Nitrogen

- Introduction
  - N Forms, Distribution, Importance
- Basic processes of N Cycles
  - Examples of current research
  - Examples of applications
- Key points learned
Nitrogen

Learning Objectives

- Identify the forms of N in wetlands
- Understand the importance of N in wetlands/global processes
- Define the major N processes/transformations
- Understand the importance of microbial activity in N transformations
- Understand the potential regulators of N processes
- See the application of N cycle principles to understanding natural and man-made ecosystems

Nitrogen Cycling

[Diagram showing nitrogen cycling processes]

- Plant biomass N
- Nitrogen Fixation
- Nitrification
- Mineralization
- Denitrification
- Volatilization
- Peat accretion
- Adsorbed NH$_4^+$

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Forms of Nitrogen

- Organic Nitrogen
  - Proteins
  - Amino Sugars
  - Nucleic Acids
  - Urea

- Inorganic Nitrogen
  - Ammonium (NH$_4^+$)
  - Nitrate N (NO$_3^-$)
  - Nitrite N (NO$_2^-$)
  - Nitrous oxide (N$_2$O)
  - Dinitrogen (N$_2$)

N Transformations

**Solid Phase:**
- Particulate N
  - Bound: NH$_4^+$
  - NO$_3^-$
  - NO$_2^-$

**Gaseous Phase:**
- N$_2$
- N$_2$O

**Aqueous Phase:**
- DIN:
  - NH$_4^+$
  - NO$_3^-$
  - NO$_2^-$
- DON
- Particulate N
Reservoirs of Nitrogen

- Lithosphere: $163,600 \times 10^{18}$ g
- Atmosphere: $3,860 \times 10^{18}$ g
- Hydrosphere: $23 \times 10^{18}$ g
- Biosphere: $0.28 \times 10^{18}$ g

Forms of Nitrogen

Total Soil N

- Organic
  - Protein
  - Amino sugars
  - Heterocyclic N

- Inorganic
  - $\text{NH}_4^+$
  - Clay-fixed $\text{NH}_4^+$
Nitrogen Transformations

1. Ammonification/Mineralization
2. Immobilization
3. Nitrification
4. Denitrification
5. Dissimilatory nitrate reduction to ammonia (DNRA)
6. Nitrogen fixation
7. Ammonia volatilization

Transformation of N Species

Oxidation Number

-3 -2 -1 0 +1 +2 +3 +4 +5
Nitrogen Cycle

Plant/Algae

Org-N → NH₄⁺ → NO₃⁻

Microbial Biomass

N₂ ↔ N₂/N₂O

Productivity
Greenhouse Gas Emissions

Figure 1. Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion air molecules, respectively, in an atmospheric sample.

Nitrogen Budget

- Biological N$_2$ fixation
- Dry and wet deposition
- Non-point sources
- Wastewaters

Inputs

Storages
- Plant biomass
- Microbial biomass
- Soil organic N
- Porewater (DIN, DON)
- Exchangeable N
- Clay fixed NH$_4$-N

Outputs
- Volatilization
- Outflow
- Gaseous losses
- Plant harvest

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Ammonium Ion Wet Deposition
1985-2003

Nitrate Ion Wet Deposition
1985-2003
**Inorganic N Wet Deposition 1985-2003**

**1985**

**2003**

**Biological Nitrogen Fixation**
### Nitrogen Fixation

<table>
<thead>
<tr>
<th>Type of fixation</th>
<th>N\textsubscript{2} fixed (10^{12} g yr\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-biological</td>
<td></td>
</tr>
<tr>
<td>Industrial</td>
<td>about 50</td>
</tr>
<tr>
<td>Combustion</td>
<td>about 20</td>
</tr>
<tr>
<td>Lightning</td>
<td>about 10</td>
</tr>
<tr>
<td>Total</td>
<td>about 80</td>
</tr>
<tr>
<td>Biological</td>
<td></td>
</tr>
<tr>
<td>Agricultural land</td>
<td>about 90</td>
</tr>
<tr>
<td>Forest and non-agricultural land</td>
<td>about 50</td>
</tr>
<tr>
<td>Sea</td>
<td>about 35</td>
</tr>
<tr>
<td>Total</td>
<td>about 175</td>
</tr>
</tbody>
</table>

\[ \text{Biological } \]

