RESEARCH LETTER

Key Points:

- Interaction of saccharides with surfactant films increases organic mass at the air-water interface
- Representing co adsorption can significantly increase the modeled organic mass in sea spray
- Co adsorption improves agreement between models and observations of sea spray chemistry

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OCEANFILMS-2: Representing coadsorption of saccharides in marine films and potential impacts on modeled marine aerosol chemistry

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Abstract Here we show that the addition of chemical interactions between soluble monosaccharides and an insoluble lipid surfactant monolayer improves agreement of modeled sea spray chemistry with observed marine aerosol chemistry. In particular, the alkane:hydroxyl mass ratio in modeled sea spray organic matter is reduced from a median of 2.73 to a range of 0.41–0.69, reducing the discrepancy with previous Fourier transform infrared spectroscopy (FTIR) observations of clean marine aerosol (ratio: 0.24–0.38). The overall organic fraction of submicron sea spray also increases, allowing organic mass fractions in the range 0.5–0.7 for submicron sea spray particles over highly active phytoplankton blooms. Sum frequency generation experiments support the modeling approach by demonstrating that soluble monosaccharides can strongly adsorb to a lipid monolayer likely via Coulomb interactions under appropriate conditions. These laboratory findings motivate further research to determine the relevance of coadsorption mechanisms for real-world, sea spray aerosol production.

1. Introduction

Nascent sea spray forms the foundation of atmospheric aerosol populations over much of the world's oceans, influencing atmospheric chemical reactions [*Athanasopoulou et al.*, 2008] and cloud properties [*de Leeuw et al.*, 2011; *McCoy et al.*, 2015; *Wilson et al.*, 2015] as well as aerosol optical depth, with implications for aerosol forcing of climate [*Jaeglé et al.*, 2011]. Observations indicate that organic matter (OM) emitted with primary sea spray aerosol can comprise a substantial fraction of the submicron aerosol mass near and downwind of strong, active phytoplankton blooms, with OM:NaCl mass ratios considerably enriched in aerosol relative to ocean surface waters [*Oppo et al.*, 1999; *Aller et al.*, 2005; *O'Dowd et al.*, 2004; *Yoon et al.*, 2007; *Claeys et al.*, 2010; *Russell et al.*, 2010; *Gantt and Meskhidze*, 2013]. This organic matter coincides with other chemical markers consistent with microbial organic material that is enriched in the sea surface microlayer [*Gaston et al.*, 2011; *Bigg and Leck*, 2001, 2008; *Leck and Bigg*, 2005a, 2005b, 2008; *Leck et al.*, 2002]. Enrichment of sea spray with organic material during phytoplankton blooms has also been observed in experiments in which sea spray aerosol was artificially produced from laboratory-cultivated phytoplankton blooms [*Prather et al.*, 2013; *Alpert et al.*, 2015] and shown to be sensitive to the microbial and chemical composition of the bloom [*Wang et al.*, 2015]. These and other observations motivate a need to understand the causal mechanisms connecting the concentration of ocean dissolved organic carbon species, and their seasonal and geographic distributions, to the mass and composition of OM in emitted particles.

