Modelling approaches to marine gel formation and their relevance for ocean-atmosphere exchanges

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GEOMAR Kiel

Leipziger Meteorologisches Kolloquium
at
Leibniz-Institut für Troposphärenforschung
December 2015

Initiation:

BMBF funded project **S**urface **O**cean **PR**ocesses in the **AN**thropocene (**SOPRAN**)

Remaining challenge:

Interrelations between:

a) organic matter (OM) production in the ocean
b) enrichment of OM in the surface microlayer (SML)
c) mass exchange between atmosphere and ocean

Surface Ocean Processes in the Anthropocene

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Ultimate goal:

→ Improved parameterisations of primary organic aerosol emission & air-sea gas exchange

Outline:

1) **Organic matter (OM) production and gel formation**

2) OM at the ocean-atmosphere interface

3) Aspects of combining OM production with air-sea exchange processes

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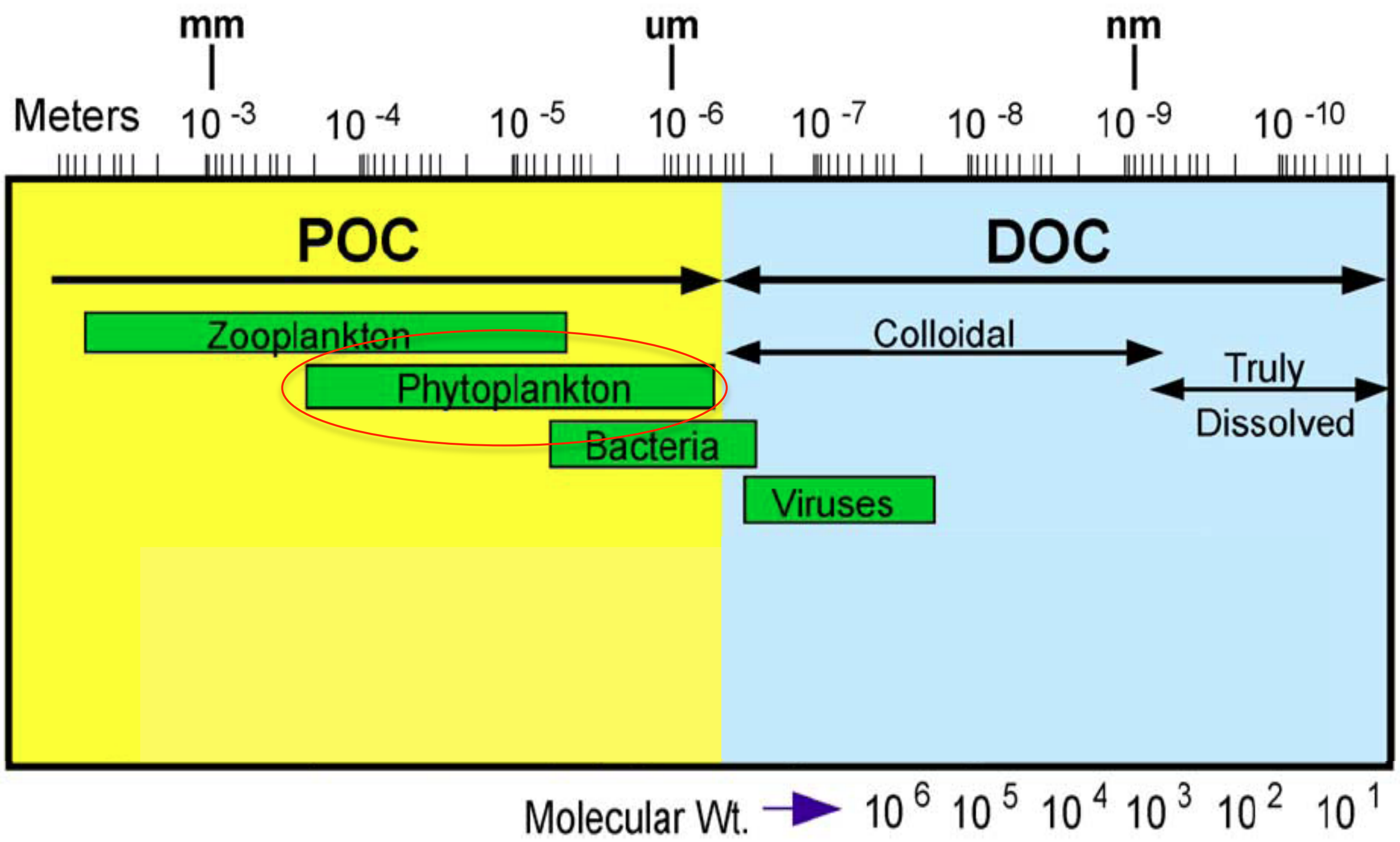
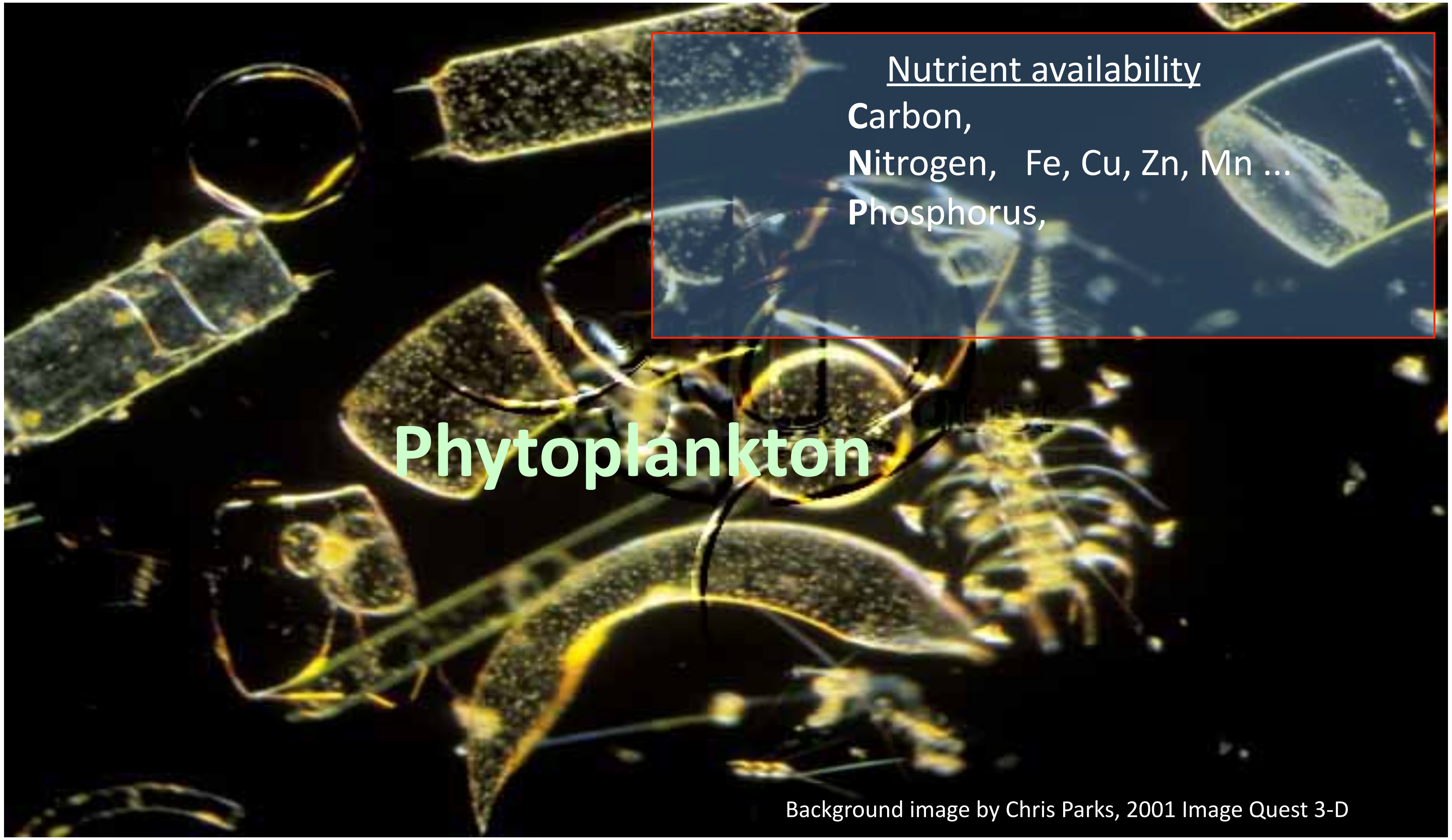
1) Organic matter (OM) production and gel formation

Particulate organic carbon (POC) Dissolved organic carbon (DOC)



Verdugo et al. (2004, Marine Chemistry)

1) Organic matter (OM) production and gel formation



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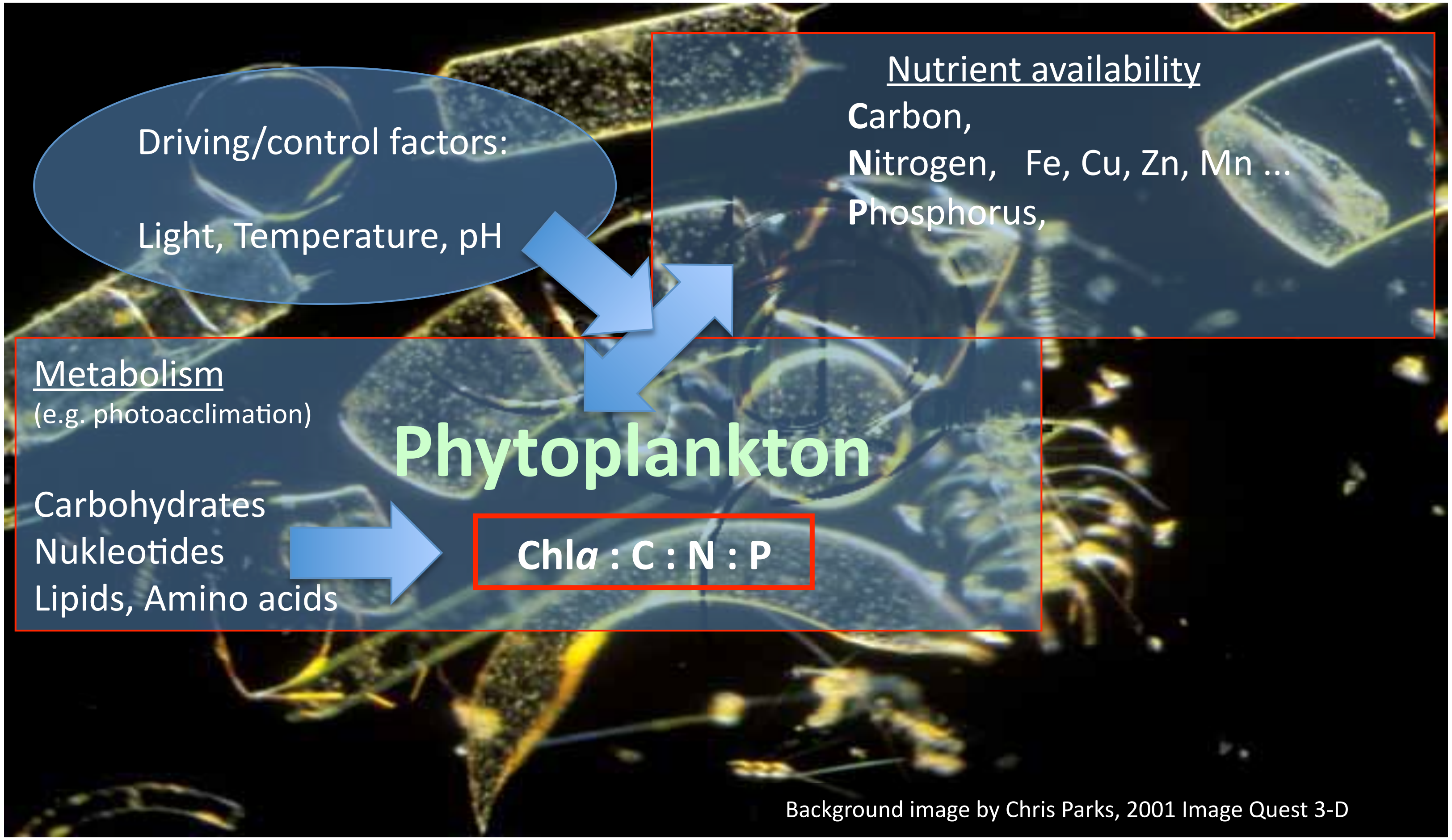
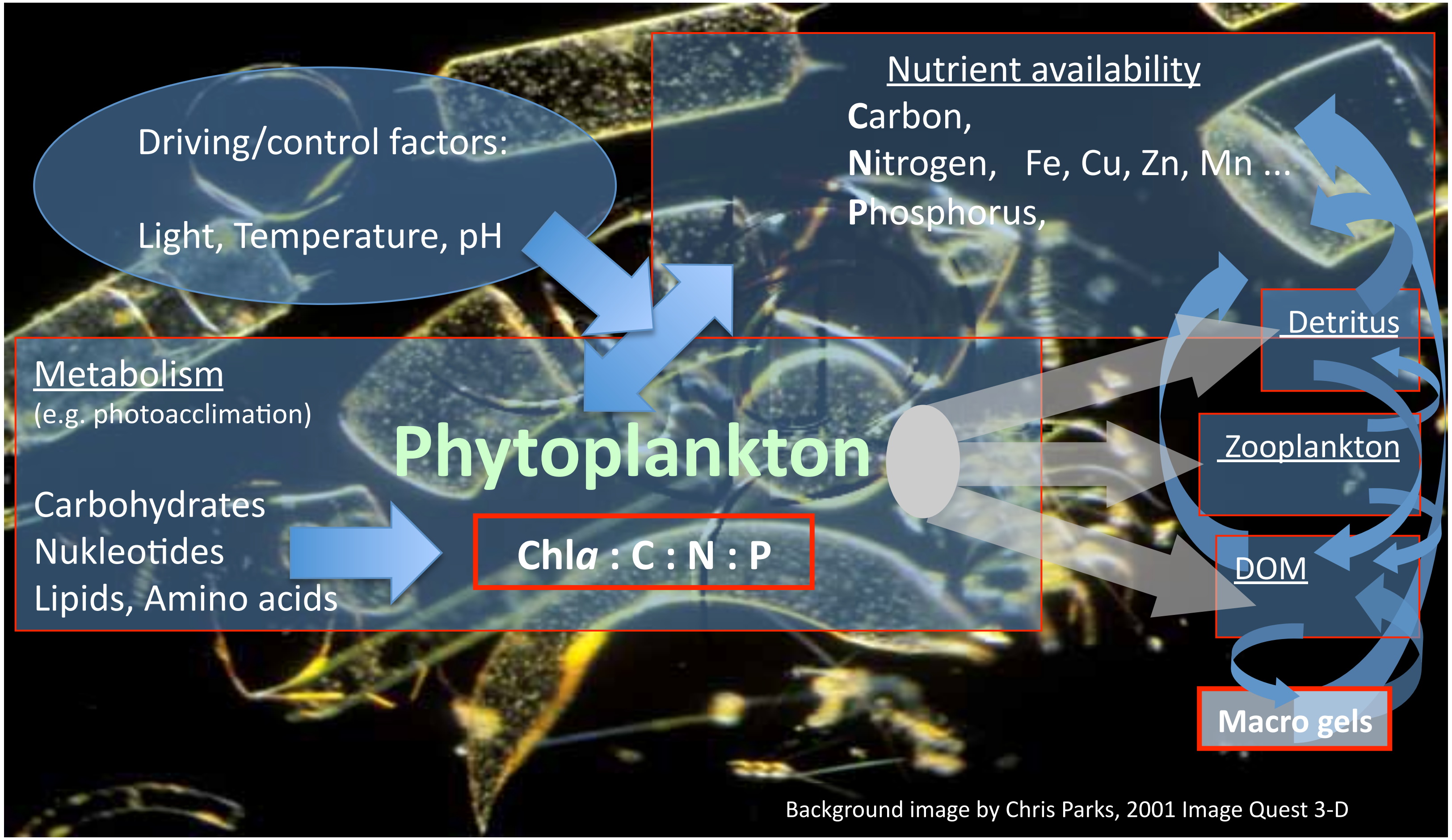


variable C : N : P assimilation ratio → variable build-up and fate of OM



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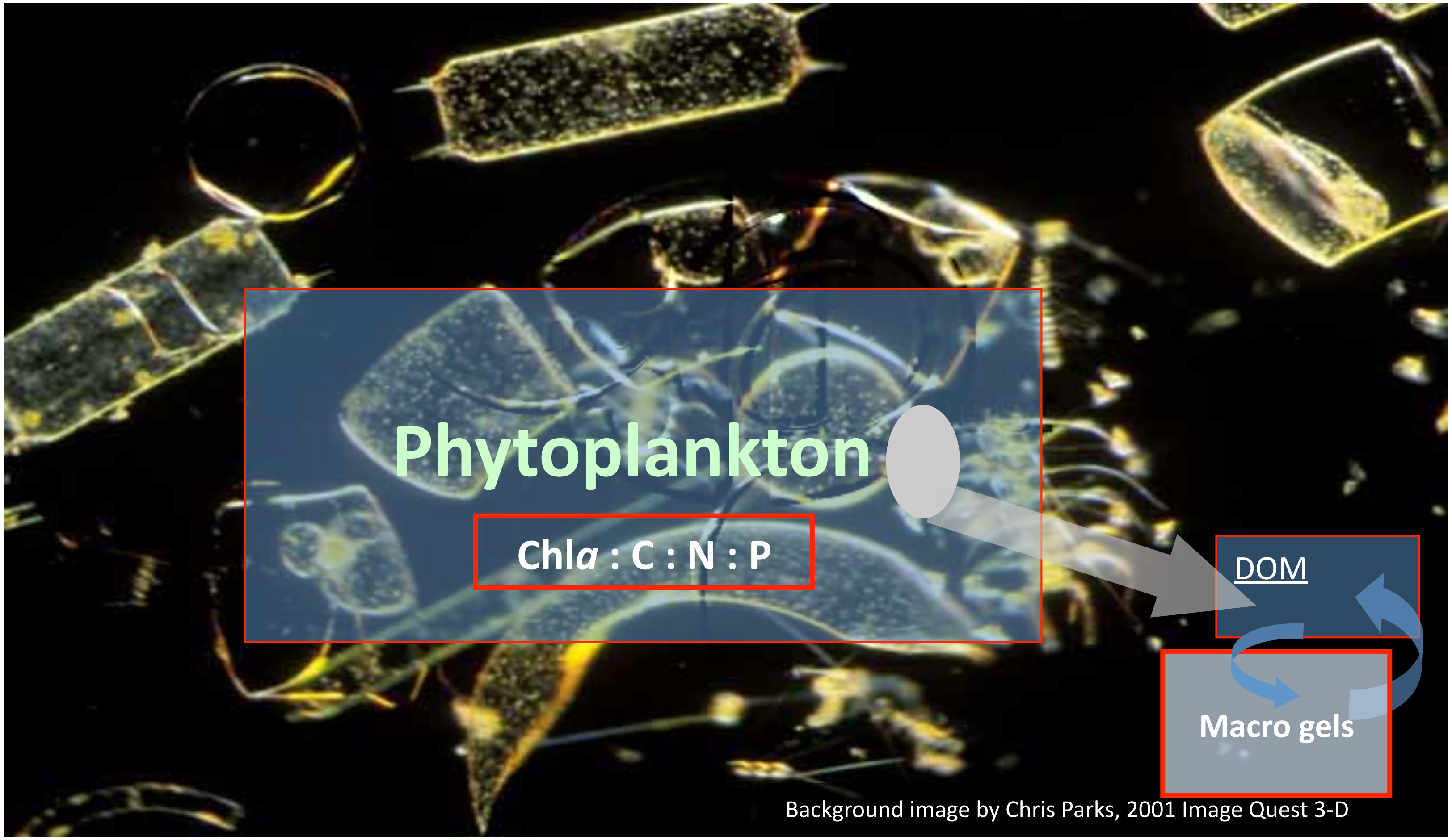

