

Cycling and Biogeochemical Transformations of N, P, S, and K

OCN 401 - Biogeochemical Systems
20 September 2016

Reading: Schlesinger & Bernhardt, Chapter 6

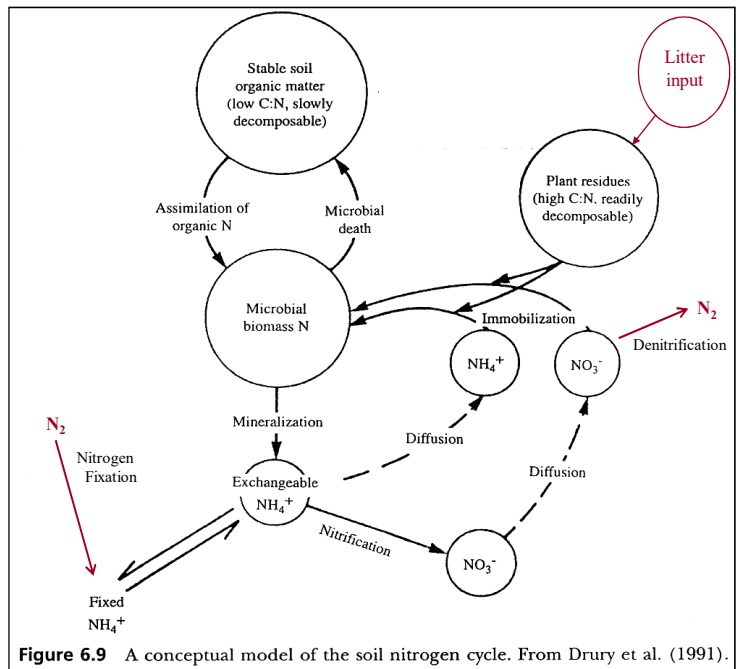
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Outline

1. Nitrogen cycle
 - Soil nitrogen cycle
 - Nitrification
 - Emissions of N gases from soils
 - Global N₂O emissions
 - Atmospheric N deposition
2. Phosphorus cycle
 - Importance of P transformations
 - Phosphorus cycling
 - Soil P transformations
 - Phosphorus pools
3. Sulfur cycle
 - The importance of sulfur cycling
 - Sulfur cycling
 - Atmospheric sulfate deposition
4. Potassium cycle

Soil Nitrogen Cycle

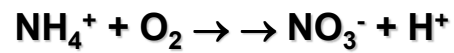
ALL OF THESE PROCESSES
ARE MICROBIALLY MEDIATED



How to Measure the Soil N Cycle

- Changes in N concentrations in plastic “**litter bags**” measured over time
- Changes in N concentrations in **trenched plots** (lined with plastic sides and bottoms) with plants removed
- Changes in $^{15}\text{NH}_4$ and $^{15}\text{NO}_3$ with and without inhibitors for specific processes
- **Acetylene reduction** measurement of nitrogen fixation
- **Acetylene block** - specific inhibitor of $\text{N}_2\text{O} \rightarrow \text{N}_2$ during denitrification (discussed later)

Nitrification



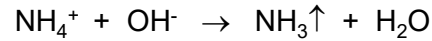
- Lower rates under these conditions:
 - low O_2
 - low pH
 - low soil moisture (can also be inhibited by too much water)
 - high litterfall C:N (slow mineralization of N due to increased immobilization of NH_4^+ by microbes)
- Higher rates in soils with high $[\text{NH}_4]$, but generally not responsive to other nutrients
- Usually higher after disturbances such as fires

Emissions of N Gases From Soils

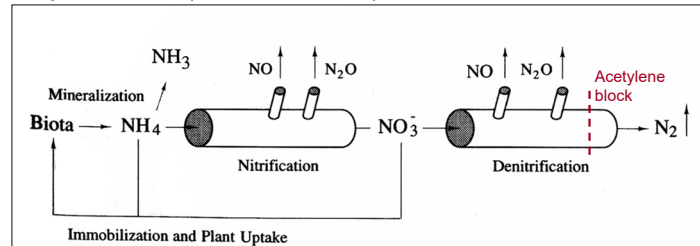
- Emitted gases include:
 - *Ammonia (NH_3)*
 - *Nitric oxide (NO)*
 - *Nitrous oxide (N_2O)*
 - *Dinitrogen (N_2)*
- Emissions are important because they remove nitrogen available for uptake by plants
- N_2O flux is also important because N_2O is a “greenhouse gas”

Processes of Nitrogen Gas Emissions

- Rapid conversion of NH_4^+ to NH_3 occurs at **high pH** and **low soil moisture**, and results in gas loss to the atmosphere:

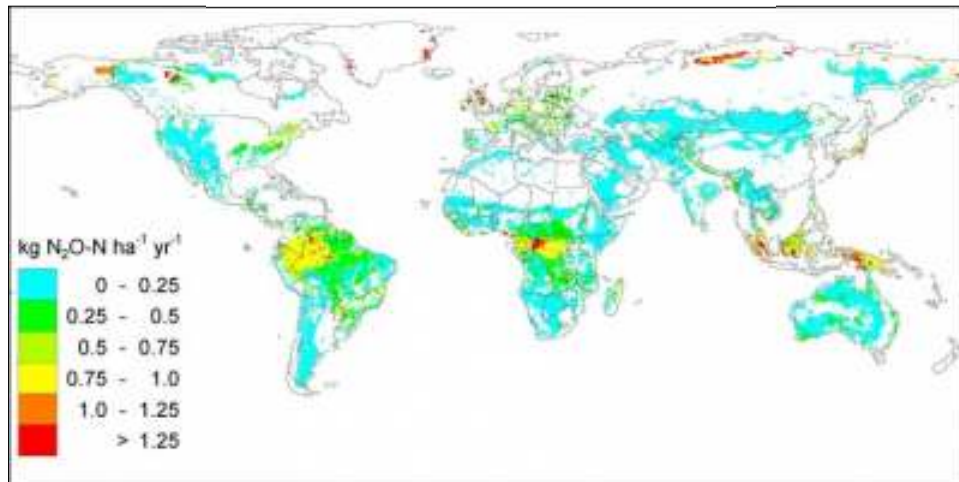


- High organic waste loads (e.g., feedlots) promote NH_3 production
- **NO** and **N_2O** are byproducts (intermediates) of **nitrification** and **denitrification**:

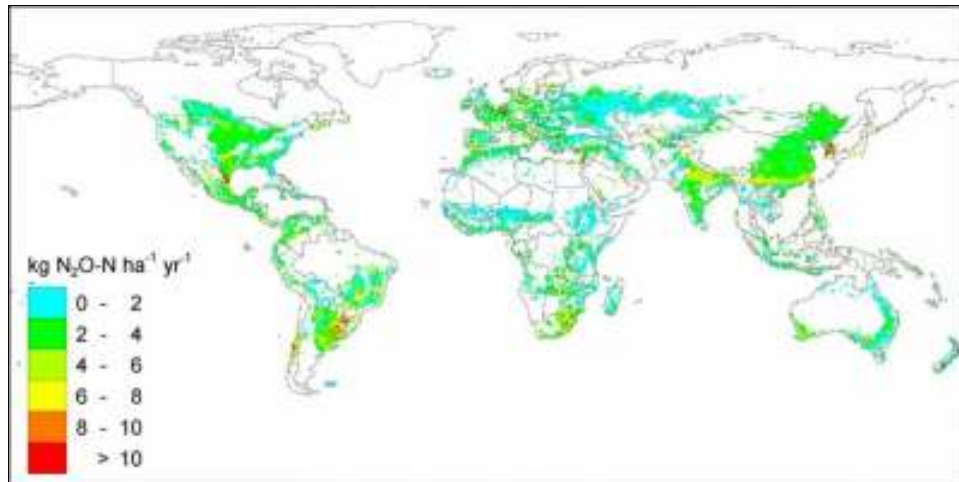


- Controls: N availability (esp NH_4^+ or NO_3^- fertilizer!), organic matter content, O_2 levels, soil moisture, pH and temperature

Global N_2O Emissions



Annual N_2O emission rates for natural ecosystems (agriculture, regrowth forests, arid climates and polar climates are excluded)



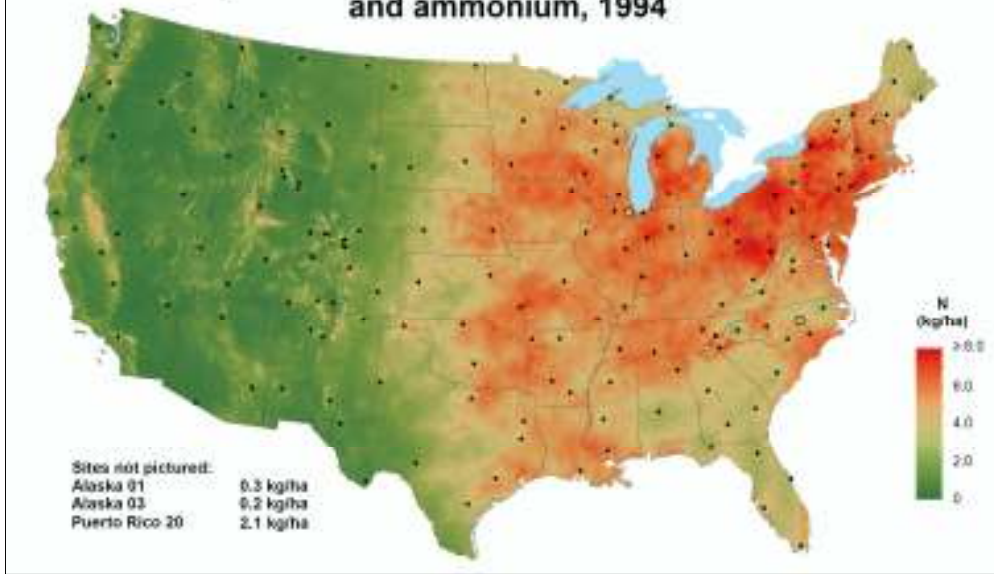
Annual N₂O emission rates for agriculture and grasslands.
Note change in scale.

www.pbl.nl/en/publications/2006/N2OAndNOEmissionFromAgriculturalFieldsAndSoilsUnderNaturalVegetation