2. Sea Spray Organic Enrichment Model and Formulation of Intermolecular Interactions

Members of our team have recently developed a process model for understanding sea spray aerosol (SSA) composition, called OCEANFILMS (Organic Compounds from Ecosystems to Aerosols: Natural Films and Interfaces via Langmuir Molecular Surfactants) [*Burrows et al.*, 2014]. OCEANFILMS uses the classic Langmuir isotherm to model the adsorption of several classes of marine organic matter: lipid-like (Lip), polysaccharide-like (Poly), protein-like (Prot), humic-like (Hum), and a refractory class of chemically processed heteropolycondensates (Proc). This approach implies several underlying assumptions including monolayer adsorption, noninteraction of adsorbed molecules, and assuming a fixed number of sites for insoluble
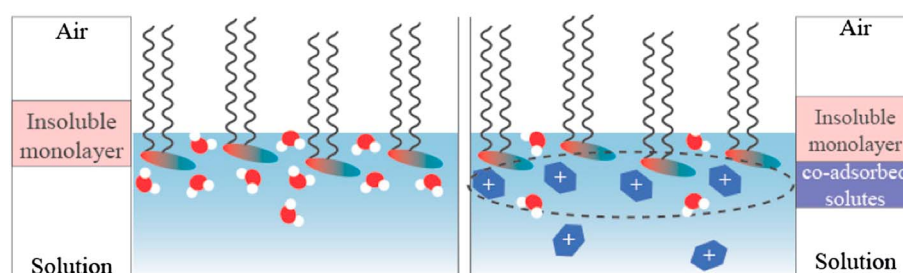
Figure 1. Schematic illustration demonstrating coadsorption. (left) A film comprised of insoluble biomolecules covers the aqueous/air interface and the zwitterionic headgroups (denoted by the blue (+ve) to red (−ve) gradient) are solvated by water. (right) Positively charged, soluble organic solutes are drawn to the insoluble film, displacing solvating water molecules and enriching the boundary's organic content.

organic surfactants. While these simplifications do not reflect the full complexity of ocean surface chemistry, they offer a first step toward describing the mechanisms that drive geographic and temporal patterns in sea spray composition. The Langmuir model captures a saturation effect in which increases in indicators of ocean biological activity and organic matter are associated with initial strong increases in aerosol organic enrichment, followed by a saturation of bubble surfaces at higher organic concentrations. This effect is observed in both the sea surface microlayer [*Marty et al.,* 1988; *Hultin et al.,* 2011; *Wurl et al.,* 2011] and sea spray aerosol [*Gantt et al.,* 2011; *Long et al.,* 2011; *Schwier et al.,* 2015].

Using estimated distributions of ocean organic compound classes, OCEANFILMS can explain an often-observed association of chlorophyll *a* concentrations [Chl *a*] with the submicron organic mass fraction (OMF; Figure 1) [*Burrows et al.,* 2014] as a consequence of the association of [Chl *a*] with the presence of marine surfactants [*Vojvodić and Ćosović,* 1996; *Gašparović and Ćosović,* 2001, 2003]. In addition, a secondary pool of less surface active but longer-lived (semilabile) organic compounds accumulates over the course of a phytoplankton bloom, leading to partial decoupling of [Chl *a*] and OMF in OCEANFILMS. This is consistent with recent laboratory and observational studies suggesting that a time lag can occur between peaks in [Chl *a*] during a bloom and in OMF of sea spray [*Laß et al.,* 2013; *Wang et al.,* 2015; *Schwier et al.,* 2015].

Another observational constraint on the mechanism of organic enrichment of SSA comes from Fourier transform infrared (FTIR) analyses of aerosols collected during ship campaigns, which show that marine particles contain high ratios of OH groups to C-H bonds, suggesting strong enrichment of carbohydrates [*Russell et al.,* 2010; *Hawkins and Russell,* 2010; *Frossard et al.,* 2014]. This result cannot be explained by the original OCEANFILMS, where highly soluble saccharides are not substantially enriched at the air-water interface [*Elliott et al.,* 2014; *Burrows et al.,* 2014].

One possible explanation of these findings involves an affinity between soluble saccharides and insoluble organic films already adsorbed to the water surface, resulting in coadsorption of the soluble saccharides, illustrated in Figure 1. Studies have shown that effective carbohydrate adsorptivity can be strongly enhanced by the presence of lipids or proteins, even for highly soluble saccharides that individually do not adsorb at the air-water interface [e.g., *Babak et al.,* 2000; *Baeza et al.,* 2005; *Parra-Barraza et al.,* 2005; *Pavinatto et al.,* 2007].

Here we introduce OCEANFILMS-2, which extends OCEANFILMS by adding a second, cooperatively adsorbed layer (following the conceptual illustration in Figure 1). OCEANFILMS-2 uses the following additional assumptions: (1) the Poly class adsorbs to monolayers formed by all five original classes, (2) adsorption behavior of Poly is independent of the composition of the monolayer, (3) classes other than Poly adsorb only in the monolayer and not in the second layer, and (4) the orientation of molecules (and their maximum surface excess) for the Poly class is the same in the second layer as in the first layer. Assumption (4) may be worth more detailed consideration in the future, since molecular interactions may alter the orientation of the molecules.

