Linking ocean biogeochemistry to marine aerosol composition

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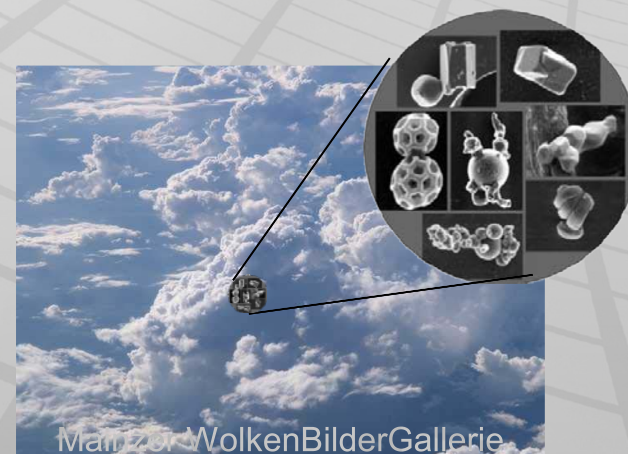

1 – Pacific Northwest National Laboratory
2 – Los Alamos National Laboratory
3 – New Mexico Institute of Mining and Technology

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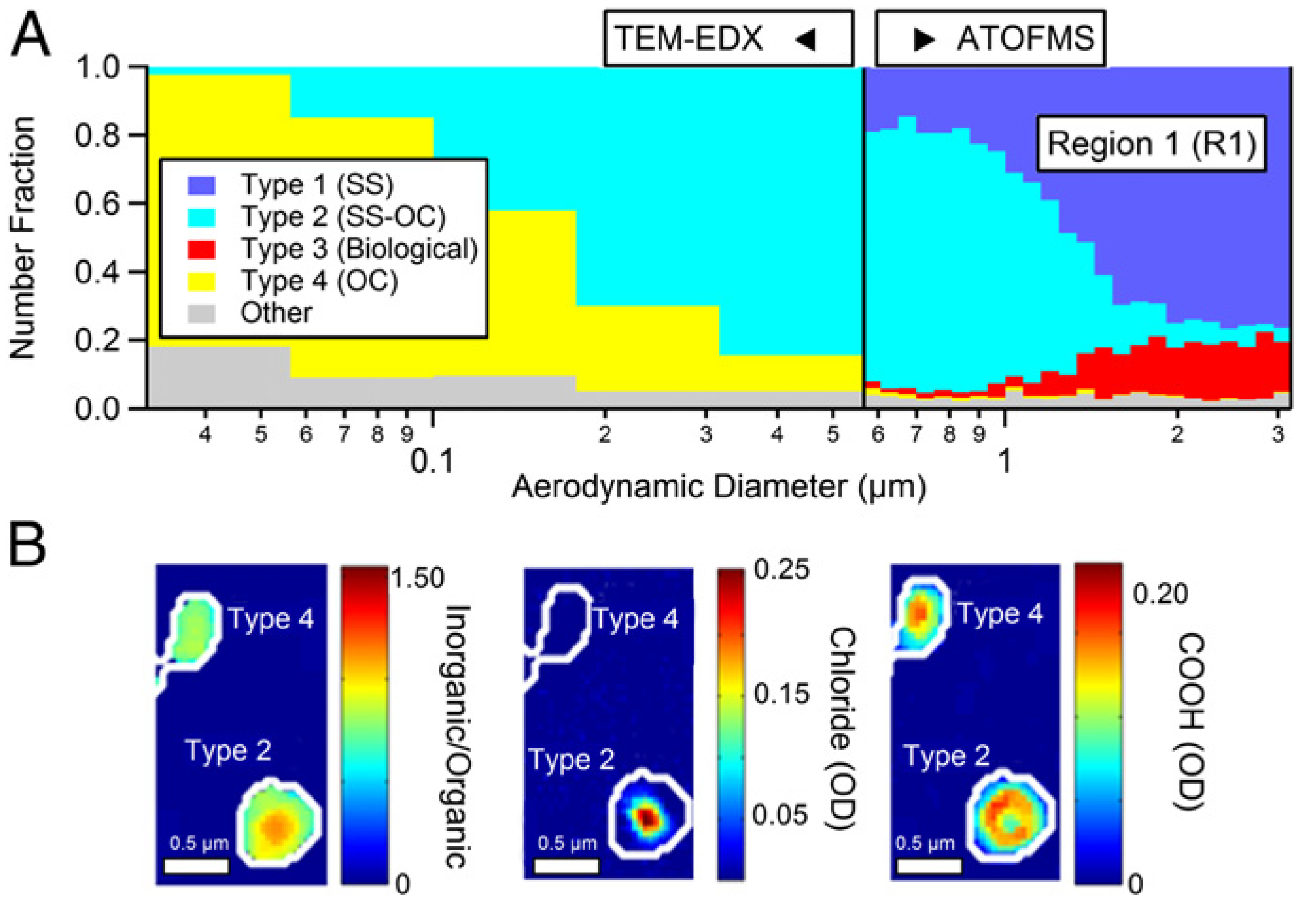
Submicron aerosol particles have distinct chemical composition – large fraction of organics

- Laboratory experiments *(Facchini et al., 2008; Prather et al., 2013)*
- Field observations *(Cavalli et al., 2004; Russell et al., 2010)*

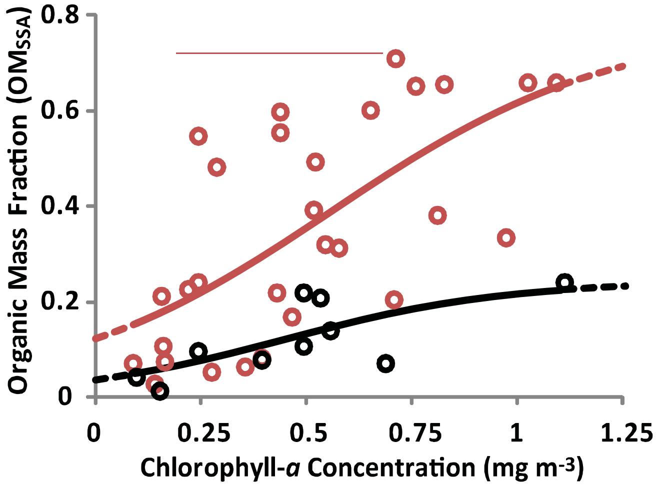


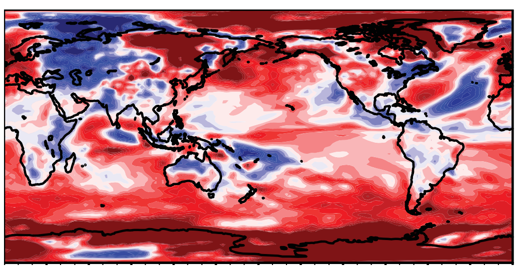
Potential impacts on:

- water uptake and growth
- activity as cloud condensation nuclei (CCN)
- heterogeneous chemistry

