Lecture 23: Marine Nitrogen Cycle

Karen Casciotti
Overview

- Why study the nitrogen cycle?
- Nitrogen pools, fluxes, and distributions
- Biogeochemical transformations
- Open questions
- Human impacts on the nitrogen cycle
Life Needs Nitrogen

Overall Phytoplankton
\[ C : N = 6.6 \]
\[ N : P = 16 : 1 \]

- \( \text{C}_{39}\text{H}_{53}\text{O}_{24}\text{N}_{15}\text{P}_{4} \)
  - \( C : N = 2.6 \)
- \( \text{C}_{61}\text{H}_{97}\text{O}_{20}\text{N}_{16} \)
  - \( C : N = 3.8 \)

Figure by MIT OCW.
## Nitrogen transformations

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Oxidation state</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{org}}$, NH$_4^+$</td>
<td>-III</td>
<td>Reduced</td>
</tr>
<tr>
<td>NH$_2$OH</td>
<td>-I</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>N$_2$O</td>
<td>I</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>V</td>
<td>Oxidized</td>
</tr>
</tbody>
</table>
Marine Nitrogen Pools

- **Nitrogen gas (N₂)**
  - Nitrous oxide (N₂O)
  - Nitric oxide (NO)

- **“Fixed” Nitrogen**
  - Inorganic nitrogen:
    - **Nitrate (NO₃⁻)**
    - Nitrite (NO₂⁻)
    - Ammonium (NH₄⁺)
  - Organic nitrogen:
    - **Detritus** and Living biomass
    - Dissolved organic matter
      - Proteins/Amino acids
      - Urea
      - Nucleic acids

- Nitrogen gas (N₂) 95.2%
- “Fixed” Nitrogen 2.5%
- Detritus and Living biomass 2.3%
Dugdale and Goering, 1967: the New Production paradigm

- **New Production**
  - Phytoplankton
  - Zooplankton

- **N$_2$ fixation**
- **Grazing**
- **Regenerated Production**
  - NH$_4^+$
  - DON

- **Export production**
  - Bacteria

- **Euphotic zone**
- **Aphotic zone**

- **Nitrification**
  - NO$_3^-$
  - NH$_4^+$

- **Ammonification**
  - Dead organic matter
Dugdale and Goering, 1967: the New Production paradigm

- Introduced the concept of balanced new and export production
- Introduced the use of $^{15}$N-labeled compounds to measure rates of new and regenerated production.

“Ammonium is an important nitrogen source... but nitrate and nitrogen fixation are the most important parameters with respect to nitrogen limitation of primary productivity.”
Eppley and Peterson. 1979: Export Production and the “Biological Pump”

- **N₂ fixation**
- **CO₂**
- Atmospheric deposition

**New Production**

**Phytoplankton**

**Regenerated Production**

**Zooplankton**

**Export production**

- NH₄⁺
- DON, DOC

**Euphotic zone**

**Aphotic zone**

- Dead organic matter

**Nitrogen Cycle**

- NH₄⁺ + CO₂ → NO₃⁻ + CO₂

**Carbon Cycle**

- CO₂ + CO₂ → CO₂ + CO₂

**Atmospheric deposition**
“Only the sinking flux due to new production associated with N₂ fixation and atmospheric sources of N can be identified as... transport of atmospheric CO₂ to the deep ocean.”

Introduced “f ratio” as ratio of new/total production
Sea Surface Nitrate Map
‘HNLC’ regions (high nutrient, low chlorophyll)

These regions are typically limited by other factors:
- Light
- Temperature
- Iron, micronutrients
Sea Surface Nitrate Map
Distribution of Nitrate in Atlantic Ocean
Nitrate section through the ETP
“Redfield Ratio”: $C_{106}:N_{16}:P_1$ applies to both the average composition of phytoplankton biomass and the ratio of nitrate and phosphate generated from organic matter remineralization under oxic conditions.

