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Marine aerosol sources: organics

- Contribution to SSA mass
- Enrichment mechanism
- Seasonal cycles
- Relevance as CCN and IN

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Atmospheric System Research (ASR) Fall Working Group
Meeting CAPI and Cloud Lifecycle Working Groups
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Organic matter makes up a significant fraction of small marine particles

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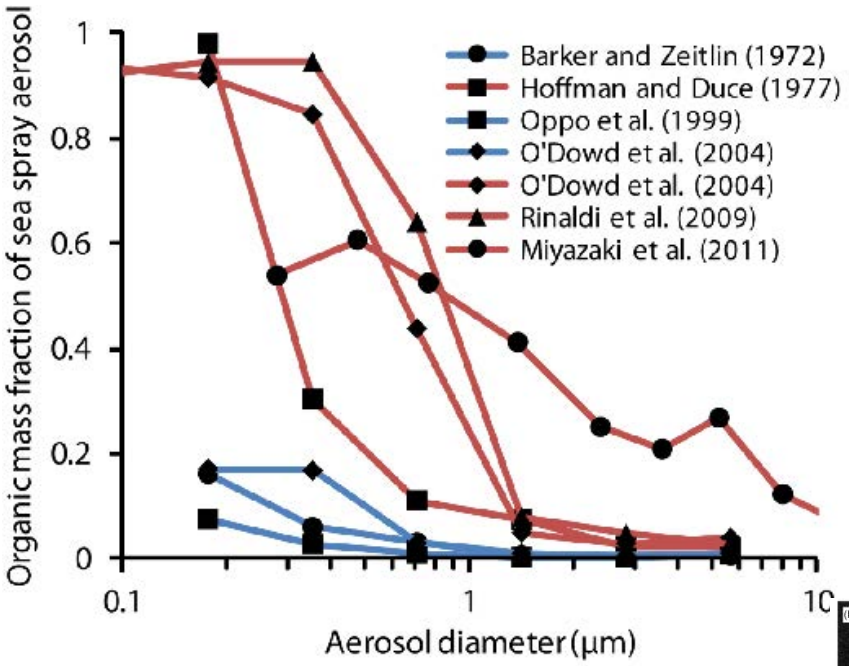
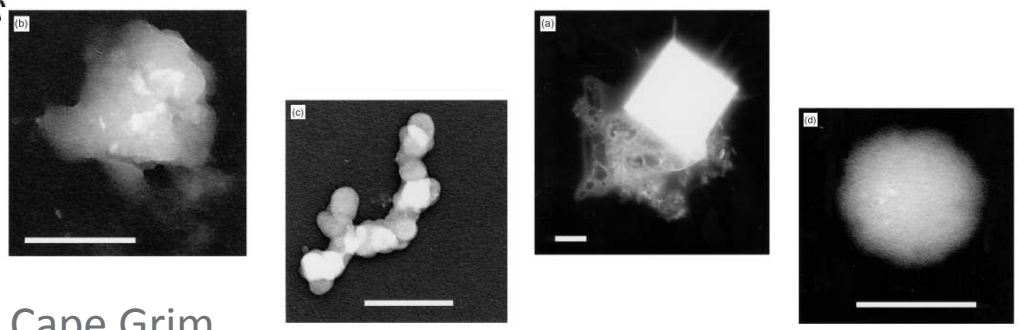
Red: biologically-active season
Blue: biologically-inactive season



Gantt et al., 2013

Attributed mainly to primary sources:

- Mostly insoluble.
- Chemical analysis (FTIR, STXM-NEXAFS) shows that much of it contains proteinaceous / polysaccharide-like material.
- Many particles contain fragments / agglomerates visible in TEM images.

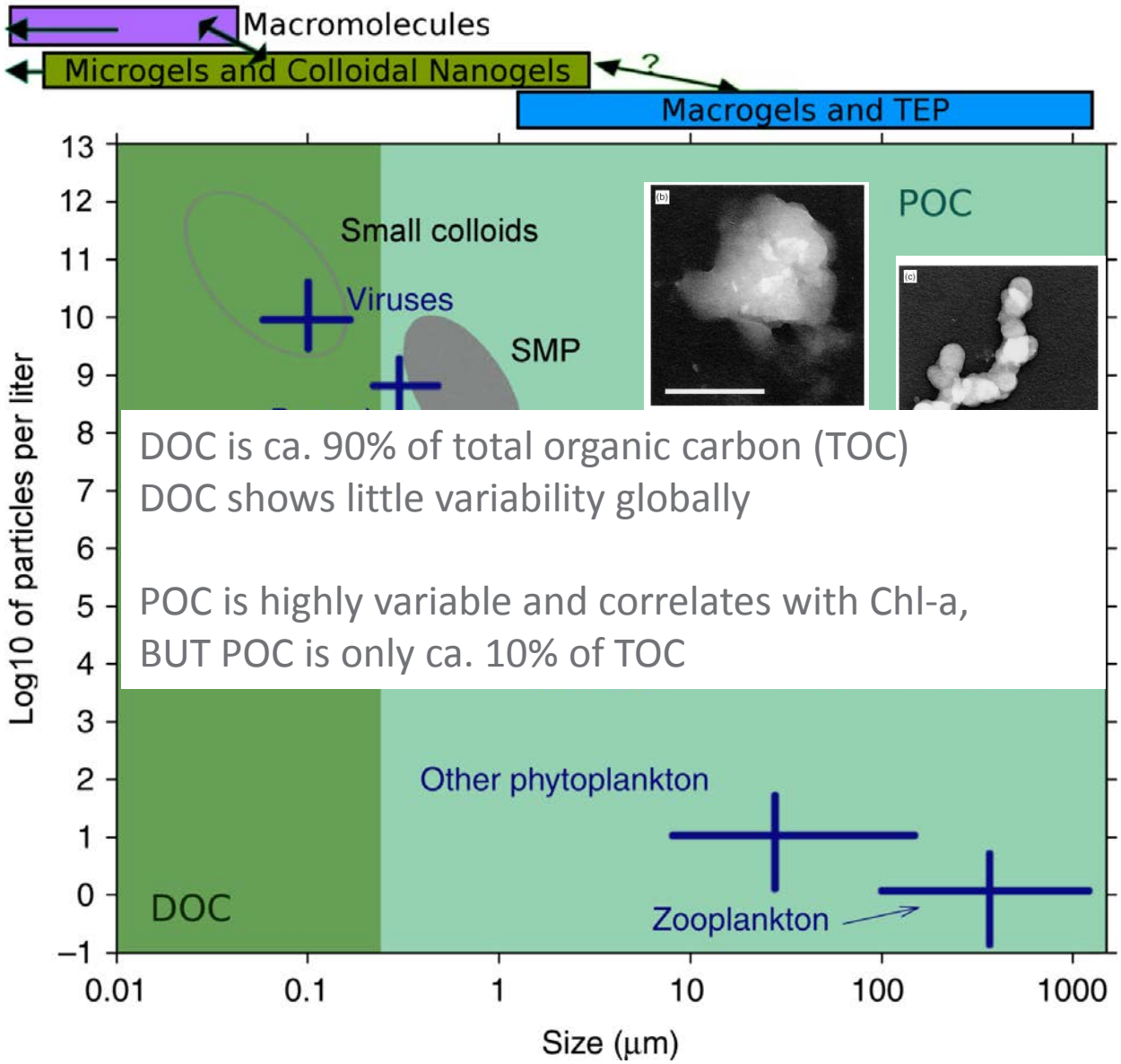


Bigg, 2007

Marine particles collected at Cape Grim

Almost all marine particulate mass is colloidal / gel-like material.

(Chin et al., 1998; Verdugo et al., 2004, 2008)



DOC is ca. 90% of total organic carbon (TOC)
DOC shows little variability globally

POC is highly variable and correlates with Chl-a,
BUT POC is only ca. 10% of TOC

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POC: particulate organic carbon

DOC: dissolved organic carbon

SMP: submicrometer particles

DYP: DAPI-positive yellow particles

TEP: transparent exopolymers stained by Alcian Blue

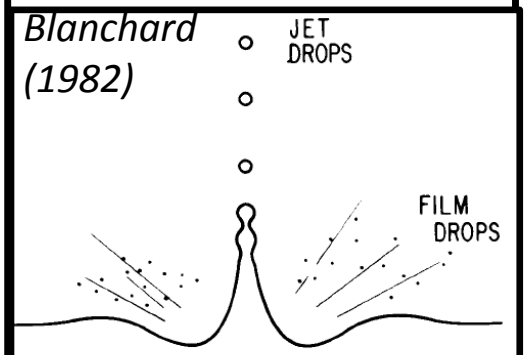
CSP: proteinaceous particles stained by Coomassie Brilliant Blue

Wells and Goldberg, 1991; Alldredge et al., 1993; Long and Azam, 1996; Mostajir et al., 1995; Yamasaki et al., 1998; Verdugo et al., 2004; Bigg, 2007; Kirchman, 2008

MBL

Particle formation from film by bubble bursting.