Atmospheric N Deposition

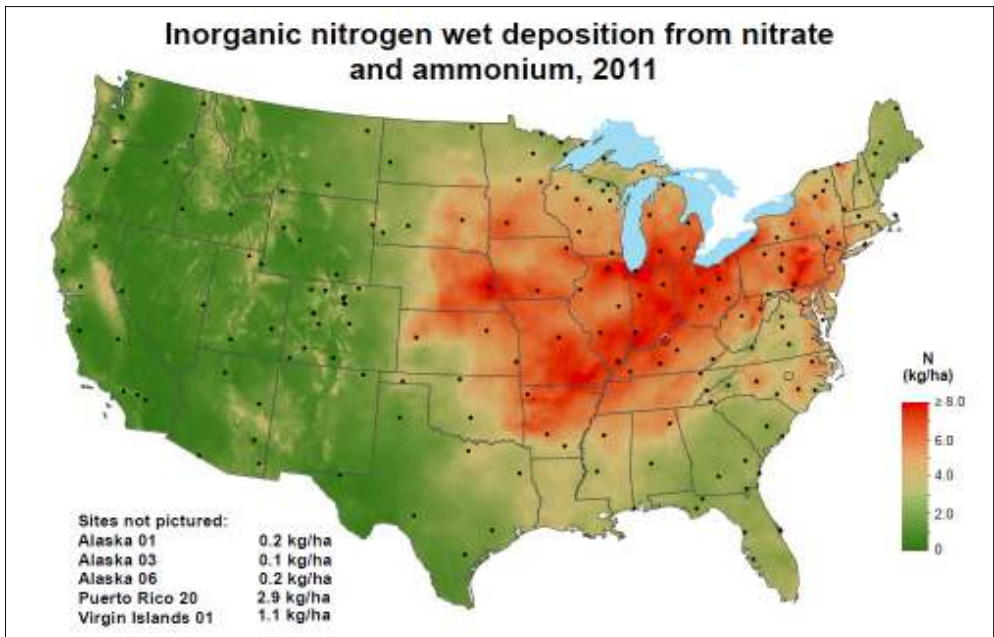
- An important source of nitrogen cycling in many systems
 - Mostly in the form of **acidic wet and dry deposition** originating from fossil-fuel and plant combustion (NO_x)
 - Some areas also have significant deposition of **ammonium**, largely originating from livestock organic waste (~85% of US ammonia emissions are from the agricultural sector)

Inorganic nitrogen wet deposition from nitrate and ammonium, 1994

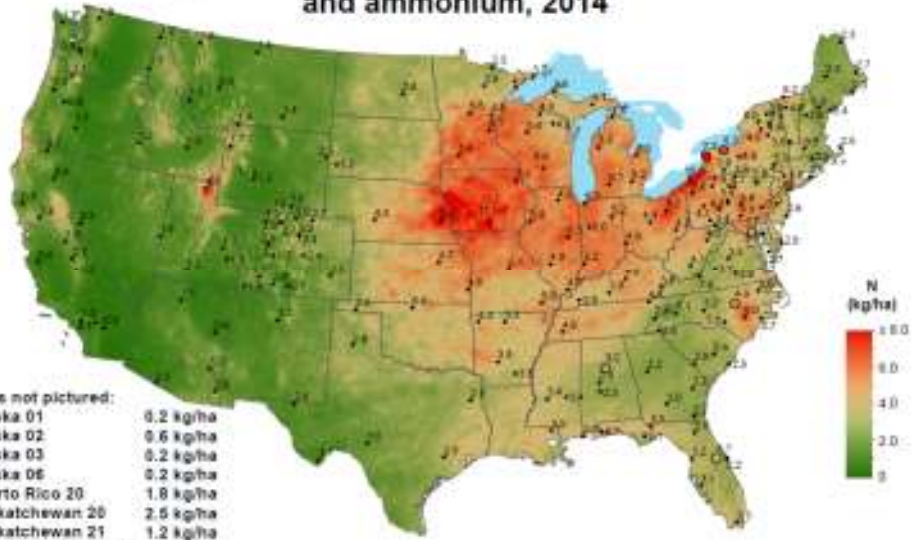


nadp.sws.uiuc.edu/ntn/maps.aspx

Inorganic nitrogen wet deposition from nitrate and ammonium, 2011



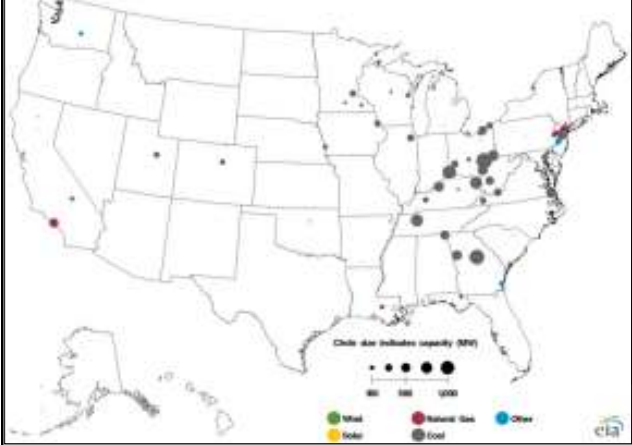
Inorganic nitrogen wet deposition from nitrate and ammonium, 2014