In OCEANFILMS, the surface-active organic matter is assumed to partially coat the surface of the bubble film, forming a monolayer according to

$$\Theta_i = \frac{K_{i,1} C_i}{1 + \sum_i K_{i,1} C_i} = \frac{C_i}{C_{\frac{1}{2},i,1} + \sum_i C_i}, \tag{1}$$
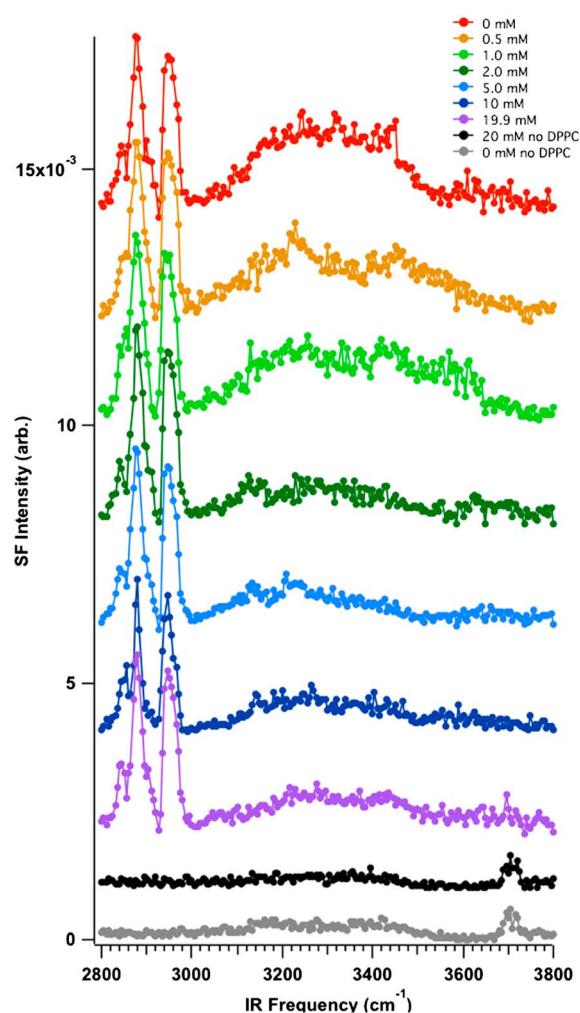
Figure 2. Raw SFG-VS spectra of 40 Å^2/molecule of DPPC on different concentrations of aqueous glucosamine in the OH stretching region. Spectra were collected in the $S_{SF}S_{vis}P_{IR}$ polarization combination and are offset for clarity.

where Θ_i is the fractional coverage of the air-water interface by the ith dissolved organic carbon component in the first monolayer (with $i = lip$, $poly$, $prot$, hum, or $proc$; as in *Burrows et al.* [2014]), σ_i is the fractional coverage of the interface of the first-monolayer's lower surface by the adsorbed polysaccharide layer, C_i is the concentration in solution of the dissolved organic carbon component, $K_{i,m}$ is the Langmuir adsorption coefficient, and $C_{\frac{1}{2},i,m}$ the half-saturation concentration of the ith component in the mth adsorbed layer.

OCEANFILMS-2 extends this treatment by adding a representation of coadsorption following *Chen et al.* [2005], who showed the applicability of a two-layer Langmuir model for surface adsorption layers in a binary liquid acetone + water system. The areal fraction covered by the second adsorbed layer is described by

$$\sigma_i = \sum_i \Theta_i \cdot \frac{K_{poly,2} C_{poly}}{1 + K_{poly,2} C_{poly}}$$

$$= \sum_i \Theta_i \cdot \frac{C_{poly}}{C_{\frac{1}{2},poly,2} + C_{poly}}. \quad (2)$$

