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

OCN 401 - Biogeochemical Systems

19 September 2016

Reading: Schlesinger & Bernhardt, Chapter 6

Outline

1. Nitrogen cycle
   - Soil nitrogen cycle
   - Nitrification
   - Emissions of N gases from soils
   - Global N_2O 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

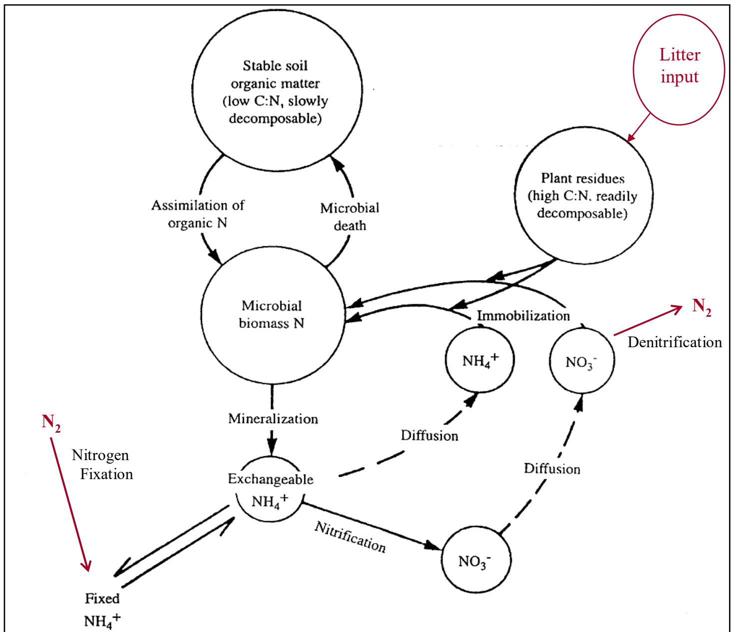


Figure 6.9 A conceptual model of the soil nitrogen cycle. From Drury et al. (1991).

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 $^{15}NH_4$ and $^{15}NO_3$ with and without inhibitors for specific processes
- Acetylene reduction measurement of nitrogen fixation
- Acetylene block - specific inhibitor of $N_20 \rightarrow N_2$ during denitrification (discussed later)

Nitrification

$$NH_4^+ + O_2 \rightarrow \rightarrow NO_3^- + H^+$$

- 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 [NH_4], but generally not responsive to other nutrients
- Usually higher after disturbances such as fires

Emissions of N Gases From Soils

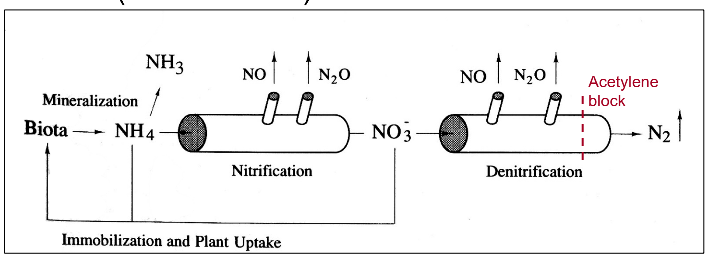
- Emitted gases include:
  - *Ammonia (NH_3)*
  - *Nitric oxide (NO)*
  - *Nitrous oxide (N_2O)*
  - *Dinitrogen (N_2)*
- Emissions are important because they remove nitrogen available for uptake by plants
- N_2O flux is also important because N_2O is a “greenhouse gas”

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:

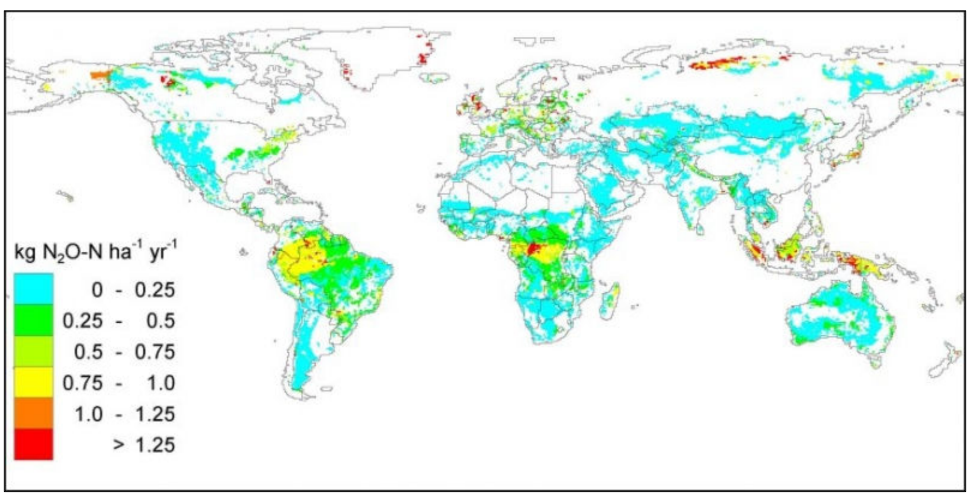
$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$$

