Why do we care about Nitrogen?

1) N is a currency to track mass transfers in marine ecosystem
2) N dynamics important to model exchange processes
Nitrogen

• N is an essential nutrient for all living organisms (nucleic acids and amino acids)
• N has many oxidation states, which makes speciation and redox chemistry very interesting
• NH$_4^+$ is preferred N nutrient

Different forms of Marine N

<table>
<thead>
<tr>
<th>Bioavailable/Fixed (oxidation state)</th>
<th>Non-bioavailable</th>
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</thead>
<tbody>
<tr>
<td>NO$_3^-$ 5.7*10$^5$ Tg N (+5)</td>
<td>Nitrate</td>
</tr>
<tr>
<td>NO$_2^-$ 500 Tg N (+3)</td>
<td>Nitrite</td>
</tr>
<tr>
<td>NH$_4^+$ 7.0*10$^3$ Tg N (-3)</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Organic N 5.3*10$^5$ Tg N (-3)</td>
<td></td>
</tr>
</tbody>
</table>

Libes, 1992

Data: eWOCE. Plot prepared with ODV

Nitrate Section in Atlantic
Marine Fixed N Budget

Codispoti et al. (2001)

Marine Reservoir: $6.3 \times 10^5$ Tg N

Sources: 287 Tg N/yr

Atmospheric deposition: 86 Tg N/yr

$N_2$ fixation: 125 Tg N/yr

River Input: 76 Tg N/yr

Oceanic Nitrogen Budget Estimates

<table>
<thead>
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<tbody>
<tr>
<td>(Tg N y$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Inputs</td>
<td></td>
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<tr>
<td>atmospheric</td>
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<td>49</td>
<td>40</td>
<td>15</td>
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<tr>
<td>runoff</td>
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<td>17</td>
<td>25</td>
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<td>$N_2$-fixation</td>
<td>10</td>
<td>30</td>
<td>125</td>
<td>125</td>
<td>125</td>
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<tr>
<td>Total Inputs</td>
<td>44.1</td>
<td>96</td>
<td>90</td>
<td>181</td>
<td>222</td>
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<tr>
<td>Outputs</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pelagic denitrification</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>85</td>
<td>150</td>
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<tr>
<td>sedimentary denitrification</td>
<td>0</td>
<td>10</td>
<td>60</td>
<td>85</td>
<td>300</td>
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<tr>
<td>burial &amp; other</td>
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<td>36</td>
<td>38</td>
<td>19</td>
<td>32</td>
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<tr>
<td>Total Outputs</td>
<td>40.2</td>
<td>96</td>
<td>158</td>
<td>189</td>
<td>482</td>
</tr>
</tbody>
</table>

Georgia Tech Biological Oceanography
**Trichodesmium**: The Usual Suspect

- Diazotrophs, including *Trichodesmium*, are broadly distributed in nutrient poor oceanic waters, but their contribution to the marine N budget remains poorly constrained.

![Trichodesmium puffs (above) and tufts (right). Photos by Hans Paerl.](image1)

![Trichodesmium blooms from aboard ship (left) and from space (below).](image2)

*Gruber & Sarmiento 1997*
Oceanic N Cycle Schematic

New vs. Regenerated Production

Organic Matter Oxidation Sequence

Mored & Herring, 1993

Respiration

\[ \frac{1}{2} CH_4O + \frac{1}{2} O_2 \rightarrow \frac{1}{2} CO_2 + \frac{1}{2} H_2O \]

AG° (kJ/mol) -119

Denitrification

\[ \frac{1}{2} CH_4O + \frac{1}{2} NO_3^- + \frac{1}{2} H^+ \rightarrow \frac{1}{2} CO_2 + \frac{1}{2} N_2 + \frac{1}{2} H_2O \]

AG° (kJ/mol) -113

MnO_2 reduction

\[ \frac{1}{4} CH_4O + \frac{1}{4} MnO_2 + H^+ \rightarrow \frac{1}{4} CO_2 + \frac{1}{4} Mn^{2+} + \frac{1}{2} H_2O \]

