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

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Leipziger Meteorologisches Kolloquium
at
Leibniz-Institut für Troposphärenforschung
December 2015
Initiation:

BMBF funded project Surface Ocean Processes in the ANthropocene (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
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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
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Particulate organic carbon (POC)  Dissolved organic carbon (DOC)

Verdugo et al. (2004, Marine Chemistry)
1) Organic matter (OM) production and gel formation

Nutrient availability
- Carbon,
- Nitrogen, Fe, Cu, Zn, Mn...
- Phosphorus,

Phytoplankton

Background image by Chris Parks, 2001 Image Quest 3-D
1) Organic matter (OM) production and gel formation

Driving/control factors:
- Light, Temperature, pH

Metabolism (e.g. photoacclimation)
- Carbohydrates
- Nucleotides
- Lipids, Amino acids

Phytoplankton

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- Carbon,
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Chlα : C : N : P

variable C : N : P assimilation ratio → variable build-up and fate of OM
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1) Organic matter (OM) production and gel formation

variable C : N : P assimilation ratio → variable build-up and fate of OM
1) Organic matter (OM) production and gel formation

Verdugo et al. (2004, Marine Chemistry)
1) Organic matter (OM) production and gel formation

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

Microscopic pictures of natural phytoplankton assemblages

Direct view  Stained with Alcian Blue

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

\[ CH_x\text{-}COO^- \]

Spontaneous assembly of marine dissolved organic matter into polymer gels

Wein-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

Binding ("ion-bridging")
acidic polysaccharides

Spontaneous assembly of marine dissolved organic matter into polymer gels
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A) Gelation by spontaneous assembly

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

Chin et al. (1998, Nature)
1) Organic matter (OM) production and gel formation

Binding ("ion-bridging")
acidic polysaccharides

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

Xavier Mari¹, Adrian Burd²

B) Aggregation of polysaccharides (coagulation dynamics)

Mari and Burd (1998, Marine Ecology Progress Series, MEPS)
1) Organic matter (OM) production and gel formation

\[
\frac{dn(s,t)}{dt} = \frac{1}{2} \int_0^s \alpha(s,s-s_1) \cdot \beta(s_1,s-s) \cdot n(s_1,t) \cdot n(s-s_1,t) \, ds - n(s,t) \int_0^\infty \alpha(s,s_1) \cdot \beta(s,s_1) \cdot n(s_1,t) \, ds_1 - \frac{w(s)}{Z} n(s,t) + \mu(s,t)
\]

Coagulation kernel \( \beta = \) Brownian motion \( (\beta_{Br}) \) + Shear stress \( (\beta_{Sh}) \) + Differential settlement \( (\beta_{Ds}) \)

Mari and Burd (1998, Marine Ecology Progress Series, MEPS)
1) Organic matter (OM) production and gel formation

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**Polysaccharide aggregation as a potential sink of marine dissolved organic carbon**

Anja Engel¹, Silke Thoms¹, Ulf Riebesell¹, Emma Rochelle-Newall², & Ingrid Zondervan³

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Coagulation dynamics with only **two** size classes

\[
\frac{d[PCHO]}{dt} = \gamma(MP_C - \mu)[cell] - \alpha_{PCHO}\beta_{PCHO}[PCHO]^2 - \alpha_{TEP}\beta_{TEP}[PCHO][TEP] \\
\frac{d[TEP]}{dt} = \alpha_{PCHO}\beta_{PCHO}[PCHO]^2 + \alpha_{TEP}\beta_{TEP}[PCHO] \times [TEP]
\]  

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

Leipziger Meteorologisches Kolloquium at Leibniz-Institut für Troposphärenforschung, December 2015
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Coagulation dynamics with only **two** size classes

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\frac{d[PCHO]}{dt} = \gamma (M_{PC} - \mu) [\text{cell}] - \alpha_{PCHO} \beta_{PCHO} [PCHO]^2 \\
- \alpha_{TEP} \beta_{TEP} [PCHO][TEP] \\
\]

(1)

\[
\frac{d[TEP]}{dt} = \alpha_{PCHO} \beta_{PCHO} [PCHO]^2 + \alpha_{TEP} \beta_{TEP} [PCHO] \\
\times [TEP] \\
\]

(2)
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)
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)

- Continuous increase in POC although algal growth N-limited
- POC increase mainly attributable to TEP(-C) formation

Schartau et al. (2007, Biogeosciences)
Summary

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

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

The ocean-atmosphere interface’s property is characterized by the ocean’s surface microlayer (SML).