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

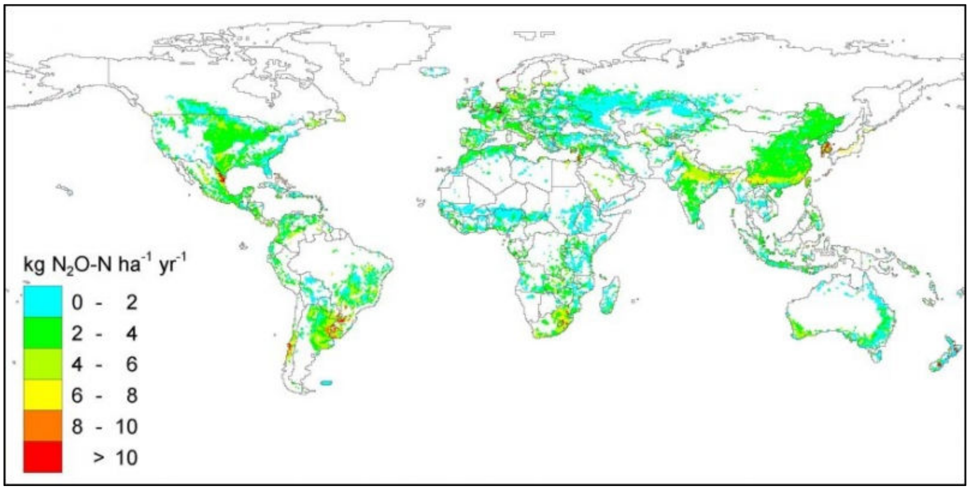


- Controls: N availability (esp NH_4^+ or NO_3^- fertilizer!), organic matter content, O_2 levels, soil moisture, pH and temperature

Global N_2O Emissions



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

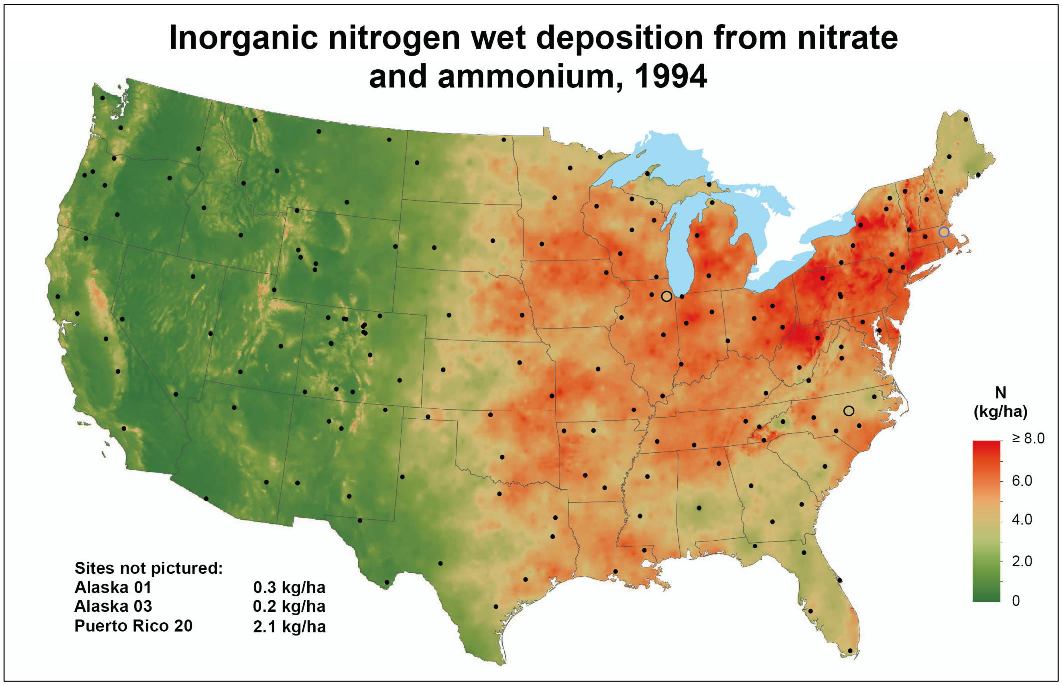


Annual N_2O emission rates for agriculture and grasslands.
Note change in scale.

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)



