

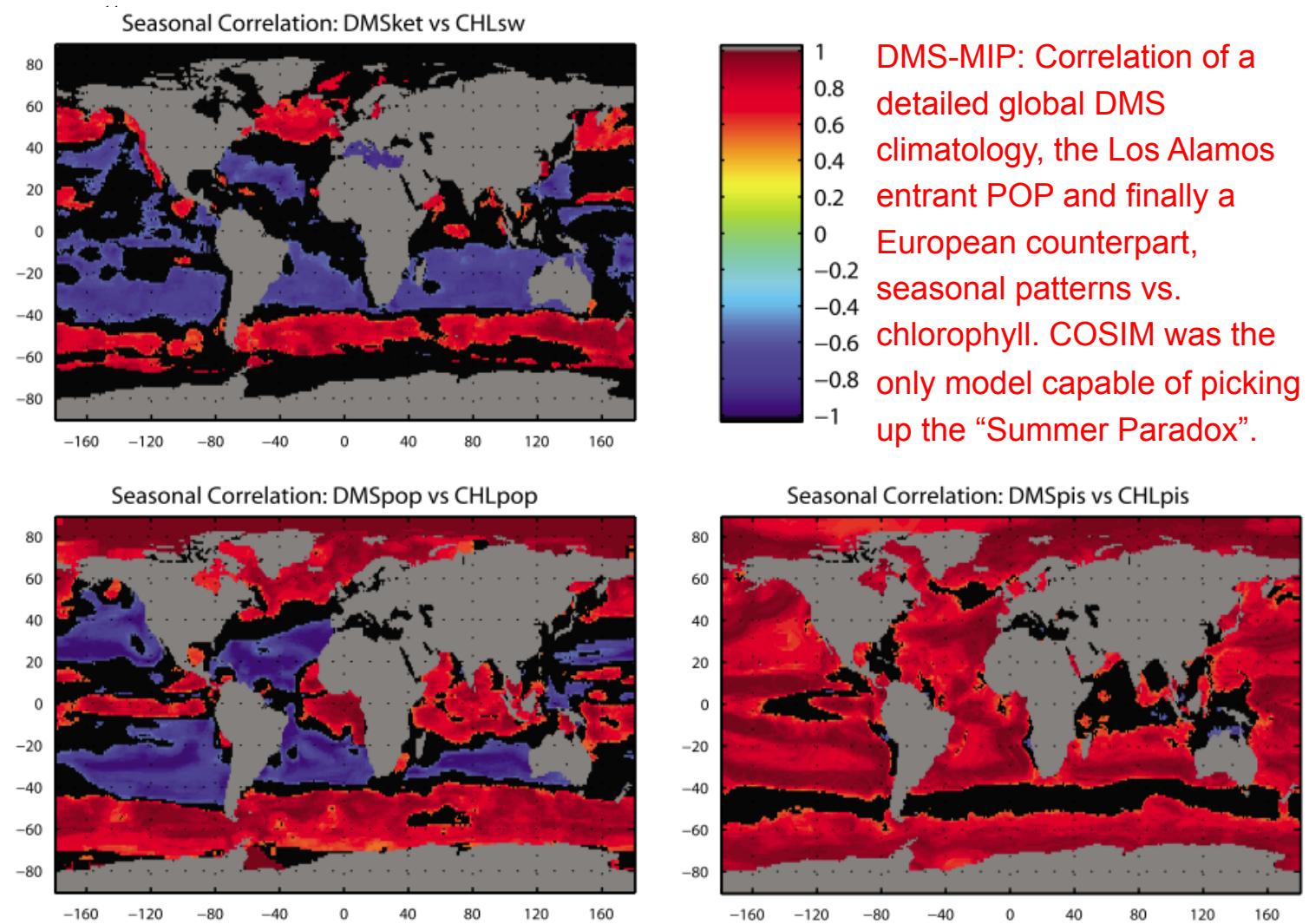
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Abstract