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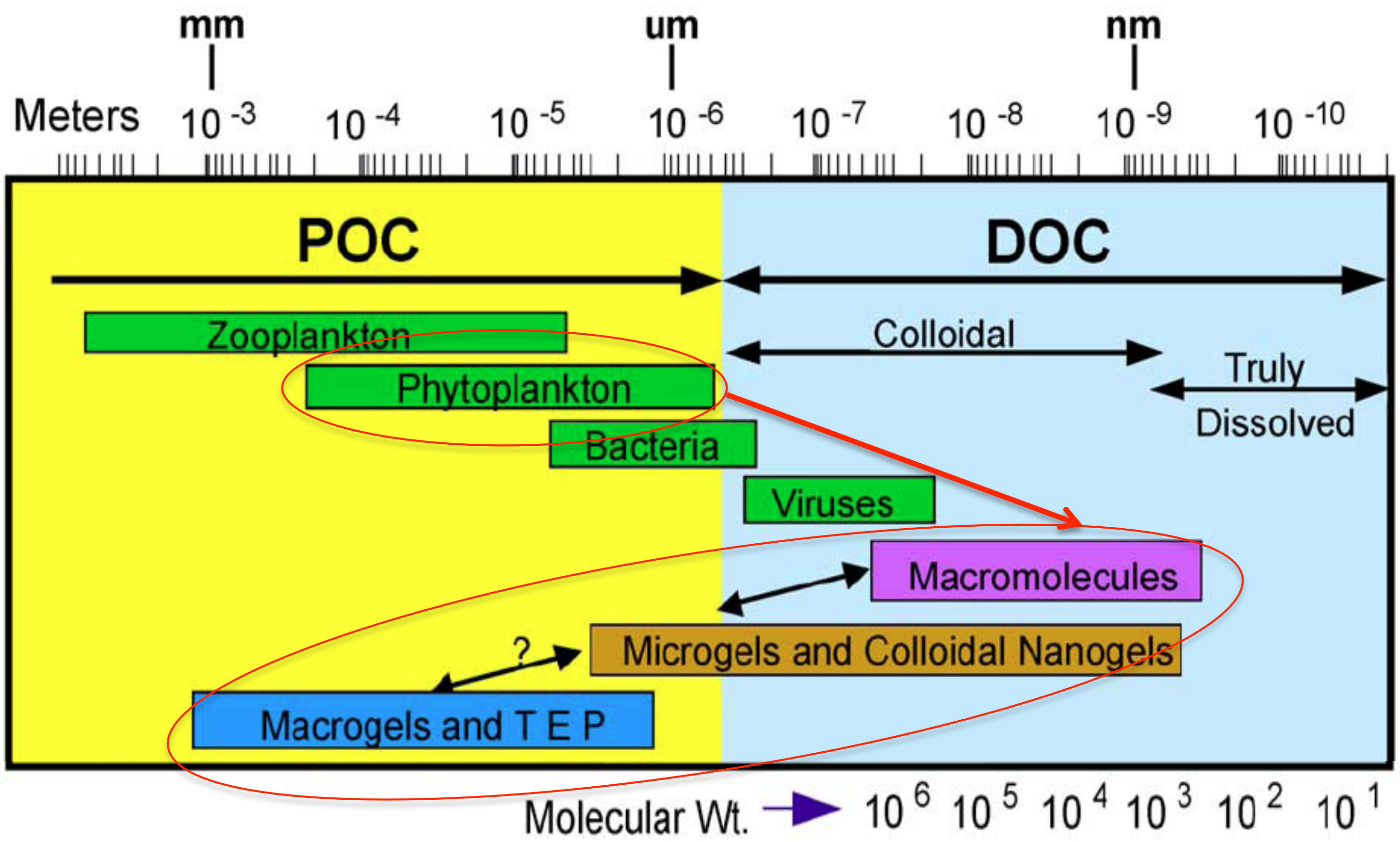
1) Organic matter (OM) production and gel formation

Particulate organic carbon (POC) Dissolved organic carbon (DOC)



Verdugo et al. (2004, Marine Chemistry)

Definition of TEP = transparent exopolymer particles

The abundance and significance of a class of large, transparent organic particles in the ocean

ALICE L. ALLDREDGE,* UTA PASSOW* and BRUCE E. LOGAN†

(*Received* 12 *February* 1993; *accepted* 17 *February* 1993)

Abstract—Polysaccharide-specific staining techniques reveal the existence and high abundance of a class of large, discrete, transparent particles in seawater and diatom cultures formed from dissolved exopolymers exuded by phytoplankton and bacteria. Transparent exopolymer particles (TEP), ranged from 28 to 5000 particles ml^{-1} and from 3 to 100s μm in longest dimension at five coastal stations off California. A high percentage of seemingly free-living bacteria (28–68%) were attached to these transparent sheets and films, suggesting that they may alter the distributions and microenvironments of marine microbes in nature. Preliminary coagulation experiments demonstrated that TEP are major agents in the aggregation of diatoms and in the formation of marine snow. The existence of microbial exudates acting as large, discrete particles, rather than as dissolved molecules or as coating on other particles, suggests that the transformation of dissolved organic matter into particulate form in the sea can occur via a rapid abiotic pathway as well as through conventional microbial uptake. The existence of these particles has far reaching implications for food web structure, microbial processes, carbon cycling and particulate flux in the ocean.

Alldredge et al. (1993, Deep Sea Research I)

a) stained acidic polysaccharides

b) extracellular and particular (>2 μm)

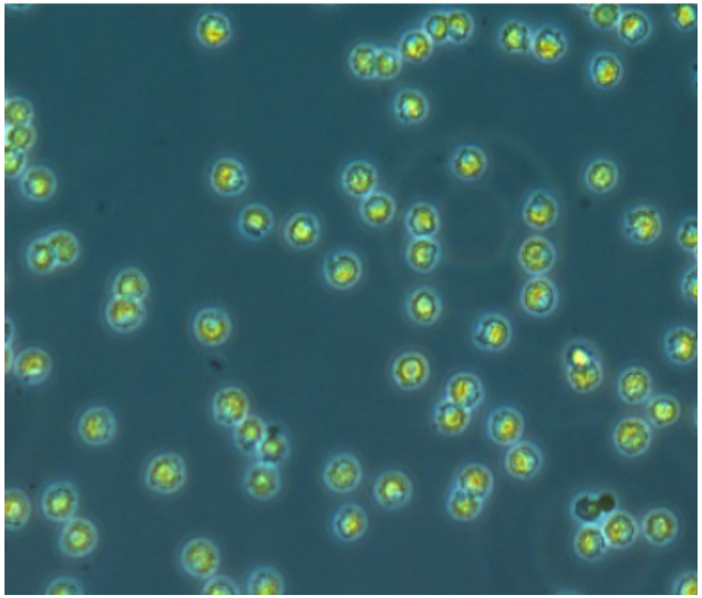
c) exuded by phyto-plankton and bacteria

d) relevant for particle aggregation and export dynamics (marine snow)

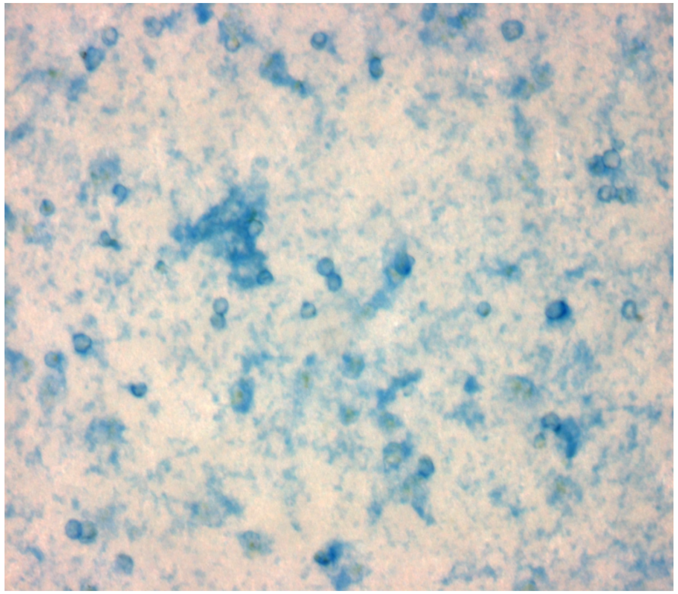
e) TEP = a subgroup of **E**xopolymeric **S**ubstances (EPS)

1) Organic matter (OM) production and gel formation

Direct view



Stained with Alcian Blue

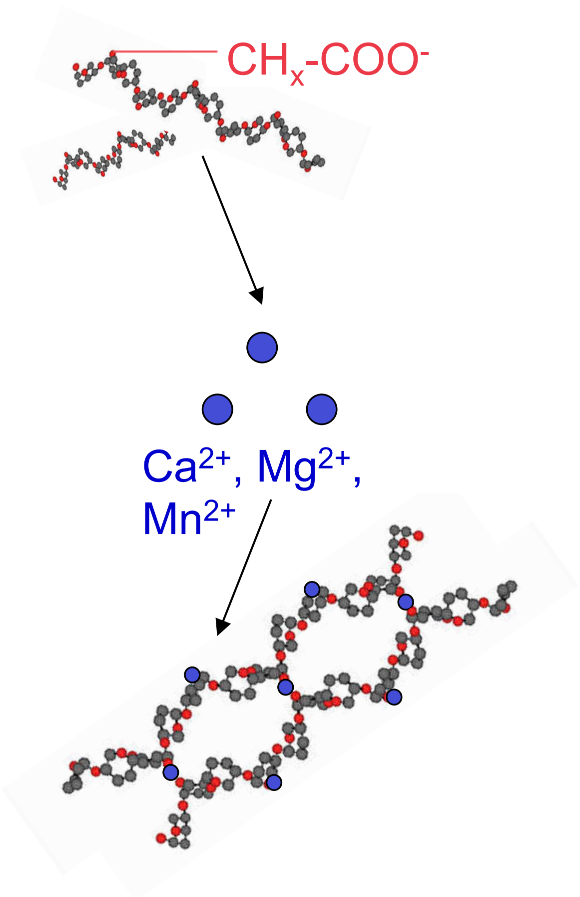


Microscopic pictures of natural phytoplankton assemblages

Figures by courtesy of Anja Engel (GEOMAR Kiel)

1) Organic matter (OM) production and gel formation

Binding ("ion-bridging")
acidic polysaccharides

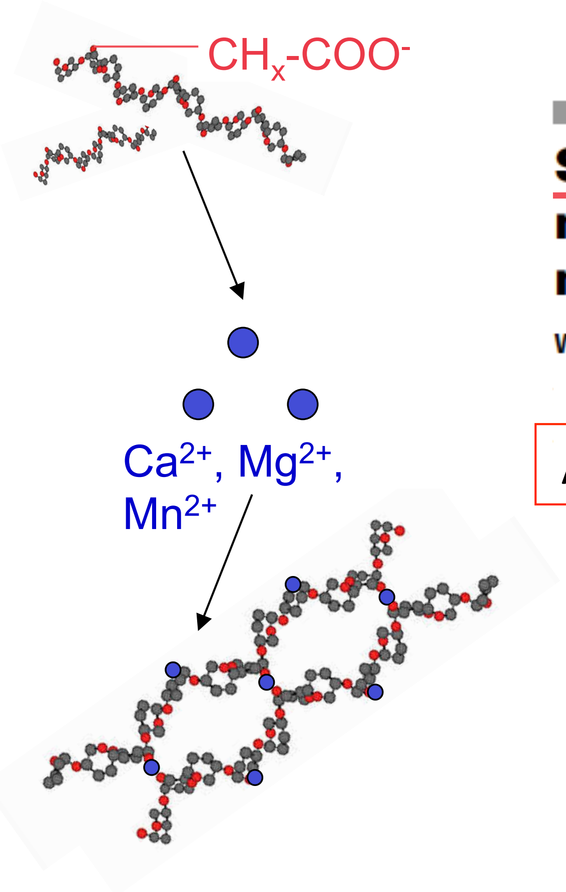


Two mechanisms to form macro-gels:

A) Theory of spontaneous assembly
B) Theory of coagulation

1) Organic matter (OM) production and gel formation

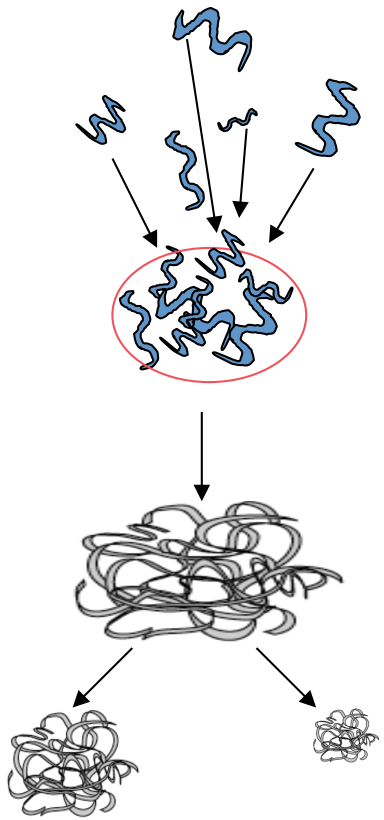
Binding ("ion-bridging")
acidic polysaccharides



Spontaneous assembly of marine dissolved organic matter into polymer gels

Wei-Chun Chin, Mónica V. Orellana & Pedro Verdugo

A) Gelation by spontaneous assembly



Chin et al. (1998, Nature)

1) Organic matter (OM) production and gel formation

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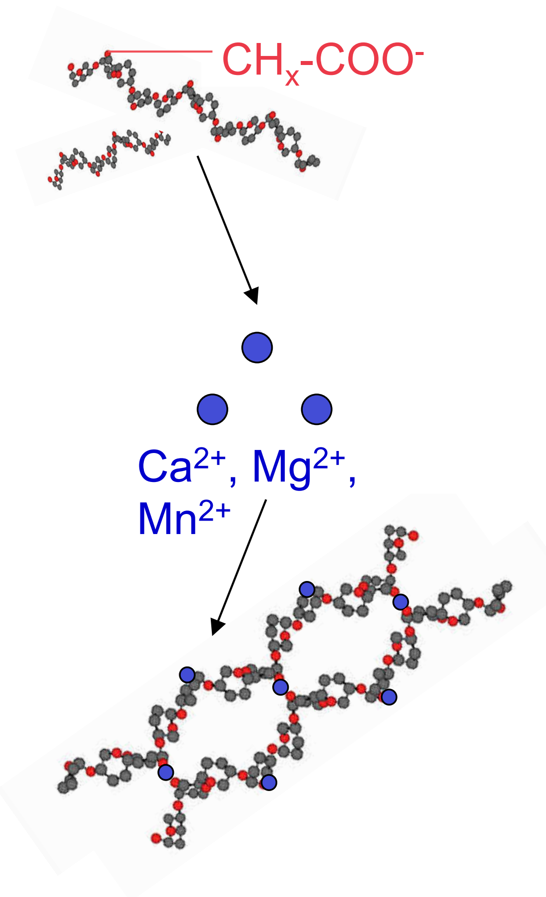
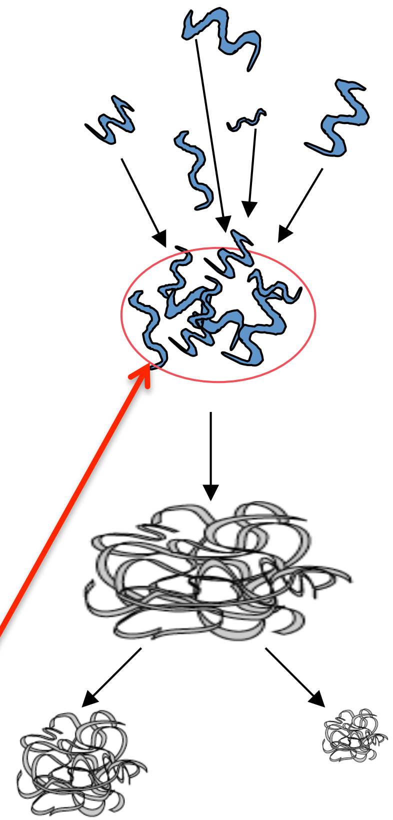


Spontaneous assembly of marine dissolved organic matter into polymer gels

Wei-Chun Chin, Mónica V. Orellana & Pedro Verdugo

A) Gelation by spontaneous assembly

→ Requires some kind of accumulation site (e.g. interface) for spontaneous assembly to occur



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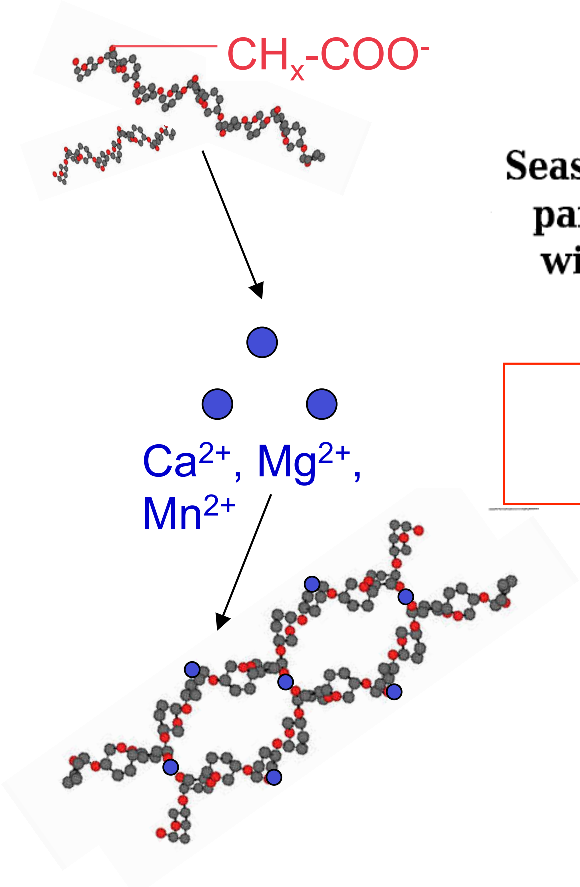
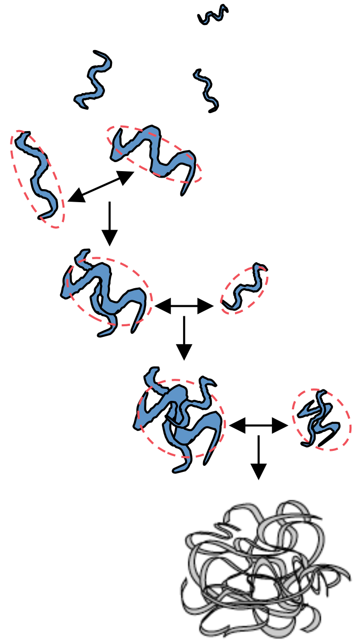


Seasonal size spectra of transparent exopolymeric particles (TEP) in a coastal sea and comparison with those predicted using coagulation theory

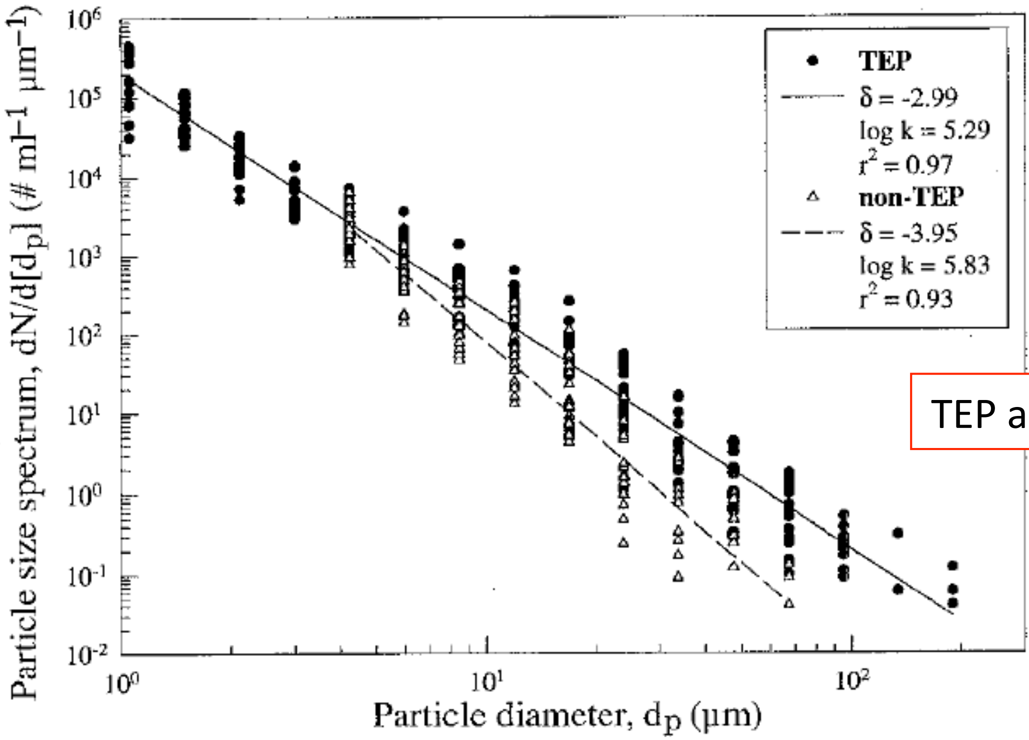
Xavier Mari[1,*], Adrian Burd[2]