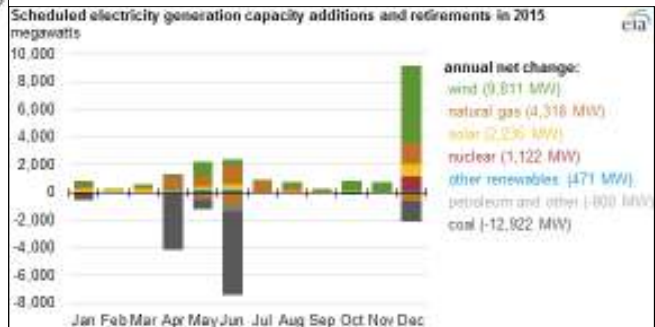
Sites not pictured:

Alaska 01	0.2 kg/ha
Alaska 02	0.6 kg/ha
Alaska 03	0.2 kg/ha
Alaska 06	0.2 kg/ha
Puerto Rico 20	1.8 kg/ha
Saskatchewan 20	2.5 kg/ha
Saskatchewan 21	1.2 kg/ha
British Columbia 22	1.3 kg/ha
British Columbia 23	0.5 kg/ha
British Columbia 24	1.0 kg/ha

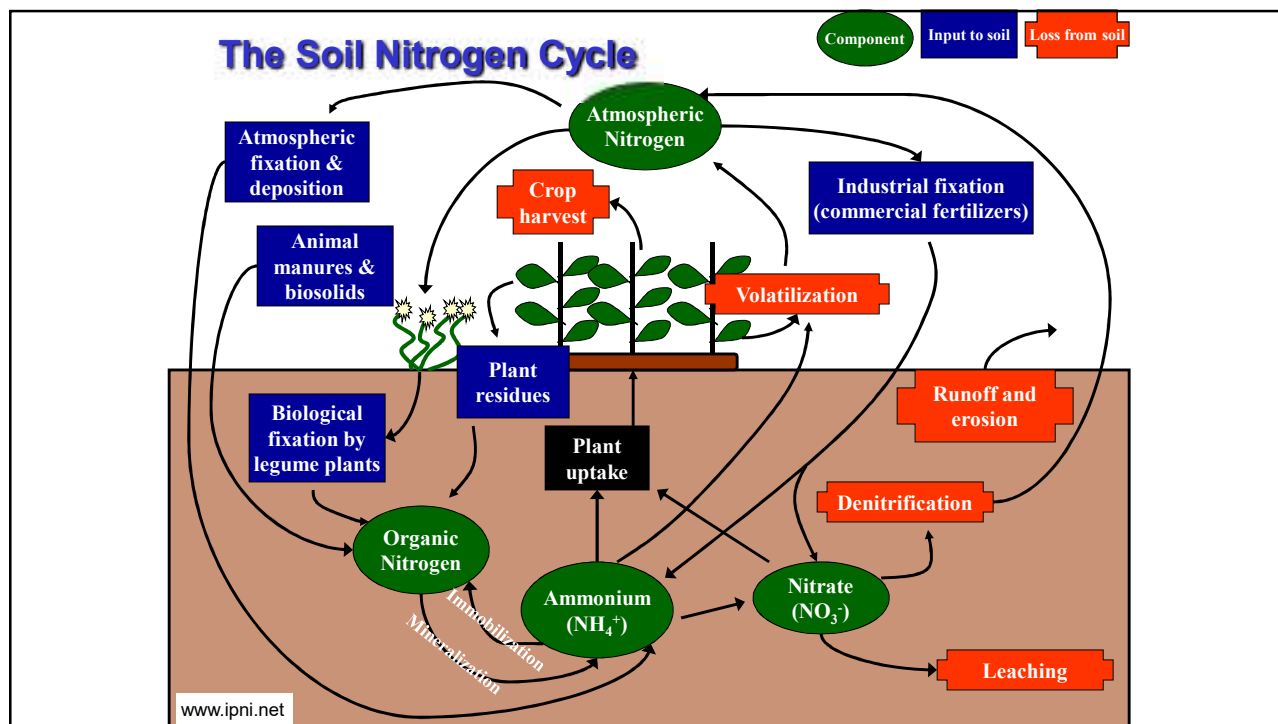
Utility-scale generating units planned to retire during 2015



U.S. Mainland



U.S. Energy Information Admin.
<http://www.eia.gov/todayinenergy/>



Importance of P Transformations

The level of available P during soil development may be the primary determinant of terrestrial NPP:

- P is present in low concentrations in **rocks**, whereas
- N is abundant in the **atmosphere**
- **Bacteria** that fix N_2 gas to biologically available N require P
- Other essential plant **nutrients** (e.g., S, K, Ca, Mg) are more abundant than P

