Nitrogen, Sulfur, Phosphorus, and Other Nutrients

- Nitrogen
- Sulfur
- Phosphorus
- Silicon, Iron, and Other Trace Nutrient Cycles
- Gradients of Redox and Nutrient Cycles and Interactions Among the Cycles

Carbon and Nitrogen cycles

A. Carbon and nitrogen cycles are tightly coupled

B. These are 2 of the most important nutrients in all ecosystems

1. Carbon
   - **a) atom that organic molecules are based upon**
   - **b) energy/redox currency**
2. Nitrogen
   - **a) limits productivity in terrestrial, marine, and many freshwaters**
   - **b) important macromolecules like proteins, DNA, and RNA are based upon N**

C. microbes are of utmost importance in nutrient cycling

Some basics about redox reactions

•Photosynthesis and respiration are the most commonly taught ones, but microbes can carry out some funky biochemical reactions.

•Reduction: when a reactant receives an electron. There is usually a hydrogen passed along with the electron, but not always. This requires energy under high redox potentials.

•Oxidation: when a reactant gives up an electron. There is usually hydrogen lost in the process, or oxygen atoms gained, but not always. This releases energy under high redox potentials.

•In biochemistry, reduction reaction is always coupled with an oxidation reaction

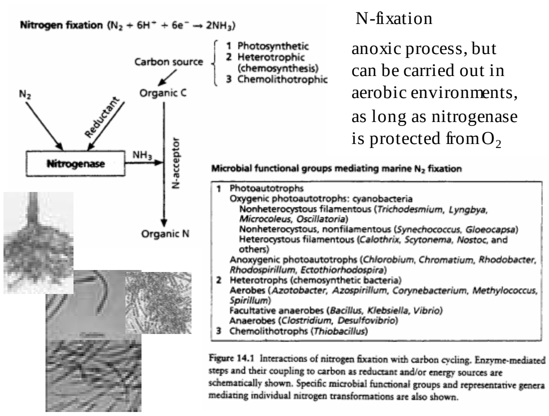
•Most organisms must oxidize fixed carbon in order to acquire energy, but the amount of energy they get from said fixed carbon depends on what gets reduced in the process, which in turn depends on the redox potential.

Nitrogen Fixation

- N_2 gas to ammonium, very expensive energetically
- Only bacteria known to fix nitrogen
- Nitrogenase sensitive to O_2, and a variety of adaptations protect it
- Lightning also fixes N_2 to NOx in the atmosphere
- Nitrogen-fixing cyanobacteria can be very important in lake N cycles

N-fixation

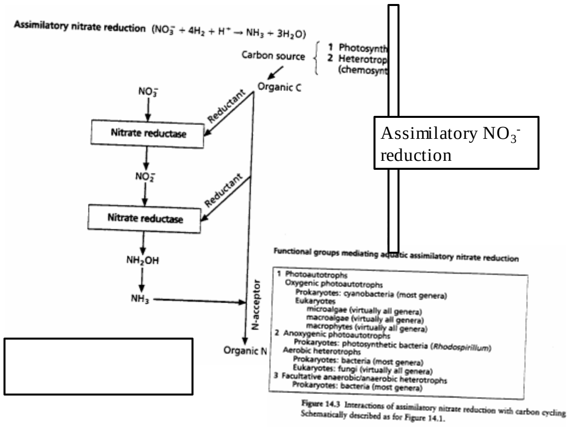
anoxic process, but can be carried out in aerobic environments, as long as nitrogenase is protected from O_2



Microbial functional groups mediating marine N_2 fixation

1 Photoautotrophs
  Oxygenic photoautotrophs: cyanobacteria
    Nonheterocystous filamentous (*Trichodesmium, Lyngbya, Microcoleus, Oscillatoria*)
    Nonheterocystous, nonfilamentous (*Synechococcus, Gloeocapsa*)
    Heterocystous filamentous (*Calothrix, Scytonema, Nostoc*, and others)
  Anoxygenic photoautotrophs (*Chlorobium, Chromatium, Rhodobacter, Rhodospirillum, Ectothiorhodospira*)
2 Heterotrophs (chemosynthetic bacteria)
  Aerobes (*Azotobacter, Azospirillum, Corynebacterium, Methylococcus, Spirillum*)
  Facultative anaerobes (*Bacillus, Klebsiella, Vibrio*)
  Anaerobes (*Clostridium, Desulfovibrio*)
3 Chemolithotrophs (*Thiobacillus*)

Figure 14.1 Interactions of nitrogen fixation with carbon cycling. Enzyme-mediated steps and their coupling to carbon as reductant and/or energy sources are schematically shown. Specific microbial functional groups and representative genera mediating individual nitrogen transformations are also shown.

