Hsu et al., 1994). Because Point Reyes has no “clean sector” filter on site like Mace Head, a wind direction filter was used on the Point Reyes aerosol data including only days with all 24 h having on-shore wind directions (between 180° and 315°) according to the buoy winds. 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 (11 total data points) in order to avoid potential influence of OM from anthropogenic sources (Clarke, 1989) and to make them consistent with the Mace Head clean sector conditions.

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 555 nm (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 Results and discussion

3.1 Factors affecting organics in SSA

3.1.1 Wind speed

A plot of OM_{SSA} against surface wind speed in Fig. 2a shows that for both the Mace Head and Point Reyes measurement stations, the OM_{SSA} decreases with increasing 10 m wind speed in a manner consistent with our conceptual picture given on Fig. 1. For wind speeds above 10 m s^{-1} , SSA 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 SSA was observed. This trend can be explained by the presence of a SML 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 h and Point Reyes over 24 h). 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, according to our conceptual picture on Fig. 1, OM_{SSA} should not change much for low wind speed values. Using the MATLAB curve fitting tool and the proposed conceptual relationship, we have developed a logistic function that is a moderate fit ($R^2 = 0.38\text{--}0.47$) for the existing ambient measurements and requires no artificial cutoff. Despite this moderate fit, the different time scales of the measurements (hours-days) and emission processes (seconds-minutes) may lead to some uncertainties in its application to sea spray production functions. However, the general relationship between OM_{SSA} and wind speed shown on Fig. 2a suggests that winds (through their effect on the SML coverage) could play a considerable role in determining the organic content of SSA.

It should be noted, that in addition to the wind speed/SML coverage relationship, the regression shown in Fig. 2a could be interpreted by having relatively constant marine POA flux, diluted by wind speed-dependent sea-salt emissions. The difference between the two hypotheses occurs when applied to a sea spray emission function for prediction of marine POA emission rates. The wind speed/SML coverage relationship predicts increasing marine POA emissions with wind speed (roughly linearly due to the combination of the negative logistic relationship between OM_{SSA} and U_{10} and the positive exponential relationship between sea spray emissions and U_{10}) whereas the dilution hypothesis predicts emissions to be

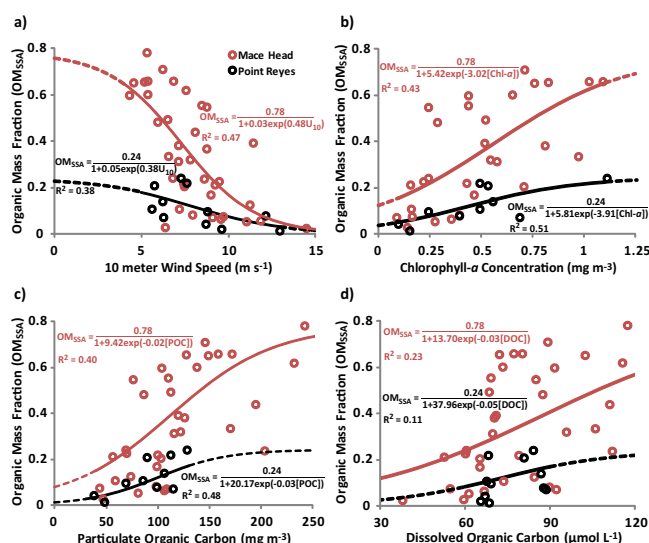


Fig. 2. Organic mass fraction of sea spray aerosol as a function of (a) observed 10 m wind speed (U_{10}) and upwind averaged ocean concentrations of 8-day averaged (b) [Chl-*a*], (c) [POC], and (d) [DOC] for Mace Head and Point Reyes. In Fig. 2b, four outlier data points for Mace Head with [Chl-*a*] > 1.25 mg m^{-3} have been excluded due to their occurrence during anomalously high chlorophyll-*a* 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.

unrelated to wind speed. As the results of the recent studies by Russell et al. (2010) and Ovadnevaite et al. (2011) suggested a positive linear relationship between wind speed and submicron marine-source organic aerosol concentration, we believe the proposed wind speed/SML coverage relationship is most consistent with the available ambient measurements.

