DON sources: methods and processes

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Department of Physical Sciences

What is DON?

<table>
<thead>
<tr>
<th>Labile</th>
<th>Semi-labile</th>
<th>Refractory</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFAA urea</td>
<td>proteins</td>
<td>humic acids</td>
</tr>
<tr>
<td>nucleic acids</td>
<td>DCAA amino</td>
<td>fulvic acids</td>
</tr>
<tr>
<td>methylamines</td>
<td>polysaccharides</td>
<td>porphorins</td>
</tr>
<tr>
<td>(chitins &amp; peptidoglycans)</td>
<td></td>
<td>amides</td>
</tr>
</tbody>
</table>

DON

Months
Years

semi-labile
& refractory
DON

Days
Weeks
Days
Months
- Autochthonous sources
- Methods to study release
- Allochthonous sources
- DON as a mode of N delivery

**Autochthonous sources of DON**

- Phytoplankton
  - Passive diffusion
  - Cell death & lysis
  - DON

**Autochthonous sources of DON**

- Zooplankton
  - Excretion
  - Sloppy feeding
  - Bactivory
  - DON
**Autochthonous sources of DON**

Bacteria

Exoenzyme release  → DON  
Cell death & lysis

**Viral lysis**

Phytoplankton

DON and $NH_4^+$

Viruses are unique in that they are “part” of the DOM pool (~<2%).


**Photochemical Ammonification**

UV radiation

Humic or fulvic acids  
Proteins  
Large organic moieties

phytoplankton

$NH_4^+$  
DPA  
$NO_2^-$

bacteria

Bushaw et al. 1996 Nature

**Methods for studying release:**

1. Bioassays
2. Radioactive tracers
3. Stable isotope tracers  
   a. Direct measures  
   b. Isotope dilution
Bioassays & Radiotracers

\((^3\text{H}, ^{14}\text{C}, ^{32}\text{P})\)

Absolute amounts

Net rates

Stable isotope tracers

\((^{15}\text{N}, ^{13}\text{C})\)

Ratios

\((^{15}\text{N}/^{14}\text{N} \text{ or } ^{13}\text{C}/^{12}\text{C})\)

Gross rates

Uptake and regeneration simultaneously

\[\text{Net Uptake} = \text{Rate} \times \text{atom}\% \ \text{PN} \times \text{Time}\]

\[\text{Rate} = \frac{\text{atom}\% \ \text{of target}}{\text{atom}\% \ \text{of source}} \times \text{Time} \times [\text{target}]\]
Gross - Net = DON Uptake - Uptake = Release

\[
\text{Gross Uptake} = \frac{^{15}\text{N in PN & DON}}{\text{Rate}} \times [\text{PN}]
\]

\[
\text{Net Uptake} = \frac{\text{atom % PN}}{\text{Rate}} \times [\text{PN}]
\]

\[
\text{Isotope dilution}
\]

\[
\text{Net Uptake} = \frac{15\text{NH}_4^+}{14\text{NH}_4^+} \times [\text{PN}]
\]
\[ P_t = P_0 + (d - u)t \]

\[ \ln (R_t - R_a) = \ln (R_0 - R_a) - \frac{d}{d - u} \ln \left( \frac{P_t}{P_0} \right) \]

\( P_t \) and \( P_0 = \) ambient \( \text{NH}_4^+ \) conc at end and start of incubation
\( R_t \) and \( R_0 = \) atom % of the \( \text{NH}_4^+ \) pool at end and start of incub.
\( u = \) absolute uptake rate
\( d = \) regeneration rate

Glibert et al. 1982 L&O

**Field Methods**

- \( \text{NH}_4^+ \)
- \( \text{NO}_3^- / \text{NO}_2^- \)
- Urea
- DFAA
- DCAA
- Humic
- DON
- chl. \( a \)

- \( ^{15}\text{NH}_4^+ \)
- \( ^{15}\text{NO}_3^- \)