### Biological N\textsubscript{2} Fixation

\[ \text{N} \equiv \text{N} + 8\text{H}^+ + 8\text{e}^- + 16\text{ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{ADP} + 16\text{P}_1 \]
Biological N\textsubscript{2} Fixation

- Prokaryotes

<table>
<thead>
<tr>
<th>Aerobic</th>
<th>Anaerobic</th>
<th>Associated w/ Plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azotobacter</td>
<td>Clostridium</td>
<td>Rhizobium</td>
</tr>
<tr>
<td>Beijerinckia</td>
<td>Desulfovibrio</td>
<td>Frankia</td>
</tr>
<tr>
<td>Klebsiella</td>
<td>Cyanobacteria</td>
<td>Azospirillum</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Heterocysts (cyanobacteria)
- Leghaemoglobin (rhizobium)
- Exopolysaccharides
- Temporal isolation

Temporal Isolation

Biological N\textsubscript{2} Fixation

Regulators?

- Light
- Concentration of Oxygen
- Growth limitation
  - Macro nutrients (C, P)
  - Co-factors (Fe, Mo)
Nitrogen Mineralization

- Plant biomass N
- Nitrogen Mineralization
- AEROBIC
  - Organic N
  - Nitrification
  - NH$_4^+$
  - Peat accretion
  - Microbial Biomass N
  - NH$_4^+$
  - N$_2$, N$_2$O (g)
  - Denitrification
- Anaerobic
  - Organic N
  - Nitrogen Fixation
  - NH$_4^+$ uptake
  - Litterfall
  - NH$_3$
  - Volatilization
  - Water Column

Organic Nitrogen

- **Proteins**
  - Amino acids (30-50% of total organic N)
- **Nucleic Acids**
  - 2-5% of total organic N
- **Amino Sugars**
  - 3-13% of total organic N
- **Urea**
Protein Decomposition

Proteins → Peptides

Proteases

Pro

Arg

Ala

Phe

Asp

Lys

Peptidases

Amino acids

Arg

Pro

Ala

Asp

Phe

Lys

Pro

Pro

Peptide Bonds

-2H₂O

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Peptide Bonds:

\[
\begin{align*}
H & \quad R_1 \quad O \\
N & \quad C & \quad C & \quad - & \quad O \\
H & \quad H & \quad H & \quad H \\
R_2 \\
N & \quad C & \quad C & \quad - & \quad O \\
H & \quad H & \quad H & \quad H \\
R_3 \\
N & \quad C & \quad C & \quad - & \quad O \\
H & \quad H & \quad H & \quad H \\
\end{align*}
\]

\[+ \ 2H_2O\]

Detrital Matter:

- **Complex Polymers**: Cellulose, Hemicellulose, Proteins, Lipids, Waxes, Lignin
- **Enzyme Hydrolysis**
- **Monomers**
- **Sugars, Amino Acids, Fatty Acids**
- **Leaching**
- **Uptake**
- **Bacterial Cell**

Electron Acceptors:
- \(O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, CO_2\)

Products:
- \(CO_2, H_2O, NH_4^+, Mn^{2+}, Fe^{2+}, S^{2-}, CH_4\)

Amino acids
- **Energy**
- **ATP**
- **NH_4^+**
- **NH_4^+**
Urea Decomposition

\[
\text{Urea} \rightarrow \text{CO}_2 + 2\text{NH}_3
\]

Urease activity (\(^{14}\text{C} \text{Tracer})

\[
y = -0.014x + 4.4 \\
R^2 = 0.99
\]

[Thorén (2007)]
**Ammonification**

[Mineralization]

*Organic N* → *Ammonium N*

[Breakdown of Organic Matter]

**Immobilization**

*Inorganic N* → *Organic N*  
*(NH₄-N and NO₃ -N)*

[Buildup of Organic Matter]
Microbial Biomass C & N

[Everglades- WCA-2A]

\[ y = 10.7 \cdot x + 2.2 \]

\[ R^2 = 0.78 \]

Microbial Biomass C (g C kg\(^{-1}\))