3.1.2 Ocean chemistry

Analysis of ambient marine aerosol chemical composition suggests that there is a maximum in OM_{SSA} that, although usually occurring at low wind speed, can be vastly different for the measurement locations. Fig. 2b–d show that each ocean chemistry parameter examined ([POC], [DOC], and [Chl-*a*]) had a positive relationship with OM_{SSA} although none of the correlations were very strong. It is worth noting that the relationship between OM_{SSA} and [POC] (Fig. 2c) was stronger than [DOC] (Fig. 2d) for Mace Head, consistent with the hypothesis of Russell et al. (2010) that [POC] influences organic mass fraction of Northern Atlantic SSA. Overall, out of the three ocean parameters examined, the strongest and most consistent relationship was found between OM_{SSA} and [Chl-*a*] (Fig. 2b). Therefore, in our new parameterization of the organic mass fraction of SSA, [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 OM_{SSA} vs. U_{10} and OM_{SSA} vs. $[Chl-a]$ were found to be very similar for both stations. The corresponding coefficients in each equation were averaged to yield:

$$OM_{SSA}(Chl-a, U_{10}) = \frac{OM_{SSA}^{\max}}{1 + \exp(-2.63[Chl-a] + 0.18U_{10})} \quad (1)$$

where $[Chl-a]$ 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_{SSA}^{\max} , is the maximum OM_{SSA} observed at the two sites during the entire measurement period (0.24 for Point Reyes and 0.78 for Mace Head). As the contribution of sea-salt to total marine aerosol mass increases considerably in supermicron mode (de Leeuw et al., 2011), the large difference in the values for the two sites is believed to be associated with the aerosol sizes that were sampled at each site ($PM_{2.5}$ at Point Reyes vs. $PM_{1.5}$ at 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. (1) in Fig. 3 shows the interdependence of $[Chl-a]$ and U_{10} in determining OM_{SSA} , where the steepest slope corresponding to highest sensitivity occurs in the intermediate $[Chl-a]$ and U_{10} values and the shallowest slopes (constant OM_{SSA}) occur at the extreme values where $[Chl-a] > 1\ mg\ m^{-3}$ and $U_{10} > 15\ m\ s^{-1}$ or $U_{10} < 5\ m\ s^{-1}$. Despite the relationship between $[Chl-a]$ and wind speed that exists because of seasonal effects (high $[Chl-a]$ and low winds in summer, low $[Chl-a]$ and high winds in winter), the inverse relationship between OM_{SSA} and U_{10} remains (albeit weak at times) even when the Mace Head measurements are binned into “low”, “moderate” and “high” $[Chl-a]$ regimes (see Fig. S2). Comparison of Eq. (1) with a short term high organic aerosol concentration episode at Mace Head described in Ovadnevaite et al. (2011) reveals remarkably good agreement (the observed and predicted OM_{SSA} were 0.57 and 0.54, respectively using $U_{10} = 10\ m\ s^{-1}$ and $[Chl-a] = 1\ mg\ m^{-3}$ based on Table 1 and Fig. 1 from Ovadnevaite et al., 2011).

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

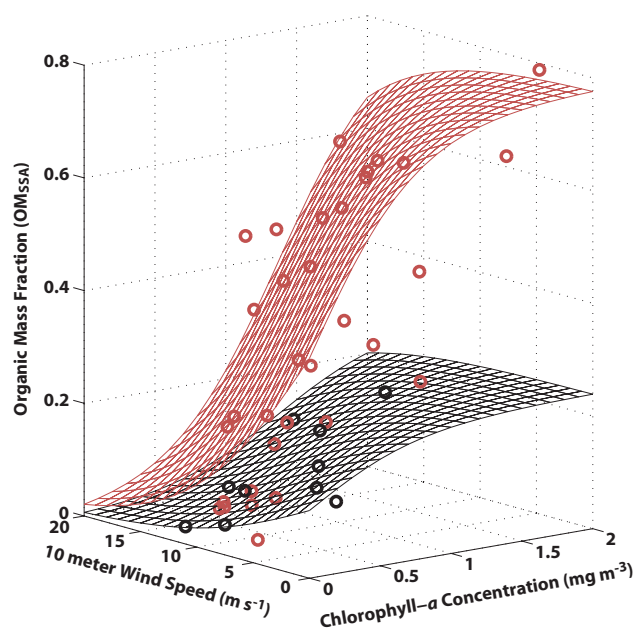


Fig. 3. Organic mass fraction of sea spray aerosol as a function of both 10 m wind speed and $[Chl-a]$ for (a) Mace Head (red) and Point Reyes (black) with the surface regression based on Eq. (1) in the same color scheme for each site.