Remineralization of generalized organic matter:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138 O_2$$

$$106 CO_2 + 16 HNO_3 + H_3PO_4 + 122 H_2O$$

$$(106 O_2)\quad (32 O_2)$$
## Global Thermohaline Circulation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLW</td>
<td>Surface layer water</td>
</tr>
<tr>
<td>SAMW</td>
<td>Subantarctic mode water</td>
</tr>
<tr>
<td>RSW</td>
<td>Red sea water</td>
</tr>
<tr>
<td>AABW</td>
<td>Antarctic bottom water</td>
</tr>
<tr>
<td>NPDW</td>
<td>North pacific deep water</td>
</tr>
<tr>
<td>ACCS</td>
<td>Antarctic circumpolar current system</td>
</tr>
<tr>
<td>CDW</td>
<td>Circumpolar deep water</td>
</tr>
<tr>
<td>NADW</td>
<td>North atlantic deep water</td>
</tr>
<tr>
<td>UPIW</td>
<td>Upper intermediate water, $26.8 &lt; \sigma_0 &lt; 27.2$</td>
</tr>
<tr>
<td>LOIW</td>
<td>Lower intermediate water, $27.2 &lt; \sigma_0 &lt; 27.5$</td>
</tr>
<tr>
<td>IODW</td>
<td>Indian ocean deep water</td>
</tr>
<tr>
<td>BIW</td>
<td>Banda intermediate water</td>
</tr>
<tr>
<td>NIIW</td>
<td>Northwest Indian intermediate water</td>
</tr>
</tbody>
</table>

Figure by MIT OCW.
Distribution of Nitrate in Atlantic Ocean
Overview

✓ Why study the nitrogen cycle?

✓ Nitrogen pools, fluxes, and distributions

• Biogeochemical transformations

• Open questions

• Human impacts on the nitrogen cycle
Microbial Nitrogen Cycle

Nitrogen fixation

Narration:

Organic matter (Org) → Ammonia (NH₃) → Ammonia oxidation → Ammonium (NH₄⁺) → Nitrite oxidation → Nitrite (NO₂⁻) → Nitrate oxidation → Nitrate (NO₃⁻) → Nitrification (N₂O, N₂)

Denitrification:

Anammox → N₂O → Denitrification → NO

Assimilation:

N₂ → Ammonia (NH₃) → Ammonia oxidation → Ammonium (NH₄⁺) → Assimilation (N₂O, N₂)

Oxidation state:

(-III) (III) (V) (I) (II) (III) (V)
Overview

- Why study the nitrogen cycle?
- Nitrogen pools, fluxes, and distributions
  - Biogeochemical transformations
  - Open questions
  - Human impacts on the nitrogen cycle
Redfield Ratios and Remineralization

“Redfield Ratio”: \( \text{C}_{106} \text{N}_{16} \text{P}_1 \) applies to both the average composition of phytoplankton biomass and the ratio of nitrate and phosphate generated from organic matter remineralization under oxic conditions.

Remineralization of generalized organic matter:
\[
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138 \text{ O}_2 \\
\downarrow \\
106 \text{ CO}_2 + 16 \text{ HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{ H}_2\text{O} \\
\uparrow \quad \uparrow \\
(106 \text{ O}_2) \quad (32 \text{ O}_2)
\]
HOTS: N$_2$ fixation may account for 30-50% of export production
Evidence for $\text{N}_2$ Fixation

- Occurrence of nitrogen fixing species, such as *Trichodesmium spp*.

- Low $\delta^{15}\text{N}$ of sinking organic matter suggestive of significant $\text{N}_2$ fixation

- Acetylene reduction or $^{15}\text{N}_2$ incorporation rate estimates
Oceanic Diazotroph Diversity

Zehr, 2000
Trends in Microbiology

Image removed due to copyright restrictions.
Water Column Denitrification Zones

Figure 7. Dissolved O$_2$ (µmol/L) at 400 m from the World Ocean Atlas [Levitus and Boyer, 1998].

