

Lecture 9 – Nitrogen and Phosphorus Cycling

Outline for today:

- I. Review of Biogeochemical cycling mechanics and Mass balance
 - a. Reservoirs and Fluxes
 - b. Sources and sinks
- II. Nitrogen
 - a. Role in biology
 - b. Reservoirs
 - c. Nitrogen Sources
 - d. Nitrogen Sinks
- III. Phosphorus
 - a. Role in biology
 - b. Reservoirs
 - c. Phosphorus Sources
 - d. Phosphorus Sinks

Study questions:

- Why is nitrogen fixation only carried out by prokaryotes? Why didn't humans and plants evolve a way to fix nitrogen from the atmosphere directly?
- Would nutrients have a longer residence time in deciduous or coniferous forests? Why?
- In today's Nitrogen cycle is nitrogen fixation balanced by denitrification?

I. Review of Biogeochemical cycling mechanics and Mass balance

a. Reservoirs and Fluxes, Sources and sinks

Inputs > outputs (sink) Inputs < outputs (source)

Mass balance: $\Sigma \text{Inputs} - \Sigma \text{Outputs} + \Sigma \text{Sources} - \Sigma \text{Sinks} = \Delta \text{Mass}$

Steady state: $\Delta \text{Mass} = 0$

II. Nitrogen Atomic # 7 ... 14.0067 g mol⁻¹ B.P. -195.8°C

a. Role in biology

N is an essential component of proteins, nucleic acids and other cellular constituents.

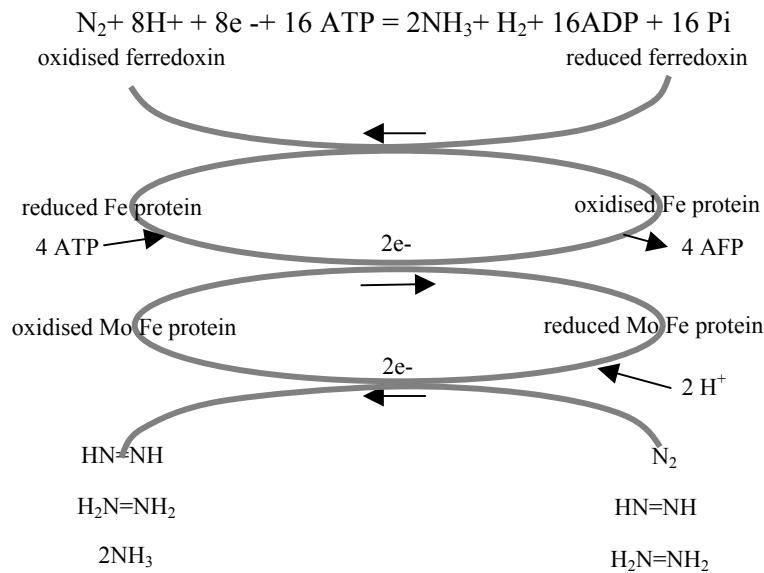
- b. Reservoirs** – 79% of the atmosphere is N₂ gas. The N≡N triple bond is relatively difficult to break, requires special conditions. As a result most ecosystems are N-limited. N₂ dissolves in water, cycles through air, water and living tissue.

c. Nitrogen Fixation

Abiotic: lightning (very high T and P) 10^7 metric tons yr^{-1} ~ 5-8% of total annual N fixation. (weathering of rocks is an insignificant source)

Biotic: Nitrogen fixation by microbes, (prokaryotic bacteria) typically either free-living *azobacter* or *rhizobium* living symbiotically with plants (such as legumes). Total N fixed by biological processes is approx. 1.75×10^8 metric tons yr^{-1}

Biological mechanism of nitrogen fixation: uses an enzyme complex called nitrogenase consisting of two proteins – an iron protein and a molybdenum-iron protein.