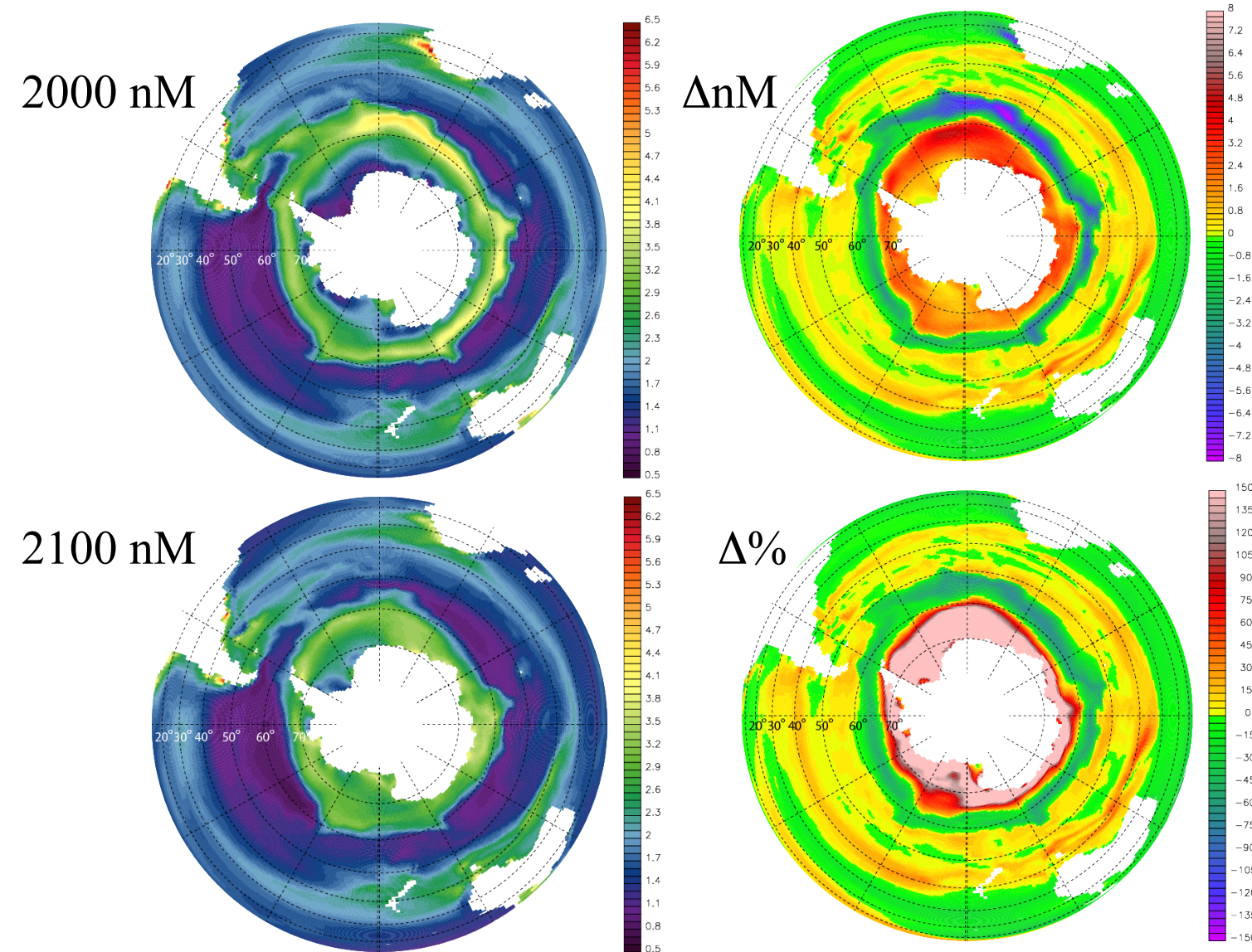
The ocean transfers numerous gaseous and condensed precursors into the global aerosol system, influencing boundary layer reflectivity over a majority of the planetary surface. The most variable and active substances involved are of biotic origin, including byproduct gases of the marine organosulfur cycle and carbon chain macromolecules within the detrital organic pool. Dimethyl sulfide, proteins, polysaccharides, lipids, humics and many permutations from within this list are all intimately involved. A unique program will be described which cuts across the DOE systems modeling community and undertakes global scale simulation for the collective marine aerosol source material. We seek through inter-laboratory collaborations to represent chemical oceanographic and atmospheric science points of view simultaneously. Marine-to-troposphere biogeochemical interactivity is thus built into our approach, so that climate feedbacks and uncertainties may be assessed as they are manifested through the aerosol direct and indirect effects. We construct a unified model for the organic metabolism of phytoplankton and heterotrophic bacteria, then superimpose the resulting chemical resolution onto distributions of the global dissolved organic matter. Individual compound volatilities and surfactant properties are estimated based on laboratory physical chemistry studies, and speciated fluxes into the atmosphere are computed for wind and bubble driven transfer. We are now closing coupled loops into the chemistry of the modal aerosol, for dimethyl sulfide and the dominant classes of biomacromolecule.

Starting Point: Dimethyl Sulfide

- LANL built an early DMS simulator, embarrassingly competitive in first/only MIP (2010)
- In CCSM runs with LLNL gas phase chemistry, global warming influences sulfur flux