Prather et al., 2013

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

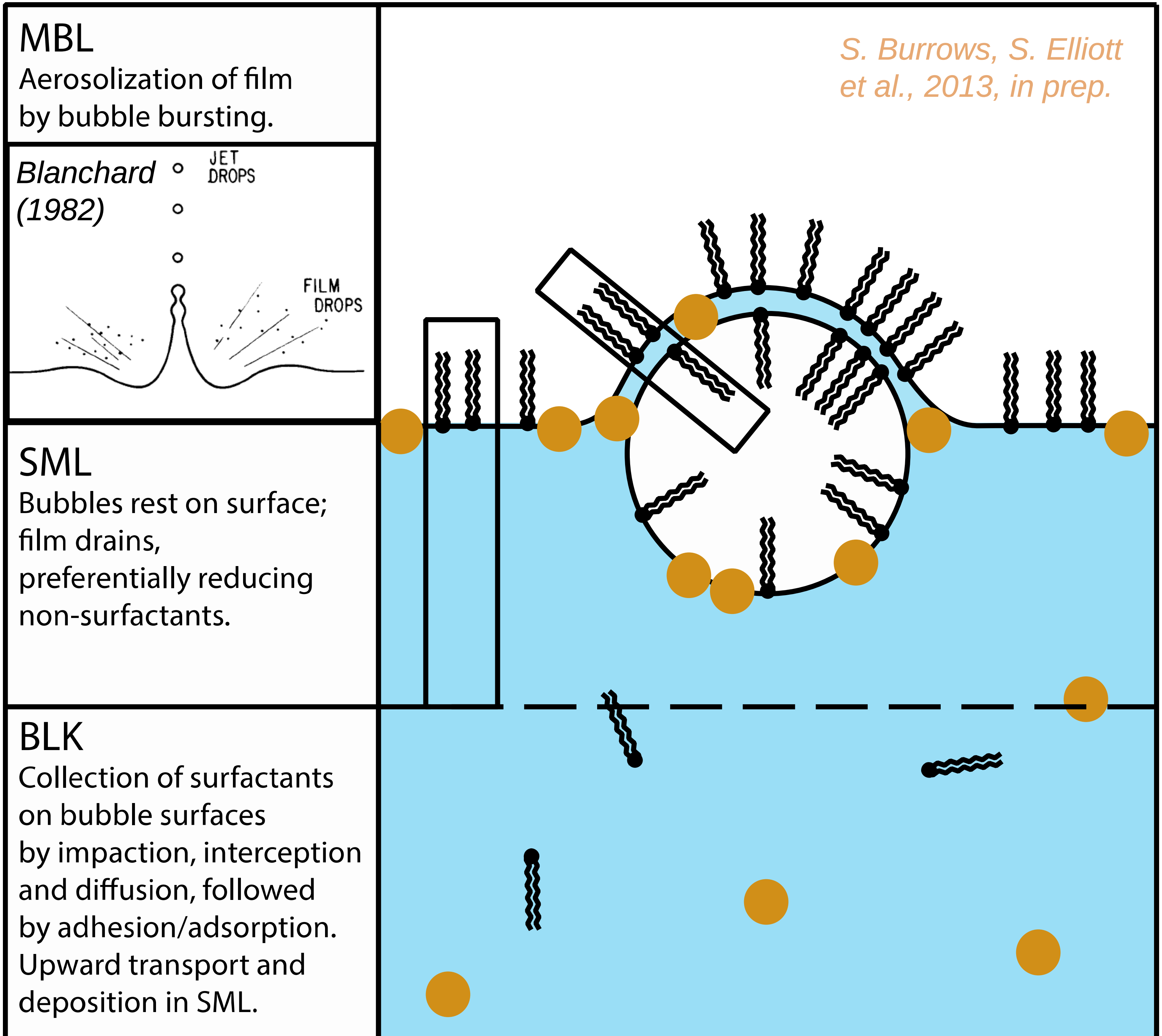




- Empirical parameterizations of OM fraction as a function of…
  - Chl-a (e.g., *Vignati et al., 2010*)
  - Chl-a, wind speed and size (e.g., *Gantt et al., 2011*; *Meskhidze et al., 2011*)
  - Extrapolate from bloom regions
- $CCN_{0.2\%}$ changes up to 20% regionally depending on aerosol mixing state (*Meskhidze et al., 2011*)

Top: Gantt et al., 2011

Bottom: Meskhidze et al., 2011


MBL
Aerosolization of film by bubble bursting.
Blanchard (1982)
JET DROPS
FILM DROPS
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.
S. Burrows, S. Elliott et al., 2013, in prep.

Langmuir adsorption isotherm

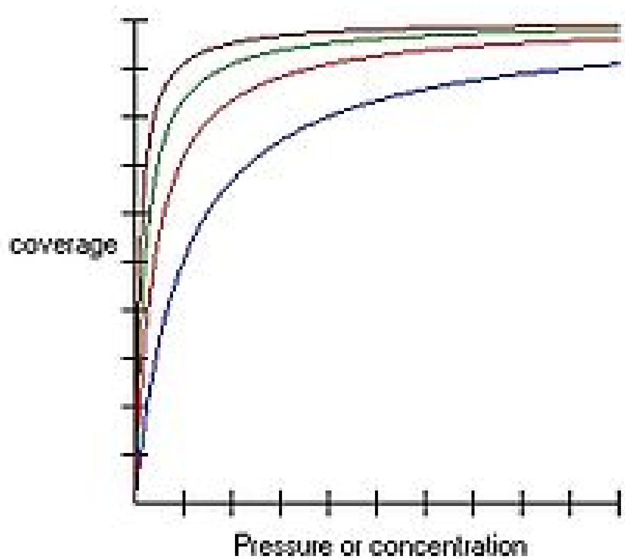
Fraction of surface area covered

Langmuir adsorption constant

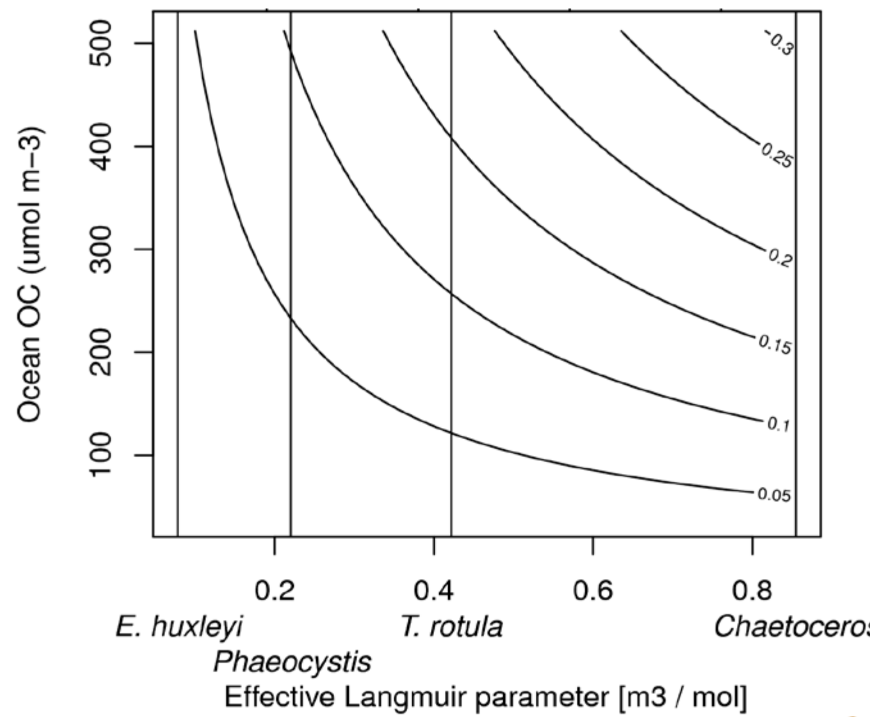
Concentration

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

1. Surface saturation
2. Competition



Example surface coverage calculations using values from Fuentes et al. (2010)



