Nitrogen Pollution and its Impacts
OUTLINE:

• Background – forms and cycling

• Sources

• Cycling, transport dynamics and loadings from watersheds

• Landuse and N exports

• Management Options to reduce N

• Effects and impacts of excess N on ecosystems
Notes based on –


• Passeport et al. 2013; Environmental Management
OUTLINE:

• Background – forms and cycling
Forms of N:

**Inorganic:**

**Reduced**
1. NH$_4^+$ (ammonium – g, aq, s)
2. N$_2$ (nitrogen – g)
3. N$_2$O (nitrous oxide – g)
4. NO (nitric oxide – g)
5. NH$_3$ (g, aq)

**Oxidized**
1. NO$_2^-$ (nitrite – aq)
2. NO$_2$ (nitrogen dioxide - g)
3. NO$_3^-$ (nitrate – aq)

**Organic N** – urea, amines, proteins and nucleic acids
Tied to carbon molecules
Reactive vs. Non-reactive species

Non-reactive – Nitrogen gas $\text{N}_2$ – atmosphere - largest N store on the planet (78%)

Reactive ($\text{N}_r$) –

- Ammonia
- Ammonium
- Nitrogen oxides
- Nitric acid
- Nitrous oxide
- Organic compounds

$\text{N}_2 \leftrightarrow \text{N}_r$

Concern – Anthropogenic activities increasing $\text{N}_r$ accumulation in environmental reservoirs – and increasing impacts on these reservoirs.
<table>
<thead>
<tr>
<th></th>
<th>million tonnes N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air</strong></td>
<td></td>
</tr>
<tr>
<td>$\mathrm{N}_2$</td>
<td>3,900,000,000</td>
</tr>
<tr>
<td>$\mathrm{N}_2\mathrm{O}$</td>
<td>1,400</td>
</tr>
<tr>
<td><strong>Land</strong></td>
<td></td>
</tr>
<tr>
<td>Plants</td>
<td>15,000</td>
</tr>
<tr>
<td>Animals</td>
<td>200</td>
</tr>
<tr>
<td>of which people</td>
<td>10</td>
</tr>
<tr>
<td>Soil organic matter</td>
<td>150,000</td>
</tr>
<tr>
<td>of which microbial biomass</td>
<td>6,000</td>
</tr>
<tr>
<td><strong>Sea</strong></td>
<td></td>
</tr>
<tr>
<td>Plants</td>
<td>300</td>
</tr>
<tr>
<td>Animals</td>
<td>200</td>
</tr>
<tr>
<td>In solution or suspension</td>
<td>1,200,000</td>
</tr>
<tr>
<td>of which $\mathrm{NO}_3^-$-N</td>
<td>570,000</td>
</tr>
<tr>
<td>of which $\mathrm{NH}_4^+$-N</td>
<td>7,000</td>
</tr>
<tr>
<td>Dissolved $\mathrm{N}_2$</td>
<td>22,000,000</td>
</tr>
</tbody>
</table>
OUTLINE:

• Background – forms and cycling

• Sources
Sources

Natural Sources:

lightning

\[ \text{N}_2 + \text{O}_2 \rightarrow 2\text{NO} \]

biological nitrogen fixation

\[ \text{N}_2 \rightarrow \text{NH}_3 \rightarrow \text{amino acids} \rightarrow \text{proteins} \]

Symbiotic bacteria in rhizobium/roots of plants
Types of plants that host these bacteria?
Other types of bacteria?
Prior to anthropogenic influences - there was a balance between BNF and denitrification which kept Nr low

**Anthropogenic sources**

- Burning of fossil fuels
- Widespread cultivation of N fixing crops
- Use of fertilizers in agriculture – synthetic and animal manures
- Urban, suburban, rural sources – wastewater, lawn fertilizers, septic tanks, CSOs.

**Human activity has had a profound effect on the N cycle.**
1. **Energy production** - under high temperature combustion processes, unreactive nitrogen is converted to reactive nitrogen by two processes.

   a. **Thermal NO\(_x\)**
      
      \[ N_2 + O_2 \rightarrow 2\text{NO} \]
      
      1000\(^\circ\)K

   b. **Fuel NO\(_x\)** - the oxidation of organic N in fuels

2. **Fertilizer** - Most anthropogenic fertilizers are either NH\(_3\) or urea produced from NH\(_3\).

   This material is produced by the **Haber-Bosch process**.

   \[ 4\text{N}_2 + 12\text{H}_2 = 8\text{NH}_3 \]

   Types of N fertilizers – Ammonium nitrate, Ammonium sulfate, Calcium nitrate, Sodium nitrate, Urea [CO(NH\(_2\))\(_2\)], Urea-ammonium nitrate
Fritz Haber

Carl Bosch

https://en.wikipedia.org/wiki/Fritz_Haber

Historical high pressure steel reactor

https://en.wikipedia.org/wiki/Haber_process
Global Population and Reactive Nitrogen Trends

What is Nitrogen Pollution?