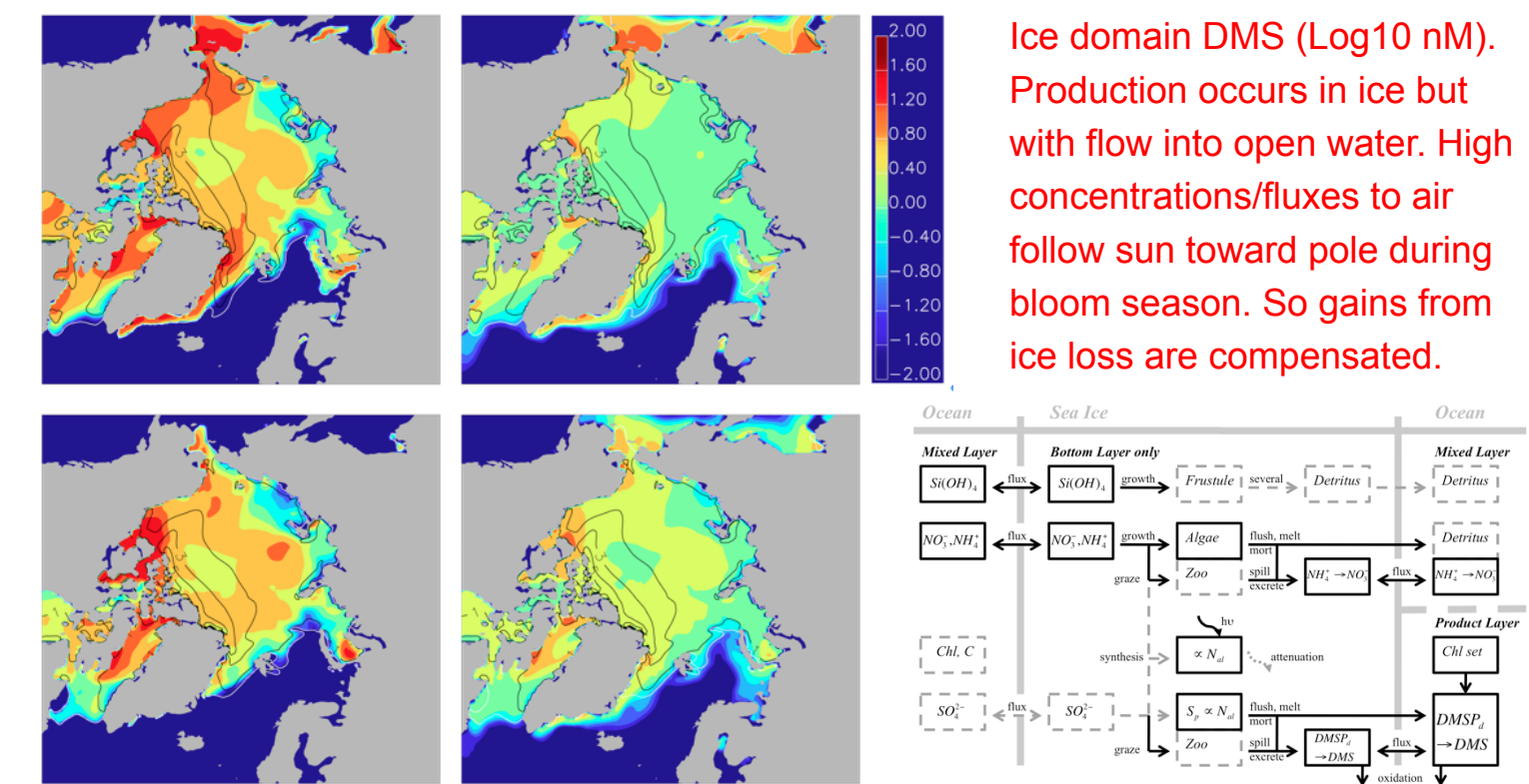


Contemporary and 2100 distributions and differences, DMS concentrations across the Southern Ocean (nanomolar). Rings of activity collapse toward Antarctica as the global ocean warms and stratifies. Major increases correspond to loss of ice coverage. Key image is lower left, showing that shifts in DMS flux may be many tens of percent.



Coupling Laboratories and ESM Components

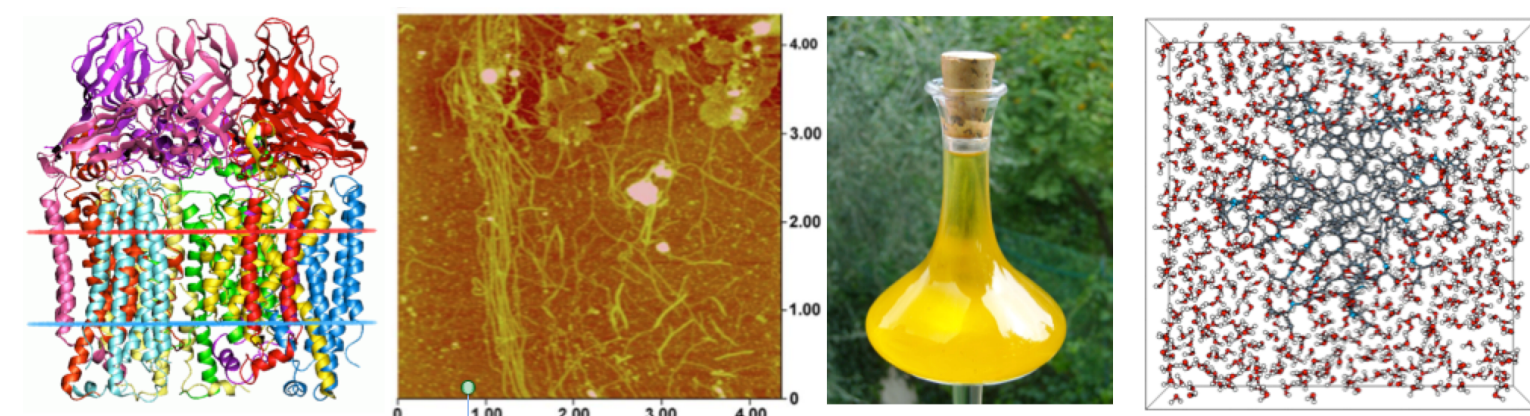
- DMS crosses ocean and ice interfaces, bridging marine biogeochemistry to the aerosol
- Requires coupling LANL ocean/ice, LLNL superfast chemistry, PNNL modal models
- For example, aerosol precursors produced strongly in brine channels, leads of sea ice
- LANL performed first ever pan-Arctic simulations of ice algae and DMS in the pack
- Releases hug the ice edge but are an order of magnitude stronger than open water