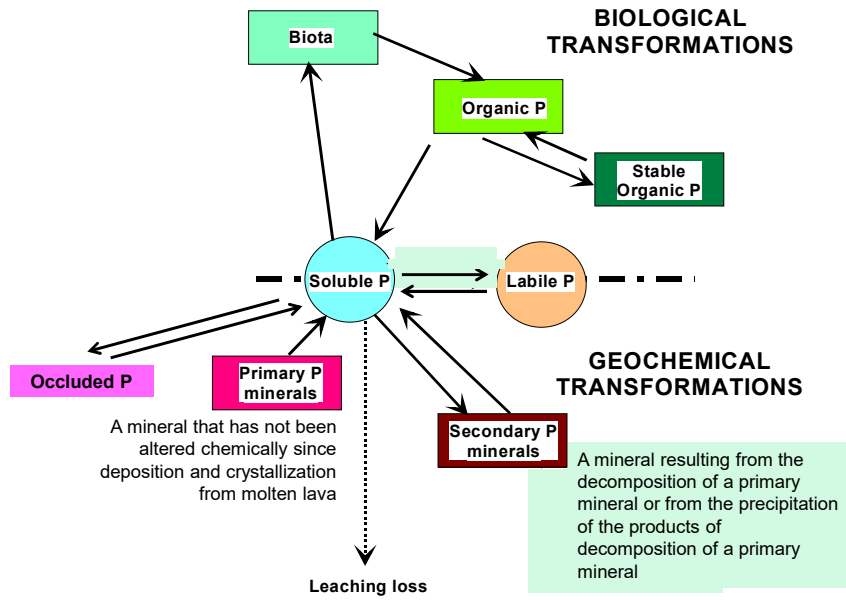
Phosphorus Cycling

- Unlike N, P cycling includes significant **inorganic** (mineral) reactions that make it much more difficult to study
 - These reactions tend to interfere with the **availability of P**
 - They also complicate the measurement of various forms of P
 - Use **sequential extractions** to determine P-mineral binding
- Unlike N, **gaseous P** (phosphine, PH_3) is negligible in biogeochemical cycles and can be ignored
- Unlike N, P does not have multiple oxidation states (no redox reactions)

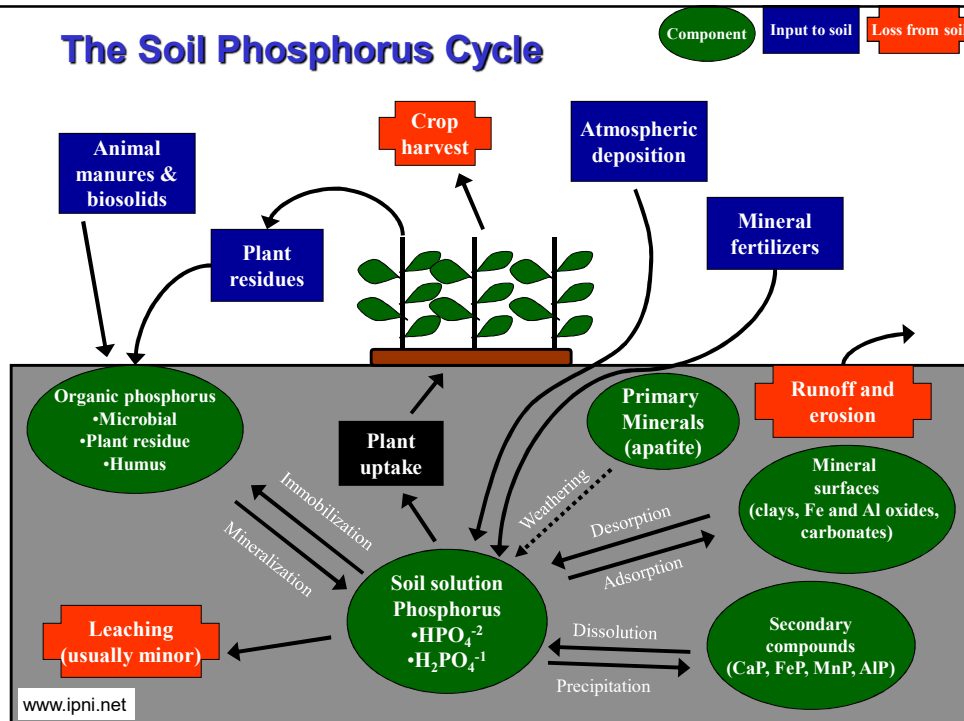
Soil Phosphorus Pools

- 1) Organic matter P
 - P in live plants and animals
 - P in microbes
 - P in dead organic matter
- 2) Soluble P (P in dissolved form)
- 3) **Labile** P (P readily released into solution)
- 4) P in minerals and **occluded** P (tightly adsorbed or absorbed)
 - Igneous apatite ($\text{Ca}_5\text{FP}_3\text{O}_{12}$)
 - Biological forms of apatite
 - P co-precipitated with CaCO_3
 - Fe- and Al-bound P, etc.