Arabian Sea

Eastern Tropical North Pacific

Eastern Tropical South Pacific
Overview

✓ Why study the nitrogen cycle?
✓ Nitrogen pools, fluxes, and distributions
✓ Biogeochemical transformations

• Open questions
• Human impacts on the nitrogen cycle
Major Questions in Marine N Cycling

• Is the nitrogen cycle in balance?
• How does the N cycle vary on glacial/interglacial timescales?
• How is N₂O produced in the ocean?
• By what mechanism is ‘extra excess N₂’ formed?
## Nitrogen Inputs to the Ocean

<table>
<thead>
<tr>
<th></th>
<th>Nitrogen Fixation</th>
<th>Atmospheric Deposition</th>
<th>Continental Runoff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluxes in Tg N/yr</td>
<td>25</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Codispoti and Christensen [1985]</td>
<td>125 ± 50</td>
<td>15 ± 5</td>
<td>41 ± 20</td>
</tr>
<tr>
<td>Gruber and Sarmiento [1997] (preindustrial)</td>
<td>125 ± 50</td>
<td>30 ± 5</td>
<td>76 ± 20</td>
</tr>
<tr>
<td>Gruber and Sarmiento [1997] (postindustrial)</td>
<td>Same as G&amp;S</td>
<td>86</td>
<td>Same as G&amp;S</td>
</tr>
<tr>
<td>Codispoti et al [2001]</td>
<td>Same as G&amp;S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Includes DON
# Nitrogen Exports from the Ocean

<table>
<thead>
<tr>
<th>Fluxes in Tg N/yr</th>
<th>Organic Burial</th>
<th>Sedimentary Denitrification</th>
<th>Water column Denitrification</th>
<th>Anammox</th>
</tr>
</thead>
<tbody>
<tr>
<td>Codispoti and Christensen [1985]</td>
<td>21</td>
<td>60</td>
<td>60</td>
<td>?</td>
</tr>
<tr>
<td>Gruber and Sarmiento [1997] (preindustrial)</td>
<td>15 ± 5</td>
<td>85 ± 20</td>
<td>80 ± 20</td>
<td>?</td>
</tr>
<tr>
<td>Gruber and Sarmiento [1997] (postindustrial)</td>
<td>25 ± 10</td>
<td>95 ± 20</td>
<td>80 ± 20</td>
<td>?</td>
</tr>
<tr>
<td>Codispoti et al [2001]</td>
<td>25 ± 10</td>
<td>300</td>
<td>150</td>
<td>?</td>
</tr>
</tbody>
</table>
Nitrogen Budgets

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sources</td>
<td>74</td>
<td>181 ±44</td>
<td>231 ±44</td>
</tr>
<tr>
<td>Total sinks</td>
<td>142</td>
<td>184 ±29</td>
<td>204 ±30</td>
</tr>
<tr>
<td>Residence time of N in the ocean</td>
<td>5,000 years</td>
<td>3,500 years</td>
<td>1,500 years</td>
</tr>
</tbody>
</table>

Is the N cycle in balance? Maybe not!
Is it a moving target?
What are the consequences?
Major Questions in Marine N Cycling

- Is the nitrogen cycle in balance?
- How does the N cycle vary on glacial/interglacial timescales?
- How is N$_2$O produced in the ocean?
- By what mechanism is ‘extra excess N$_2$’ formed?
Higher δ15N in diatom-bound organic matter suggests higher degree of nitrate utilization in the Antarctic zone during glacial times.

Sigman et al., 1999
Southern ocean nitrate utilization changes

Figure by MIT OCW.

Sigman and Boyle, 2000
Changes in Denitrification

Sedimentary $\delta^{15}$N changes from the ETNP

Chart removed due to copyright restrictions.
Changes in Denitrification

Present

High $\delta^{15}$N

High $\delta^{15}$N-PN

LGM

Lower $\delta^{15}$N

Lower $\delta^{15}$N-PN
Major Questions in Marine N Cycling

- Is the nitrogen cycle in balance?
- How does the N cycle vary on glacial/interglacial timescales?
- How is $N_2O$ produced in the ocean?
- By what mechanism is ‘extra excess $N_2$’ formed?
Anticorrelation of N\textsubscript{2}O and O\textsubscript{2} concentrations suggests N\textsubscript{2}O is produced during organic matter remineralization (nitrification)

Vertical NO\textsubscript{2} and O\textsubscript{2} profiles at three different stations in the western North Atlantic, a, slope water of off Nova Scotia (42° 18' N, 61° 24' W); b, Gulf Stream (39° 07' N, 62° 21' W); c, Sargasso Sea (35° 52' N, 63° 44' W)

Figure by MIT OCW.

