“Basic to the understanding of any ecosystem is knowledge of its food web, through which energy and materials flow. If microorganisms are major consumers in the sea, we need to know what kinds are the metabolically important ones and how they fit into the food web.” - Lawrence Pomeroy (Bioscience, 1974)
Cycling and composition of marine
Dissolved organic matter: A primer

1) What is the global distribution of dissolved organic matter?

2) How do we approach an understanding of its cycling and reactivity?

3) What techniques are used to characterize DOM composition?

4) Can we link composition to source and putative sinks?
Typical 1D profile of dissolved organic carbon in the ocean

Often measured as TOC

Surface values typically 60-80 µM

Deep water values @ 40 ±1 µM
(implies some unknown feedback/control of DOC values)

Global inventory about 660 GT C

Data from Peltzer and Hayward (1996) DSR
Global circulation and the distribution of DOC

Hansell et al. Oceanography 2009
Time series analysis of DOC (µM C) at Bermuda

Data from Dennis Hansell and Craig Carlson
Seasonal dynamics of SAR11 populations in the euphotic and mesopelagic zones of the northwestern Sargasso Sea

Craig A Carlson¹,⁵, Robert Morris¹,²,⁵, Rachel Parsons³,⁵, Alexander H Treusch⁴,⁵, Stephen J Giovannoni⁴ and Kevin Vergin⁴

How do we measure carbon fluxes in DOC?
Natural radiocarbon production has changed over time, and is influenced by changes in the flux of cosmic rays, solar activity, and the earth's magnetosphere.

Atmospheric radiocarbon is adsorbed by the ocean through CO₂ gas exchange, but the rate of adsorption varies in space and time. Penetration of radiocarbon into the ocean interior is affected by mixing and circulation.

Atmospheric testing of nuclear weapons in the period of 1945-1962 introduced a large amount of anthropogenic radiocarbon into the atmosphere. This “bomb signal” is still being adsorbed by the ocean and incorporated into Organic matter.
DOC cycling via $^{14}$C

**UV photooxidation**

<table>
<thead>
<tr>
<th>Depth</th>
<th>$\Delta^{14}$C(‰)</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>1880m</td>
<td>-351 ‰</td>
<td>-3470±330 ybp</td>
</tr>
<tr>
<td>1920m</td>
<td>-341 ‰</td>
<td>-3350±300 ybp</td>
</tr>
</tbody>
</table>

Williams, Oeschger, and Kinney; Nature v224 (1969)
Radiocarbon in the Atlantic and Pacific Oceans

Peter M. Williams and Ellen Druffel; Nature 1987, JGR 1992
Radiocarbon in the Atlantic and Pacific Oceans

DIC $^{14}$C in surface waters of the Atlantic and Pacific have similar isotopic values.

DOC is always older than DIC (by 2-3 kyrs in surface water)

DIC $\rightarrow$ POC $\rightarrow$ DOC
Radiocarbon in the Atlantic and Pacific Oceans

DIC $^{14}$C in surface waters of the Atlantic and Pacific have similar isotopic values.

DOC is always older than DIC (by 2-3 kyrs in surface water)

$\Delta \Delta^{14}$C of DIC and DOC is about the same in the deep Atlantic and Pacific.
Radiocarbon based models of DOC cycling in the water column

\[
[\text{DOC}]_z(C14)_z = [\text{Deep}](C14)_D + [Z-Deep](C14)_{DIC}
\]

Atlantic surface water
\[ ^{14}\text{C}_{\text{calc}} = -120 \ \% \]
\[ ^{14}\text{C}_{\text{obs}} = -127 \ \% \]

Pacific surface water
\[ ^{14}\text{C}_{\text{calc}} = -147 \ \% \]
\[ ^{14}\text{C}_{\text{obs}} = -148 \ \% \]
Under this perspective, DOM is produced and rendered recalcitrant by marine microbes. Combined with the two component model of radiocarbon and deep sea DOC, it suggests no or at best very slow removal of DOM in the deep sea.
Southern Ocean DOC-14 data suggests the two component model cannot be correct.
Very rapid degradation of DOC in the Mediterranean Sea. If DOC is refractory, why does this happen?

C. Sanitelli et al. 2013
The diagram illustrates the carbon cycle in aquatic ecosystems. It shows the flow of dissolved organic carbon (DOC) between different compartments.

1. **Atmospheric deposition**:
   - DOC enters the system from the atmosphere.

2. **Phytoplankton**:
   - Photosynthetic organisms that produce organic matter.

3. **Grazers**:
   - Consumers that feed on phytoplankton.

4. **Sinking particles**:
   - Organic material sinks to the ocean floor.

5. **Hydrothermal DOC**
   - DOC from hydrothermal vents.

6. **Sedimentary DOC**
   - DOC from sedimentation.

7. **Methane seeps**
   - DOC from methane emissions.

8. **Terrestrial organic matter (DOM, POM)**
   - Organic material from land.

9. **Semi-labile DOC**
   - DOC that is relatively labile, with a turnover rate of 5-10 µM and a Δ¹⁴C value of approximately -150‰.