Macromolecule distributions – mapping from BEC model output

µM C

µM C

S. Elliott, S. Burrows, et al., 2013, in prep.

Model compounds for marine organic matter

Table 1. Marine and laboratory model compounds selected to represent the ocean macromolecules, along with reference concentrations $C_{1/2}$ and carbon surface excess Γ_{max}. Except as stated in the text, data are for room temperature and low ionic strength. Concentrations and surface densities are given in moles per liter carbon and then atoms per square angstrom. Parenthetical values were estimated based on others in the same class.

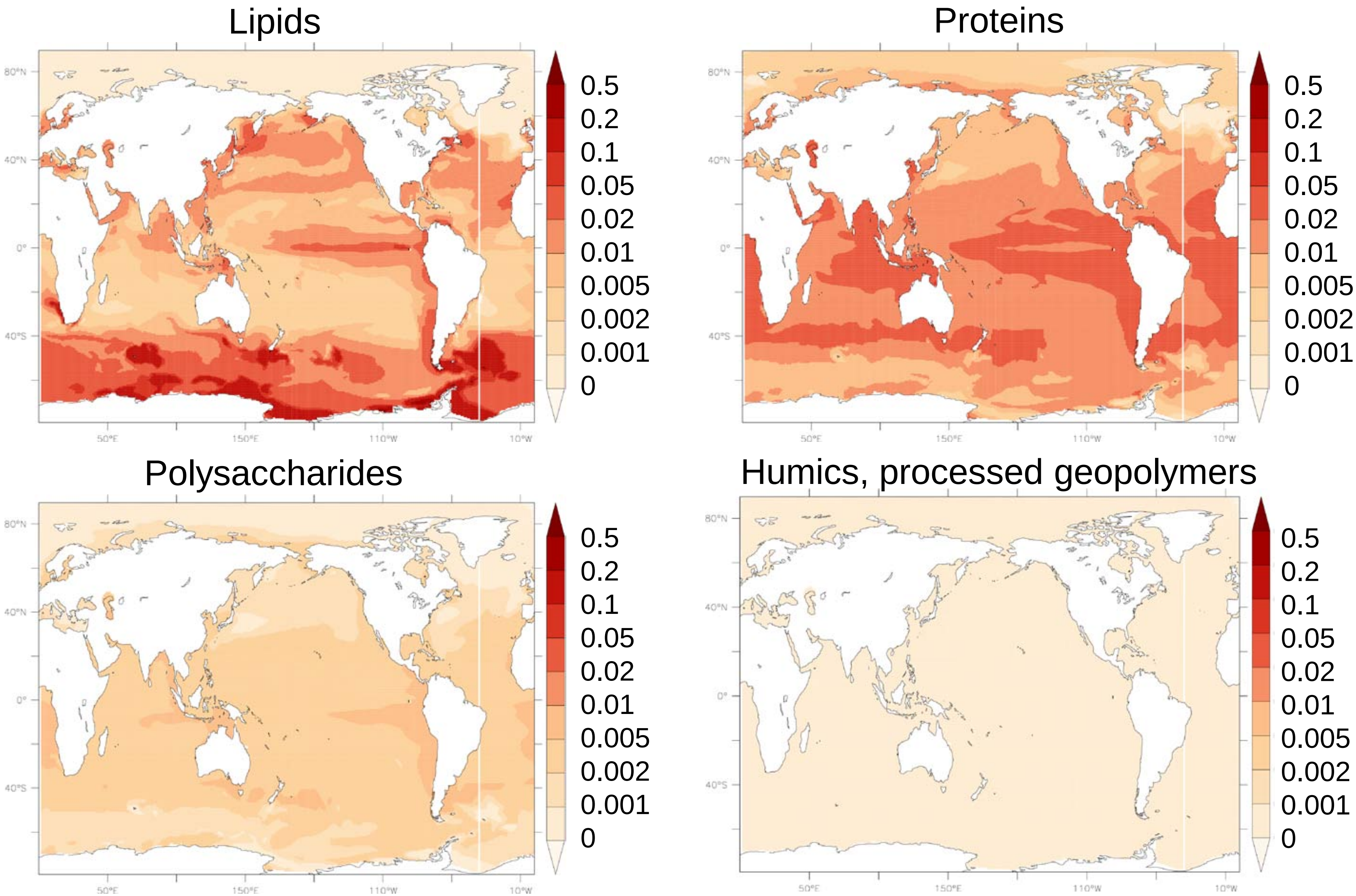
Structure	Ocean Analogs	Laboratory Analogs	$C_{1/2}$	Carbon Γ_{max}	References
Prot	Generic enzymes	Lysozyme	10^{-4}	1.0	F97, GP79b
	Albumin	BSA	10^{-5}	0.5	GP79b, VW83, Z81
	Denatured strands	Casein	10^{-5}	0.5	BM85, DR03, GP79b
Poly	Soluble starch	Maltodextrin	$>10^{0}$	(10-100)	SB07, VW83
	Alginate	Natural alginate	10^{-1}	50-100	B00, VW83, Z81
	Generic glucans	Pectin	10^{-1}	Close packing	F97, NB06, RB00, P11
		Gum Arabic	10^{-2}	50	DR03, G91, NB06
Lip	Commercial surrogate	SDS	10^{-2}	4	CT52, L98, T70, T07
	C18 fatty acids	Oleic and Stearic	$<10^{-6}$	1.0	B10, CD68, H70, G70, L91
	Sterols	Cholesterol	$<10^{-6}$	1.5	A86, BM85, MB78, P88, P05
Hum	Fulvic acid	Riverine Standard	10^{-1}	1.0	A89, D06, S06, T07, VW83
	Humic acid	Commercial	10^{-1}	1.0	M90, T07, TC04

General abbreviations: BSA –Bovine Serum Albumin, SDS –Sodium Dodecyl Sulfate

Reference abbreviations: A86 –Alexander et al. 1986; A89 –Averett et al. 1989; B00 –Babak et al. 2000; B10 –Brzozowska et al. 2010; BM85 –Barger and Means 1985; CD68 –Christodoulou and Rosano 1968; CT52 –Cook and Talbot 1952; D06 –Dinar et al. 2006a; DR03 –Damodaran and Razumovsky 2003; F97 –Frew 1997; G70 –Garrett 1970; G91 –Gaonkar 1991; GP79b –Graham and Phillips 1979b, H70 –Heikkila et al. 1970; L91 –Lindsley et al. 1991; L98 –Li et al. 1998; M90 –Malcolm 1990; MB78 –McGregor and Barnes 1978; Nilsson and Bergenstahl 2006; P88 –Parrish 1988; P05 –Parra-Barraza et al. 2005; P11 –Perez et al. 2011; RB00 – Rosilio and Baszkin 2000; S06 –Svenningsson et al. 2006; SB07 –Shogren and Biresaw 2007; Tajima et al. 1970; T07 –Tuckermann 2007; TC04 –Tuckermann and Cammenga 2004; VW83 –Van Vleet and Williams 1983; Zutic et al. 1981

