The Biosphere: Biogeochemical cycling of C,N,P in freshwater lakes and wetlands
OR: Some basic metabolic processes

Outline:
- Introduction
- Redox
- The basic nitrogen cycle
  - Inorganic nitrogen cycle
  - Nitrogen fixation
  - Other nitrogen reactions
- Sulfate Reduction
- Methanogenesis
- Lakes

Please note that the majority of the text below is taken from Chapter 7 in:

Introduction

Oxygen is only sparingly soluble in water and diffuses about $10^4$ times more slowly in water than in air
  - Problem for organisms living in water

Plus, heterotrophic respiration may totally deplete O$_2$ in some aquatic and wetland systems

As a result, nutrient cycling in freshwater lakes and wetlands controlled by both:
1. reduction potential (redox)
2. microbial transformations of nutrient elements that occur under conditions in which O$_2$ is not always abundant

Examples:
- Availability of phosphorus in lakes differs between surface waters saturated with atmospheric O$_2$ and deeper waters in which O$_2$ may be depleted
- Anaerobic microbial processes (denitrification, sulfate reduction, methanogenesis) are responsible for the release of N$_2$, H$_2$S and CH$_4$ from wetland sediments
  - Also coupled to changes in oxidation state of Fe and Mn in wetland soils
- Anaerobic decomposition is often incomplete, so many wetlands (e.g., bogs) store significant amounts of organic carbon (net ecosystem production)
  - Wet soils contain ~1/3 of all organic matter stored in soils of the world (but only cover ~3.6% of world’s land area

Redox
Redox potential is used to express the tendency of an environment to receive or supply electrons

- Oxic environments are said to have high redox potential because $O_2$ is available as an electron acceptor
  - E.g., Fe oxidizes when it shares electrons of its outer shell with $O_2$ to become rust ($Fe_2O_3$)

Heterotrophic organisms in oxic environments capitalize on use of $O_2$ as a powerful electron acceptor

- Electrons are derived from metabolism of reduced organic compounds that are obtained from the environment and oxidized to $CO_2$

The oxidation state of an environment (redox potential) is determined by particular suite of chemical species that is present

Oxidized species + e^- + H^+ $\leftrightarrow$ reduced species

Few oxic environments have redox potentials less than +600 mV

- Progressive decrease in redox potential occurs when flood soils (Figure 7.3)
  - Redox potential drops as heterotrophic respiration of organic carbon depletes soil $O_2$
- Where organic carbon is abundant, a strong gradient of redox potential may develop in sediments over a depth as small as 2 mm

Studies suggest that a particular sequence of reactions is expected as progressively lower redox potentials are achieved

- After $O_2$ is depleted by aerobic respiration, denitrification begins when redox falls to +747 mV (at pH 7)
  - Denitrifying bacteria use nitrate as an alternative electron acceptor during oxidation of organic matter
- When nitrate is depleted, reduction of $Mn^{4+}$ begins below a redox of +526 mV, followed by reduction of $Fe^{3+}$ at < -47 mV

In many cases there is some overlap between zones of denitrification and zones of $Mn$ reduction in sediments

- Most microbes in this zone are facultative anaerobes that can tolerate periods of aerobic conditions

There is little overlap between zones of $Mn$ reduction and $Fe$ reduction, because soil bacteria show an enzymatic preference for $Mn^{4+}$, and $Fe^{3+}$ reduction will not begin until $Mn^{4+}$ is depleted

- Below zone of $Mn^{4+}$ reduction, most redox reactions are performed by obligate anaerobes

Use of $Fe$ is widespread in the transition zone from mildly oxidizing to strongly reducing conditions
• Certain obligate anaerobes use energy derived from fermentation/Fe$^{3+}$ reduction to engage in nitrogen fixation

\[
C_6H_{12}O_6 \rightarrow CH_3COOH + CH_3CH_2COOH + CO_2 + H_2
\]

\[
2Fe^{3+} + H_2 \rightarrow 2Fe^{2+} + 2H^+
\]

Such nitrogen fixation essential to augment meager supplies of N that result from anaerobic mineralization

Below depth of Fe reduction
• Get sulfate reduction occurring around –221 mV
• Methanogenisis occurs around –244 mV

These reactions preferred by obligate anaerobic bacteria (some of which also engage in N fixation)

The free energy of reaction (\(\Delta G\)) is greatest for aerobic respiration (-29.9) and least for methanogenisis (-5.6) (Table 7.1)

At any redox potential, the microbial community conducting the metabolism with greatest energy yield will usually outcompete the rest.
• Low energy yields accounts for the inefficiency of anaerobic metabolism and preservation of organic matter in sediments
Fluctuating water tables in wetlands (move around zones of oxidation):

- Example:
  - Total rate of denitrification is enhanced when seasonal periods of aerobic conditions stimulate mineralization and nitrification of organic nitrogen
  - This makes NO₃ more available for denitrifiers when water level rises later
    - In continually flooded soils, nitrate must diffuse downwards from aerobic layers to anaerobic layers where denitrification occurs
  - Reduced elements may also diffuse upwards to be oxidized.