Soil P Transformations



The Soil Phosphorus Cycle



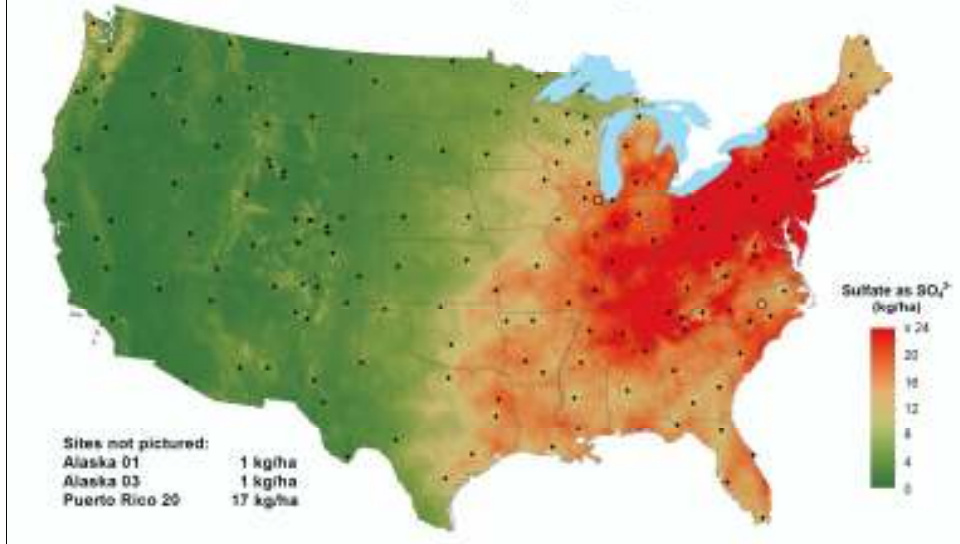
The Importance of Sulfur Cycling

- S, along with C, H, O, N, and P, is one of the major constituents of living tissue
- While essential to life, S is also relatively abundant
- It is therefore an **essential** plant nutrient, but not ordinarily a **limiting** plant nutrient
- Plants take up SO_4^{2-} by reduction and incorporation into amino acids
- S is released in many forms during decomposition

Sulfur Cycling

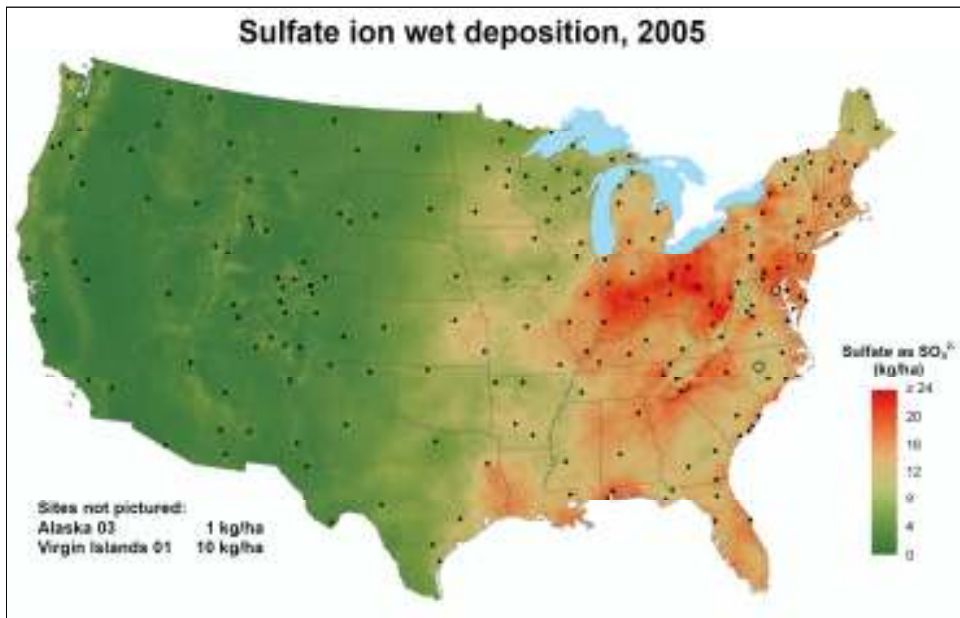
- Like P, sulfur undergoes important geochemical, as well as biological, cycling
- Like N, and unlike P, sulfur occurs in **multiple oxidation states**
- SO_4^{2-} [**sulfate**] is abundant in seawater (28 mM)
- Like N and unlike P, sulfur has significant gas phases:
 - H_2S [**hydrogen sulfide**]
 - Organic gases
 - COS [carbonyl sulfide]
 - $(\text{CH}_3)_2\text{S}$ [dimethylsulfide]
- A locally important S source is H_2SO_4 [**sulfuric acid**] in acid rain