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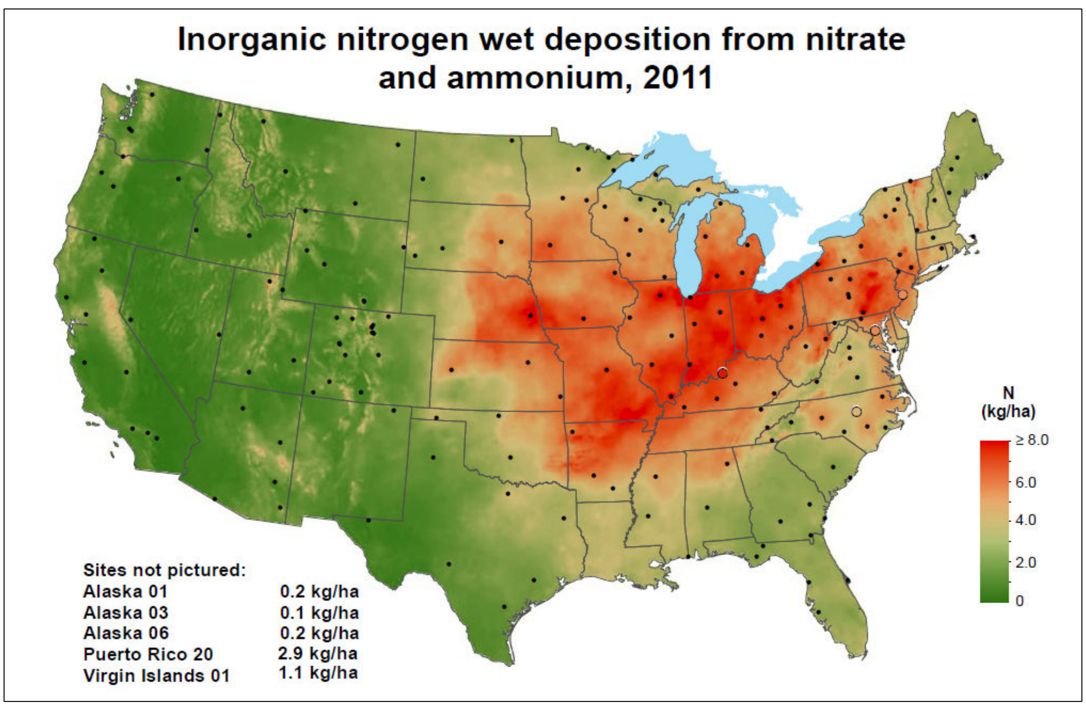
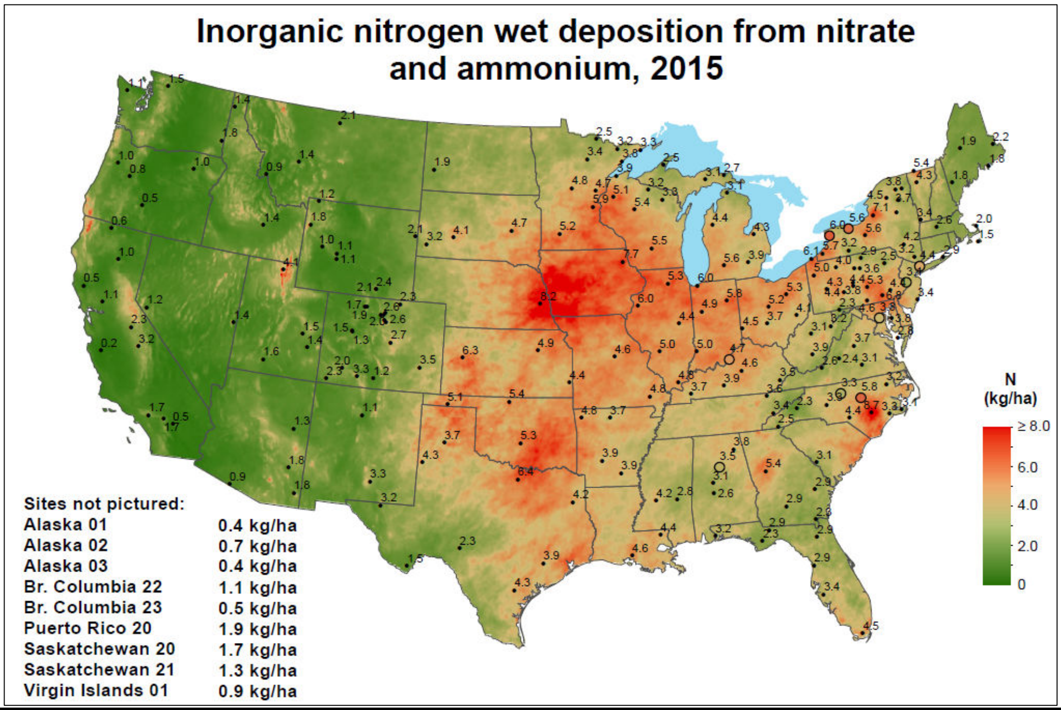
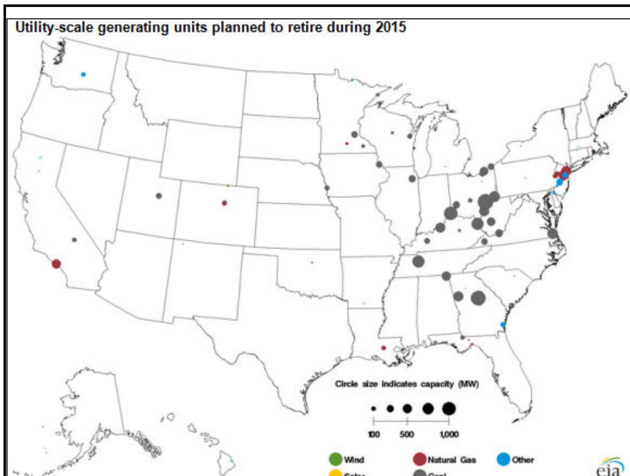
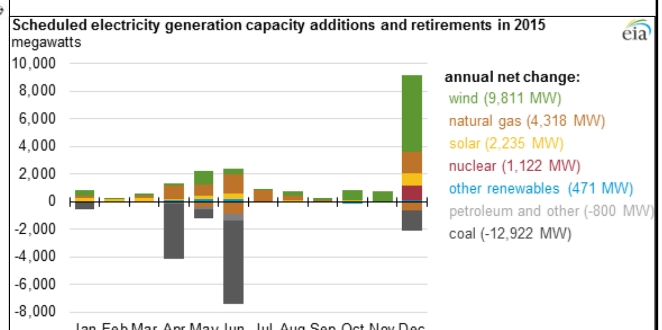


