U.S. DEPARTMENT OF ENERGY

Office of Science

Ocean Macromolecules and the Aerosol

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Also Scripps, HU

Sponsorship: DOE SciDAC, SFA

OUTLINE

BACKGROUND –DMS spills from phytoplankton…

NEW CONNECTION –So why shouldn't biopolymers?

VISUALS –SeaWiFS vs. DOC

POP OFFLINE –Chemical resolution of macromolecules

1st CUT –Enrich, diameters, Gibbs layers

NEXT –Map into spray emission, CAM-MAM tests

Los Alamos
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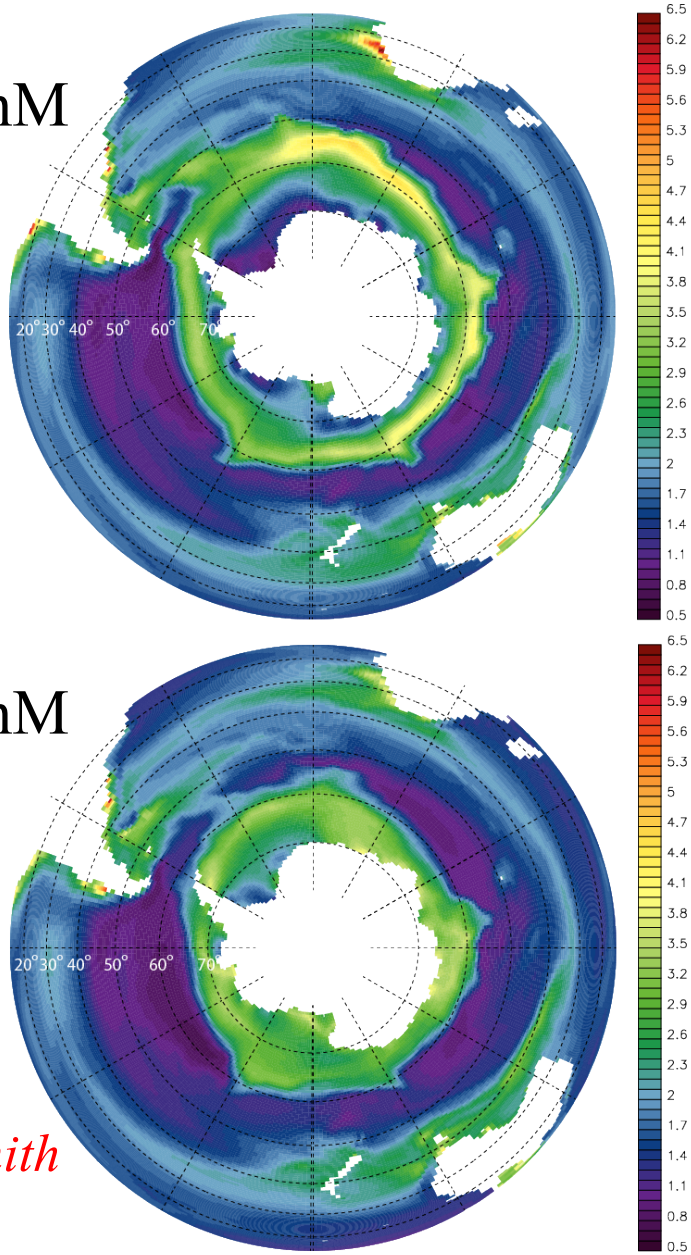
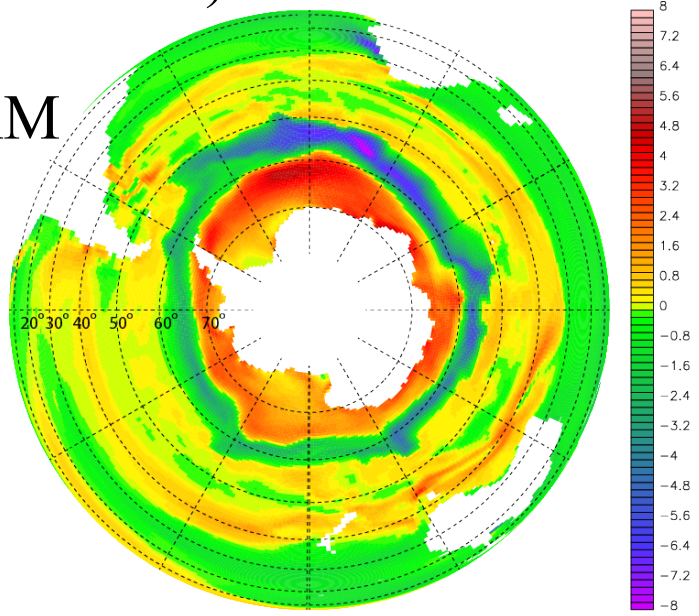
Once and future DMS (*LLNL and LANL in CESM*)