3. Experimental Evidence From SFG-VS

The utility of this approach for systems of organic species having markedly different solubilities is qualitatively supported by laboratory experiments that our team has performed on a dipalmitoylphosphatidylcholine (DPPC)-glucosamine model system (Figure 2). DPPC is a common model biological membrane phospholipid with similar vibrational spectral sign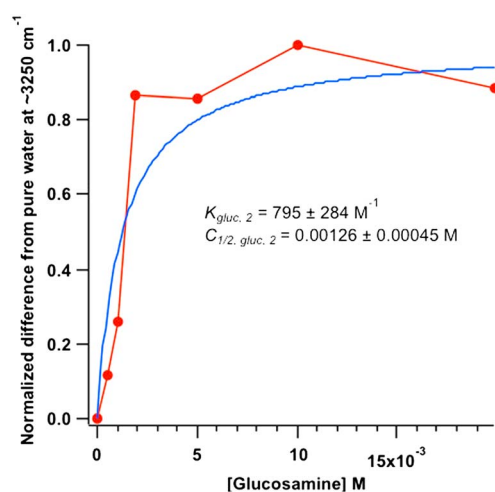atures as those observed with sum frequency generation vibrational spectroscopy (SFG-VS) in studies of sea surface microlayer material [*Laß et al.*, 2013]. In these surface-specific vibrational spectroscopy experiments, DPPC monolayers were studied at the aqueous/vapor interface as glucosamine concentrations varied between 500 μM to 19.9 mM. Experiments were performed using a polarization combination ($S_{SF}S_{vis}P_{IR}$) that probes vibrations aligned normal to the surface. A strong methyl signature (at 2875 cm^{-1}) and a relatively weak methylene signature (at 2850 cm^{-1}) demonstrated that these DPPC monolayers (~45 Å^2/molecule) were tightly packed, consisting of ordered acyl chains aligned perpendicular to the surface. Since direct measurement of the glucosamine vibrational spectral signature is not possible because of the strong DPPC signal in the same C-H vibration region around 2800–3000 cm^{-1}, the interfacial hydrogen-bonded water signal in the 3000–3600 cm^{-1} range is used to probe the glucosamine adsorption. As glucosamine concentrations increased, signal intensity from the surface water molecules was reduced in the 3220–3240 cm^{-1} O-H stretching region. This suppression of water signal depended on glucosamine concentration in a manner consistent with a Langmuir isotherm saturation effect (Figure 3). Such a correlation suggests strong association between the highly soluble glucosamine monomers and the insoluble DPPC film. The deviation of the experiment from the fitted Langmuir curve suggests that fitting a modified Langmuir or other alternative isotherm may lead to a stronger modeled adsorption; this will be investigated in more thorough studies in the future. We note that the driving force behind this association is likely to be Coulombic. At the pH where experiments were performed (5.5), glucosamine is positively charged

Figure 3. Red points and connecting line: SFG intensity, normalized difference from pure water spectrum at ~3250 cm^{-1}. Blue line: Langmuir fit to points, with fit parameter b.

($pK_a = 7.58$) [*Bichsel and von Gunten*, 2000] meaning that glucosamine cations will have strong affinity for the negatively charged phosphate of DPPC's zwitterionic headgroup. Fitting the change in water intensity (at ~3250 cm^{-1}) as a function of glucosamine concentration to a Langmuir model leads to a value for C$_{1/2,gluc,2}$ in this system of C$_{1/2,gluc,2}$ = [0.00126 ± 0.00045 M glucosamine] or [0.00756 ± 0.0027 mol C L^{-1}]. During the aerosol production process, bubbles sit on the surface for some period of time [*Modini et al.*, 2013], during which their film caps drain, and water and soluble molecules (e.g., salts) are removed from the bubble film, a process thought to play an important role in producing high OMF. These experiments suggest that strong Coulombic binding occurs between glucosamine and DPPC molecules, such that the glucosamine molecules would likely remain bound to the DPPC monolayer, and not be washed out as the film cap drains.