Sulfate ion wet deposition, 1994

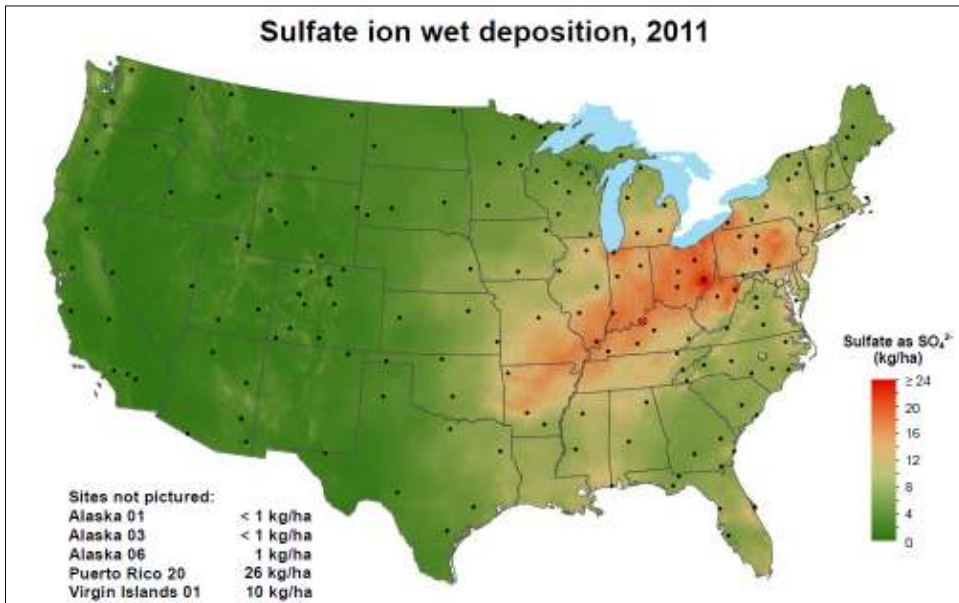


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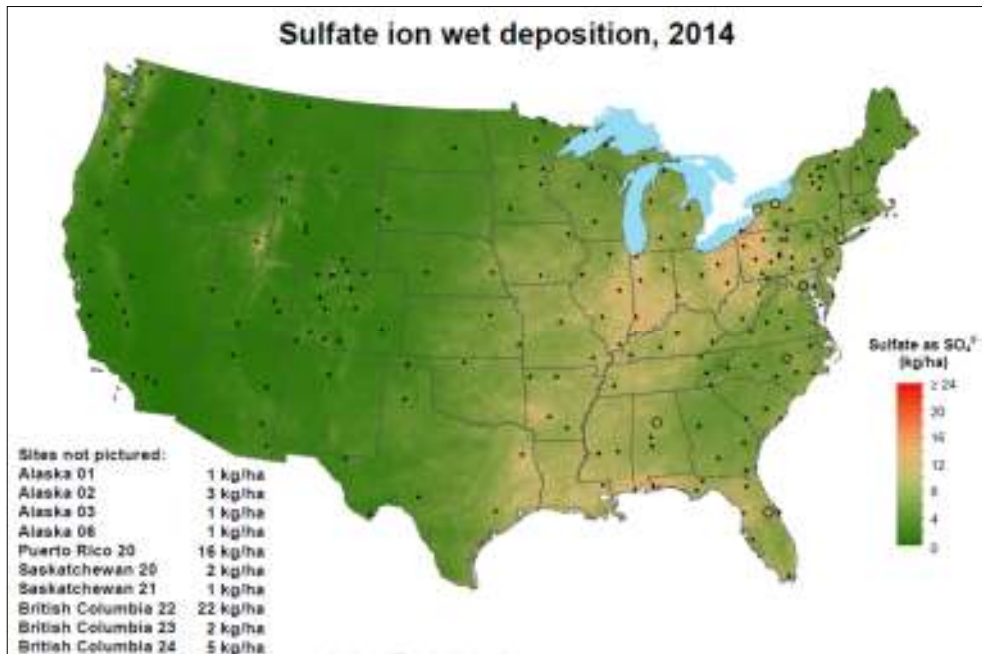
Sulfate ion wet deposition, 2005