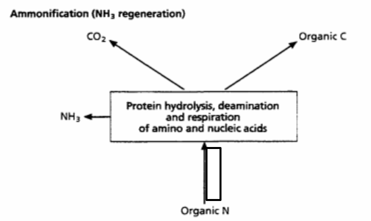


Assimilatory NO_3^- reduction

Functional groups mediating aquatic assimilatory nitrate reduction

1 Photoautotrophs
  Oxygenic photoautotrophs
    Prokaryotes: cyanobacteria (most genera)
    Eukaryotes
      microalgae (virtually all genera)
      macroalgae (virtually all genera)
      macrophytes (virtually all genera)
2 Anoxygenic photoautotrophs
    Prokaryotes: photosynthetic bacteria (*Rhodospirillum*)
  Aerobic heterotrophs
    Prokaryotes: bacteria (most genera)
    Eukaryotes: fungi (virtually all genera)
3 Facultative anaerobic/anaerobic heterotrophs
    Prokaryotes: bacteria (most genera)

Figure 14.3 Interactions of assimilatory nitrate reduction with carbon cycling Schematically described as for Figure 14.1.



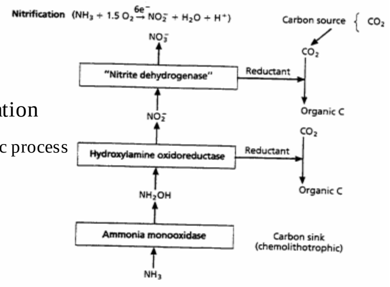
Microbial functional groups mediating marine ammonification

1 Photoautotrophs
  Oxygenic photoautotrophs
    Prokaryotes (cyanobacteria)
    Eukaryotes (all phyla and genera)
  Anoxygenic photoautotrophs (all genera)
2 Heterotrophs (chemosynthetic bacteria)
  Aerobes (most genera)
  Facultative anaerobes (most genera)
  Anaerobes (most genera)
3 Chemolithotrophs (most genera)

Figure 14.4 Interactions of ammonification with carbon cycling. Schematically described as for Figure 14.1.

Nitrification

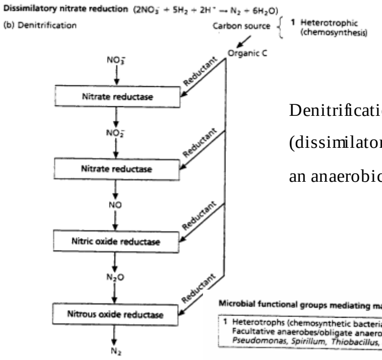
an aerobic process



Microbial functional groups mediating marine nitrification

1 Chemolithotrophs
  Aerobes (*Nitrosomonas*: $NH_3 \rightarrow NH_2OH \rightarrow NO_2^-$)
  (*Nitrobacter*: $NO_2 \rightarrow NO_3^-$)

Figure 14.5 Interactions of nitrification with carbon cycling. Schematically described as for Figure 14.1.



Denitrification

(dissimilatory nitrate reduction)

an anaerobic process

Microbial functional groups mediating marine denitrification

1 Heterotrophs (chemosynthetic bacteria)
  Facultative anaerobes/obligate anaerobes (*Bacillus, Corynebacterium, Pseudomonas, Spirillum, Thiobacillus,* and others)

Figure 14.2 Interactions of dissimilatory nitrate reduction with carbon cycling. Schematically described as for Figure 14.1.