Blanchard (1982)



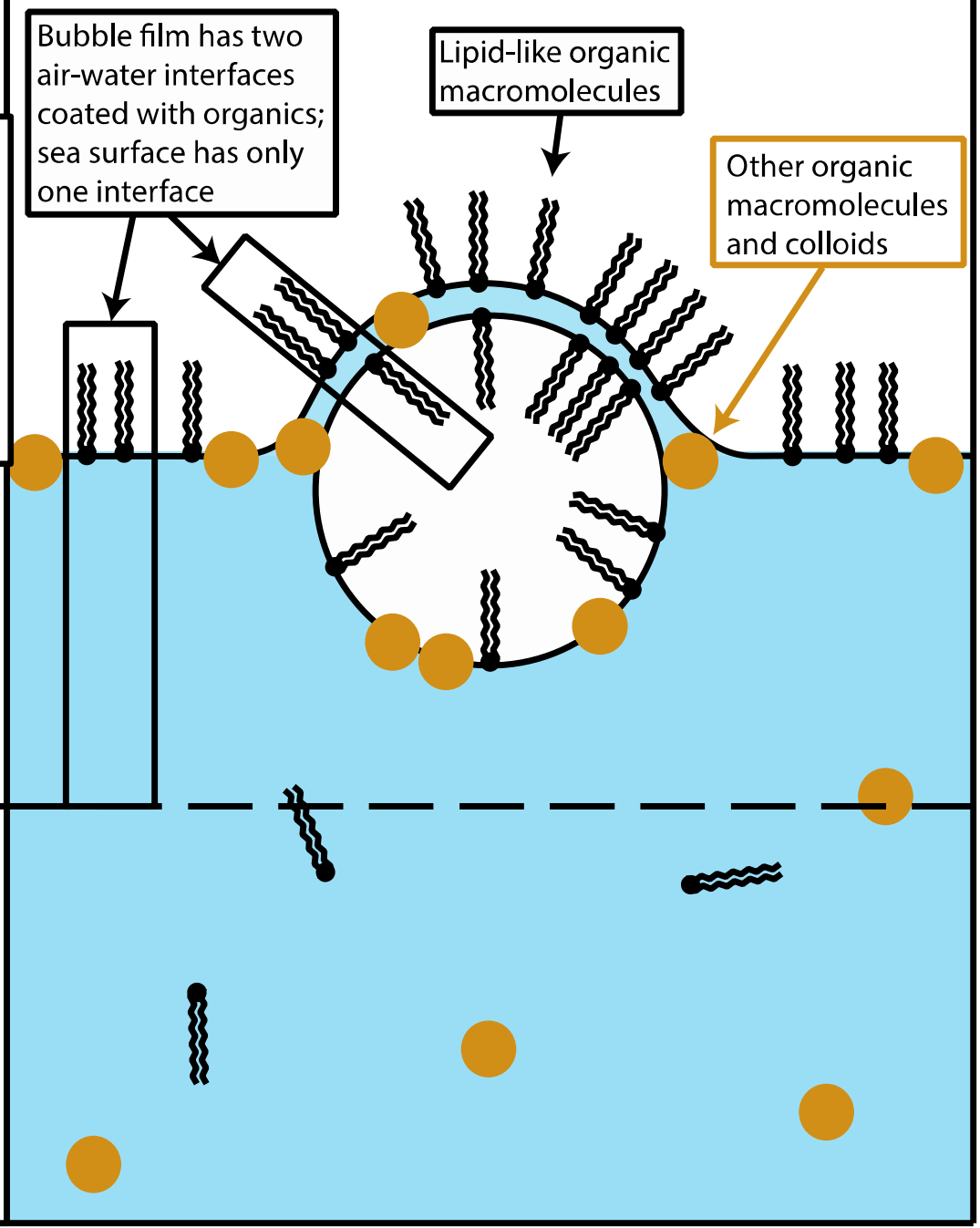
SML

Bubbles rest on surface; film drains, preferentially reducing non-surfactants.

BLK

Collection of surfactants on bubble surfaces by impaction, interception and diffusion, followed by adhesion/adsorption. Upward transport and deposition in SML.

Burrows et al., ACP, 2014, in press



Organic enrichment of sea spray: First fully mechanistic parameterization

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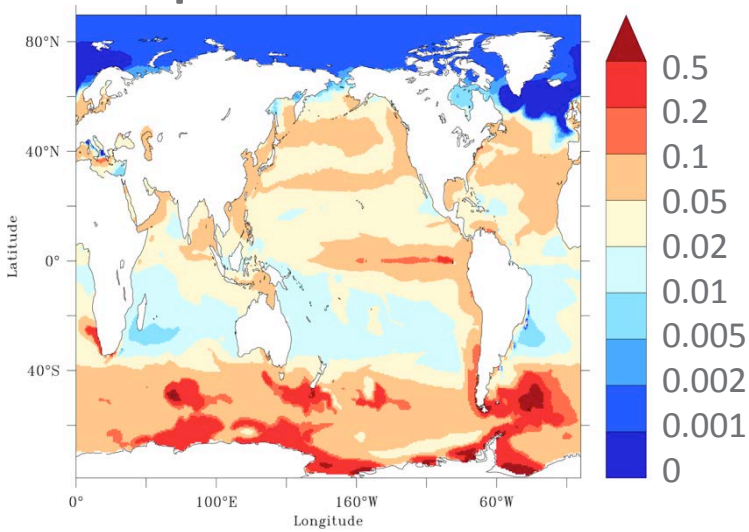
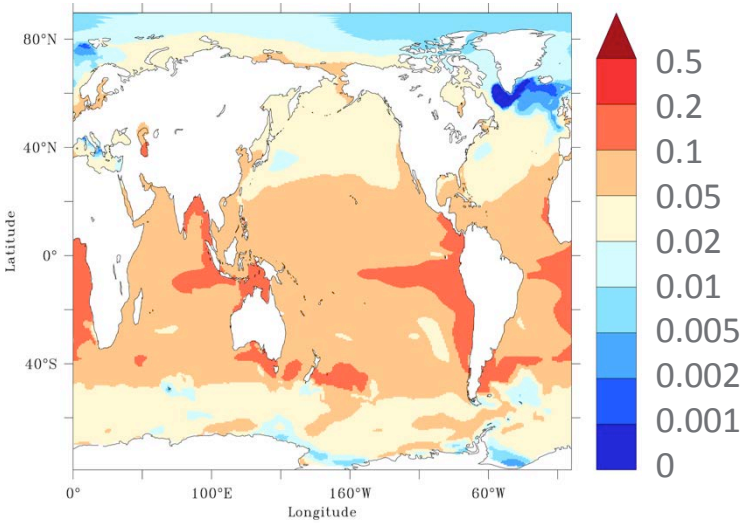
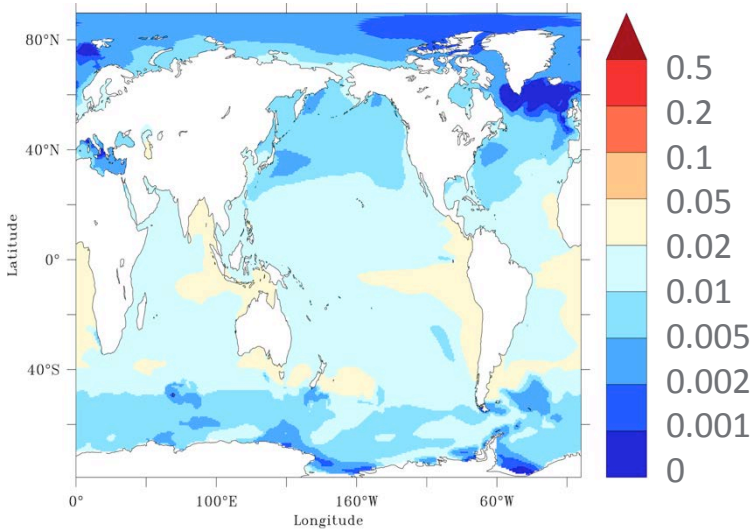
Lipid-like mixture