B) Aggregation of polysaccharides
(coagulation dynamics)



Mari and Burd (1998, Marine Ecology Progress Series, MEPS)

1) Organic matter (OM) production and gel formation



TEP as size frequency distribution!

$$\frac{\mathrm{d}n(s,t)}{\mathrm{d}t} = \frac{1}{2}\int_0^s \alpha(s_1, s-s_1)\cdot\beta(s_1, s-s_1)\cdot n(s_1,t)\cdot n(s-s_1,t)\,\mathrm{d}s - n(s,t)\int_0^\infty \alpha(s,s_1)\cdot\beta(s,s_1)\cdot n(s_1,t)\,\mathrm{d}s_1 - \frac{w(s)}{z}n(s,t) + \mu(s,t)$$

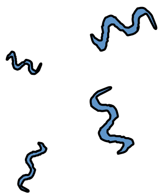
Coagulation kernel β = Brownian motion (β_{Br}) + Shear stress (β_{Sh}) + Differential settlement (β_{Ds})

Mari and Burd (1998, Marine Ecology Progress Series, MEPS)

Plankton

PCHO

dissolved



TEP(C)

particulate

Polysaccharide aggregation as a potential sink of marine dissolved organic carbon

Anja Engel[1*], Silke Thoms[1], Ulf Riebesell[1*], Emma Rochelle-Newall[2*] & Ingrid Zondervan[1]

Coagulation dynamics with only **two** size classes

dissolved

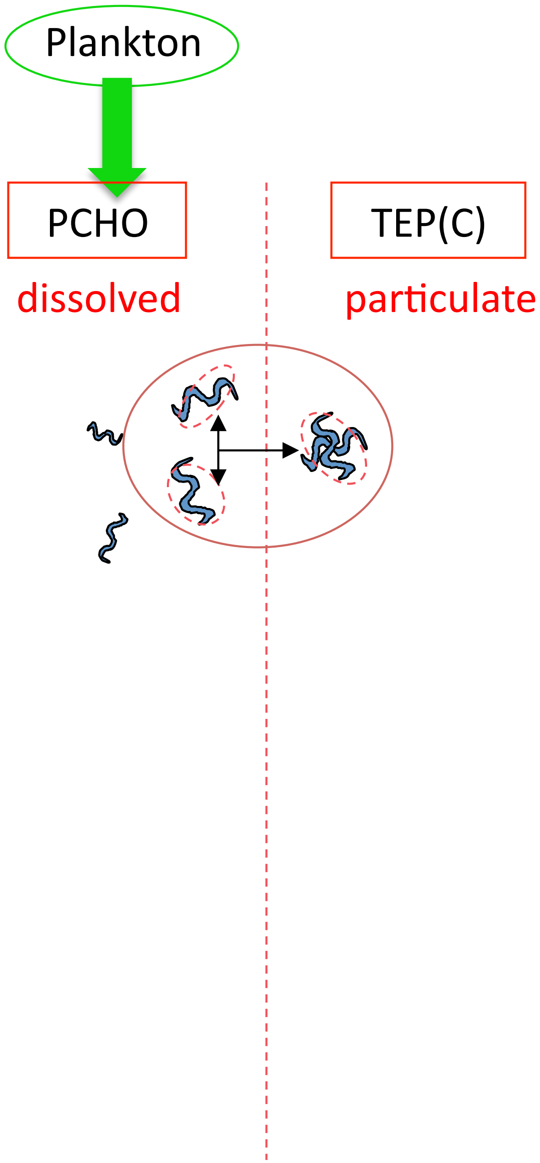
Net source

$$\mathrm{d[PCHO]/d}t = \gamma(MP_C - \mu)[\mathrm{cell}] - \alpha_{\mathrm{PCHO}}\beta_{\mathrm{PCHO}}[\mathrm{PCHO}]^2 - \alpha_{\mathrm{TEP}}\beta_{\mathrm{TEP}}[\mathrm{PCHO}][\mathrm{TEP}] \quad (1)$$

particulate

$$\mathrm{d[TEP]/d}t = \alpha_{\mathrm{PCHO}}\beta_{\mathrm{PCHO}}[\mathrm{PCHO}]^2 + \alpha_{\mathrm{TEP}}\beta_{\mathrm{TEP}}[\mathrm{PCHO}] \times [\mathrm{TEP}] \quad (2)$$

1) Organic matter (OM) production and gel formation



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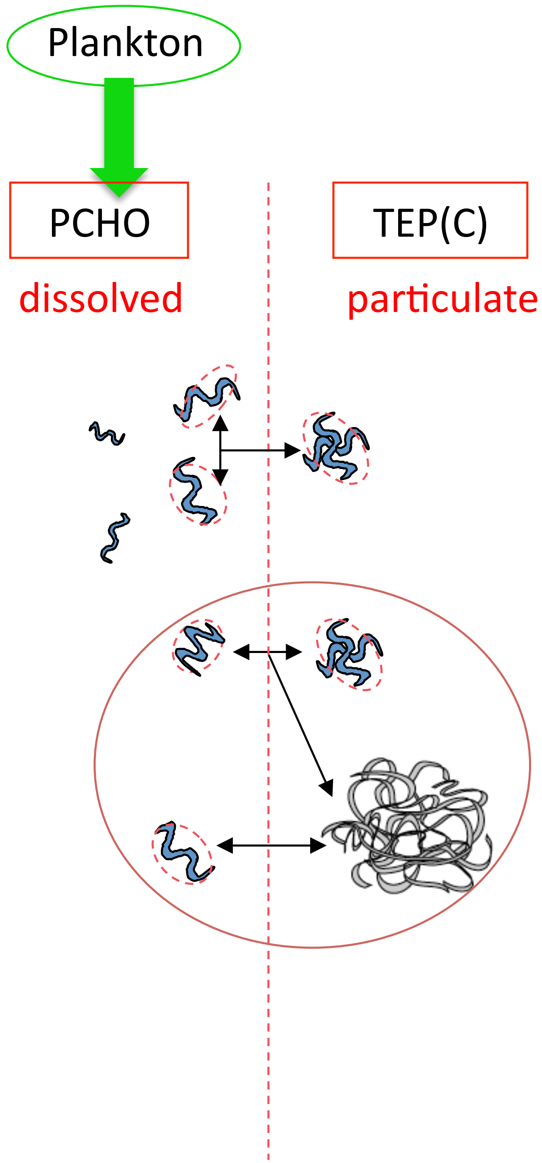

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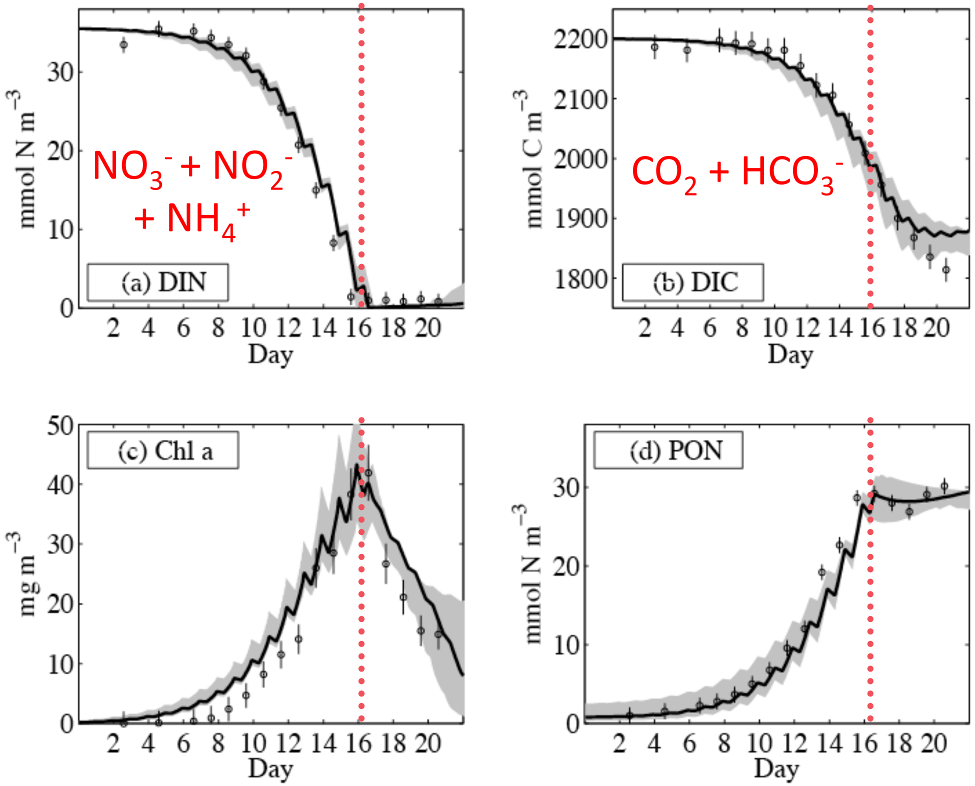
1) Organic matter (OM) production and gel formation

Assessment of plankton growth model + TEP formation against data of a mesocosm experiment

Mesocosm = enclosure (tank or bag) of seawater (e.g. 2 m diameter, 1.5 m depth, or larger)



Schartau et al. (2007, Biogeosciences)

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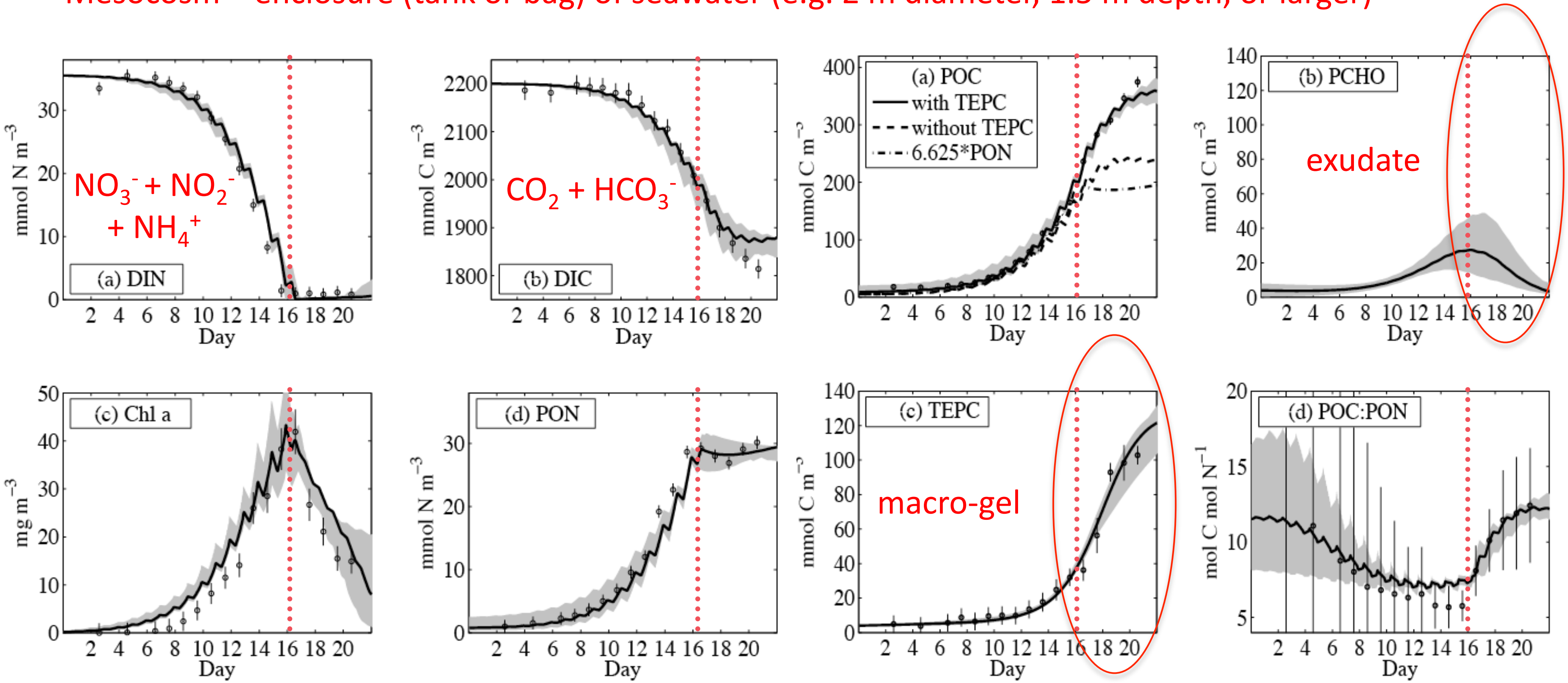


Schartau et al. (2007, Biogeosciences)

→ Continuous increase in POC although algal growth N-limited

→ POC increase mainly attributable to TEP(-C) formation

Summary

→ Organic matter production depends on algal growth condition (e.g. light, nutrient availability and temperature)

→ Exudation and thus gel formation (TEP) is accelerated when algal growth becomes nutrient limited while carbon fixation (photosynthesis) continues

2) Organic matter (OM) at the ocean-atmosphere interface (the surface microlayer, SML)

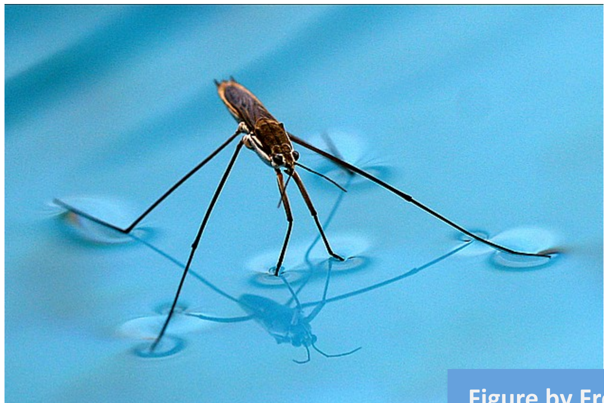


Figure by Fred Liebenberg
http://www.eyefetch.com

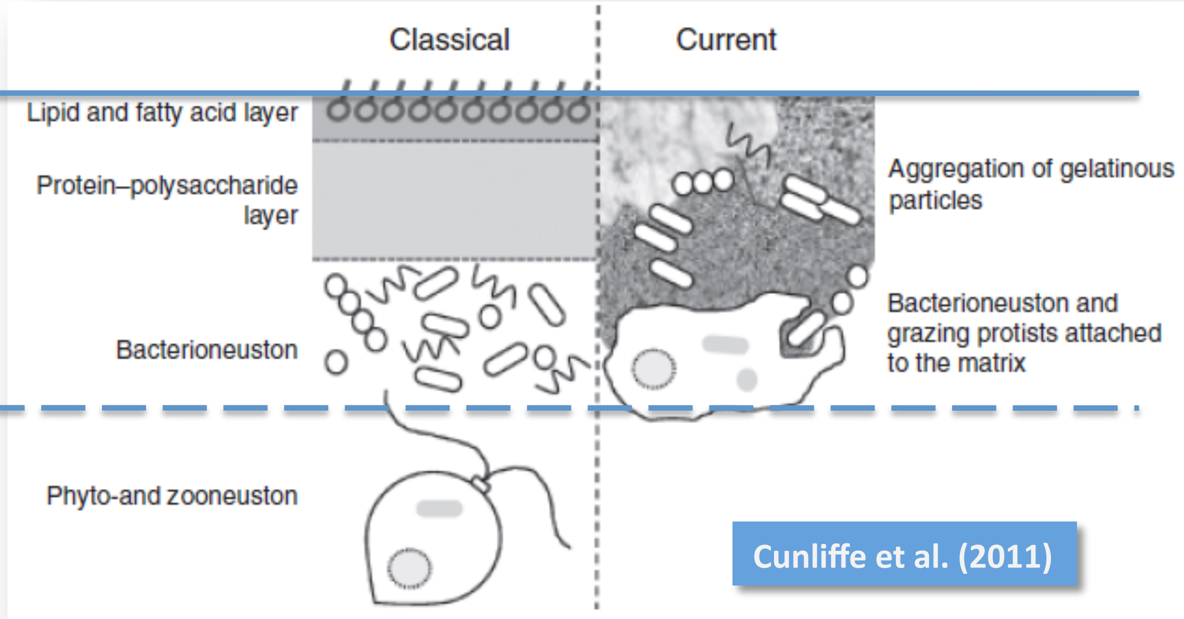
2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

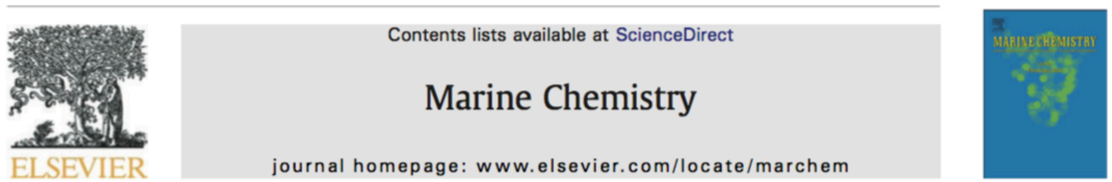
The ocean-atmosphere interface's property is **characterised by of the ocean's surface microlayer (SML).**

Atmosphere

Ocean

Surface microlayer (SML)
thickness ≈ 200 - 1000 µm




Marine Chemistry 110 (2008) 89–97

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Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

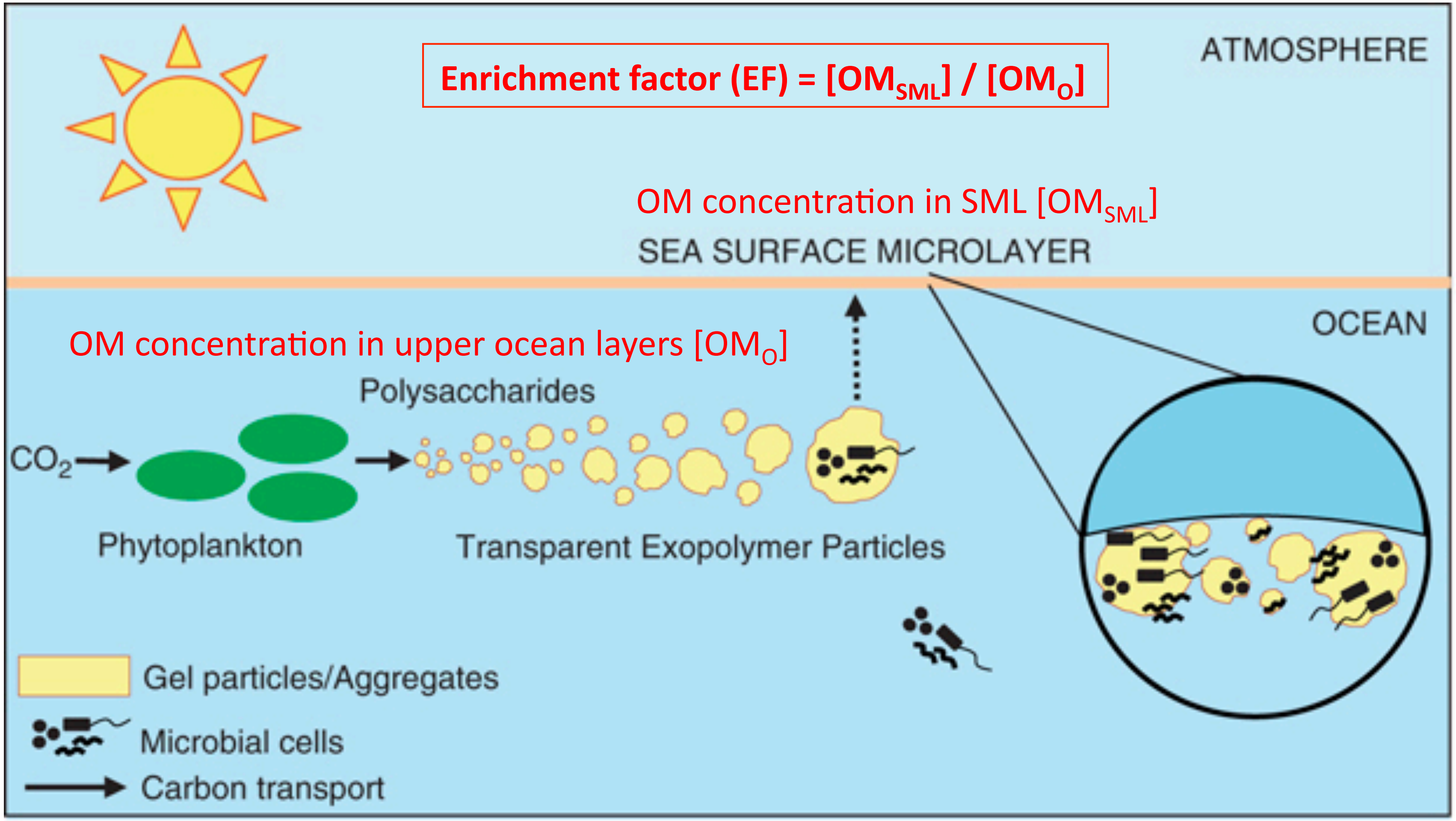
The gelatinous nature of the sea-surface microlayer

