Organics

Ocn 623

Reading: Libes, Chapters 22 & 23
ORGANIC MATTER POLARITY

A Useful Tool For Predicting DOM Behavior

Polar - molecule has a net ionic dipole - dissolves well in polar solvents such as water

\[
\text{H}^\delta+ \quad \text{O}^{2\delta-} \quad \text{H}^\delta+ \\
\text{Net dipole} \quad \text{(sum of two bond dipoles)}
\]

(\(\delta^+\) and \(\delta^-\) indicate partial charges)

Non-polar - molecule has no net ionic dipole - "surface active" in polar solvents (i.e., wants to come out of solution)
Demonstration - models of:

- CH$_4$ - methane (non-polar)
- CH$_3$COOH - acetate (polar)
- C$_{16}$ - n-hexadecane (non-polar)
- CH$_3$-(CH$_2$)$_{16}$-COOH - stearate

(polar carboxyl group + non-polar wax = "fatty acid")

Fatty acids in water tend to form micelles:
Figure 3.5 Relative aqueous solubility of different functional groups. 
Thurman (1985).
Figure 1.1 Approximate concentrations of dissolved and particulate organic carbon in natural waters. Thurman (1985).
Organic Matter Size Fractionation
(or, what do we mean by dissolved vs. particulate?)

Operational definitions based on filter retention:

1. **Particulate organic matter** (POM or POC/PON/POP) -- membrane (e.g., Millipore) or Nuclepore filtration

2. **Colloidal organic matter** (COM) -- tangential flow ultra-filtration (Amicon filters)
3. Dissolved organic matter (DOM)

a. Dissolved organic carbon (DOC)
   - Oceanic concentrations = µg-C/L to mg-C/L
   - Turnover time ranges from days to centuries, depending on compound
   - Can be very fast during blooms, when large amounts of DOC are excreted
   - Typical upper ocean DOC residence time: 3 - 40 days.

b. Dissolved organic nitrogen (DON)
   - Oceanic concentrations = µg-N/L
   - Much shorter turnover time

c. Dissolved organic phosphorus (DOP)
   - Oceanic concentrations = ng-P/L to µg-P/L
   - Presumably very fast turnover time

Note: If you are using mass/vol units, be sure you specify if you mean mass of atoms or mass of molecules!
Figure 5. Rainwater as a part of the ocean dissolved organic carbon cycle. Fluxes are in $10^{12} \text{ g C yr}^{-1}$. Wiley et al. (2000).
“Biomarkers” – relatively unchanged during sedimentation and diagenesis.
A Few Examples of Biomarkers

Figure 2. Compound structures, names and biological origins of examples of indicators of algal contributions to sedimentary organic matter. Sohn (1986).
Sources And Sinks Of Marine Organic Matter

1. **Autochthonous** vs. **Allochthonous** organic matter
   (locally produced vs. imported)
   
   Greek roots: "auto" = self
   "allo" = other
   "chthonous" = earth, ground

2. In general, the major source of open ocean OM is planktonic primary producers (**autochthonous**).
   Most OM exported from coastal systems is consumed in stratified continental shelf waters during the summer (**allochthonous**).
3. OM abundance in the open ocean is controlled by grazing:
   • 85% of primary production is recycled through consumers
   • 15% is released from primary producers by extracellular release
   • This extracellular release supplies \( \geq 50\% \) of bacterial growth requirements

4. Humic materials – chromophoric or colored fraction of dissolved organic matter (CDOM) – “Gelbstoffe”
   Read Libes for description of sources, composition & fates
   • Humic acids
   • Fulvic acids
   • Humin
Fig. 2. Cumulative biochemical class distributions (compound class-C as percent of total C$_{org}$). Values at 9°N, 5°N, and the equator have been averaged; values for the 105-m traps represent means for the two surveys. Carbon contents were calculated directly for amino acids and sugars, while the measured lipids were estimated to be 85% C. Chlorophyll and its degradation products are included with lipids but are quantitatively negligible. Residual "uncharacterized" carbon was obtained as the difference between total C$_{org}$ and the sum of carbon in amino acid + sugar + lipid.
Fig. 1. Fluxes (mg/m²d) of organic carbon and biochemical classes at 9°N, 5°N, and the equator. Compound class fluxes are in mg of compound, not mg C. Fluxes for net-plankton are derived from primary production rates (Barber et al., 1996) and our measurements of biochemical content of net-plankton. Floating sediment trap fluxes at 5°N and the equator are means of two surveys (there was only 1 measurement at 9°N). Fluxes into surface sediments were calculated using the sediment Corg content and accumulation rates (Demaster et al., 1997) and our biochemical measurements. There are no accumulation rate data for 10–12 cm sediments.
DOC Dynamics and Size Fractionation

DOC – Passes through Whatman GF/F filter (0.7 um)

- Downward DOC flux – a significant fraction of OC flux

- Mixed layer – high DOC

- Subsurface layer – steep DOC gradient

- Deep water – Low and constant DOC conc.