10. **Chemoautotrophs**
    - Microorganisms that use chemical energy to fix carbon.

11. **Semi-labile DOC meso- and bathypelagic microbial loop**
    - DOC with a turnover rate of 10-15 µM and a Δ¹⁴C value of >0‰.

12. **Recalcitrant DOC**
    - DOC that is resistant to degradation, with a turnover rate of 25 µM and a Δ¹⁴C value of approximately -800‰.
The cycling and composition of marine dissolved organic matter: a primer
Dissolved Organic Matter Composition – The Problem

Salt

DOC
Cross or tangential flow filtration, Ultra- or nanofiltration

Separation based on size

1 nm pore @ 1 kD

Selects for larger size (High Molecular Weight) fraction

About 30-35% TOC (now up to 60% using electrically assisted UF)

Membrane effects what is collected
Ultrafiltration of high molecular weight DOM (HMWDOM)
Isolation of DOM by adsorption onto hydrophobic resins.

Selective chemical Adsorption

Seawater (filtered; pH = 2)

10-20% of DOC

Methanol or Ammonium hydroxide wash
Nuclear Magnetic Resonance Spectroscopy (NMR)

Can be tuned to different Nuclei of interest (C,N,P…).

Gives information on functional groups which, combined with a knowledge of biochemicals can be used to deduce composition and origin.

Internally quantitative.
$^{13}$C Nuclear Magnetic Resonance Spectrum of high molecular weight dissolved organic matter (C/N = 15)
$^{13}$CNMR of plankton tows

1. Southern Ocean #1
2. Arabian Sea

Chemical shift (ppm)

$^{13}$CNMR of HMWDOM

Sargasso Sea (surface)

Chemical shift (ppm)

Hedges et al GCA 2001
$^{13}$CNMR spectra of HMWDOM

Sargasso Sea

3 m

North Pacific Subtropical Gyre

3 m
HMWDOM in the deep sea

Sargasso Sea

3 m

2500 m

NPSG

3 m

1800 m
$^{15}$N-NMR of DOM shows most N is in aminopolysaccharides

-mild acid hydrolysis
Composition of HMWDOP

Organic phosphorus nomenclature

- Phosphonate
- (ortho) phosphate
- Phosphate monoester
- Polyphosphate

12°S, 134°W UDOM

Phosphate mono- & di-esters

A

BATS UDOM

C

Surface
100 m
200 m
375 m
4000 m

Surface
900 m
2400 m

Chemical shift (ppm)

30 25 20 15 10 5 0 -5 -10 -15 -20

50 40 30 20 10 0 -10 -20 -30 -40 -50

Kolowith et al., L&O 2001
Spectral modeling of major biochemicals in DOM

Proteins

Carbohydrates

Lipids (CRAM)

Surface Water

Deep Water
Proteomics of dissolved proteins

Station

<table>
<thead>
<tr>
<th>Molecular weight (KDa)</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>66</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>45</td>
</tr>
<tr>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>36</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>18.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.4</td>
</tr>
<tr>
<td>14.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.3</td>
</tr>
</tbody>
</table>
Proteomics of dissolved proteins

Molecular weight
(KDa)

Station

<table>
<thead>
<tr>
<th>Molecular weight (KDa)</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Typical 1D profile of dissolved organic carbon in the ocean

Often measured as TOC

Surface values typically 60-80 $\mu$M

Deep water values @ 40 $\pm$1 $\mu$M
(implies some unknown feedback/control of DOC values)

Global inventory about 660 GT C

Data from Peltzer and Hayward (1996) DSR
gas sample enters here

ions accelerate towards charged slit

magnetic field deflects lightest ions most

filament current ionizes the gas

ions separated by mass expose film

http://antoine.frostburg.edu/chem/senese/101/glossary/m.shtml
Substitute CH$_4$ for O

