Nitrogen transport and cycling in watersheds
Outline

**Nitrogen** –
- Environmental Significance
- Forms
- Sources
- Cycling
- Transport pathways
- Annual/Seasonal patterns
- Storm event patterns – sources and flow paths
Environmental Significance

Nitrogen – a nutrient; pollutant at high levels!
- > 10 mg/L of NO3-N – Blue baby syndrome
- Excess conc. – eutrophication and algal growth
- Impacts on plants and forests
- Acidification of soils
N Forms

**Inorganic:**

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

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

**Organic N** – urea, amines, proteins and nucleic acids
N Forms

Reactive vs. Non-reactive species

Non-reactive – Nitrogen gas $N_2$ – atmosphere - largest N store on the planet (78%)

Reactive (Nr) –
- Ammonia
- Ammonium
- Nitrogen oxides
- Nitric acid
- Nitrous oxide
- Organic compounds
Sources of N

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

biological nitrogen fixation

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

Prior to anthropogenic influences - there was a balance between BNF and denitrification which kept Nr low
Sources of N

**Anthropogenic sources**

- Burning of fossil fuels – atmospheric deposition
- Widespread cultivation of N fixing crops
- Use of fertilizers in Agriculture
N Cycle

Nitrogen Cycle

- Nitrification
- Wet & dry deposition
- Denitrification

Plant
Organic N

Organic matter & microbial N

NH₄⁺

NO₃⁻

NO₂⁻

NH₃ gas

atmosphere

Symbiotic N fixation

Litterfall, & other sources

Plant uptake

Immobilization

Ammonification

Erosion loss

Leaching loss

Nitrification

Adsorption

Erosion loss

Clay
N Cycle

- Nitrate – high mobility
- Ammonium – low mobility, fixation with clay particles in subsoils
- Organic N – moderate mobility
N Cycle

Mineralization & Immobilization:

Mineralization: Conversion of \textbf{organic N into inorganic N forms} (NH$_4^+$, 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 \textbf{inorganic N forms to organic N forms} (via processes like plant & biological uptake)

The \textbf{carbon and nitrogen pool ratios in soils} and implications for mineralization and immobilization
Lignin: Nitrogen ratio
Organic & Inorganic C, N, P, pools in soil

Decomposition – 2/3rd of C is lost as CO2

C:N < 24:1 – mineralization
C:N > 24:1 – immobilization

C:N ratios -
Microbes = 8:1
Litter ~ 10:1 to 30:1
Sawdust ~ 600:1
C/N ratio of the residues – Nitrogen in the residue is used by the microbes.

Microbes need a required quantity of N to consume or decompose C. – if the level of N is less than that required level decomposition will slow down or stop.

• C/N ratios of legumes & young green leaves = 10:1 to 30:1
• C/N of sawdust = 600:1

• A low value of C/N ratio means – more N – faster decomposition
• Typically, microbes have a C:N ratio of 8:1

• 2/3rd of the C is lost – for decomposition the residue should have at least a ratio of 24:1

• If C:N ratio is greater than 24:1 – the microbes will scavenge the soil solution for N – which means removal of N from the soil solution – Nitrate depression.
• If C:N ratio is less than 24:1 – excess N from the decomposing residue will be added to the soil.

Example – C:N ratio of residue and potential for mineralization or immobilization.
**Case 1:** Assume C:N ratio of residue = 36:1
Carbon burnt away (CO2) due to decomposition = 24 parts
Carbon available for microbes = 12
C:N ratio of microbes = 8:1
Therefore N needed = 12 / (8:1) = 1.5 parts
N available from organic matter = 1
Therefore excess N needed = 1.5-1 = 0.5 (**immobilization!**)  

**Case 2:** Assume C:N ratio of residue = 12:1
Carbon burnt away (CO2) due to decomposition = 8 parts
Carbon available for microbes = 4
C:N ratio of microbes = 8:1
Therefore N needed = 4 / (8:1) = 0.5 parts
N available from organic matter = 1
Therefore excess N released = 1-0.5 = 0.5 (**mineralization!**)
N Cycle