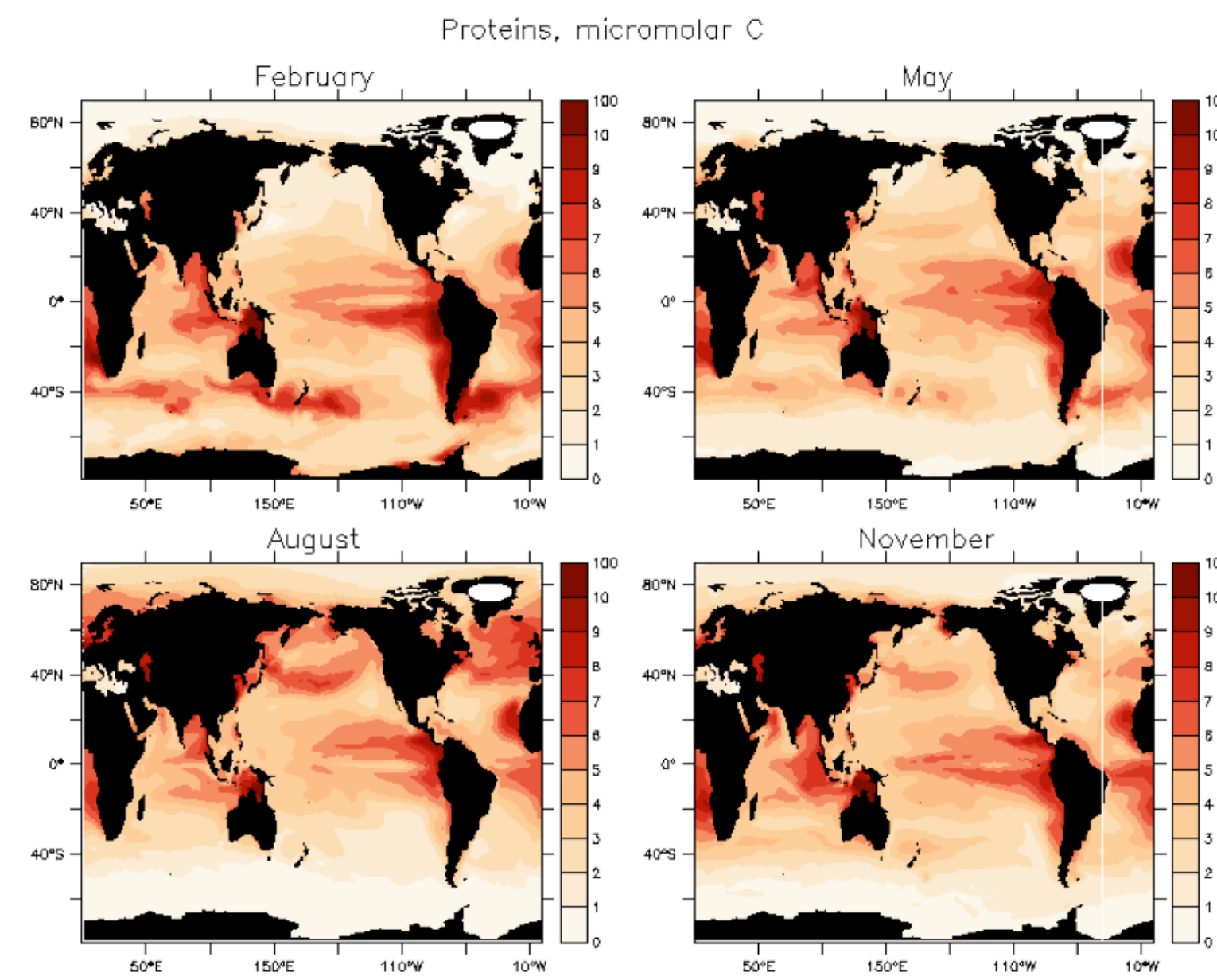
Ice domain DMS (Log₁₀ nM). Production occurs in ice but with flow into open water. High concentrations/fluxes to air follow sun toward pole during bloom season. So gains from ice loss are compensated.

On to the Sea Spray Organics

- Over last decade, primary organics shown to comprise major fraction of remote aerosol
- Affects on Kohler curve properties strong but multiple, complex, highly uncertain
- LANL/PNNL conducting first ever simulations of chemically resolved DOC in ocean
- Macromolecule types differ in basic surfactant behaviors and some stick to bubbles
- PNNL/LANL compute wave driven sourcing for competitive Langmuir monolayers
- The calculations provide a novel approach to parameterization of marine POA