Fig. 4. A DOC profile from open-ocean station 11 in the Atlantic. Guo et al. (1995).
Fig. 6. Vertical distribution of COC concentrations in seawater from the Gulf of Mexico and off Cape Hatteras (MAB).
Fig. 5. Variations of COC concentrations from nearshore to offshore stations in the Gulf of Mexico and off Cape Hatteras.
PHOTO-OXIDATION

Two main processes affecting DOM:

- $\text{H}_2\text{O}_2$ production:

  \[ \text{O}_2 + 2\text{e}^- + 2\text{H}^+ + \text{h}_\nu \rightarrow \text{H}_2\text{O}_2 \]

  (~50\% of $\text{O}_2$ consumption by photo-oxidation)

- DOM oxidation to $\text{CO}_2$ and oxidatively altered DOM
<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>Structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low MW Organic Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>44</td>
<td>H₂C⋅·C = O</td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td></td>
<td>59</td>
<td>H₂C⋅·C = O</td>
<td>Mopper et al. 1991</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>H₂C⋅·C = CH₂</td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Chlorate</td>
<td>189</td>
<td>O⋅·C⋅·CH₂⋅·CH₂⋅·C⋅·O−</td>
<td>Wetzel et al. 1995</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>30</td>
<td>H₂C = O</td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Formate</td>
<td>45</td>
<td>H₂C = O</td>
<td>Mopper et al. 1991</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>58</td>
<td>O⋅·O⋅·C⋅·CH</td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Glyoxalate</td>
<td>73</td>
<td>O⋅·O⋅·C⋅·O−</td>
<td>Kieber and Mopper 1987</td>
</tr>
<tr>
<td>Levulinic</td>
<td>115</td>
<td>H₂C⋅·C⋅·CH₂⋅·CH₂⋅·C⋅·O−</td>
<td>Wetzel et al. 1995</td>
</tr>
<tr>
<td>Malonate</td>
<td>102</td>
<td>O⋅·C⋅·CH₂⋅·CH₂⋅·C⋅·O−</td>
<td>Dahlen et al. 1996</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>72</td>
<td>H₂C⋅·C⋅·CH₂</td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Oxalate</td>
<td>88</td>
<td>O⋅·O⋅·C⋅·O−</td>
<td>Dahlen et al. 1996</td>
</tr>
<tr>
<td>Propanal</td>
<td>59</td>
<td>H₂C⋅·CH₂⋅·CH</td>
<td>Kieber and Mopper 1987</td>
</tr>
<tr>
<td>Pyruvate</td>
<td>87</td>
<td>H₂C⋅·C⋅·C⋅·O−</td>
<td>Kieber et al. 1989</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Carbon Dioxide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>28</td>
<td>CO</td>
<td>Mopper et al. 1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Jones 1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Valentine and Zepf 1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Schmidt and Conrad 1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Miller and Zepf 1995</td>
</tr>
<tr>
<td><strong>Nutrients</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>17</td>
<td>NH₄⁺</td>
<td>Bushaw et al. 1996</td>
</tr>
<tr>
<td>Phosphate</td>
<td>95</td>
<td>PO₄³⁻</td>
<td>Franck and Heath 1982</td>
</tr>
</tbody>
</table>

Mopper and Stahovec (1986)
Mopper et al. 1991
Kieber et al. 1990
Wetzel et al. 1995
Dahlen et al. 1996
Mopper and Stahovec 1986
Mopper et al. 1991
Kieber et al. 1990
Kieber and Mopper 1987
Mopper et al. 1991
Kieber et al. 1990
Levulinic acid
Mopper and Stahovec 1986
Mopper et al. 1991
Kieber et al. 1990
Formaldehyde
Mopper and Stahovec 1986
Mopper et al. 1991
Kieber et al. 1990
Malonate
Mopper and Stahovec 1986
Mopper et al. 1991
Kieber et al. 1990
Methylglyoxal
Mopper and Stahovec 1986
Mopper et al. 1991
Kieber et al. 1990
Oxalate
Mopper and Stahovec 1986
Mopper et al. 1991
Kieber et al. 1990
Propanal
Mopper and Stahovec 1986
Mopper et al. 1991
Kieber et al. 1990
Pyruvate
Mopper and Stahovec 1986
Mopper et al. 1991
Wetzel et al. 1995
Carbon Dioxide
Mopper et al. 1991
Jones 1991
Valentine and Zepf 1993
Schmidt and Conrad 1993
Miller and Zepf 1995
Ammonium
Bushaw et al. 1996
Kieber et al. 1990
Phosphate
Franck and Heath 1982