Ammonium Fixation 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 than ammonium.
Ammonia Volatilization

- Conversion of ammonium from the soil to ammonia gas – NH$_3$
- Typical sites for occurrence – locations where animal manures are spread on land.
- Moist and high pH conditions increase the rate of volatilization.
N Cycle

Nitrification

Conversion of Ammonium $\rightarrow$ Nitrate

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

Two types of bacteria involved – *Nitrosomonas* and *Nitrobacter* – two stage process of conversion

Ammonium $\rightarrow$ Nitrite $\rightarrow$ Nitrate

Nitrification reaction results in the release of hydrogen ions – which means nitrification increases soil acidity!
Factors that regulate Nitrification:

- **Availability of ammonium**
- **Aeration** – nitrifying bacteria are aerobic and need O2
- **Moisture** – nitrification is retarded at high soil moisture conditions (poor aeration)
- **Carbon** – don’t need carbon as an energy source
- **Temperature** – optimum 20C to 30C.
- **Exchangeable base forming cations**: Nitrification proceeds at a higher rate in soils that have an abundance of exchangeable base forming cations like Ca$^{2+}$ and Mg$^{2+}$
- **Clay types**: (e.g., smectite & allophane) Clays that stabilize organic matter and hold ammonium ions tightly can result in reduced rates of nitrification
- **Pesticides & nitrification inhibitors**
N Cycle

Watershed sites for Nitrification:
N Cycle

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)
N Cycle

Conditions for Denitrification:

- **Nitrate availability**
- **Energy source** – Carbon
- **Anaerobic conditions** – soil air less than 10% O2 or less than 0.2 mg/L
- **Temperature** between 2 and 50°C – optimum is between 25 and 35°C.
- **Acidity** – acidic conditions (pH < 5.0) can inhibit denitrification
N Cycle

Watershed sites for Denitrification:
N Cycle

• Denitrification can occur in large saturated expanses of soil or even in small pockets of saturation called *micro-sites*

• Denitrification rates could vary from 5 to 15 kgN/ha/yr for agricultural fields to as high as 30 to 60 kgN/ha/yr for wetlands, saturated soils receiving high N loads or riparian soils.

• During a year - denitrification losses will be high when there is sufficient moisture in the soil and the soil is warm.
N Transport pathways

Primary pathways of transport for various N forms

- **Surface runoff** – DON, diss-NH$_4^+$, NO$_3^-$
- **Vertical drainage** - DON, diss-NH$_4^+$, NO$_3^-$
- **Near subsurface flow** - DON, diss-NH$_4^+$, NO$_3^-$
- **Groundwater flow** - DON, diss-NH$_4^+$, NO$_3^-$
- **Sediment** - PON, particulate-NH$_4^+$

DON – dissolved organic N
PON – particulate organic N

*The amount transported via the various pathways depends on the sources of inputs and the nature of application*
Factors affecting N in watersheds

Factors affecting N in forested watersheds

- Inputs – atmospheric deposition
- Climate
- Geology
- Topography – gradient, aspect, wetlands
- Vegetation type
- Soils
- Hydrologic flow paths
- Management
Factors affecting N in forested watersheds

- **Inputs** – atmospheric deposition

<table>
<thead>
<tr>
<th>Location</th>
<th>Precipitation (mm)</th>
<th>NH₄-N kg N ha⁻¹ yr⁻¹</th>
<th>NO₃-N kg N ha⁻¹ yr⁻¹</th>
<th>DON kg N ha⁻¹ yr⁻¹</th>
<th>Total N kg N ha⁻¹ yr⁻¹</th>
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<td>1.54</td>
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2011 N deposition estimates – Inamdar et al 2011. * only inorganic N
Factors affecting N in watersheds

Topography – gradient, aspect, wetlands

Steeper slopes may drain more NO₃

Catchments with flat valley-bottom locations (with wetlands) may encourage denitrification loss
Factors affecting N

Topographic index may provide a catchment-scale index to characterize N potential?! 