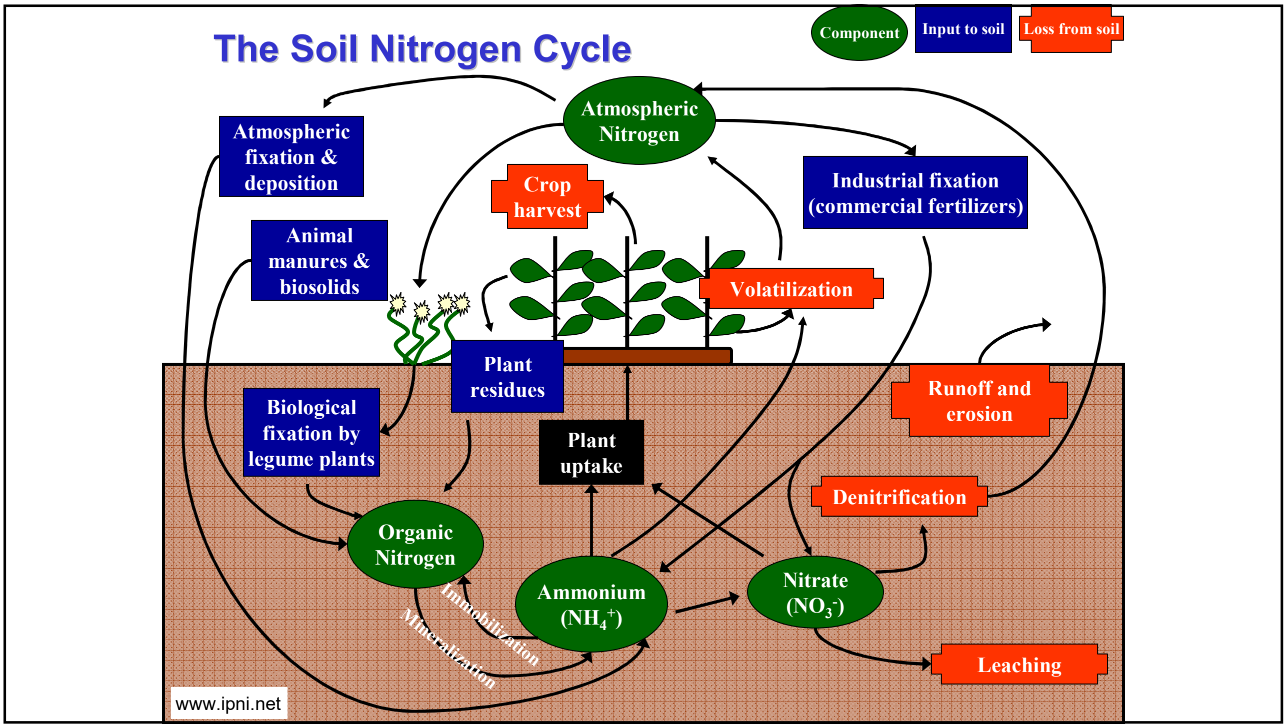




U.S. Mainland



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

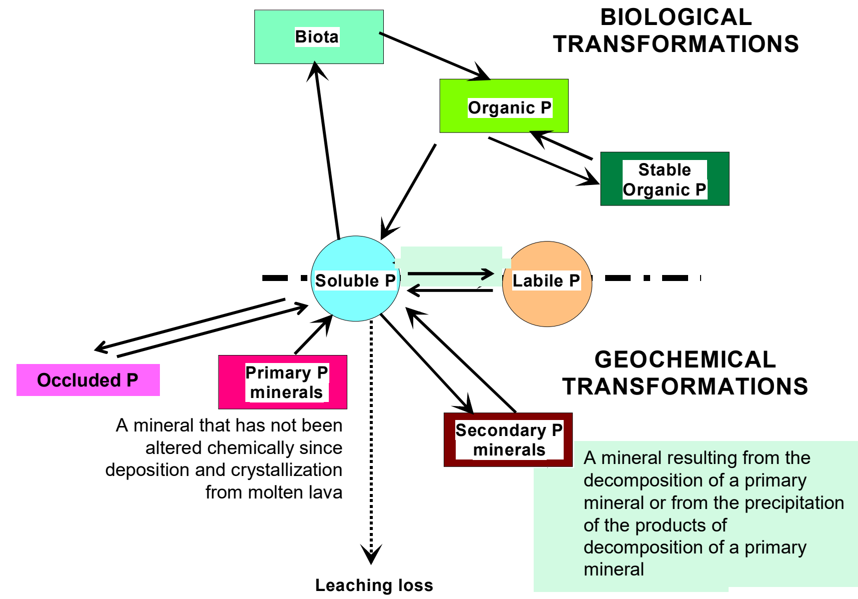
1) Organic matter P
   - P in live plants and animals
   - P in microbes
   - P in dead organic matter