**Turnover time = conc/rate**

<table>
<thead>
<tr>
<th>Location</th>
<th>Compound Considered</th>
<th>Turnover Time</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceanic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Northeastern Pacific</td>
<td>DON</td>
<td>0.91</td>
<td>years</td>
</tr>
<tr>
<td>Equatorial Atlantic (15N-25N)</td>
<td>DON</td>
<td>0.4 to 13.2(^{\circ})</td>
<td>years</td>
</tr>
<tr>
<td>Equatorial Atlantic (15S-15N)</td>
<td>DON</td>
<td>12.7 ( \pm 26.1^{\circ} )</td>
<td>years</td>
</tr>
<tr>
<td>Equatorial Atlantic (35S-15S)</td>
<td>DON</td>
<td>2.1 to 300(^{\circ} )</td>
<td>years</td>
</tr>
<tr>
<td>Caribbean Sea</td>
<td>DON</td>
<td>40.7 ( \pm 10.4 )</td>
<td>days</td>
</tr>
<tr>
<td>Southern California Bight</td>
<td>DON</td>
<td>11 to 62</td>
<td>days</td>
</tr>
<tr>
<td>where?</td>
<td>HMW DON ( &gt;1kD )</td>
<td>( \sim 238^{\circ} )</td>
<td>days</td>
</tr>
<tr>
<td>Northern Sargasso Sea</td>
<td>Protein</td>
<td>0.38 to 3.42</td>
<td>days</td>
</tr>
<tr>
<td>Northern Sargasso Sea</td>
<td>Modified protein(^d)</td>
<td>9.04 to 32.71</td>
<td>days</td>
</tr>
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<td>Northern Sargasso Sea</td>
<td>Modified protein(^d)</td>
<td>9.04 to 32.71</td>
<td>days</td>
</tr>
<tr>
<td>Northern Sargasso Sea</td>
<td>DFAA</td>
<td>0.03 to 0.29</td>
<td>days</td>
</tr>
<tr>
<td>Central Arctic</td>
<td>DFAA</td>
<td>( \sim 2.72 )</td>
<td>days</td>
</tr>
</tbody>
</table>

Bronk 2002 Book chapter

**Monterey Bay**

- Total Gross DIN Uptake and DON Release (\( \mu \text{g-at N}^3/d \))

- Depth (m)

- March

- September

Bronk & Ward 1999 L&O
DOMINO
Dissolved Organic Matter IN the OceanS

DOC
DON
NH$_4^+$

Measurements

NH$_4^+$
NO$_3^-$/NO$_2^-$
DOC/TDN
Urea
Chl. $a$
VA
BA
PA
$\mu$mZooA

Field Study Site

Chesapeake Bay
July 23-30, 2004
Grace Henderson

Southern California Bight

Bronk & Ward 2005 DSRI

DOC/TDN
15N$_4$H$^+$

Grazing Rates

6 hr incubation
< 150 $\mu$m

15N$_4$H$^+$ Regeneration
DON

15NO$_3^-$ Regeneration
DON

14HCO$_3^-$ Regeneration
DOC

Grace Henderson
**Ambient Conditions**

- NH$_4^+$ ~9 µM
- NO$_3^-$ ~10 µM
- DOC ~185 µM
- DON ~10 µM  (C:N 18)
- urea ~ 0.6 µM

**Treatments**

- Control
- + Grazers
- 0 Virus
- 0 Virus + Grazers
- 2X Virus
- 2X Virus + Grazers

- Grazers and viruses increased the rate of NH$_4^+$ regeneration.
  - Additive effect.
• Both grazers and viruses depressed primary production.
  • Additive effect.

• Grazers increased the % of primary production released as DOC.
  • Viruses tended to decrease it.

