

Pollution of Natural Waters

Outline:

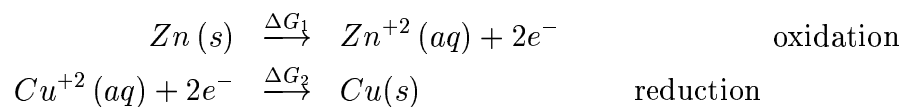
1. Redox chemistry
2. Redox potential in aquatic systems
3. Eutrophication
4. Water treatment

1. Redox chemistry

- Principle of equilibration of chemical system

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

- 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:



- 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:

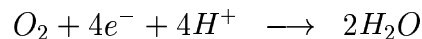
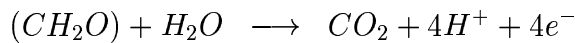
$$\epsilon = \epsilon^0 - RT/nF \log Q_R$$

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

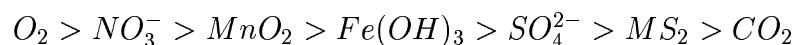
- Examples: Battery and Copper plating
- Cell potential depends on pH since Q_r often dependent on pH

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:



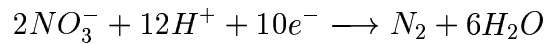
- Oxygen as oxidizer of carbohydrates: electrochemical driving force
- Problem: Oxygen not very soluble in H_2O : 9 mg/l at $T = 20C$: 2.7 mg/l O_2 necessary to oxidize 1 mg organic carbon
- When concentration of organic compounds is high, water is depleted of O_2
 - * Oxygenation depends on mixing of water with air: Turbulent surfact 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:



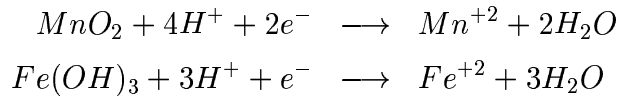
- Microbes use other oxidants in metabolism under anaerobic conditions

1. Nitration ion: NO_3^- used by denitrifying bacteria

- Important as soon as O_2 concentrations drop
- Normally inert: enzyme catalysis of half-reaction

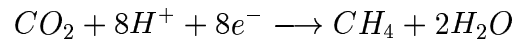


2. Metal oxides and hydroxides



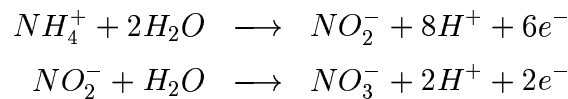
3. SO_4^{2-} : sulfate reducing bacteria

4. Methanogens: reduce CO_2 into methane



- Ubiquitous in sediments
- Substantial source of methane: swamps

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



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 \downarrow available 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 phosphate 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 → acid rain → excessive nitrates in water

Water Treatment

- Settling and screening processes to remove solids in primary treatment
- Bacterial metabolism 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. Fertilizer: 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