2000 nM

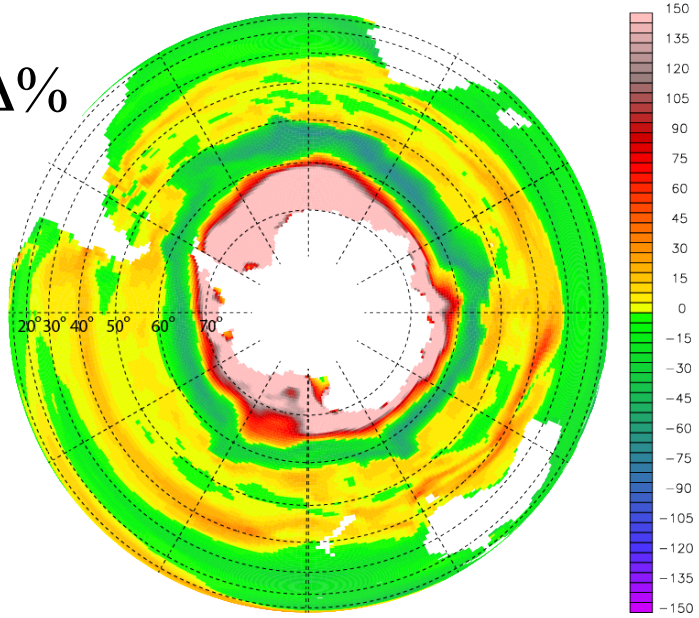


ΔnM

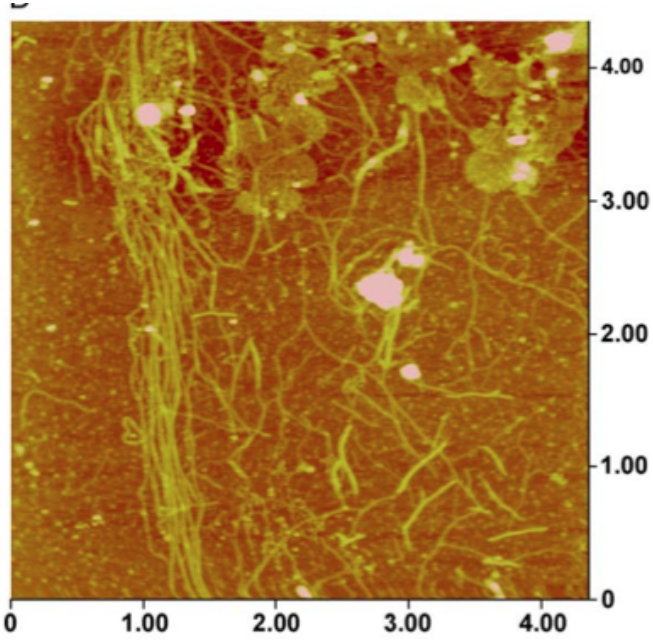


2100 nM

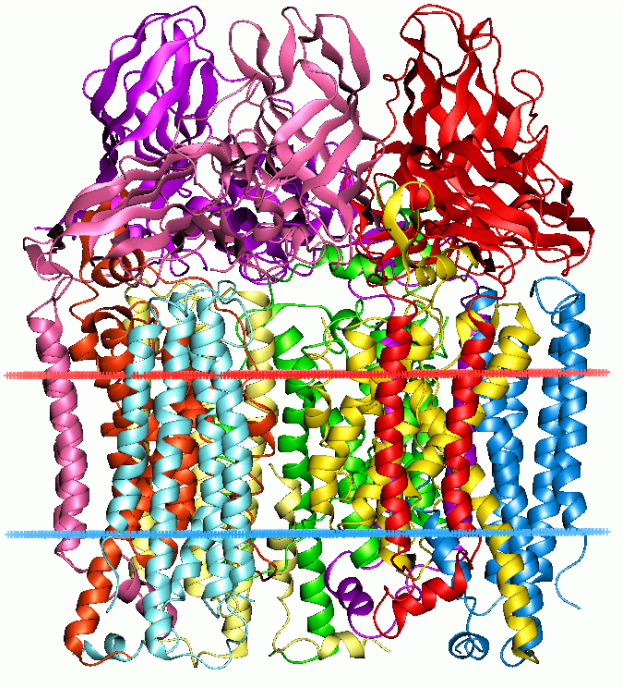
Δ%

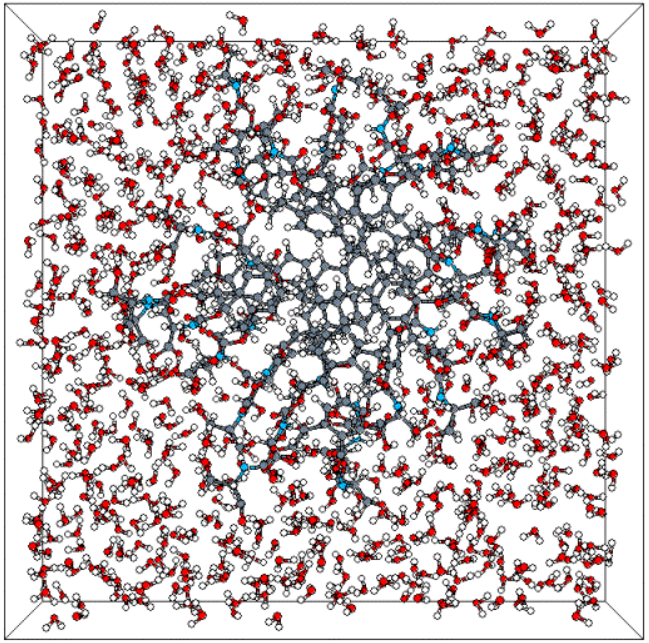


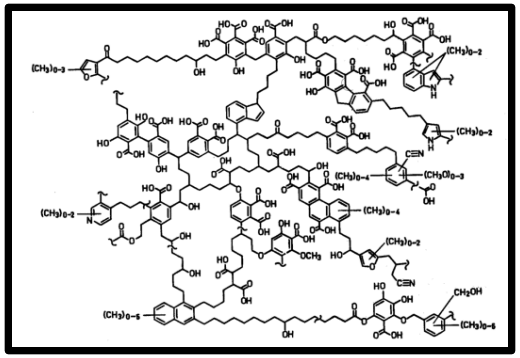
Cameron-Smith et al. 2010

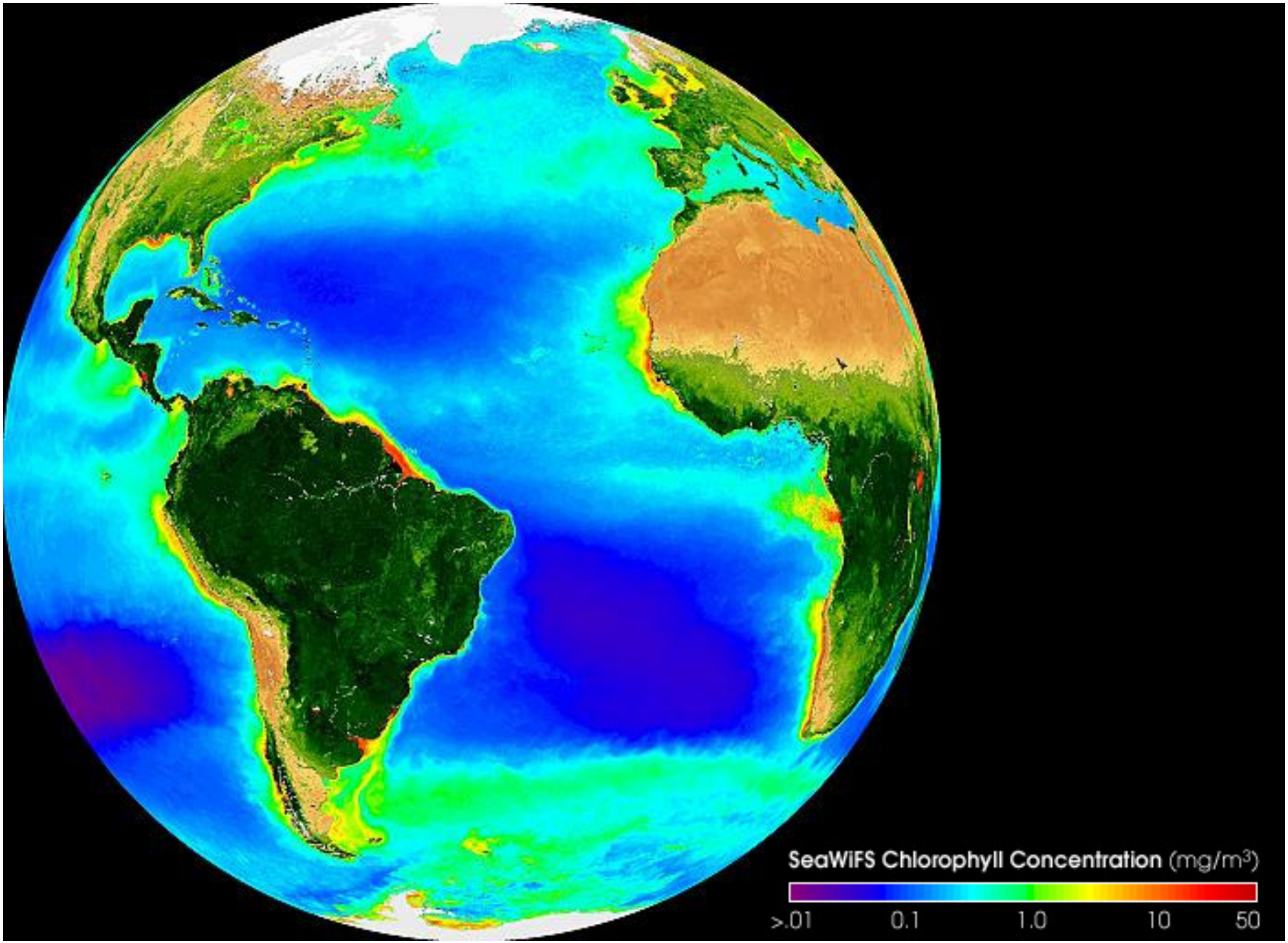


Polysaccharides,
Proteins,
Lipids,
Humic acids,
(and geopolymers…








SeaWiFS Chlorophyll Concentration (mg/m3)
>.01
0.1
1.0
10
50

Hansell et al. 2012 Global DOC

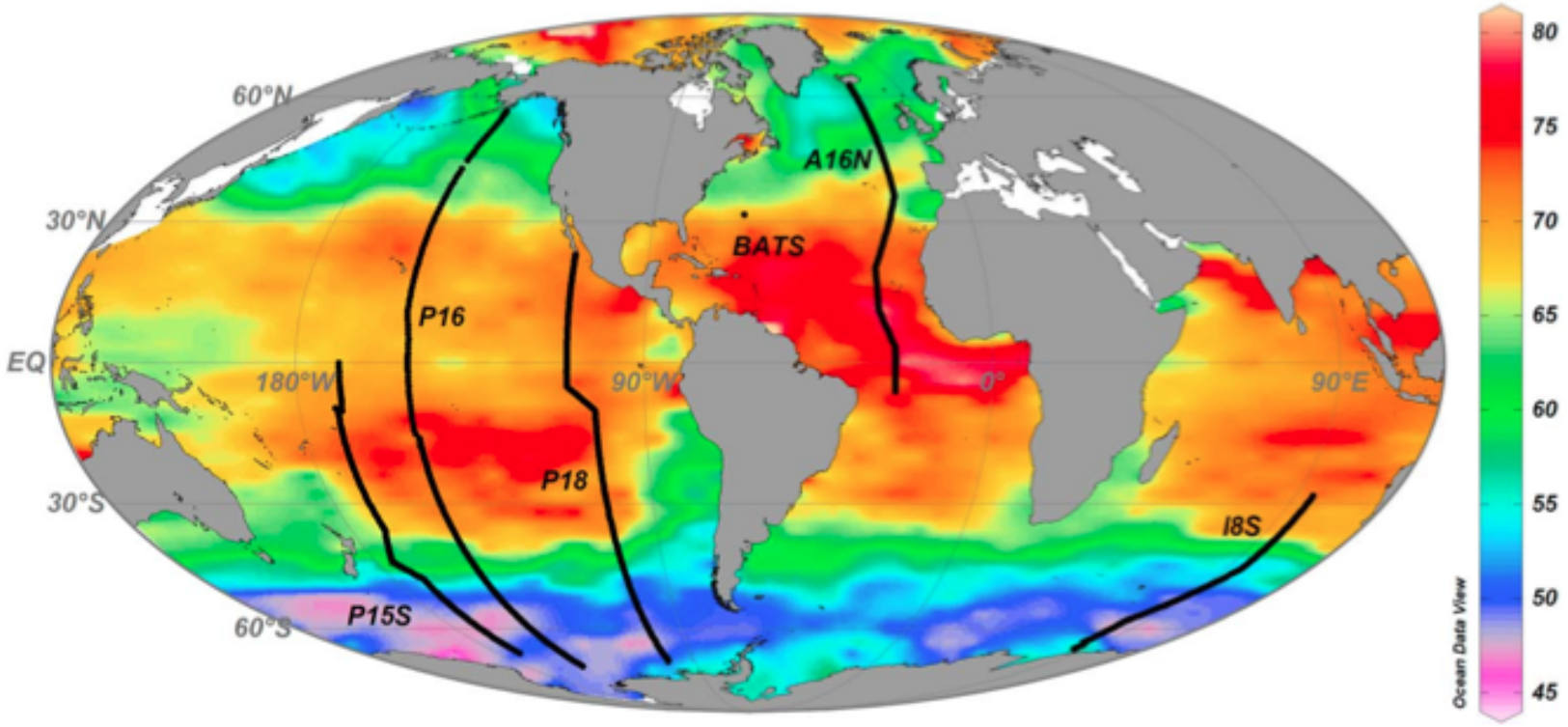
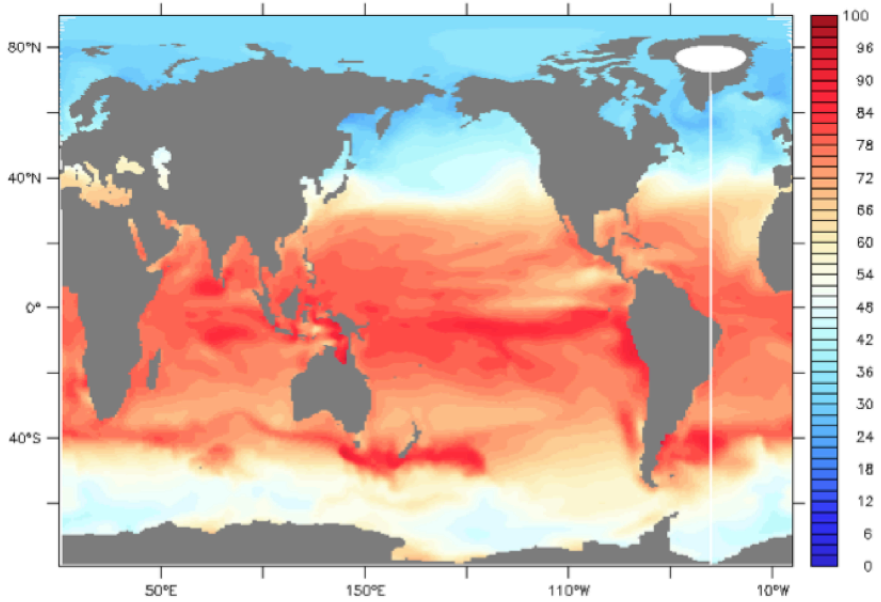


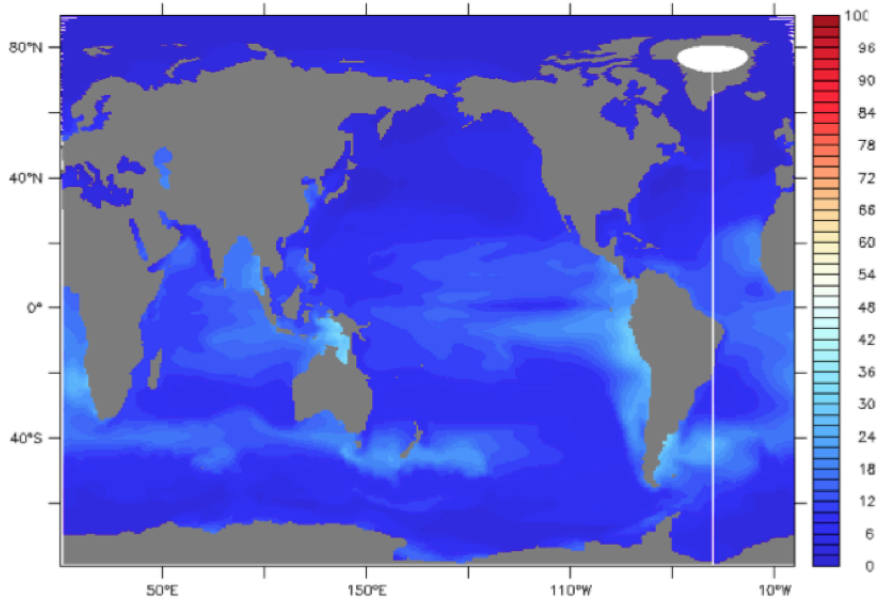
Figure 1. Locations of the BATS site and hydrographic sections A16N (North Atlantic), P16 (central Pacific), P18 (eastern Pacific), I8S (Indian Ocean) and P15S (western South Pacific) over a modeled field of DOC (μmol C kg^{-1}) at 30 m throughout the global ocean [from *Hansell et al.*, 2009]. A16N 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.