S. Elliott, S. Burrows, et al., 2013, in prep.

Chemically-resolved submicron sea spray aerosol organic mass fraction – February



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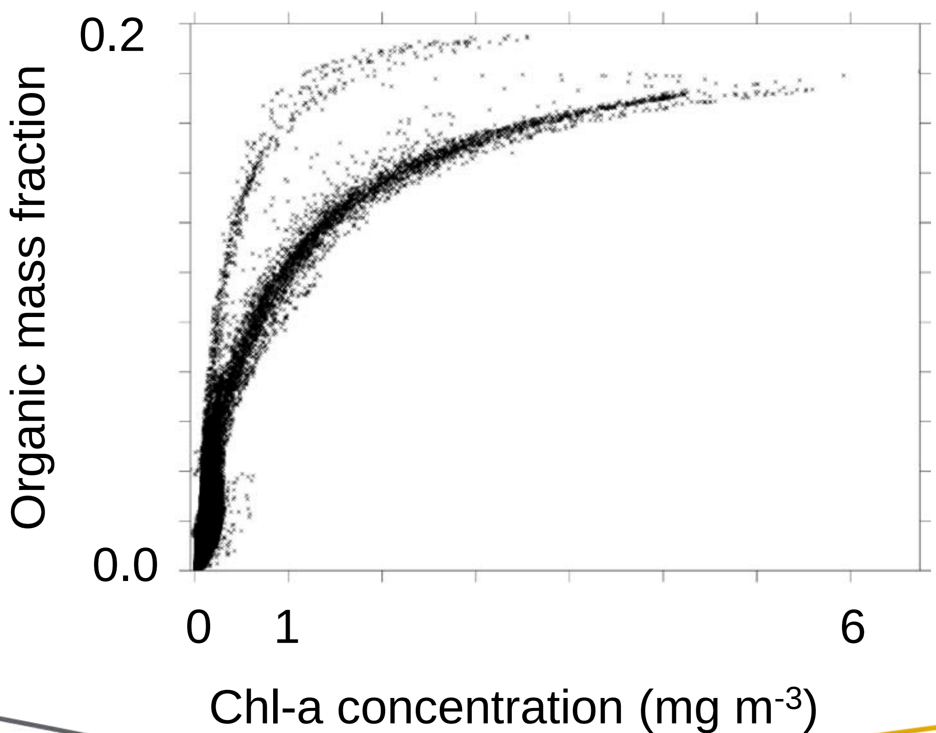
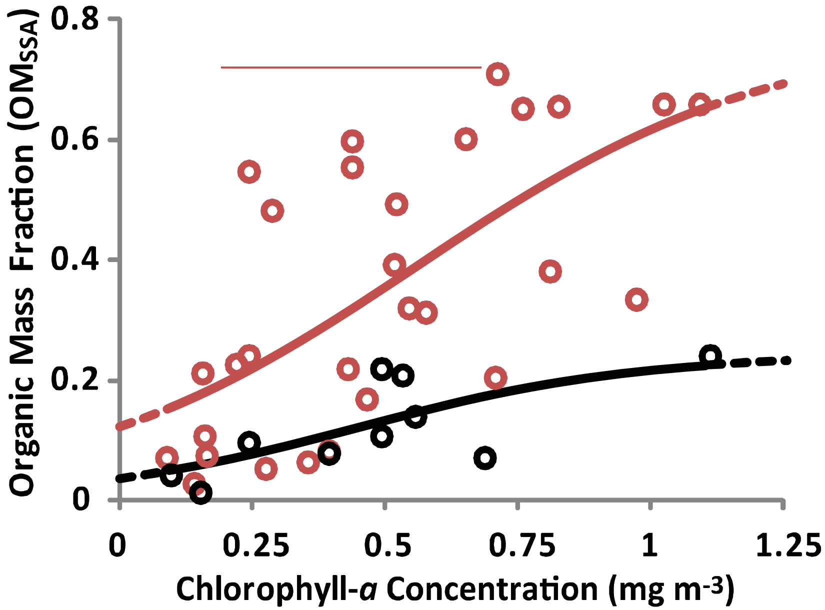
OM fraction vs chlorophyll with marine biogeochemistry

Langmuir model -- February



Empirical fit (Gantt et al., 2011)



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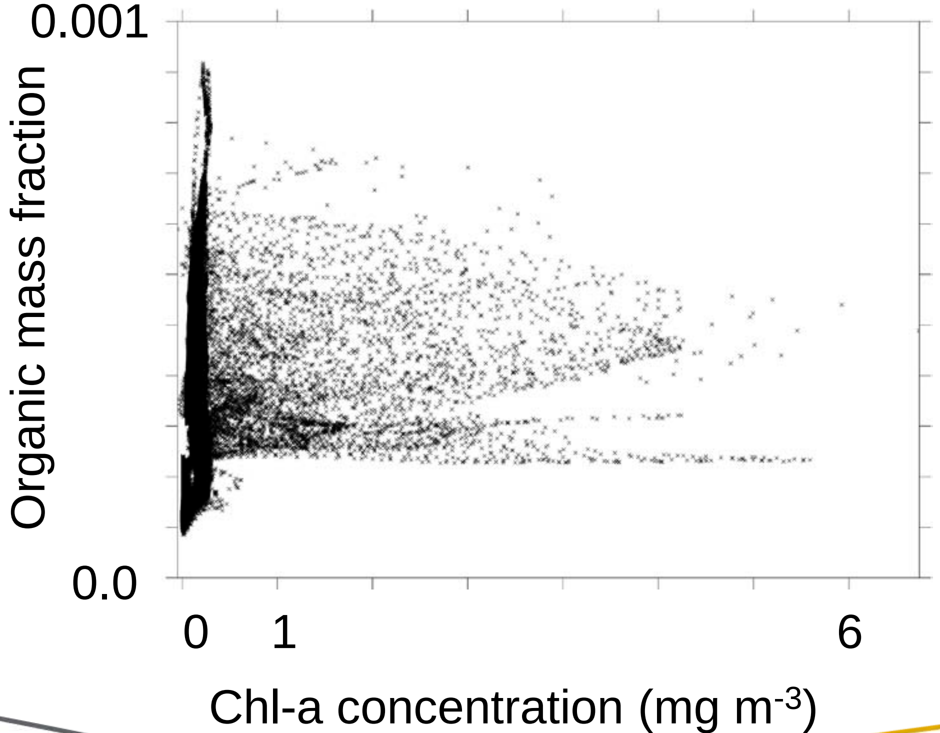
OM fraction vs chlorophyll no chemical distinctions