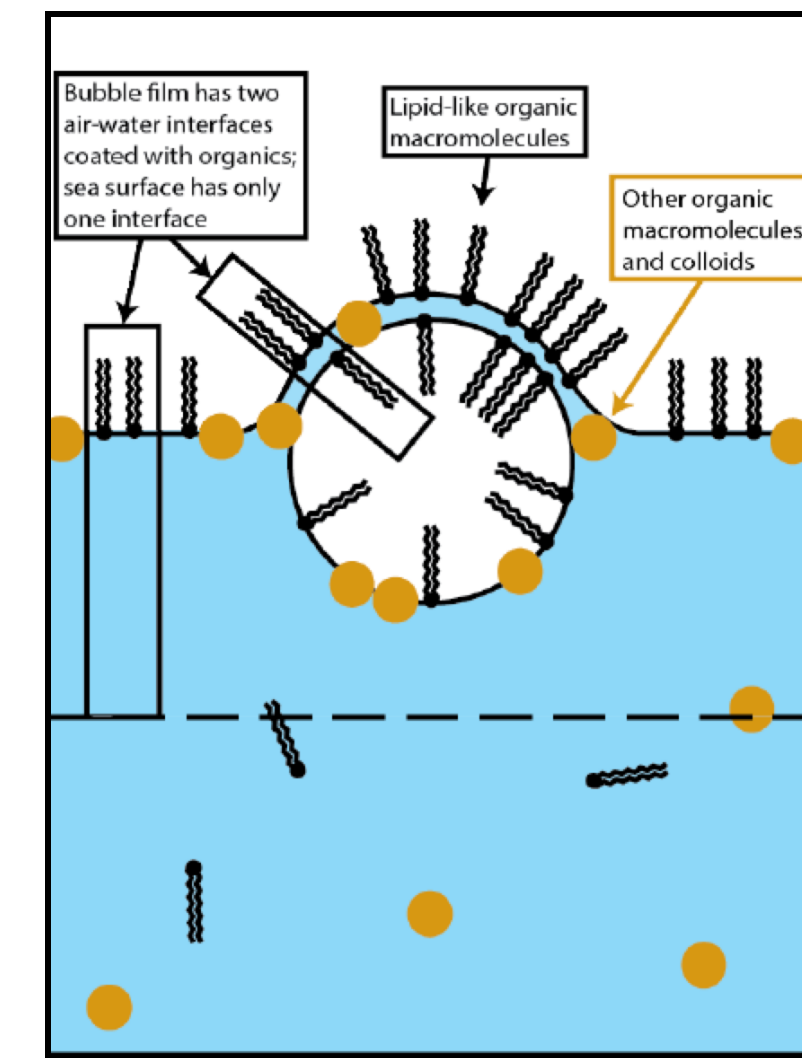


Above: Compound types initially simulated in the LANL ocean with handoffs to MAM include -proteins, polysaccharides, lipids, humics. More recently added -chitin, chitosan, peptidoglycan, deep amphiphiles. Below: Sample distributions for proteins, which are emitted directly as a high proportion of grazed cell biomass and given an intermediate time constant of 10 days. Sugars mix farther from the source, heteropolycondensates are constructed as decay products and may be completely refractory in the deep sea.

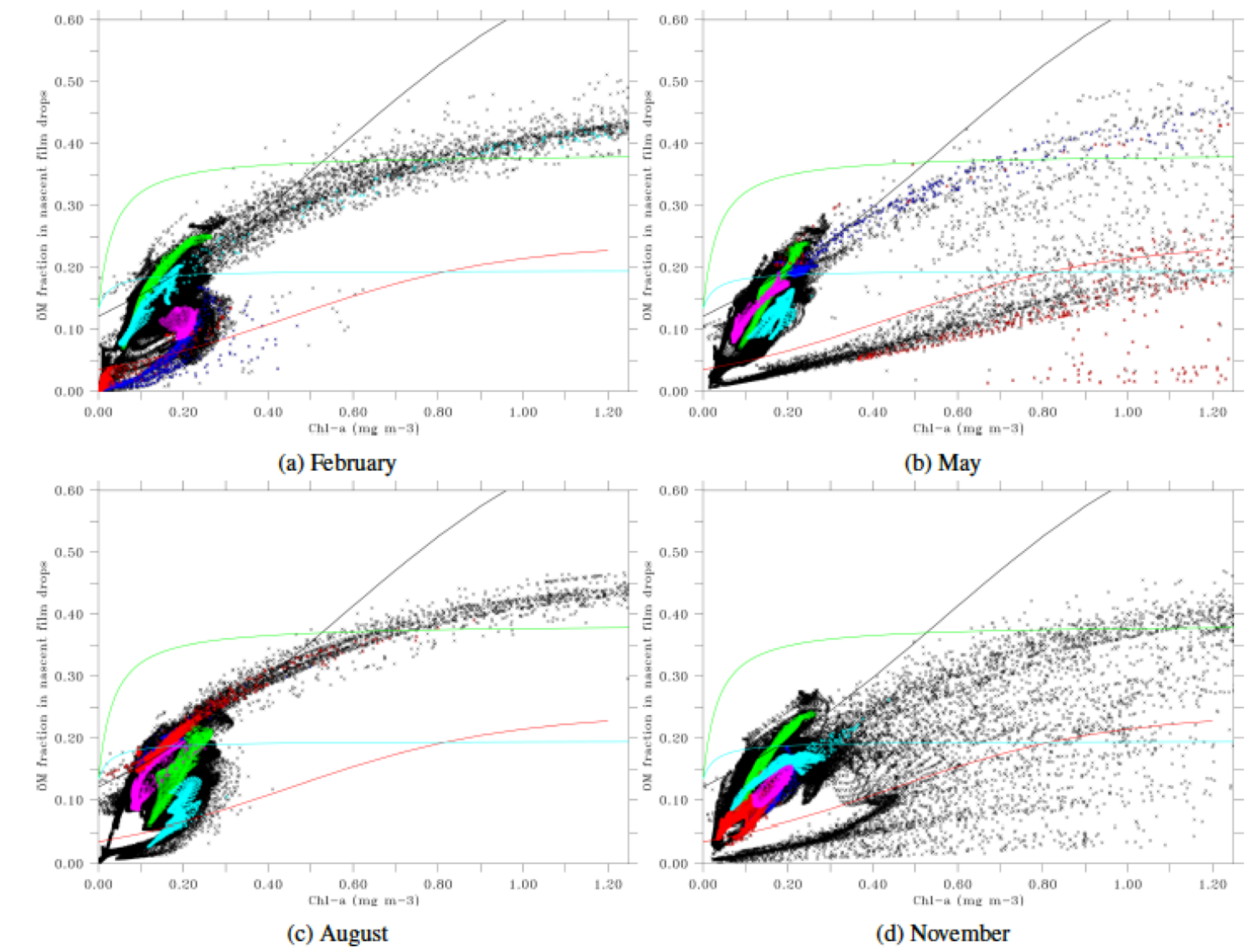


Global Marine Surfactant Chemistry

- First keep it simple -competitive Langmuir monolayers for cavities and interfaces
- Wave generated bubbles burst and drive several thicknesses into the boundary layer
- There organics can affect mass, hygroscopicity, surface tension, vapor transport, more
- Injections into spray aerosol highly nonlinear -not simple functions of biotic activity

