Pollution of Natural Waters

Outline:

1. Redox chemistry
2. Redox potential in aquatic systems
3. Eutrophication
4. Water treatment

1. Redox chemistry

- Principle of equilibration of chemical system

$$\begin{aligned} R &\overset{K_{eq}}{\rightleftharpoons} P \\ Q_R &= \frac{[P]}{[R]} \\ \Delta G &= \Delta G^0 + RT \log Q_R \end{aligned}$$

- ΔG acts as a chemical potential for chemical change.
- Spontaneous process: $\Delta G < 0$ -lowering of free energy
- Reaction proceeds until $\Delta G = 0$ when $Q_R = K_{eq}$
- Direction of process (towards reactants/products) depends on Q_R
- Electrochemistry: Chemical potential drives electron flow from one species to another.
  - Oxidant: Electron acceptor
  - Reductant: Electron donor
- Half-reactions:

$$\begin{aligned} Zn\,(s) &\xrightarrow{\Delta G_1} Zn^{+2}\,(aq) + 2e^- & \text{oxidation} \\ Cu^{+2}\,(aq) + 2e^- &\xrightarrow{\Delta G_2} Cu(s) & \text{reduction} \end{aligned}$$

- Standard cell potential: $\epsilon^0 = -\Delta G^0/nF$ where $F = 96485$ Coul/mol is Faraday's constant and n is the number of moles of electrons flowing in reaction.
  - Measured in volts

- Nernst equation:

$$\epsilon = \epsilon^0 - RT/nF \log Q_R$$

  - Reaction proceeds until $\epsilon = 0$: concentrations of cations adjust until $Q_r = K_{eq}$.

- Examples: Battery and Copper plating
- Cell potential depends on pH since Q_r often dependent on pH

2. Redox potential in natural waters

- Can be viewed as chemical switch determining metabolic pathways
- Oxidation of carbohydrates (CH_2O)
- Redox potential describes energy that can be obtained from pathway: Kinetics also important (enzyme catalysis)
- Half-reactions:

$$\begin{aligned} (CH_2O) + H_2O &\longrightarrow CO_2 + 4H^+ + 4e^- \\ O_2 + 4e^- + 4H^+ &\longrightarrow 2H_2O \end{aligned}$$

  - Oxygen as oxidizer of carbohydrates: electrochemical driving force
  - Problem: Oxygen not very soluble in H_2O: 9 mg/l at $T = 20C$: 2.7 mg/l O_2 necessary to oxidize 1 mg organic carbon
  - When concentration of organic compounds is high, water is depleted of O_2
    * Oxygenation depends on mixing of water with air: Turbulent surface leads to good mixing; stagnant water leads to poor mixing.
  - Biological oxygen demand (BOD): measures reducing powers of water containing organics: number of mg of O_2 required to carry out oxidation.

- What happens when little O_2 present? Other oxidants provide alternative metabolic pathways
- Order of driving potential:

$$O_2 > NO_3^- > MnO_2 > Fe(OH)_3 > SO_4^{2-} > MS_2 > CO_2$$

- Microbes use other oxidants in metabolism under anaerobic conditions

1. Nitration ion: NO_3^- used by denitrifying bacteria
   - Important as soon as O_2 concentrations drop
   - Normally inert: enzyme catalysis of half-reaction

$$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$$

2. Metal oxides and hydroxides

$$\begin{aligned} MnO_2 + 4H^+ + 2e^- &\longrightarrow Mn^{+2} + 2H_2O \\ Fe(OH)_3 + 3H^+ + e^- &\longrightarrow Fe^{+2} + 3H_2O \end{aligned}$$

3. SO_4^{2-}: sulfate reducing bacteria
4. Methanogens: reduce CO_2 into methane

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$$

   - Ubiquitous in sediments
   - Substantial source of methane: swamps

- Other important processes: Nitrification for source of nitrates for plants

$$\begin{aligned} NH_4^+ + 2H_2O &\longrightarrow NO_2^- + 8H^+ + 6e^- \\ NO_2^- + H_2O &\longrightarrow NO_3^- + 2H^+ + 2e^- \end{aligned}$$

Water quality and Nutrient cycles

- Supply of O_2 in water is limited: complex dynamical easily disturbed
- O_2 concentration falls with distance from surface: sediments rich with anaerobic bacteria
- Vegetation on surface can lead to higher O_2 levels
- Photosynthetic algae limited to *euphotic* zone where light can penetrate
- Below euphotic zone, O_2 concentration drops rapidly
- Partitioning of lakes: euphotic and “deep water” zones
  - Stabilized by thermal stratification
    * Boundary and thermocline in summer: warm water less dense

  - Mixing primarily in euphotic zone
  - In winter, temperature gradient disappears: good mixing of nutrients
  - In Spring, sunlight brings rapid growth in nutrient-rich water
    * Growth slows as nutrient supply decreases
    * Bacteria decompose dead plant matter: nutrient supply grows again
  - Generally, nutrient supply limited and BOD ¡ avaiable O_2

- Cycle disruption: excessive nutrient loading
- High populations of algae and photoplankton form algal blooms
  - Aerobic bacterial decomposition of dead algae depletes O_2 supply
  - Kills fish and other aquatic life
  - Shift to anaerobic metabolic mechanisms
- Eutrophication: aging and filling in of lake-natural process
- *Cultural eutrophication:* Accelerated aging due to excessive nutrients
  - Over time, clear lakes (oligotrophic) fills in with sediment to become a marsh and then dry land
- Nutrients
  - Assimilated by primary producers which support photosynthesis and nitrogen fixation
  - Primary producers serve as food for secondary producers, such as fish
  - Limiting nutrient: element least available in required abundance in biological species: $C : N : P \sim 106 : 16 : 1$
  - Usually N or P is limiting nutrient: On land N_2 generally is but N_2 fixing bacteria common in water
  - Phosphorus usually limiting in water
  - Excessive phophate input in water: sources- sewage, agricultural runoff, detergents, synthetic fertilizers
- Notorious examples of nutrient-overloading
  1. Phosphate-induced eutrophication of lake Erie

- Most fish died and fouled shoreline in 1960's
- US and Canada spent 8 million on sewage treatment and detergent restrictions
- Commercial fisheries now operational and beaches open

2. Chesapeake bay: Maryland and Virginia
   - Excessive nitrates: NO_x production from traffic $\rightarrow$ acid rain $\rightarrow$ excessive nitrates in water

Water Treatment

- Settling and screening processes to remove solids in primary treatment
- Bacterial metabolysis of organics in secondary treatment
  - CO_2 released and BOD decreased
  - Wastewater sprayed on sediments containing aerobic bacteria
  - Algae sludge produced: disposal problem
  - Disposal options:
    1. Fertizer: problem is may contain toxic metals
    2. Incineration
    3. Convert sludge to methane with anaerobic bacteria: expensive and smelly
    4. Landfills: toxic metals in landfills