Microbial biomass N (g N kg\(^{-1}\))

White and Reddy, 2000

Decomposition

- **Microbial Biomass**
  - C/N ratio = 10
  - Efficiency of carbon assimilation
    - Aerobic = 20-60%
    - Anaerobic = 10%

- **Plant Detritus [100 units]**
  - 40% carbon (dry weight basis) = 40 units C
  - Amount of C assimilated during decomposition
    - Aerobic = 16 units [40% efficiency]
    - Anaerobic = 4 units [10% efficiency]
Carbon/Nitrogen Ratio

Nitrogen Demand?
- Microbial Biomass C/N ratio = 10
  - Aerobic = 1.6 units
  - Anaerobic = 0.4 units

Critical Plant Detritus Nitrogen?
- Aerobic = 1.6 %
- Anaerobic = 0.4%

Critical Carbon/Nitrogen Ratio?
- Aerobic = \([40\% \text{ C}]/[1.6\% \text{ N}] = 25\)
- Anaerobic = \([40\% \text{ C}]/[0.4\% \text{ N}] = 100\)

Carbon/Nitrogen Ratio

Mineralization [M] vs. Immobilization [I]

- **Aerobic**
  - \(I > M = \text{C/N ratio} > 25\)
  - \(M > I = \text{C/N ratio} < 25\)

- **Anaerobic**
  - \(I > M = \text{C/N ratio} > 100\)
  - \(M > I = \text{C/N ratio} < 100\)
N Mineralization/Immobilization
[Aerobic]

Decomposition (days)

C/N = 15
C/N = 35
C/N = 100

Inorganic N Release

N Mineralization/Immobilization
[Aerobic]

Decomposition Period [days]

Carbon/Nitrogen Ratio

0 10 20 30 40

Immobilization

Mineralization

C/N ratio of soil humus/
microbial biomass

0 150
Regulators of Ammonification

Substrate quality
- C/N ratio of the substrate
- Secondary compounds
- N forms (soluble vs. structural compounds)

Microbial Activity
- Extracellular enzyme activity
- Supply of electron acceptors (Redox)
- Temperature
- pH

Mineralizable Nitrogen
[Everglades-WCA-2A]

\[ y = 0.317x + 52.4 \]
\[ R^2 = 0.76 \]
Fate of Ammonium

Nitrogen Uptake by Rice (\(^{15}\text{N}\))
Ammonium Adsorption - Aerobic

Ammonium Adsorption - Anaerobic
**Ammonium Fixation**

Illite - Clay Mineral

- Fixed Ammonium
- Interlayer Space
- Si-O layer
- Al-OH layer

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Adsorption/Desorption Equilibrium

Fixed Exchangeable Solution

\[ \text{NH}_4^+ \xrightarrow{\text{adsorption}} \text{NH}_4^+ \]

\[ \text{NH}_4^+ \xrightarrow{\text{desorption}} \text{NH}_4^+ \]

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Adsorption/Desorption Equilibrium

\[ \text{NH}_4^+ \xrightarrow{\text{adsorption}} \text{NH}_4^+ \]

\[ \text{NH}_4^+ \xrightarrow{\text{desorption}} \text{NH}_4^+ \]

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\[ S = K \times C + S_0 \]

\[ \text{NH}_4^+_{\text{ads}} = K \times [\text{NH}_4^+] + \text{NH}_4^+_{\text{fixed}} \]

**Ammonium Adsorption - Salinity**

Environmental Geology (2003) 45:72–78
Increasing salinity

### Table 1

The parameters of ammonium adsorption isotherm equation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sampling site</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K^*$ (mL g$^{-1}$)</td>
<td>XP</td>
</tr>
<tr>
<td>$q$ (µg g$^{-1}$ dry wt.)</td>
<td>2.32</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.939</td>
</tr>
</tbody>
</table>

* $K^*$ (mL g$^{-1}$) is the slope of the regression line; $q$ (µg g$^{-1}$ dry wt.) is the fixed ammonium in the sediments; $r$ is the correlation coefficient, $a=0.01$

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Environmental Geology (2003) 45:72–78

