The Global Nitrogen Cycle, and Linkages Between C, N, and P Cycles

• The Contemporary N Cycle
  - Basic Facts
  - Reservoirs and Fluxes

• Global N Budget
  - balance between N-fixation and denitrification sets the level of bioavailable N
  - anthropogenic impacts
  - temporal changes, paleoceanography

• Linking the Global N Cycle to Global Cycles of C and P

Basic Nitrogen Facts

• An essential (limiting) nutrient:
  - enzymes
  - amino acids, proteins
  - pigments (e.g., Chlorophyll)

• Range of valance (oxidation) states: \(\text{NH}_3\) (-3) to \(\text{NO}_3^-\) (+5)
  - microbes capitalize on potential transformations of N
  - use energy released by changes in redox potential

• Microbial reactions drive the N cycle
  - Nitrogen fixation:
    \[\text{N}_2 + 8\text{H}^+ + 8e^- + 16 \text{ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + 16 \text{ADP} + 16 \text{P}_i\]
  - Denitrification:
    \[5\text{CH}_2\text{O} + 4\text{H}^+ + 4\text{NO}_3^- \rightarrow 2\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O}\]
  - Anammox:
    \[\text{NH}_4^+ + \text{NO}_2^- \rightarrow 2\text{N}_2 + 2\text{H}_2\text{O}\]
Microbial Transformations in the N Cycle

Fig. 12.1

Nitrogen Redox Chemistry

Figure 1 The processes of nitrogen fixation, assimilation, nitrification, decomposition, ammonification, and denitrification (after Karl, 2002).
Role of N in Biogeochemistry

- Bioavailability of N (and/or P) can limit NPP on land/oceans; controls size of biomass
- N has multiple oxidation states:
  - -3 in NH$_3$ ammonia
  - 0 in N$_2$ nitrogen
  - +1 in N$_2$O nitrous oxide
  - +2 in NO nitric oxide
  - +3 in NO$_2^-$ nitrite ion
  - +4 in NO$_2$ nitrogen dioxide
  - +5 in NO$_3^-$ nitrate ion
- Microbial processes exploit redox gradients (for energy purposes) and thereby mediate fluxes
- Most abundant form of N is atmospheric N$_2$
  - N$_2$ is “fixed” (oxidized) by bacteria and plants in N-poor regions
  - Denitrifying bacteria reverse process.

Global Nitrogen Reservoirs

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>3.5 x 10$^{21}$ g</td>
</tr>
<tr>
<td>Soil organic matter</td>
<td>95-140 x 10$^{15}$ g</td>
</tr>
<tr>
<td>Terrestrial biomass</td>
<td>3.5 x 10$^{15}$ g</td>
</tr>
<tr>
<td>Total ocean DIN (NO$_3^-$)</td>
<td>570 x 10$^{15}$ g</td>
</tr>
<tr>
<td>Ocean dissolved N$_2$ gas</td>
<td>1.1 x 10$^{19}$ g</td>
</tr>
<tr>
<td>Oceanic biota</td>
<td>4.7 x 10$^{14}$ g</td>
</tr>
</tbody>
</table>

- Soil inorganic N pool (NO$_3^-$, NH$_4^+$) small, but annual flux large
- Annual terrestrial N requirement 1200 x 10$^{12}$ g N yr$^{-1}$
  - 12% from N fixation
  - 88% from recycling
The Global Nitrogen Cycle: Fluxes Between Reservoirs

Fig. 12.2. Units are $10^{12}$ g N/yr (Tg)

### N-bioavailability: ‘fixed N’

- Balance of fixation and denitrification affects global N bioavailability
- Pool of available inorganic N is always small. Like P, bioavailable N is rapidly taken up
- All biologically available N originally came from atmospheric N, via lightning, meteorite impacts etc., or by biological fixation
- Current rates are dominated by biological fixation:
  - Lightning $<3 - 5 \times 10^{12}$ N yr$^{-1}$
  - Biological fixation $140 \times 10^{12}$ yr$^{-1}$
Nitrogen Fixation