Oliver Wurl*, Michael Holmes

Wurl and Holmes (2008)

2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

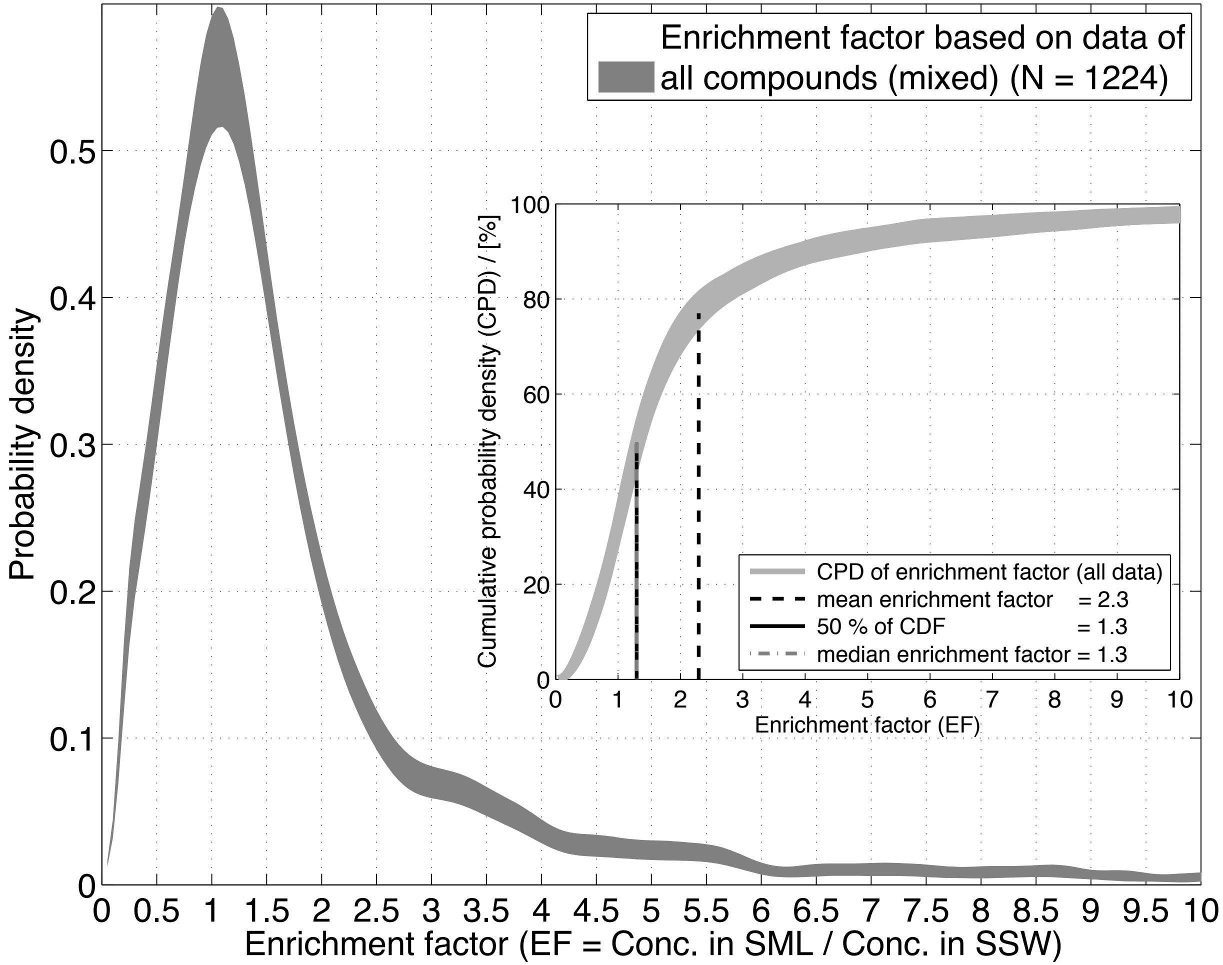
Linkage between phytoplankton production and accumulation of OM within SML



Modified figure from Cunliffe and Murrell (2009, Nature)

2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

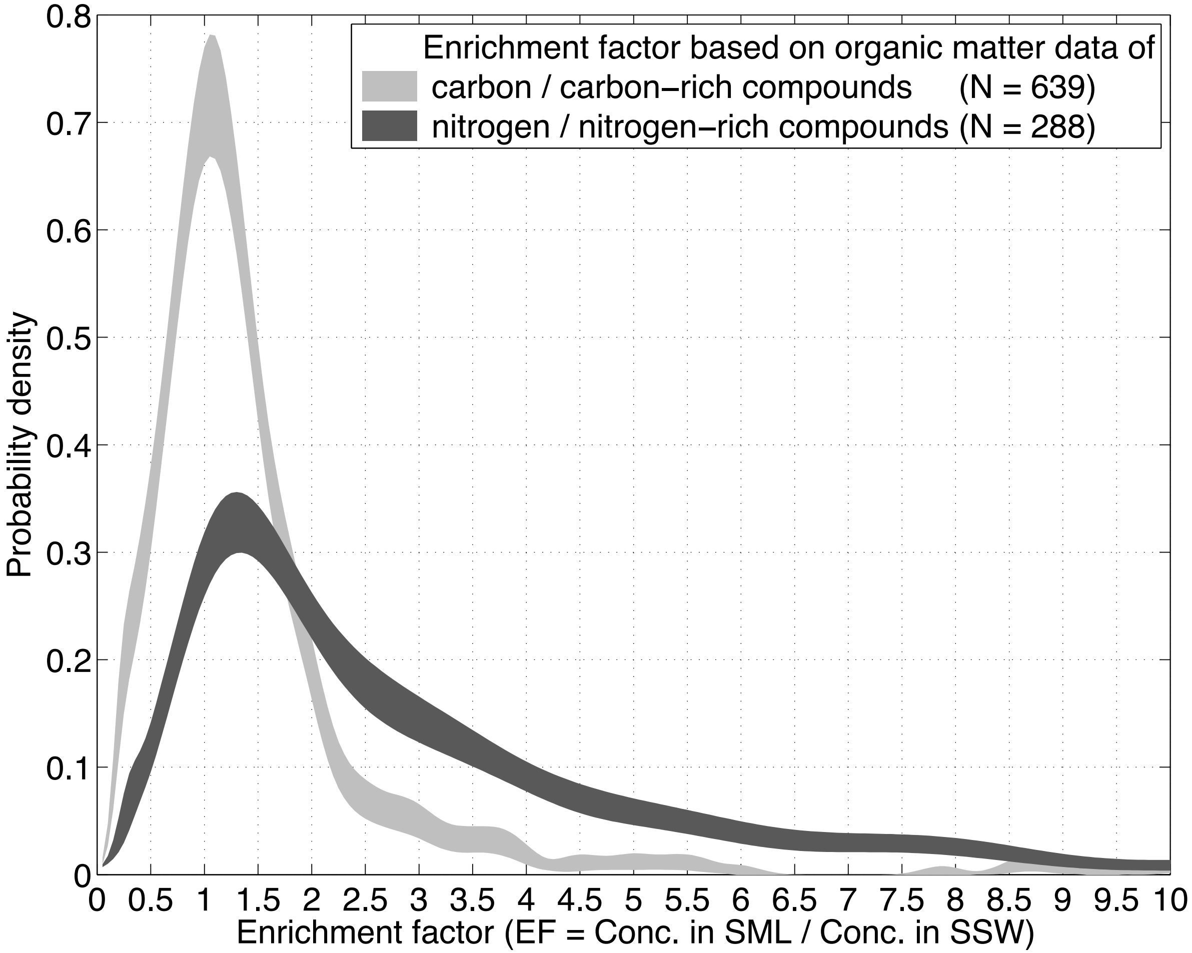
Enrichment factor (**EF** = OM concentration in SML / OM concentration subsurface water)
Probability density estimates of **EF** based on published data collection (by Surandokht Nikzad) with OM measurements of the SML



2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

Enrichment factor (**EF** = OM concentration in SML / OM concentration subsurface water)

Conditional probability density estimates of **EF**, distinguishing between **carbon-enriched** and **nitrogen-enriched** compounds (C-enriched versus N-enriched OM)



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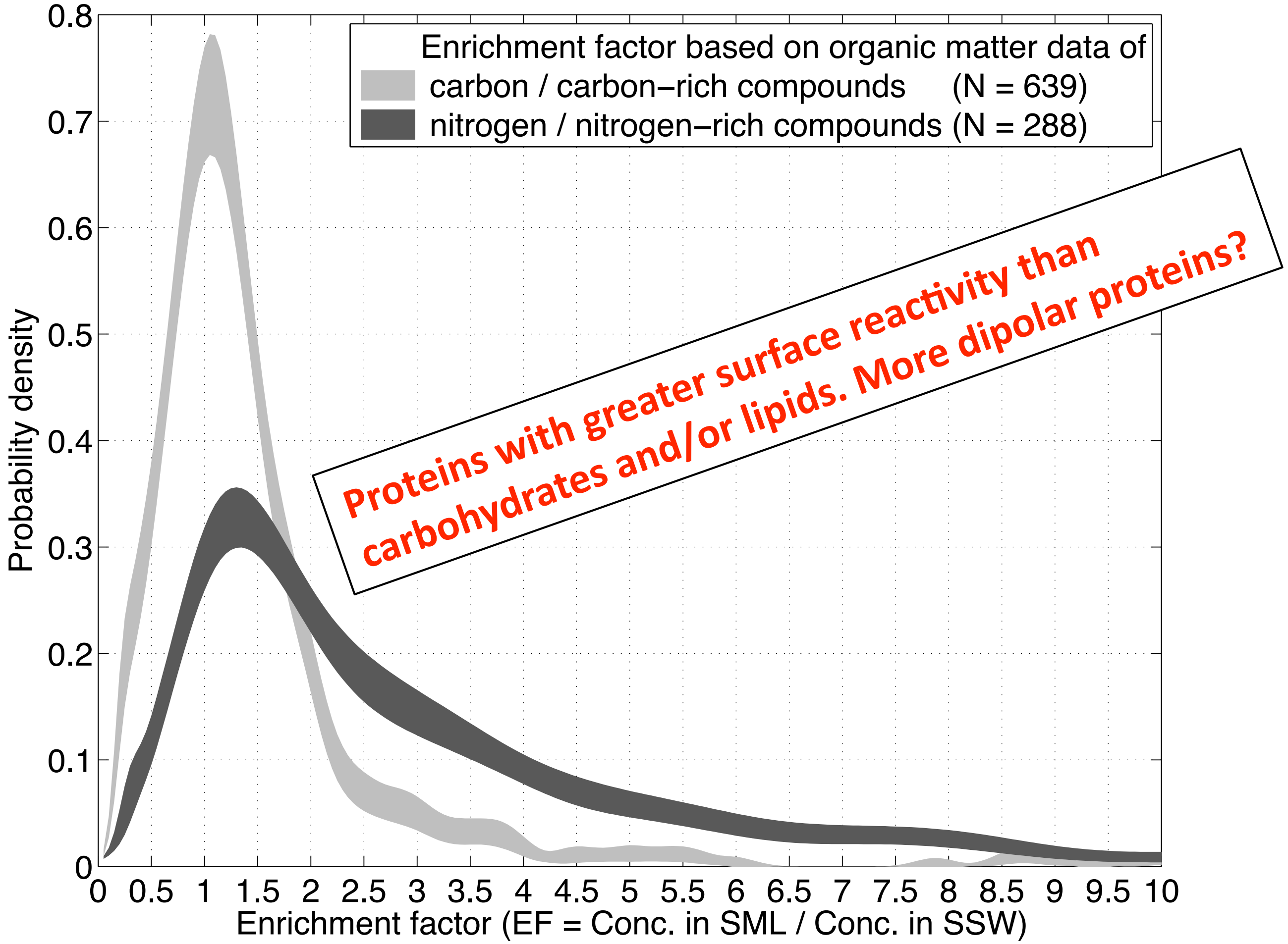
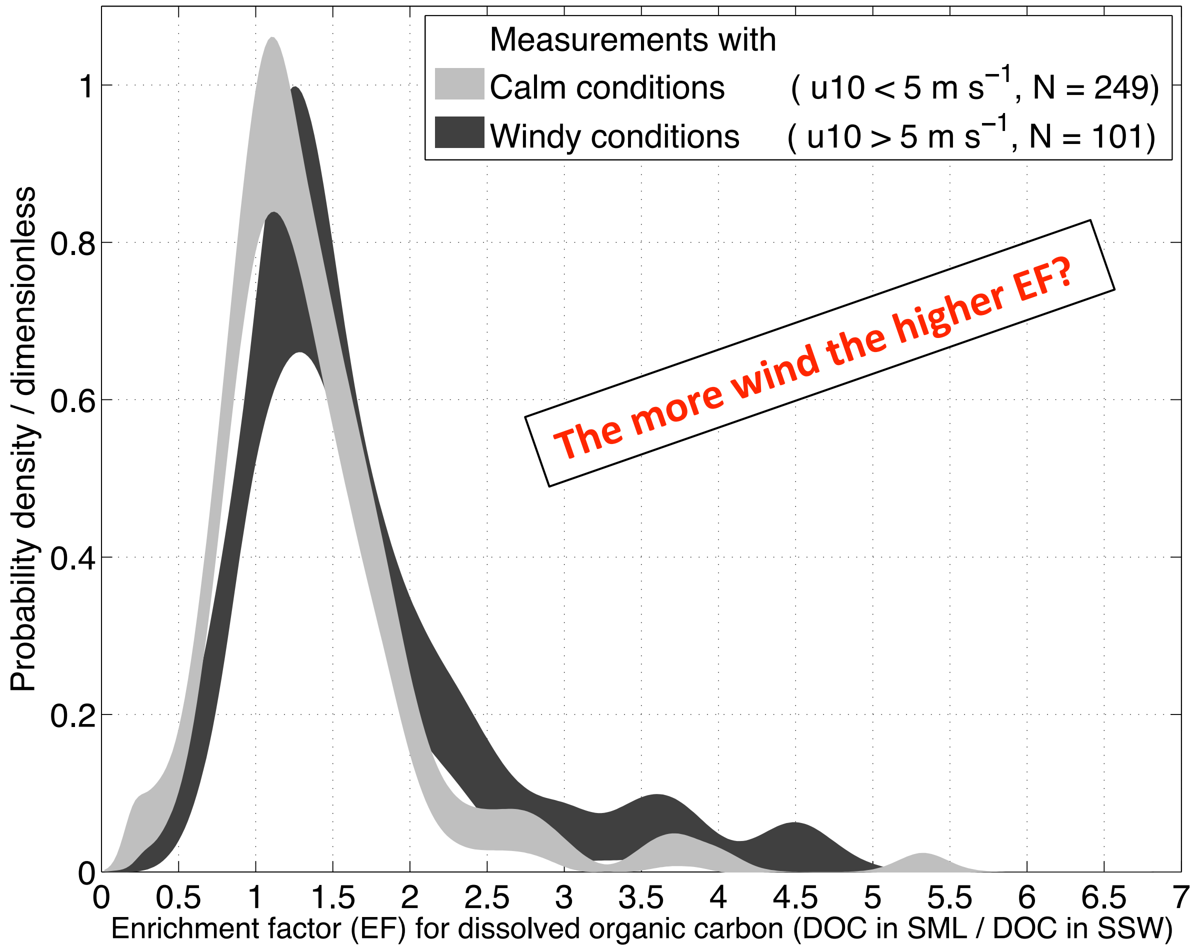


2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

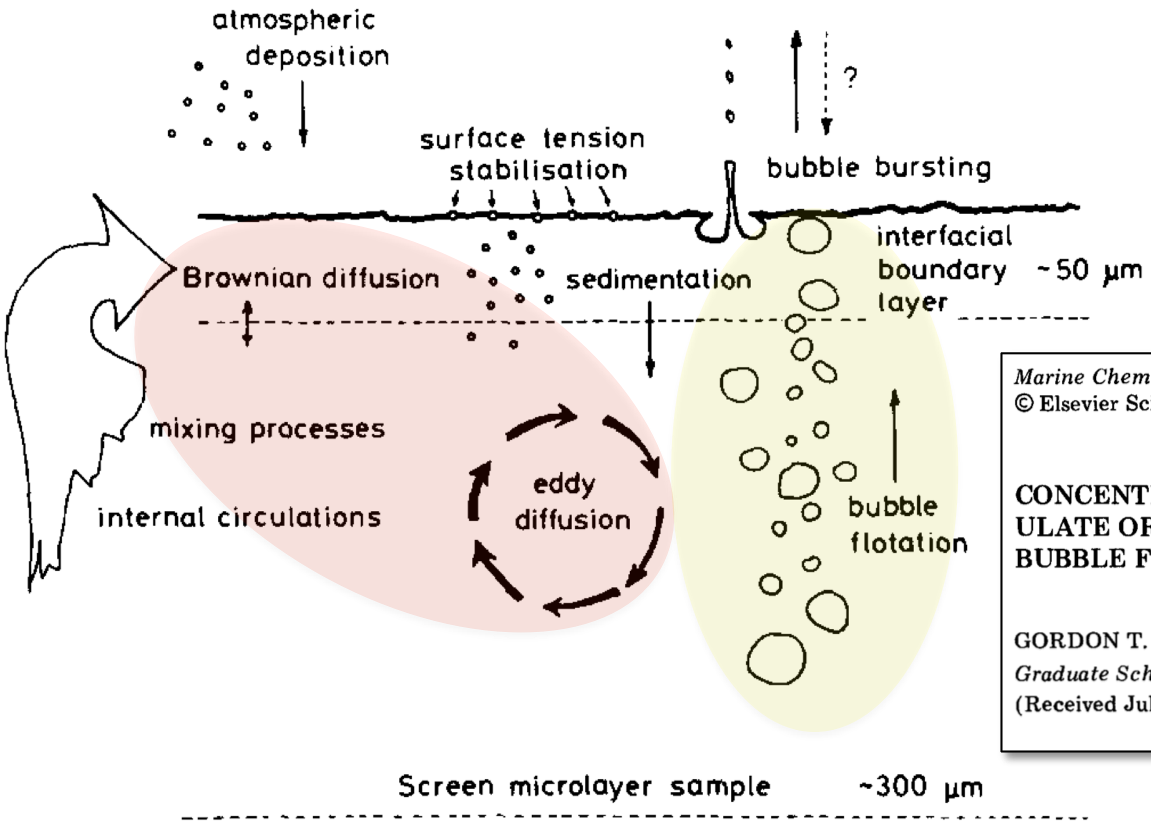
Enrichment factor (**EF** = OM concentration in SML / OM concentration subsurface water)
Conditional probability density estimates of **EF of DOC data**, distinguishing between **wind conditions** **($u_{10} < 5\ m\ s^{-1}$ versus $u_{10} > 5\ m\ s^{-1}$)**



2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

Mechanism:

→ OM (e.g. DOC & POC) adsorption to bubbles then transport with bubbles to interfacial boundary layer



Marine Chemistry, 3(1975) 157—181

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CONCENTRATION OF PARTICULATE TRACE METALS AND PARTICULATE ORGANIC CARBON IN MARINE SURFACE WATERS BY A BUBBLE FLOTATION MECHANISM

GORDON T. WALLACE, Jr. and ROBERT A. DUCE

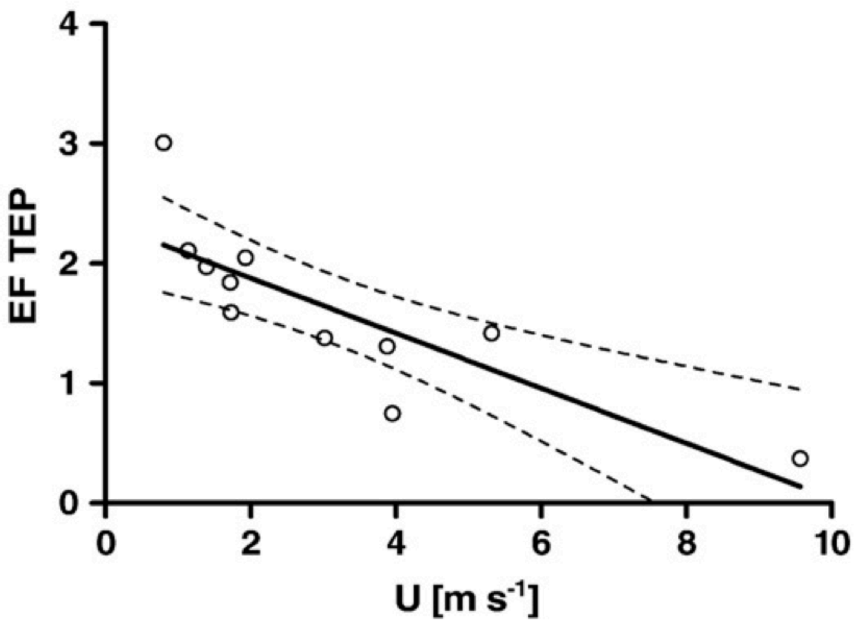
Graduate School of Oceanography, University of Rhode Island, Kingston, R.I. (U.S.A.)