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**Ammonia Flux**

\[ \text{NH}_3(g) \] (Volatilization)

\[ \text{NH}_3(g) \quad \rightarrow \quad \text{NH}_3(aq) + \text{H}^+ \]

Photosynthesis

\[ \text{O}_2 + \text{CH}_2\text{O} \quad \leftrightarrow \quad \text{CO}_2 + \text{H}_2\text{O} \]

Respiration

\[ 2\text{H}^+ + \text{CO}_3^{2-} \quad \leftrightarrow \quad \text{CO}_2 + \text{H}_2\text{O} \]

Water

\[ \text{NH}_4^+ \]

Soil

\[ \text{NH}_4^+ \text{ (adsorbed)} \]

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Diel pH changes in the Water Column

Ammonia Volatilization
(assuming high pH)

- Floodwater depth
- Plant density
- SAV/Periphyton Density
- Temperature
- Wind speed
- Soil CEC
Ammonia Volatilization

- $\text{NH}_4^+ = \text{NH}_3 + \text{H}^+$
- Temperature
- High floodwater pH
- Cation exchange capacity of soil
- High soil pH
- Wind speed
- High algal activity
- Floodwater depth
- Plant density

Nitrification

- Nitrogen Fixation
- Nitrification
- Denitrification
- Peat accretion
- Microbial Biomass N
- Adsorbed $\text{NH}_4^+$
- Organic N
- $\text{NH}_4^+$
- Chemical Equilibrium
- $\text{NH}_3$
- $\text{NO}_3^-$
- $\text{NH}_4^+$
- $\text{NH}_3$
- $\text{NO}_3^-$
- $\text{N}_2$
- $\text{N}_2$
Nitrification

\[ \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^- \]

Obligate aerobes (O₂ e⁻ acceptor)
- Common nitrifiers (autotrophs)
- Methanotrophs
- Heterotrophs

Sites of Nitrification

- Aerobic Water column
- Aerobic Soil/Floodwater Interface
- Aerobic Root Zone
Nitrification

- $\text{NH}_4^+ \rightarrow \text{NO}_2^- \quad \text{Nitrosomonas (‘Nitroso’ spp.)}$
- $\text{NO}_2^- \rightarrow \text{NO}_3^- \quad \text{Nitrobacter (‘Nitro’ spp.)}$
- Obligate aerobes (O$_2$ e$^-$ acceptor)
- Energy/e$^-$ source: $\text{NH}_4^+$
- Carbon source: $\text{CO}_2$

**Step I: Nitrosomonas** $\Delta G^o = -65 \text{ kcal/mole}$

$$\begin{align*}
\text{NH}_4^+ + 2\text{H}_2\text{O} & \rightarrow \text{NO}_2^- + 6\text{e}^- + 8\text{H}^+ \\
\frac{1}{2} \text{O}_2 + 6\text{e}^- + 6\text{H}^+ & \rightarrow 3\text{H}_2\text{O} \\
\text{NH}_4^+ + \frac{1}{2}\text{O}_2 & \rightarrow \text{NO}_2^- + 3\text{H}_2\text{O} + \text{H}^+
\end{align*}$$

**Step II: Nitrobacter** $\Delta G^o = -18 \text{ kcal/mole}$

$$\begin{align*}
2\text{NO}_2^- + 2\text{H}_2\text{O} & \rightarrow 2\text{NO}_3^- + 4\text{e}^- + 4\text{H}^+ \\
\text{O}_2 + 4\text{e}^- + 4\text{H}^+ & \rightarrow 2\text{H}_2\text{O} \\
2\text{NO}_2^- + \text{O}_2 & \rightarrow 2\text{NO}_3^-
\end{align*}$$
Heterotrophic Nitrification

- Bacteria and fungi
- Poorly studied
- Only dominant under high C/low N conditions
- Many facultative (reduce oxidized N to N\(_2\))
  “Nitrifier denitrification”

Nitrification

- Ammonia
  NH\(_3\) toxic to nitrifying bacteria
- pH
  7 - 8.5 optimum
- Sulfide
  S\(^2\)- toxic to nitrifying bacteria
Nitrification