Yoshinari, 1976
Nitrification

Ammonia-oxidizing nitrifiers:  
*Nitrosomonas, Nitrosospira, Nitrosococcus*

\[ \text{NH}_3 + \frac{3}{2} \text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2 \text{H}^+ \]

Nitrite-oxidizing nitrifiers:  
*Nitrobacter, Nitrospira, Nitrospina*

\[ \text{NO}_2^- + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_3^- \]

\[ \text{NH}_3 + 2 \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2 \text{H}^+ \quad \text{Overall} \]
Chart removed due to copyright restrictions.
Major Questions in Marine N Cycling

- Is the nitrogen cycle in balance?
- How does the N cycle vary on glacial/interglacial timescales?
- How is $N_2O$ produced in the ocean?
- By what mechanism is ‘extra excess $N_2$’ formed?
Nitrate deficits

“N*” based on Redfield relationship of NO$_3^-$ and PO$_4^{3-}$:

$\text{(CH}_2\text{O)}_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138 \text{ O}_2$
$106 \text{ CO}_2 + 16 \text{ HNO}_3 + \text{H}_3\text{PO}_4 + 119 \text{ H}_2\text{O}$

N* = [NO$_3^-$] - 16 [PO$_4^{3-}$] + constant

Denitrification: N* ↓ (lower [NO$_3^-$], unchanged [PO$_4^{3-}$])
Also, higher N$_2$/Ar because of N$_2$ production from nitrate production/accumulation of N$_2$ yields “excess N$_2$”

But, there’s more N$_2$ than expected from nitrate deficits!!
this phenomenon has been termed “extra excess N$_2$”
“Extra Excess N”

What is it?
- Discrepancy between N deficit based on N:P ratios and N\textsubscript{2} excess from N\textsubscript{2}/Ar ratios

How could it be explained?
- Remineralization of organic matter with high N:P ratio
- Lateral mixing of N\textsubscript{2} from sedimentary denitrification
- Anammox
Anammox

\[ \text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} \]

**Who:** Bacteria in the order *Planctomycetales*

**What:** anaerobically combine NH\(_4^+\) and NO\(_2^-\) to form N\(_2\)

**Where:** anoxic sediments and watercolumns; Black Sea; Gulfo Dulce, Chile; Benguela Upwelling System

**When:** ??

**Why:** ??

**How:** Anammoxosome; enzymology known incompletely, but genome sequencing is providing targets for biochemical analysis.
Measurement of Anammox

**Anammox**

Organic geochemistry:
unique ladderane lipids

Isotopic tracers:
$^{15}\text{NH}_4^+ + ^{14}\text{NO}_2^-$ → $^{15}\text{N}^{14}\text{N}$

Molecular biology:
Detection of anammox
16S rRNA genes

Kuypers et al., Nature 2003
Isotopic Tracers of Anammox

Masses For N₂

14-14
14-15
15-15

15NH₄⁺ 14NO₃⁻ 14NH₄⁺ 15NO₃⁻
Isotopic Tracers for Anammox

15N-NH4 addition

15N-NO3 addition

anammox2
denitrif2

14-14 14-15 15-15
Overview

- Why study the nitrogen cycle?
- Nitrogen pools, fluxes, and distributions
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  - Human impacts on the nitrogen cycle
Human perturbation of the N cycle

Nitrogen fixation by humans is now equivalent to natural terrestrial nitrogen fixation (~140 Tg N/yr).

The amount of human-produced N entering the oceans is not well known, but is on the order of 20-40 Tg N/yr.
Eutrophication and Anoxia

Mississippi River nitrate loads and Gulf of Mexico Hypoxia
Sea Surface Chlorophyll a