Summary

\[
\begin{array}{c}
\text{NH}_4^+ \text{ uptake} \\
\text{NO}_3^- \text{ uptake} \\
\text{NH}_4^+ \text{ regeneration} \\
\text{Primary Production} \\
\text{DOC release} \\
\% \text{DOC released}
\end{array}
\]

+ Grazers + Viruses

\[
\begin{array}{c}
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\downarrow
\end{array}
\]

Time scales?

\[
\text{Slope} = 0.24
\]

Bronk & Steinberg In press N in the Mar Env.
DON in atmospheric deposition

<table>
<thead>
<tr>
<th>Source/Location</th>
<th>% org N</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walker Branch, TN</td>
<td>34</td>
<td>Kelly and Meagher 1986</td>
</tr>
<tr>
<td>Coastal plain, FL</td>
<td>40–63</td>
<td>Rickert 1983</td>
</tr>
<tr>
<td>Cascade Mtns., OR</td>
<td>46–72</td>
<td>Fredrikson 1976</td>
</tr>
<tr>
<td>Coastal plain, SC</td>
<td>49</td>
<td>Richter et al. 1983</td>
</tr>
<tr>
<td>Philadelphia, PA*</td>
<td>19–52</td>
<td>This study</td>
</tr>
<tr>
<td>Chesapeake Bay</td>
<td>57</td>
<td>Smilowitz et al. 1982</td>
</tr>
<tr>
<td>Rhode River, MD</td>
<td>18–44</td>
<td>Jordan et al. 1995</td>
</tr>
<tr>
<td>New Brunswick, NJ**</td>
<td>2–44</td>
<td>Scheckinger and Sanders unpubl. data</td>
</tr>
<tr>
<td>Narragansett, RI</td>
<td>19</td>
<td>Nixon et al. 1995</td>
</tr>
<tr>
<td>U.K.</td>
<td>21</td>
<td>Cornell et al. 1995</td>
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<tr>
<td>Czech Rep.</td>
<td>27</td>
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<tr>
<td>N. Carolina</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Amazonia</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Recife, Brazil</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Bermuda</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Tahiti</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>NE Atlantic</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>NE Atlantic</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Cape Cod, MA</td>
<td>43</td>
<td>Valiela et al. 1997</td>
</tr>
<tr>
<td>Lewes, DE</td>
<td>23</td>
<td>Scaulk et al. 1998</td>
</tr>
</tbody>
</table>

Seitzinger & Sanders 1999 L&O

Seitzinger et al. 2005 GBC

Allochthonous sources of DON

Atm deposition

DON

Groundwater

Galloway et al. 2008 Science

Rivers & Terrestrial run-off

DON

Sediments

Seitzinger & Sanders 1999 L&O

Refactory??
DON in rivers

The rise of urea

Allochthonous sources of DON

Effluent Organic Nitrogen

Nitrogen in Wastewater

Compounds poorly removed by treatment
Humics in source
Recalcitrant organics

Compounds formed during treatment

Dave Sedlak
Composition of EON

**TABLE 1.** Total Amino Acid Concentrations in the Secondary Treated Wastewater Effluents (Scully et al., 1988b; Confer et al., 1995; Grohmann et al., 1998; Pehlivanoglu and Sedlak, in preparation)

<table>
<thead>
<tr>
<th></th>
<th>Wagott</th>
<th>Parkin</th>
<th>Elissar</th>
<th>Hejzlar</th>
<th>Scully</th>
<th>Scully*</th>
<th>Confer</th>
<th>Pehlivanoglu</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg N/L</td>
<td>0.017</td>
<td>0.025</td>
<td>0.013</td>
<td>0.034</td>
<td>0.042-0.084</td>
<td>0.02</td>
<td>0.26</td>
<td>0.14-0.17</td>
</tr>
<tr>
<td>μM N</td>
<td>1.23</td>
<td>1.79</td>
<td>0.93</td>
<td>2.45</td>
<td>3-6</td>
<td>1.43</td>
<td>18.76</td>
<td>10-12</td>
</tr>
</tbody>
</table>

Note: Wagott, Parkin, Elissar, Hejzlar, and Scully data are obtained from Grohmann et al. (1998).

*Primary effluent.

Humic Extraction Method

Acidified Sample (pH < 2)

Humic Substances stick to the acidified resin

XAD-8 Resin

Humic fraction elutes from column with NaOH

C:N Ratio of Saturated Humics Before and After XAD Extraction

Samples Saturated at 4 μmol NH₄⁺ (mg humic-C)⁻¹

See & Bronk 2005 Mar Chem
When humics hit ~15 % they dump NH$_4^+$