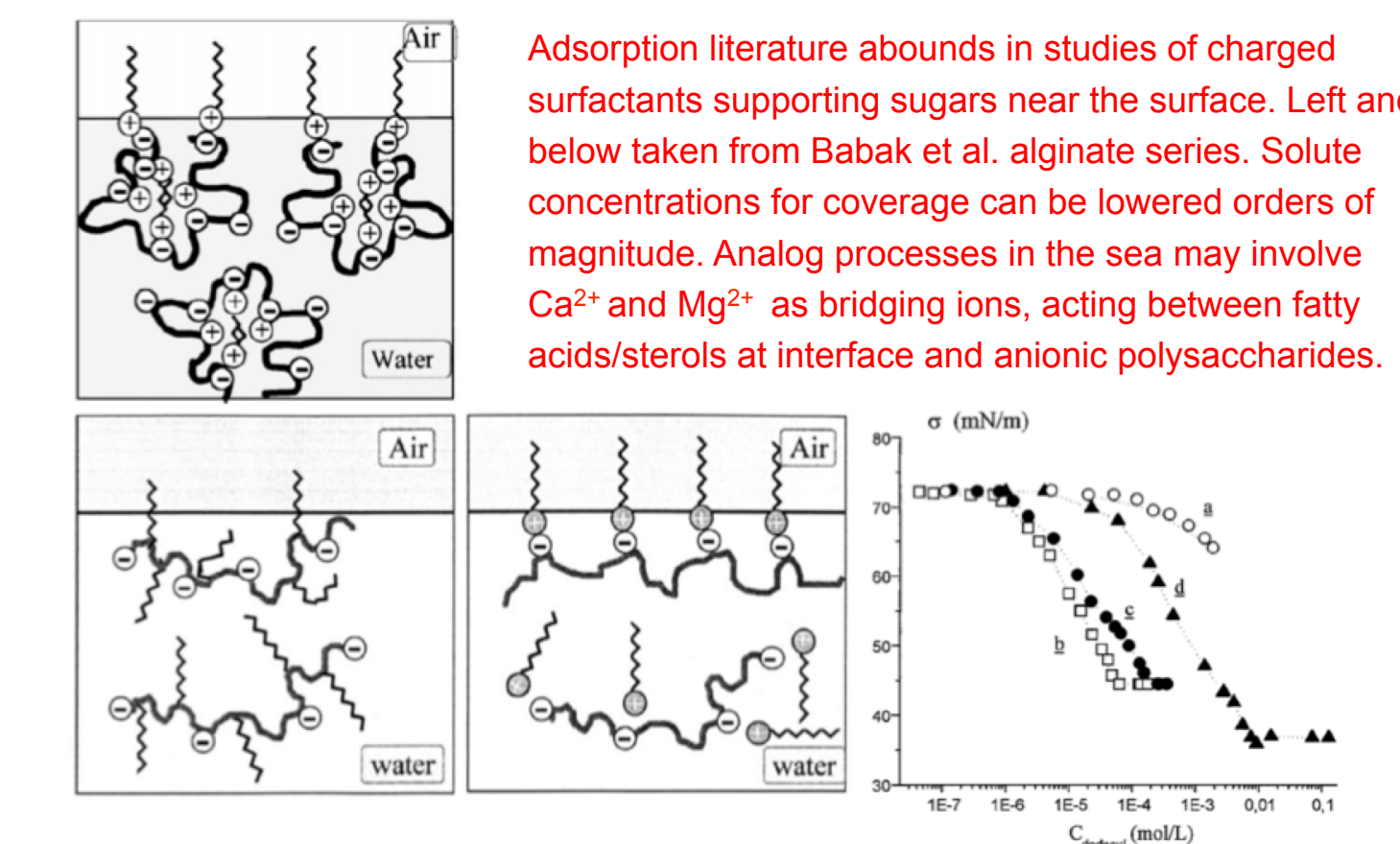


Left: Schematic of the first order process set for the surface sea. Adsorbates among the dissolved organic matter have distinct Langmuir parameters. We compute relative coverage and surface excess (mass per area) based on available laboratory studies. Below: Global results for organic mass fraction in the aerosol versus the usual master variable chlorophyll. Different ecogeographic zones colored e.g. red Arctic, green Southeast Pacific. Black and red lines are fits to the best studied site internationally, Mace Head (Ireland). Blue and green lines are Langmuir to chlorophyll parameterizations of Long at Harvard. Macromolecular chemical distinctions promise representation of saturation, geographic complexity.