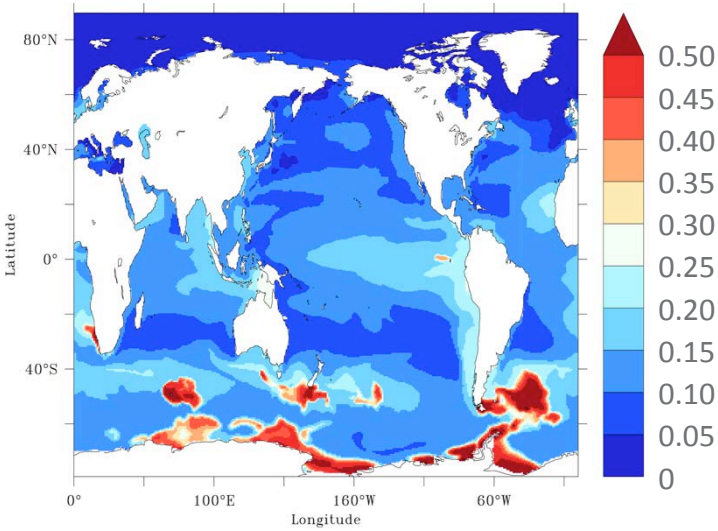
Protein-like mixture



Polysaccharide-like mixture

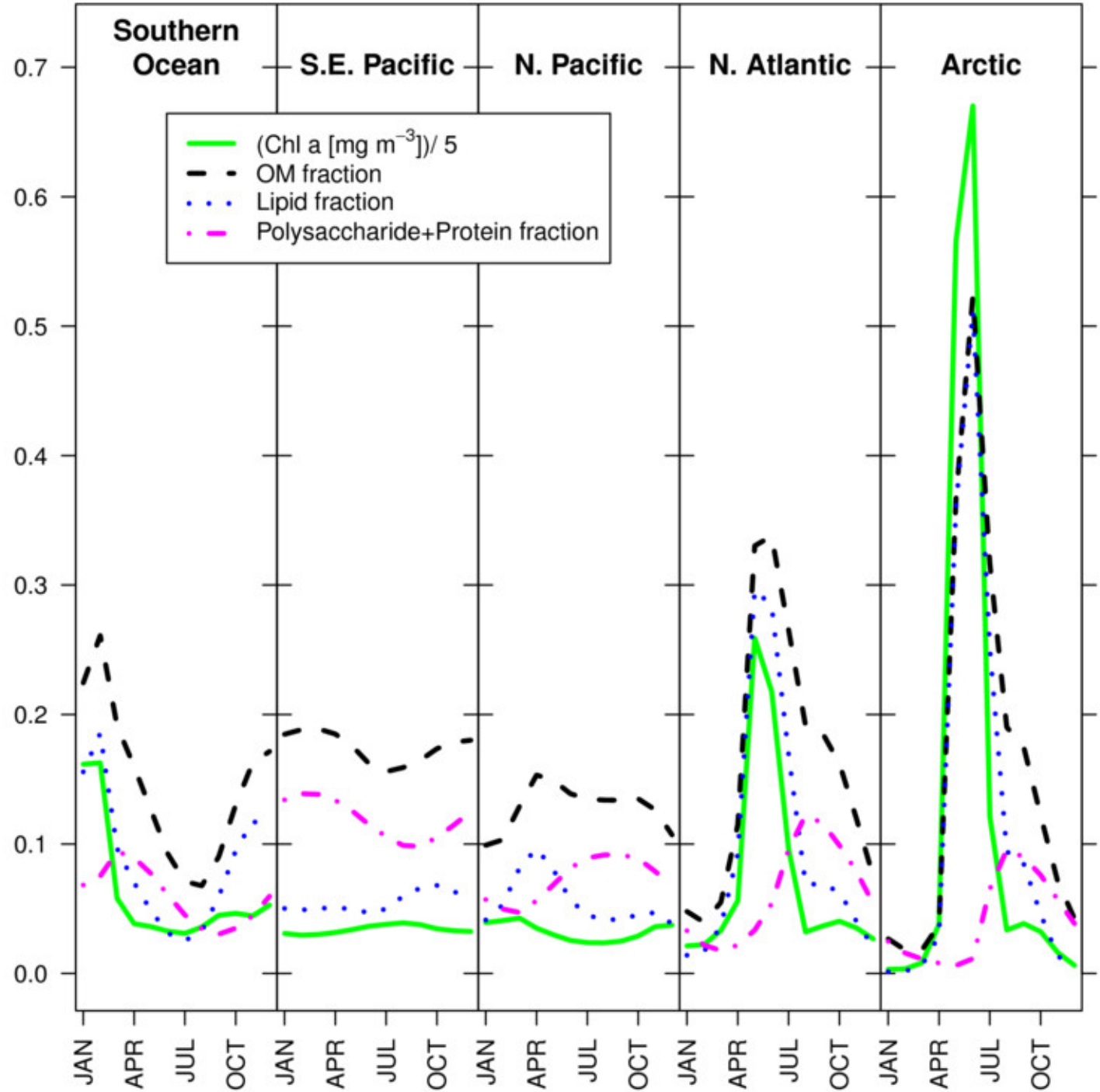


Total organic mass fraction



Elliott et al., ERL, 2014; Burrows et al., ACP, 2014, in press

Seasonal cycles of marine biota vary regionally



Burrows et al., 2014, ACP, in press

Evidence that marine organics affect CCN: SO4 and OM fraction predict cloud-top droplet concentration (Nd) over Southern Ocean

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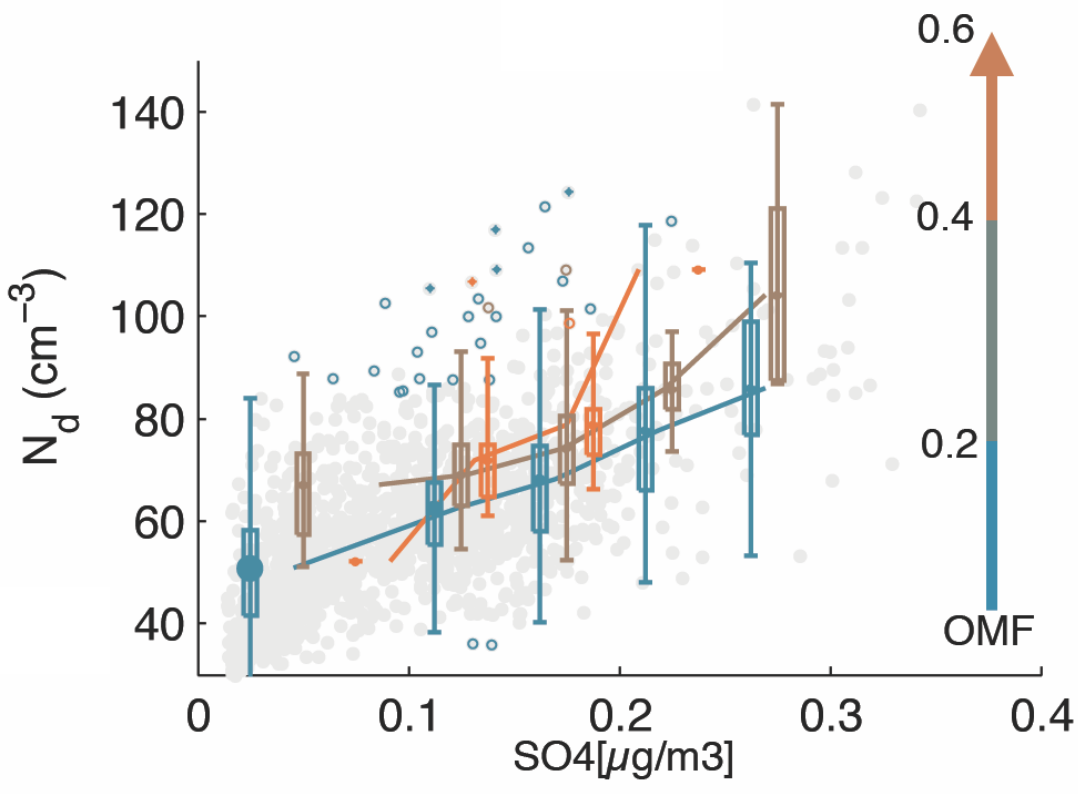
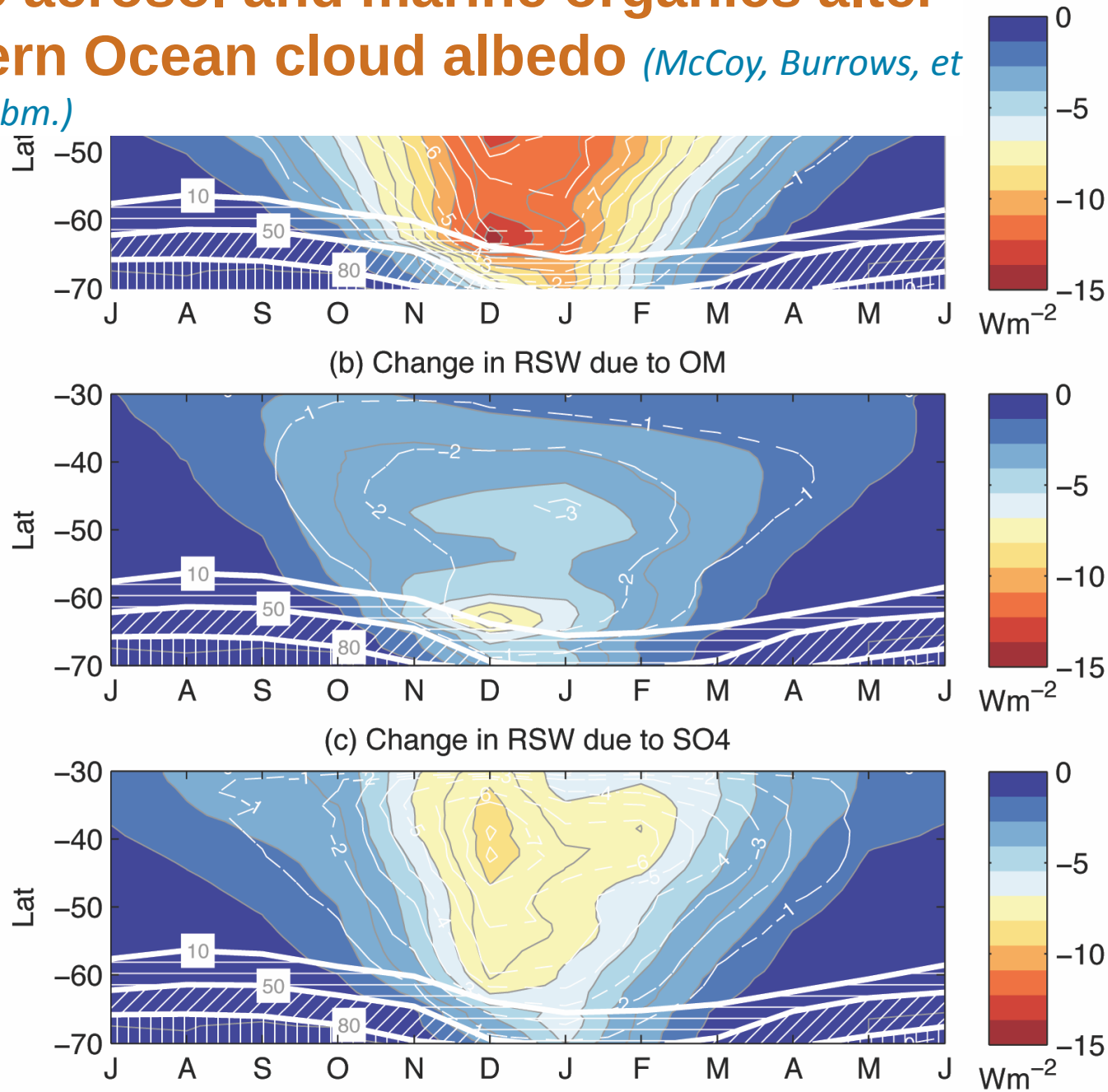
Nd vs. SO4, binned into low-OMF, intermediate OMF, and high-OMF groups