Moran and Zepf (1997)
Table 3. Estimated formation of biologically labile photoproducts from DOM in seawater from the continental shelf of the southeastern U.S. during exposure to 1 h of noontime summer sunlight at 32°N latitude. Calculations were made by normalizing for light intensity, length of exposure, and light absorption properties of the DOM among a number of studies. Daily production rates given in the text were calculated by assuming 7.6 h of noontime sunlight per day.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Production (nM (C or N) h(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low-MW organic compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>11</td>
<td>Kieber et al. 1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mopper et al. 1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Acetate</td>
<td>5</td>
<td>Wetzel et al. 1995</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>14</td>
<td>Kieber et al. 1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Formate</td>
<td>1</td>
<td>Wetzel et al. 1995</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>6</td>
<td>Mopper et al. 1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Glyoxylate</td>
<td>22</td>
<td>Kieber et al. 1990</td>
</tr>
<tr>
<td>Levulinate</td>
<td>46</td>
<td>Wetzel et al. 1995</td>
</tr>
<tr>
<td>Propanal</td>
<td>3</td>
<td>Mopper et al. 1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mopper and Stahovec 1986</td>
</tr>
<tr>
<td>Pyruvate</td>
<td>12</td>
<td>Mopper et al. 1991</td>
</tr>
<tr>
<td><strong>Carbon gases</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>108</td>
<td>Mopper et al. 1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Valentine and Zepp 1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Miller and Zepp 1995</td>
</tr>
<tr>
<td><strong>Nutrients</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>17</td>
<td>Bushaw et al. 1996</td>
</tr>
</tbody>
</table>

Moran and Zepp (1997)
Fig. 3. Depth profiles of relative rates of formation of biologically available DOM photoproduction for representative marine and freshwater ecosystems. Estimates of diffuse attenuation coefficients for the boreal pond sample (A) were based on an absorption spectrum obtained on a Shimadzu spectrophotometer using a 0.2-μm filtered water sample. Diffuse attenuation coefficients for water from the Gulf of Mexico (B), moderately productive seawater (C), and the Sargasso Sea (D) are from Smith and Baker (1979). The assumed action spectrum is based on that of Valentine and Zepp (1993) for CO photoproduction. Moran and Zepp (1997).
Fig. 4. Estimated depth-integrated photochemical formation of biologically available carbon photoproducts from DOM and surface area of the ocean for 10° latitude bands. Photoproduction calculations assume particle-free water of sufficient depth for all sunlight to be absorbed, the action spectrum of Valentine and Zepp (1993), and cloud-free skies. Ocean area is from Sverdrup et al. (1942). Annual depth-integrated production for 10° increments in latitude are based on fluxes that were computed for each month using a previously described model (Valentine and Zepp 1993) and recent total ozone data (Harris et al. 1995).
1. **Bulk analysis:**

- Oxidize or combust DOC to convert CO$_2$ (detect with IR spec or coulometer),

  Three methods commonly used:

  a. **UV-oxidation** (traditional)
  
  b. **Persulfate oxidation** (traditional)

  c. **High temperature catalytic oxidation** (recent) (Suzuki's "magic platinum catalyst"). Supposedly gave results up to 2.5x higher than for other methods (esp. in surface waters), but now all results are similar (Actually a blank problem).

- Oxidize DON to N$_2$ (chemiluminescence detector) or hydrolyze DON to DIN (colorimetric analysis)

- Hydrolyze DOP to DIP (colorimetric detector)

**Note:** DOC: Must be corrected for pre-existing DIC, DIN, and DIP in the seawater

POM: Must corrected for C in carbonate minerals
2. **Fluorescence detection** - *In situ* analysis of chromophoric or colored fraction of dissolved organic matter (CDOM)
3. Molecular analysis:

Problems:  - Great number of compounds
            - Very low concentrations

Methods:  need to worry about SEPARATION and IDENTIFICATION

- Extract and concentrate OM from seawater (liquid-liquid or solid-phase extraction)
- Fractionate OM into individual compound classes (chromatography or extraction)
- Separate individual compounds in classes (chromatography)
- Identify compounds:  ***Has been done for maybe 30% of DOM***
  Mass spectroscopy
  Nuclear magnetic resonance
  Infrared spectroscopy
  X-ray diffraction
  Ultraviolet-visible light spectroscopy