Figure 4 compares the geographic distribution of polysaccharide mass as a percentage of total OM in the single-layer OCEANFILMS model with the two-layer OCEANFILMS-2 model (C$_{1/2,poly,2}$ = 0.001 mol C L^{-1}), i.e., for a polysaccharide-surfactant cooperative adsorption interaction that is moderately stronger than that observed for glucosamine. This stronger adsorption would likely be achieved for marine polysaccharides, where the linking of multiple monosaccharide units can increase the opportunities for coulombic or hydrogen-bond interactions between the polysaccharide and the surfactant monolayer. The relative contribution of polysaccharides to sea spray OM increases from between 20 and 50% over most of the globe in the single-layer case, to over 50% over most of the globe in OCEANFILMS-2 (not shown). The estimated alkane:hydroxyl mass ratio of aerosol emitted in the model was calculated following *Burrows et al.* [2014]. Reported mean ratios from FTIR measurements of ambient aerosol composition under clean marine conditions are 0.24 (Pacific Ocean off the central coast of California; July–August 2011) [*Russell et al.*, 2013] and 0.38 (North Atlantic, March–April 2008) [*Russell et al.*, 2010]. In the OCEANFILMS, the median
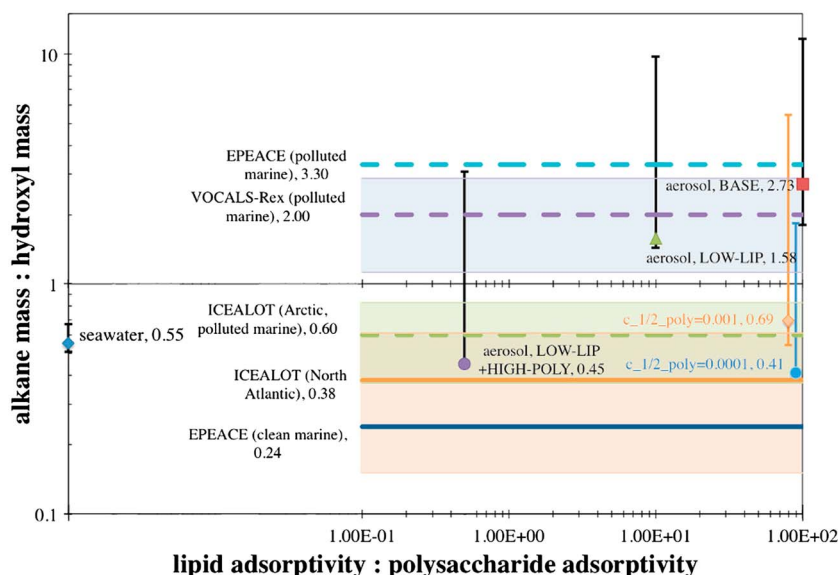