**Ideal Conditions**

- $\text{NH}_4^+$
- $\text{NO}_2^-$
- $\text{NO}_3^-$

**Inhibited**

- $\text{NH}_4^+$
- $\text{NO}_2^-$
- $\text{NO}_3^-$

Oxygenases

- $\text{NH}_4^+$ $\rightarrow$ $\text{NH}_2\text{OH}$
- $\text{NH}_2\text{OH}$ $\rightarrow$ $[\text{NOH}]$

Hydroxylamine oxidoreductase

- $[\text{NOH}]$ $\rightarrow$ $\text{N}_2\text{O}$
- $\text{NO}_2^-$ $\rightarrow$ $\text{NO}_3^-$

Oxygen stress

- $\text{NH}_2\text{OH}$ $\rightarrow$ $\text{NH}_3$

Chemical

Nitrification reductase

- $\text{N}_2\text{O}$ $\rightarrow$ $\text{N}_2$
- $\text{NO}_3^-$ $\rightarrow$ $\text{O}_2$

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Inhibited Nitrification

‘Leaky Pipe’ Model:

\[
\begin{array}{c}
\text{NH}_4^+ \rightarrow \text{NO}_2^{-} \rightarrow \text{NO}_3^{-} \rightarrow \text{N}_2 \\
\text{Nitrifiers} \quad \text{Nitrifiers} \quad \text{Denitrifiers}
\end{array}
\]

Regulators:
- Ammonia concentration
- Oxygen availability
- Alkalinity and CO\(_2\)
- Temperature
- Nitrifying population
- pH
- CEC
Anaerobic Ammonium Oxidation: Anammox

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

Anaerobic Ammonium Oxidation (ANAMMOX)

$$5\text{NH}_4^+ + 3\text{NO}_3^- \rightarrow 4\text{N}_2 + 9\text{H}_2\text{O} + 2\text{H}^+$$

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

Mechanism of anaerobic ammonium oxidation. NR is a nitrite-reducing enzyme (NH$_2$OH is the assumed product); HH (hydrazine hydrolase) condenses hydrazine out of ammonia and hydroxylamine; HZO is a hydrazine-oxidising enzyme (which might be equivalent to hydroxylamine oxidoreductase).

*Current Opinion in Biotechnology* 2001, 12:293–288

“Nitrates, which the juice of beetroot naturally includes, decompose, and great quantities of nitrous vapor form at the surface of the vats”

“From experience”:

Nitrate is reduced under certain conditions in arable land releasing nitrogen gas

Nitrate reduction occurs in arable soil which contains a high organic matter

We have observed that this reduction occurs when the soil atmosphere is completely stripped of oxygen

Nitrate Reduction

- Denitrification
  - \( \text{NO}_3^- \overset{5e^-}{\rightarrow} \text{N}_2 \)

- Dissimilatory nitrate reduction to ammonia (DNRA)
  - \( \text{NO}_3^- \overset{8e^-}{\rightarrow} \text{NH}_4^+ \)

- Assimilatory nitrate reduction to ammonia
  - \( \text{NO}_3^- \rightarrow \text{NH}_4^+ \rightarrow \) Proteins
## Nitrate Reduction

### Assimilatory
- NH\(_4^+\) uptake for growth - biosynthesis
- NH\(_4^+\) concentration- main regulator
- Growth linked
- Occurs mainly in aerobic soils
- Insensitive to O\(_2\)

### Dissimilatory
- Functions as an electron acceptor
- Oxygen concentration main regulator
- Linked to catabolic reactions
- Occurs in anaerobic soils
- Sensitive to O\(_2\)

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## Nitrate Reduction

### Denitrification
- NO\(_3^-\)/NO\(_2^-\) → N\(_2\)
  - 5 e- transferred
- Low electron pressure
- Eh = 200 – 300 mV
- O\(_2\) transient conditions
- Facultative anaerobes

### DNRA
- NO\(_3^-\) → NH\(_4^+\)
  - 8 e- transferred
- High electron pressure
- Eh = < 0 mV
- Lake sediments or permanent wetlands
- Obligate anaerobes

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Regulators of Denitrification

