Nutrient Cycling 1: The nitrogen cycle

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I. Intro to the Nitrogen Cycle

Productivity of many ecosystems (managed & unmanaged) is limited by nitrogen availability:
- terrestrial - temperate, boreal, arctic
- aquatic - open oceans

Fluxes: several important biosphere-atmosphere N exchanges
- biological: fixation, denitrification, nitrification
- abiotic: industrial fixation, lightning fixation, fossil fuel and biomass burning, deposition

Biological cycling within systems greatly outweighs inputs/outputs (i.e., N cycle is much more "closed" than the C cycle)

A. Global Pools:
- most in the atmosphere, but not biologically available
- reactive N in atmosphere: trace gases
- lots in sediments and rocks, but not available
- inorganic N in ocean is next largest
- organic pools in plants and soils follow that

B. Human-mediated fluxes in the global N cycle now exceed 'natural' (pre-industrial) fluxes
How much N is added in agriculture?

- Cotton: 56-78 Kg/ha
- Iowa corn: 170-225 Kg/ha
- Taiwan rice: 270 Kg/ha

\[ \text{N fert} \rightarrow \text{increasing prod.} \]

\[ \text{N fert} \rightarrow \text{increasing dominance, decreasing diversity} \]

\[ \text{N} \text{ NO} + \text{ NO}2 (\text{NOx}): \text{fossil fuel combustion} \]

\[ \text{NO} (\text{highly reactive}) \rightarrow \text{smog, tropospheric O3 formation} \]

\[ \text{Acid rain} (\text{NO} + \text{OH} \rightarrow \text{HNO3}) \]

\[ \text{N2O: increased fertilizer application} \rightarrow \text{denitrification} \]

\[ \text{Potent greenhouse gas (200x more effective than CO2, 6% of total forcing)} \]

\[ \text{Chemically inert in troposphere, but catalyzes destruction of O3 in stratosphere} \]

\[ \text{NH3: domestic animals, ag fields (fert), biomass burning} \]

\[ \text{Atmospherically active aerosols, air pollution} \]

\[ \text{Deposition, N availability downwind} \]

\[ \text{N deposition} \rightarrow \text{increased growth (C sequestration)...to a point.} \]

\[ \text{N saturation: availability exceeds demand} \]

- Associated with decreases in forest productivity, potentially due to indirect effects such as acidification, altered plant cold tolerance

\[ \text{N saturation} \rightarrow \text{N losses} \rightarrow \text{“opening” of the N cycle} \]
B. Overview of Ecosystem N cycle (Ch. 9)

1. Major pools & fluxes
2. Main Points
   1. Inputs-outputs
   2. Open (C) vs. closed (N)
   3. Plant needs met by internal recycling
   4. Available soil pools are small relative to organic pools
   5. Microbes rule by

II. Controls on N cycle fluxes in soil
A. N Inputs

1. Biological N Fixation
   a. What is it?
      - Conversion of atmospheric N₂ to NH₄⁺ (actually, amino acids)
      - Under natural conditions, nitrogen fixation is the main pathway by which new, available nitrogen enters terrestrial ecosystems

   b. Who does it?
      - Carried out by bacteria
      - Symbiotic N fixation (e.g., legumes, alder)
      - Heterotrophic N fixation (rhizosphere and other carbon-rich environments)
      - Photosynthetic (bluegreen algae)

      - The characteristics of nitrogenase, the enzyme that catalyzes the reduction of N₂ to NH₄⁺, dictate much of the biology of nitrogen fixation
        - High-energy requirement (N triple bond)
        - Requires abundant energy and P for ATP
        - Inhibited by O₂
        - Requires cofactors (e.g., Mo, Fe, S)

Types of N-fixers

- There’s no such thing as a N-fixing plant
- Symbiotic N-fixers
  - High rates of fixation (5-20+ g-N m⁻² y⁻¹) with plants supplying the C (and the plant receiving N)
  - Protection from O₂ via leghemoglobin (legumes)
  - Microbial symbiont resides in root nodules
    - Bacteria (Rhizobia) - Legumes (Lupinus, Robinia)
    - Actinomycetes (Frankia) - Abies, Ceanothus (woody non-legumes)