Figure 4. Ratio of alkane mass to hydroxyl mass from model macromolecules and from shipborne FTIR observations, modified from *Burrows et al.* [2014]. Points and error bars indicate the model's global median (median values also printed) and 5–95th percentile range of model estimates for seawater (displayed at the left of the figure) and for emitted submicron SSA in several sensitivity cases, i.e., with modifications to the adsorption of noninteracting lipid and polysaccharide groups (LOW-LIP and LIP-LIP + HIGH-POLY) [*Burrows et al.*, 2014] and with the new two-layer model, using C$_{1/2,poly}$ of 0.0001 and 0.001.
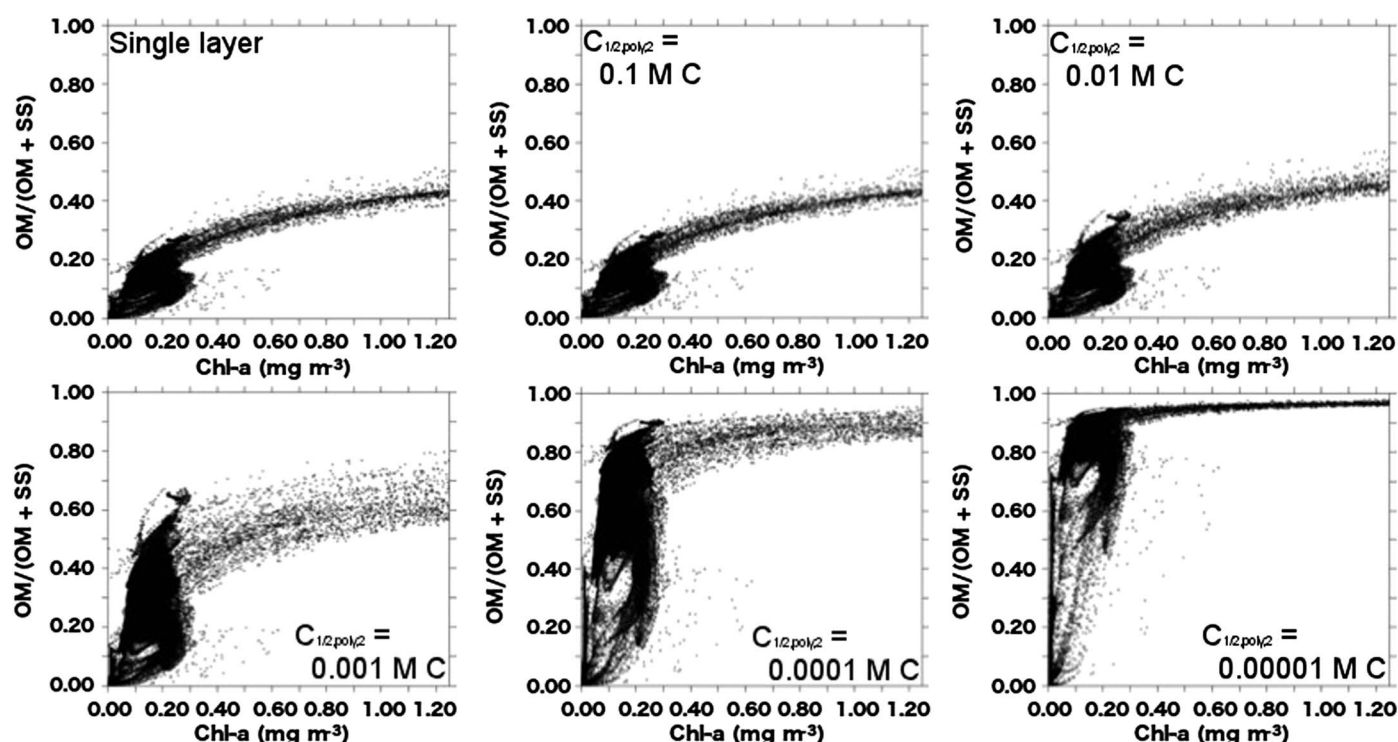
Figure 5. Sensitivity of the OMF: Chl a relationship to assumed value of $C_{1/2,poly,2}$ (in units of $mol\,C\,L^{-1}$). (upper left panel) OMF versus Chl a is shown for the single-layer model; all other panels are for two-layer model with values of $C_{1/2,poly,2}$ as shown.

ratio is 2.73; in OCEANFILMS-2, the ratio is reduced to 0.41–0.69, reducing the discrepancy with FTIR measurements.

The relationship between the organic mass fraction (OMF) of emitted submicron aerosol and oceanic Chl a concentration $(mg\,m^{-3})$ is a conventional correlation because Chl a is a readily observed and widely available proxy for phytoplankton biomass. In Figure 5, we show how including two-layer adsorption of polysaccharides with different parameter values changes the OMF:Chl a relationship. The changes are small for $C_{1/2,poly,2} = 0.1$–$0.01\,mol\,C\,L^{-1}$ but become much larger with stronger assumed adsorption, i.e., $C_{1/2,poly,2} = 0.001\,mol\,C\,L^{-1}$ and greater. Results from the DPPC-glucosamine model system laboratory studies (Figures 2 and 3) support a value for $C_{1/2,poly,2}$ of order 0.001–$0.01\,mol\,C\,L^{-1}$, corresponding to the bottom left and top right panels of Figure 5. With a single monolayer, the maximum OMF reached is about 0.4, even for very strong phytoplankton blooms (Figure 5, upper left). However, with addition of a strongly adsorbing second layer, the maximum OMF is increased to as much as approximately 0.8 or more, in better agreement with high OMF values observed at Mace Head, Ireland, and in the Arctic. This improved agreement with measurements in the North Atlantic and Arctic is shown in Figure 6 (middle column). However, the two-layer model agrees less well with aerosol generated using the SeaSweep mechanism during two field campaigns (CalNex, near coastal California and Western Atlantic Cloud Study (WACS), in the Western Atlantic).