- Total terrestrial biological N fixation ≈ 140 x 10^{12} g N yr^{-1}
  40 x 10^{12} g N yr^{-1} from leguminous crops (enzyme-mediated) and
  > 80 x 10^{12} g N yr^{-1} from fertilizer addition
  Haber process:
    natural gas (CH_4) is burned to produce H_2
    H_2 + N_2 (under high T and P) = NH_3
  20 x 10^{12} g N yr^{-1} from fossil fuel combustion
- N ≡ N, triple bond takes massive energy to break
- In total, 240 x 10^{12} g N yr^{-1} of newly fixed N is delivered from the atmosphere to the Earth’s land surface:
  40% via natural processes
  60% via human-derived sources

Terrestrial Nitrogen cycle

- Allochthonous N inputs:
  ° Terrestrial N fixation 240 x 10^{12} g N yr^{-1}
- N-removal from terrestrial soils:
  ° Rivers carry ~ 36 x 10^{12} g N yr^{-1} to the oceans
  ° Denitrification in soils approximately balances N inputs
- Global terrestrial denitrification: 13-233 x 10^{12} g N yr^{-1}
  - Wetlands account for ~50%
  - Pre-industrial denitrification ≈ 70 x 10^{12} g yr^{-1}
- Denitrification produces N_2 and N_2O in a ratio of 22:1
- Biomass burning causes denitrification, ~ 50 x 10^{12} g N yr^{-1}(as N_2)
Oceanic Nitrogen Cycle

• **Allochthonous N inputs:**
  - Rivers to oceans, $\sim 36 \times 10^{12}$ g dissolved N yr\(^{-1}\)
  - Biological fixation, $\sim 15 \times 10^{12}$ g N yr\(^{-1}\)
  - Precipitation, $\sim 30 \times 10^{12}$ g N yr\(^{-1}\) (ammonium and nitrate)

• **Autochthonous N input:**
  - Deep water N pool, $570 \times 10^{15}$ g N yr\(^{-1}\)

• Most NPP supported by recycling

• Little burial of N in marine sediments

• Oceanic N cycle closed by denitrification in low O\(_2\) environments
  $\sim 110 \times 10^{12}$ g N yr\(^{-1}\)

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Anthropogenic activity

• Planting of N fixing crops and fertilizer production (from N+H at high T)
  $>80 \times 10^{12}$ g yr\(^{-1}\)

• Fossil fuel combustion: $\sim 20 \times 10^{12}$ g yr\(^{-1}\)
  - produces NO\(_x\)
  - Some NO\(_x\) transported long distances -- seen in Greenland ice

• Total flux of fixed N = $240 \times 10^{12}$ g yr\(^{-1}\)
  - 40% natural
  - 60% anthropogenic

• Groundwater N increasing from fertilizer leaching: $11 \times 10^{12}$ g yr\(^{-1}\)

*Image from Holland et al., 2005 EOS 86, 254*
Nitrous oxide ($N_2O$)

- $N_2O$ is a by-product of nitrogen fixation and denitrification
- $N_2O$ is an important greenhouse gas; has $300x$ the impact of $CO_2$, also destroys $O_3$
- $N_2O$ sink: stratospheric destruction via photolysis
  - $80\% \rightarrow N_2$
  - $20\% \rightarrow NO$, which destroys $O_3$
- MRT $N_2O$ in atmosphere ~ 120 yrs -- uniformly distributed
- Seawater is a source of $N_2O$ to the atmosphere, but some $N_2O$ is denitrified within water column

Anthropogenic Impact on $N_2O$ Cycle

- Soils are main source of $N_2O$ to atmosphere,
- Cultivation increases $N_2O$ production rate as increases nitrification and denitrification rates
- Manure production tracks $N_2O$ increases

But NOAA says

- Sinks exceed identified sources, yet we observe an increase in atmospheric $N_2O$ -- more research needed