AG° (kJ/mol) -96.9

Fe oxide reduction

\[ \frac{1}{4} CH_4O + Fe(OH)_3 + 2H^+ \rightarrow Fe^{2+} + \frac{1}{4} CO_2 + \frac{1}{4} H_2O \]

AG° (kJ/mol) -46.7

Sulfate reduction

\[ \frac{1}{4} CH_4O + \frac{1}{4} SO_4^{2-} + \frac{1}{4} H^+ \rightarrow \frac{1}{4} HS^- + \frac{1}{4} CO_2 + \frac{1}{4} H_2O \]

AG° (kJ/mol) -20.5

Methanogenesis

\[ \frac{1}{4} CH_4O \rightarrow \frac{1}{6} CH_4 + \frac{1}{6} CO_2 \]

AG° (kJ/mol) -17.7

Gorgia Tech Biological Oceanography
Redfield Ratio

- C:N:P
- 106:16 :1 (Redfield, 1958)
- Could there be other essential micro-nutrients?
  - Trace metals such as Fe, Zn, Co are important!

Iron and Biogeochemical Cycles

High Nutrient, Low (Medium) Chlorophyll Regions

Why aren’t the nutrients being completely utilized by phytoplankton?
Hypotheses

- Light
- Grazing
- Micronutrient limitation

In situ Fertilization experiments: Is iron limiting?

Iron needed for enzymes that facilitate electron transport, \( \text{O}_2 \) transport and other important functions.

‘Dissolved’ Iron distribution

Why are there so few measurements?
- Difficult to measure

Iron Profile

Iron has a profile between a typical metal and nutrient

What controls the distribution (vertically and horizontally) of Iron?
Sources of Iron

- Riverine
- Continental Shelves
- Dust

Riverine

- $\text{[Fe']}$ decreases further from coast.
- This is due to scavenging of Fe by particles.
- We can conclude that rivers are not an important source for the open ocean.

Scavenging: Iron sink

- Iron lost to the ocean by scavenging – the process of sticking onto particles
- Rate of scavenging not well-known
- $\text{loss} = -\text{ksc}[\text{Fe'}][P]$

Continental Shelves

1. Resuspension of sediments can release Fe
2. When organic matter decomposes, Fe can diffuse or be bio-irrigated into the water column

$$C_{106}H_{263}O_{110}N_{16}P_{1}Fe_{0.0001} + 138O_2 = 106CO_2 + 16NO_3^- + H_2PO_4^- + 0.0001Fe(OH)_2$$

Estimate global flux of $0.2-9 \times 10^{15}$ mol y$^{-1}$

Is this Fe upwelled to the surface before being scavenged?

Active area of research
Aeolian-derived Iron

- Major source of iron
- How much of the iron is soluble?
  - 1-10%
  - Active area of research: differences by provenance, processing in cloud, surface waters
- Flux: $0.2-1.2 \times 10^{10}$ mol y$^{-1}$ (assuming 2% solubility)

Iron Speciation: Complexation

- Inorganic iron: $\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Fe(OH)}_3$
  - Since ocean is oxidizing medium, reduced iron ($\text{Fe}^{2+}$) concentrations are low.
  - Most $\text{Fe}^{2+}$ produced by photochemistry, has a short lifetime
- 99% of Fe found bound to organic ligands
  - Increases solubility of iron in water column

Complexation: Active areas of research

- What is the structure of the ligand?
  - Messy organic molecular structure
- How do organisms produce it?
  - Current research suggests marine bacteria produce the ligands.
- How do organisms utilize $\text{FeL}$?
  - Light breaks down $\text{FeL}$ so organisms can grab the $\text{Fe}^{3+}$