3.1.3 Aerosol size

The differences in aerosol sizes ($< 1.5\ \mu m$ from Mace Head and $< 2.5\ \mu m$ at Point Reyes) measured at each site were likely to contribute to the differences in OM_{SSA}^{\max} . Since neither the Mace Head nor Point Reyes datasets had size-resolved aerosol composition, to better constrain OM_{SSA} 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). These emission measurements, taken offshore up to 400 km, were comparable to size-resolved ambient samples from Mace Head during the same period (Facchini et al., 2008). Figure 4 shows the OM_{SSA} measurements from Facchini et al. (2008) fitted by the following equation:

$$OM_{SSA}(D_p) = \frac{OM_{SSA}^{\max}(D_p)}{1 + 0.03\exp(6.18D_p)} + OM_{SSA}^{\min}(D_p) \quad (2)$$

where D_p is the ambient ($RH = 80 \pm 8\%$) aerosol aerodynamic diameter in micrometers, and $OM_{SSA}^{\max}(D_p)$ and $OM_{SSA}^{\min}(D_p)$ are size-dependent maximum and minimum organic mass fraction of SSA with values of 0.82 and 0.03, respectively. Although Eq. (2) is based on measurements of aerosols from 0.125 to $8.0\ \mu m$ in diameter, the asymptotic nature of the high and low end of the logistic curve gives confidence that it can be extrapolated to the size range of SSA commonly used by global climate models ($< 25\ \mu m$ in diameter) (de Leeuw et al., 2011). Section 4.2 describes how

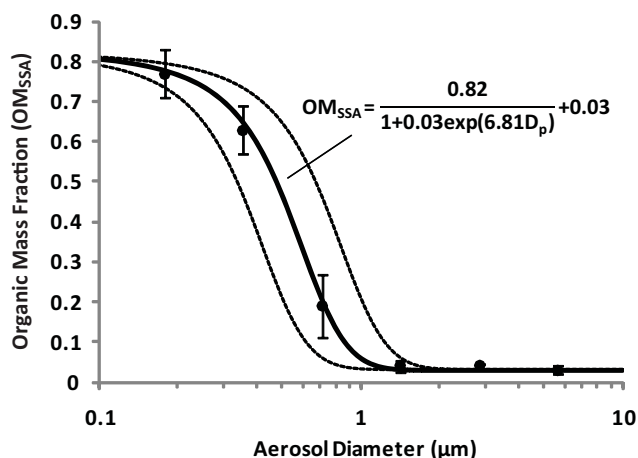


Fig. 4. Observed organic mass fraction of sea spray aerosol (solid circles) as a function of ambient aerosol aerodynamic diameter from Facchini et al. (2008). The solid curve shows a logistic fit to the geometric mean of the diameter range, with the dashed curves corresponding to the logistic fit of the high and low end of the individual aerodynamic size ranges. Vertical bars show one standard deviation from the mean as described in Facchini et al. (2008).

this assumption is most important and highly uncertain at the largest aerosol sizes.

Our size-dependent OM_{SSA} formulation in Eq. (2) is consistent with other measurements/parameterizations. Size-resolved measurements from Keene et al. (2007) give similar results for the organic fraction of SSA, but the reported OC (as water soluble only) is potentially incompatible with the data from Mace Head. Both Oppo et al. (1999) and Long et al. (2011) describe similar size-dependent OM_{SSA} through adsorption models, while Ellison et al. (1999) shows a comparable size-dependence using the “inverted micelle” model of an organic aerosol. There is some uncertainty associated with the applicability of these measurements as high OM_{SSA} values of submicron SSA have not been always observed (Modini et al., 2010a; Fuentes et al., 2010) and were often characteristic of smaller (~ 20 to 70 nm in diameter) sized particles (Modini et al., 2010b; Fuentes et al., 2010); see Sect. 4 for a brief summary of some of the caveats and uncertainties in OM_{SSA} calculations.