2) Soluble P (P in dissolved form)

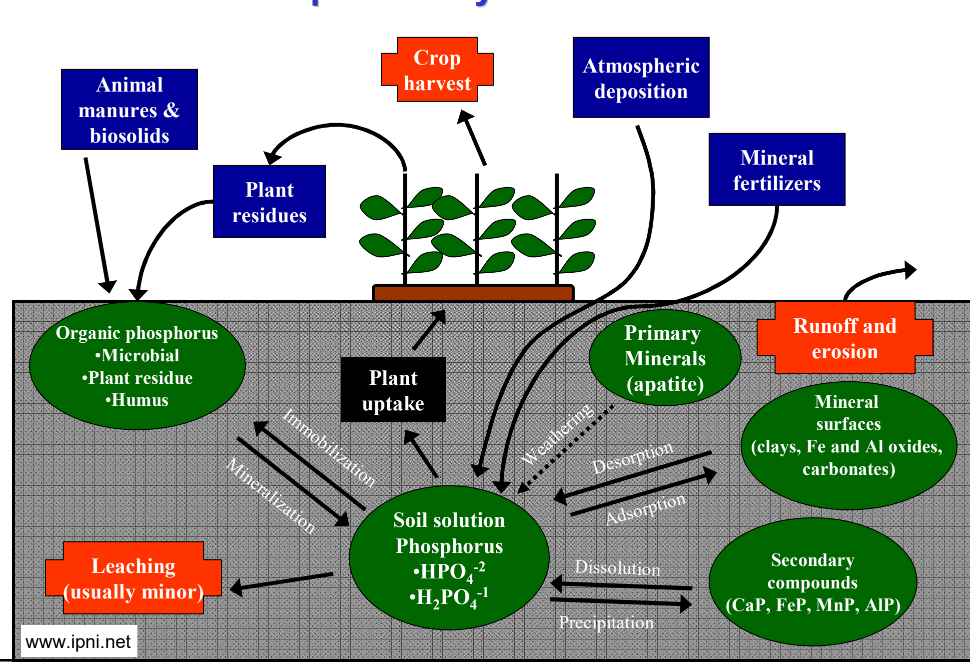
3) *Labile* P (P readily released into solution)

4) P in minerals and *occluded* P (tightly adsorbed or absorbed)
   - Igneous apatite ($Ca_5FP_3O_{12}$)
   - Biological forms of apatite
   - P co-precipitated with $CaCO_3$
   - Fe- and Al-bound P, etc.

Soil P Transformations



The Soil Phosphorus Cycle



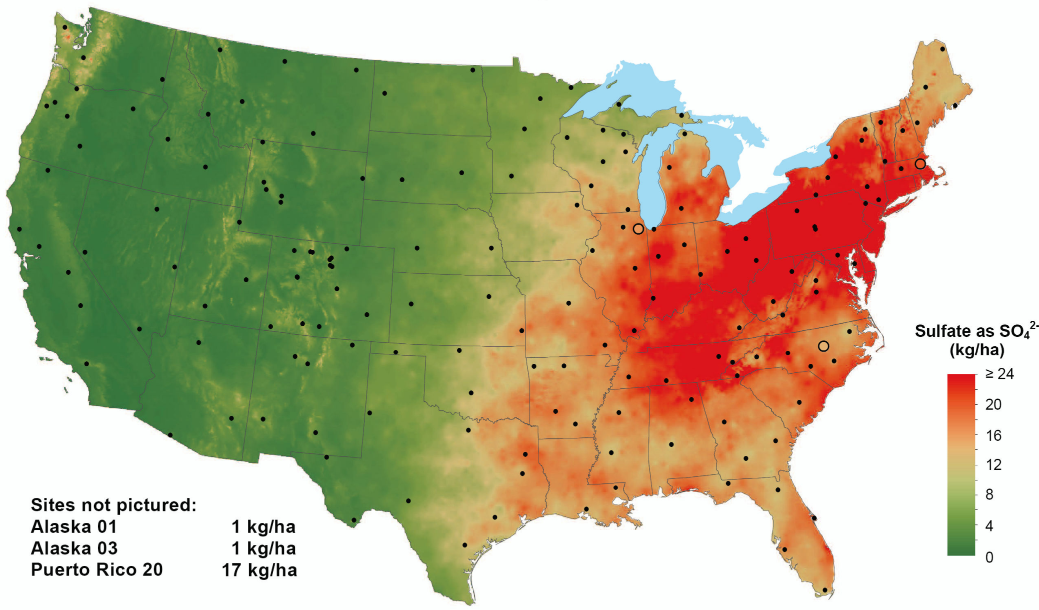
The Importance of Sulfur Cycling

- 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]
    - $(CH_3)_2S$ [dimethylsulfide]
- A locally important S source is H_2SO_4 [*sulfuric acid*] in acid rain