Langmuir model -- February



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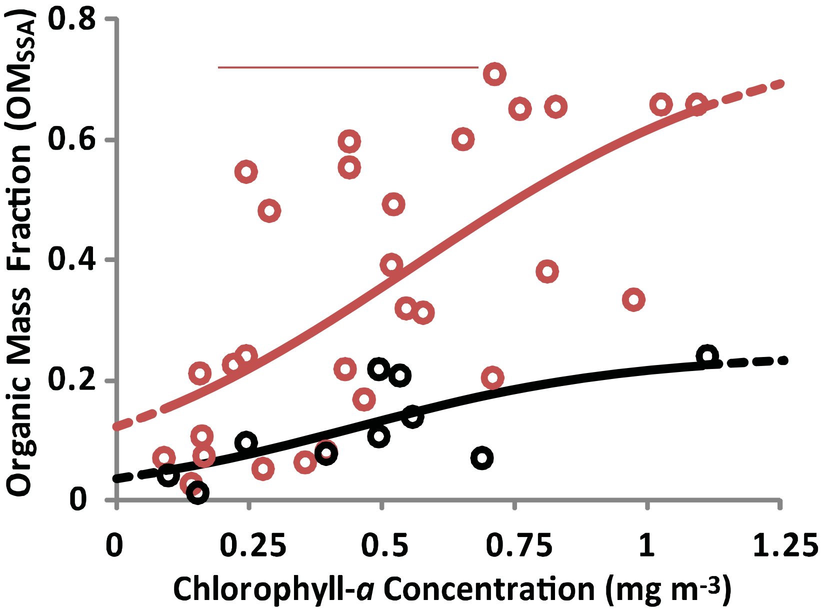

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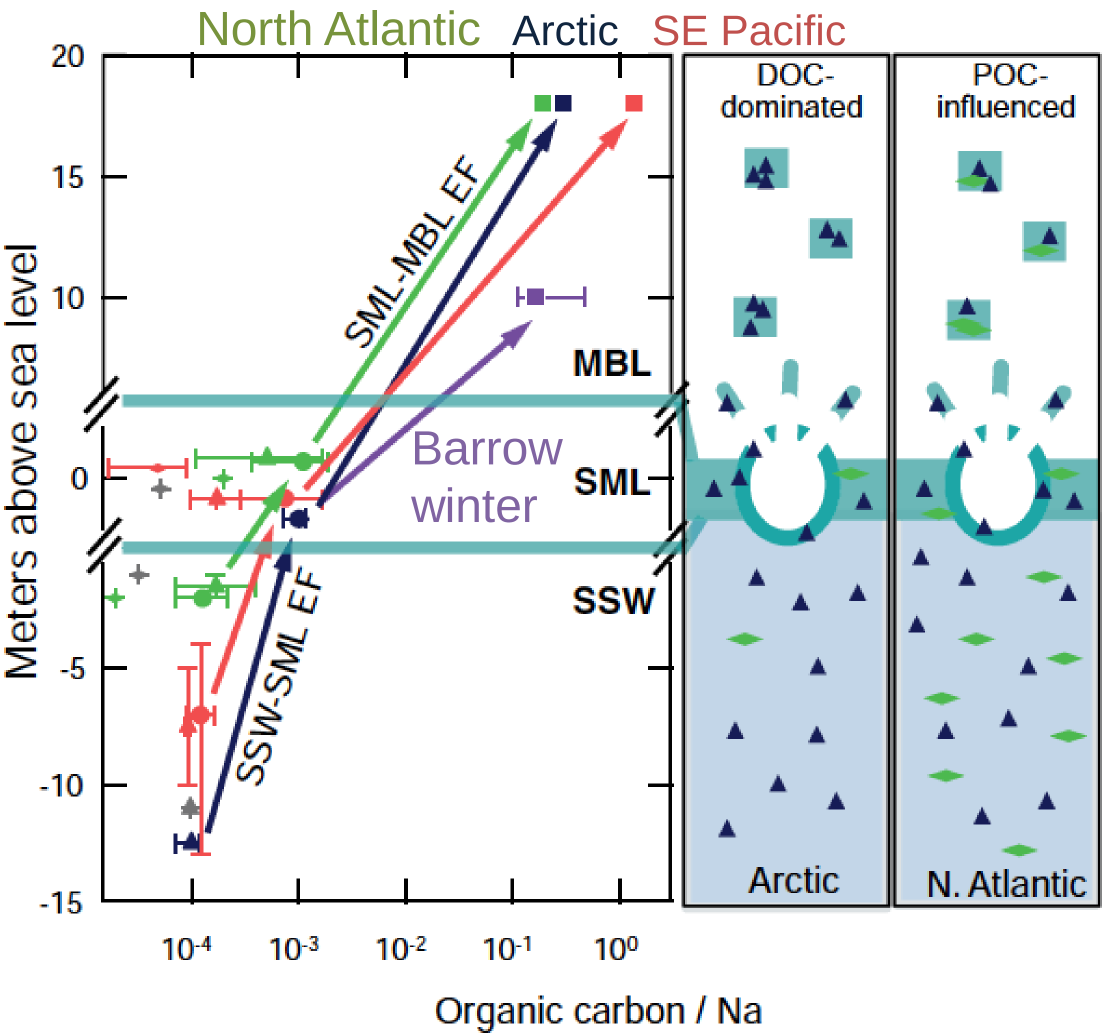
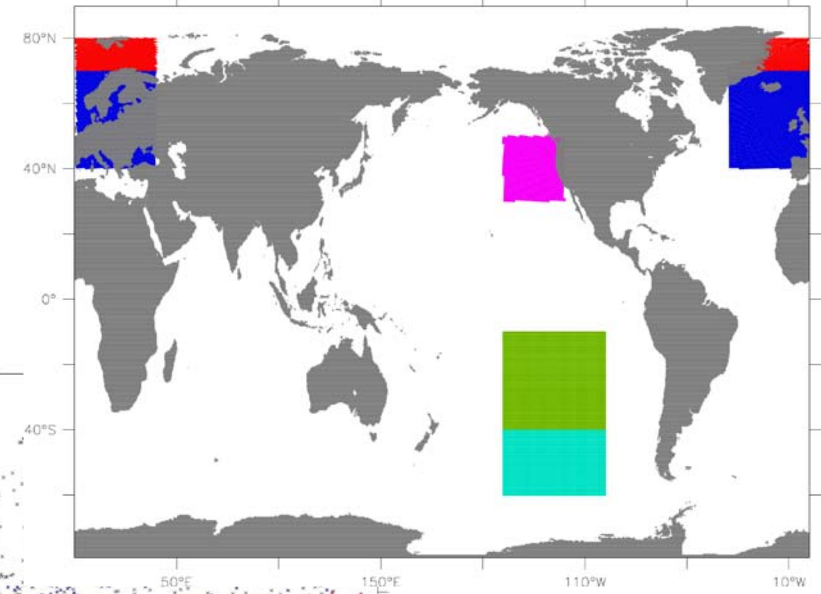
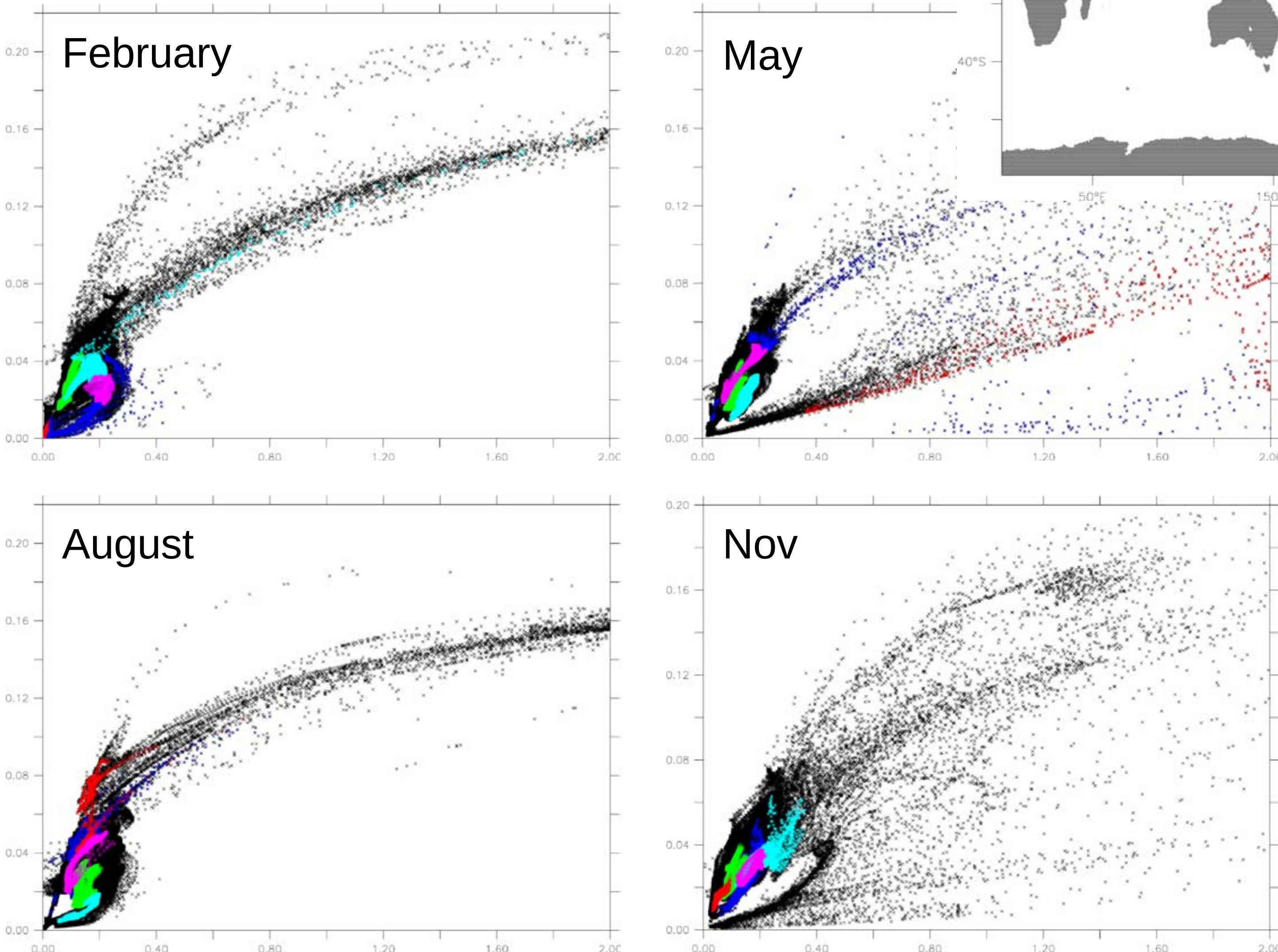
Enrichment from bulk to SML
+ additional enrichment from SML to MBL