Carbon carriers, 0-100 µM except Bacteria *(All SH summer)*

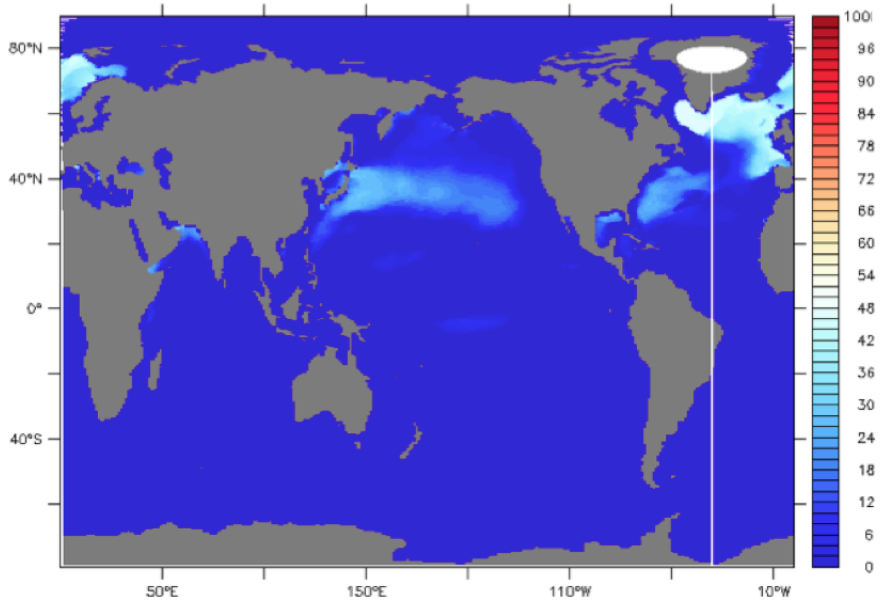
DOC



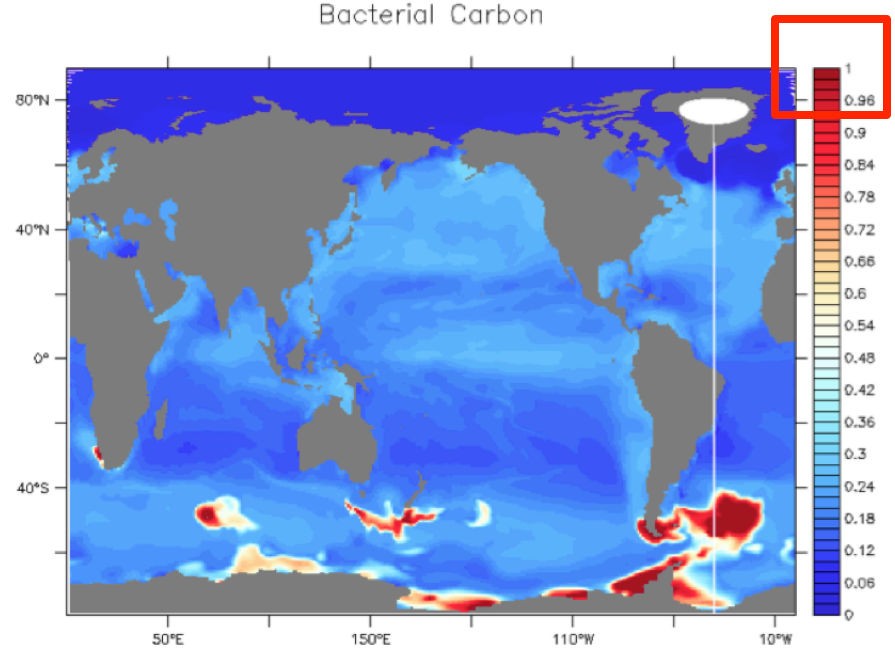
Proteins

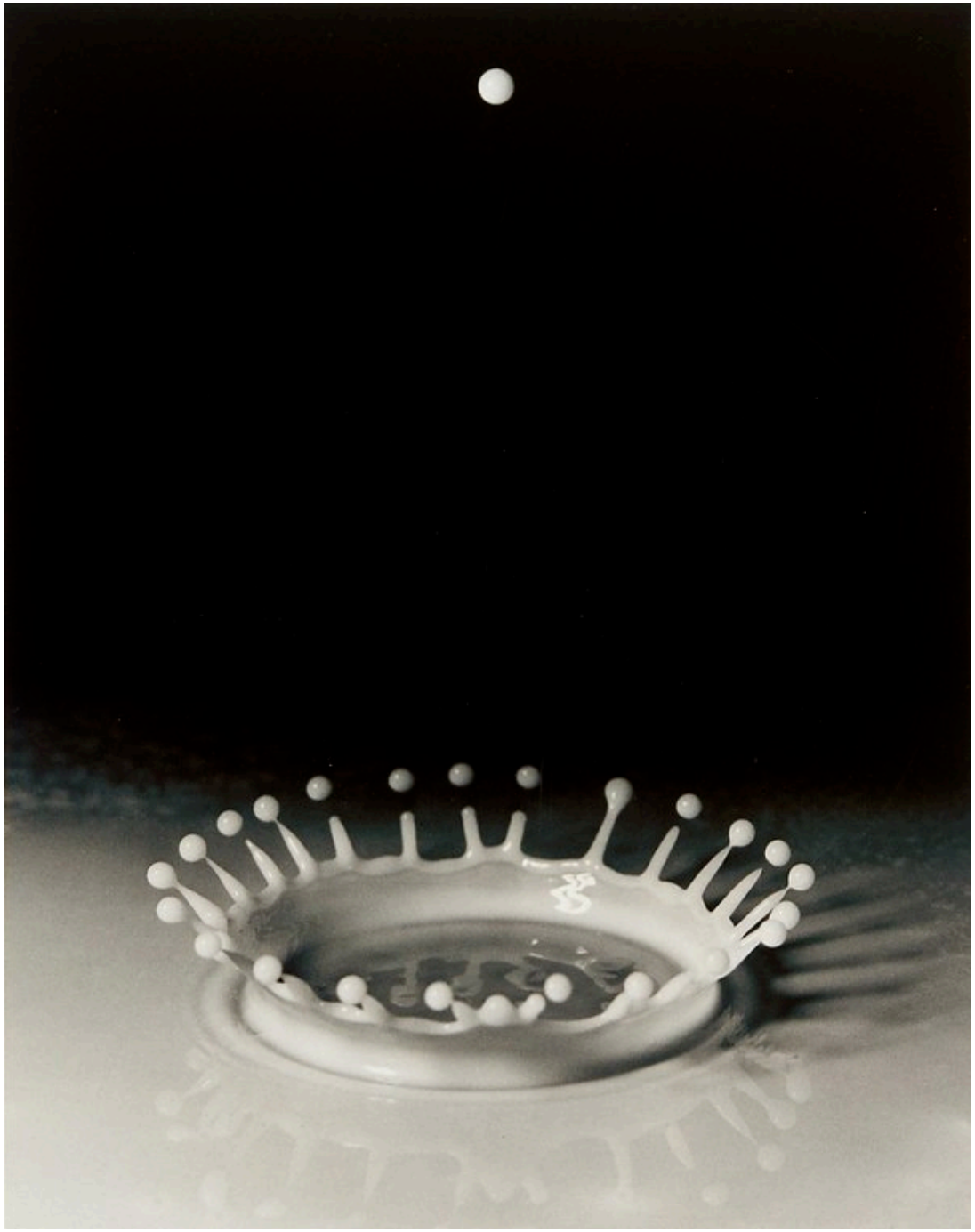


Humics



Bacterial Carbon



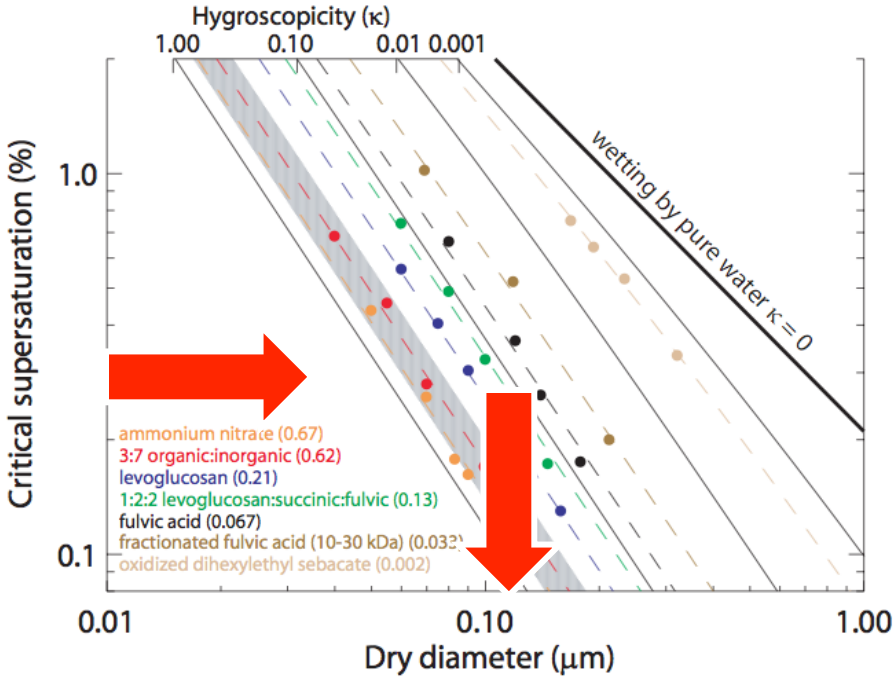


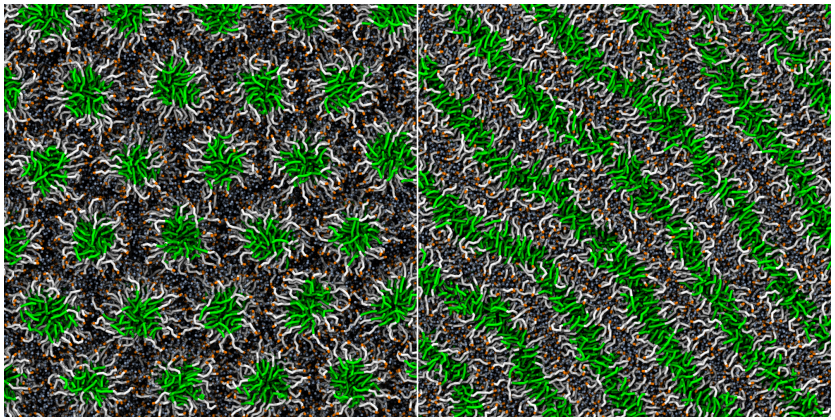
Simple Tests for CCN Effects

SPRAY ONLY –This guy is no aerosol modeler…

ACTIVATION –Variability in threshold diameter for growth

AMPHIPHILIC LAYERS –Cover 3 to 10 times at 0.1 micron

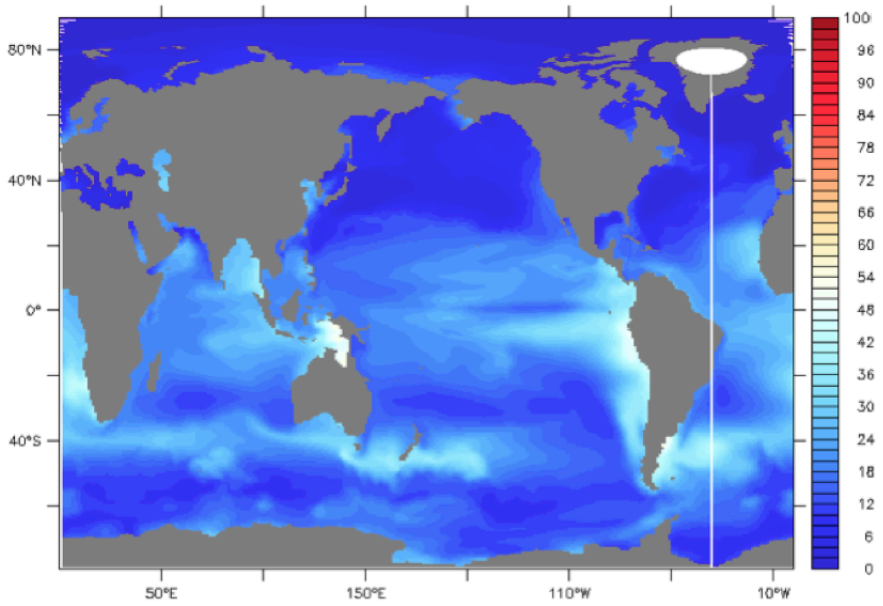




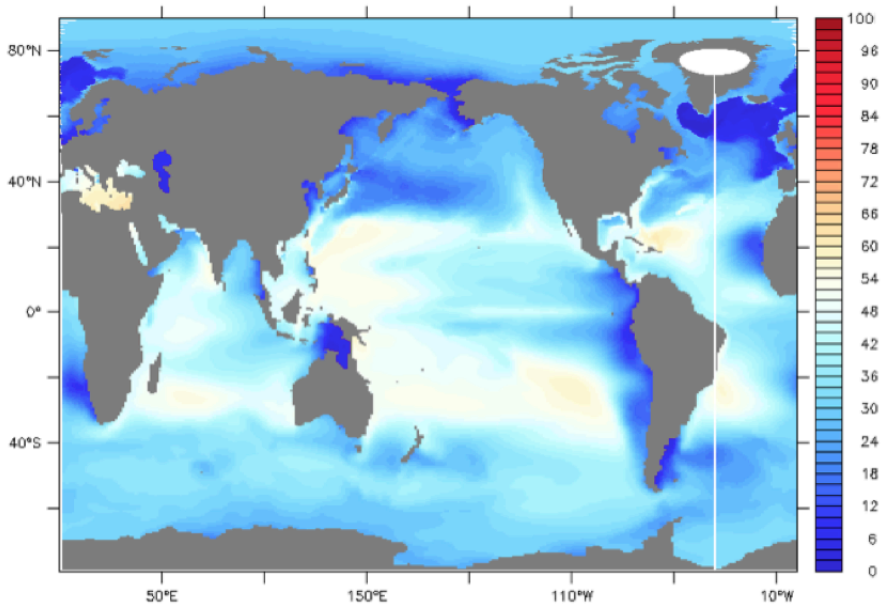
SDS as model amphiphile

Concentrations (0-100 μM) and diameters (0.1-0.2 microns)

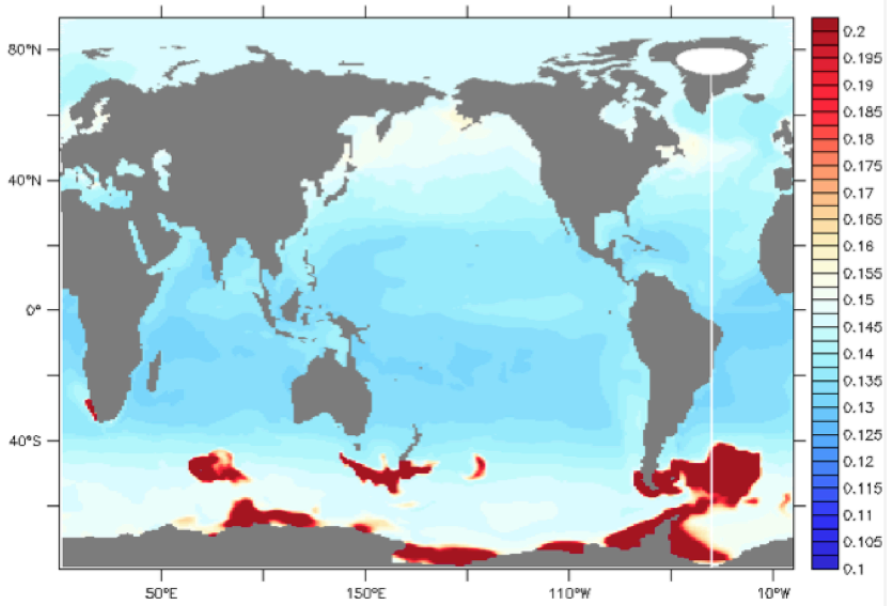
Polysaccharides



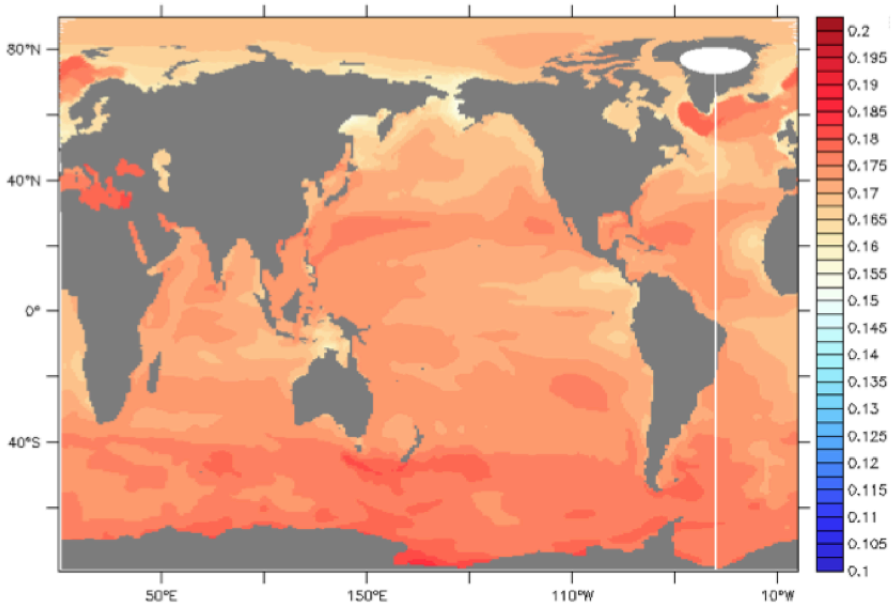
Unidentified Intermediates



Chlorophyll Proxy Diameter



Surfactants x3 Hi Hi



SUMMARY

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1st CUT –Enrich, diameters, Gibbs layers