Sulfate ion wet deposition, 1994



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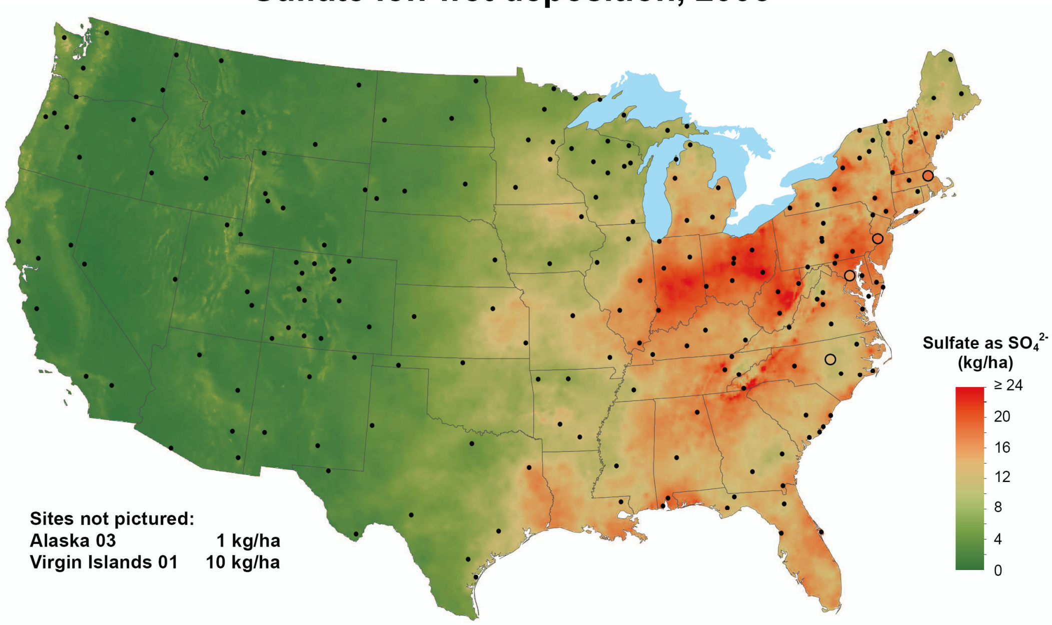