Influence of plants on coupled nitrification/denitrification

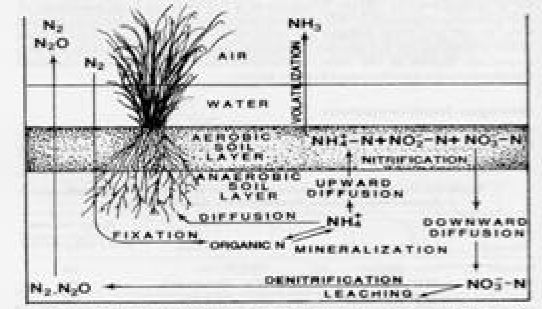
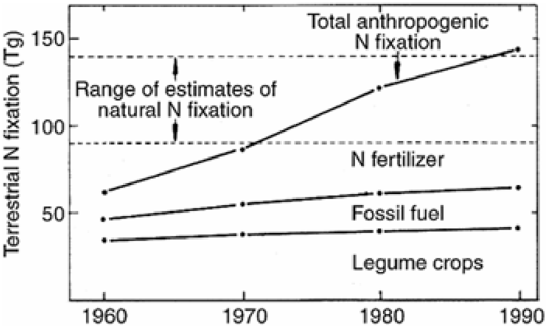


Figure 5-4. *Nitrogen transformations in wetland soils. (From Gambrell and Patrick, 1978, p. 393; Copyright © 1978 by Technomics Publication Co., reprinted with permission)*

Human's impact on global Nitrogen cycle: possible to have too much of a good thing?

- Natural inputs of fixed N
  - Terrestrial 100 Tg/yr
  - Marine - 5-20 Tg/yr
  - Lightning - 10 Tg/yr
- Human inputs -
  - Fertilizer - > 80Tg/yr
  - Internal combustion engine - 25Tg
  - Legume crops - 30 Tg/yr
    - Half of all N fertilizer used throughout human history through 1992 has been applied since 1982
- Human activity mobilizes other nitrogen
  - Biomass burning
  - Land clearing and conversion
  - Wetland draining



Nitrate Contamination

- Nitrate not allowed in drinking water in U.S. over 10 mg/L
- Can lead to methhemoglobinemia, blue baby syndrome
- Can be converted to carcinogenic nitrosamines in the stomach

Sulfur

- Forms (only some listed)
  - S^{2-}, sulfide; S^0, elemental sulfur; $S_2O_3^{2-}$, thiosulfate; SO_4^{2-}, organic S, dimethyl sulfide
- Sulfur Transformations
  - Abiotic oxidization (spontaneous conversion to sulfate, slow)
  - Biotic oxidation (chemoautotrophic bacteria)

More Sulfur Transformation

- Dissimilatory sulfur reduction
  - sulfate and successively reduced sulfur compounds used as electron acceptors for carbon oxidation
- Disproportionation
  - two sulfurs in thiosulfate, one used to oxidize the other and energy is produced
  - $S_2O_3^{2-}$? $S^{2-} + SO_4^{2-} + H^+$ + energy
- Precipitation of metal sulfides
  - Iron sulfide is a black precipitate that gives anoxic soils their dark black color
- Sulfide oxidation causes acid mine drainage
- Anoxygenic photosynthesis- uses sulfide as an electron donor for photosynthesis and produces sulfate

Phosphorus

- Forms
  - Organic P
    - Dissolved or particulate
  - Inorganic P
    - SRP
      - orthophosphate, PO_4^{3-}
      - Available to plants
  - TDP = SRP + DOP
  - TPP = total particulate phosphorus
- Transformations
  - uptake
  - remineralization (phosphatases)
  - precipitation with oxidized iron

Silicon, Iron, and Other Trace Nutrient Cycles

- Silicon
  - key element in diatom frustules
  - can become limiting in lakes
- Iron
  - ferric, Fe^{3+}, oxidized; ferrous, Fe^{2+} reduced
  - iron oxidation by microorganisms important chemoautotrophic pathway, but also will happen abiotically, so must occur at oxic/anoxic interface
  - oxidized iron precipitates with phosphate, but dissociates again in anoxic conditions
  - Chelators can keep iron in oxic solutions

Sulfur-Iron Dynamics and Wetland Eutrophication

- Phosphorus pollution in peaty lowlands of Netherlands encouraged unwanted algal blooms and hurt macrophyte populations
- Put low P, high sulfate river water in
- Sulfate was reduced to sulfide, which precipitated iron and poisoned roots of macrophytes
- Iron was not present to bind to phosphates and phosphate concentrations actually increased
- Interactions among nutrient cycles can be complex