Low $a/\tan B$ – dry positions – favor nitrification – elevated NO3 leaching?
High $a/\tan B$ – wet positions – anoxic, favor denitrification – low NO3?
Factors affecting N in watersheds

Vegetation type

- Hardwoods – especially N-rich species may enhance N cycling and leaching
- Conifers – low cycling, low N cycling
Factors affecting N in watersheds

Vegetation type
- Invasive species? – alter N cycling for their benefit?

Multiflora rose

Japanese stilt grass
Seasonality in N

Seasonal patterns of runoff N may vary with climate and watershed location

- Biotic factors – plant uptake, dormancy, autumn leaf fall
- Hydrologic factors
Seasonality in N

Stream water N for the Adirondack watershed in NY

Accumulation of NO3 over the winter dormant period!

NO3-N (mg/L) = NO3 (ueq/L) * (14/1000)

NO3-N = 0-0.84 mgN/L
Seasonality in N

Stream water N for the Fairhill watershed in MD

![Graph showing seasonal variations in stream water N for the Fairhill watershed in MD from 2008 to 2010. The graph includes data for NH4, NO3, and DON, with distinct peaks and troughs indicating seasonal changes.]
Seasonality in N

30-minute instream sensor readings!
Watershed pools of N

How does N concentration vary across watershed sources?

Will dictate the expression of N in runoff – as hydrologic flow paths intersect these pools.
Export patterns of nitrogen (N) in runoff are determined by –

- **Size of the N pools and their location** and the intersection of these pools by hydrologic paths

- **Size of the N pools** – determined by site conditions and associated biogeochemical processes
Dilution pattern in N with high flow

Large N source at depth

Low flow

High flow

N pool

Q

Dilution pattern in N with high flow
Concentration pattern in N with increased flow

Large N source near the surface

Low flow

High flow

Concentration pattern in N with increased flow
Dissolved N concentrations in watersheds sources at Fair Hill 12 ha watershed
Storm event patterns of particulate and dissolved n in stream runoff
Factors affecting N in watersheds

Factors affecting N in forested watersheds

- Inputs – atmospheric deposition
- Climate
- Geology
- Topography – gradient, aspect, wetlands
- Vegetation type
- Soils
- Hydrologic flow paths
- Management
N saturation of forest ecosystems

- Elevated atmospheric deposition
- Mature forests that are not providing net uptake of N
  - Results in elevated pools of N in soils
  - Elevated exports of N via runoff and groundwaters
N saturation of forest ecosystems

- Elevated exports of N via runoff and groundwaters
Isotopic tracers to study N sources

- Isotopes = elements with different number of neutrons
- Heavy versus light isotopes. Proportions different in various sources – expressed as ratios
- Biological processes lead to changes in proportions of the isotopes
- Application of stable isotopes can help us identify the sources of NO3-N
Isotopic tracers to study N sources

\[ \delta^\text{H}X = \left[ \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000 \]

\( X \) – element
\( H \) – heavy isotope
\( R \) – is ratio; \( \text{heavy}R / \text{light}R 
\( R_{\text{sample}} \) - ratio term for sample
\( R_{\text{standard}} \) - ratio term for the standard; set by the IAEA

\[ \times 1000 \text{ – per mil or } \%\]

\[ \delta^{15}\text{N} = \left[ \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000 \]

\[ \delta^{15}\text{N} = \left[ \left( \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} \right) - 1 \right] \times 1000 \]
Isotopic tracers to study N sources

Typical isotopes used for NO$_3^-$N - $^{15}$N, $^{18}$O, $^{17}$O

Most studies use – $^{15}$N, $^{18}$O

Biggest challenges with isotopic analyses –

- Different sources have overlapping isotopic compositions
- Considerable spatial and temporal variation
- Fractionations can blur initially distinctive isotopic compositions
Isotopic tracers to study N sources

\[ \delta^{15}N = \left[ \frac{(^{15}N/^{14}N)_{\text{sample}}}{(^{15}N/^{14}N)_{\text{standard}}} - 1 \right] \times 1000 \]