- Russell et al. (2010)
  - Chl-a correlation in N. Atlantic, but not in Arctic

Regional differences in OM fraction dependence on Chl





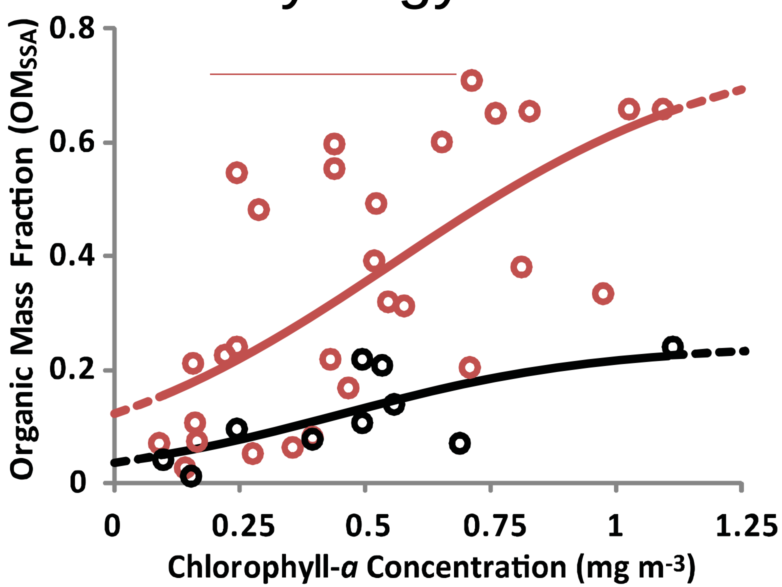
Moving sea spray chemistry forward

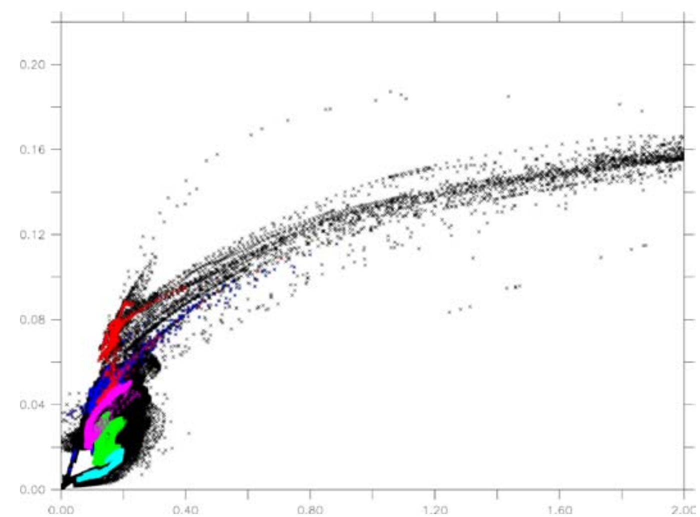
- Empirical parameterizations → semi-mechanistic

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

- Chl-a (correlated) → surfactants (causal)

- Extrapolate from blooms → Account for different chemistry in gyres





Coast of southeastern Australia, July 2011 (S. Burrows)

Additional slides

Ocean biogeochemistry mapping

- Ocean general circulation from POP/BEC (Maltrud et al., 1998; Moore et al., 2004)
- Regions of primary production – cellular breakdown provides organic mass.
- Partitioning (Parsons et al. 1984; Benner, 2002):
  - 60% polysaccharides
  - 20% proteins
  - 20% lipids
- Lipids – short lifetime ➔ phytoplankton
- Polysaccharides & proteins ➔ semi-labile dissolved organic compounds (DOC) (lifetime 100 days)
- Convective turnover ➔ humics
- Remaining DOC ➔ "processed"