Surface microlayer (SML) thickness ≈ 200 - 1000 μm

Cunliffe et al. (2011)

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

\[ \text{Enrichment factor (EF)} = \frac{\text{OM}_{\text{SML}}}{\text{OM}_O} \]

OM concentration in SML [OM_{SML}]

OM concentration in upper ocean layers [OM_O]

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 ($EF = \text{OM concentration in SML} / \text{OM concentration subsurface water}$)

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

Proteins with greater surface reactivity than carbohydrates and/or lipids. More dipolar proteins?
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 ($u_{10} < 5 \text{ m s}^{-1}$ versus $u_{10} > 5 \text{ m s}^{-1}$)

![Graph showing probability density estimates of EF of DOC data, distinguishing between wind conditions.](image)

- **Measurements with Calm conditions** ($u_{10} < 5 \text{ m s}^{-1}$, $N = 249$)
- **Windy conditions** ($u_{10} > 5 \text{ m s}^{-1}$, $N = 101$)

*The more wind the higher EF?*
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

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

Sketch from Hunter (1980, Marine Chemistry)

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

What about TEP?

- Wurl et al. (2009, Marine Chemistry)
- Engel and Galgani (2015, Biogeosciences Discussion)
2) Organic matter (OM) at the ocean-atmosphere interface (surface microlayer, SML)

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

Soloviev and Lukas (2006)
Case 2 (physics) –

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

Approximately 0.5 m

$T_{z=1}(\text{day}) < T_{z=2}(\text{day}) < T_{z=3}(\text{day})$
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

- Daytime stratification
- Night-time cooling

Light

$T_{z=1}^{\text{(day)}}$ $T_{z=1}^{\text{(night)}} < T_{z=1}^{\text{(day)}}$

$T_{z=2}^{\text{(day)}}$ $T_{z=2}^{\text{(night)}} < T_{z=2}^{\text{(day)}}$

$T_{z=3}^{\text{(day)}}$ $T_{z=3}^{\text{(night)}}$ $T_{z=3}^{\text{(day)}}$

$\approx 0.5 \text{ m}$
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
3) Aspects of combining OM production with air-sea exchange processes

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)
Gas transfer velocity ($k_{660}$) varies with seasonal changes of surface tension ($\sigma$):

$\Rightarrow$ 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): $\sigma (\text{mN m}^{-1}) = 75.64 - 0.144T + 0.0399\text{Cl}\%$

Open/closed circles = different measurement techniques
3) Aspects of combining OM production with air-sea exchange processes

b) emission of primary organic aerosols
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)

Sizes between 116 and 520 nm

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

\[ \text{OM}_{\text{SSA}}(\text{Chl} - a, U_{10}) = \frac{\text{OM}_{\text{SSA}}^{\text{max}}}{1 + \exp(-2.63[\text{Chl} - a] + 0.18U_{10})} \]

Gantt et al. (2011)
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)

- 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

Quinn et al. (2014, Nature)
3) Aspects of combining OM production with air-sea exchange processes

Chla 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 Chla concentration during exponential growth phase
→ but maximum in TEP concentration is achieved shortly after the bloom (post-bloom period)
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- TEP carbon increases linearly with Chl $a$ concentration during exponential growth phase
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→ hysteresis!
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Recalling linkage between OM production, chlorophyll $a$ concentration and gel formation:

→ hysteresis!
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 \(\rightarrow\) transport via bubbles and bubble bursting might be more relevant

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