Adapted from <http://helios.bto.ed.ac.uk/bto/microbes/nitrogen.htm#Top>

The Fe protein gets reduced by electrons donated by ferredoxin. Then the reduced Fe protein binds ATP and reduces the molybdenum-iron protein, which donates electrons to N_2 , producing $\text{HN}=\text{NH}$. In two further cycles of this process (each requiring electrons donated by ferredoxin) $\text{HN}=\text{NH}$ is reduced to $\text{H}_2\text{N}=\text{NH}_2$, and this in turn is reduced to 2NH_3 .

- ferredoxin is generated by either photosynthesis, respiration or fermentation, depending on the type of organism
- nitrogenase is inhibited in the presence of oxygen. N-fixing prokaryotes operate either anaerobically (*Clostridium*, *Desulfovibrio*, *Purple sulphur Bacteria*) or develop special mechanisms such as extremely high respiratory rates (*Azobacter*) and/or cellular features to limit oxygen diffusion, or else develop symbiotic relationships (*Rhizobium*) where the host plant scavenges oxygen. Cyanobacteria, protect nitrogenase in special heterocysts which possess only PS I.

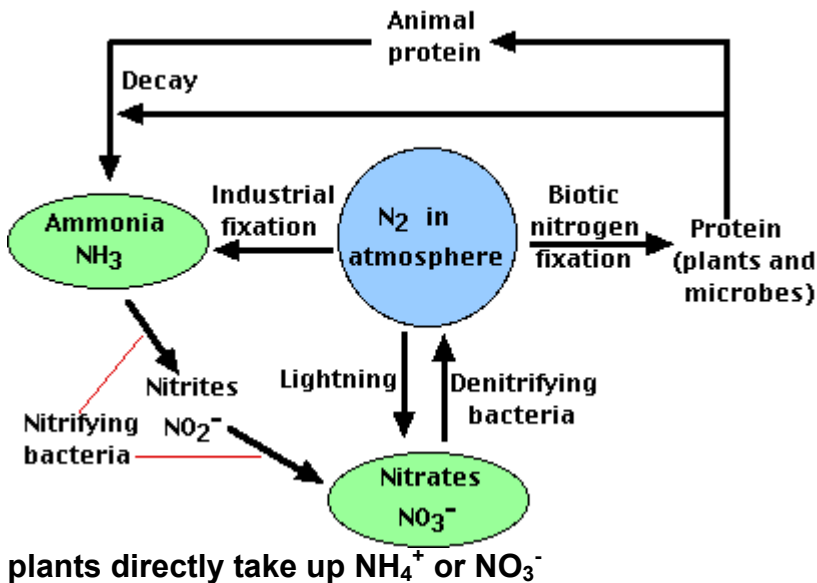
Industrial: The Haber-Bosch process (1909)– high P and relatively high T, uses Iron as a catalyst to convert N_2 to ammonia (usually further processed to urea and ammonium nitrate (NH_4NO_3) – still the cheapest means of industrial N fixation. 5×10^7 metric tons yr^{-1}

Combustion Side Effect: High T and P oxidizes N_2 to Nox 2×10^7 metric tons yr^{-1}

Since 1940s amount of N available for uptake has more than doubled. Anthropogenic N

inputs are now equal to biological fixation.

d. Nitrogen Cycling



Nitrification by chemoautotrophs

Bacteria of the genus *Nitrosomonas* oxidize NH_3 to NO_2^-

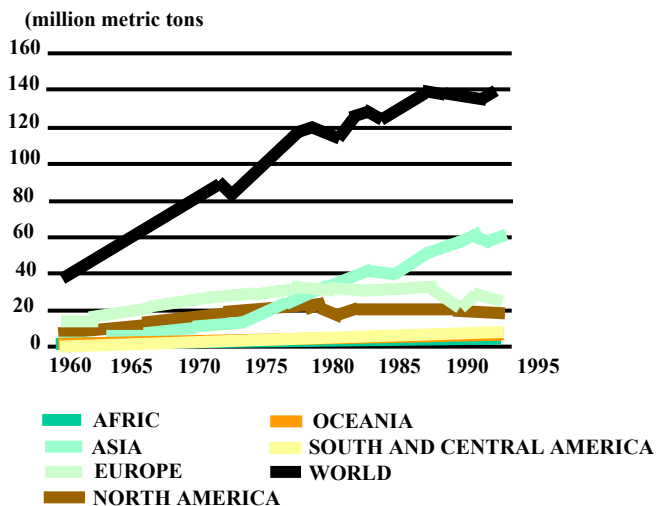
Bacteria of the genus *Nitrobacter* oxidize the nitrites to NO_3^-