(Received July 18, 1974; revision accepted February 27, 1975)

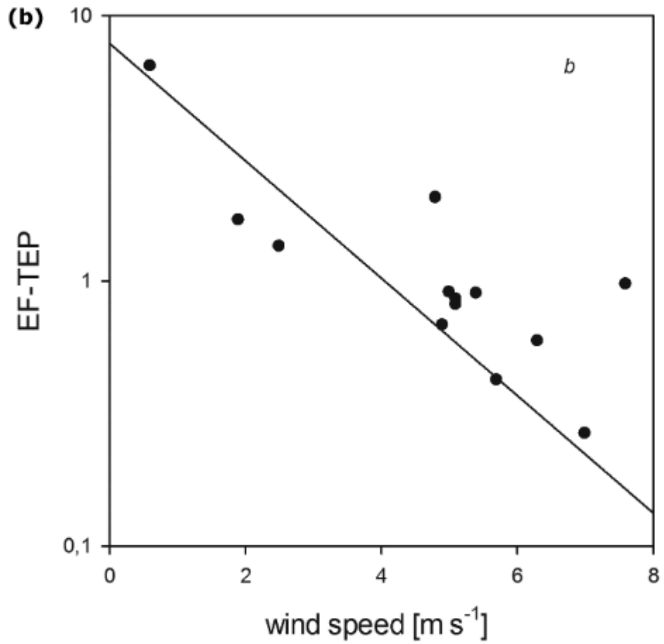
Fig.1. Transport processes for particulate matter in the microlayer.

Sketch from Hunter (1980, Marine Chemistry)

What about TEP?



Wurl et al. (2009, Marine Chemistry)



Engel and Galgani (2015, Biogeosciences Discussion)

Mechanism seem more complex

Some ideas:

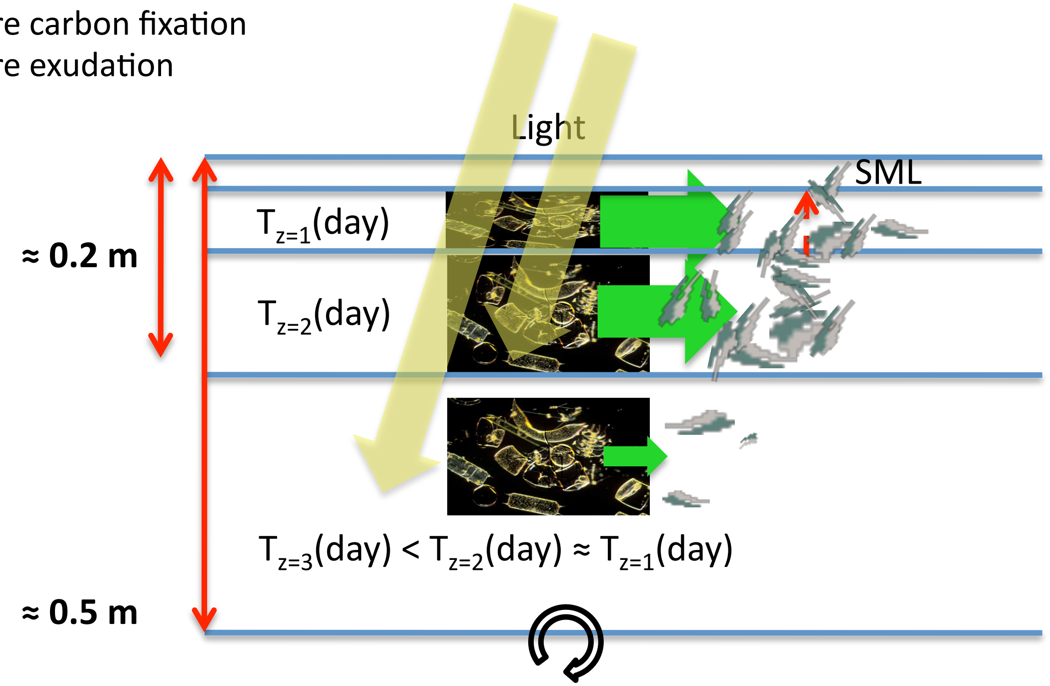
Case 1 (biology) **–**

Upper layers: negligible mixing between upper e.g. 0.2 m and the layers below (> 0.2 m)

→ more *net* light

→ more carbon fixation

→ more exudation

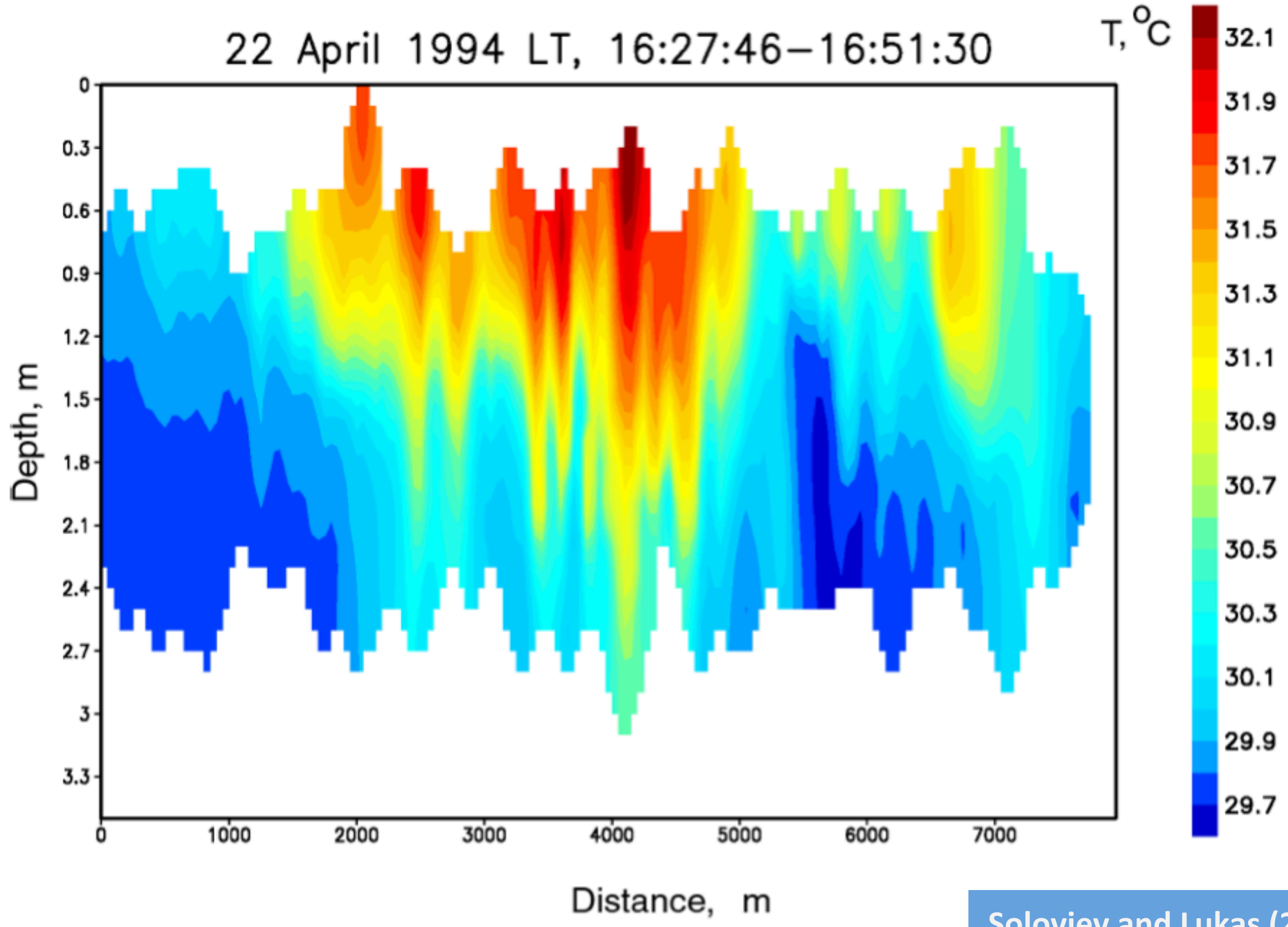


→ **more TEP is produced within upper 0.1 – 0.2 m, which remains unresolved by sampling at z > 0.2 m → high EF of TEP**

2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

Case 2 (physics) **– patches that retain signal from diurnal thermocline**

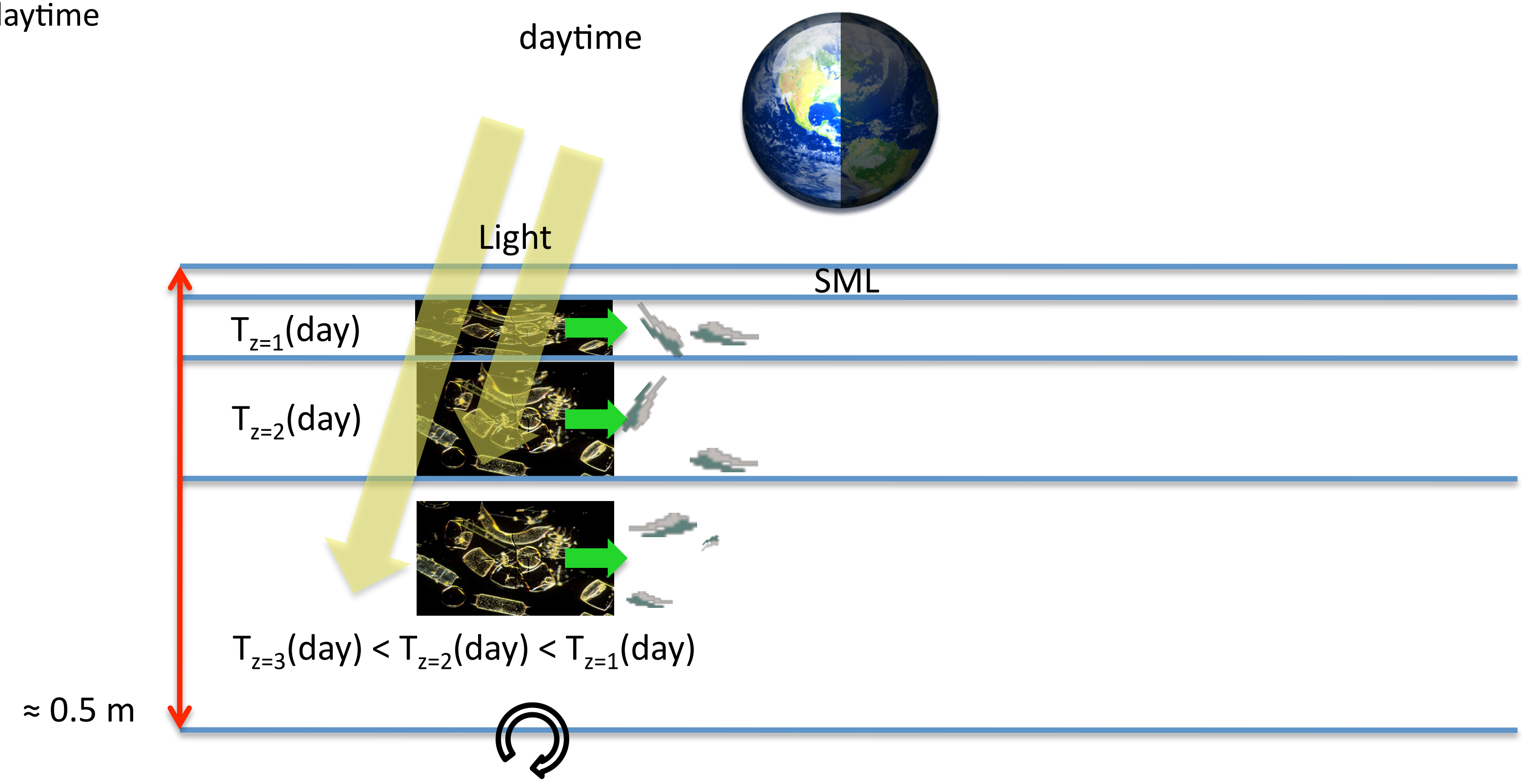
≈ 0.5 m



Soloviev and Lukas (2006)

Case 2 (physics) **–**

a) Exudates and thus TEP neutrally buoyant when formed during daytime

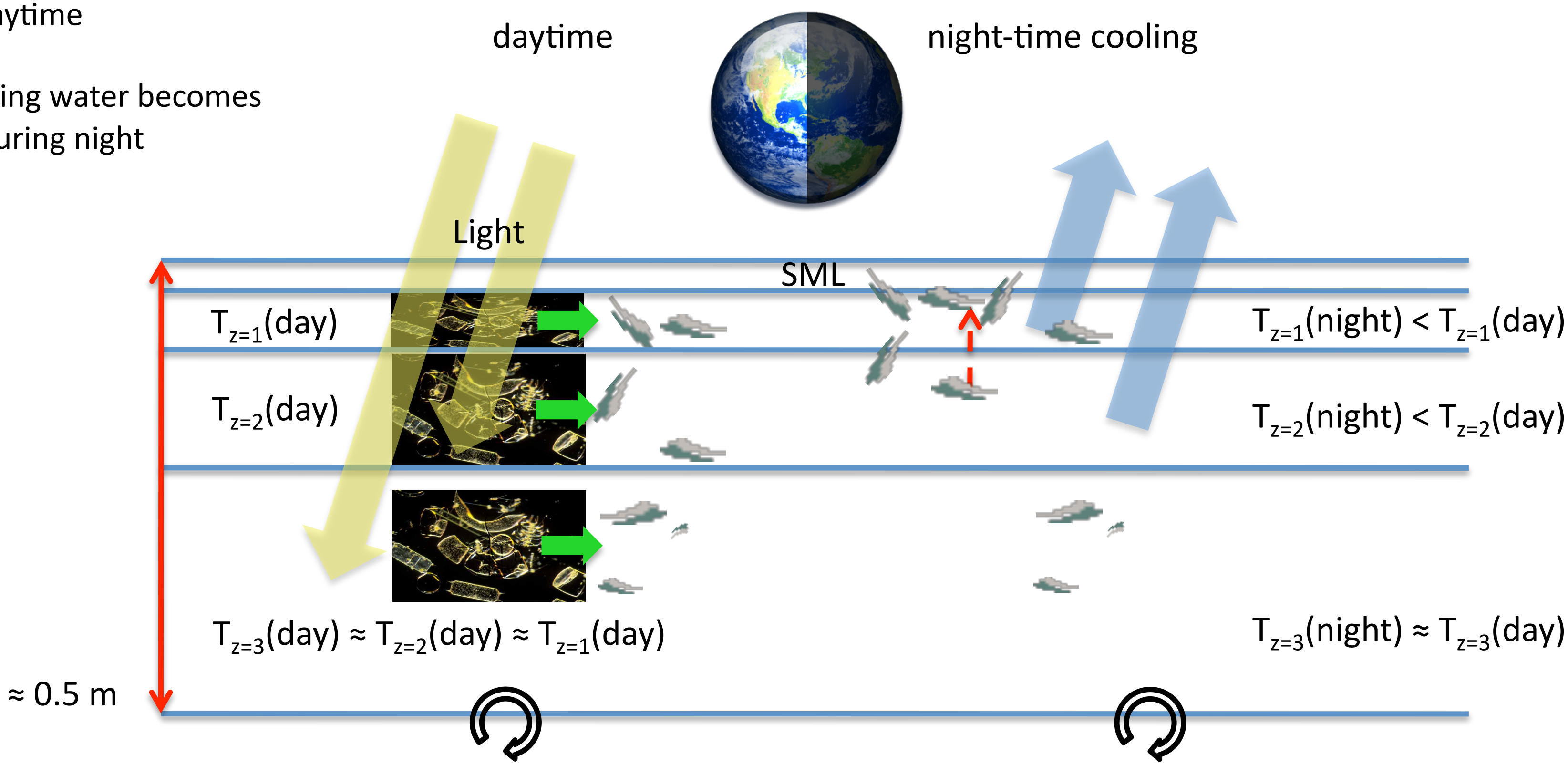


2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

Case 2 (physics) **–**

a) Exudates and thus TEP neutrally buoyant when formed during daytime

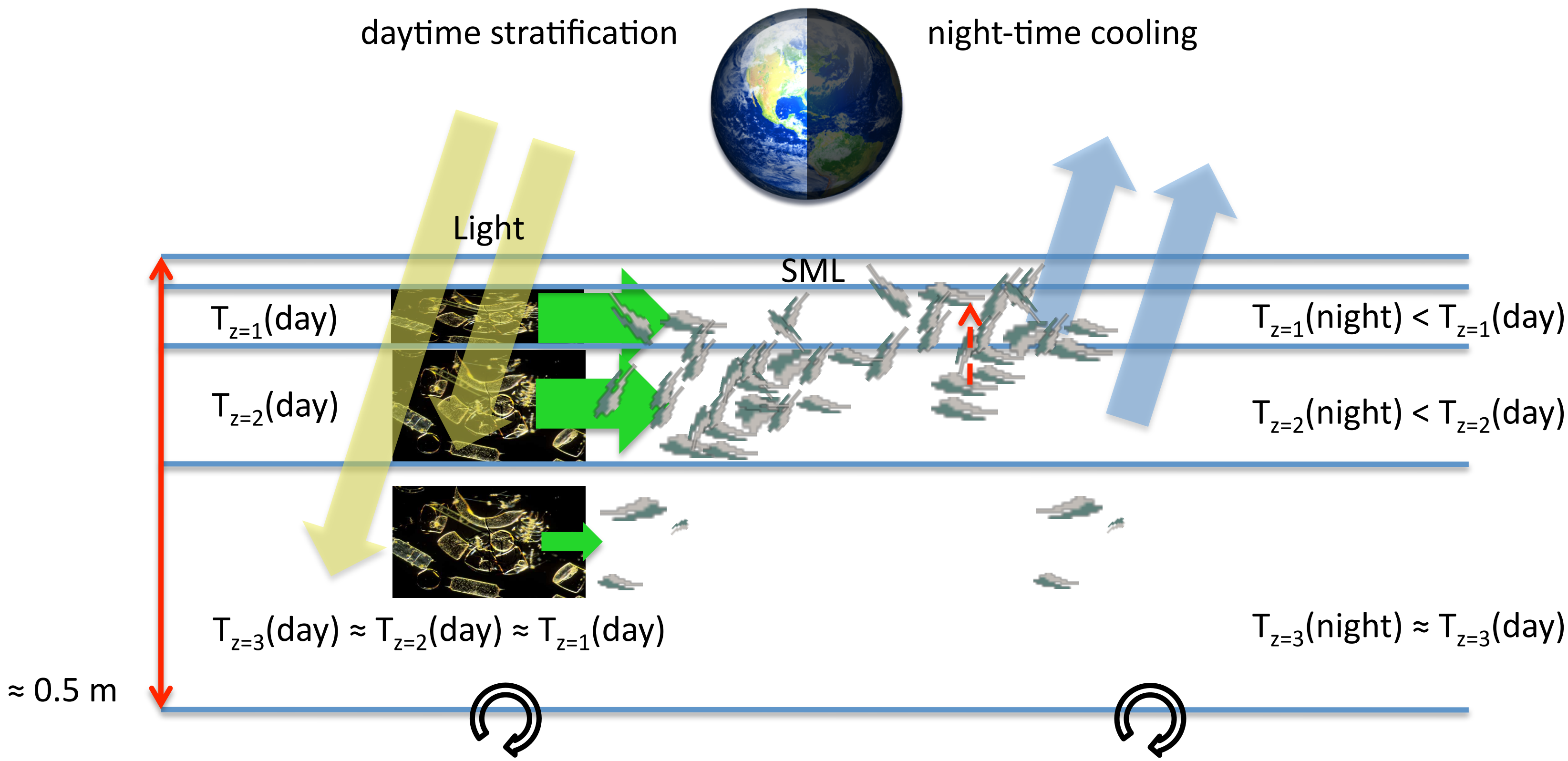
b) surrounding water becomes denser during night (cooling)