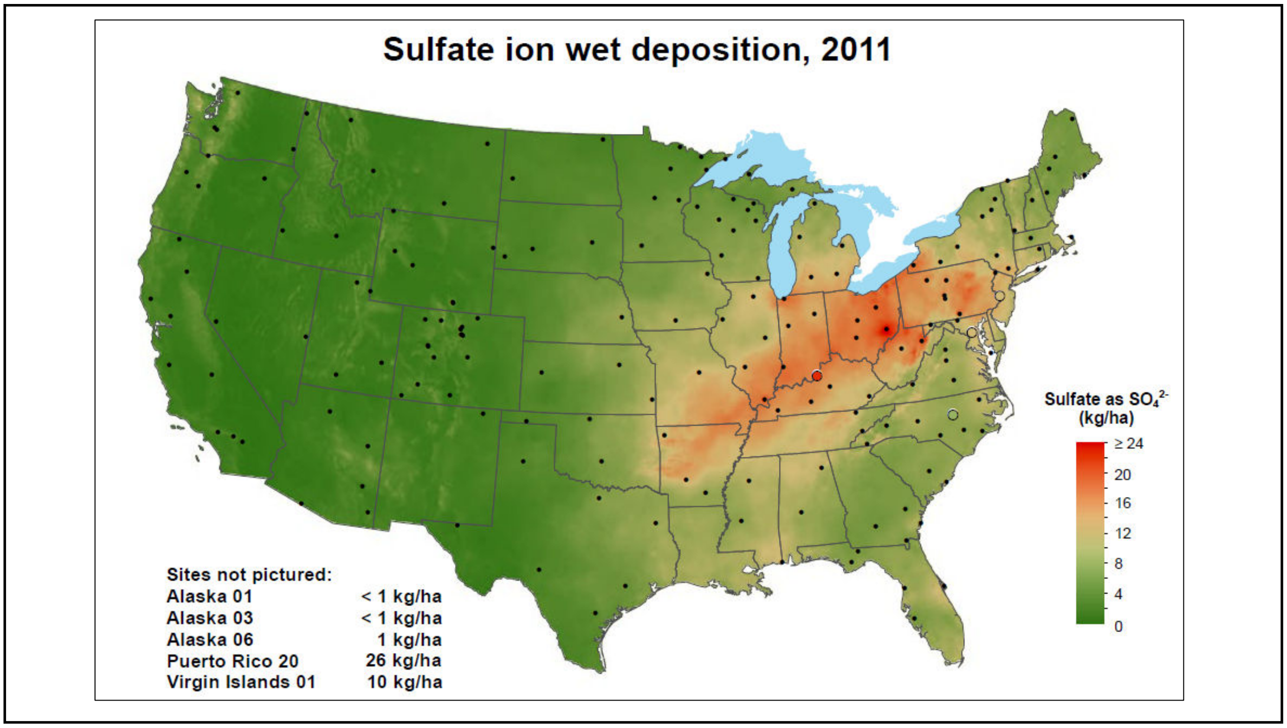
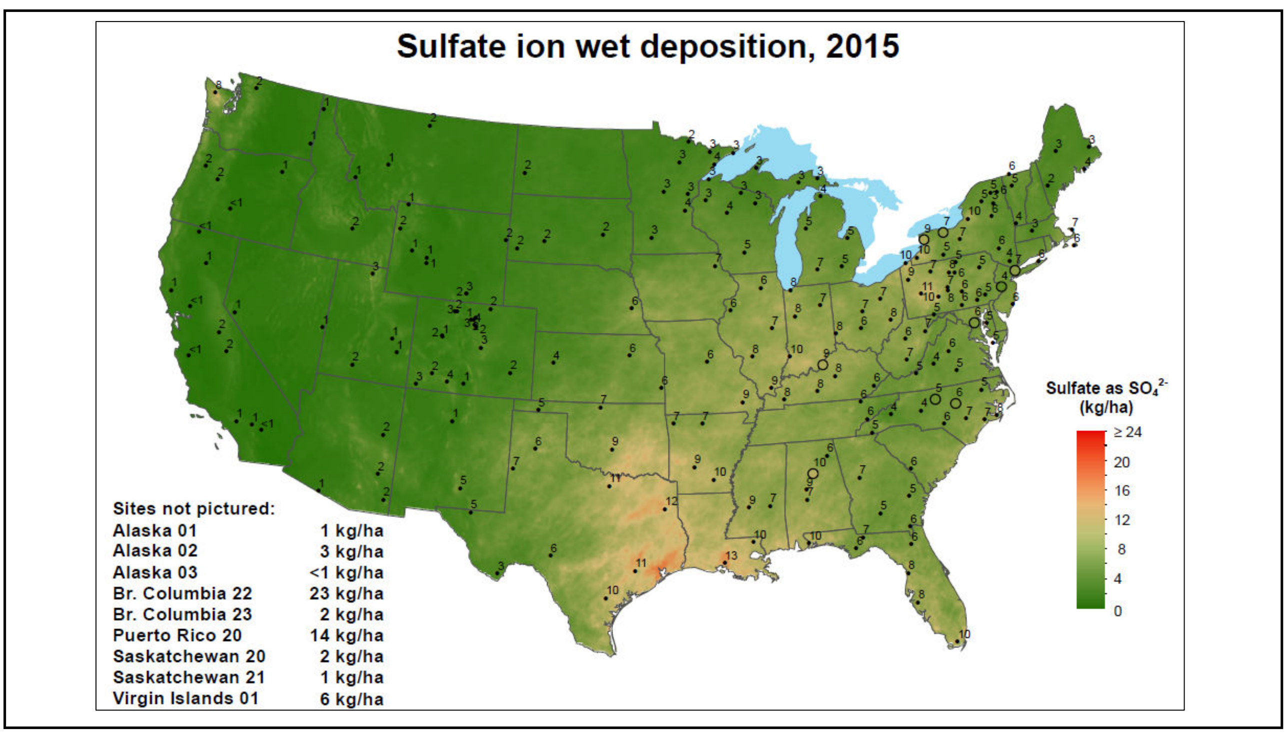
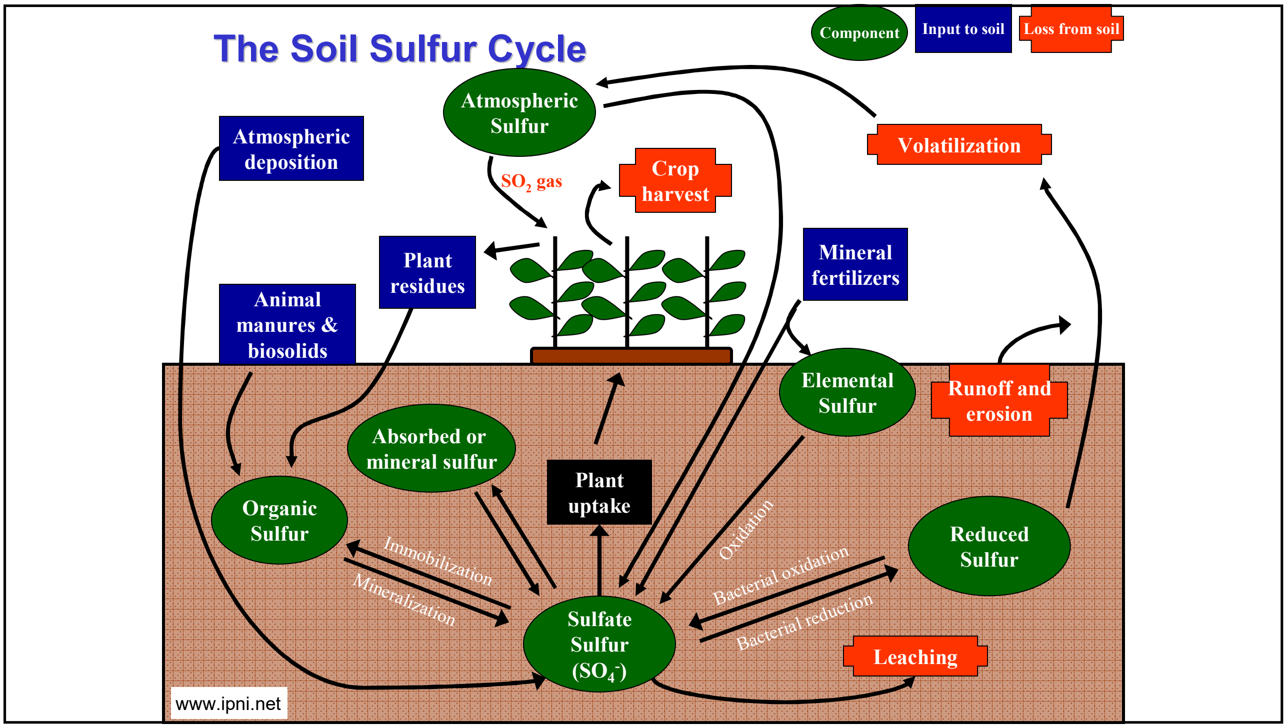
Sulfate ion wet deposition, 2005