Denitrification

Anaerobic respiration of NO_3^- to dinitrogen gas by several species of *Pseudomonas*, *Alkaligenes*, and *Bacillus*

Sources of anthropogenic N loads: Fertilizers, Legume Crops, Atm Deposition, Sewage, Deforestation, Draining of wetlands

Trends in Fertilizer Use



Adapted from the Food and Agriculture Organization of the United Nations (FAO), *FAOSTAT Statistical Database* (FAO, Rome, 1997).

Fate of N? In most terrestrial and freshwater ecosystems N is a limiting nutrient, gets cycled efficiently. What happens when plants have enough N (i.e. greater 16:1 N:P ratio)?

Flushing/erosion – dissolved and particulate matter in streamwater, (DIN, DON, TN, Org N)

leaching to groundwater – NO_3^- is an anion, does not sorb well to clays, highly water soluble. When N saturation of ecosystem occurs, excess N tends to leave the system in the form of nitrate.

, VOCs, denitrification, burning, emigration, harvesting

Effects of Increased N loading:

Eutrophication in aquatic systems, coastal algal blooms and “Dead Zone”, fish kills, increased turbidity, selective pressures in terrestrial systems favoring species-poor grasslands and forests

Nitrate MCL – 10mg L^{-1} ...

Nitric oxide – precursor of acid rain and smog

Nitrous oxide – long lived greenhouse gas that can trap 200 times as much heat as CO_2

III. Phosphorus – Atomic # 15 ... 30.97 g mol^{-1} B.P. 280°C

P is very reactive, does not exist in pure elemental form. In contact with air, it forms phosphate PO_4^{3-} .

In water, phosphates are protonated to form HPO_4^{2-} , H_2PO_4^- and H_3PO_4 .

PO_4^{3-} orthophosphate, the most simple molecular form of phosphate, aqueous form under very basic or alkaline conditions

HPO_4^{2-} : aqueous form under basic or alkaline conditions

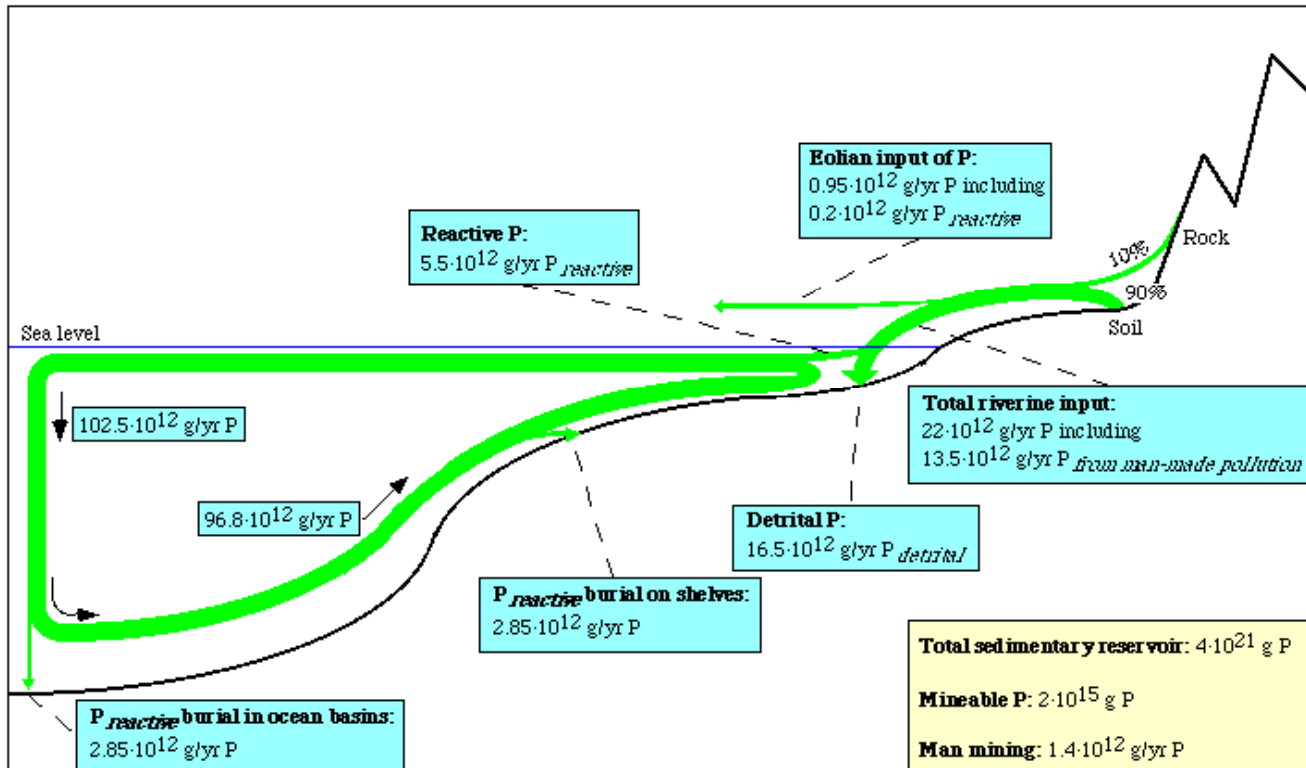
H_2PO_4^- : aqueous form under neutral conditions