→ TEP become positive buoyant during night-time cooling → high EF of TEP (for calm wind conditions)

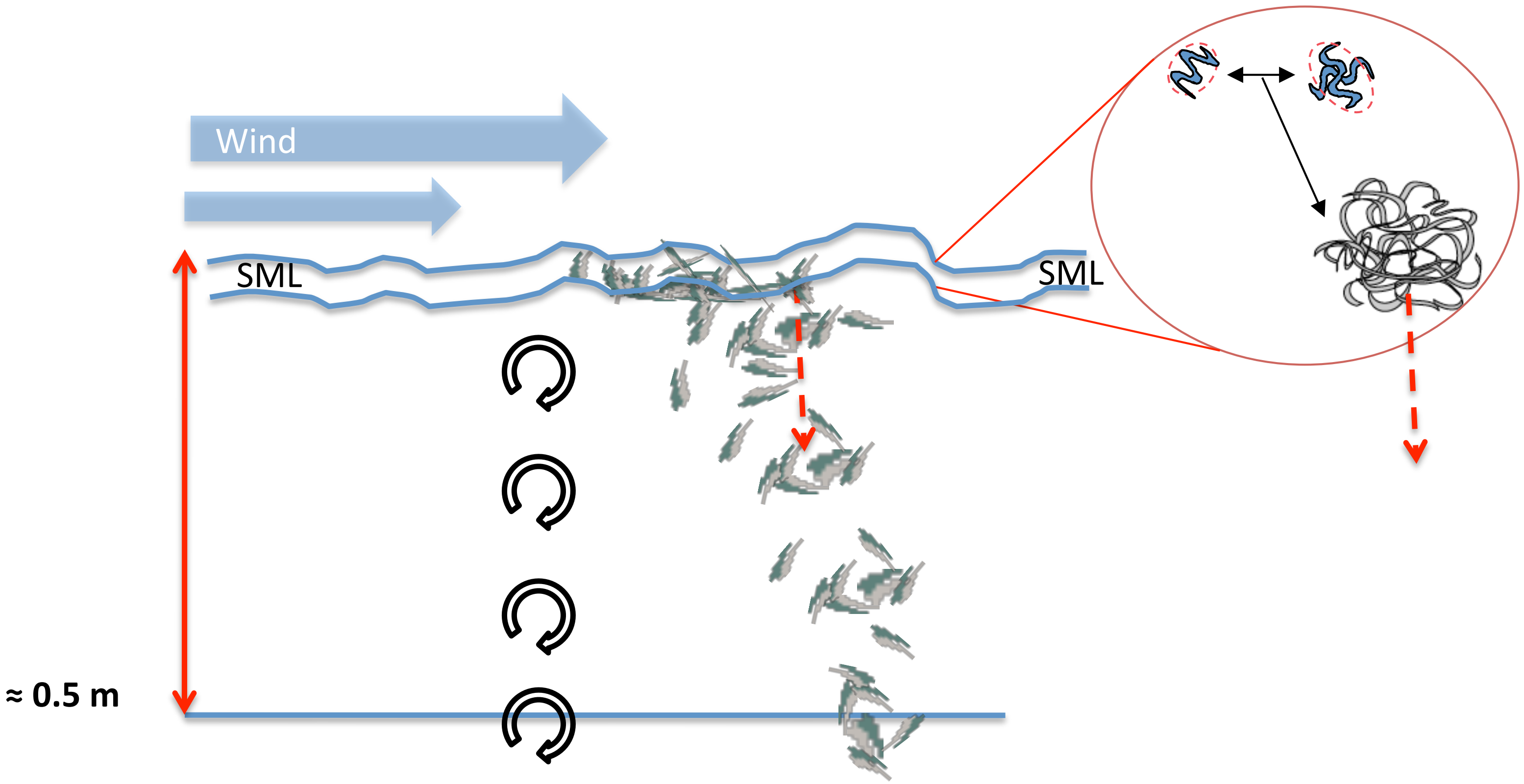
2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

Case 3 (biology & physics) **–** a combination of **case 1** and **case 2**



2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

Case 4 (physics & chemistry) **–** with increasing wind larger TEP aggregates are formed that are removed from SML (sink out)



3) Aspects of combining OM production with air-sea exchange processes

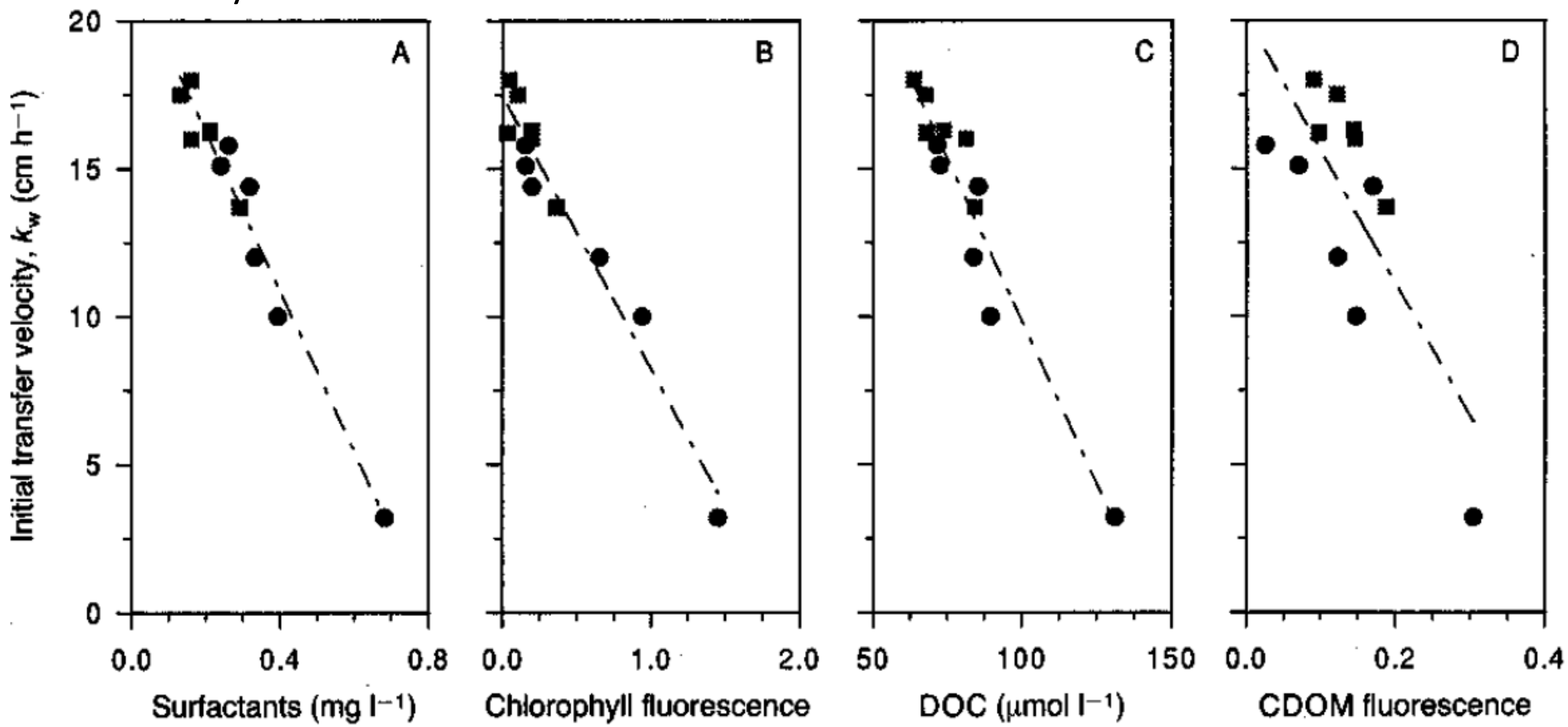
3) Aspects of combining OM production with air-sea exchange processes

a) air-sea gas exchange

3) Aspects of combining OM production with air-sea exchange processes

Air-sea gas exchange (only briefly):
→ **gas transfer is known to be sensitive to OM concentrations in the surface waters**

Gas transfer velocity



Frew (2005) in *The Sea Surface and Global Change*, edited by Liss and Duce

Air-sea gas exchange is sensitive to OM enrichment within SML:

→ damping effects of surface films (e.g. artificial surfactants) on small-scale surface gravity & capillary waves

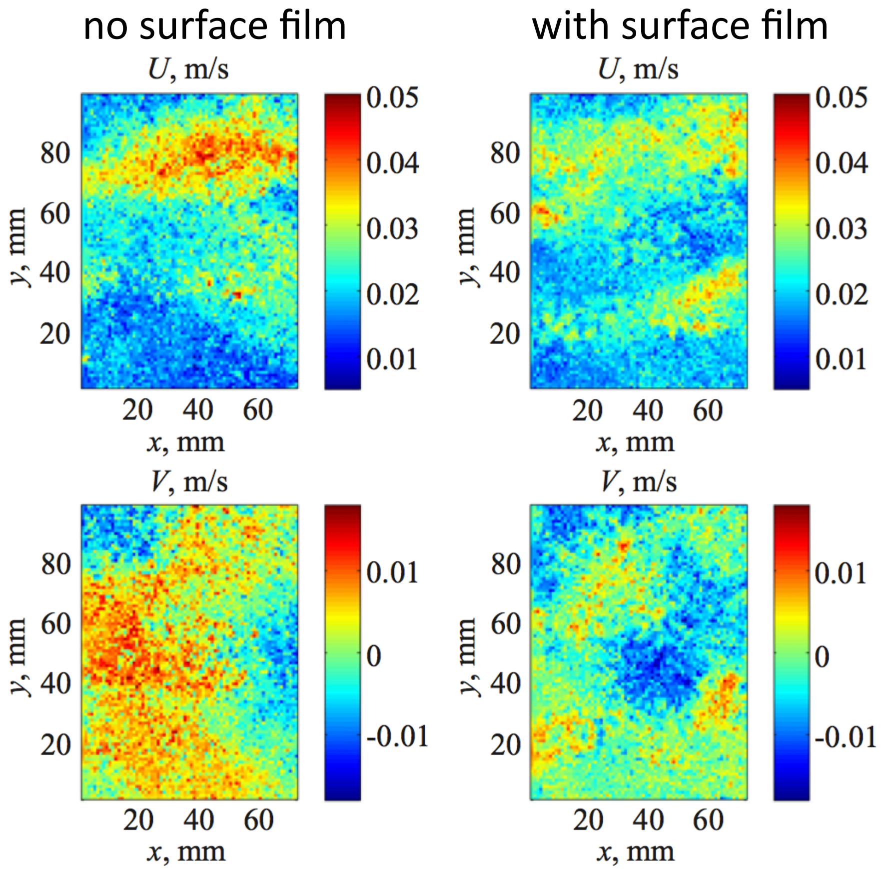
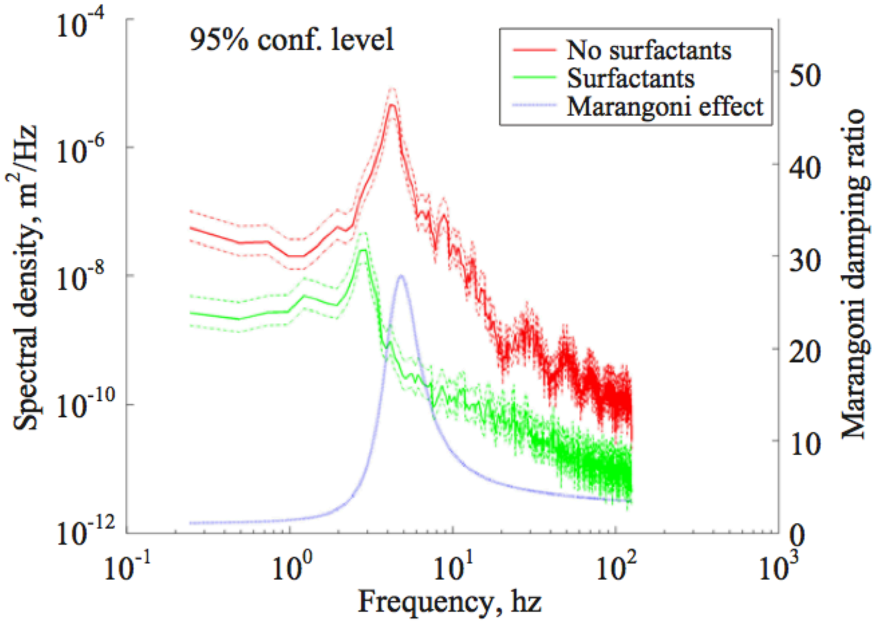


Figure 9 Contour plots of velocity components (top: along tank, bottom: across tank) from horizontal DPIV with the laser sheet at $z = -2$ cm



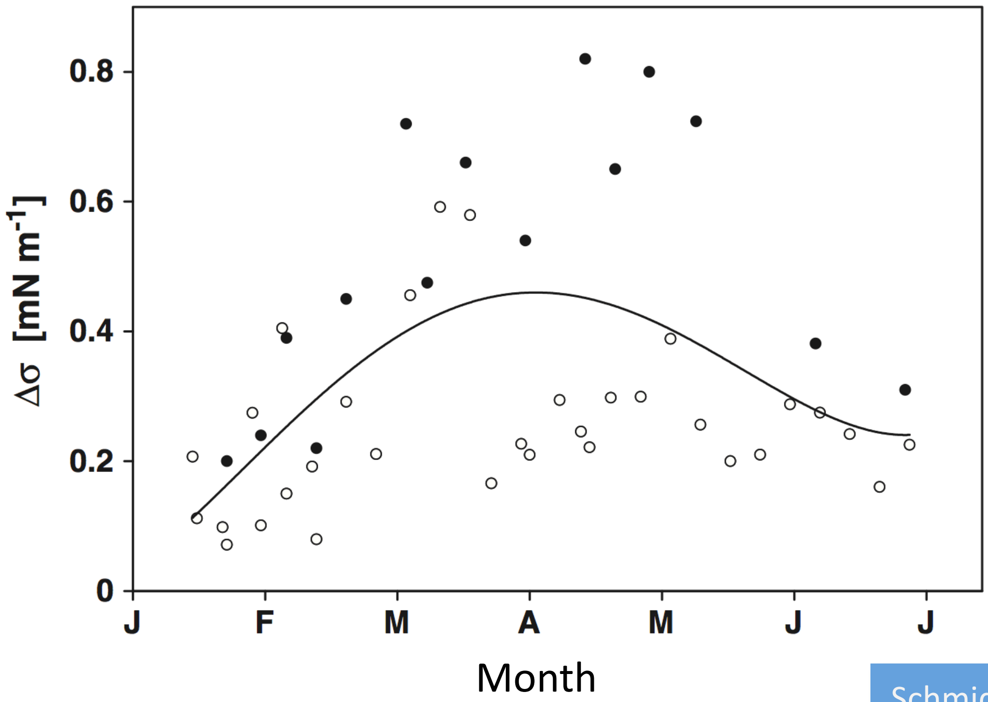
Soloviev et al. (2011)

3) Aspects of combining OM production with air-sea exchange processes

Gas transfer velocity (k_{660}) varies with seasonal changes of surface tension (σ):
→ seasonally modulated O_2 and CO_2 air-sea flux (example Baltic Sea, Schmidt and Schneider, 2011)

changes in surface tension: $\Delta\sigma = \sigma_0 - \sigma$

reference surface tension
(no biofilm): $\sigma\left(\mathrm{mN\ m^{-1}}\right) = 75.64 - 0.144\,T + 0.0399\,Cl‰$



Open/closed circles = different measurement techniques

Schmidt and Schneider (2011)

3) Aspects of combining OM production with air-sea exchange processes

b) emission of primary organic aerosols

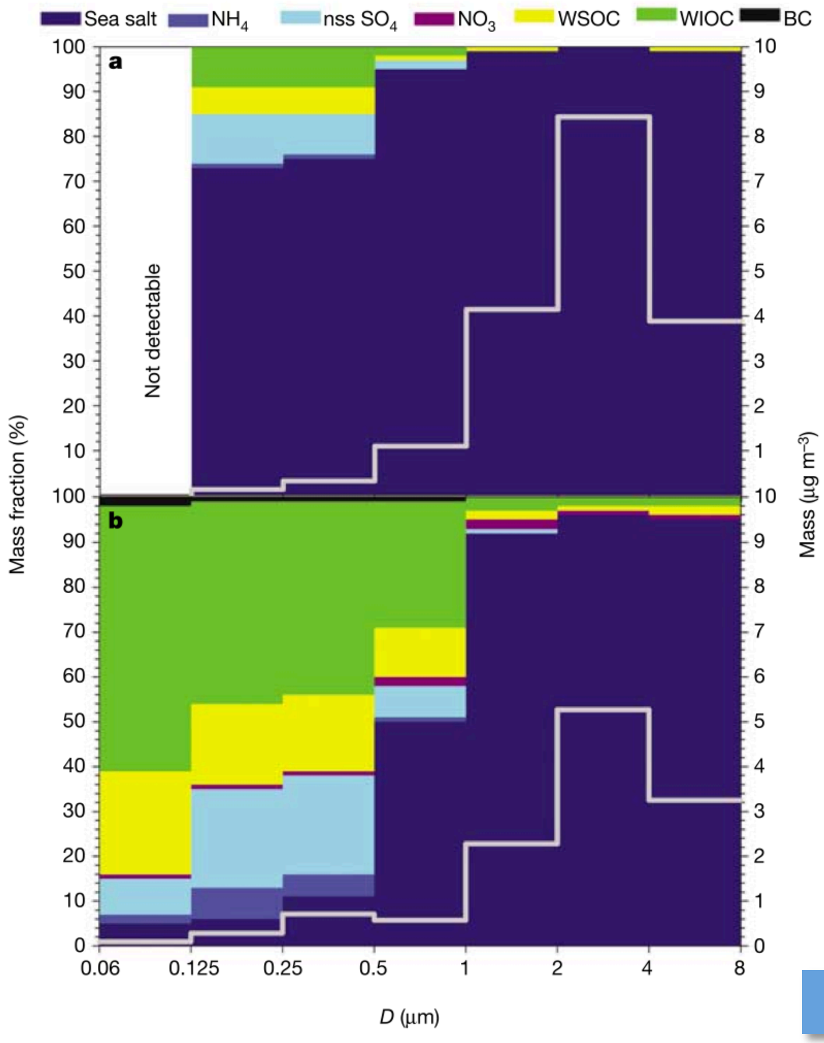
3) Aspects of combining OM production with air-sea exchange processes

Emission of aerosols:

→ **small size aerosols contain water-soluble & water-insoluble organic carbon (WSOC & WIOC)**

Low biological activity

High biological activity



O'Dowd et al. (2004, Nature)

3) Aspects of combining OM production with air-sea exchange processes

Characteristics of organic aerosols:

→ Transmission electron microscopy reveal small size aerosols with gels (here EPS; note that TEP is subgroup of EPS)

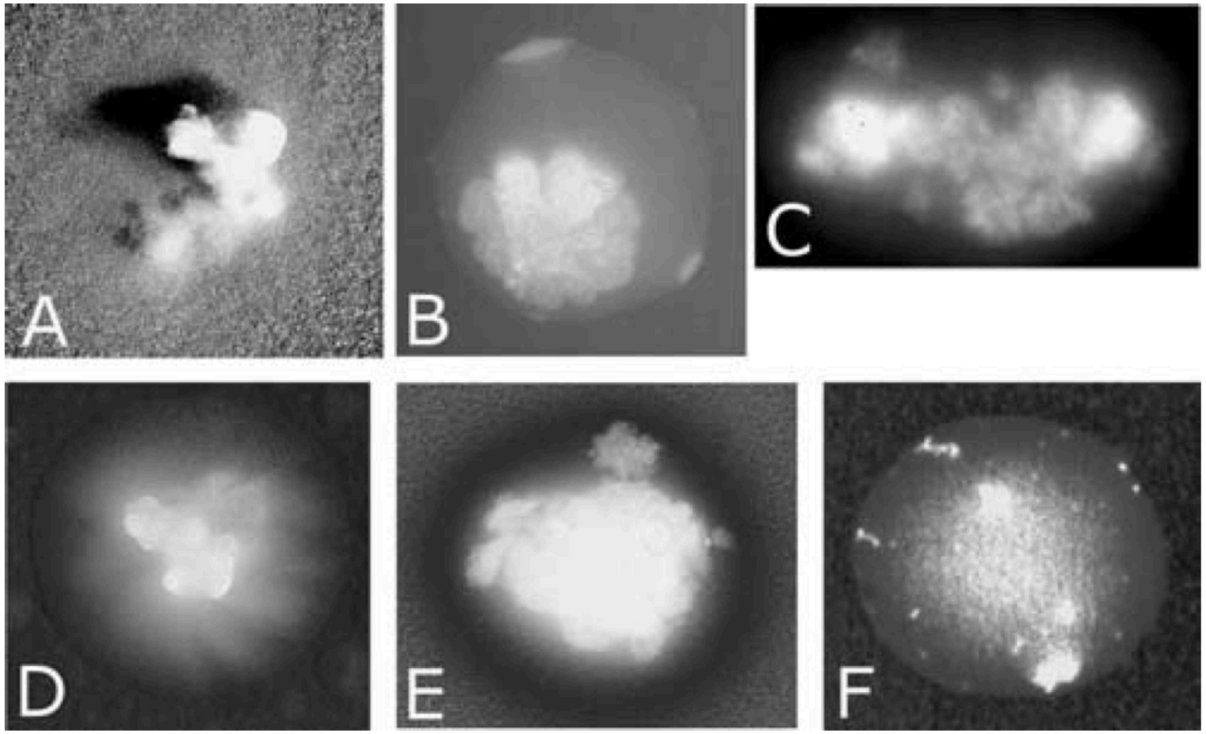


Figure 1. EPS gel surrounding airborne microcolloid aggregates: (a) 89°N, 0°, (b) 87°N, 145°E, (c) 53°S, 80°E,

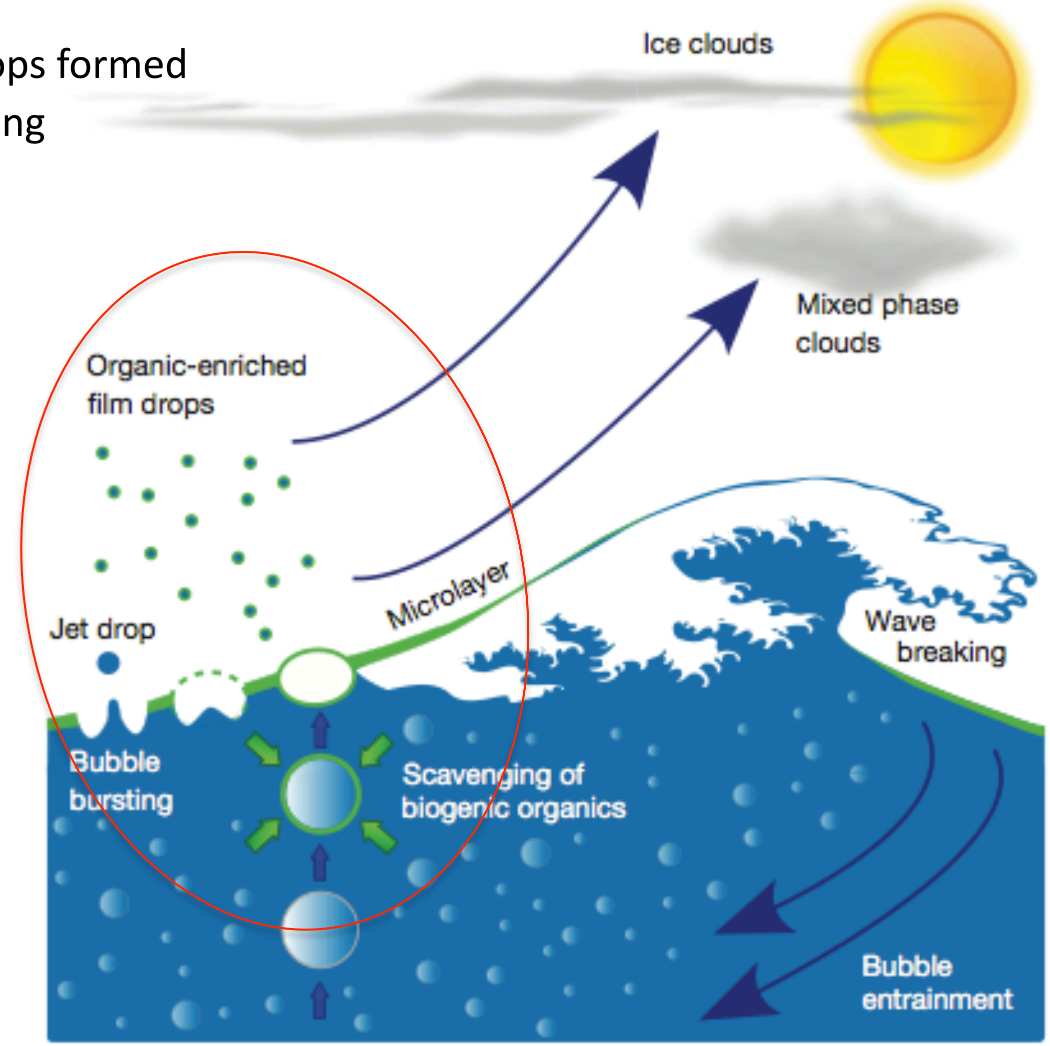
Sizes between 116 and 520 nm

Leck and Bigg (2005, JGR)

3) Aspects of combining OM production with air-sea exchange processes

Emission of primary organic aerosols from the ocean depends on:

1) scavenging (adsorption) of OM onto bubbles and transport towards surface
2) OM within SML
3) number of film drops formed from bubble bursting

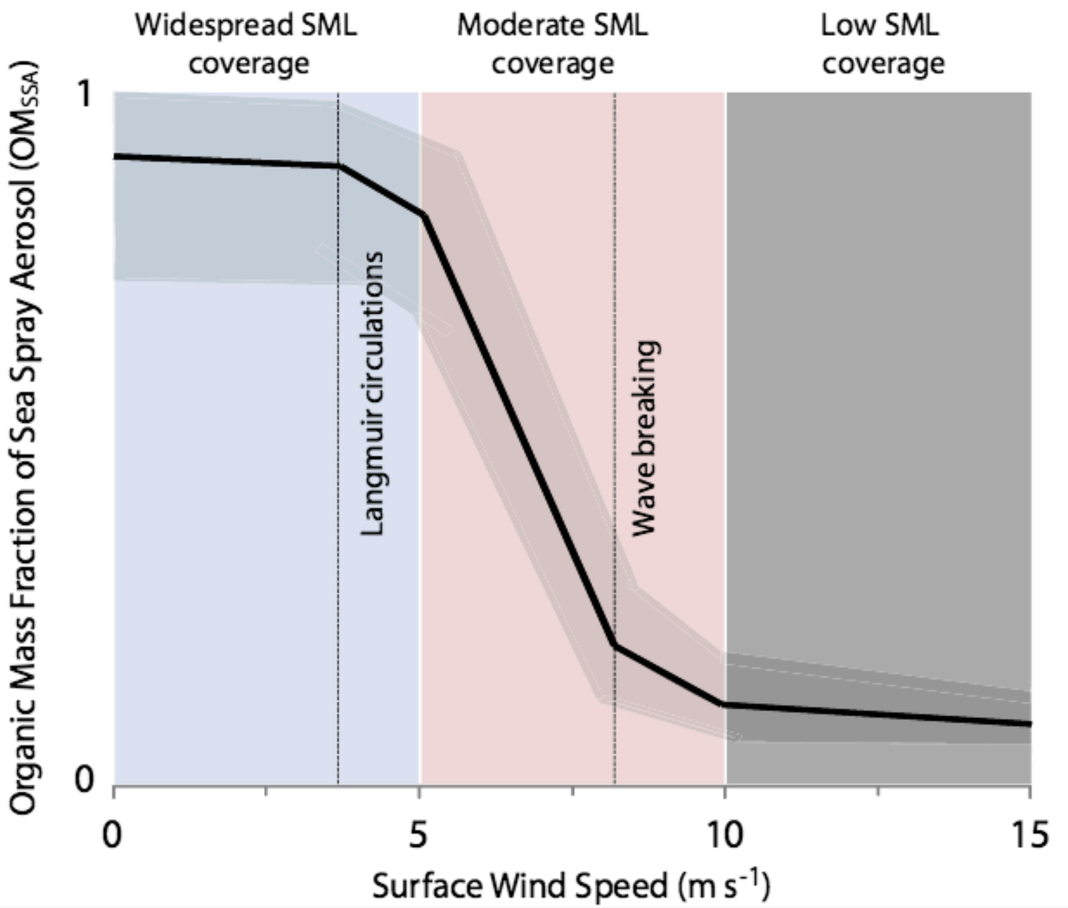


Wilson et al. (2015, Nature)

3) Aspects of combining OM production with air-sea exchange processes

Linking oceanic biological production to OM mass fraction of primary organic aerosols:

→ parameterisation based on wind speed (u_{10})

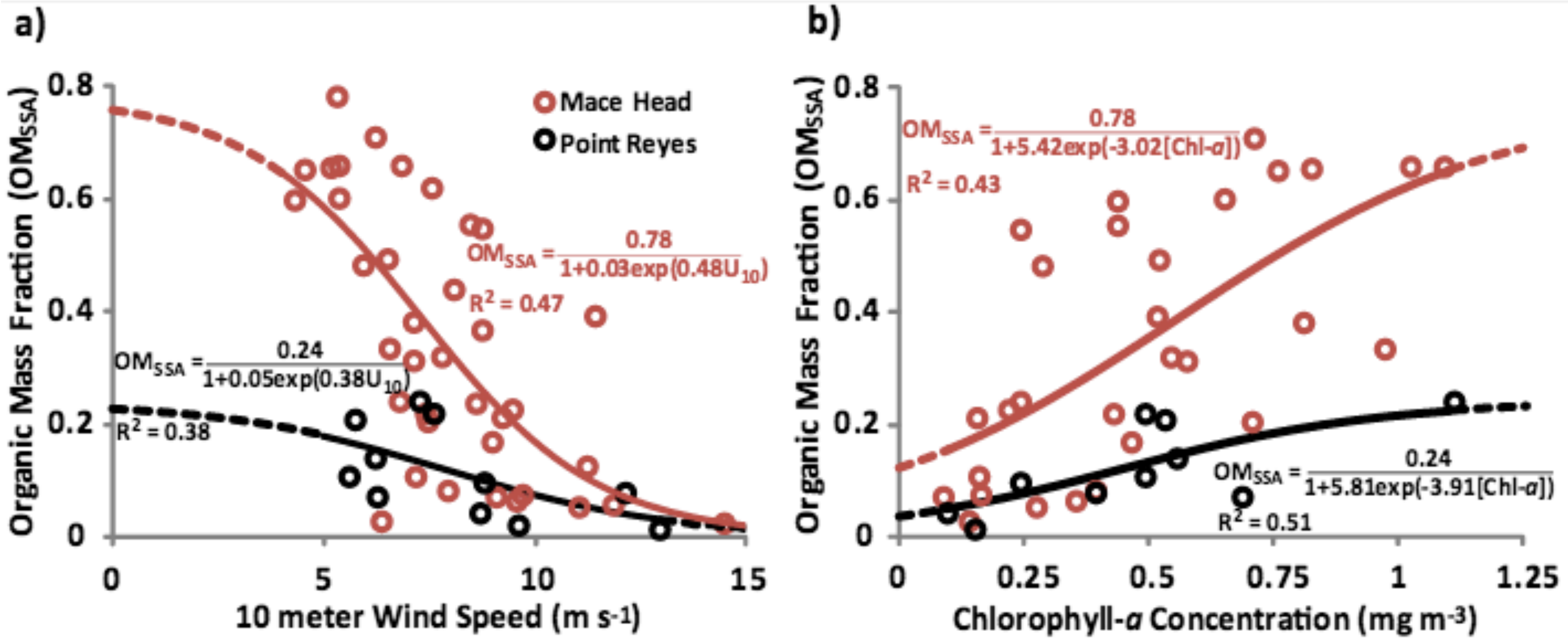


Gantt et al. (2011)

3) Aspects of combining OM production with air-sea exchange processes

Linking oceanic biological production to OM mass fraction of primary organic aerosols:

→ parameterisation based on wind speed (u_{10}) and Chl*a* concentration

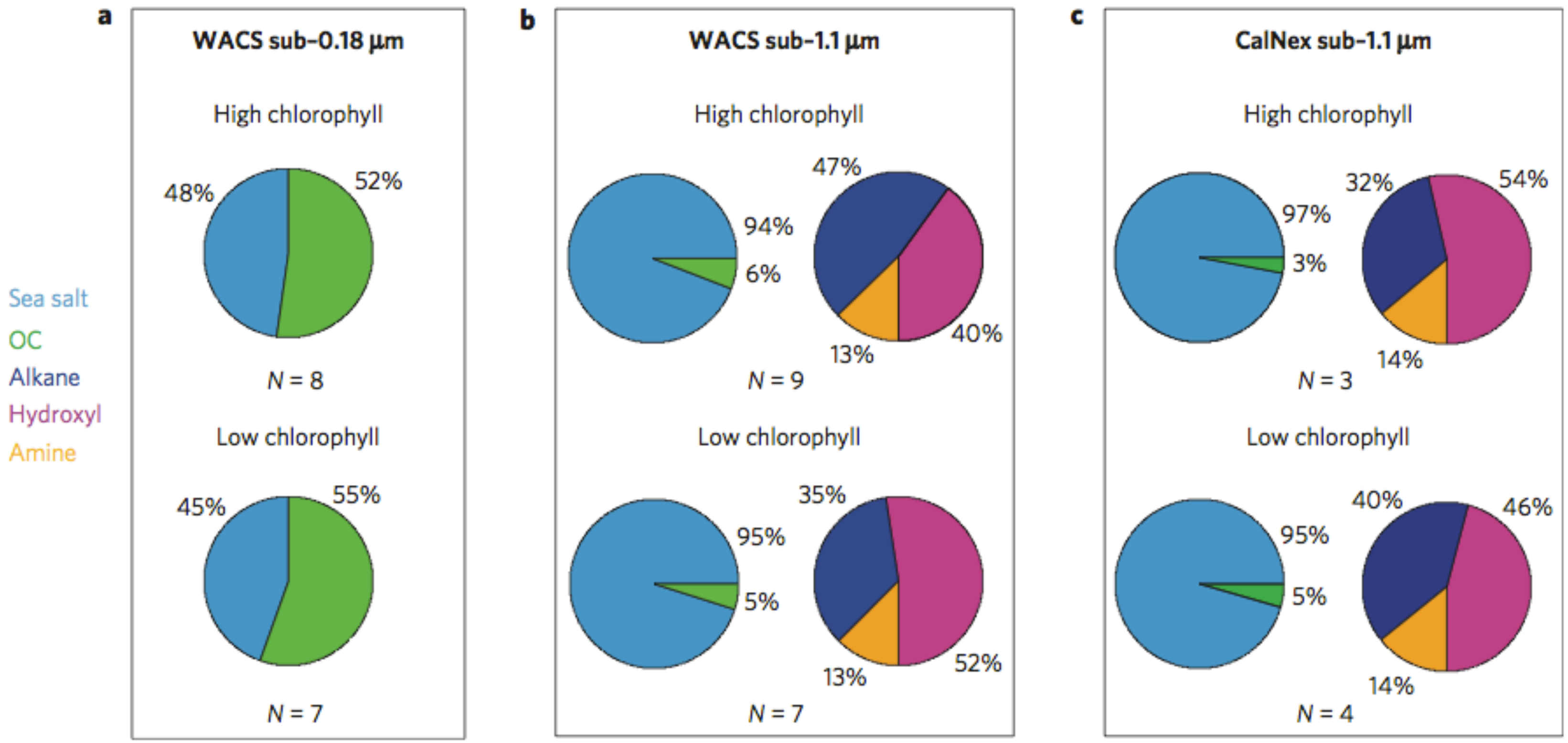


Gantt et al. (2011)

$$\rightarrow \quad \mathrm{OM_{SSA}}(\mathrm{Chl}-a, U_{10}) = \frac{\mathrm{OM_{SSA}^{max}}}{1+\exp(-2.63[\mathrm{Chl}-\mathrm{a}]+0.18U_{10})}$$

3) Aspects of combining OM production with air-sea exchange processes

Chl*a* concentration is not a good indicator for OM enrichment in sea spray aerosols (Quinn et al., 2014)



Quinn et al. (2014, Nature)

→ SSA organics are not significantly different for high- and low-chlorophyll waters

→ OM enrichment in SSA is uncoupled from "local biological activity" as measured by Chl*a* over large ocean regions

Chl*a* concentration is not a good indicator for OM enrichment in sea spray aerosols (Quinn et al., 2014)

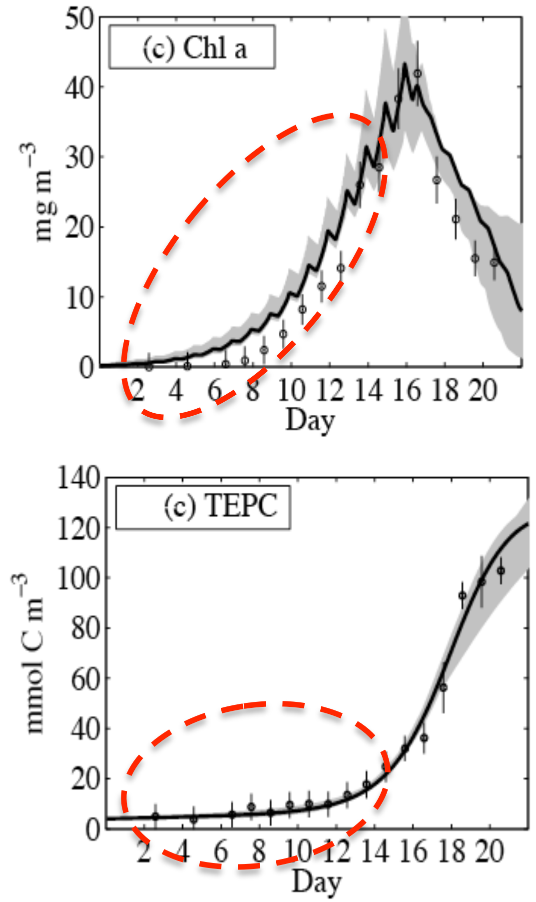
?