- Low $O_2$ content - Low Eh
- Presence of Electron Acceptor - N Oxides
- Facultative Anaerobes - Enzymes
- Electron Donor - Carbon Source
  - Organic carbon compounds
  - Reduced sulfur compounds
- Temperature
- Nitrate diffusion/flux to anaerobic zones
- Plant root density

Sites of Nitrification/Denitrification
**Dissimilatory Nitrate Reduction**

\[
\begin{align*}
\text{NO}_3^- & \rightarrow \text{NO}_2^- \rightarrow [\text{HNO}] \rightarrow [\text{H}_2\text{N}_2\text{O}_2] \\
\text{NH}_2\text{OH} & \rightarrow \text{NH}_4^+ \rightarrow \text{N}_2 \\
\text{N}_2\text{O} & \rightarrow \text{N}_2
\end{align*}
\]

[Biological]

[HNO] = Nitroxy1
[H\(_2\text{N}_2\text{O}_2\)] = Hypno1rite
NH\(_2\)OH = Hydroxylamine

**Abiotic Nitrate Reduction**

(‘Chemo-denitrification’)

\[
\begin{align*}
5 \text{Mn}^{2+} + 2 \text{NO}_3^- + 4 \text{H}_2\text{O} & \rightarrow 5 \text{MnO}_2 + \text{N}_2 + 8 \text{H}^+ \\
\Delta G^\circ & = -14.20 \text{ kJ/mole} \quad (1) \\
5 \text{Mn}^{2+} + 2 \text{NO}_3^- + 8 \text{OH}^- & \rightarrow 5 \text{MnO}_2 + \text{N}_2 + 4 \text{H}_2\text{O} \\
\Delta G^\circ & = -653.22 \text{ kJ/mole} \quad (2) \\
2 \text{NH}_3 + 3 \text{MnO}_2 + 6 \text{H}^+ & \rightarrow 3 \text{Mn}^{2+} + \text{N}_2 + 6 \text{H}_2\text{O} \\
\Delta G^\circ & = -658.64 \text{ kJ/mole} \quad (3)
\end{align*}
\]

*Geochemistry and Cosmochronology Acta, Vol. 61, No. 19, pp. 4043–4052, 1997*
Abiotic Nitrate Reduction

Lithotrophic Nitrate Reduction

Other potential e- donors: S^{2-}, H_2

Fig. 1. Potential Fe-N redox pathways in anoxic sediments: Organotrophic NO_3^- reduction to N_2 (1) or to NH_4^+ (2); organotrophic dissimilatory Fe(III) reduction (3); lithotrophic [Fe(II)-driven] NO_3^- reduction to N_2 (4) or to NH_4^+ (5). Thick lines denote external loading of NO_3^- and organic carbon (CH_2O). Temporal variations in NO_3^- and CH_2O loading have the potential to cause temporal/spatial overlap of organotrophic and lithotrophic pathways. (Figure from Environmental Microbiology, vol. 9, pp. 100–113, 2006.)
N.R. Coupled to Fe(II) Oxidation:
Paddy Soils

\[
\text{NO}_3^- + \text{Fe(II)} \rightarrow \text{NO}_2^- \rightarrow \text{Fe(III)} + \text{N}_2
\]


\[
\text{NO}_3^- \text{-control} \quad \text{Fe(III)-culture} \quad \text{NO}_3^- \text{-culture} \quad \text{Fe(III)-control}
\]

### Ecosystem Denitrification rate, mg N m⁻² day⁻¹ Reference

<table>
<thead>
<tr>
<th>Ecosystem</th>
<th>Denitrification rate, mg N m⁻² day⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater wetlands</td>
<td>7 – 5,914</td>
<td>Buresh et al. 2006</td>
</tr>
<tr>
<td>Constructed wetlands</td>
<td>3-1,020</td>
<td>Martin and Reddy, 1996</td>
</tr>
<tr>
<td>River and stream sediments</td>
<td>18-116</td>
<td>Seitzinger, 1988</td>
</tr>
<tr>
<td>Lakes</td>
<td>34-57</td>
<td>Seitzinger, 1988</td>
</tr>
<tr>
<td>Coastal and marine sediments</td>
<td>&lt;0.1 - 559</td>
<td>Seitzinger, 1988</td>
</tr>
</tbody>
</table>
Regulators of Denitrification