From Holland et al., 2005 EOS 86, 254
### Global Budget of Atmospheric Ammonia

<table>
<thead>
<tr>
<th>Sources</th>
<th>&quot;Best&quot; estimate</th>
<th>Potential range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domestic animals</td>
<td>32</td>
<td>24–40</td>
</tr>
<tr>
<td>Sea surface</td>
<td>13</td>
<td>8–18</td>
</tr>
<tr>
<td>Undisturbed soils</td>
<td>10</td>
<td>6–45</td>
</tr>
<tr>
<td>Fertilizers</td>
<td>9</td>
<td>5–10</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>5</td>
<td>1–9</td>
</tr>
<tr>
<td>Human excrement</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Coal combustion</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Automobiles</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td><strong>Total inputs</strong></td>
<td><strong>75</strong></td>
<td><strong>50–128</strong></td>
</tr>
</tbody>
</table>

**NH₄⁺ sources:**
- 70% anthropogenic
- 30% natural

**Natural inputs:**
- 22.8

**Natural sinks:**
- 57

### Global Emissions of NOₓ

<table>
<thead>
<tr>
<th>Sources</th>
<th>Magnitude (10^{12}) g N/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel combustion</td>
<td>24¹</td>
</tr>
<tr>
<td>Soil release (natural and anthropogenic)</td>
<td>12²</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>8⁴</td>
</tr>
<tr>
<td>Lightning</td>
<td>5</td>
</tr>
<tr>
<td>NH₃ oxidation</td>
<td>3⁵</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0.4</td>
</tr>
<tr>
<td>Transport from stratosphere</td>
<td>0.1 (0.6 total NOₓ)</td>
</tr>
</tbody>
</table>
**Relationship between NO$_3^-$ in Ice Cores and NO$_x$ Emissions**

- Early atmosphere dominated by N$_2$ and CO$_2$
- N fixation by lightning and meteor shock waves (6% of current rate); May have been important for origin of life
- Lack of N may have lead to early evolution of N fixers
- MRT of N in atmosphere wrt fixation by lightning ~ 1.3 x 10$^9$ y
  Add in biological fixation MRT decreases to ~ 2 x 10$^6$ y
- Denitrification important for maintaining atm N$_2$ level
- Unclear whether denitrification evolved before or after O$_2$ in atm; since denitrifiers tolerate low O$_2$, perhaps after
- Nitrification evolved after O$_2$ in atmosphere--process requires it
- Both processes are at least 1 x 10$^9$ yrs old

**Global N cycle on the Early Earth**
N isotopes in Paleoceanography

- $^{15}\text{N}/^{14}\text{N}$ in sedimentary organic N and forams is useful for assessing paleo N chemistry
- Denitrification preferentially removes $^{14}\text{NO}_3^-$ from the ocean, increases $^{15}\text{N}/^{14}\text{N}$ in DOM, residual $\text{NO}_3^-$ is heavy (enriched in $^{15}\text{N}$)
- MRT of N in ocean water is $\sim 8000$ yrs
- N may not be in steady state:
  - High N inputs during LGM supported high NPP during LGM
  - Low $^{15}\text{N}/^{14}\text{N}$ in LGM sediment OM supports this notion
  - Denitrification rates today exceed inputs, a re-adjustment to the perturbation to the N-cycle during the LGM
  - Changes in N cycling may accompany climatic changes

N versus P Biogeochemistry

- N occurs in valance states ranging from (-3) to (+5), and microbes capitalize on transformations of N from one state to another for energy
- P is almost always at a valance of (+5) as $\text{PO}_4^{3-}$
## N versus P Biogeochemistry (cont’ d.)