- More than half of the variance in monthly mean Nd is attributable to SO4, OM
- Variables that do NOT correlate significantly with Nd over Southern Ocean (in monthly mean): observed SST, observed wind speed, model sea salt concentration.

McCoy, Burrows, et al.; 2014, subm.

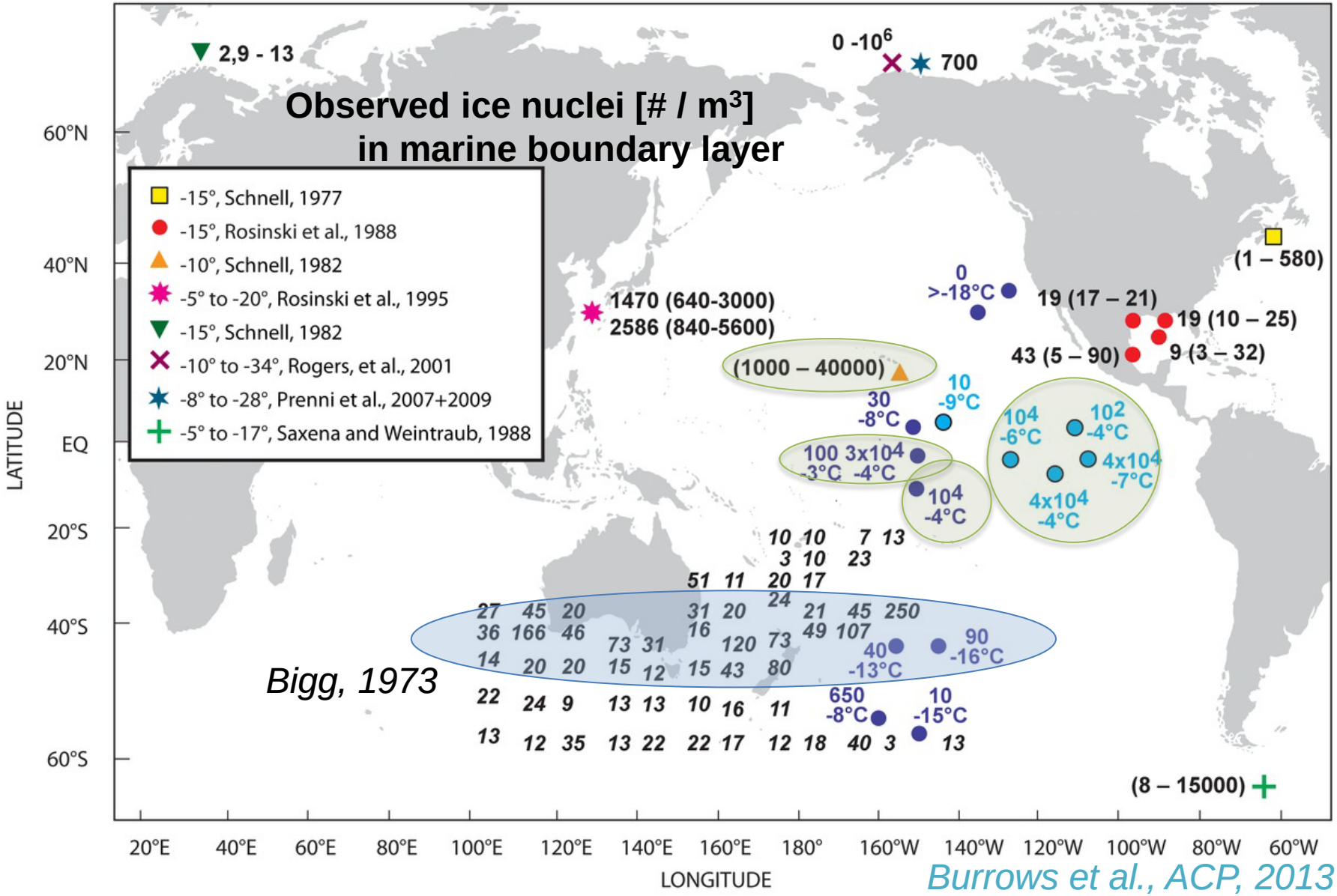
Sulfate aerosol and marine organics alter Southern Ocean cloud albedo *(McCoy, Burrows, et al. 2014, subm.)*



Marine organics dominate remote marine IN?

Observed marine IN concentrations are higher over phytoplankton bloom regions.

Occasionally, very high IN concentrations have been reported over active blooms.



Burrows et al., ACP, 2013

Why think about marine organic aerosol sources?

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- Significant mass in CCN-relevant size range.
- Mostly derived from marine dissolved and colloidal matter.
- SO4 + marine organics predict significant variability in mean Nd over Southern Ocean
- Marine organics may dominate remote MBL ice nuclei.

(Some) open questions:

- What is the mechanism by which organics *increase* CCN number?
- Are organics the primary source of IN in remote marine boundary layer? How important are sources from long-distance transport?

Thanks for your attention!

... Questions?