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CAM Modal Aerosol

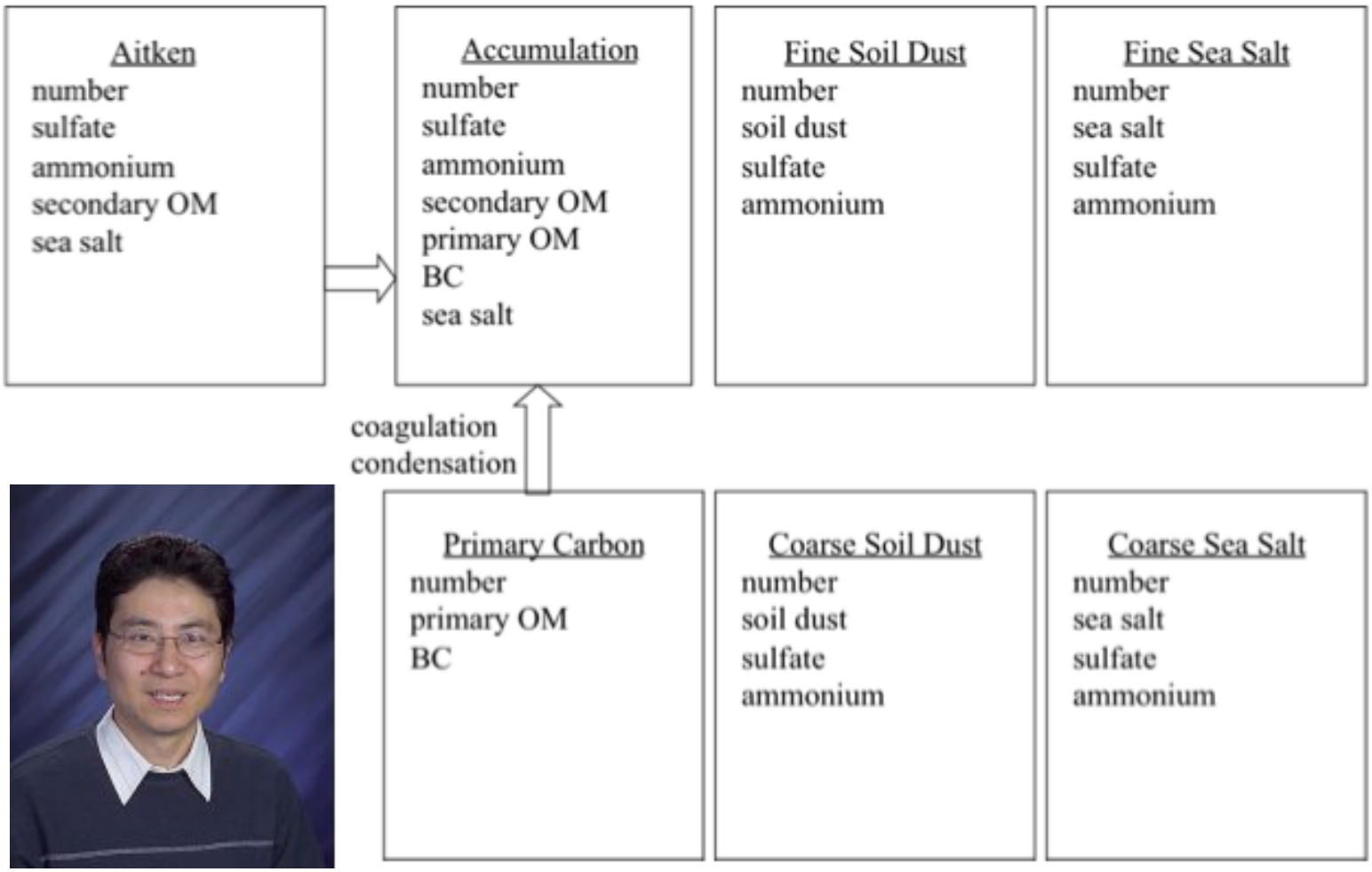
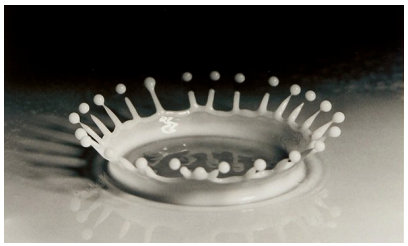
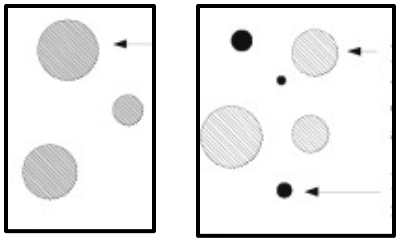


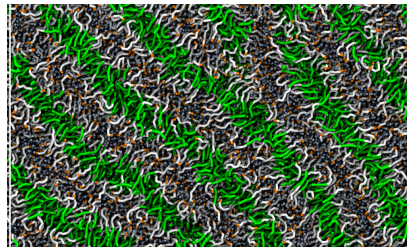
Fig. 1. Predicted species for interstitial and cloud-borne component of each aerosol mode in MAM7. Standard deviation for each mode is 1.6 (Aitken), 1.8 (accumulation), 1.6 (primary carbon), 1.8 (fine and coarse soil dust), and 2.0 (fine and coarse sea salt).

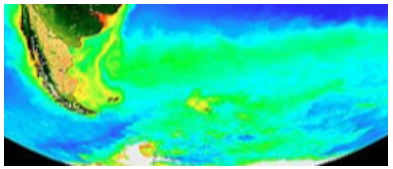
Thresholds for Activation S=0.1% and Monolayer

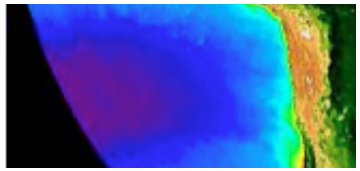
Enrichment and Hygroscopicity Settings			Diameter (microns)					
			Activation				Monolayer	
			Rings		Gyres		Rings	Gyres
P&P	Surf	κ	Int	Ext	Int	Ext	Int	Int
x1	x1	Lo Lo	0.18	0.32	0.16	0.28	0.07	0.05
		Hi Lo	0.16	0.25	0.15	0.24		
		Lo Hi	0.17	0.27	0.15	0.23		
		Hi Hi	0.16	0.23	0.15	0.21		
/3	x1	Lo Lo	0.15	0.31	0.15	0.27	0.06	0.05
		Hi Hi	0.15	0.23	0.14	0.20		
x1	x3	Lo Lo	0.19	0.31	0.20	0.27	0.04	0.03
		Hi Hi	0.18	0.23	0.17	0.20		