4. Discussion and Conclusions

Organic macromolecules in the ocean interact in ways that may affect the amount and composition of organic matter (OM) present in the surface microlayer and bubble films. Here we have considered a cooperative adsorption mechanism and shown how this mechanism impacts OCEANFILMS predictions of the organic enrichment in ocean bubble interfaces and emitted sea spray aerosol. We have shown that soluble saccharides may chemically adsorb to insoluble surfactant monolayers. Such association will likely be even stronger with polysaccharides due to multivalent interactions between the polysaccharide and the insoluble film [*Kundu et al.*, 2008; *Li and McClements*, 2014]. Results also suggest that a two-layer Langmuir adsorption model may be an appropriate first-order representation for such interactions. Further experiments are needed to
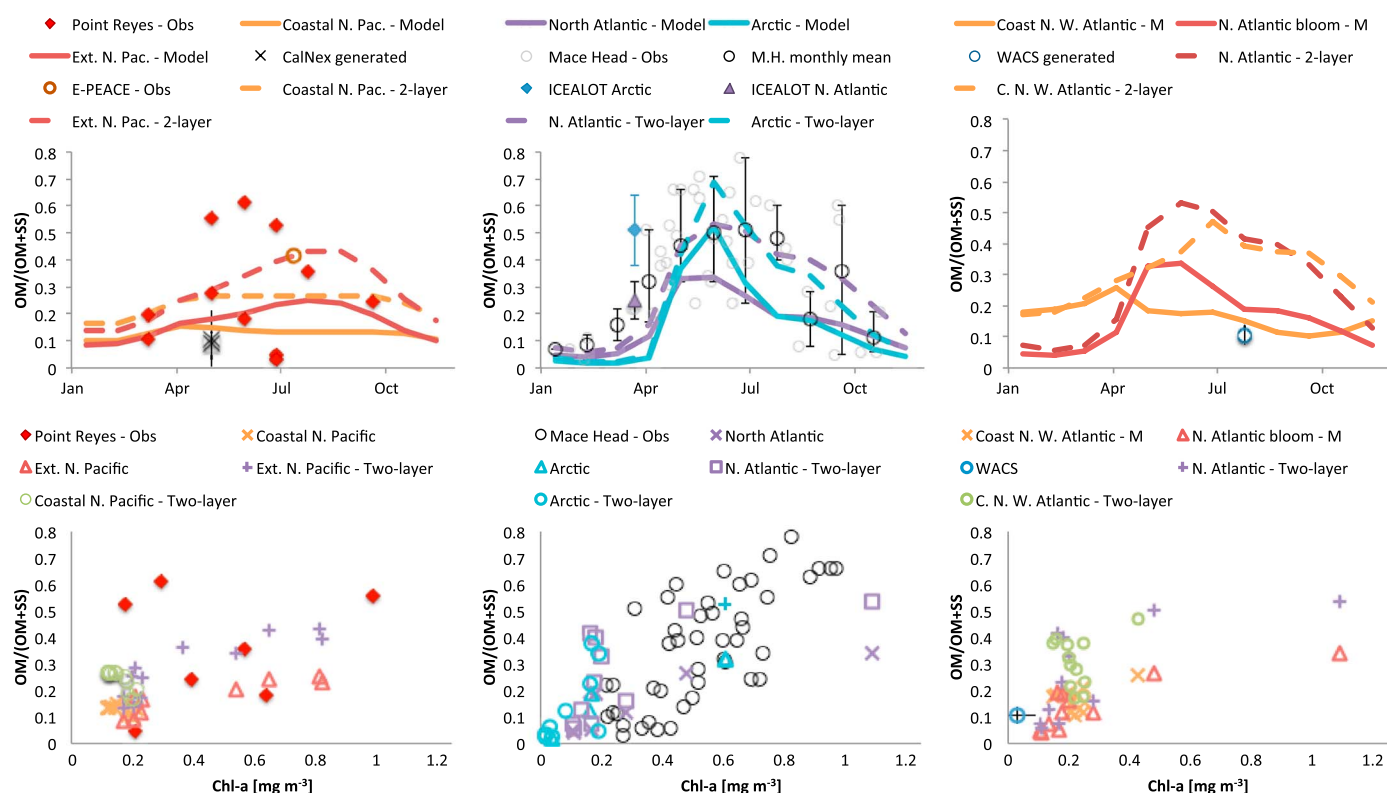
Figure 6. Observed OM or water insoluble organic matter (WIOM) fraction and modeled OM fraction in three regions, with model values from the single-layer model (OCEANFILMS) and the two-layer model (OCEANFILMS-2). (left column) Coastal California and North Pacific, compared with observations from Point Reyes ($N = 10$) [*Gantt et al.*, 2011] and the Eastern Pacific Emitted Aerosol Cloud Experiment (E-PEACE) campaign [*Russell et al.*, 2013]. (middle column) North Atlantic bloom region and Arctic, compared with observations from Mace Head ($N = 42$) [*Rinaldi et al.*, 2013] and the International Chemistry Experiment in the Arctic LOwer Troposphere (ICEALOT) campaign [*Russell et al.*, 2010]. (right column) Northwest North Atlantic, compared with the WACS campaign [*Quinn et al.*, 2014]. (top row) Seasonal cycle. (bottom row) Relationship with observed or modeled [Chl *a*]. Model region boundaries are shown in *Burrows et al.* [2014, Figure 9]. Error bars for WACS and CalNex are 95% confidence intervals based on a *t* test; error bars for ICEALOT are 1 standard deviation; error bars for monthly mean Mace Head observations are the range of observed values in the calendar month.