Additional slides

Field observations: chemically distinct particle classes

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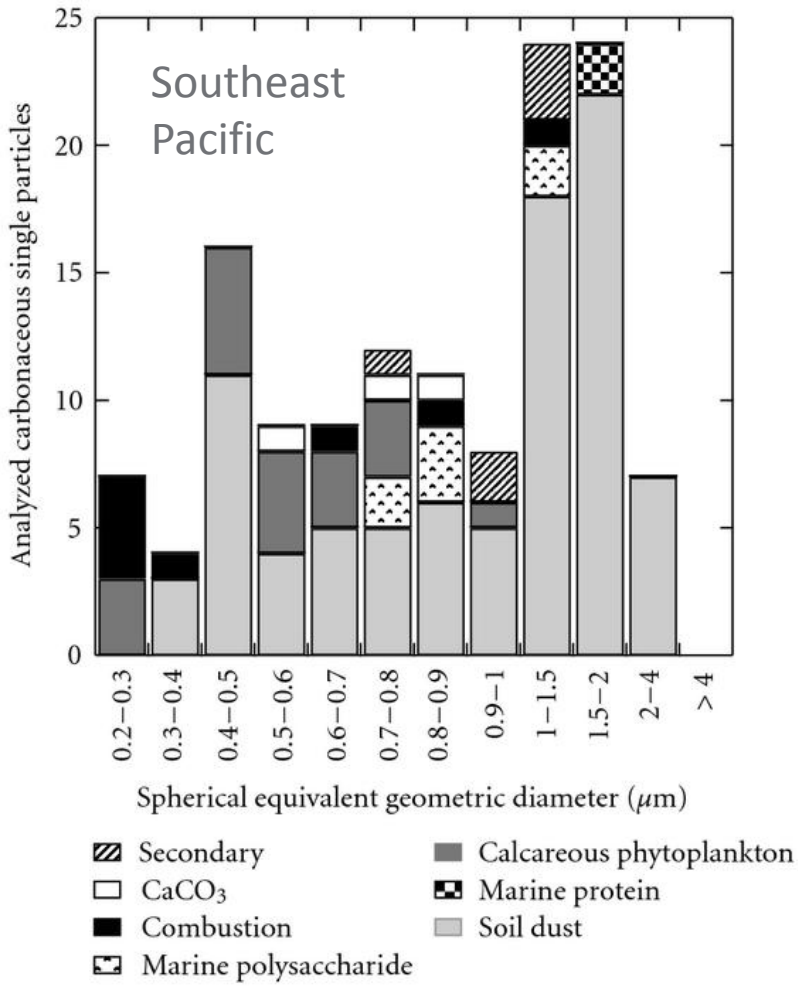
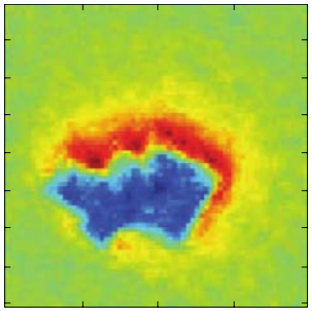
Field observations – NEXAFS single particle spectromicroscopy *(Hawkins and Russell, 2010)*



Arctic marine poly



Southeast Pacific marine poly

Calcareous phytoplankton (SE pac. Only)

Marine protein

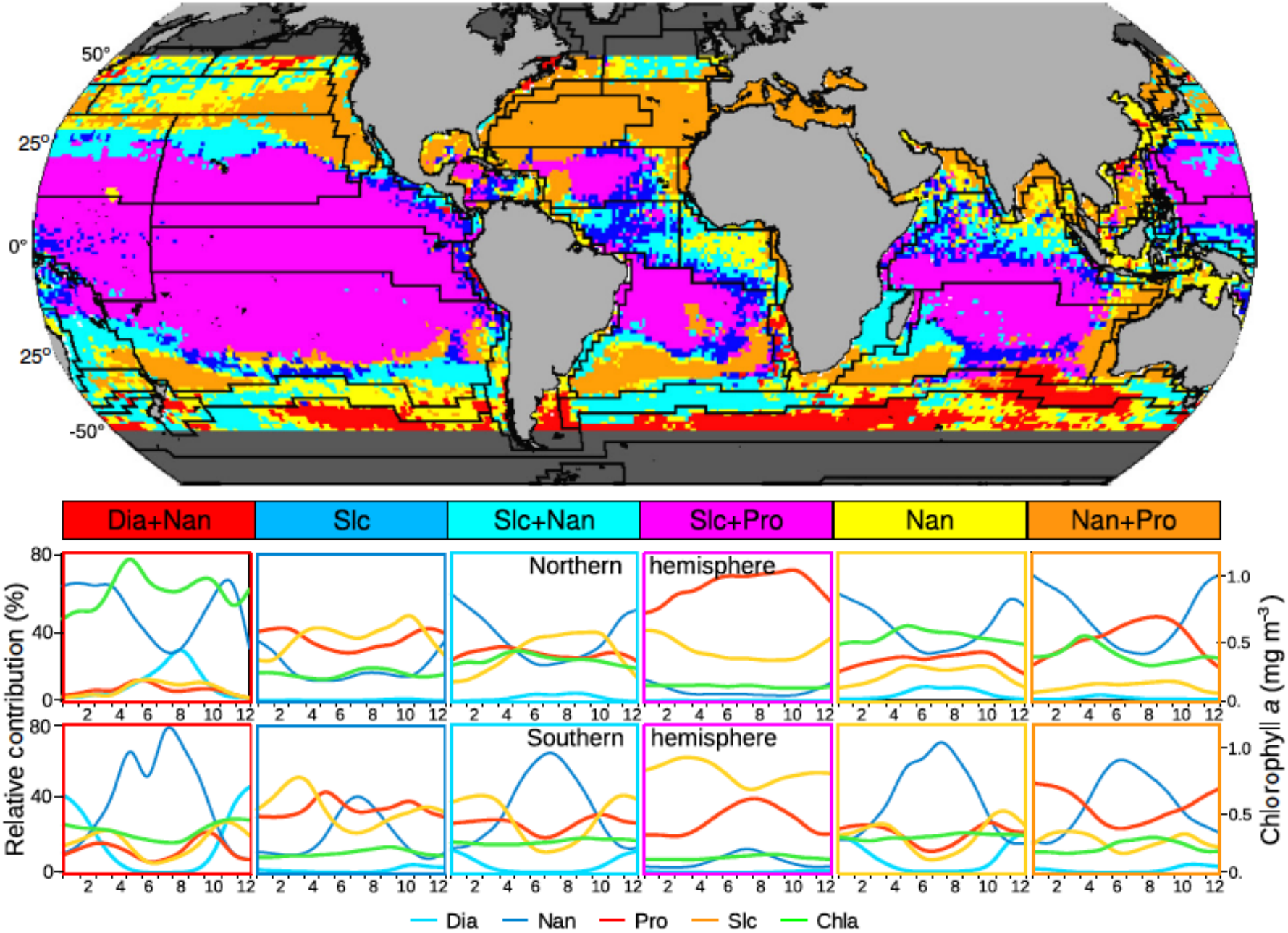


Fig. 6. Spatial distribution of the main associations of Phytoplankton Functional Types that predominantly contribute to the seasonal oscillation of chlorophyll-a concentration detected by ordinary statistical procedure (PCA), as described in the material and methods section. The time series show the average monthly dynamic of each of the 4 Phytoplankton Functional Types and chlorophyll-a concentration for each association, separately for both hemispheres.