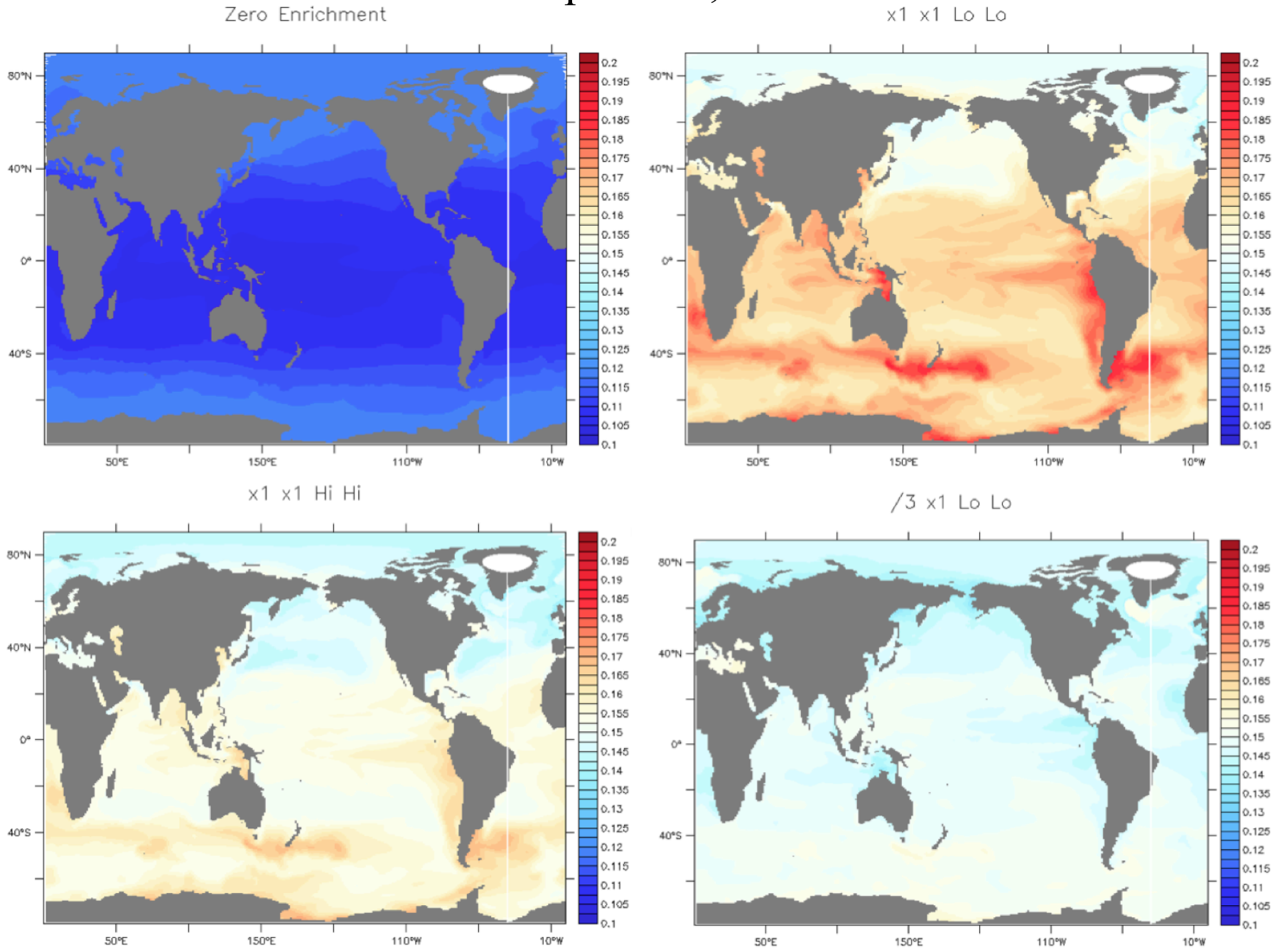








Selected threshold diameter patterns, microns



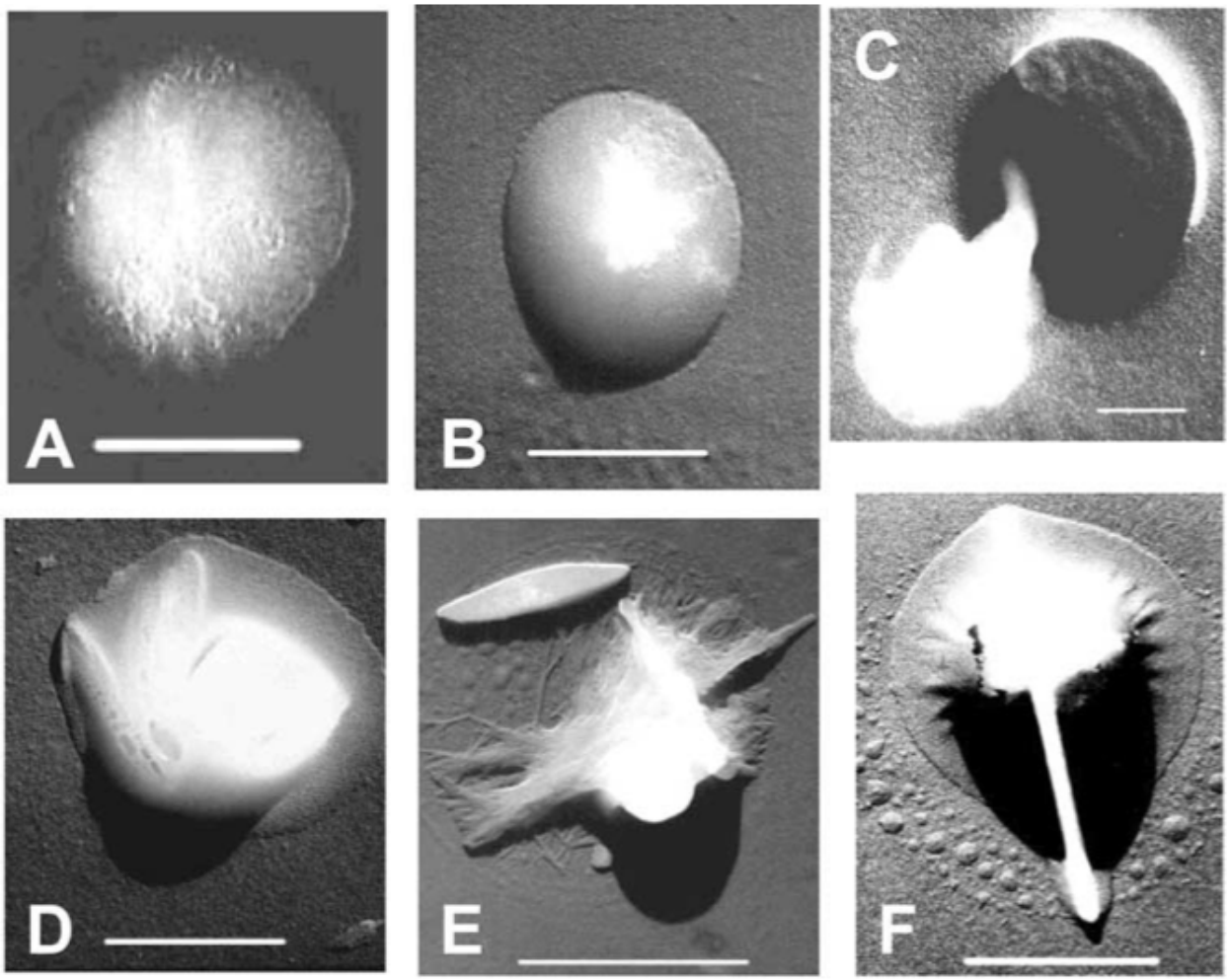
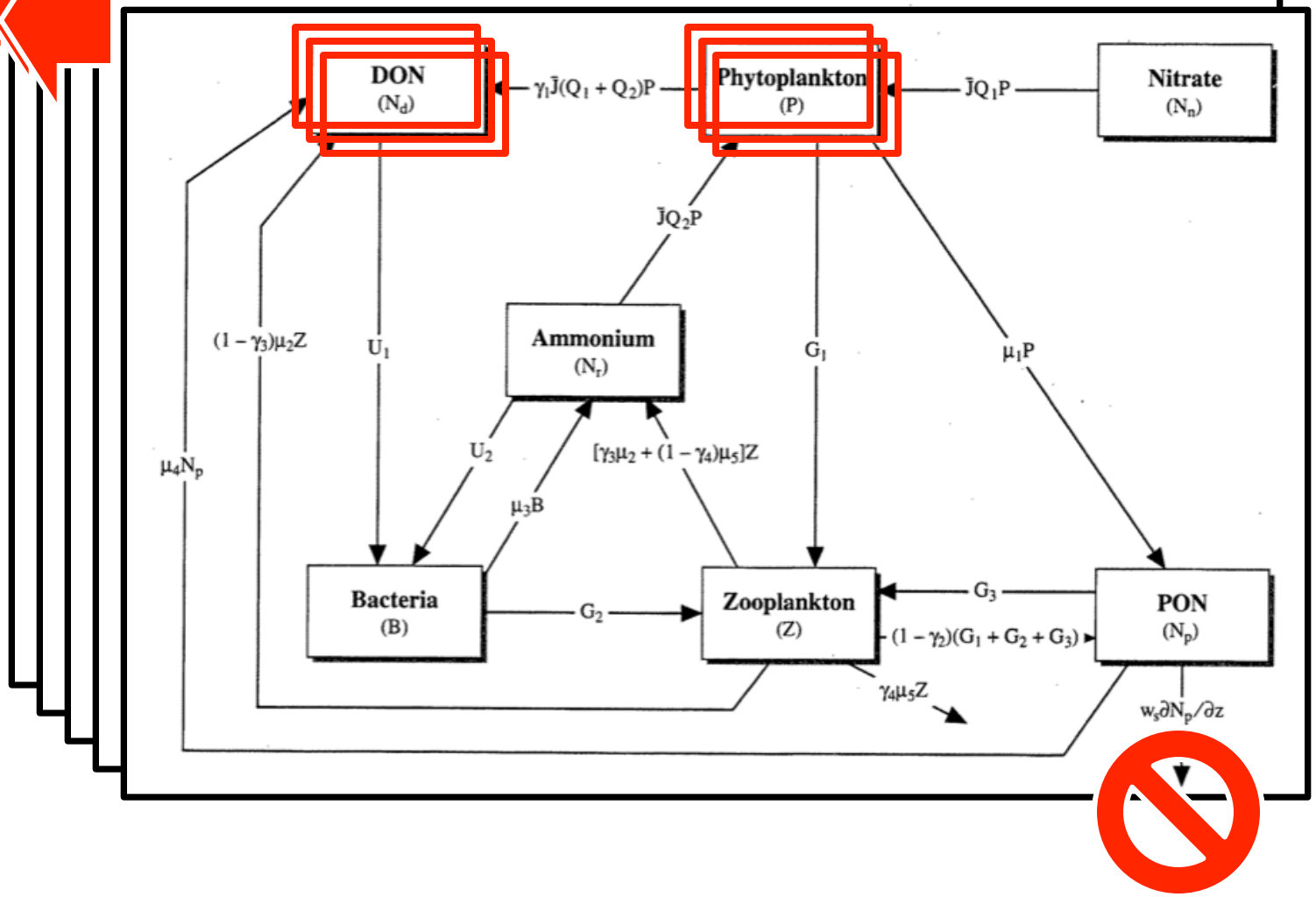


Figure 6. Transmission electron microphotographs of (a–c) film drop particles and (d–f) jet drops. Film drop particles (Figures 6a–6c) were liquid when collected and spread on the surface showing surfactant properties. The liquid had evaporated from the particle in Figure 6a, but not from the particle in Figure 6b. In Figure 6c, the particle had been subjected to decane vapor, and its organic content revealed by the stream of liquid from its interior. The jet drop particles (Figures 6d–6f) are typical sea-salt particles together with an organic content. In Figure 6f, the particle had been longer in the atmosphere and had acquired a coating of sulfuric acid. The rod through its center is thought to be a bacterium. Scale bars are 200 nm for Figures 6a–6c, 1 μm for Figures 6d–6e, and 500 nm for Figure 6f.

EXTRAS

Schematic Systems Model

$S_C P_{Si} Fe N$



Vallina/Simo: DMS model

$$SRD = I_{\text{uml}} = \frac{1}{MLD}\int_0^{MLD} I_0 \times \exp(-k \times z)dz$$

$$= \frac{I_0}{MLD \times k} \times (1 - \exp(-k \times MLD)). \quad [1]$$

I_0 is assumed to be 50% of the daily averaged solar irradiance at the top of the atmosphere (I_{toa} W m^{-2}) (40), which is calculated following Brock (41). We assume a general solar-radiation extinction coefficient (k) of 0.06 m^{-1}, which is a reasonable approximation for spectrum-centered wavelengths in open ocean waters (42).

DMS Diagnostic Models.

- SRD-model:

$$DMS = 0.492 + 0.019 \times SRD. \quad [2]$$

Science 2008

SE Attempts to Debunk

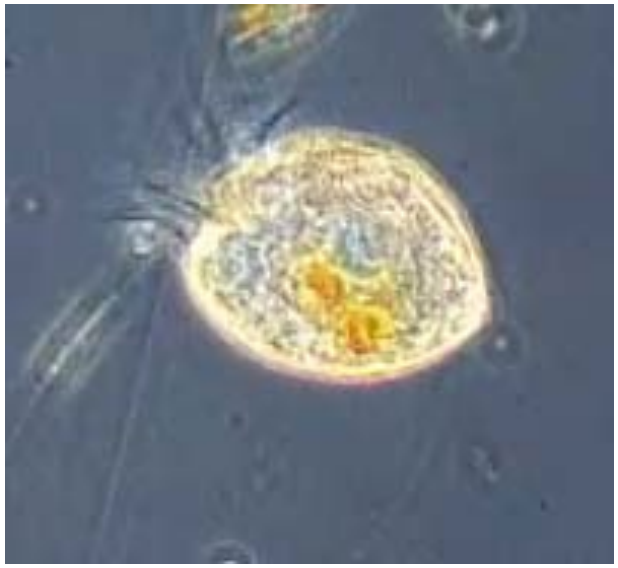
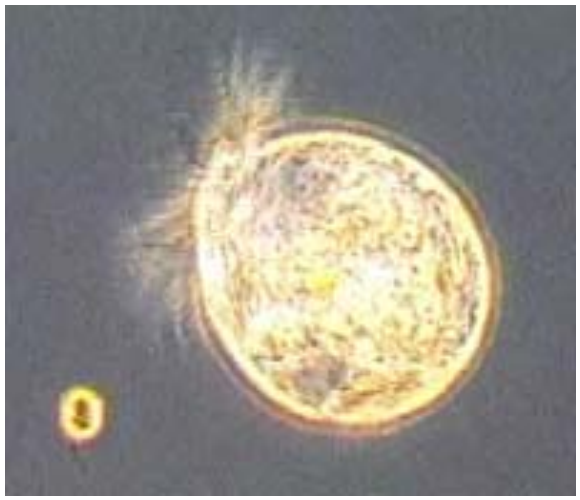
Table 1. Annual Average Increase in DMS Flux Going From a Present-Day Climate to a Future Climate, in 10° Latitude Bands, for the Models Described in the Auxiliary Material[a]

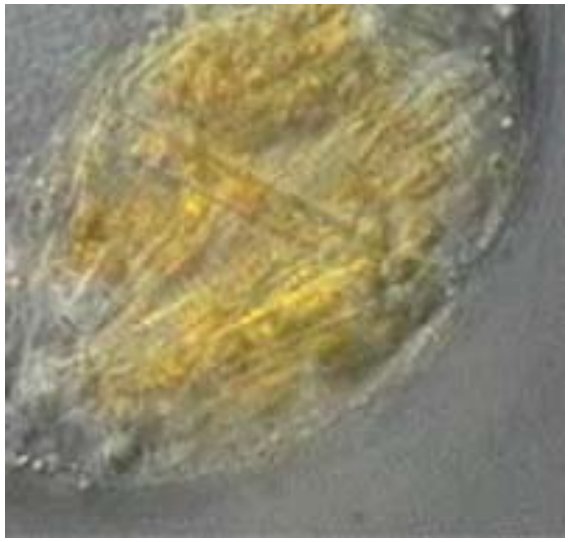
Generation	Reference	Degrees South Latitude								Interpretation
		80-70	70-60	60-50	50-40	40-30	30-20	20-10	10-Eq	
1st	*Gabric et al.* [2001, 2003]		+30		+5					Ice cover domiates
2nd	*Gabric et al.* [2004]		+50	+105	+30	+10	+5	+5	+5	ML[b] changes dominate
2nd	*Vallina et al.* [2007]	−5	0	+5	+5	0	0	+5	+5	ML[b] changes dominate, notes[c,d]
3rd	*Bopp et al.* [2003]		0	(+10)	+30	+10	(0)	(−10)	−15	See text, notes[e,f,g]
3rd	*Kloster et al.* [2007]	>+30	+10	−20	0	0	−10	−10	−10	See text, notes[e,g]
4th	This study	+170	+70	−15	+5	0	−10	−10	−10	See text.

[a]The percentage changes are taken directly from text interpretations in the original work wherever possible, and rounded to the nearest 5%.
[b]ML stands for 'mixed layer'.
[c]No zonal integrations presented so that samples were taken along meridians central to the Pacific, Atlantic and Indian basins.
[d]Their run duration was fifty years, which therefore had less greenhouse gas buildup than the other models (see Table S1).
[e]Zonal average flux perturbations reported most directly in the text.
[f]Parenthetical values indicate interpolation.
[g]Checks performed against zonal concentration integrations.

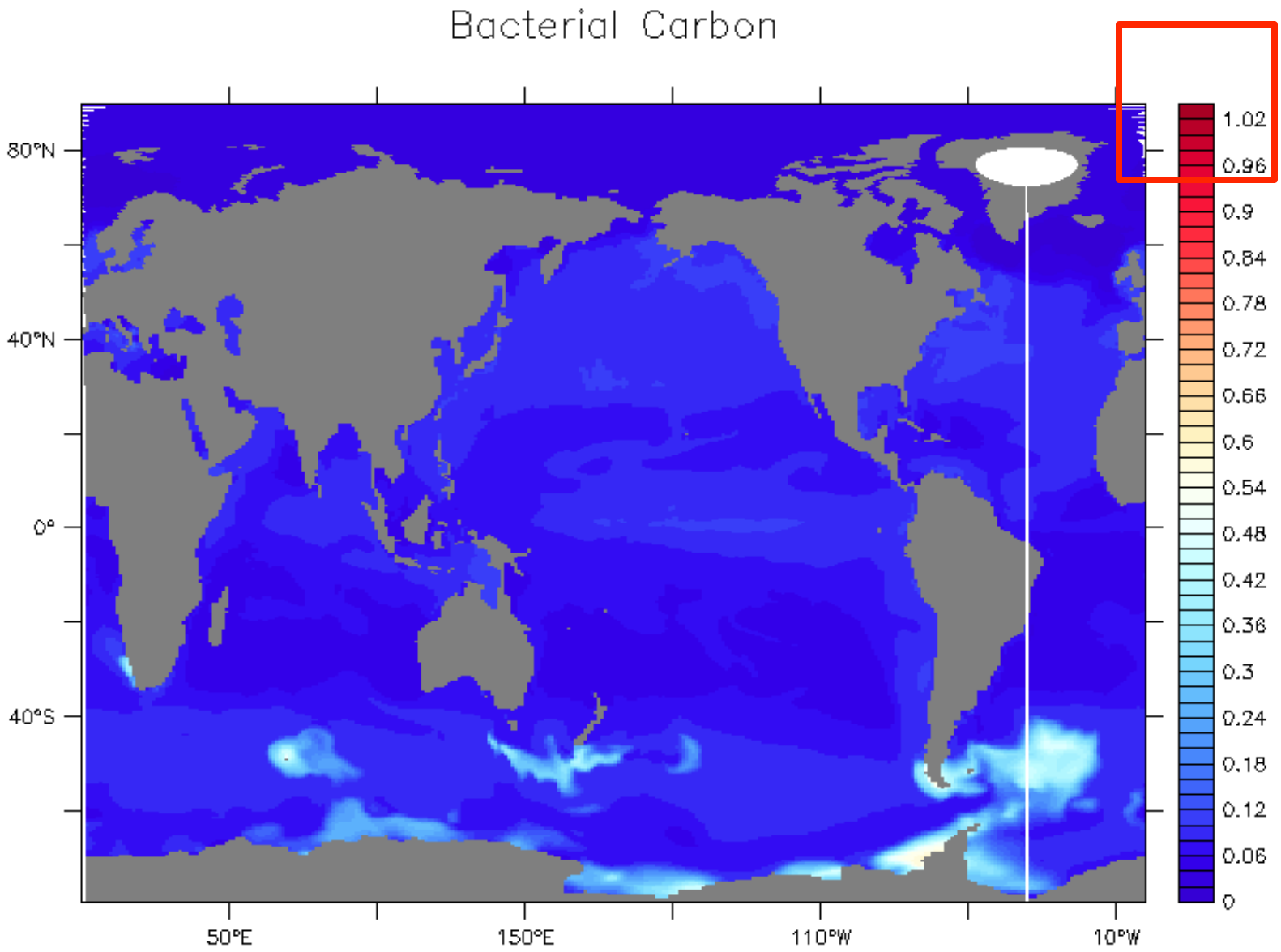
Thanks to Levasseur for feature in Nature