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Mass N (in grams)</th>
<th>Mass P (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>$3.5 \times 10^{21}$</td>
<td>$0.00003 \times 10^{12}$</td>
</tr>
<tr>
<td>Soil Organic Matter</td>
<td>$95-140 \times 10^{15}$</td>
<td>$100-200 \times 10^{12}$</td>
</tr>
<tr>
<td>Terrestrial Biomass</td>
<td>$3.5 \times 10^{15}$</td>
<td>$3 \times 10^{12}$</td>
</tr>
<tr>
<td>Total oceans (NO$_3^-$, DIP)</td>
<td>$570 \times 10^{15}$</td>
<td>$93.5 \times 10^{12}$</td>
</tr>
<tr>
<td>Ocean dissolved N$_2$ gas</td>
<td>$1.1 \times 10^{19}$g</td>
<td>N/A</td>
</tr>
<tr>
<td>Oceanic biota</td>
<td>$4.7 \times 10^{14}$</td>
<td>$0.05-0.1 \times 10^{12}$</td>
</tr>
</tbody>
</table>

### Major Differences in Reservoirs & Fluxes:
- No gaseous forms of P, whereas N$_2$(g) is largest pool.
- Ultimate N bioavailability via microbial transformations, whereas ultimate P bioavailability via weathering.
- N more enriched than P in organic matter, relative to C:
  - N:P ratio in marine (16:1) primary producer biomass.

## Linked N-, P-, and Carbon-Cycling

- P as ATP important in all biochemical processes, including C-fixation, protein (nitrogenous compound) production.
- Primary production requires both N & P, both tend to be present at low - limiting levels.
- Redfield C:N:P used to predict biomass production.
- N-fixation rates inversely related to N:P in soil.
Interlinkages Between Global Cycles

Example: Links between the global cycles of carbon, oxygen, nitrogen and phosphorus:

Photosynthesis and respiration ... *Redfield-Richards Equation:*

\[ \text{CO}_2 + N + P + H_2O \xrightarrow{P \_ R} \text{Organic matter} + O_2 \]

106 \( \text{CO}_2 \) + 16 HNO\(_3\) + 1 H\(_3\)PO\(_4\) + 122 H\(_2\)O

\[
[(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)] + 138 \text{O}_2
\]

The *stoichiometric* changes in dissolved species during respiration:

\[
\begin{array}{cccc}
\Delta C & \Delta N & \Delta P & \Delta O \\
+106 & +16 & +1 & -276
\end{array}
\]
Thus ... global C fluxes imply associated N, P, and O fluxes

Looking just at ocean – atmosphere interactions.....
What are the associated nitrogen and phosphorus fluxes?
The interlinked fluxes can be computed from another cycle if the stoichiometry of the transformation is known.....as in the case of photosynthesis / respiration:

\[
106 \text{CO}_2 + 16 \text{HNO}_3 + 1 \text{H}_3\text{PO}_4 + 122 \text{H}_2\text{O} \xrightarrow{\Delta} [(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)] + 138 \text{O}_2
\]

Stoichiometric changes in dissolved species during respiration:

<table>
<thead>
<tr>
<th>(\Delta C)</th>
<th>(\Delta N)</th>
<th>(\Delta P)</th>
<th>(\Delta O_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+106</td>
<td>+16</td>
<td>+1</td>
<td>-138</td>
</tr>
</tbody>
</table>

Thus, ratios of respiration fluxes:

\[
\frac{C}{N} = \frac{106}{16} = 6.6 \quad \frac{C}{P} = \frac{106}{1} = 106
\]

\[
\frac{N}{P} = \frac{16}{1} = 16 \quad \frac{O_2}{C} = -\frac{138}{106} = -1.3
\]

**Linked N-, P-, and Carbon-Cycling**

- High demand for P by N-fixing organisms links global C-N-P cycles, with P being the ultimate limiting nutrient

- Despite this, NPP often shows an immediate response to N additions

- It continues to be a puzzle, and source of debate
Lecture Summary

• Microbial reactions drive the N cycle, taking advantage of the various valences in which N occurs in the environment

• Atmospheric N\(_2\) (gas) is the largest N-reservoir, but inaccessible to organisms unless converted to ‘fixed-N’

• Unclear whether the global N budget is balanced: Denitrification is used to balance N-fixation, but global estimates of both are not well constrained

• \(^{15}\text{N}/^{14}\text{N}\) in sedimentary organic N and forams is useful for assessing paleo N chemistry

• Anthropogenic impacts on the global N cycle have been substantial

• Nature of N & P reservoirs and processes that impact their bioavailability are fundamentally different, can be linked through stoichiometry

Term Project Oral Presentations

• 10-minute PowerPoint or Acrobat oral presentation of your term paper on either December 10 or 12.
  