Extensions of Langmuir: Multilayers

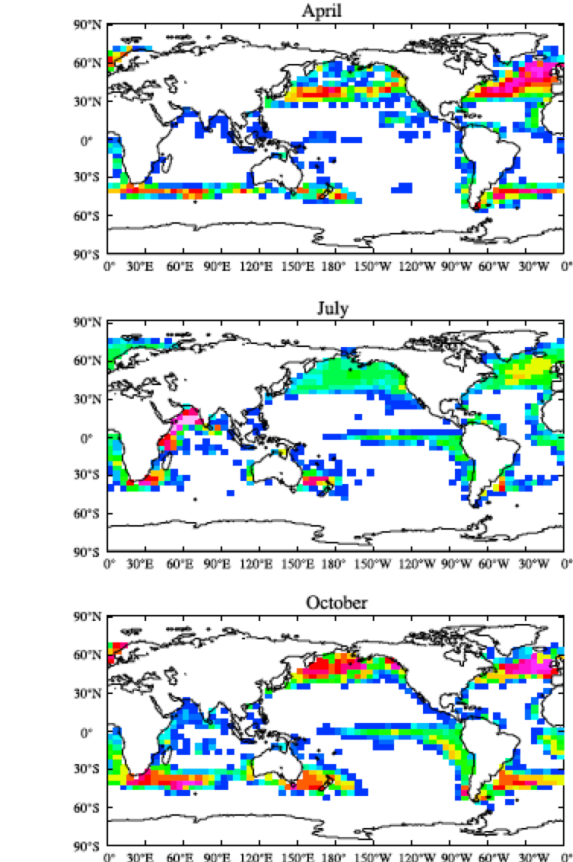
- Polysaccharides turn out to be extremely hydrophilic, hence they resist adsorption
- Yet the marine organic aerosol is rich in hydroxyl moieties (Elliott or Frossard, right)
- We are now exploring cooperative, electrostatic adsorption processes to explain



Adsorption literature abounds in studies of charged surfactants supporting sugars near the surface. Left and below taken from Babak et al. alginates series. Solute concentrations for coverage can be lowered orders of magnitude. Analog processes in the sea may involve Ca²⁺ and Mg²⁺ as bridging ions, acting between fatty acids/sterols at interface and anionic polysaccharides.

Extensions of Macromolecular Chemistry

- Even where waves don't form bubbles, surfactants coat the ocean interface
- Gas transfer rates strongly altered by viscoelasticity near the air border, e.g. CO₂, DMS
- Also the DOC surfactant spectrum overlaps that of transition metal ligands, chelators
- Hence our computations are relevant to bioavailability of iron in the Southern Ocean



Left: Chlorophyll used to estimate general surfactant effects on the global carbon dioxide flux (Tsai and Liu 2003). We will distinguish effects for lipids, proteins, humics etc. Below: Many of the organic substituent groups coordinate trace metals, e.g. carboxylic acids, protein R groups, amines. We will ask whether our polymer distributions can explain patterns of iron bioavailability. Complexation shown for deferaserioux as model siderophore.

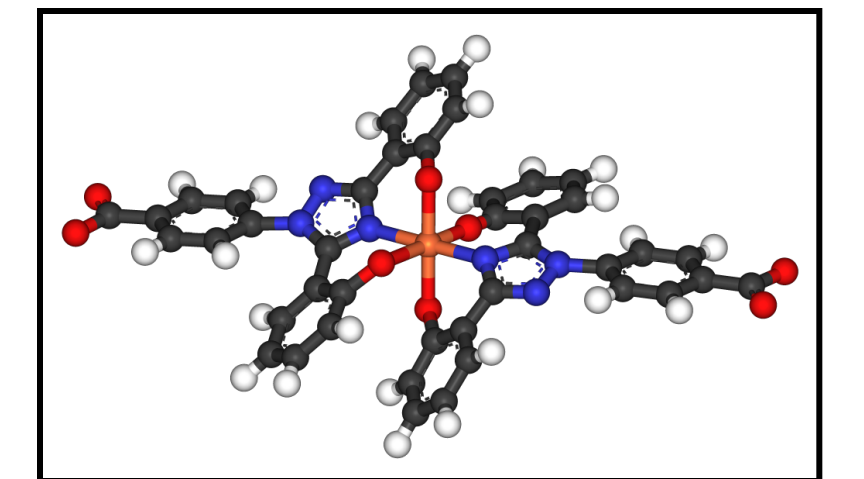
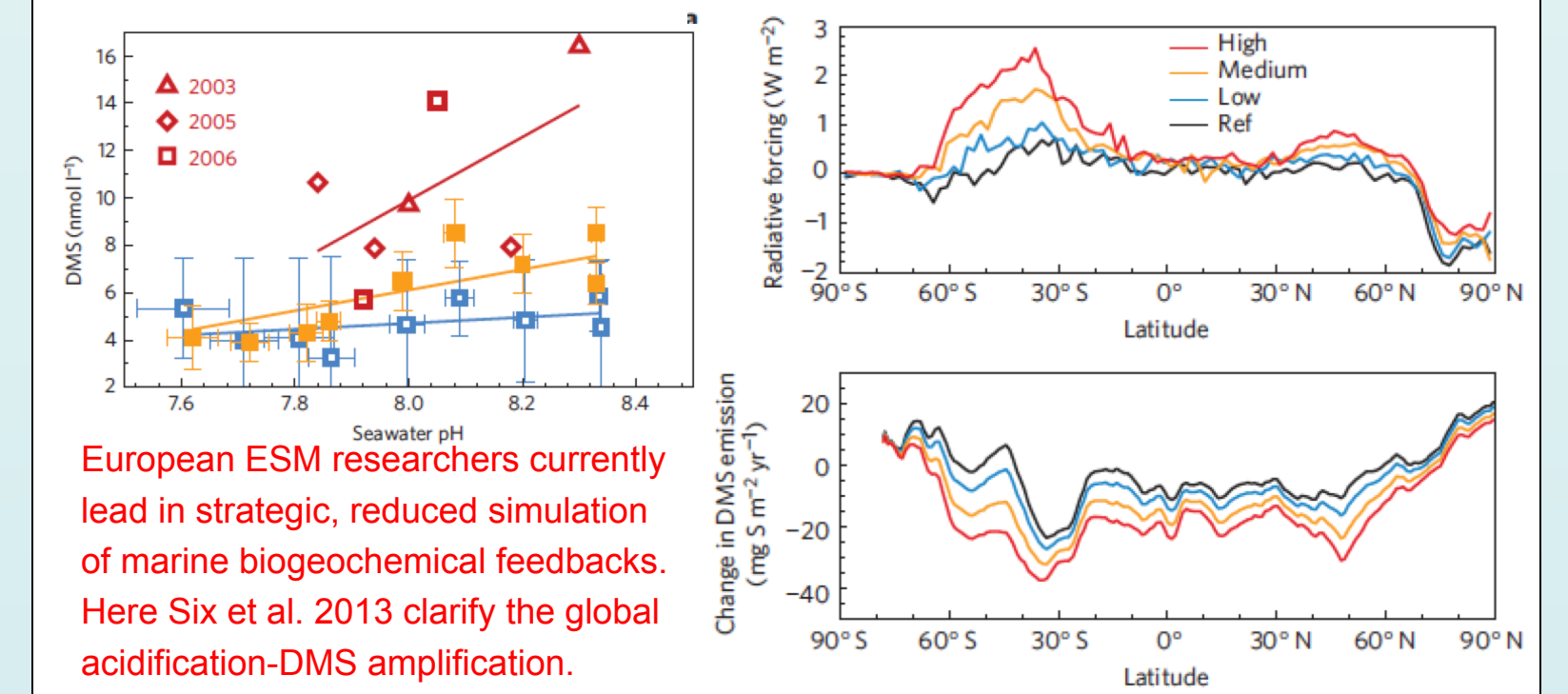