- Associative N-fixers
  - Occur in rhizosphere of plants (non-nodulated)
  - Moderate rates with C supply from plant root turnover and exudates (1-5 g-N m⁻² y⁻¹)
  - Reduced [O₂] by rapid respiration from plant roots
  - Azotobacter, Bacillus

Types of N-fixers

- There’s no such thing as a N-fixing plant
Types of N fixers

- **Free-living N fixers**
  - Heterotrophic bacteria that get organic C from environment and where N is limiting (e.g., decaying logs)
  - Rates low due to low C supply and lack of O₂ protection (0.1-0.5 g-N m⁻² y⁻¹)
- Also, *cyanobacteria* (free-living photo-autotrophs); symbiotic *lichens* (cyanobacteria with fungi offering physical protection)

C. When/where does it happen?
N-fixing species are common in early succession

- Lichens early in primary succession following deglaciation in Alaska.
- Alder at later stages.

Red alder in secondary succession following clearcutting near Lake Whatcom

Alder and the other woody hosts of *Frankia* are typical pioneer species that invade nutrient-poor soils. These plants probably benefit from the nitrogen-fixing association. 

d. Paradox of N limitation

- Nitrogen is the element that most frequently limits terrestrial NPP
- N₂ is the most abundant component of the atmosphere
- Why doesn’t nitrogen fixation occur almost everywhere?
- Why don’t N fixers have competitive advantage until N becomes non-limiting?

Environmental limitations to N fixation

- Energy availability in closed-canopy ecosystems
- N-fixers seldom light-limited in well-mixed aquatic ecosystems (e.g., lakes)
- Nutrient limitation (e.g., P, Mo, Fe, S)
  - These elements may be the ultimate controls over N supply and NPP
- Grazing
  - N fixers often preferred forage
A. Inputs
2. Nitrogen Deposition

- **Wet deposition**: dissolved in precipitation
- **Dry deposition**: dust or aerosols by sedimentation (vertical) or impaction (horizontal)
- **Cloud water**: water droplets to plant surfaces immersed in fog; only important in coastal and mountainous areas

Wet deposition typically scales with precipitation.

Dry deposition can be significant even in humid climates.

Dry deposition a greater proportion of total deposition in more arid climates (Pawnee, CO)

Deposition depends on upwind sources

3. Rock weathering as a source of N?

- Some sedimentary rocks contain substantial amounts of N with high rates of N release (up to 2 g-N m\(^{-2}\) y\(^{-1}\)); however, most rocks contain little N.

N species in deposition depends on type of source

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B. Internal Cycling of Nitrogen

- In natural ecosystems, most N taken up by plants becomes available through decomposition of organic matter
  - Over 90% of soil nitrogen is organically bound in detritus in a form unavailable to organisms
  - The soil microflora secrete **extracellular enzymes** (exoenzymes) such as proteases, ribonucleases, and chitinases to break down large polymers into water-soluble units such as amino acids and nucleotides that can be absorbed

http://pah.cert.ucr.edu/aqm/ndep/results.shtml
The pools
- Plant biomass
- SOM (solid, including litter)
- Microbial biomass
- DON (a variable portion "plant available")
- NH$_4^+$ (plant available)
- NO$_3^-$ (plant available)

The processes:
- (Gross) N mineralization
- (Gross) N immobilization
- (Gross) autotrophic nitrification
- N uptake (and assimilation) by plants

Internal Cycling of Nitrogen

Net Ain't Gross
- Net rates of N transformations (mineralization and nitrification)

Net N mineralization = $\Delta$ (NH$_4^+$ + NO$_3^-$ pools) = gross N mineralization - gross N immobilization

Net Ain't Gross
- Similarly...
  Net nitrification = $\Delta$ NO$_3^-$ pool = gross nitrification - gross NO$_3^-$ immobilization

1. Mineralization/immobilization
- Mineralization is closely linked to decomposition.
- Plant functional types: effects via litter quality influence on both breakdown of plant material and immob by microbes.
- Climate affects mineralization via decomposition (microbial activity).
- Species effects can be much greater than differences in climate.