  12/10: Babiano, Jerolmon, Kleven, Ko
  12/12: Mura, Roberts, Sato, Shimabukuro

• ≈ 5 minutes after each talk for questions.

• Email me your powerpoint the day before your presentation, by 5 p.m.

• Grading (30% of your Term Project grade):
  Comprehensiveness of the material covered – 20%
  Organization of talk, including the quality of the conclusions given – 20%
  Quality and use of figures – 20%
  Keeping within the allotted time – 15%
  Participation in discussions – 15%
  Quality of speaking style – 10%
Tips for Oral Presentations

1. Comprehensiveness of Material Covered
   - Was the subject matter covered comprehensively?
   - Did the speaker tell a complete story? or were there loose ends?

2. Talk Organization
   - Was the talk well organized?
   - Did one slide flow logically into the next?
   - Could you easily follow the speaker’s reasoning?
   - Were the main points summed up in a conclusions slide?

Tips for Oral Presentations (cont’d.)

3. Talk Delivery
   - Was the speaker well-spoken, avoiding ‘ahs’ and ‘uhms’
   - Was the speaker easy to understand? Why or why not?
   - Did the speaker emphasize the main points for each slide, without rambling on about less central details?
   - Did the speaker make clear declarative statements, rather than making statements sound like a question?

4. Quality & Use of Figures
   - Were the figures legible and interesting?
   - How well were the figures used to support the points made in the talk?
   - Did the speaker adequately explain each figure?

5. Did the speaker keep within the allotted time?
Peer Review of Oral Presentations

Please provide a rating and comments on the following criteria. Try to give the speaker a balanced summary of the things they are doing well, and things they should try to improve.

Peer Evaluator: __________________________ Presentator: __________________________

Topic: __________________________

<table>
<thead>
<tr>
<th>Evaluation Criterion</th>
<th>Score (1 to 5)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Was the talk well organized?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Could you easily follow the speaker’s reasoning?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Were the figures legible, of good quality, useful?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Did the speaker adequately explain each figure?</td>
<td></td>
<td></td>
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<tr>
<td>Did the speaker seem to be adequately prepared?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Did the speaker adequately communicate the significance of topics?</td>
<td></td>
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</tr>
<tr>
<td>What was the best aspect(s) of the talk?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>What aspect(s) of the talk could use the most improvement?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Rating</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Draft Term Paper Common Edits

- Figures must be cited in order
- Do not begin a sentence with ‘Figure X shows…’
- Really integrate figures & tables into text
- Grammar:
  - avoid possessives
  - avoid indefinite articles/pronouns
  - only use ‘which’ after a comma; otherwise use ‘that’
  - ‘data’ is a plural noun; make sure verb agrees
  - define all acronyms 1st time used
  - improper use of the word ‘uptake’:
    - ‘iron uptake by phytoplankton’ (OK)
    - ‘phytoplankton uptake iron’ (Not OK), rather ‘phytoplankton take up iron’
New Due Dates for Term Paper!!

- Drafts will be returned **Thursday, 12/5** in class

- Final papers are due **Monday, 12/16**, an extra 4 days
  - printouts either in my mailbox in the Ocean office mailroom or under my door by 5 p.m. on Monday 12/16

Draft Term Paper Common Edits (cont’d.)

- An abstract is not part of the body of the paper, so it is not given a heading #.

- References in Bibliography must ALL be in the same format, must be in alphabetical order by last name of 1st author, all must cite year

- In-text references must show 1st author ‘et al.’, if # authors >2, both authors if a 2-authored paper, and MUST cite year: e.g., ‘Wang et al. (2009) demonstrated that the mineral was dissolving…’

- Do not anthropomorphize! E.g., ‘The carbon cycle suggests that the ocean is a sink for CO$_2$’ – NOT OK. Rather, ‘Examination of fluxes between carbon reservoirs clearly shows that the oceans are a sink for atmospheric CO$_2$.’