Demarcq et al., 2012

Hansell et al. 2012 Global DOC

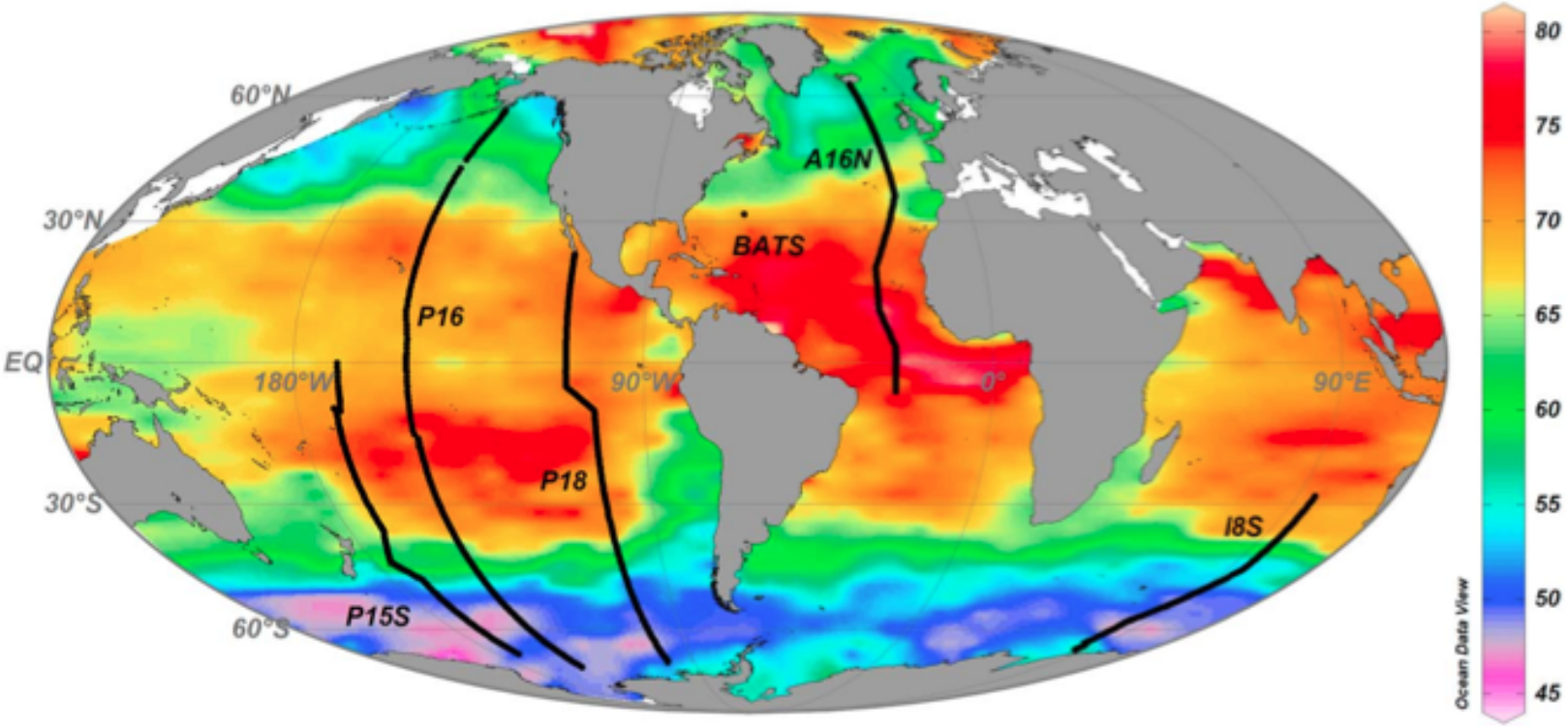
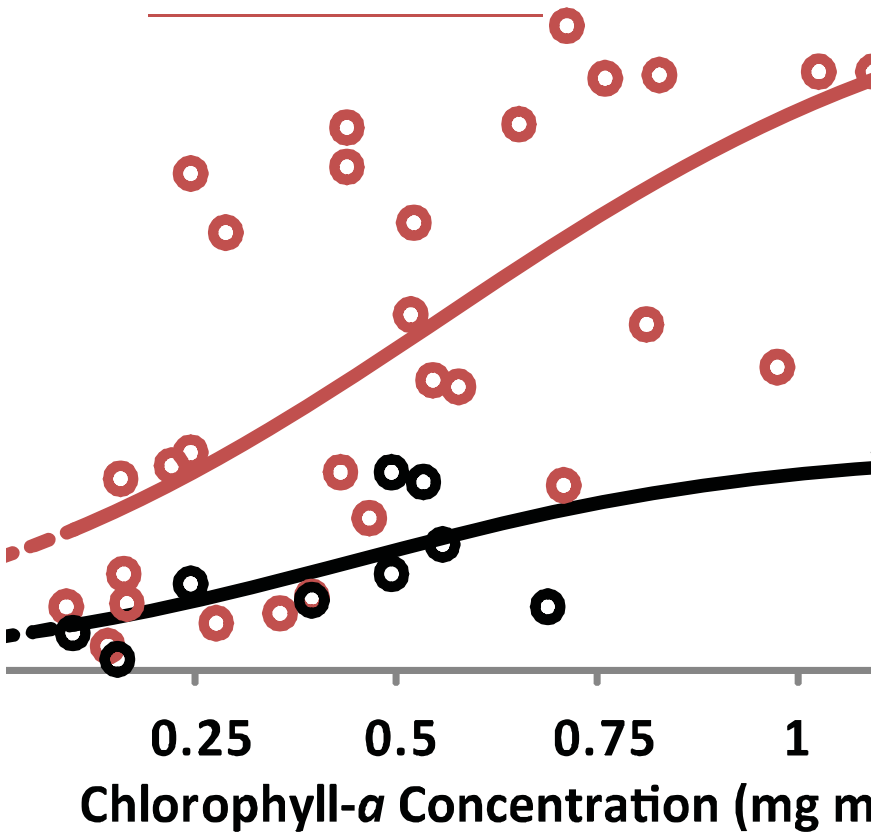


Figure 1. Locations of the BATS site and hydrographic sections A16N (North Atlantic), P16 (central Pacific), P18 (eastern Pacific), I8S (Indian Ocean) and P15S (western South Pacific) over a modeled field of DOC (μmol C kg^{-1}) at 30 m throughout the global ocean [from *Hansell et al.*, 2009]. A16N was occupied in June and July, 2003; P16 in January and February, 2005 (southern hemisphere) and February and March, 2006 (northern hemisphere); P18 in December 2007 and January 2008; I8S in February 2007; P15S in January and February 1996.

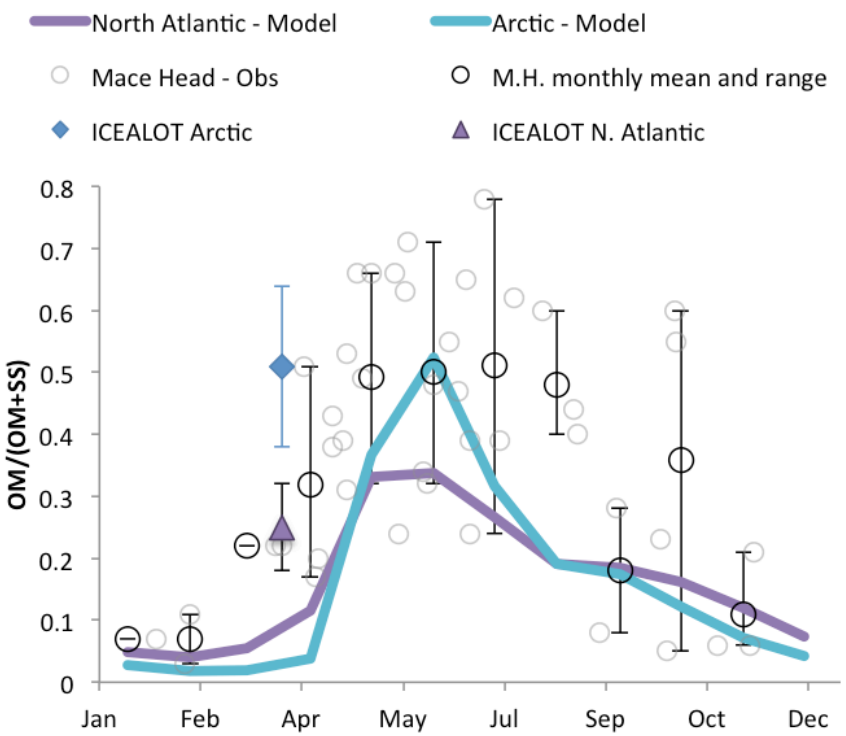
State-of-the-art in sea spray OM modelling

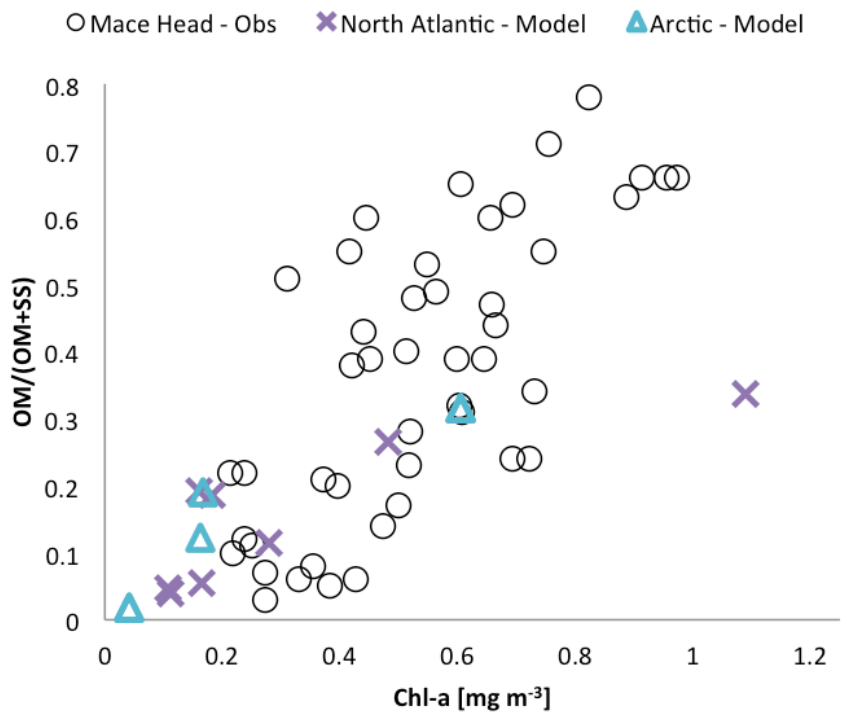


Gantt et al., 2011

- Empirical parameterizations of submicron OM fraction as a function of
  - Chl-a (e.g., *Vignati et al., 2010)*
  - Chl-a + physical variables; (e.g., *Long et al., 2011; Gantt et al., 2011*; *Meskhidze et al., 2011*)
- All rely on only 1-3 sites dominated by mid-latitude seasonal blooms