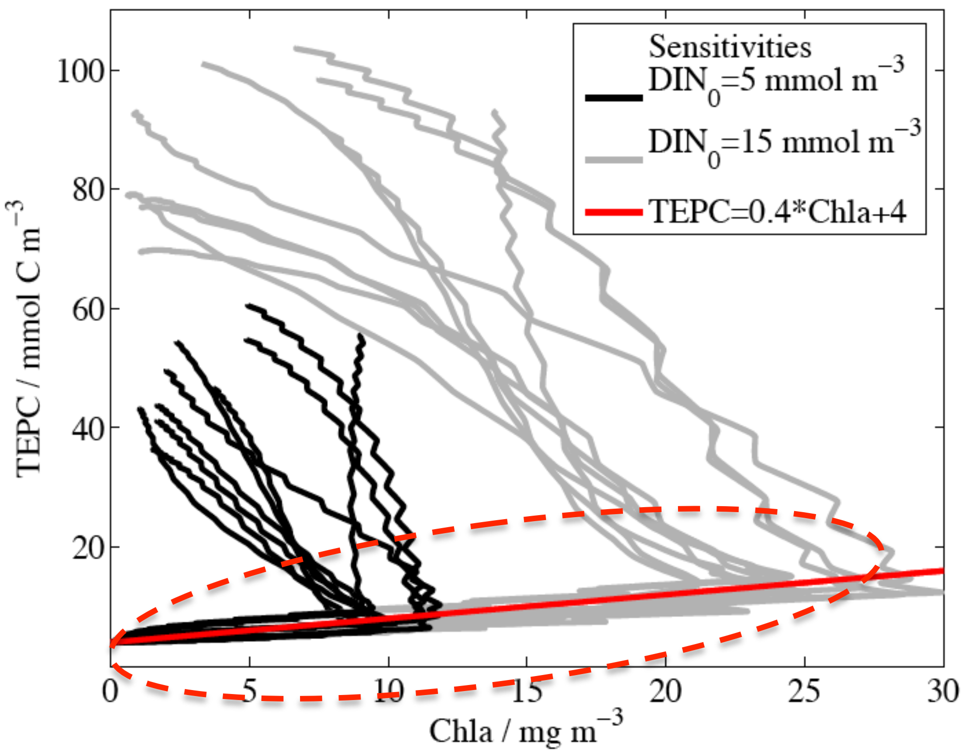
3) Aspects of combining OM production with air-sea exchange processes

Recalling linkage between OM production, chlorophyll *a* concentration and gel formation:

→ TEP carbon increases linearly with Chl*a* concentration during exponential growth phase

→ but maximum in TEP concentration is achieved shortly after the bloom (post-bloom period)





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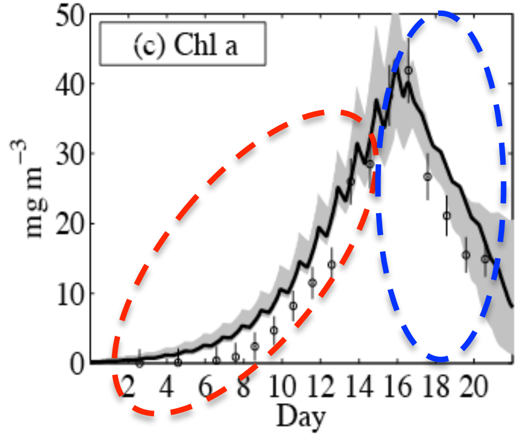
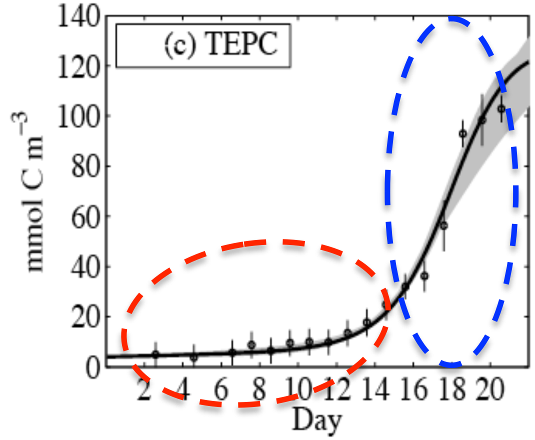
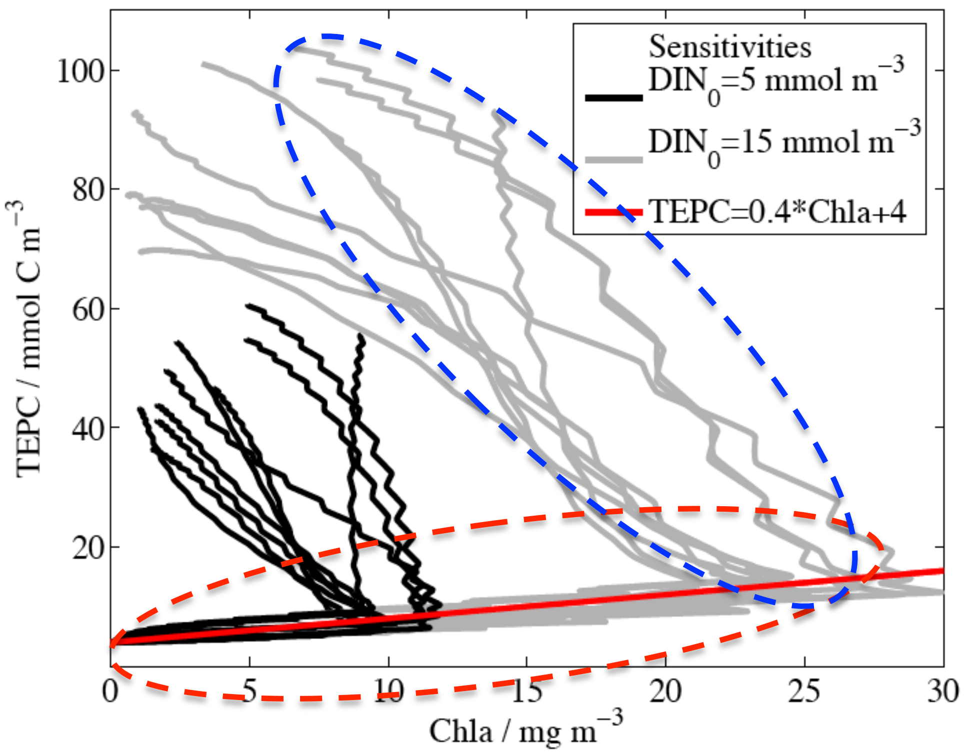
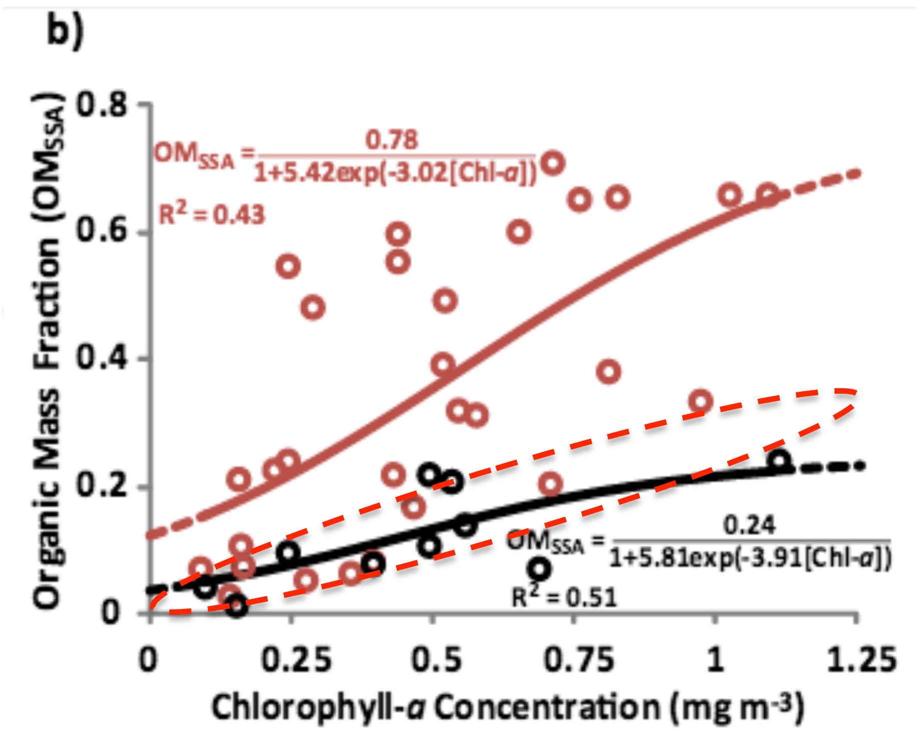
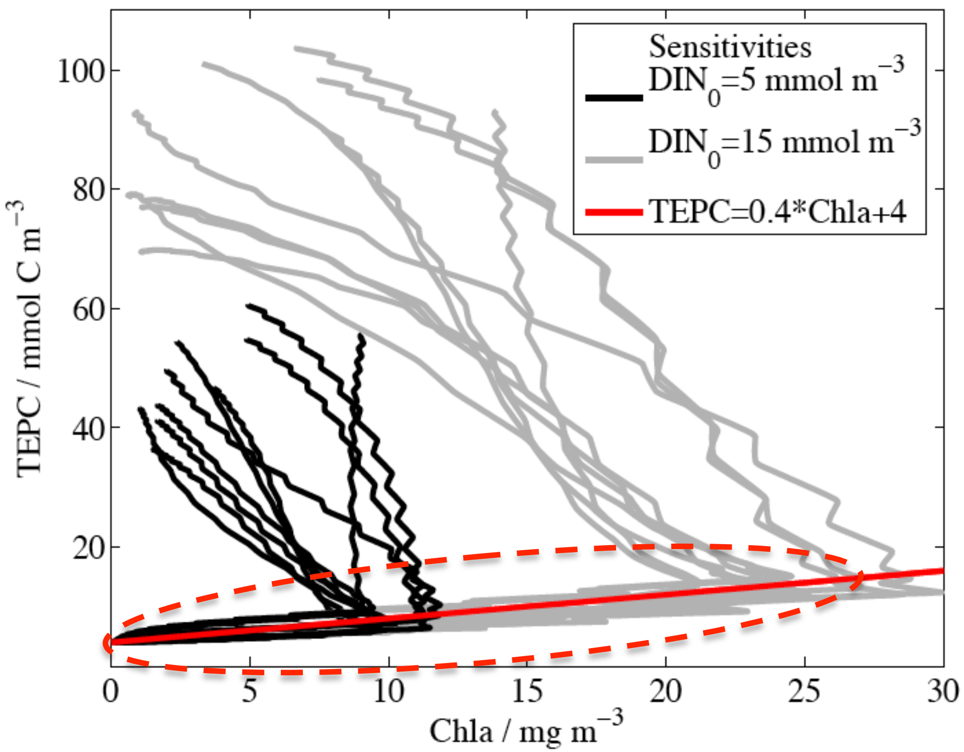






Recalling linkage between OM production, chlorophyll *a* concentration and gel formation:
→ hysteresis!





3) Aspects of combining OM production with air-sea exchange processes

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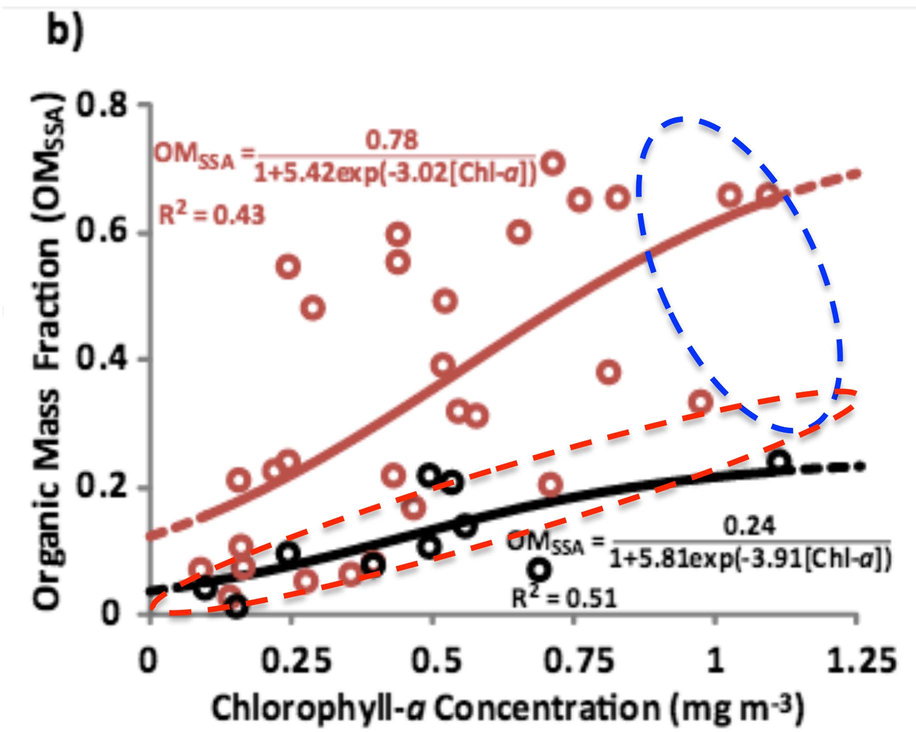

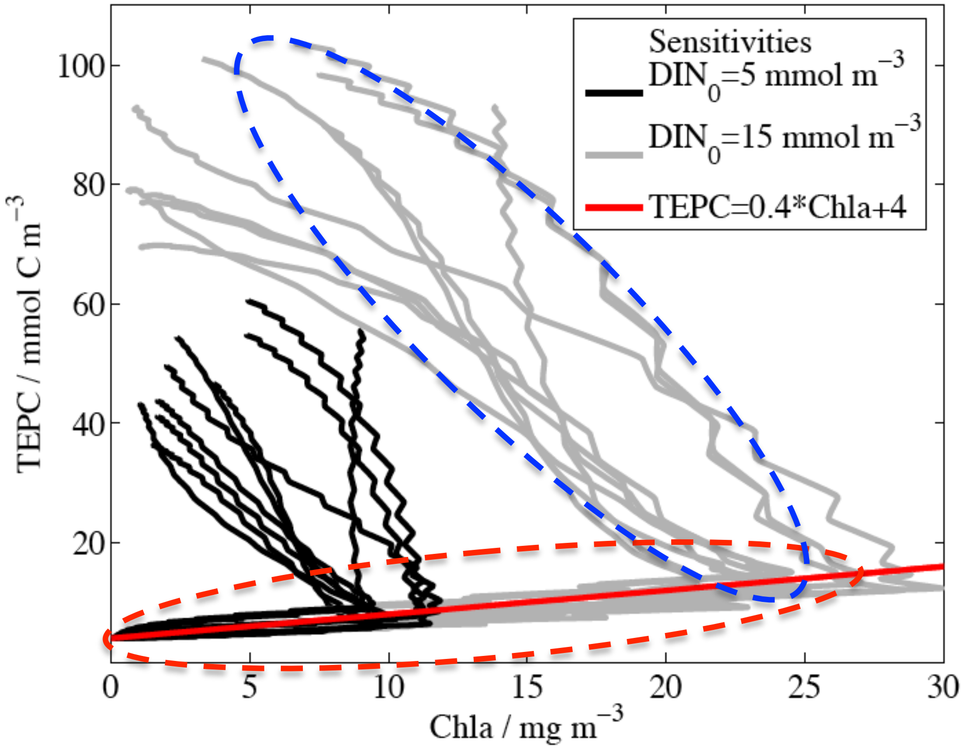

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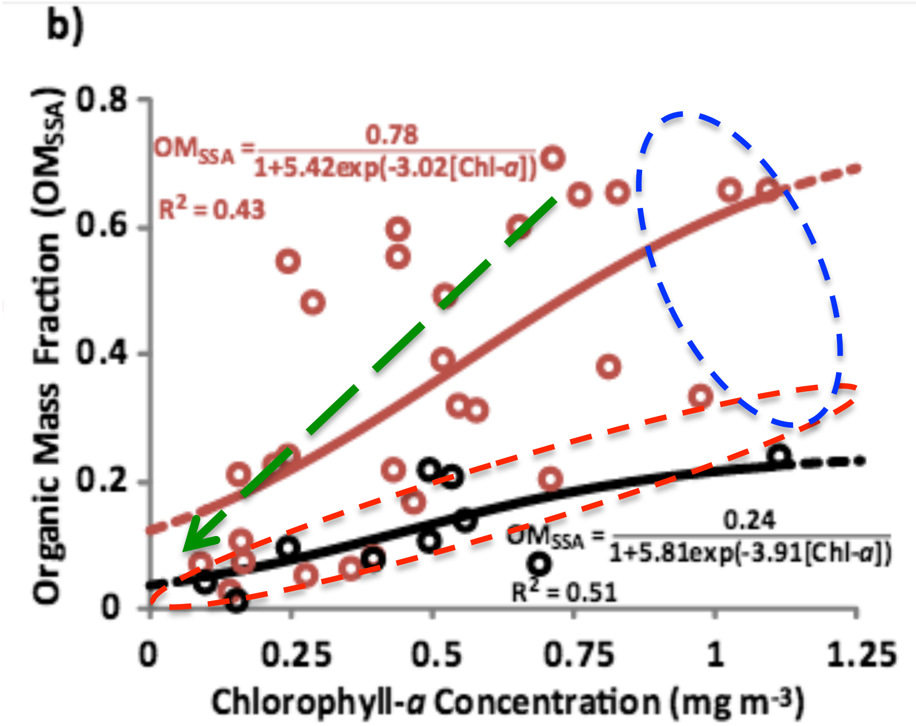

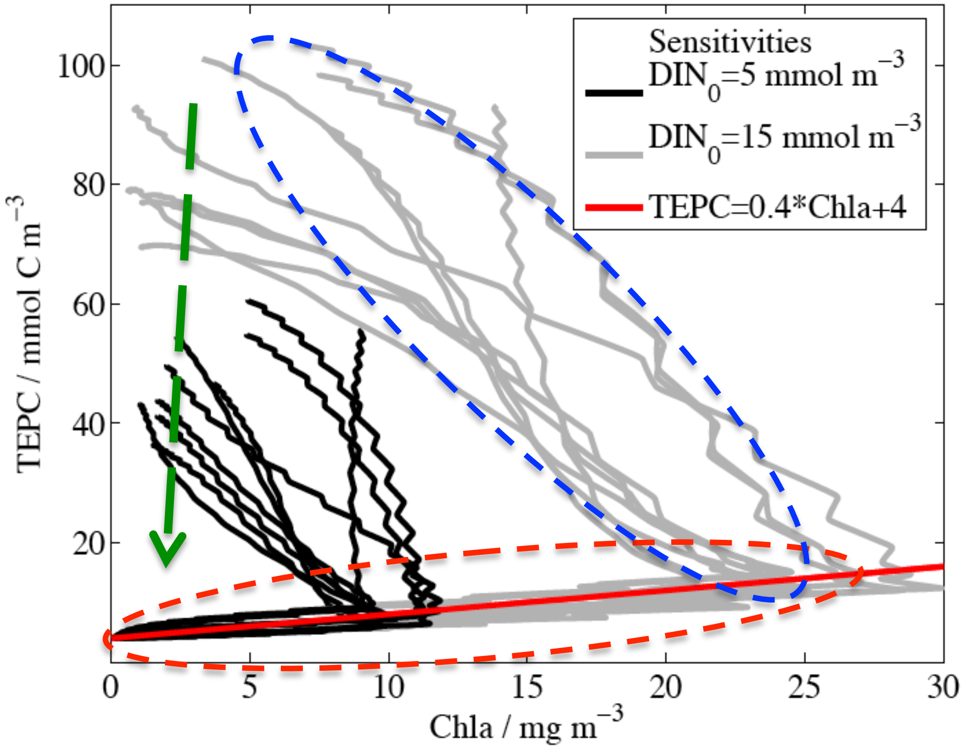

Summary and conclusions

1) Organic matter (OM) production relevant for air-sea exchange processes involves the formation of extracellular gels (e.g. TEP)

2) Chlorophyll *a* concentration and TEP formation are well correlated as long as primary production is not nutrient limited

3) OM within the surface microlayer (SML) modulates air-sea gas exchange at low wind speeds via damping of small gravity and capillary waves

4) The role of gels (like TEP) in the SML for emission of primary organic aerosols is still unclear → transport via bubbles and bubble bursting might be more relevant

5) Chlorophyll *a* concentration is an inappropriate indicator for possible emission of organic aerosols → refined parameterisations should distinguish between **pre**-, **bloom**, and **post-bloom** conditions