**The basic Nitrogen cycle**

![Nitrogen cycle diagram]

**Inorganic nitrogen cycle**

- no nitrogen is found in native rock
- the **ultimate source of nitrogen for ecosystems** is molecular nitrogen (N₂) in the **atmosphere** (78.1% by volume)
- N₂ may dissolve in water
- virtually all nitrogen would occur as N₂ if not for biological processes occurring in the presence of oxygen

Molecular nitrogen enters biological pathways through **nitrogen fixation** by certain microorganisms:

\[
\text{molecular nitrogen (N}_2\text{)} \rightarrow \text{ammonia (NH}_3\text{).}
\]

**Nitrogen Fixation**

- Lightning can fix nitrogen:
• produces momentary conditions of high pressure and temperature to allow N₂ to be fixed

However:
• Done primarily by bacteria; Example:
  • A zotobacter (free-living)
  • Rhizobium (lives in symbiotic association with roots of some leguminous plants (e.g., clover))
  • blue-green algae

Biological fixation of nitrogen much greater than abiotic fixation. Of the N fixed biologically:
• about 30% comes from asymbiotic fixation
• remainder comes from symbiotic fixation in the higher plants.

Biological nitrogen fixation requires energy:
• N₂ fixing microorganisms get energy by oxidizing sugars or other organic compounds
• free-living bacteria get energy by metabolizing organic detritus
• Rhizobium lives symbiotically with leguminous plants because plants provide them with sugars produced from photosynthesis.

Other nitrogen reactions

Nitrogen has numerous oxidation states. A large number of biochemical transformations of N are possible since N is found at valence states ranging from -3 (ammonia: NH₃) to +5 (nitrate: NO₃⁻).

Nitrification involves the oxidation of nitrogen by specialized bacteria:
• first from ammonia to nitrite (NO₂⁻) by e.g., Nitrosomonas in soil
• then from nitrite to nitrate by e.g., Nitrobacter in soil

Nitrification steps are oxidation and require oxygen to act as an electron acceptor.

Denitrification: In anoxic environments, nitrate and nitrite can act as electron acceptors (oxidizers), and the nitrification reactions reverse:

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

Denitrification is accomplished by such bacteria as Pseudomonas denitrificans

Additional physical reactions under anaerobic conditions can produce molecular nitrogen:

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

Ammonification
• begin with organic nitrogen such as protein
• hydrolysis of protein and the oxidation of amino acids produces ammonia (NH₃)
• done by all organisms

**Sulfate reduction**

Dissimilatory sulfate reduction in anaerobic environments is analogous to denitrification, in which SO₄²⁻ acts as an alternative electron acceptor during the oxidation of organic matter by bacteria in the genera *Desulfovibrio* and *Desulfotomaculum*:

\[
2H^+ + SO_4^{2-} + 2(CH_2O) \rightarrow 2CO_2 + H_2S + 2H_2O
\]

These bacteria produce variety of sulfur gases, including:

- Hydrogen sulfide (H₂S)
- Dimethylsulfide [(CH₃)₂S]
- Carbonyl sulfide (COS)

Prior to human industrialization, the release of biogenic gases from anaerobic wetland soils was dominant source of sulfur gases in the atmosphere.

- Release of H₂S from wetland soils is often much less than rate of sulfate reduction as depth
  - H₂S can react with Fe²⁺ to precipitate FeS
    - FeS may subsequently be converted to pyrite:
      \[
      FeS + H_2S \rightarrow FeS_2 + 2H^+ + 2e^-
      \]

When H₂S diffuses upward through the zone of Fe³⁺, pyrite (FeS₂) is precipitated:

\[
2Fe(OH)_3 + 2H_2S + 2H^+ \rightarrow FeS_2 + 6H_2O + Fe^{2+}
\]

During periods of low water, specialized bacteria may reoxidize FeS₂, releasing SO₄²⁻ that can then be used by sulfate-reducing bacteria