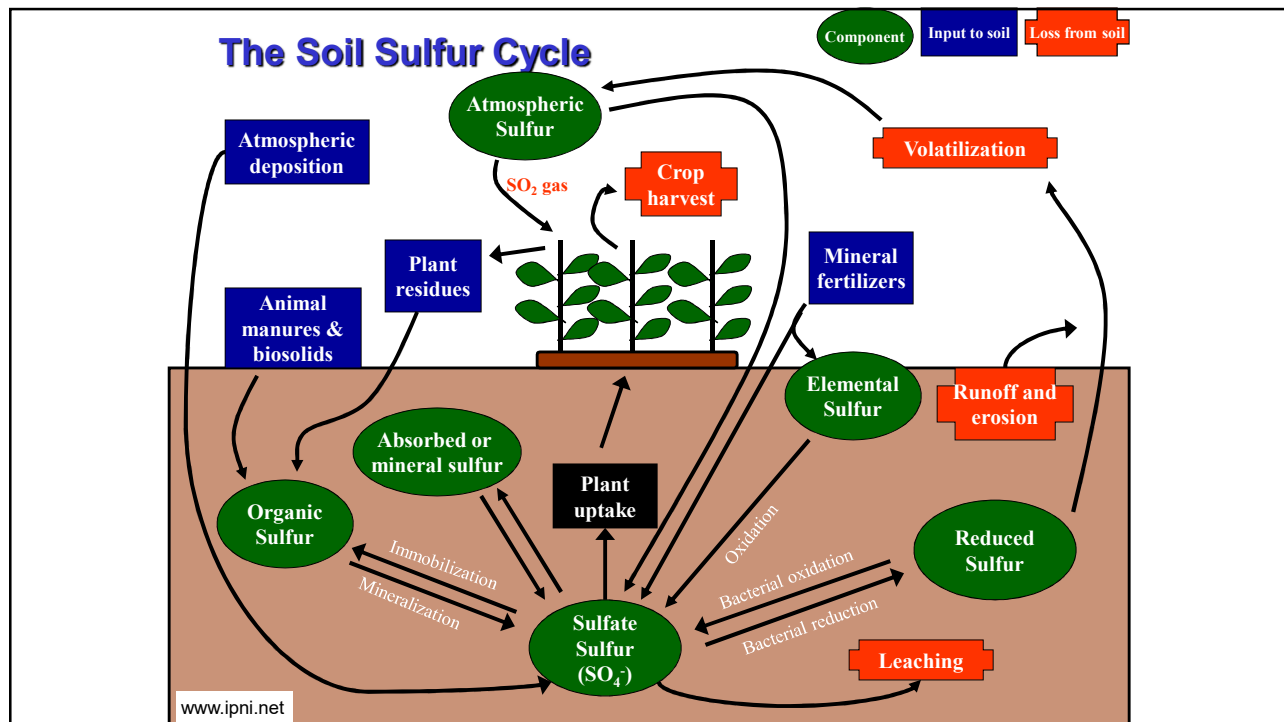


Sulfate ion wet deposition, 2011



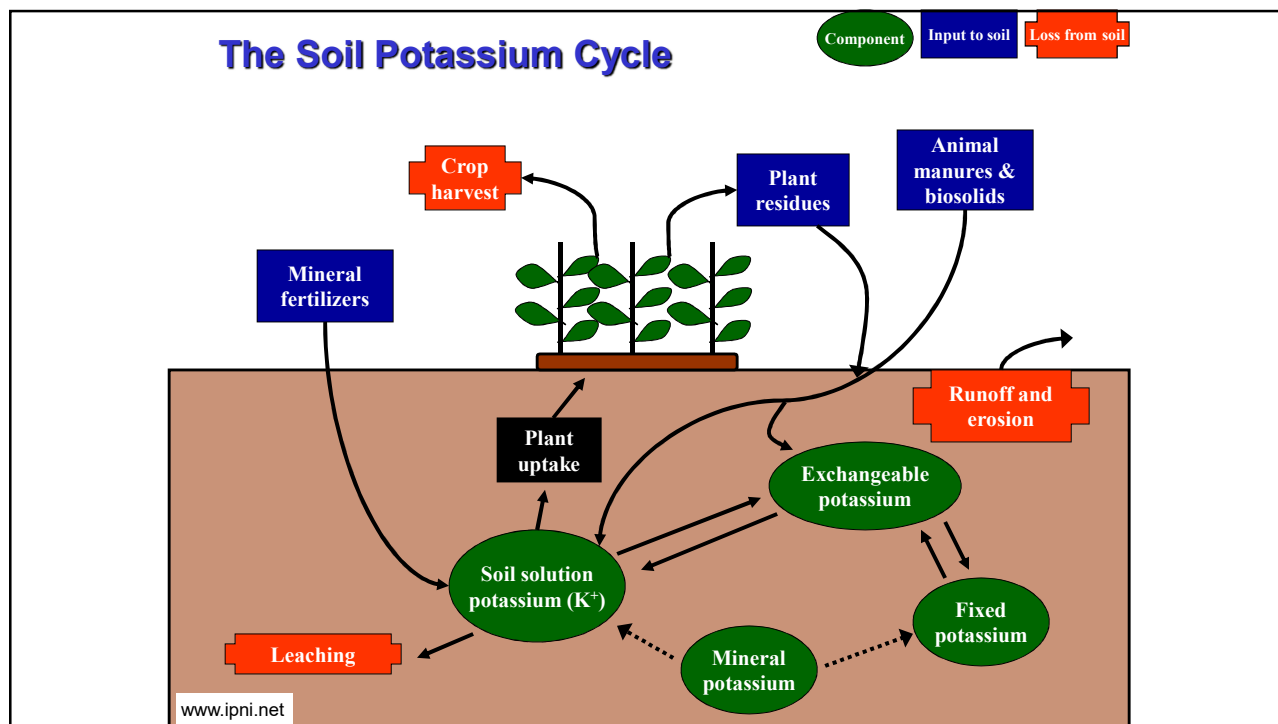
Sulfate ion wet deposition, 2014





Potassium Cycling

- The potassium (K) cycle is almost entirely inorganic
- The major role of K in living organisms is osmotic control
- K is taken up, retained and excreted in ionic form (K⁺)
- The amount of K in soil solution is relatively small but is in near equilibrium with the much larger amount of **readily exchangeable K**, from which it is replenished
- Soils also contain K in more slowly exchangeable forms (**fixed K**) which act as sources for crops
- K present in **clay minerals** becomes available as these minerals weather



Lecture Summary

- Nitrogen cycling is biologically mediated among soil pools (organic N, NH_4 , NO_3), with important shunts to gaseous forms
- Unlike N, phosphorus is also involved in geochemical (mineral) reactions that may make P less available for biotic cycling
- Sulfur has important analogies with both N and P, including both biological and geochemical reactions, and gas-phase reactions
- Potassium is a required nutrient with a variety of possible inorganic sources