EPSS C113/213 Biological and Environmental Chemistry
Feb 12, 2018

The biosphere – terrestrial ecosystems.
Reading: Chapter 5 of Schlesinger

Ch. 5: The biosphere (cont'd).

Lecture 11

1. Global Changes to Net Primary Production
    a. Present human use of active biomass is ~3.3×10^{15} gC/yr.
        i. % total?
    b. Historic consumption of biomass since 1860 ~1.1×10^{17}gC
        i. Mostly conversion of forest to grassland/farmland
    c. Quantifying biomass/fossil fuel loss
        i. $^{14}C/^{12}C$, $^{13}C/^{12}C$
            1. ^{14}C formed by cosmic rays in atmosphere
                a. mean lifetime 8300 years
                b. captured by photosynthesis, but all decayed away in ~10-100 Myr old fossil fuels.
                c. Use as signature of fossil fuel burning
            2. $^{13}C/^{12}C$ – partially separated by chemical processes
                a. $^{12}CO_2$ diffuses ~1% faster than $^{13}CO_2$
                b. CO_2 penetrating stomata has low $^{13}C/^{12}C$
                c. $^{12}CO_2$ also easier to photosynthesize
                d. Biomass, fossil fuel $^{13}C/^{12}C$ lower than atmosphere.
                e. Use as signature of ??
2. Secular change in biomass
    a. Succession from barren land → brush → forest: net storage of NPP
    b. Mature ecosystem reaches steady state
        i. NEP = NPP – (Rh + Rd) = GPP – (Rh + Rd + Rp)
        ii. Fig. 5.13 Chapman et al. (1975)
        iii. Rh < 20% NPP
        iv. Rp ≈ NPP
        v. Therefore Rd ≈ 70-80% NPP in steady-state ecosystem
        vi. Reset by wildfire/harvest.
        vii. Long-term NPP storage possible only if Rd inhibited
            1. Medium-term storage in wood (forest), humus (O-horizon in soil)
            2. Decomposition radically slowed below 15cm, by low T, low H_2O, or low $O_2 + SO_4^{2-}$
            3. Peatland/swampland
    c. Effects of cultivation (Fig. 5.9)
        i. Exponential loss (mean T ~15years) of ~1/2 to 2/3 stored C.

Reading: Chapter 6 of Schlesinger

Ch. 6: Biogeochemical Cycles on Land.

1. Inter-system cycling
    a. Class so far has focused on transport between systems (atmosphere → oceans (precipitation), Soils → runoff (weathering)
    b. Limiting nutrients tend to be strongly recycled *within* ecosystems, to compensate for insufficient input, and scavenge against loss.
        i. (Table 6.1) Fixed nitrogen in forests may cycle 10-20 times before export/destruction.
2. Nutrients in land plants
    a. Common ions taken up by adsorption/osmosis of soil water.
    b. Over-common ions may be excluded (Ca2+ in semi-arid soil, Na+ in saline soils).
    c. Limiting nutrients (esp. N, P, K) actively "pumped" into root systems
    d. Phosphorus (PO_4^{3-}) scarcity → higher root/leaf ratio (also slower growth)
    e. Nitrogen (NH_4^+ or NO_3^-)
        i. Relative ammonium/nitrate vs. soil water oxidation state?
        ii. Nitrate usually more mobile (in silicate soil)
        iii. Biological Nitrogen typically $R\text{-}NH_2$
            1. Both forms rare in most soils/soil waters.
        iv. Production of NH3: N2 + 2H+ + 3H2 → NH3
            1. DG0 = –16 KJ/mol at 298K (gas phase)
            2. NH3 stable, but reaction is sssslllloooowwww
            3. Inorganic production only significant at high temperatures (lightning >> volcanoes)
            4. Inorganic production mainly by lightning
        v. Organic nitrogen fixation vital
            1. Cyanobacteria, bacteria most common N-fixers
            2. Some free-living, some symbiotic with plants
                a. Rhizobia -- Legumes (beans, kudzu)
            3. Consumes energy
            4. Requires Fe, Mo for nitrogenase enzymes.

Proposed Steps In Nitrogenase Mechanism (from David Clark, SIU – not required for class, just added if you're interested in more detail):

The mechanism is largely based on work with non-protein MoFe complexes, some of which will fix N_2 chemically (but very inefficiently).
a) Mo in active site is reduced from Mo^{6+} to Mo^{5+} to Mo^{4+} by sequential electron transfer from azoferredoxin.