Major Sources
1. Power plant emissions
2. Vehicle emissions
3. Septic tank leakage
4. Manure/livestock runoff
5. Agricultural emissions
6. Fertilizer runoff (e.g. lawns and fields)
7. Wastewater effluent
8. Food and feed imports
What happens to inputs of Nr?

- Denitrification (loss as N₂ gas)
- Biomass storage (crops, forests, animals)
- Soil storage
- Groundwater storage
- Exported to streams/estuaries
- Exported in food and feed
OUTLINE:

• Background – forms and cycling

• Sources

• Cycling, transport dynamics and loadings from watersheds
Cycling, Transport Dynamics and N loadings from watersheds

- Nitrate – high mobility
- Ammonium – low mobility, fixation with clay particles in subsoils
- Organic N – moderate mobility
- Particulate versus dissolved species (?)
Key N Cycle Processes:

Mineralization & Immobilization:

- **Mineralization**: Conversion of organic N into inorganic N forms ($\text{NH}_4^+$, $\text{NO}_3^-$) – via processes like decomposition -- organic N forms decompose and form ammonium first.
- 1.5 to 3.5 % of the organic N may mineralize annually
- **Immobilization**: Conversion of inorganic N forms to organic N forms (via processes like plant & biological uptake)
  - NH$_4^+$ preferably immobilized compared to NO$_3^-$

The carbon and nitrogen pool ratios in soils and implications for mineralization and immobilization
Fixation/Sorption by Clay Minerals

- Positively charged ammonium ions are adsorbed on the negatively charged clay & humus sites – remember the CEC!
- Because of the adsorption of ammonium to clay particles ammonium is the less mobile form of N --- nitrate (negatively charged) is more mobile that ammonium.
- Thus soils with higher clay content will retain or tie-up more ammonium (compared to sandy soils)
Ammonia Volatilization

- Conversion of ammonium from the soil to ammonia gas – NH₃

- Typical sites for occurrence – locations where animal manures are spread on land.

- Moist and high pH conditions increase the rate of volatilization.
Nitrification

- Conversion of Ammonium → Nitrate

- Performed by bacteria classed as *autotrophs* – because they obtain their energy from the oxidation of ammonium ions.

- Ammonium → Nitrite → Nitrate

- Occurs in dry soils
Denitrification

- Process of conversion of nitrate NO$_3^-$ to nitrogen gas N$_2$

- Typically occurs in saturated soils – like wetlands, riparian soils, flooded rice fields, ……

- Bacteria involved – are *heterotrophs* – extract their energy from carbon (as opposed to autotrophs)

- Conditions for Denitrification:
  - Nitrate availability
  - Energy source – Carbon
  - Anaerobic conditions – soil air less than 10% O$_2$ or less that 0.2 mg/L
Hydrologic delivery processes:

1. Precipitation
2. Surface runoff
3. Sediment and soil associated
4. Vertical drainage, leaching
5. Groundwater flow
Primary pathways of transport for various N forms

Either in dissolved or particulate forms

**Dissolved < 0.45 or 0.7 micron**

**Particulate > 0.45 or 0.7 micron**

- Surface runoff – **DON**, diss-**NH₄⁺**, NO₃⁻
- Vertical drainage - **DON**, diss-**NH₄⁺**, NO₃⁻
- Near subsurface flow - **DON**, diss-**NH₄⁺**, NO₃⁻
- Groundwater flow - **DON**, diss-**NH₄⁺**, NO₃⁻
- Sediment - **PON**, particulate-**NH₄⁺**

**DON** – dissolved organic N
**PON** – particulate organic N
OUTLINE:

• Background – forms and cycling

• Sources

• Cycling, transport dynamics and loadings from watersheds

• Landuse and N exports
N exports with landuse

Baltimore Ecosystem Study LTER Watersheds

Kaushal et al. (2011)
Figure 5. Box Plots of Nitrogen Export Coefficients From Various Land Uses.
Forested watersheds:

- Primary inputs – atmospheric deposition (nitrate, ammonium)
- Atmospheric deposition for Newark region ~ 3-4 kgN/ha/yr

- Primary N species exported – nitrate and DON; PN could be high during large storms or watersheds with significant erosion and sediment export

- Inorganic N species constitute 50 to 80%

- In some undisturbed tropical forested watersheds – DON is the predominant form of N (could be as high as 60-80%)

- Nitrate-N concentrations less than 1.0 mg/L

- Exports occur with surface as well as with groundwater flow
  - DON – surface waters
  - Nitrate – groundwaters
Agricultural watersheds:

- Primary inputs – fertilizers, manure, atmospheric deposition

- Poultry manure N:P = 3:1 << that required for plant uptake ~ 8:1. Manure application rate for corn ~ 214 kgN/ha/yr

- N species – nitrate, ammonium, organic N

- Nitrate concentrations in runoff and groundwater may be as high as 10 mg/L

- Particulate concentrations could be high if soil erosion occurs
Chicken manure on Delaware farm to be applied in spring
N exports from an Agricultural Watershed in Coastal Plain of Virginia

QN1

- pre-BMP: 52 kg/ha particulate, 27 kg/ha dissolved-organic, 16 kg/ha nitrate, 5 kg/ha nitrate, 2 kg/ha ammonium
- post-BMP: 52 kg/ha particulate, 17 kg/ha dissolved-organic, 29 kg/ha nitrate, 2 kg/ha ammonium
Urban watersheds:

- Primary sources – wastewater, leaking septic tanks, leaking sewer lines, CSOs, lawn fertilizers, golf courses, atmospheric deposition

- Golf course N application rate = 173 kgN/ha/yr!