$Fer = Fe^{3+} + FeL$

$Fe^{3+} + L' \rightleftharpoons FeL$

$K = \frac{[FeL]}{[Fe^{3+}][L']}$

$K = \text{cond. stability constant}$

specifies strength of ligand
Forms of Iron

- Dissolved iron: <0.02 µm
- Colloidal: 0.02-0.4 µm
- Particulate: >0.4 µm

Active area of research: Role of colloidal matter

Data from Boyle, 10N (Atlantic)

Putting it all together

Developing mathematical model to understand the various processes affecting Fe

Biological Uptake of Iron

- Oceanic species have higher growth rates at lower [Fe]
- They have adapted
  - Their Fe requirement is lower (small Fe:C ratio)
  - Oceanic species are smaller, so they have higher surface area:volume ratio

Data from Boyle, 10N (Atlantic)

Model Results: Iron

- >0.6 nM
- 0.4 – 0.6 nM
- 0.2 – 0.4 nM
- 0.1 – 0.2 nM
- <0.1 nM
Link between dust flux and CO₂?

Air

Dust Flux

CO₂

+ dust → + Fe → + bio. Productivity → + Export → + CO₂ drawdown

Atmospheric CO₂ Sensitivity to Increased Dust Flux

‘Paleo’ dust estimate from Mahowald et al. (1999)
Dust flux greater 5.5 times globally

Model result

Difference in primary production (gC m⁻² yr⁻¹) between high and low dust sensitivity studies. Solid line is zero contour. Positive values indicate higher production when aeolian dust supply is enhanced.

Time series of total global primary production (GtC yr⁻¹) for high (solid line), medium (dashed line), and low (dash-dotted line) dust sensitivity studies.
Convergence of Macro Nutrients in surface waters

Low Dust

High Dust

Changes in Biogeochemical Cycling

Macro Nutrients

Export of Organic Matter

Model result

Iron Fertilization

- Adding Fe artificially to transfer CO$_2$ from atmosphere to the sea

Open questions:
- How effective will it be?
- Effect on marine ecology?

The effect of additional Fe is quite small.
~11 ppm

$\Delta$pCO$_2$
(Pre-industrial - LGM)
= 80 ppm

0 100 200 300 400 500 600 700 800 900
-10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2

\[ \text{time (years)} \]
End
Alternative pathways to $N_2$

### Microbially mediated

**Nitrification**

$\text{NH}_4^+ + 2\text{O}_2 \rightleftharpoons \text{NO}_2^- + \text{H}_2\text{O} + 2\text{H}^+$

**Anammox**

$\text{NH}_4^+ + \text{NO}_2^- \rightleftharpoons N_2 + 2\text{H}_2\text{O}$

**Heterotrophic Denitrification**

$5\text{CH}_4\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightleftharpoons 2\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O}$

**OLAND**

$\text{NH}_4^+ + \frac{1}{2}\text{O}_2 \rightleftharpoons \frac{7}{5}\text{N}_2 + \frac{7}{5}\text{H}_2\text{O} + \text{H}^+$

**Nitrogen Fixation**

$\text{N}_2 + 5\text{H}_2\text{O} \rightleftharpoons 2\text{NH}_3 + 2\text{OH}^- + \frac{3}{2}\text{O}_2$

### Chemical Reactions

**MnO$_2$ Reduction**

$3\text{MnO}_2 + 2\text{NH}_4^+ + 4\text{H}^+ \rightleftharpoons 3\text{Mn}^{2+} + \text{N}_2 + 6\text{H}_2\text{O}$

$4\text{MnO}_2 + \text{NH}_4^+ + 6\text{H}^+ \rightleftharpoons 4\text{Mn}^{2+} + \text{NO}_3^- + 5\text{H}_2\text{O}$

**Mn$^{2+}$ Oxidation**

$5\text{Mn}^{2+} + 2\text{NO}_3^- + 4\text{H}_2\text{O} \rightleftharpoons 5\text{MnO}_2 + \text{N}_2 + 8\text{H}^+$

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