3.1.4 Combination of wind speed, [Chl-*a*], and SSA size

To create an OM_{SSA} equation as a function of [Chl-*a*], U_{10} , and SSA size, we have combined Eqs. (1) and (2) in a way that retains the size dependence of OM_{SSA} from Eq. (2) but scales with [Chl-*a*] and U_{10} as described in Eq. (1). Specifically, the $OM_{SSA}^{\max}(D_p)$ and $OM_{SSA}^{\min}(D_p)$ values from Eq. (2) were scaled with the OM_{SSA} from Eq. (1) after setting $OM_{SSA}^{\max}(D_p)$ to 1 reflecting the highest potential enrichment of 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*], and removes the need for a site-specific OM_{SSA}^{\max} . The resulting final OM_{SSA} parameterization is:

$$OM_{SSA}(\text{Chl}-a, U_{10}, D_p) = \frac{1}{1 + \exp(-2.63[\text{Chl}-a] + 0.18U_{10})} + \frac{0.03}{1 + \exp(-2.63[\text{Chl}-a] + 0.18U_{10})} \quad (3)$$

There are two main advantages of Eq. (3): (i) it does not require any artificial cutoffs of wind speed, [Chl-*a*], or aerosol size and (ii) it can give the size-resolved organic mass fraction of SSA solely from globally-available U_{10} and [Chl-*a*] data. However, it should also be recognized that Eq. (3) is based on limited available observational data and does not incorporate parameters such as sea surface temperature and marine ecosystem type that have been suggested to influence other types of marine emissions (Mårtensson et al., 2003; Gantt et al., 2009). Figure 5 examines the dependence of OM_{SSA} on three parameters: SSA size (D_p), chemical composition of ocean seawater ([Chl-*a*]), and the 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. 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.

3.2 Estimated emission rate

To estimate marine POA fluxes in different parts of the oceans, we have used Mårtensson et al. (2003) and Monahan et al. (1986) 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 $2.8 \mu\text{m}$ and the Monahan et al. (1986) function for diameters from ~ 2.8 to $10 \mu\text{m}$. Both the Mårtensson et al. (2003) and Monahan et al. (1986) functions are assumed to represent SSA whose effective densities are determined by the fractional contribution of sea-salt and organics ($\rho_{\text{organic}} = 1 \text{ g cm}^{-3}$ according to Cavalli et al. (2004) and $\rho_{\text{NaCl}} = 2.165 \text{ g cm}^{-3}$). Since the magnitude of OM_{SSA} can

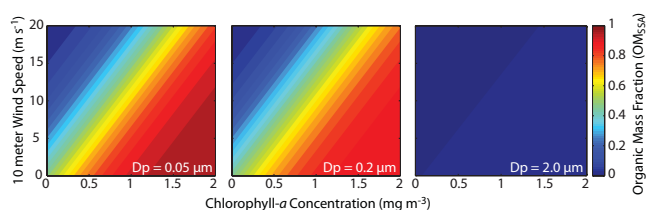


Fig. 5. Contour plots of the organic mass fraction of sea spray aerosol as a function of [Chl-*a*] and 10 m wind speed (U_{10}) for sea spray aerosols with ambient aerodynamic diameters of (a) 0.05, (b) 0.2, and (c) 2 μm .

also influence the hygroscopicity (κ) and resulting growth factor (GF) of the SSA, a conversion between dry and ambient aerosol diameters was achieved by changing the OM_{SSA} from Eq. (3) to an organic volume fraction using the effective density and deriving a GF at a relative humidity of 80 % assuming $\kappa_{\text{organic}} = 0$ and $\kappa_{\text{NaCl}} = 1.12$ (Petters and Kreidenweis, 2007).

The model-predicted global annual submicron (dry aerosol diameter $< 1 \mu\text{m}$) marine POA emission rate shown in Fig. 6 reveals some of the important similarities and differences between our parameterization and those of other studies using only [Chl-*a*] as a proxy for the organic mass fraction of submicron SSA (O'Dowd et al., 2008; Langmann et al., 2008; Gantt et al., 2009; Vignati et al., 2010). Like other parameterizations, the highest emissions occur over the mid latitude waters such as the southern and northern Atlantic Ocean where strong winds and high [Chl-*a*] are common throughout the year and the lowest emissions occur in ocean gyres where winds are weak and [Chl-*a*] is low. Our parameterization is more distinct in areas with strong winds and low [Chl-*a*] and vice versa. Under similar [Chl-*a*] conditions, marine POA emissions in our parameterization always increase with increases in surface wind speed (due to the exponential wind speed dependence of sea spray emissions). However, due to reduction in SML coverage, the predicted enhancement of OM_{SSA} and thus emission rates of marine organics under high wind conditions is lower compared to other parameterizations. On the other hand, the predicted emission rates in equatorial waters, which can have lower winds and elevated [Chl-*a*], are larger than those from previous studies because of the higher OM_{SSA} predicted by our parameterization. As there have been no marine POA flux measurements in different oceanic regions, the predicted organic emission rates are difficult to verify. Comparisons of model-predicted marine-source POA concentrations with observations at the Northern and Southern Hemispheric coastal sites (Meskhidze et al., 2011) show that including wind speed, in addition to [Chl-*a*], as a factor in determining OM_{SSA} yields a more accurate representation for the seasonal cycle of marine organic aerosol mass concentrations.