Processes that remove 14N – make \( \delta^{15}N \) greater (positive values) – enrichment

Processes that add 14N - make \( \delta^{15}N \) lower (towards negative values) – depletion
Isotopic tracers to study N sources

15N, 14N

NH3

volatilization

Cropland receiving animal manure
Figure 16.9. Schematic of typical ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of nitrate from various sources, simplified from data presented in Figure 16.6. Nitrification of ammonium and/or organic-N in fertilizer, precipitation, and organic waste can produce a large range of $\delta$ values, as shown. Soil waters tend to have higher $\text{NO}_3$-$\delta^{18}\text{O}$ values, and a larger range of $\text{NO}_3$-$\delta^{18}\text{O}$ values, than groundwaters because of the higher $\delta^{18}\text{O}$ values of $\text{O}_2$ and/or $\text{H}_2\text{O}$ in soils.
Isotopic tracers to study N sources

- **Atmospheric sources**: $\delta^{15}N$ of nitrate decreases while $\delta^{18}O$ increases

- **Fertilizer**: $\delta^{15}N$ of nitrate is low and $\delta^{18}O$ remains low

- **Wastewater**: $\delta^{15}N$ of nitrate is +10 to 20 and $\delta^{18}O$ remains low

- **Denitrification**: $\delta^{15}N$ of nitrate increases while $\delta^{18}O$ increases
Isotopic tracers to study N sources

- Anthropogenic NOx sources generally have positive $\delta^{15}N$
- NOx emissions from power plants - +6 to +13 ‰
- Vehicle NOx emissions have lower $\delta^{15}N$ values than stationery sources
- Natural NOx sources (lightening, soil emissions) have lower $\delta^{15}N$ than anthropogenic sources
Isotopic tracers to study N sources

Fossil Fuel Emissions (point & nonpoint sources) vs. Agricultural activities (animal waste & fertilizers)

- NOx
- NH₃

Will have distinct isotopic signatures
Evidence has shown that:

- $\delta^{15}N$ of $NO_x$ pollution tends to be $+$
- $\delta^{15}N$ of $NH_3$ pollution tends to be $-$

Source – Tara Tramell
Isotopic tracers to study N sources

- Seasonal and inter-event variability of $\delta^{15}\text{N}$

- Winter values of $\delta^{15}\text{N}$ of N deposition may be higher than summer values
Isotopic tracers to study N sources

- Ammonium fertilizers have low $\delta^{15}\text{N}$ values indicating their origin from N2 via the Haber-Bosch process.

- Microbial processing of the fertilizers increases the $\delta^{15}\text{N}$ values.

- Crop residues, composts, animal manure have greater $\delta^{15}\text{N}$ than inorganic fertilizers.

- $\delta^{15}\text{N}$ of total soil N ranges -10 to +15 ‰.
Isotopic tracers to study N sources

- Higher $\delta^{15}N$ values of soils in lower slopes or valley bottoms are attributed to denitrification or higher rates of immobilization and nitrification.

- Lower foliar $\delta^{15}N$ on ridgetops versus higher $\delta^{15}N$ foliar N in valley bottoms.

- Foliar $\delta^{15}$ values could also vary between urban and rural areas.
Isotopic tracers to study N sources

Processes affecting $\delta^{15}N$ -

• Key processes that affect $\delta^{15}N$ - fixation, assimilation, nitrification, mineralization and denitrification.

• Reactions commonly increase of $\delta^{15}N$ of substrate and decrease of $\delta^{15}N$ in product.

• Bacterial fixation produces $\delta^{15}N$ values slightly less than 0‰.
Isotopic tracers to study N sources

Processes affecting δ^{15}N -

• Assimilation favors N of lower mass.

• Mineralization typically does not cause large fractionation of N.

• Volatilization – high fractionation process – NH3 gas produced has lower δ^{15}N than the residual NH4+.

• Denitrification – causes significant fractionation – δ^{15}N of residual NO3 increases.
Isotopic tracers to study N sources

Small forested watershed studies –

- Lot of interest in differentiating between atmospheric N and soil N from nitrification

- Difficult to make distinction using only $\delta^{15}N$. Hence $\delta^{18}O$ is valuable.