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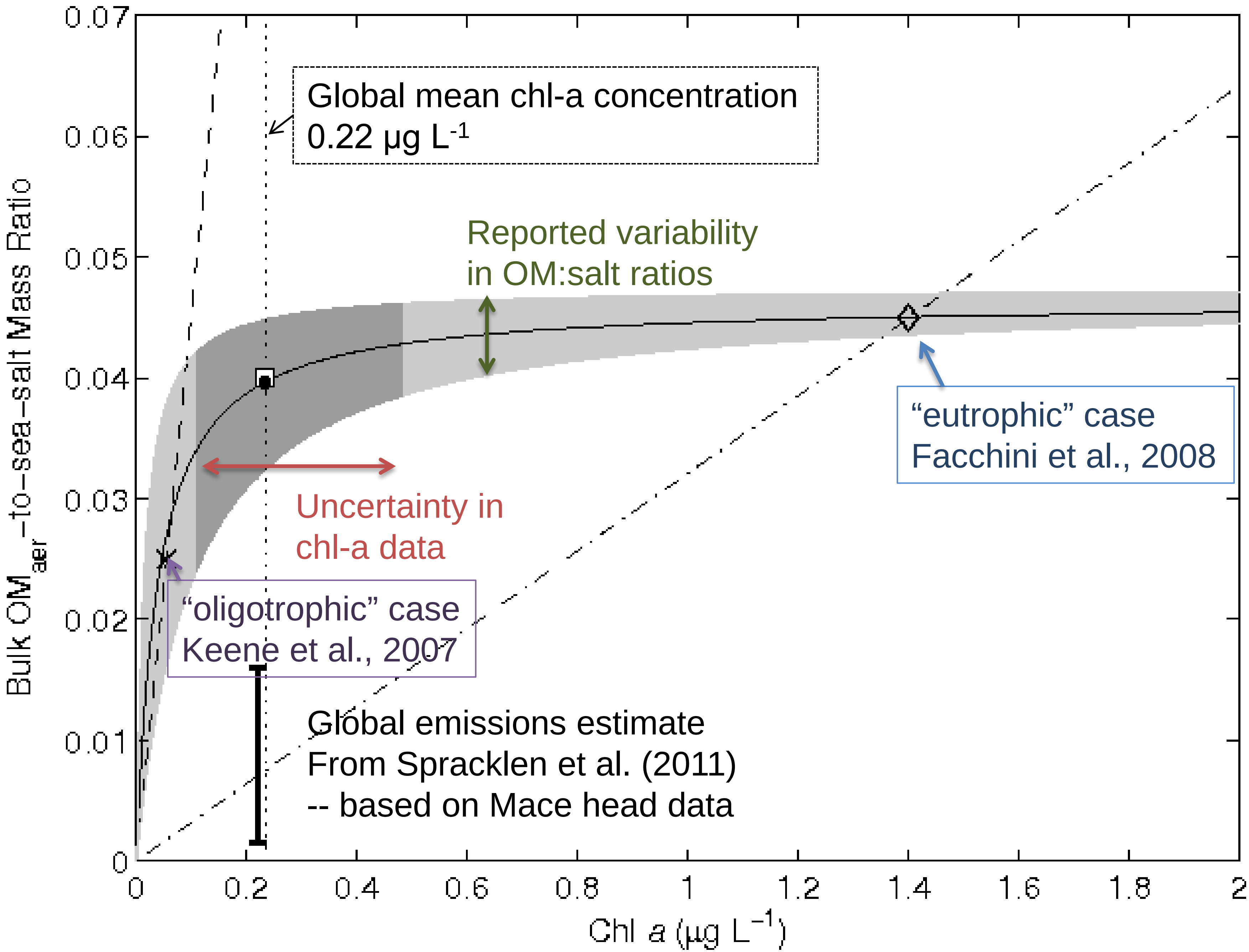
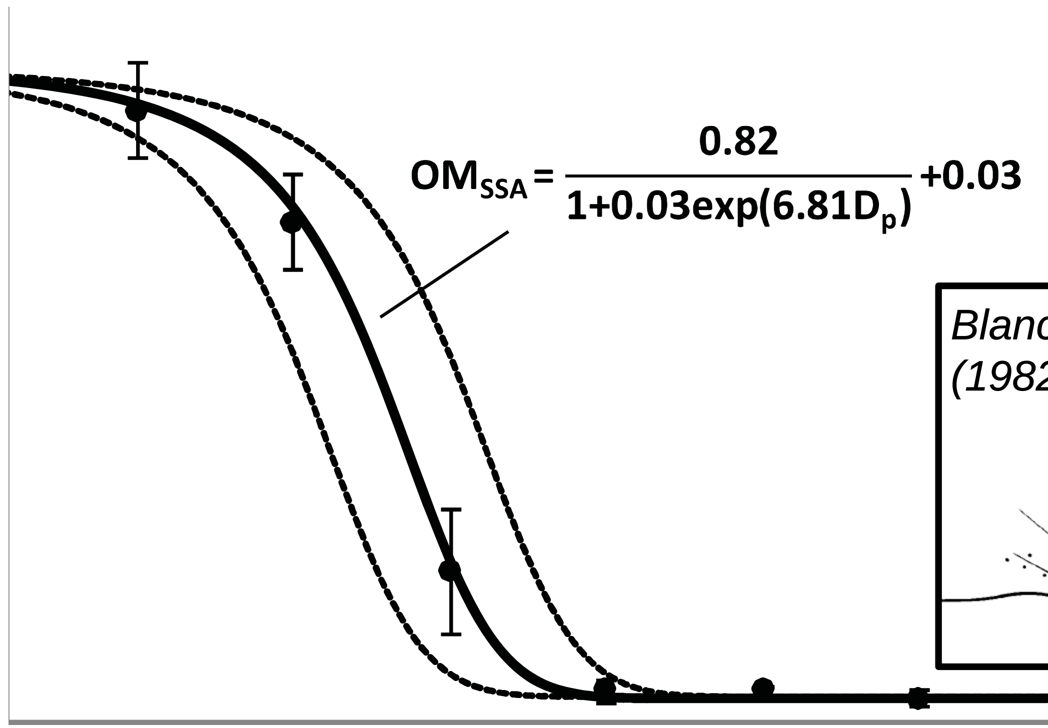


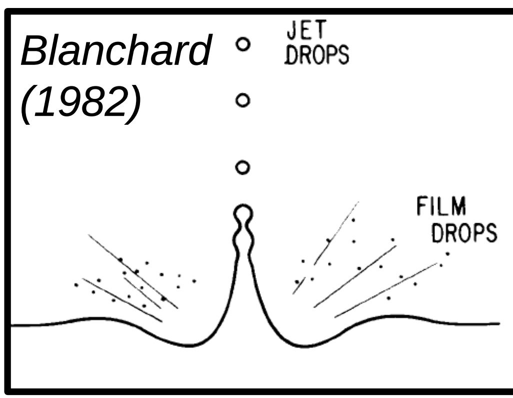
1.