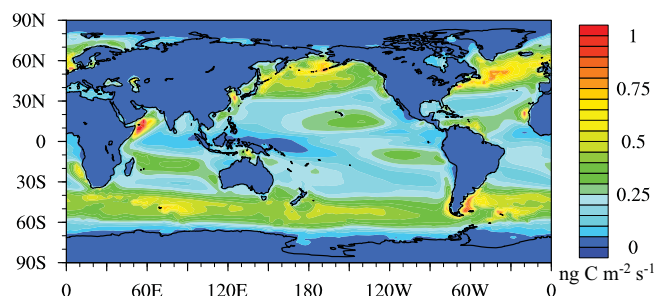


Fig. 6. Annual average submicron marine POA emission rate in units of $\text{ng C m}^{-2} \text{s}^{-1}$ using the Mårtensson et al. (2003) sea spray function, monthly average climatological [Chl-*a*] from SeaWiFS, modeled U_{10} from the CAM5 “current climate” (not based on any particular year), and the estimated global submicron marine POA emissions of 2.8Tg C yr^{-1} . See text for more details.

The estimated global marine POA emissions range from 15.9 to 18.7Tg C yr^{-1} with 2.8 to 5.6Tg C yr^{-1} emitted in the submicron mode. The high end value of this range is obtained when using a growth factor of aerosols composed of 100 % organic ($\text{GF} = 1$). A GF of 1 effectively assumes that the aerosol diameter measurements of Facchini et al. (2008) and thus the D_p in Eq. (2) represent the dry aerosol diameter. This assumption is based on some drying of SSA occurring from the pressure drop at different stages of the Berner impactor used in Facchini et al. (2008). The measurements of Facchini et al. (2008) have only extended to particles with an aerodynamic diameter of $8.0 \mu\text{m}$ and therefore model estimates beyond that are highly uncertain. Overall, global estimates of submicron marine POA emissions are similar to some recently published values (5.5 and 5.8Tg C yr^{-1} for Spracklen et al. (2008) and Vignati et al. (2010), respectively) but lower than the 17.7Tg C yr^{-1} suggested by Westervelt et al. (2011). The considerable organic mass fraction in the largest aerosol sizes (up to 40 % organic mass for aerosols with a geometric mean diameter of $25.5 \mu\text{m}$) reported in size-dependent measurements of Keene et al. (2007), as well as a recently estimated global value for total marine POA emissions of 29Tg C yr^{-1} by Long et al. (2011), suggests that our value for global marine POA emissions (sub- and supermicron together) could be viewed as a low-end estimate.

4 Caveats and uncertainty

One of the main caveats in our study arises from the use of observed or estimated WIOC at two coastal sites as a proxy for global marine POA. To derive OM_{SSA} , we have used values reported by Facchini et al. (2008) which show 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 cases. Recently there have been several studies measuring the hygroscopic growth

of SSA that derived lower organic fractions (Sellegrì et al., 2008; Modini et al., 2010a, b; Fuentes et al., 2010, 2011). 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 coastal seawater was $8 \pm 6\%$ for aerosols between 71–77 nm in diameter and less than 20% (with up to 40%) for 40 nm particles at remote coastal location of Australia. 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. 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), for example, reports a WIOC/OC ratio of $\sim 40\%$ from western North Pacific submicron marine aerosols. Aerosol samples collected during 2006 at Mace Head have revealed that the WIOC/OC ratio reported in previous studies is not consistently observed, averaging $\sim 23\%$ and $\sim 50\%$ during periods of high and low biological activity (Rinaldi et al., 2010).

