Marine Microgels

Orellana and Leck, 2015
The dissolved-particulate continuum

Thermodynamic yield of assembly

- **DOC** polymers: ~5–50 nm
- **Nanogels**: ~100–200 nm
- **Microgels**: ~3–6 μm

**DOC** ↔ **POC**

Orellana and Verdugo, 2003
Verdugo, 2012
Dissolved Organic Matter

662 Pg C (Hansell et al. 2009)

Operationally defined
filter: 0.7, 0.45, 0.22 (μm)

Complex pool (mostly unknown)
- carbohydrates,
- proteins
- lipids,
- nucleic acids
- metabolites
- lignins
- DOC/ DON/CDOM

Sources (?) Sinks (?) Dynamics (?) Role of polymers (?)
Primary Production: 48.5 PgC (20-50%) released as DOM

Processes: DOM

- Extracellular release
- Viral lysis
- Regulated secretion and exocytosis
- Apoptosis, programmed cell death
- Grazing
- Dissolution of large particles
<table>
<thead>
<tr>
<th>Process</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct release</td>
<td>(Decho, 1990),</td>
</tr>
<tr>
<td>Viral lysis</td>
<td>(Suttle, 2007; Vardi et al., 2012),</td>
</tr>
<tr>
<td>Apoptosis and programmed cell death</td>
<td>(Berman-Frank et al., 2004; Bidle &amp; Falkowski, 2004; Orellana et al., 2013), Biddle 2015.</td>
</tr>
<tr>
<td>Microbial degradation of POM</td>
<td>(Nagata and Kirchman, 1997),</td>
</tr>
<tr>
<td>Grazing</td>
<td>(Strom, 2008; Strom et al., 1997),</td>
</tr>
<tr>
<td>Zooplankton sloppy feeding</td>
<td>(Jumars et al., 1989),</td>
</tr>
<tr>
<td>Particle dissolution</td>
<td>(Azam and Long, 2001; Carlson, 2002b; Kiørboe and Jackson, 2001; Nagata et al., 2010; Smith et al., 1992),</td>
</tr>
<tr>
<td>Vesicle production and regulated exocytosis</td>
<td>(Biller et al., 2014; Chin et al., 2004)</td>
</tr>
</tbody>
</table>
Can we predict polymer production?

*T. pseudonana*

Ashworth et al. PNAS 2013
Inferred gene regulatory relationships

Ashworth et al. PNAS 2013
DOC- POC continuum is influenced by the community structure and metabolic state.

Southern Ocean diatom communities produce larger gels.

Cyanobacteria and other prokaryote communities produce smaller gels.

Orellana et al. unpubl
How do gels assemble?

Nanogels (20nm)  Microgel (µm)
Microgel spontaneous assembly

Flow cytometry

DLS with & w/o azide

EDTA-treated

Chin et al., 1998 Nature
Assembly
$\alpha L^2$ polymer length

Atomic Force Microscopy

ESEM (environmental scanning electron microscope)

Verdugo and Santschi, 2010
Chemical composition

Chlortetracycline  Nile Red

Verdugo & Santschi 2010
Does the polymer composition affect assembly?

Polymer assembly as a function of time in the high Arctic surface waters (87-88°N, 2-10°W).

Orellana et al. PNAS 2011
Hydrophobic moieties in polymer gels

Orellana et al., PNAS, 2011
Spontaneous assembly: hydrophobic moieties in *Emiliania huxleyi*

Ding et al. 2009

![Graph showing hydrodynamic diameter over time for ASW and Ca$^{2+}$ free ASW](graph.png)
Dispersion of microgels: synergistic effect of pH and temperature

Chen et al. PLOS one 2015
Does polymer size matter?

Assembly of marine polymers degraded by UV light exposure

Orellana & Verdugo 2003
Equilibrium polymer size of assembly and concentration of microgels decreases exponentially when irradiated with UV

Orellana & Verdugo, L&O 2003
Exponential decrease of microgels with UVB exposure

Orellana and Verdugo, L&O 2003
Volume phase transition

Electric field

Light

Pollutants

Heat

Change in environment

(Ions and pH, temperature, solvent, pH, ions, light)

Biochemicals

T. Tanaka, 1993
Bacterial degradation

Assembly of microgels after microbial degradation (Orellana et al. unpub.)

Ditt et al., submitted

South Atlantic

500 m

1000 m

4000 m
Microgel volume phase transition

(a) 

(b) 

Orellana et al.
2011
Marine Microgels
Mónica V. Orellana,
University of Washington/Institute for Systems Biology

RuBisCO Microgels
Deep Pacific Ocean (3000m)

Orellana and Hansell 20

Graph showing microgel concentration vs pH

Image of RuBisCO protein structure

Image of microgels under a microscope
RuBisCO in the deep Pacific Ocean

Orellana & Hansell 2012
Microgels in clouds, fog and aerosol particles.

Immunostained cloud microgels

Field Emission Scanning microscope

Unstained samples

1 3 um

2

3 500 nm

Confocal microscope

Tangled nanometer sized gels

Primary colloids: 5-25 nm

Marine polymer gel

Immunostained samples

Fractal structure

Orellana et al. 2011
<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Gels</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural units bend, fold, reptate and intertwine</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Internal dialectric properties different from the bulk</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Non-Newtonian Rheology &amp; porous structure</td>
<td>Yes</td>
<td>?</td>
</tr>
<tr>
<td>Defined internal topology of their polymer network</td>
<td>Yes</td>
<td>?</td>
</tr>
<tr>
<td>Defined mechanisms of assembly and stability</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Defined kinetics of assembly/dispersion and swelling</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Characteristic polymer gel phase transitions</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Defined ion (Donnan) and hydrophobic partition properties</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>
DOM-POM continuum

Adapted from Verdugo et al.
Elucidating the DOM-POM Continuum

• Soft matter physics allows understanding structure and dynamics of DOC biopolymer
• Assembly: explains formation of particles in seawater
• Emergent properties (phase transition) explain chemical landscape
Thank you!