Critical litter C:N for net N min. (box 9.1)
- Microbial C:N ~10:1
- Microbial growth efficiency ~40%
- So, for 100 units C, 40 units $\rightarrow$ mic biomass, 60 units respired.
- For mic C:N of 10:1, need 4 units of N per 40 units C.
- So substrate needs C:N of 100:4 (i.e., 25:1) for net N mineralization.

2. Nitrification
  a. Why is Nitrification Important?
- Nitrate is more mobile than ammonium, so more readily leached from soil
- Substrate for denitrification (N loss as a gas)
- Generates acidity if nitrate is lost from soil
- Loss of nitrate results in loss of base cations
2.b. Controls on Nitrification

- \( \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \)
- Two-step process conducted by chemosynthetic bacteria:
  - First step conducted by \( \text{Nitrospora} \) (other Nitroso-), \( \text{NH}_4^+ \rightarrow \text{NO}_2^- \), ammonia mono-oxygenase, needs \( \text{O}_2 \)
  - Second step conducted by \( \text{Nitrobacter} \), \( \text{NO}_2^- \rightarrow \text{NO}_3^- \)
- Controls:
  - \( \text{NH}_4^+ \)
  - \( \text{O}_2 \)
  - Slow growth of nitrifiers

Nearly all nitrogen that is mineralized in these systems is nitrified on a net basis.

- In contrast, net nitrification is frequently less than 25% of net mineralization in temperate coniferous forests.
- Semi-arid forests tend to show more net nitrification relative to net N mineralization.

- Controls:
  - \( \text{NH}_4^+ \)
  - \( \text{O}_2 \)

- Substrate limitation is common.
- Nitrifiers are obligate aerobes.

C. N outputs

1. Gaseous losses
   - Ammonia gas (pK = 8.2, \( \text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+ \))
   - Fire
   - Oxides of \( \text{N} \) (\( \text{NO}, \text{N}_2\text{O}, \text{N}_2 \))
     - \( \text{NO} \) and \( \text{N}_2\text{O} \) from autotrophic nitrification
     - \( \text{NO}, \text{N}_2\text{O}, \text{N}_2 \) from denitrification
   - Most denitrification conducted by heterotrophic bacteria (many are facultative anaerobes that use \( \text{NO}_3^- \) as a terminal e- acceptor in the absence of \( \text{O}_2 \))
   - Controls: \( \text{NO}_3^- \), \( \text{C} \) availability, \( \text{O}_2 \)

- Nitrification and denitrification occur under different conditions.
- Gaseous losses for both follow the "hole-in-the-pipe" model.
- H-in-the-P depends on rate of flux and percent of losses.

- High nitrate concentration, much labile \( \text{C} \), and lack of oxygen together lead to high denit. rates.
Denitrification - where?

- Very important in wetlands, riparian areas.
- Spatially very patchy in well-drained soils.

C. N outputs

2. Leaching

- Erosional losses
- Solution losses
  - $\text{NO}_3^-$ $\gg$ DON $\gg$ $\text{NH}_4^+$
  - Greatest when water flux is high and biological demand for N is low (e.g., after snowmelt!)

- Leaching losses of nitrate and cations decrease with forest regrowth at Hubbard Brook.
- Plant and microbial demand

Leaching increases when plant and microbial demand are exceeded (e.g., N saturation).

Consequences of Mississippi River N runoff: The Gulf of Mexico "Dead Zone"

Summary: small $\rightarrow$ big

- Controls on mineralization (C quality, AET) are similar to those for decomposition, and this is the major source of plant nutrients for rainfall ecosystems.
- Increased N inputs to ecosystems: N fixation, N deposition
- Higher N availability $\Rightarrow$ greater plant growth, until demand saturated
- Microbes compete with plants for nutrients
- Presence of substrate ($\text{NH}_4^+$) is a major control on nitrification; nitrate is much more susceptible to loss than ammonium.
- Losses of N cause
  - Nitrate and nitrate pollution in groundwater
  - Chemically active N species (NO $\times$) in atmosphere
  - Radiatively active N species ($\text{N}_2\text{O}$) in atmosphere
  - Increased output to aquatic ecosystems (eutrophication).