$\Delta m = 36.4 \text{ m Da}$

C$_{17}$H$_{24}$O$_8$Na

379.1369 Da

C$_{16}$H$_{20}$O$_9$Na

379.1005 Da

C$_{18}$H$_{28}$O$_7$Na

379.1732 Da

m/z
Elemental Analysis of DOM in Weddell Sea Seawater

<table>
<thead>
<tr>
<th>Count</th>
<th>A (Exp)</th>
<th>B (Theory)</th>
<th>C (Error ppm)</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>415,10141</td>
<td>415,10236</td>
<td>2.29</td>
<td>21</td>
<td>18</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>415,13797</td>
<td>415,13874</td>
<td>1.85</td>
<td>22</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>415,17405</td>
<td>415,17513</td>
<td>2.6</td>
<td>23</td>
<td>26</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>417,08070</td>
<td>417,08162</td>
<td>2.21</td>
<td>20</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>417,11720</td>
<td>417,11801</td>
<td>1.94</td>
<td>21</td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>417,15349</td>
<td>417,15439</td>
<td>2.16</td>
<td>22</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>417,19014</td>
<td>417,19078</td>
<td>1.53</td>
<td>23</td>
<td>28</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>419,09650</td>
<td>419,09727</td>
<td>1.84</td>
<td>20</td>
<td>18</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>419,13277</td>
<td>419,13366</td>
<td>2.12</td>
<td>21</td>
<td>22</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>419,16910</td>
<td>419,17004</td>
<td>2.24</td>
<td>22</td>
<td>26</td>
<td>8</td>
</tr>
<tr>
<td>11</td>
<td>419,20525</td>
<td>419,20643</td>
<td>2.81</td>
<td>23</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>12</td>
<td>421,07604</td>
<td>421,07654</td>
<td>1.19</td>
<td>19</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>13</td>
<td>421,11206</td>
<td>421,11292</td>
<td>2.04</td>
<td>20</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>421,14848</td>
<td>421,14931</td>
<td>1.97</td>
<td>21</td>
<td>24</td>
<td>9</td>
</tr>
<tr>
<td>15</td>
<td>421,18488</td>
<td>421,18569</td>
<td>1.92</td>
<td>22</td>
<td>28</td>
<td>8</td>
</tr>
<tr>
<td>16</td>
<td>423,09139</td>
<td>423,09219</td>
<td>1.89</td>
<td>19</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td>17</td>
<td>423,12766</td>
<td>423,12857</td>
<td>2.15</td>
<td>20</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>423,16415</td>
<td>423,16496</td>
<td>1.91</td>
<td>21</td>
<td>26</td>
<td>9</td>
</tr>
<tr>
<td>19</td>
<td>423,20011</td>
<td>423,20194</td>
<td>4.32</td>
<td>22</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>425,10689</td>
<td>425,10784</td>
<td>2.45</td>
<td>19</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>21</td>
<td>425,14331</td>
<td>425,14422</td>
<td>2.14</td>
<td>20</td>
<td>24</td>
<td>10</td>
</tr>
<tr>
<td>22</td>
<td>425,17971</td>
<td>425,18061</td>
<td>2.12</td>
<td>21</td>
<td>28</td>
<td>9</td>
</tr>
</tbody>
</table>
Unusual molecular masses in DOM

Surprisingly, there is a population of very low H/C and O/C organic matter.
Dittmar & Paeng Nature 2009
### Composition, reactivity, flux and distribution of DOM

<table>
<thead>
<tr>
<th>Non-reactive DOM</th>
<th>Semi-reactive DOM</th>
<th>Very reactive DOM</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td><img src="image3" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><strong>Aliphatic or “Humic” substances</strong></td>
<td>Biopolymers (polysaccharides, proteins)*</td>
<td>Simple biomolecules (amino acids, sugars)*</td>
</tr>
<tr>
<td>Concentration 40 µM</td>
<td>Concentration 0-40 µM</td>
<td>Concentration 1-2 µM</td>
</tr>
<tr>
<td>Inventory = 640 GT C</td>
<td>Inventory = 10-20 GT C</td>
<td>Inventory = 0.1-0.3 GT C</td>
</tr>
<tr>
<td>$\Delta^{14}C = -400$ to $-600%$</td>
<td>$\Delta^{14}C =$ modern (DIC)</td>
<td>$\Delta^{14}C =$ modern (DIC)</td>
</tr>
<tr>
<td>Annual flux = 0.1 GTC</td>
<td>Annual flux = 10’s GT C?</td>
<td>Annual flux = 10’s GT C?</td>
</tr>
</tbody>
</table>

* = 80% of cell C, N

* = 10-20% of cell C, N

---

**Notes:**

- Biopolymers and Simple biomolecules are major components of DOM.
- The reactivity and flux of DOM vary significantly among different categories.
Lecture 2. Summary

There is a large vertical gradient in DOC between surface and deep waters. Net production in the euphotic zone, net respiration in the mesopelagic zone.

Radiocarbon measurements show that there is “new” DOC in the surface ocean, very “old” DOC at depth.

Loss of about 30% of deep DOC between the North Atlantic and the North Pacific, along the path of deep water drift.

Studies of chemical composition are handicapped with by our ability to sample DOM. DOM is sampled by two techniques, ultrafiltration which is based on the larger molecular size of some DOM relative to water and salt (high molecular weight DOM; HMWDOM) and solid phase extraction (SPE) that relies on chemical adsorption onto a hydrophobic surface.
Lecture 2. Summary

Of the ~ 50-60% of DOM that can be recovered, and therefore characterized. Major techniques used to characterized DOM are nuclear magnetic resonance spectroscopy (NMR) and high resolution mass spectrometry (HR-MS). HMWDOM is largely “new” DOC and has a modern radiocarbon age when purified. HMWDOM is largely carbohydrate with a small amount of protein. HMWDOM carbohydrate has an unusual composition that has not been fully characterized. The source of the carbohydrate is not known.

SPE extracted DOM has an old radiocarbon age. So far this is very hard to analyze and characterize. It is clearly a complex mixture of organic matter with a significant amount of aliphatic character. The source of this DOM and the pathways that lead to its formation are not known.