M. Long et al. (2011)

Size distribution

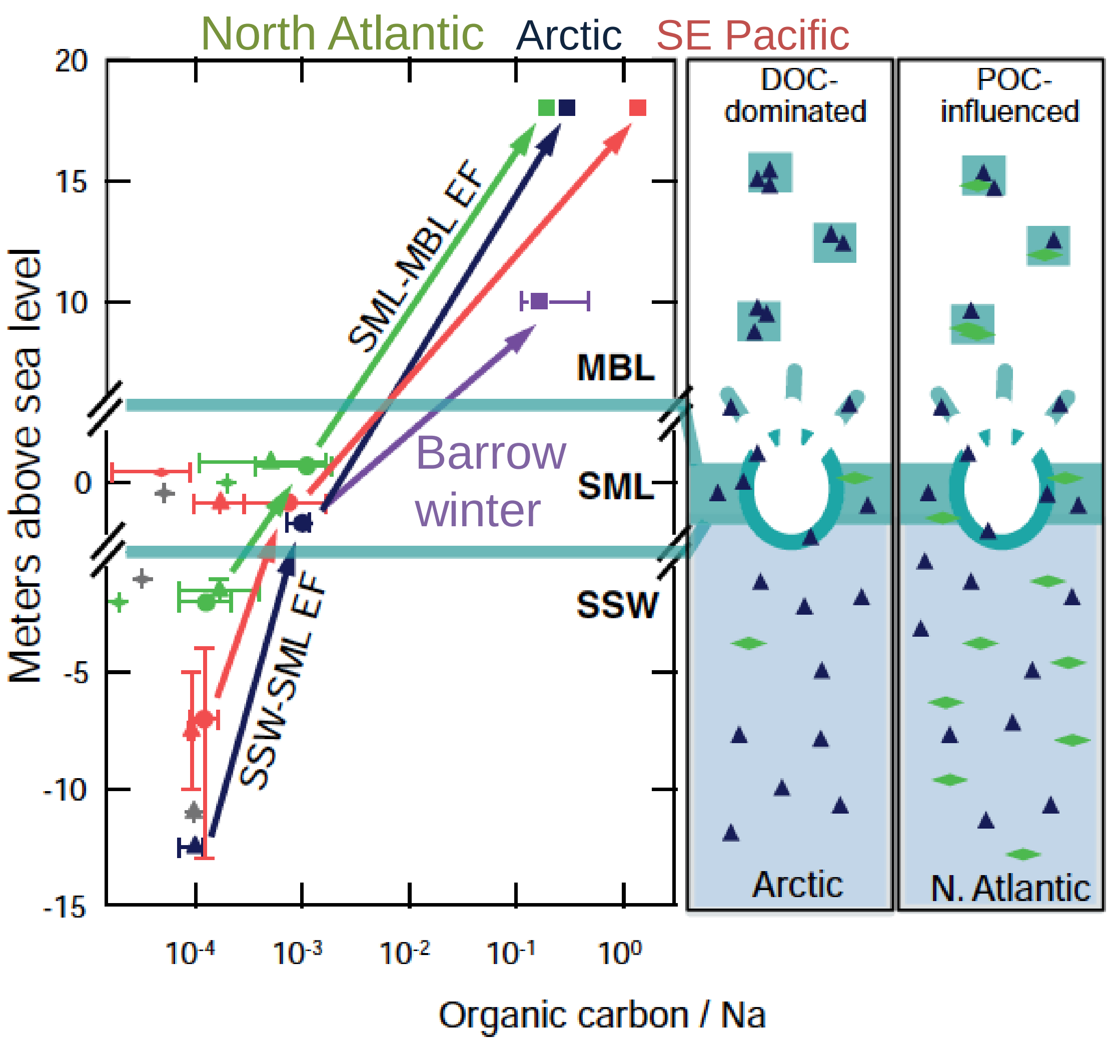
SML: 20 – 200 µm





Gantt et al. (2011); Facchini et al. (2008)

Enrichment from bulk to SML + additional enrichment from SML to MBL



- Russell et al. (2010)
  - Chl-a correlation in N. Atlantic, but not in Arctic
  - Attributed to POC influence vs. DOC influence

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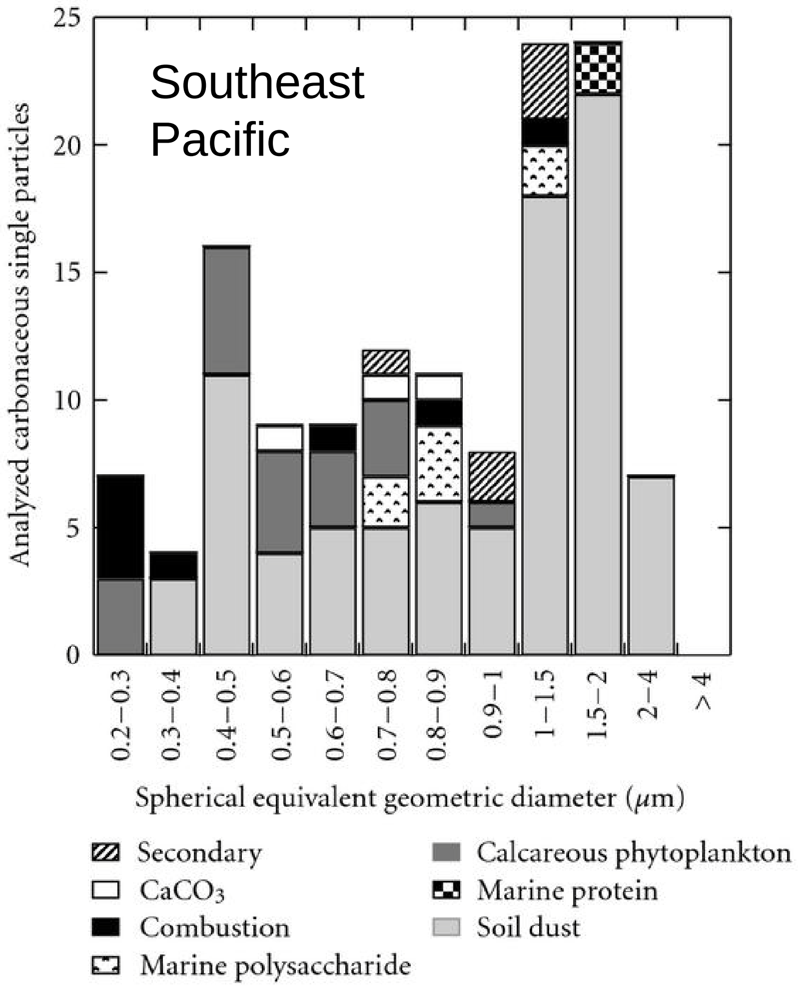
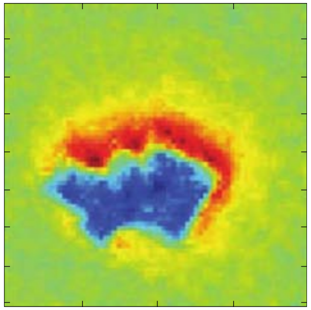
Chemically distinct particle classes

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



Arctic marine poly



Southeast Pacific marine poly

Calcareous phytoplankton (SE pac. Only)

Marine protein