- Most studies show that NO3 in runoff is of microbial origin (including atmospheric N that is recycled)

- Some recent data with high-frequency snow-melt sampling has show atmospheric origin of NO3.
Isotopic tracers to study N sources

Urban watersheds –

• Interest in differentiating N from - fertilizer vs. wastewater or septic tanks vs. atmospheric inputs
Isotopic tracers to study N sources

Kaushal et al. (2011) applied isotopes of nitrate to trace the sources of N in forested, urban, and agricultural watersheds.

Following notes from Kaushal’s paper and presentation made in 2012 at UD.
Isotopic tracers to study N sources

Figure 16.9. Schematic of typical ranges of $\delta^{18}O$ and $\delta^{15}N$ values of nitrate from various sources, simplified from data presented in Figure 16.6. Nitrification of ammonium and/or organic-N in fertilizer, precipitation, and organic waste can produce a large range of $\delta$ values, as shown. Soil waters tend to have higher NO$_3$-$\delta^{18}O$ values, and a larger range of NO$_3$-$\delta^{18}O$ values, than groundwaters because of the higher $\delta^{18}O$ values of O$_2$ and/or H$_2$O in soils.
Isotopic tracers to study N sources

Study/sampling sites in Baltimore LTER
Isotopic tracers to study N sources

Watersheds represented a range of watershed N export

- Largest exports of N and nitrate from agricultural watershed
- Lowest from forested watershed
- Urban systems indicated intermediate values
Isotopic tracers to study N sources

Various sources of N
Isotopic tracers to study N sources

Figure 16.9. Schematic of typical ranges of $\delta^{18}O$ and $\delta^{15}N$ values of nitrate from various sources, simplified from data presented in Figure 16.6. Nitrification of ammonium and/or organic-N in fertilizer, precipitation, and organic waste can produce a large range of $\delta$ values, as shown. Soil waters tend to have higher NO$_3$-$\delta^{18}O$ values, and a larger range of NO$_3$-$\delta^{18}O$ values, than groundwaters because of the higher $\delta^{18}O$ values of O$_2$ and/or H$_2$O in soils.
Isotopic tracers to study N sources in watersheds.
Isotopic tracers to study N sources

Forested watershed (POBR)

- Nitrate was derived from microbial uptake, mineralization, and nitrification processes.
- Some indications of atmospheric deposition source during high flows.

Agricultural watershed (MCDN) and Low residential (BARN)

- Represent a “soil” N source. Fertilizer source not seen since it’s so similar to the soil signature.
- Denitrification likely modified isotopic N signatures
- In low residential watersheds – septic tanks were the primary source of N, but this signature was modified by denitrification along the flow path
Isotopic tracers to study N sources

Suburban watersheds (GFGL)

• Wastewater was the primary source of nitrate – sanitary sewers.

• Sanitary sewer lines were running close to and parallel to the stream and were likely leaking.

• Lawn fertilizers not seen. Likely retained in the lawns OR the problem in distinguishing between soil and fertilizer isotopic signatures.
Isotopic tracers to study N sources

Changes in N sources with flow conditions in urban watershed – Dead Run (DRKR)

Kaushal et al. (2011)
Isotopic tracers to study N sources

- Low flow (< 1 mm/day) – N is from wastewater
- Moderate flow (2-8 mm/day) – atmospheric deposition N increases
- High flows (> 8 mm/day) – mixture of atmospheric deposition and wastewater N!
Isotopic tracers to study N sources

Key Points from Kaushal et al 2011 –

Forest watersheds

• Nitrate derived from soil microbial processes
• During high flow – shift to atmospheric deposition

Urban/suburban watersheds –

• Wastewater sources – leaking septic tanks and sanitary sewers during baseflow
• Atmospheric deposition N becomes significant during storms
• Lawn fertilizer was not being seen in streamflow (maybe be difficult to distinguish from soil N)