- Key N species – nitrate, ammonium N

- N concentrations may vary considerably with season and hydrologic conditions (baseflow versus stormflow)

- Runoff and N – short-circuited, bypasses natural sinks in the landscape

Increasing concerns in regions like the Chesapeake Bay watershed.
OUTLINE:

• Background – forms and cycling
• Sources
• Cycling, transport dynamics and loadings from watersheds
• Landuse and N exports
• Management Options to reduce N
Management strategies for N

Source Control

- Emissions Control
  - Reduce emissions from power utilities
  - Transportation

- Fertilizer applications
  - Reduce applications rates
  - Timing and location of fertilizer application
  - Retardants (e.g., nitrification inhibitors)
Management strategies for N

Source Control

- Manure management & application
  - Storage
  - Timing of applications – winter manure ban in some states
  - Location and amount of application

- Suburban & rural areas –
  - Septic tanks
  - Homeowner lawn fertilizers – timing and amounts
  - Golf courses
Transport & delivery controls

Intercept and reduce nutrients during transport

- Riparian zones, wetlands, buffer strips
  
  *Ripar* – beside the stream
  - Denitrification of N
  - Vegetative uptake of N
  - Deposition of sediment & sediment-N
  - Conversion of inorganic N to $\text{N}_2$ & organic N

Riparian forest on a Midwestern farm
Effectiveness of riparian zones as N sinks is site specific

- Flow paths
  - Deep versus shallow
- Carbon availability/vegetation
  - Why?
- Vegetation growth status
Other types of management practices for N control

(notes and graphics from Passeport et al., 2013, Environmental Management)
Urban landscape management practices

- Reduce management intensity
- Increase biodiversity
- Enhance native species
Intensively Managed Landscape
Water quality and other ecosystem services concerns are associated with managed lawn.

Mixed Planting with Abundance and Diversity
Improved water quality and other ecosystem services are associated with mixed vegetation landscapes including meadows and reforested edges.

Concerns
1) chemical inputs increase fertilizer and herbicide runoff into watershed
2) increasing impervious surface area increases runoff, and
3) removal of natural vegetative zones disables water infiltration

Benefits
1) reducing fertilizer and herbicide inputs,
2) enabling water infiltration,
3) stabilizing stream base-flow,
4) increasing dissolved oxygen, and
5) decreasing turbidity

Figure 1. Illustrates change from the current lawn-based suburban landscaping paradigm to one that encourages less-intensive management and allows for a greater abundance and diversity of native flora and fauna.
OUTLINE:

• Background – forms and cycling

• Sources

• Cycling, transport dynamics and loadings from watersheds

• Landuse and N exports

• Management Options to reduce N

• Effects and impacts of excess N on ecosystems
Effects of Excess N:

Human health and non-ecosystem effects:

• Particulate matter (PM) – especially < 2.5 μm
• Ozone formation (NO$_x$ triggers ozone)
  o 80 ppb – for 8hrs – can cause problems
• Acid deposition (deterioration of exposed structures)
• Nitrate concentrations in waters (blue baby syndrome)
Ecosystem Effects of Nitrogen Deposition

1. change in species composition
2. changes in soil chemistry
3. reduction in forest growth

Nitrogen Inputs

1. N saturation
2. reduction in water quality

terrestrial ecosystems

freshwater ecosystems

watersheds

estuaries

1. toxicity to fish and other fauna
2. loss of acid neutralizing capacity

1. eutrophication
2. nuisance algal blooms
3. fish kills
4. habitat loss
N-poor terrestrial landscapes and impacts of N enrichment

e.g., Ombrotrophic Bogs and carnivorous plants
Eutrophication – Coastal & inland

- Eutrophication – excess growth of algae (N, P)
- N especially a concern for coastal water bodies – N limited.
- N deposition plays a greater role
Symptoms and Consequences of Nutrient Enrichment

Nutrient Inputs                  Primary Effects                  Secondary Effects                  Consequences of Symptoms

Increased Nitrogen Load  

Increased Primary Production  
Loss of Habitat  
Low D.O.  
Algal Blooms

Fish kills  
Human health risks  
Loss of Tourism  
Closed fishing areas
Dead Zones → Anoxic or Hypoxic waters – an increasing problem!

- Hypoxic – when dissolved $O_2 < 2$ to $3$ mg/L
- Anoxic – when devoid of $O_2$

Dead zones occur in:
- Gulf of Mexico
- Chesapeake Bay
- Florida Bay
- Long Island Sound
- Adriatic sea
- Baltic sea
Gulf of Mexico Hypoxic zone 20,000 sq km! – attributed to N loadings from the Mississippi River watershed.