Coastal sites also suffer from uncertainties related to the influence of the surf zone and continental aerosols. Even though SSA 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), the greatest differences were with the coarse size particles that are not included in this study. Previous studies have suggested that aerosol chemical composition derived from Mace Head measurements can provide a suitable proxy for open ocean conditions (Ceburnis et al., 2008; Rinaldi et al., 2009), although the comparatively higher offshore OM_{SSA} ($63 \pm 12\%$ and $54 \pm 10\%$ for the open ocean and Mace Head sites, respectively) reported by Rinaldi et al. (2009) suggests a potential underestimation of organic aerosol mass in our parameterization. At Point Reyes, no such studies have been conducted but the site is similar to Cape Grim Baseline Air Monitoring Station in Tasmania (both are ~ 90 m a.s.l. over a rocky cliff on a grassy plain) which had similar aerosol chemical composition to offshore ship measurements within measurement uncertainties (Huebert et al., 1998). 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 SSA 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. This uncertainty may not result in large errors in the magnitude and direction of our wind speed dependence due to the similarity between Mace Head and Point Reyes nearshore and offshore wind speeds derived from NASA's Quick Scatterometer (QuikSCAT) (see Fig. S4) when averaged over the sampling period. Continental sources of organic aerosols can 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 OM_{SSA} parameterization (derived using limited spatiotemporal measurements) to the global scale.

When we compared our conceptual model to measurement data from Mace Head and Point Reyes, we assumed consistency between measured and estimated WIOM and POA. Such an assumption may lead to additional uncertainty in marine POA emissions, as it disregards the fraction of marine SOA that may be water insoluble or POA that is water soluble (even though these contributions are expected to be minimal). A well recognized SOA component of marine aerosol derived from ocean-emitted BVOCs is methanesulfonate (MS^-) from the oxidation of 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.

These individual uncertainties in the calculation of OM_{SSA} and subsequent marine POA emissions, combined with the uncertainties in SSA production (e.g., O'Dowd and de Leeuw, 2007) and extremely limited number of long-term measurements can add up to a large uncertainty when applying to global emissions. However, different parameter values used in this study are within commonly accepted range. For example, if we change the effective value of OM_{SSA}^{max} in Eq. (3) from 1 to ~ 0.1 based on Modini et al. (2010a), the result is a factor of 10 decrease in the submicron global marine POA emissions. On the other hand, using different assumptions for the density and OM/OC ratio of marine POA such as 1.4 g cm^{-3} (Moore et al., 2008) and 2.0 (Turpin and Lim, 2001) would lead to a factor of 2 increase in the emissions. Although accurately estimated for the global annual mass emission of marine organic aerosol have not been established, recent modeling efforts have shown that global marine POA emissions of $\sim 5.5 \text{ Tg C yr}^{-1}$ lead to reasonable predictions of surface concentrations (Spracklen et al., 2008; Vignati et al., 2010).

5 Conclusions

A conceptual relationship between wind speed and sea spray aerosol (SSA) 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 organic enrichment of SSA during calm winds when marine aerosol production is at a minimum and large fraction of water surface is covered by the sea-surface microlayer (SML). Under such low wind conditions marine aerosol POA emission rates are at minimum and contribute little to overall marine organic aerosol budget. An increase in wind speed (above $3\text{--}4\text{ m s}^{-1}$) increases sea spray and associated marine POA emission rates, although reduction in OM_{SSA} is also predicted due to the initiation of Langmuir circulations that starts breaking up the microlayer and formation of slicks and streaks, consequently reducing the sea surface area covered by the SML. Wave breaking caused by wind speeds in excess of 8 m s^{-1} , while enhancing sea spray and marine POA emissions, thoroughly mixes the SML with the underlying water and considerably reduces OM_{SSA} . Derived relationships between observed 10 m 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 the three most important parameters regulating OM_{SSA} from among the variables examined in this study.

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. Our model-predicted submicron marine POA 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); although the wind speed dependence of our parameterization gives a distinct spatial distribution for marine POA emissions. Like other studies focused on organic enrichment of SSA, the exponential wind speed dependence of the sea spray emission function combined with the positive relationship between enrichment and [Chl-*a*] in our study leads to the highest marine POA emissions in productive areas with strong winds; however, compared to other emissions formulations the inverse relationship between wind speed and OM_{SSA} employed in our parameterization leads to higher emissions in areas with lower winds. 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) and process-based laboratory and field studies, are needed to determine the accuracy of this wind speed dependent size-resolved parameterization for the organic mass fraction of SSA.

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/11/8777/2011/acp-11-8777-2011-supplement.pdf>.

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