

OCEANFILMS: Chemically explicit modeling of marine biogeochemical influence on submicron sea spray aerosol

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1. Introduction and motivation

- The submicron primary sea spray aerosol often contains a significant fraction of organic matter (OM) associated with marine biological activity.
- Existing parameterizations of this organic fraction use chlorophyll-a as a predictive variable and extrapolate from nutrient-rich mid-latitude oceans and coastal sites to the global ocean, including polar biomes and oligotrophic gyres.
- Existing approaches have limitations:
 - can not account for regional and seasonal differences in the relationship between chlorophyll-a and OM fraction.
 - do not include chemical speciation of organics.
- As a first step to address these issues, we propose a novel, semi-mechanistic parameterization framework for submicron sea spray composition, using the Langmuir adsorption isotherm to model fractionation of surface-active macromolecules on the film of bursting bubbles and into the aerosol.
- In an initial application, we partition marine organic matter into several model classes of macromolecules, estimate their global distributions, and assign each a molecular weight, surface excess, and Langmuir adsorption parameter.

3. Partitioning of ocean dissolved organic carbon (DOC)

Based on fields from the Parallel Ocean Program (POP).

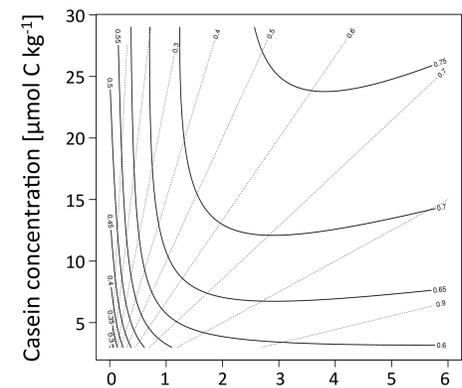
- Lipids:** $\tau \approx 10$ days; scaled with phytoplankton disruption by zooplankton.
- Polysaccharides and proteins:** $\tau \approx 100$ days; scaled with semi-labile DOC.
- Processed:** Long-lived; used climatology of refractory DOC.
- Humics:** Deep humic substance; in convective overturning regions.

4. Langmuir adsorption isotherm model

- Each macromolecule class is assigned five physical parameters based on literature data describing model compounds.
- Bubble surface coverage follows the Langmuir isotherm:

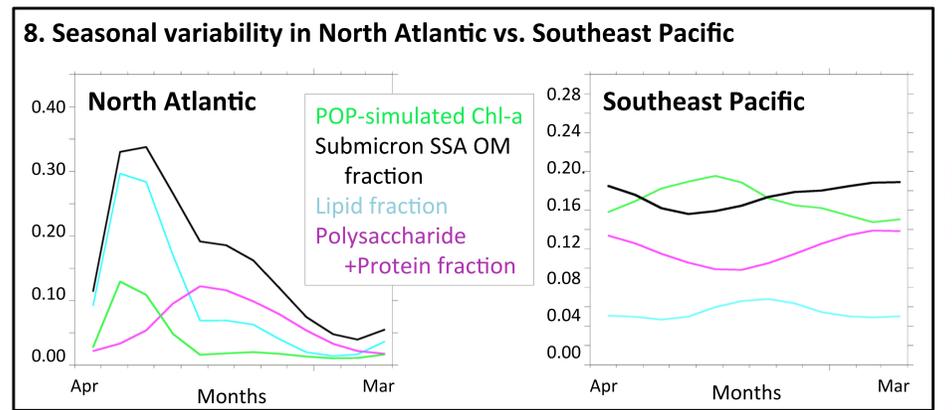
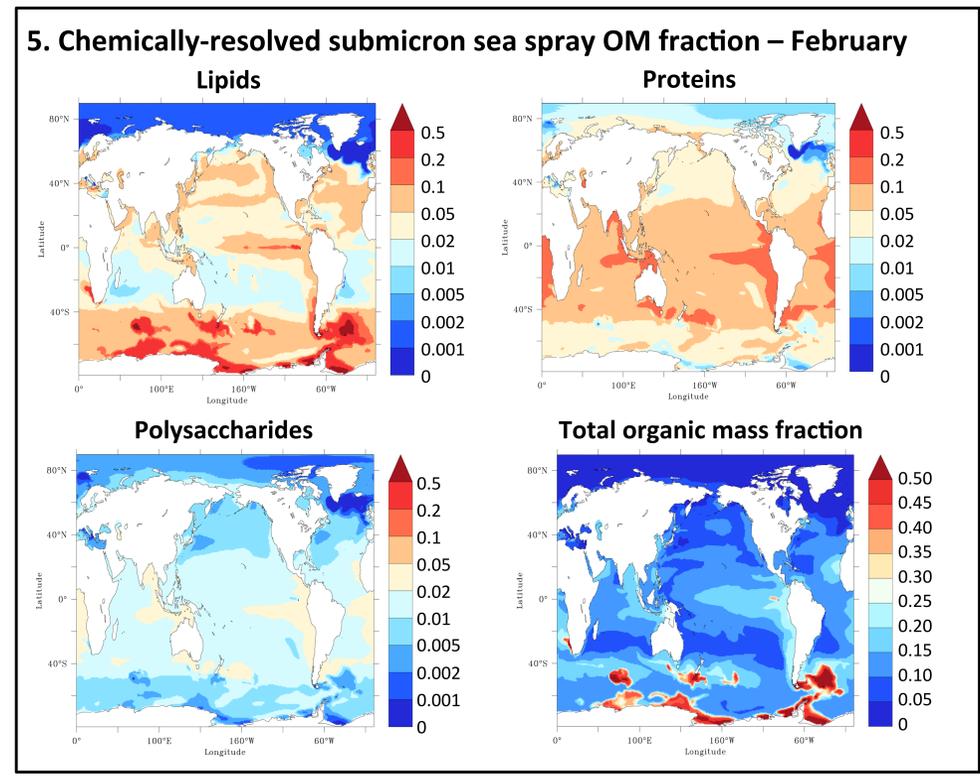
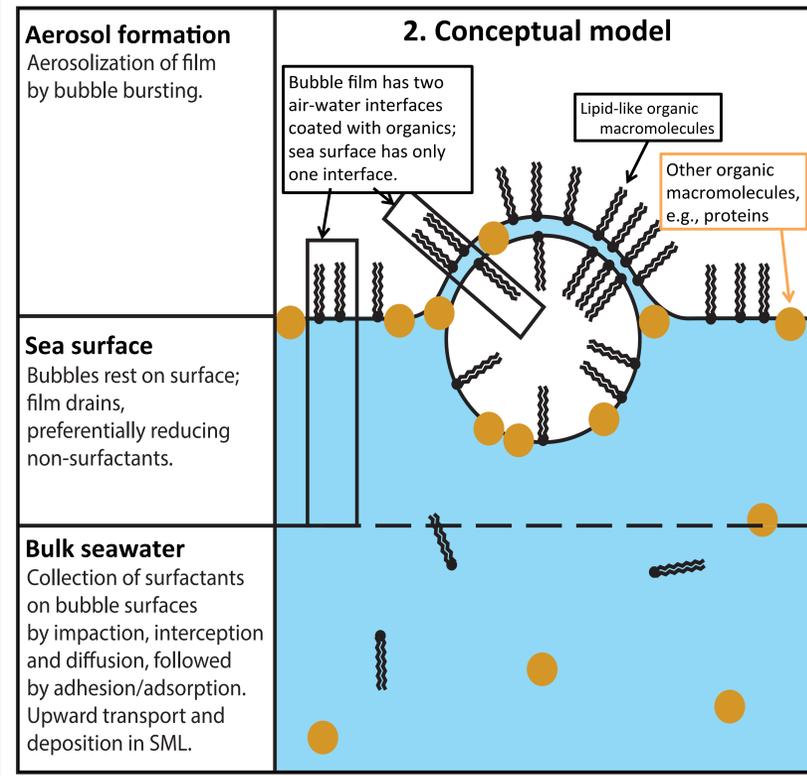
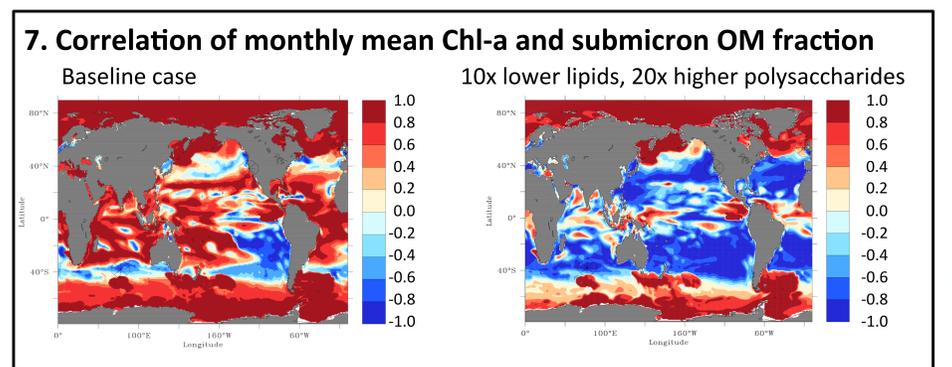
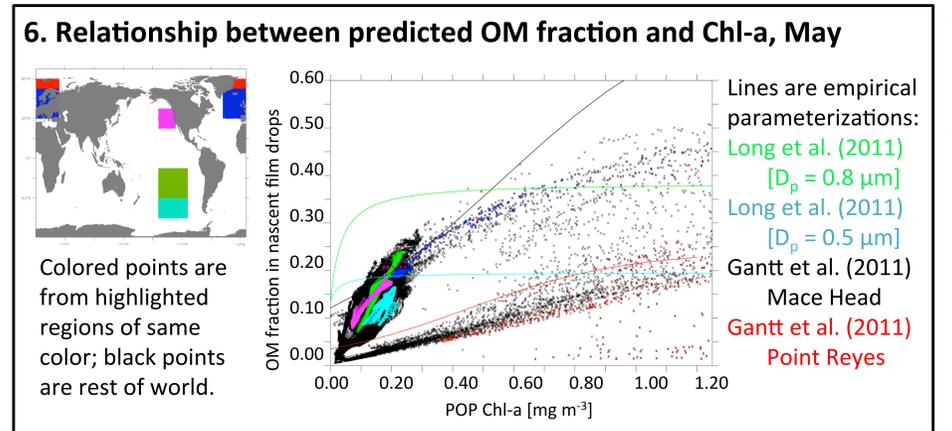
$$\theta_i = \frac{\alpha_i C_i}{1 + \sum_{i'} \alpha_{i'} C_{i'}}$$

Casein concentration [$\mu\text{mol C kg}^{-1}$]



Stearic acid concentration [$\mu\text{mol C kg}^{-1}$]

Two-component system example



9. Summary and outlook

- Developed a mechanistically-based parameterization for primary sea spray aerosol composition based on surface activity of macromolecules.
- OM fraction relationship with chlorophyll is qualitatively similar to observations and existing parameterizations.
- Potential to explain different behavior in different ocean biomes and basins, e.g., Arctic, N. Atlantic, Southeast Pacific.
- Parameters need better observational constraints.

Papers submitted and in press:
 Burrows, S. M., et al.: A framework for modeling the organic fractionation of the sea spray aerosol, *under discussion*, ACPD, 2014.
 Elliott, S., et al., Prospects for the simulation of macromolecular surfactant chemistry in the ocean-atmosphere, *accepted.*, ERL, 2014.
 Frossard et al., Sources and composition of submicron organic mass in marine aerosol particles. *JGR*, submitted