confirm that the adsorbed saccharides are transferred into the sea spray aerosol. However, tentatively assuming that this transfer does occur, including such a mechanism into a global parameterization of marine organic enrichment in sea spray aerosol (OCEANFILMS-2) lowers alkane:hydroxyl ratios in the emitted spray from a median of 2.73 to a range of 0.41–0.69, reducing the discrepancy with FTIR measurements of freshly generated and ambient sea spray aerosol (ratio: 0.24–0.38). Furthermore, this process increases the OMF of emitted aerosol, improving agreement with ambient OMF observed under "clean" conditions in the Arctic and eastern North Atlantic. However, in aerosol generated by the SeaSweep device during two campaigns (the WACS campaign in the western North Atlantic and CalNex, near coastal California), where the observed OMF is lower than the model prediction, the discrepancy is exacerbated in the two-layer model.

Beyond the mechanism discussed here, alternative possible explanations for the observed highly oxidized state of ambient marine organic aerosol include (1) more oxidized chemical composition of labile (lipid-like) organic mixtures (i.e., higher hydroxyl and carboxyl fractions for the lipid group in Table 1), (2) rapid oxidation of emitted primary OM in the atmosphere, and/or (3) formation of secondary aerosol from volatile precursors.

Our results suggest that chemical interactions between surface-active molecules and soluble saccharides could explain the saccharide-like composition of sea spray aerosol. Potential future research directions include investigation of the impacts of variations in temperature and pH on surface interactions, broadening the scope of chemical interactions considered, including monosaccharides and polysaccharides of varying molecular weights, and interactions with divalent cations (Mg^{2+} and Ca^{2+}) that can bridge between anionic head groups of surfactant molecules and the carboxyl or hydroxyl groups of soluble macromolecules [*Chin et al.*, 1998; *Verdugo et al.*, 2004; *Casillas-Ituarte et al.*, 2010; *Casper et al.*, 2016].

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