Model vs. obs: seasonal cycles and Chl-a vs. OM fraction



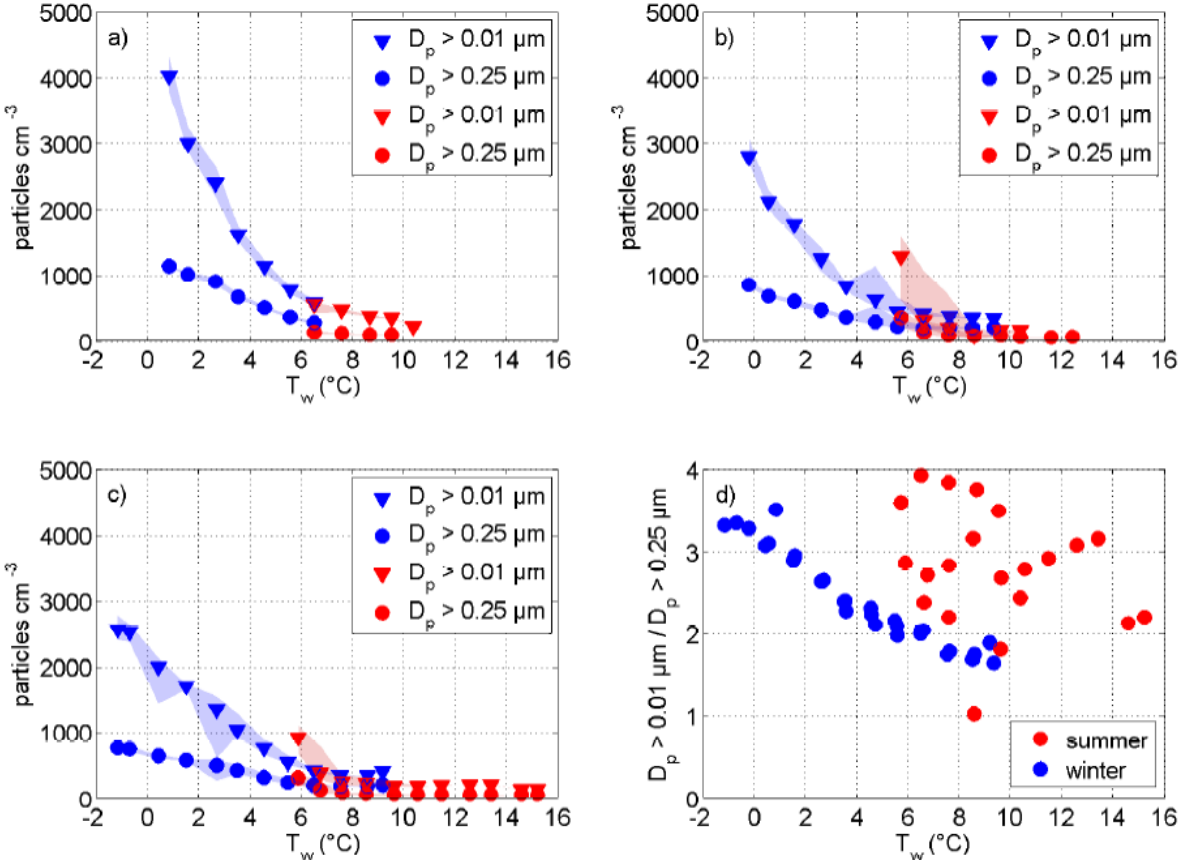


Burrows et al., 2014, ACP, in press

Sea spray emissions increase for SST < 8° C

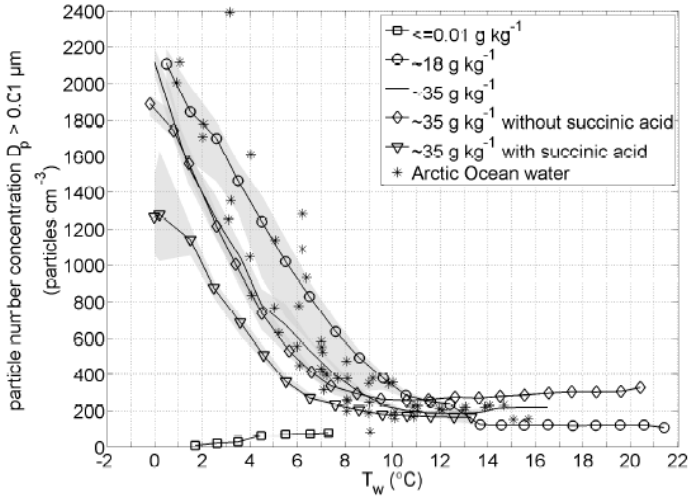
Laboratory experiments with Arctic seawater

red = summer ; blue = winter



Zábori et al., 2013

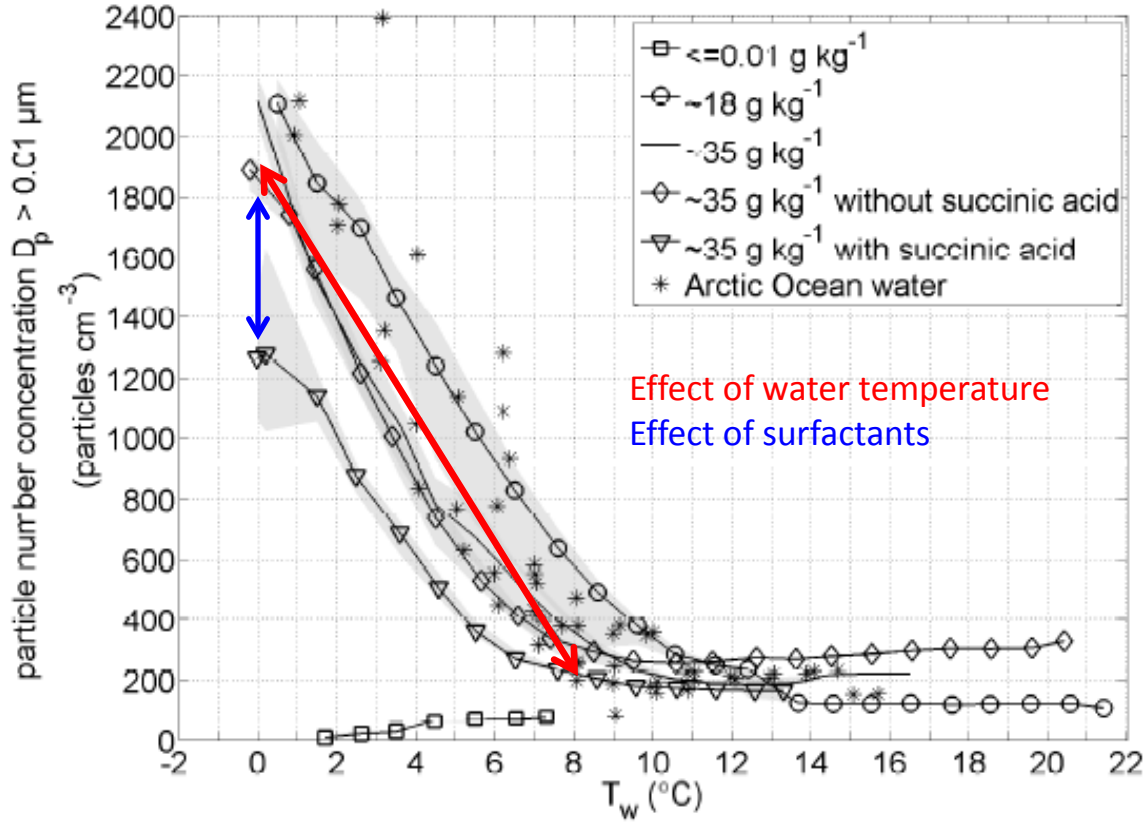
Laboratory experiments with artificial seawater, varying salinity and surfactants



Zábori et al., 2012b

Sea spray emissions at low SST

- Laboratory experiments indicate sea spray production depends on SST and surfactants *(e.g., Zábori et al., 2012a,b)*
- missing from most models