H_3PO_4 : aqueous form under very acidic conditions

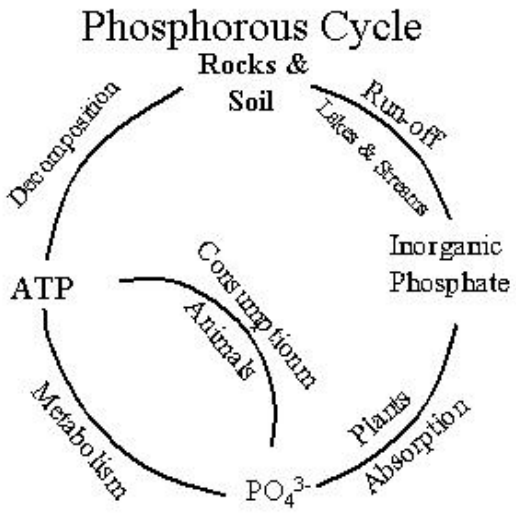
a. Role in biology

Phosphorus is an essential nutrient for plants and animals in the form of ions PO_4^{3-} and HPO_4^{2-} . It is found in DNA-molecules (it binds deoxyribose sugars together forming the backbone of the DNA molecule), ATP and ADP, and lipid cell membranes (phospholipids). P is also a fundamental to tissues such as bones and teeth.

- b. Reservoirs** – Unlike C, N and other important bioelements P does not exist in a gaseous state at typical environmental Temps and Pressures. Cycles through water (DOP and DIP), soils and sediments (adsorption to mineral surfaces) and organic tissue/humic material.



- c. **Phosphorus Sources** – Found in sedimentary rocks such as apatite ($\text{Ca}_x(\text{OH})_y(\text{PO}_4)_z$), fossilized bone or guano. Weathering from phosphate rocks found in terrestrial rock formations and some ocean sediments (PO_4 is soluble in H_2O). Guano (excrement of fish-eating birds) mining for fertilizers and sewage. Detergents have historically contained Na_3PO_4 , though newer types are avoiding it.
- d. **Phosphorus Sinks** – uptake of orthophosphate by plants through the roots, incorporation into plant tissue and heterotroph tissues, decomposition returns P to water and soils via microbial mineralization; eventually it is washed out to the oceans, sinks to the floor (becomes limestone) and is not recycled for millions of years.



Adapted from: http://www.starsandseas.com/SAS%20Ecology/SAS%20chemcycles/cycle_phosphorus.htm