Sulfate ion wet deposition, 2011
Sulfate as SO_4^{2-} (kg/ha)
≥ 24
20
16
12
8
4
0
Sites not pictured:
Alaska 01 < 1 kg/ha
Alaska 03 < 1 kg/ha
Alaska 06 1 kg/ha
Puerto Rico 20 26 kg/ha
Virgin Islands 01 10 kg/ha

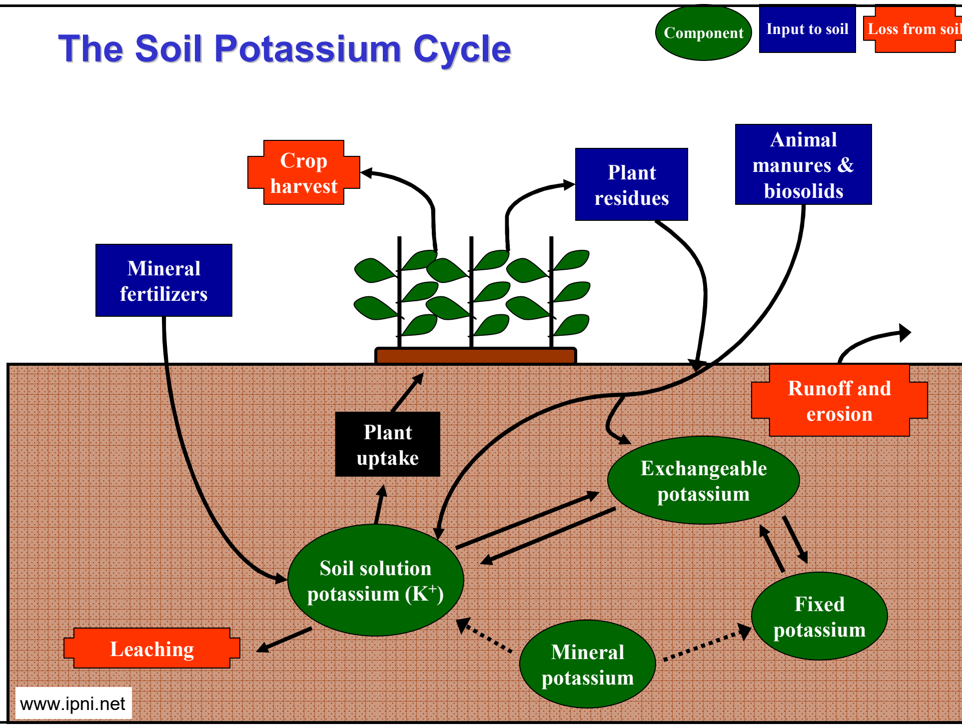

Sulfate ion wet deposition, 2015
Sulfate as SO_4^{2-} (kg/ha)
≥ 24
20
16
12
8
4
0
Sites not pictured:
Alaska 01 1 kg/ha
Alaska 02 3 kg/ha
Alaska 03 <1 kg/ha
Br. Columbia 22 23 kg/ha
Br. Columbia 23 2 kg/ha
Puerto Rico 20 14 kg/ha
Saskatchewan 20 2 kg/ha
Saskatchewan 21 1 kg/ha
Virgin Islands 01 6 kg/ha



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

The Soil Potassium Cycle



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

The next lecture:

"Ecosystem Mass Balances and Models of Terrestrial Nutrient Cycling"

- We will use what we've learned so far to look at element fluxes at the ecosystem scale

- This will be done by creating ecosystem mass balances, which are a powerful way of looking at ecosystem function in an integrated manner