Zábori et al., 2012b

Effect of sea surface temperature on sea spray emissions

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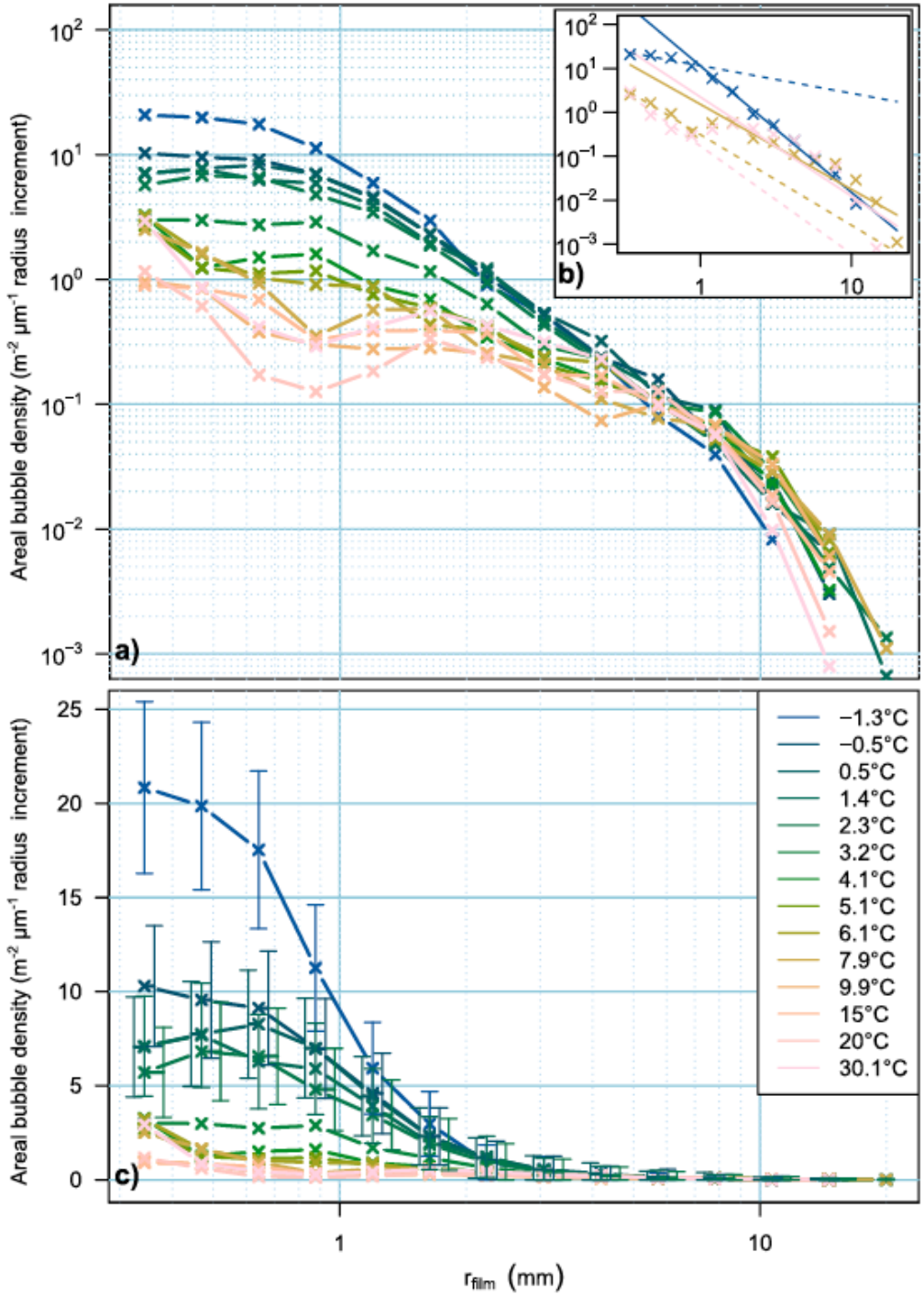
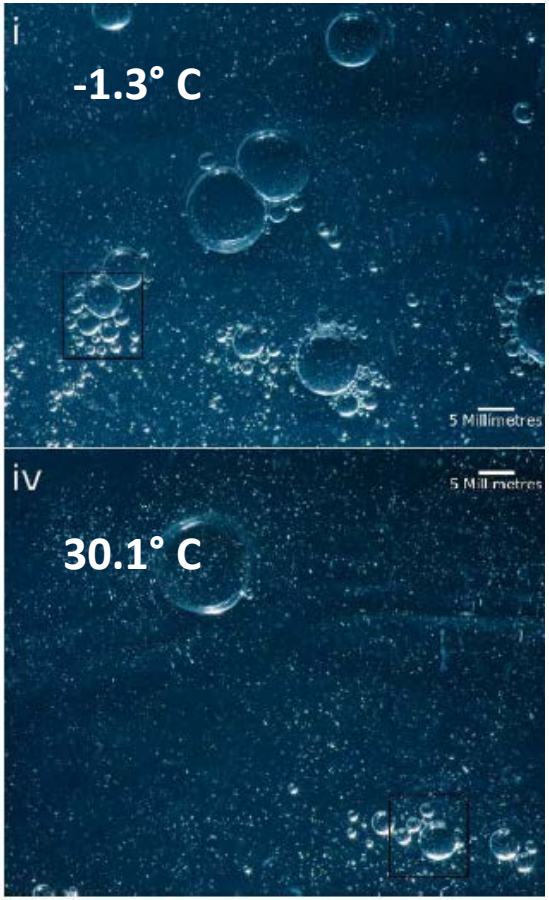
SST affects bubble size distribution
Colder water => more small bubbles

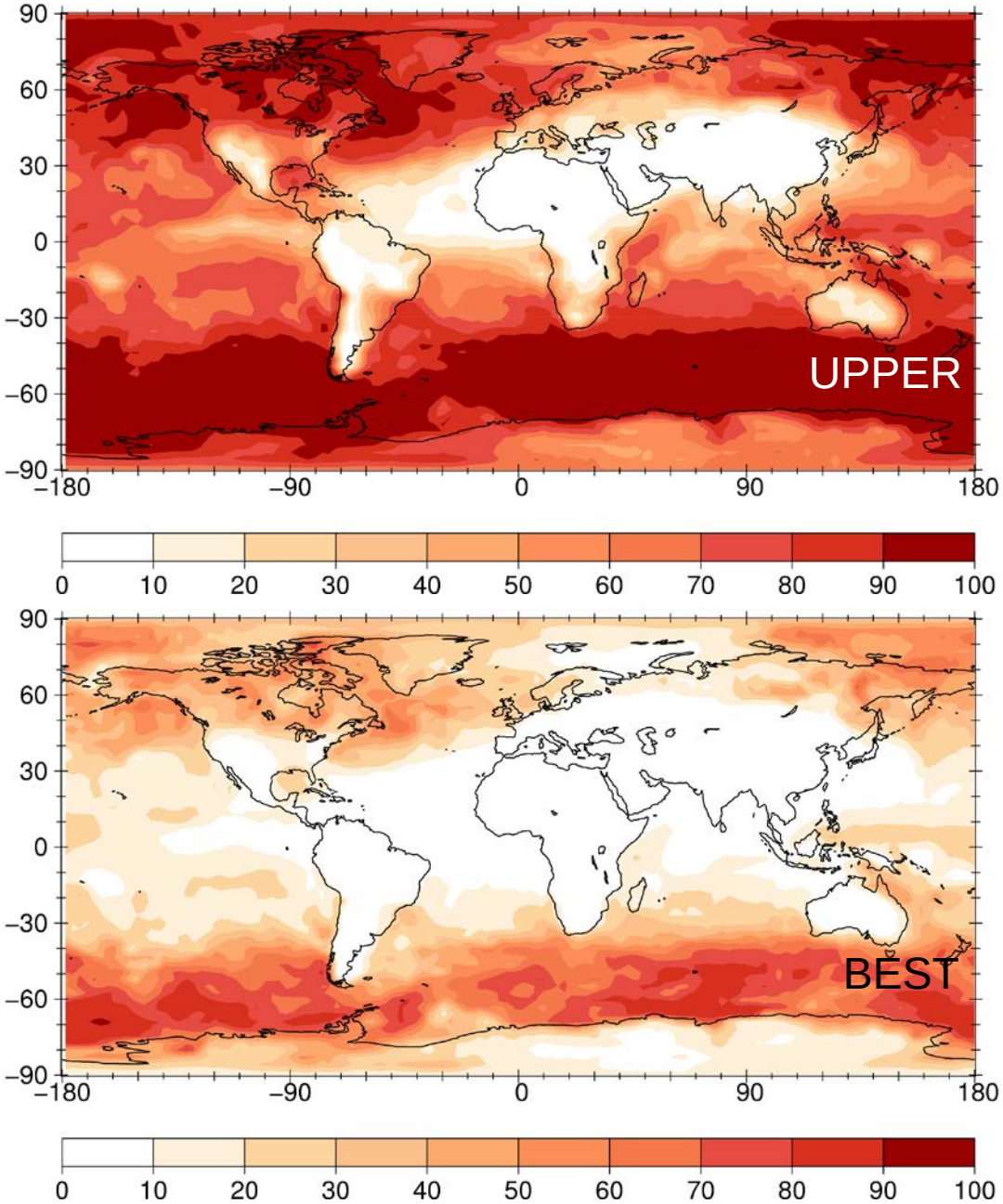




Salter et al., 2013

Estimated percentage contribution of biogenic sea spray to MBL IN population at -15 deg C

- Nature of IN unknown, but only need ca. 1 IN per 10^3-10^4 marine bacteria to reach observed IN concentrations in air / water. *(Schnell and Vali, 1977; Rosinski et al., 1988; Li et al., 2004; Burrows et al., 2013)*



Burrows et al., ACP, 2013