Figure 5. Maps of CO₂ exchange coefficient reduction in units of mol m⁻² yr⁻¹ "juts" by surfactants using the threshold value of $\beta = 15 \text{ g-C m}^{-3} \text{ mol}^{-1}$ for the months of January, April, July, and October. Blank areas of the oceans are free of surfactants, and therefore no reduction in the exchange coefficient is found.

Feedbacks through the Earth System

- Marine bio-emissions dominate aerosol precursor inputs over most of the planet
- Potential for CLAW-like feedback abounds and we are well positioned to simulate
- LANL/PNNL/LLNL coupling both DMS and macromolecules into MAM within CESM
- Reduced models regularly demonstrate the need for complete climate system runs
- Hopefully upcoming in the new ACME model, emphasizing fast forcing agents



European ESM researchers currently lead in strategic, reduced simulation of marine biogeochemical feedbacks. Here Six et al. 2013 clarify the global acidification-DMS amplification.

Relevant Recent Publications

Elliott, S., Burrows, S., Deal, C., Liu, X., Long, M., Russell, L., Ogunro, O. and Wingerter, O. 2014. Prospects for the simulation of macromolecular surfactant chemistry at the ocean-atmosphere boundary. *Environmental Research Letters*, in press.

Frossard, A. with Elliott, S. and 7 others. 2014. Sources and composition of submicron organic mass in marine aerosol particles. *Journal of Geophysical Research - Atmospheres*, submitted.

Burrows, S., Ogunro, O., Russell, L., Rasch, P. and Elliott, S. 2014. A physically based framework for modeling the organic fractionation of sea spray aerosol from bubble film Langmuir equilibria. *Atmospheric Chemistry and Physics*, ACP-2014-32, under discussion.

Meskhidze, N. with Elliott, S. and 27 others. 2013. Production, number concentration, size distribution, chemical composition and optical properties of sea spray aerosol. *Atmospheric Science Letters*, doi:10.1002/asl2.441.

Elliott, S., Deal, C., Humphries, G., Hunke, E., Jeffery, N., Jin, M., Levasseur, M. and Stefels, J. 2012. Pan-Arctic simulation of coupled nutrient-sulfur cycling due to sea ice biology. *Journal of Geophysical Research - Biogeosciences*, 2011JG001649.

Humphries, G., Elliott, S., Deal, C. and Huetmann, F. 2012. Spatial prediction of sea surface dimethylsulfide concentrations in the high Arctic. *Biogeochemistry* 110, 287-301.

Deal, C. with Elliott, S. and 12 others. 2012. Progress in biogeochemical modeling of the Pacific Arctic Region. In *Pacific Arctic Region Post-IPY Synthesis*, Grebeiner, J., Maslowski, W. and Zhao, J. (Editors), Springer.

Cameron-Smith, P., Elliott, S., Maltrud, M., and Wingerter, O. 2011. Shifts in oceanic dimethyl sulfide due to climate change. *Geophysical Research Letters* 2011GL047069.

Loose, B., Miller, L., Elliott, S. and Papakyriakou, T. 2011. Sea ice biogeochemistry with transfer of CO₂ and other gases. *Oceanography* 24, 202-218.

Le Clainche, Y. with S. Elliott and 17 others. 2010. A first appraisal of prognostic ocean DMS models and prospects for their use in climate simulations. *Global Biogeochemical Cycles* 24, doi:10.1029/2009GB003721.

Elliott, S. 2009. Dependence of DMS global sea-air flux distribution on transfer velocity and concentration field type. *Journal of Geophysical Research - Atmospheres*, 2008JG000710.

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