

The biosphere – terrestrial ecosystems.

1. Acid Rain

- a. Acidity downwind of fossil-fuel burning mainly due to H_2SO_4 , HNO_3 .
- b. HNO_3 is expected to fertilize forest, increasing NPP, but long term exposure to acid rain actually causes productivity decline, illness.
- c. Increase in soil-water Al^{3+} at low pH may inhibit (poison) nutrient uptake.
- d. High N-availability may stunt mycorrhizal fungi growth, impeding P-acquisition.
- e. Leaf N/P ratios in SoCal forest appear to follow “d”.
- f. Some excess N accumulates in soil, much loss to nitrification, runoff.

Aqueous reduction/oxidation; biogeochemistry of wetlands and lakes

Reading: Chapter 7 of Schlesinger

Ch. 7: Wetlands biogeochemistry.

1. Streams and soil water

- a. Streams and groundwater flow affect availability of water for land plants, but also create wetland environments with distinct biogeochemical properties
- b. Stream load is the non- H_2O component of stream chemistry, includes
 - i. Dissolved ions (from rainfall and soil dissolution/weathering)
 - ii. Particulates (from mechanical weathering/erosion)
- c. C/N/P in wetlands/streams
 - i. Small streams – most organic carbon washed in.
 - ii. Large rivers – more organic carbon generated in place, but still typically dominated by external sources
 - iii. N/P typically limit productivity.
 1. Rapid internal cycling – nutrient “spiraling”
 2. Indicates rapid biological assimilation, decomposition, and “remineralization” (i.e., restoration to inorganic form)
- d. Inorganic ions
 - i. Many streams and rivers seem to have roughly constant dissolved ion concentrations, so transport scales in proportion to streamflow.
 - ii. Rivers in different climate / weathering environments show somewhat characteristic dissolved ion compositions (i.e., Zones A, B, C on fig. 8.7)
- e. Suspended material
 - i. Highly dependent on streamflow

- ii. Most suspended matter (~90%) settles out before reaching the ocean

2. Oxygen limitation

- a. The modern atmosphere and ocean are oxygen-rich. The atmosphere due to rapid mixing, the ocean due to relatively large volumes of water and low rates of productivity/decomposition.
 - i. even in stagnant air, O_2 diffusivity $D(O_2, \text{air}) \approx 0.2 \text{ cm}^2/\text{sec}$
 - ii. diffusion length scale $d \approx (Dt)^{0.5}$, $\sim 130 \text{ cm (day)}$; 25 m (year)
- b. Oxygen mixing into wetland/lake/sedimentary environments is often slow or incomplete – setting up strong redox gradients.
 - i. in water, O_2 diffusivity $D(O_2, \text{water}) \approx 2 \times 10^{-5} \text{ cm}^2/\text{sec}$
 - ii. diffusion length scale $d \approx (Dt)^{0.5}$, $\sim 1.3 \text{ cm (day)}$; 25 cm (year)
- c. Production of reduced gasses (N_2 , H_2S , CH_4 , H_2) from low- pO_2 environments globally significant, as in incomplete decomposition/respiration/mineralization of organic matter.

3. Reduction/oxidation reactions

- a. Oxidation \rightarrow loss of electrons
- b. Reduction \rightarrow gain of electrons
- c. $4Fe + 3O_2 \rightarrow 2Fe_2O_3$ $Fe^0 \rightarrow Fe^{3+}$, oxidation of iron (reduction of O_2)
- d. Fe^{3+} oxidized, Fe^{2+} reduced. If connected electrically, electrons will flow from a solution of Fe^{2+} to a solution of Fe^{3+} to equalize redox state – redox potential.
 - i. $Fe^{2+} - e \rightarrow Fe^{3+}$
 - ii. $Fe^{3+} + e \rightarrow Fe^{2+}$
- e. Oxidation “power” can be measured by voltage of electrons from solution of interest to a standard solution (H_2 g + H^+ aq) – called Eh.
- f. $O_2 + 4e + 4H^+ \rightarrow 2H_2O$ has standard redox potential of 1.1V at pH of 2.
- g. Fe^{3+} has a lower redox potential, meaning O_2 will oxidize Fe^{2+} to Fe^{3+} but Fe^{3+} will not split water to make O_2 .
- h. $Fe^{2+} \rightarrow Fe^0$ has lower potential still....