- i.e., recycling of S between oxidized and reduced forms

H₂S also reacts with organic matter to form carbon-bonded S that accumulates in peat and lake sediments

- Carbon-bonded forms include:
  - Original plant material
  - Reaction of H₂S with organic matter
  - Direct immobilization of SO₄ by soil microbes

**Methanogenesis**

The concentration of SO₄²⁻ in most freshwater wetlands is not high

- Zone of SO₄²⁻ is closely underlain by zone of active methanogenic bacteria
CH$_4$ production in freshwater environments:

\[ \text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4 \]

- Acetate-type compounds produced from cellulose by fermenting bacteria coexisting at same depth

Methane also produced by CO$_2$ reduction:

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]

in which the H is available as a by-product of fermentation

CO$_2$ is found as HCO$_3^-$
- Methanogenesis by CO$_2$ reduction accounts for the limited release of H$_2$ from wetland soils

Methanogenic bacteria can only use certain organic substances for acetate splitting
- In many cases there is evidence that sulfate-reducing bacteria are more effective competitors for same compounds

Sulfate-reducing bacteria also use H$_2$ as a source of electrons, and are more efficient in uptake of H$_2$ than methanogens engaging in CO$_2$ reduction
- Therefore in most environments, little overlap between zone of methanogenesis and zone of sulfate-reduction
  - Methanogenesis begins when sulfate is depleted

In marine environments, methanogenesis is inhibited by high concentrations of SO$_4$ in seawater
- Where methanogenesis occurs in marine environments, CO$_2$ reduction is much more important than acetate splitting, because acetate is entirely depleted within zone of sulfate-reducing bacteria

A number of bacteria also consume CH$_4$ (CH$_4$ oxidation or methanotrophy)
- Therefore loss of CH$_4$ from ecosystem determined by balance between methanogenesis at depth and methane oxidation as it diffuses up through aerobic zones of higher redox potential

In some marine sediments, anaerobic CH$_4$ oxidation is also performed by sulfate-reducing bacteria that use CH$_4$ as a source of reduced carbon

\[ \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O} \]

Figure 7.8
Lakes

Physical properties of water exert a significant control on net primary productivity and nutrient cycling in lakes.

Sunlight warms water, but light energy is rapidly attenuated at depth:
- Have thermal stratification of lakes because water is densest at 4°C
  - Upper layer: epilimnion
  - Lower layer: hypolimnion
  - Zone of rapid temperature change between two layers is thermocline or metalimnion

Primary production by phytoplankton usually confined to epilimnion when lake stratified:
- Depends on direct nutrient inputs to surface waters and regeneration of nutrients there
  - Because of high redox potential in epilimnion, organic materials decompose rapidly due to aerobic respiration
    - Still have low quantities of available nutrients due to rapid uptake by phytoplankton

Phytoplankton not bathed in atmospheric CO₂, and must depend on that dissolved in water:

\[
CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}
\]
- At pH < 4.3, mostly CO₂
- Between pH 4.3 and 8.3, as HCO₃⁻
- At pH > 8.3 as CO₃^{2-}

Usually a strong relationship between lake production and total concentration of nutrients, especially phosphorus.

Figure 7.10

Under most natural conditions, P input to lakes is relatively small:
- Little P in precipitation
- P effectively retained in terrestrial watersheds by vegetation and chemical interactions with soil minerals
- Available P may also precipitate with Fe and Mn minerals that are insoluble at high redox potentials of surface waters

Continued NPP by phytoplankton depends on rapid cycling of P between dissolved (e.g., HPO₄^{2-}) and organic forms in the epilimnion:
- Turnover of P in epilimnion dominated by bacterial decomposition of organic matter
  - Phytoplankton and bacteria excrete extracellular phosphatases to aid in mineralization of P
- Planktonic bacteria may immobilize P when C/P ratio of their substrate is high
  - Globally, N/P ratio of freshwater phytoplankton between 20-40, and net P mineralization begins at N/P < 16

During lake stratification, P pool in surface waters is progressively depleted as phytoplankton and other organisms die and sink to hypolimnion (Figure 7.11)
  - P mineralization continues in hypolimnion and sediments
    - Some is returned to surface during periods of seasonal mixing of lakes

When phytoplankton communities grow in limited supplies of nitrogen (often the case if there is sufficient P), there is a shift to algal dominance from green algae to blue-green algae
  - Blue-green algae fix nitrogen, adding to its availability and raising the N/P ratio
    - CO2 can be drawn in from the atmosphere

**Figure 7.13**