Detonators, Piercers, Biters, Sweepers, Engulfers

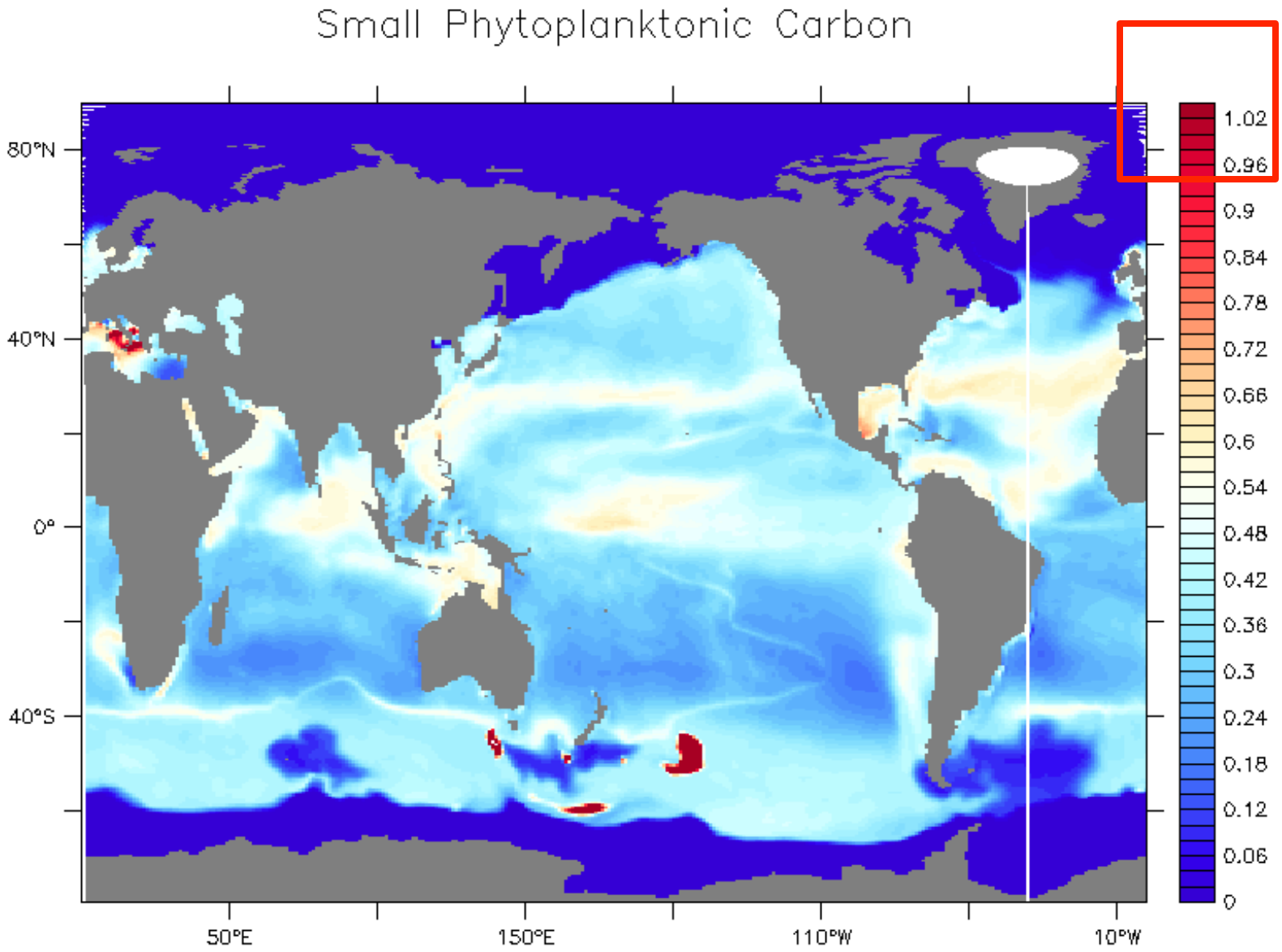



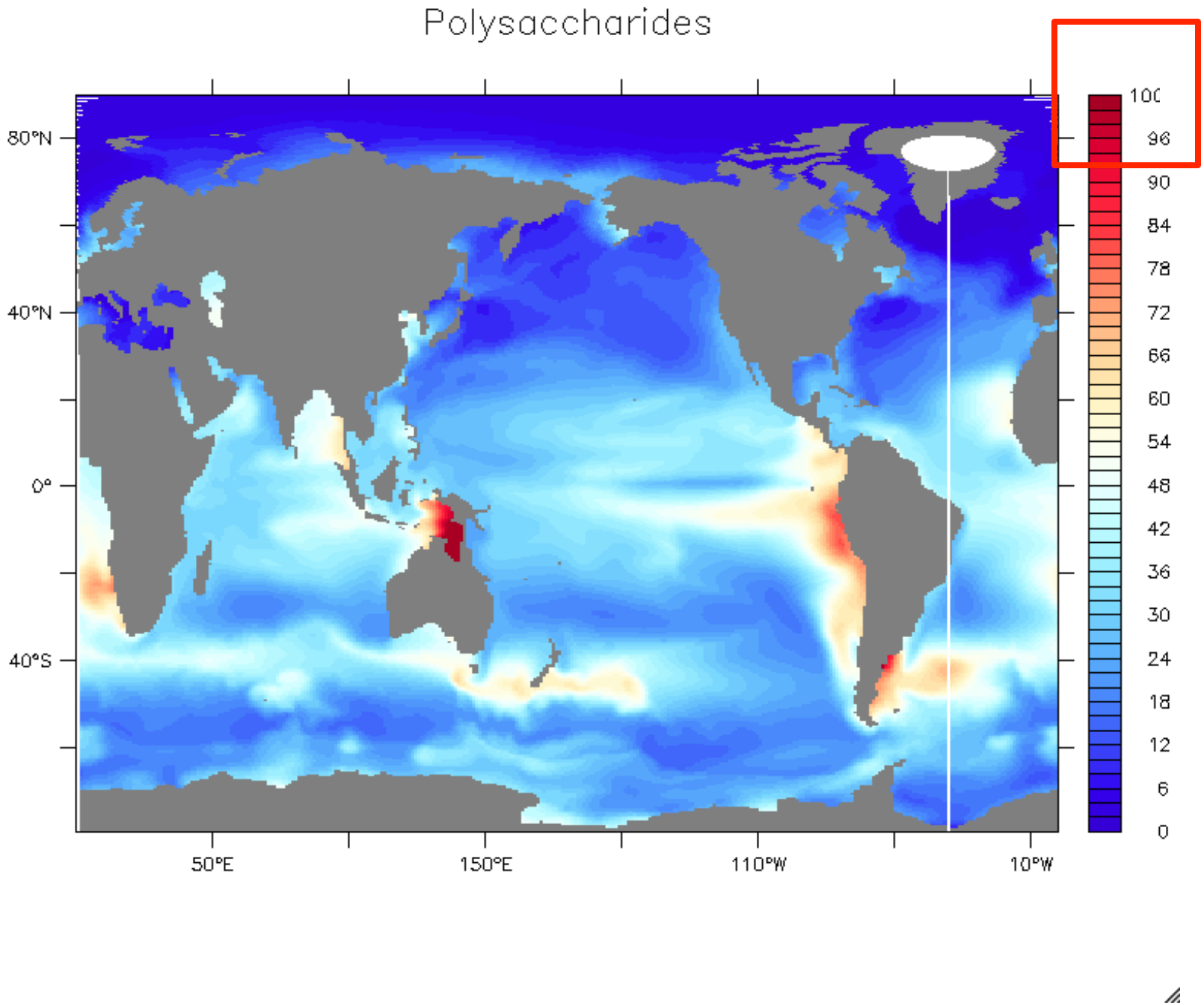



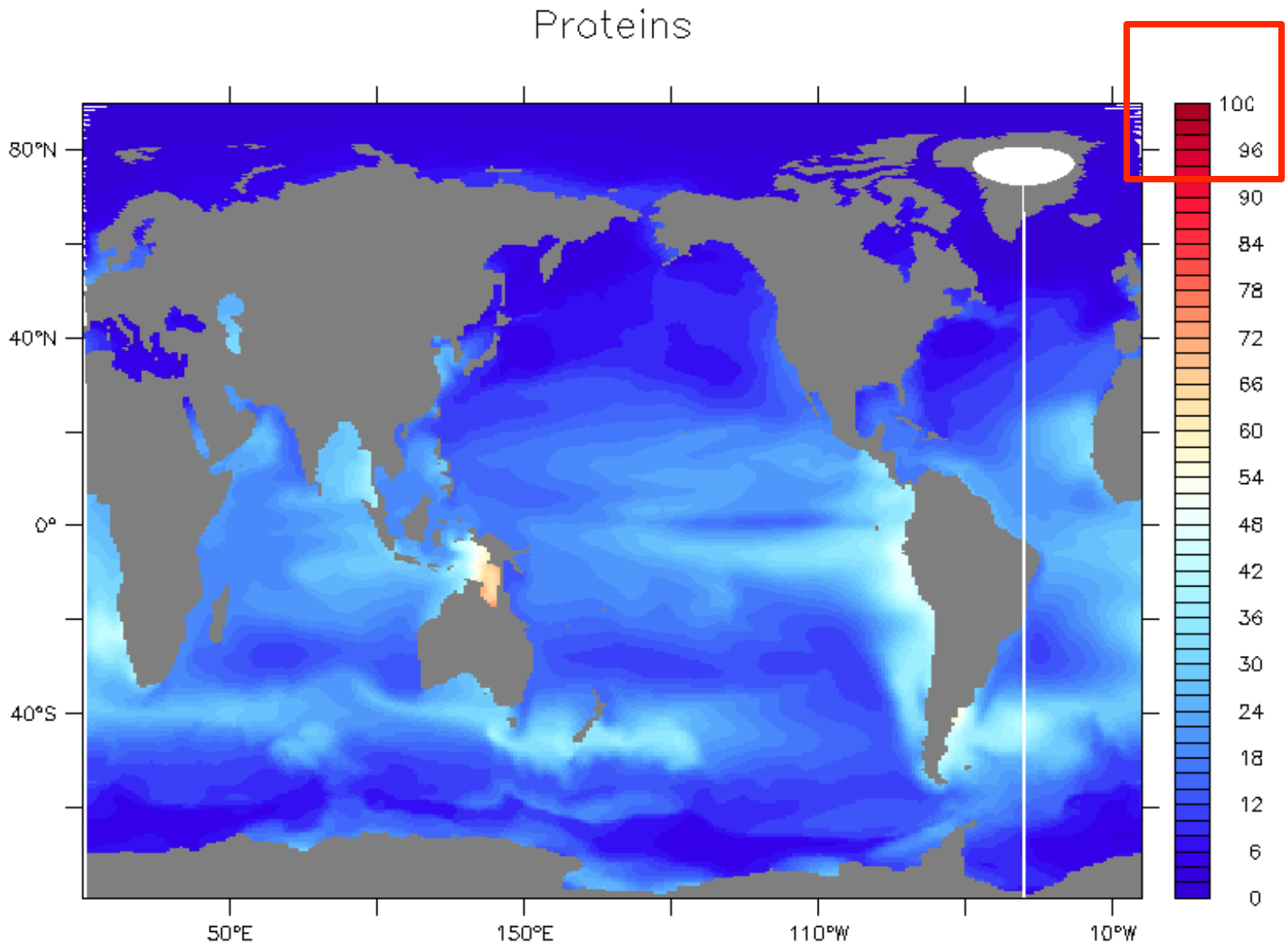

Australian Antarctic Division

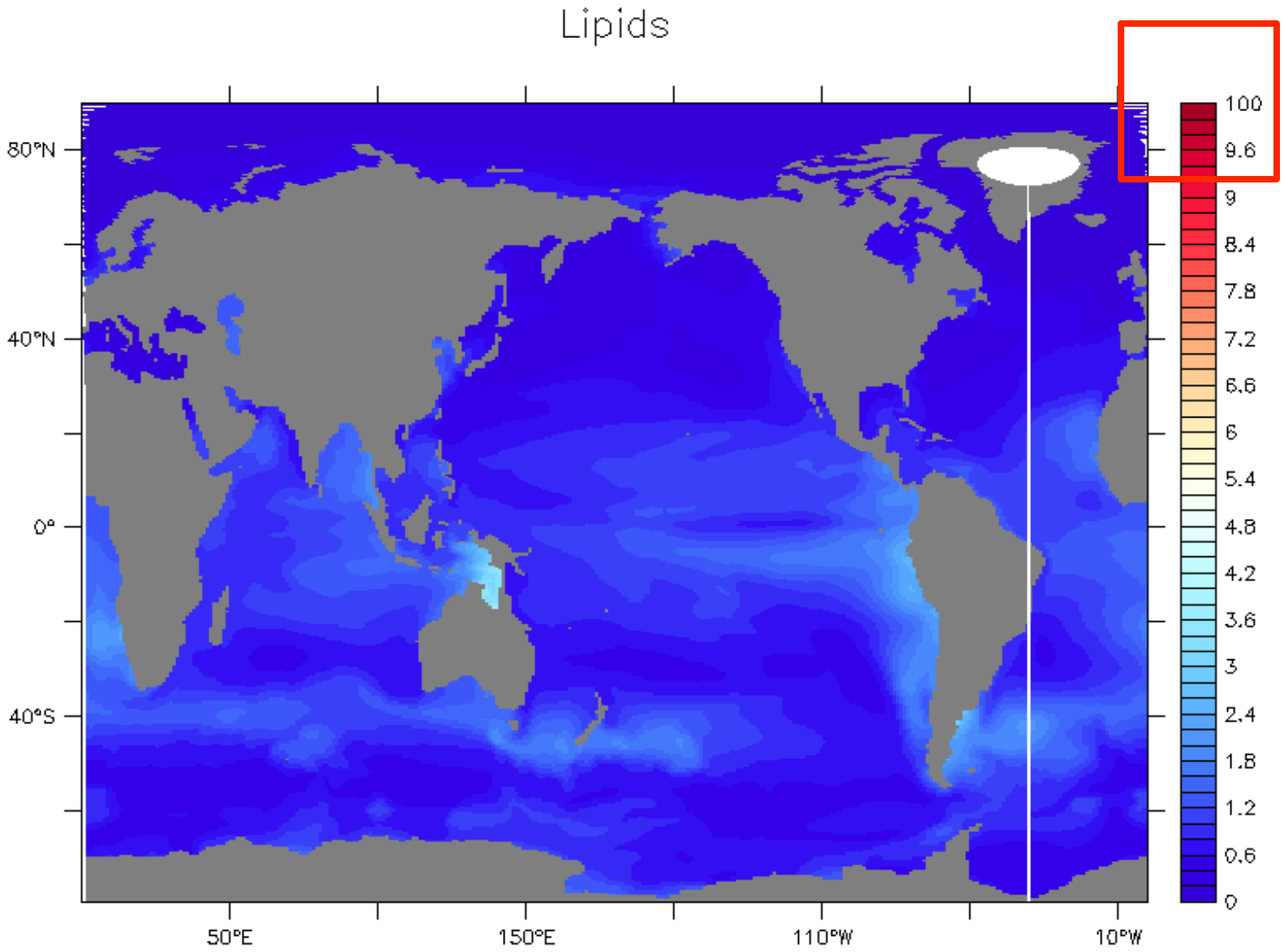


All Southern Ocean summer, concentration units micromolar…

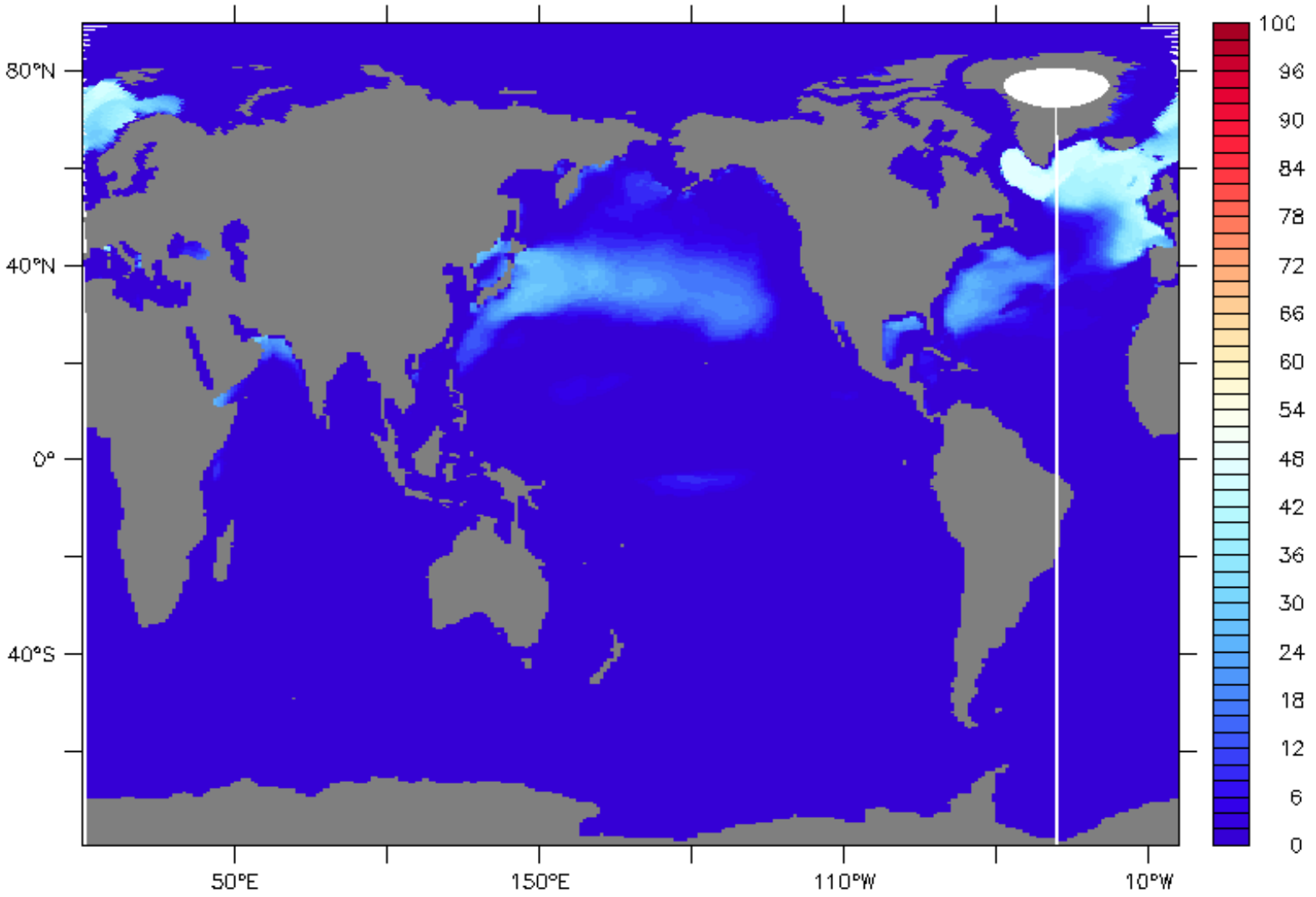

Small Phytoplanktonic Carbon
80°N
40°N
0°
40°S
50°E
150°E
110°W
10°W
1.02
0.96
0.9