- Low O₂ content - Low Eh
- Presence of Nitrogenous Oxides
- Heterotrophs: Carbon Source
  Organic carbon compounds, DOC
- Lithotrophs: Electron Source
  Reduced Fe, Mn, S compounds, H₂
- Temperature
- Nitrate diffusion/flux to anaerobic zones
- Plant root density
  Nitrate uptake, O₂ loss

Denitrification

<table>
<thead>
<tr>
<th>Wetland</th>
<th>Denitrification Rate (mg N kg⁻¹ day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Houghton Lake Wetland</strong></td>
<td></td>
</tr>
<tr>
<td>Inflow Zone</td>
<td>74</td>
</tr>
<tr>
<td>Interior Zone</td>
<td>11</td>
</tr>
<tr>
<td><strong>Orange County ESAWT</strong></td>
<td></td>
</tr>
<tr>
<td>Inflow Zone</td>
<td>9</td>
</tr>
<tr>
<td>Interior Zone</td>
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<td></td>
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<td>Inflow Zone</td>
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</table>

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**Coupled Nitrification-Denitrification**

**Nitrification rate depends on:**
- Ammonification rate
- Ammonium flux into aerobic zone

**Denitrification rate depends on:**
- Nitrification rate
- Nitrate flux into anaerobic zones

**Nitrification-denitrification occurs in:**
- Flooded soil-water column with aerobic-anaerobic interfaces
- Aerobic-anaerobic interfaces in the root zone
- Water-table fluctuations/ alternate flooding and draining

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**From:** Reddy (1989)
Everglades –WCA-2A

Nitrate source/
High C/Low Eh

Nitrate depleted/
High C/Low Eh

Nitrate source/
Low C,P/Low Eh

Denitrification Rate
(mg N kg⁻¹ hr⁻¹)

Distance (km)

With Glucose

Without Glucose

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Denitrification Walls:
(Schipper et al. 2003)
ANAMMOX vs. Denitrification

- Supply of NO$_2^-$
  - Low NO$_2^-$ favors Denitrification, High NO$_2^-$ (>10mM) inhibits ANAMMOX

- Organic matter availability
  - Higher DOC favors Denitrification

- Temperature
  - ANAMMOX dominant @ low Temp.

FIG. 3. Rates of dinitrogen production by anaerobic oxidation of NH$_4^+$ with NO$_2^-$ and by denitrification as a function of temperature (A) and the production of dinitrogen by the oxidation of NH$_4^+$ with NO$_2^-$ relative to the total dinitrogen production in the sediment (B). Error bars indicate standard errors.
Denitrification vs. DNRA

- Supply of NO$_3^-$
  - Low NO$_3^-$ favors DNRA

- Organic matter availability
  - High DOC favors DNRA

- Hydropattern
  - Denitrifiers are largely facultative
Fig. 3—Relationship between NO₃⁻ loss and CO₂ production in mineral and organic soils. Middle line represents the average linear regression for all soils. Two outside lines represent the regression in 2 extreme soils.

Reddy et al. (1982)
Potential Fate

Low Organic Matter (Low C:EA)

NO

NO\textsubscript{3}^{-}

N\textsubscript{2}O

N\textsubscript{2}

N\textsubscript{2}O

NH\textsubscript{4}^{+}

NO\textsubscript{2}^{-}

H^{+}

N\textsubscript{2}

Anaerobic

Aerobic

High Organic Matter (High C:EA)

Permanently Anaerobic

Anaerobic

Dissimil

Potential Fate


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Nitrogen Cycling

- **Plant biomass N**
- **Litterfall**
- **Volatilization**
- **N2, N2O (g)**
- **N2**
- **NH3**

**AEROBIC**
- **Nitrification**
- **NH4+**
- **Mineralization**
- **Plant uptake**
- **[NH4+]s**
- **Peat accretion**
- **Microbial Biomass N**
- **Adsorbed NH4+**

**ANAEROBIC**
- **Denitrification**
- **NO3-**
- **[NH4+]a**
- **N2, N2O (g)**

**Nitrogen Fixation**

Water Column

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