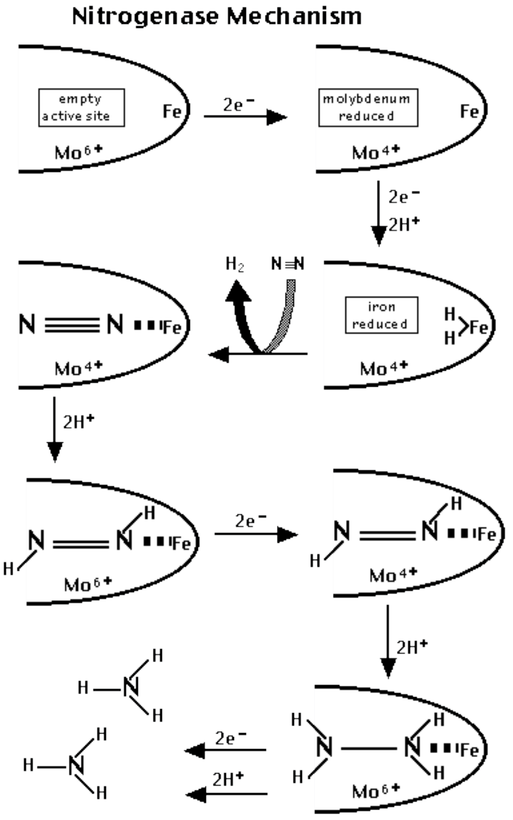
b) Semi-activated nitrogenase can reduce easy substrates such as acetylene.

c) Further transfer of two electrons activates the Fe of the MoFe cofactor in the active site, which carries 2[H].

d) N_2 binds end on to the $Fe[H]_2$ complex and releases H_2.

e) The bound N_2 is reduced to HN=NH by sideways transfer of 2e- (plus $2H^+$) from the active site Mo^{4+}.

f) Conversion of N_2H_2 to $2NH_3$ requires two further $2e^-$ steps, but partial activation of the enzyme is sufficient (i.e. ATP is no longer needed to hype up the redox potential) since only step (e) requires extreme reducing power.



This mechanism also explains why acetylene, C_2H_2, is a non-competitive inhibitor of N_2 fixation. Acetylene reduction discharges nitrogenase before it ever reaches full activation. Although N_2 fixation wastes reducing power when H_2 is evolved, most N_2 fixing bacteria contain hydrogenase which uses gaseous H_2 to reduce NAD(P). Hence they recycle the hydrogen at least partly.

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5. Nitrogenase activity measured via acetylene hydrogenation to ethylene (HCCH chemical analogue to N2)
6. Typical free-living N-fixation ~0.1-0.5 g N/m2/yr
    a. Potentially supports ~10-250 g C/m2/yr net production
7. N-fixation highest in recovering ecosystems

3. Fungal symbiosis (N, P uptake)
    i. Fungi increase soil contact
    ii. Deliver increased nutrients
    iii. Fixed carbon obtained from plants
4. Nutrient loss
    a. Acquired N, P, K concentrated in areas of growth (new leaves).
    b. Nutrients withdrawn from mature/senescent tissue (old leaves, stems), deciduous trees evacuate leaves in preparation for winter.
    c. Nutrients lost through rainfall leaching (leaves, esp. K)

    d. Litterfall exports some N, P, K, much Mg, Ca.
    e. Both losses may reconcentrate nutrients in soil near parent plant.
5. Biogeochemical cycling in soil
    a. Most available nitrogen comes from the soil, via decomposition of dead organic matter
        i. Decomposition – breakdown of organic matter
        ii. *Mineralization* more specific – conversion of organic matter to inorganic compounds. I.e., CO2, PO43–, NO3–
        iii. Mostly result from fungi, bacteria
        iv. Decomposition rates correlate with decomposer biomass
            1. Measured by fumigation! CHCL3 kills bugs, breaks cells, releasing extra N, P. Decomposer "Redfield-like" ratio allows back-extrapolation of soil decomposer biomass.
        v. Decomposer accumulate liberated N, P – *immobilization* – particularly in high C/N, C/P soils and materials (e.g., log falls)
        vi. Soil N, P mineralization slow, ~1-3% per year.
        vii. Therefore ~70-90% of N, P bound in soils, only ~10-30% above ground!
6. Nitrogen cycling
    a. Decomposition: R-NH2 → NH4+ → NH4+(decomposer)
    b. Nitrification: NH4+ + bact → NO3–
        i. NO3– → runoff or plants
    c. Soil gas emission: NH4+ + OH– → NH3 + H2O
        i. Favorable conditions?
        ii. Ammonia loss typically < 1 kg/ha/yr (100 mg/m2/yr)
        iii. N2, N2O, NO lost as by products of nitrification
        iv. Metabolism of NO3– → N2O, NO, N2: denitrification
            1. N2 loss greatest, ~2kg/hayr (200 mg/m2/yr)
7. Transformations in Fire
    a. Heat and oxidation capable of removing volatile components, esp. N-species
        i. N2 most common product; N2O, Nox less common, but substantial contributors to global atmospheric N-oxide budget.
        ii. CH4, H2, SO2 also liberated.
        iii. P, cations less intensively remove
        iv. N, P remaining often rendered more available, but may also be likely to run off with precipitation.
        v. Human activity probably substantially increasing incidence and intensity of fire.
8. Acid Rain
    a. Acidity downwind of fossil-fuel burning mainly due to H2SO4, HNO3.
    b. HNO3 is expected to fertilize forest, increasing NPP, but long term exposure to acid rain actually causes productivity decline, illness.

c. Increase in soil-water Al3+ 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.
   ii.