0.84
0.78
0.72
0.66
0.6
0.54
0.48
0.42
0.36
0.3
0.24
0.18
0.12
0.06
0


Polysaccharides
80°N
40°N
0°
40°S
50°E
150°E
110°W
10°W
100
96
90
84
78
72
66
60
54
48
42
36
30
24
18
12
6
0

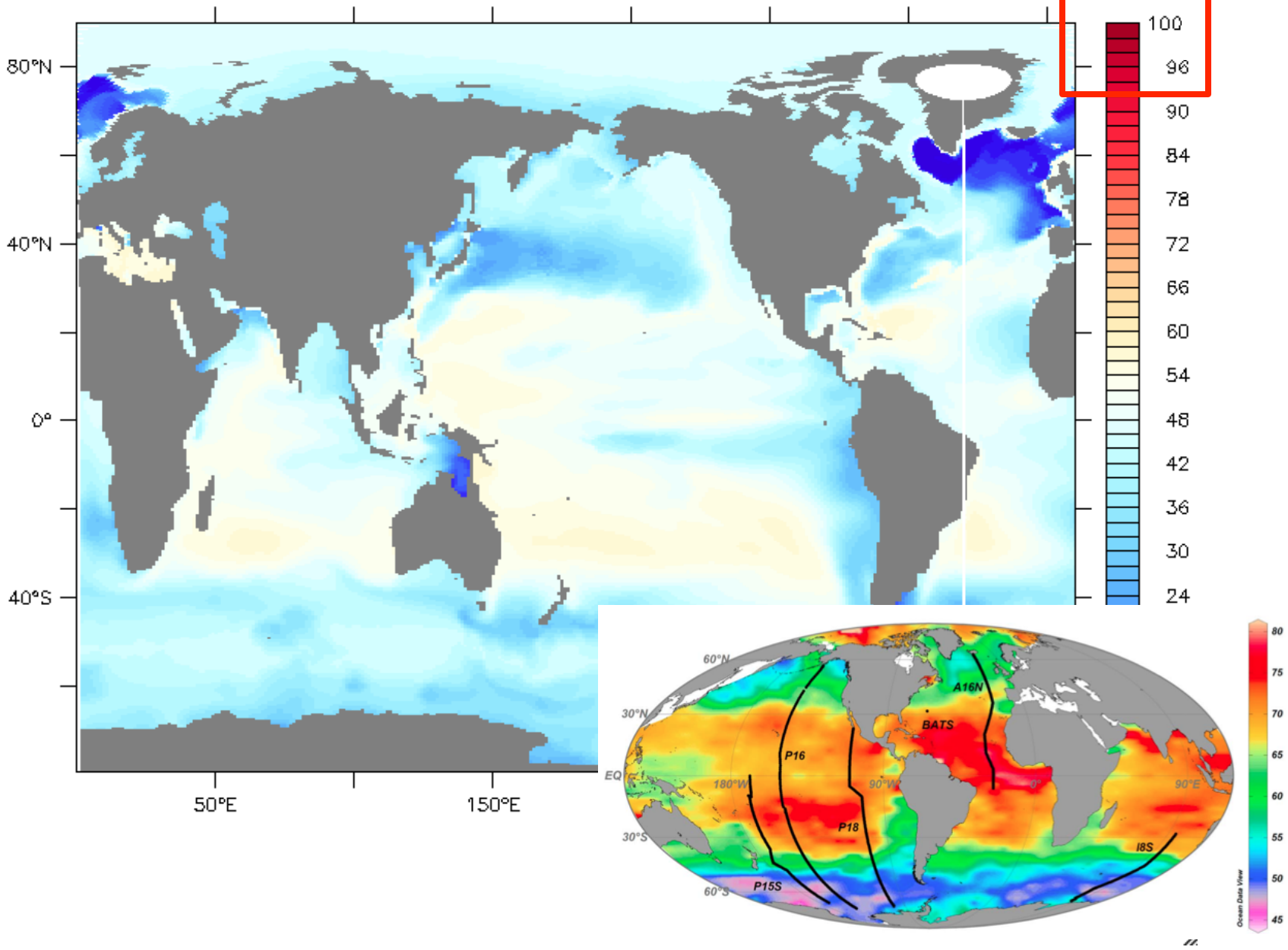

Proteins
80°N
40°N
0°
40°S
50°E
150°E
110°W
10°W
100
96
90
84
78
72
66
60
54
48
42
36
30
24
18
12
6
0


Lipids
80°N
40°N
0°
40°S
50°E
150°E
110°W
10°W
100
9.6
9
8.4
7.8
7.2
6.6
6
5.4
4.8
4.2
3.6
3
2.4
1.8
1.2
0.6
0

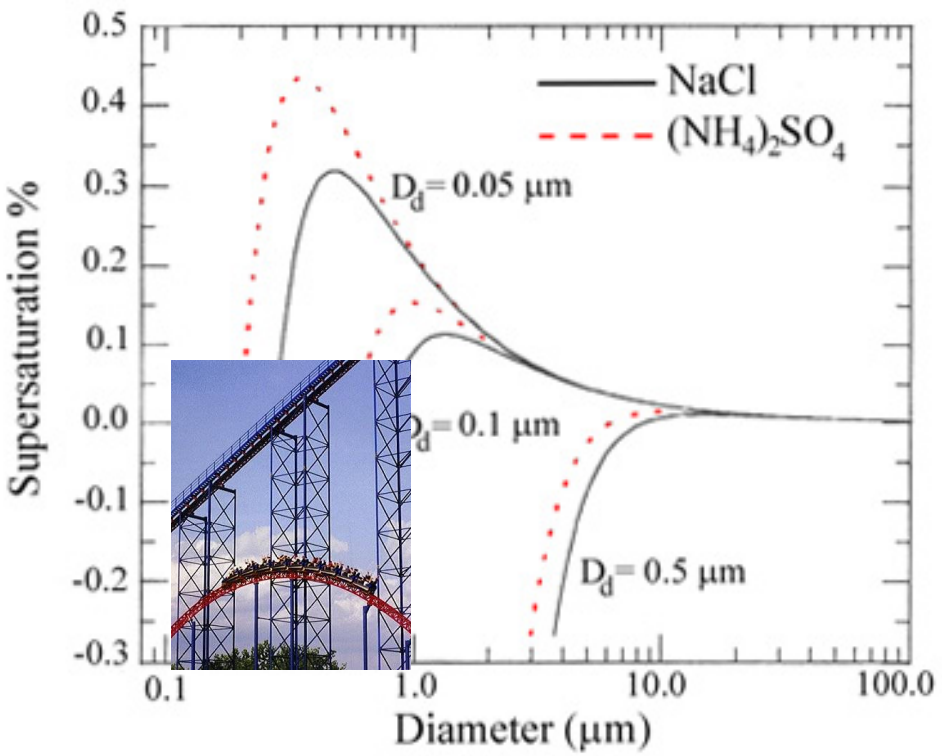
Humics


80°N
40°N
0°
40°S
50°E
150°E
110°W
10°W
100
96
90
84
78
72
66
60
54
48
42
36
30
24
18
12
6
0

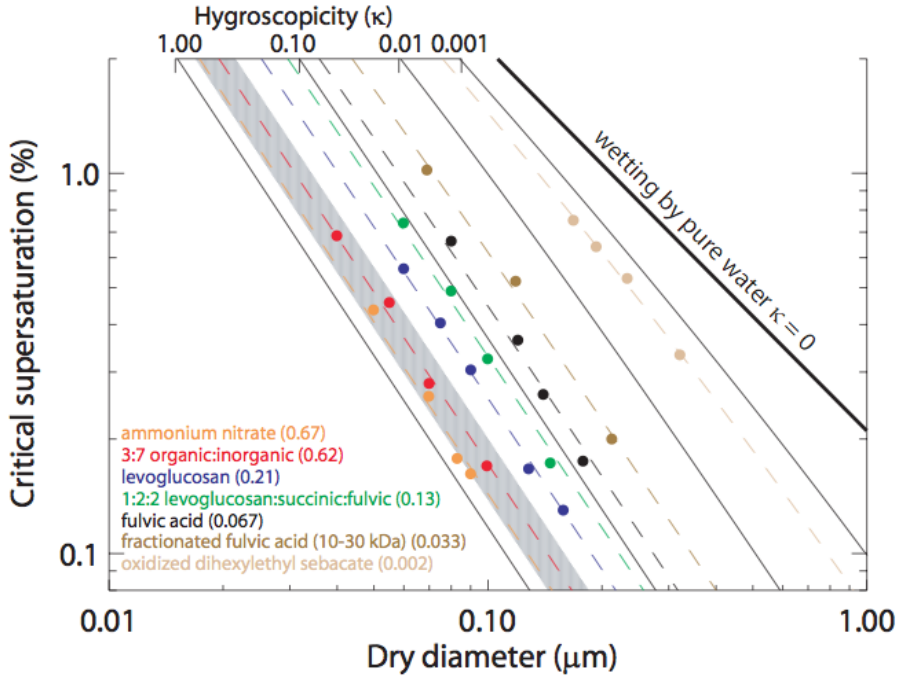
Unidentified Intermediates



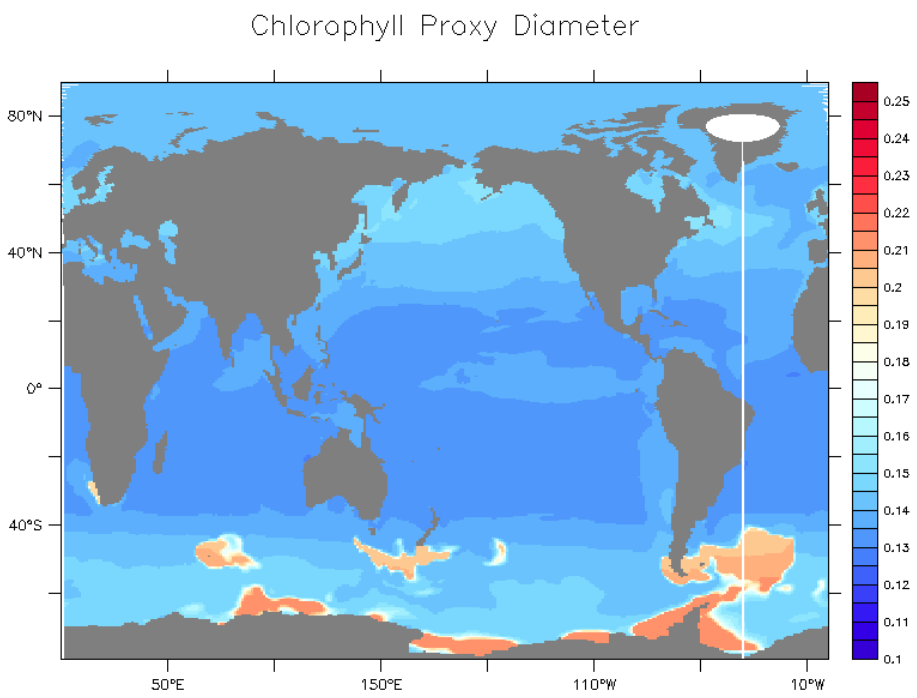
Kohler Curves and Hygroscopicity

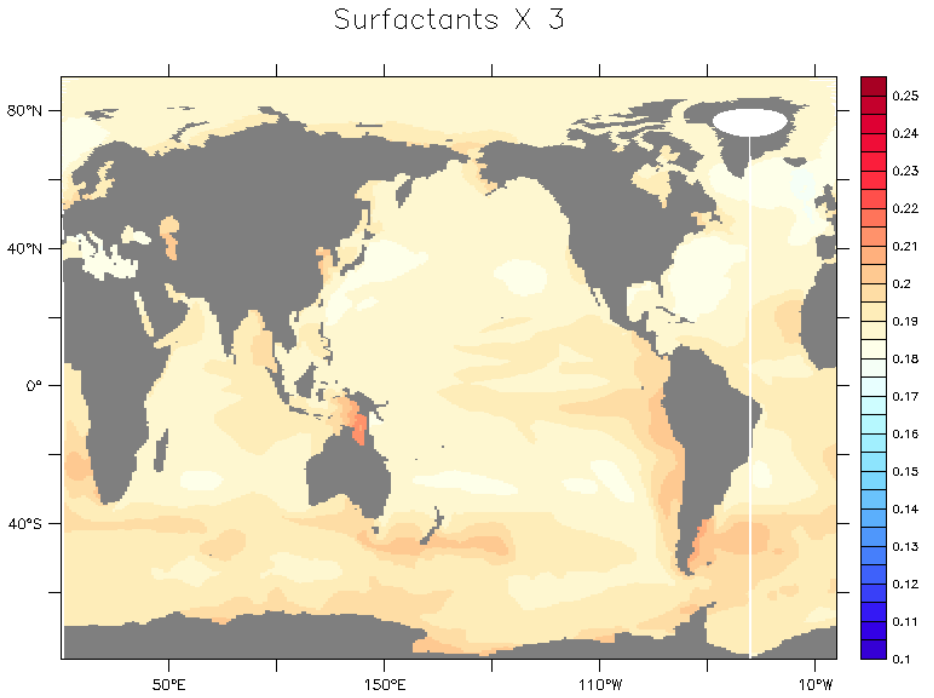


All calculations analytical



Petters & Kreidenweiss κ

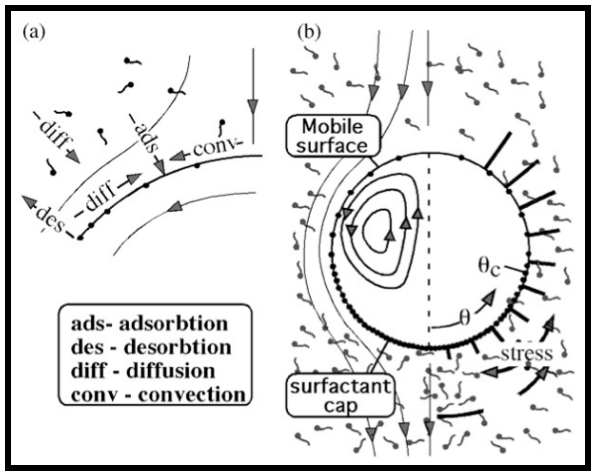




Drama King image:
Threshold diameters for growth (microns):
Standard chlorophyll proportionality vs. detailed O-chem

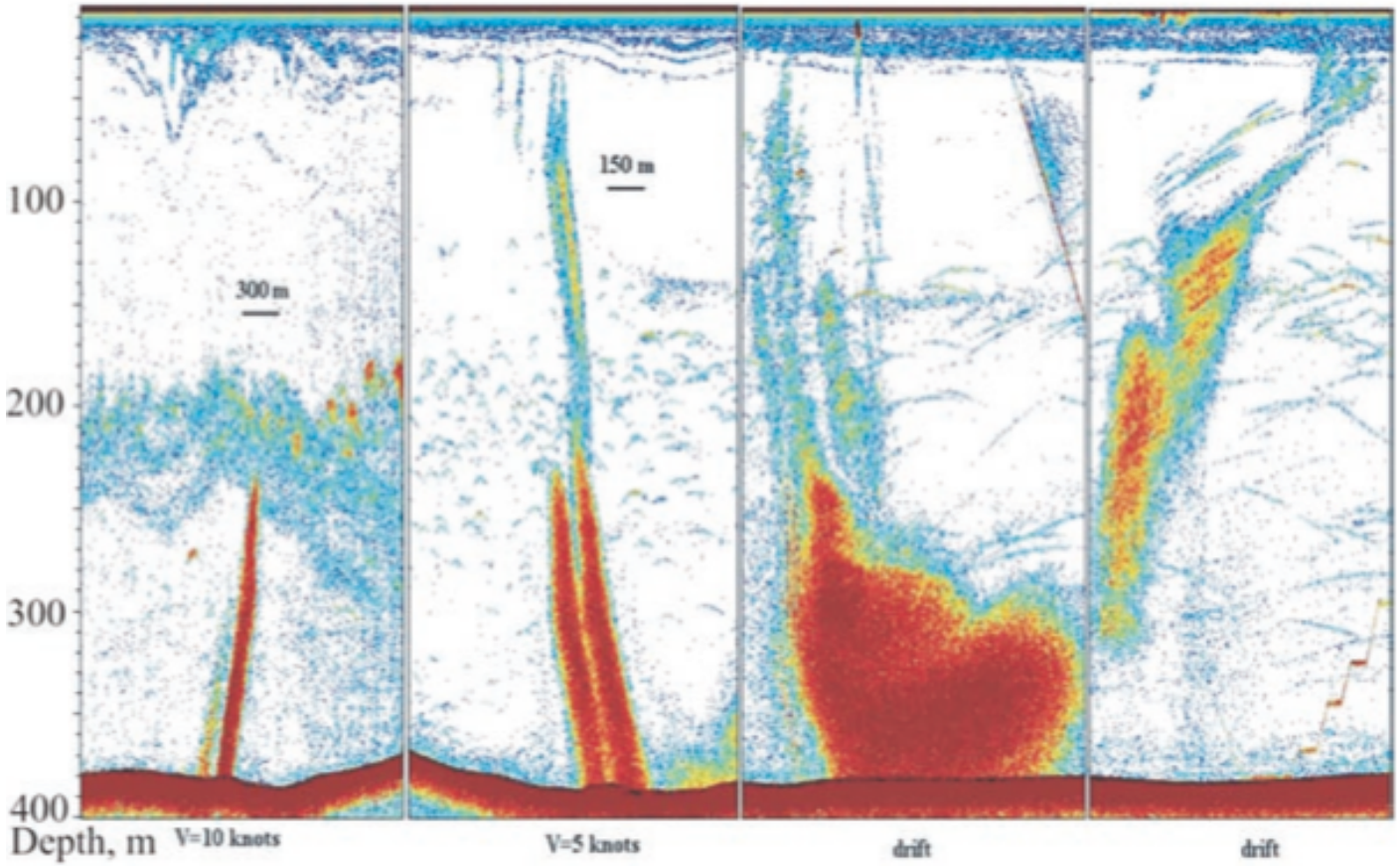
Selected monolayer computations

3



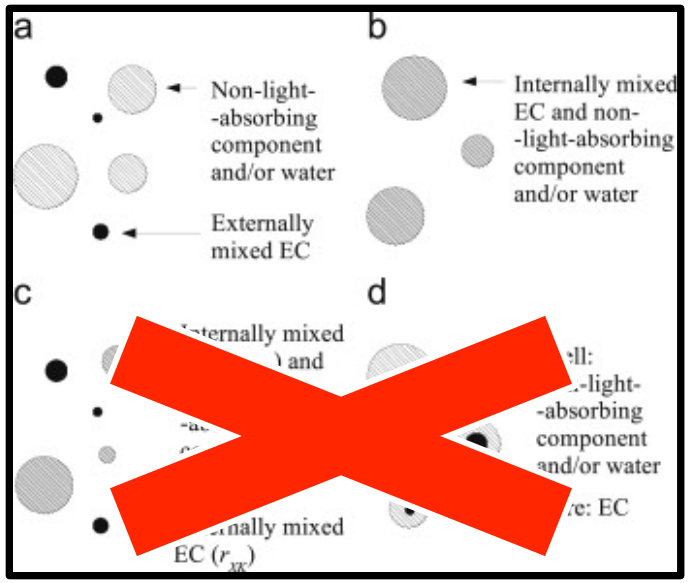
Bubbles, Organics

CH_4 flare rise:
Determined by surfactants



Obzhirov 04
Methane Flares
100-300 meters

Final Issues: Mixing State, Films



Diode Mixing

Test lipid, humic films and also lipid-derived mystery compound- Coat their own particles externally (mass balance a given)

Self Assembly