

# Lecture 6a, Dissolved Oxygen Modeling and Introduction to Biotransformation and Biodegradation

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# Dissolved Oxygen= DO Dissolved Oxygen Modeling in Surface Waters

- DO is critical for the sustainability of aquatic ecosystems (freshwater, brackish water, seawater) and the terrestrial ecosystems ecological receptors (osprey, gulls, raccoons etc.) that depend on them.
- Most organisms in water require O<sub>2</sub> for respiration so the DO level determines if the water is suitable for inhabitation by appropriate species.
- At equilibrium with atmospheric pressure DO is approximately = 10 ppm or 10 mg/L
- At 760 mm Hg-water saturated air

DO (T,[chloride])  $\Rightarrow$  T $\downarrow$  than DO $\uparrow$  and as [Chloride]  $\uparrow$  than DO  $\downarrow$

See Table 2.4 on page 91 of Hemond Text from APHA 1960

# Dissolved Oxygen Modeling in Surface Waters

- If temperature is held constant and chloride concentration increases then DO decreases. If chloride concentration is held constant and temperature increases then DO decreases.
- Why does O<sub>2</sub> solubility increase as the water temperature decreases—O<sub>2</sub> slips into pockets that exist in the loose hydrogen bonded network of H<sub>2</sub>O molecules without forcing them apart. The O<sub>2</sub> is then caged by the H<sub>2</sub>O molecules—weakly pinning them in. The dissolution of O<sub>2</sub> is weakly exothermic—so cooling shifts the reaction equilibrium more to the dissolved form.

# Mechanisms of O<sub>2</sub> to DO

1. Diffusion from surrounding air-The DO in water obeys Henry's Law where the mass of a gas that will dissolve into a solution is proportional to the partial pressure of the gas over the solution. So the higher the air pressure than the higher is the O<sub>2</sub> partial pressure.
  - Given this-Does water at sea level or in a mountain stream dissolve more oxygen at the same temperature?----Why?
  - See Handout 6.2-6 Solubility of Oxygen in Water at Various Temperatures and Pressures-Source USGS, Weiss 1970
  - Also—high humidity lowers O<sub>2</sub> partial pressure therefore all things being equal will lower DO slightly.

# Deriving DO in mg/L or ppm

- A simple empirical equation that will give DO in mg of oxygen per liter of water (ppm) is:
  - $0^{\circ}\text{C} < t < 30^{\circ}\text{C}$        $\text{DO} = (P - p) \cdot 0.678 / (35 + t)$
  - $30^{\circ}\text{C} < t < 50^{\circ}\text{C}$        $\text{DO} = (P - p) \cdot 0.827 / (49 + t)$
- Where P is barometric pressure in torr, temperature is t in centigrade and H<sub>2</sub>O vapor pressure is p in torr.  
Remember that 1 atmosphere is equal to 760 mm Hg = 760 torr = 14.7 psi
- From Standard Methods for the Examination of Water and Wastewater, 12th Edition, APHA, NY, NY, 1965, pp. 408-410.

# Mechanisms of O<sub>2</sub> to DO

2. Aeration – rapid movement, waterfalls. Natural water courses with stones, producing eddy currents etc.
3. Photosynthesis – As a waste product of the photosynthetic cycle.

# DO and Effect on Aquatic Life

- If DO goes over 110 ppm it can be very harmful to fish life-fish can develop gas bubble disease.
- As DO goes less than 5 ppm aquatic life is put under stress
- If DO is under 1-2 ppm even for a few hours fish kills can result.
- **So thinking question:**
  - What could happen to trout in a mountain stream if a mining operation uses water for cooling and releases water 10 degrees C above input temperatures?

# Conductivity and DO Relationship

- **Another Factor-** Conductivity in water is proportional to the concentration of total dissolved solids (TDS). As water conductivity increases than DO decreases
- TDS are most usually sulfates, bicarbonates and chlorides of calcium, magnesium and sodium.
- What is the biggest threat to conductivity increases in the Monongahela River watersheds and why???

# Loss of DO in Water

- **DO is a Function of the Organic Waste Concentration or Sewerage in Water**
  - DO decreases as [sewerage-organic waste] increases.
  - Why; Bacteria use O<sub>2</sub> to oxidize this waste thus releasing CO<sub>2</sub> and mineralizing the organic waste.
  - Therefore if O<sub>2</sub> is consumed faster than it can be replenished (by diffusion, photosynthesis or aeration) than DO will of course decrease.

# Biochemical or Biological Oxygen Demand (BOD)

- Measure of the amount of O<sub>2</sub> required by bacteria to degrade dissolved or suspended organic matter per unit volume of H<sub>2</sub>O.
- Therefore it is an indirect measure of the organic content in the water.
- BOD(5) - A five day test where a fully saturated water sample is incubated at 20°C and the amount of DO that has been consumed is measured.
- BOD(5) is expressed as the mg of DO used to oxidize the organic waste in one Liter of water (mg/L).
- Review Figure 2-22 in Text page 136 This is quite a problem in Pittsburgh because of Combined Sewer Overflows (CSO), Sanitary Sewer Overflows (SSO) and Wastewater Treatment Plant Overflows (WWTPO)
- At Outfalls the O<sub>2</sub> demand is greatest where BOD is maximum. The rate of decay and recovery is a factor of the dissolution of O<sub>2</sub> from the atmosphere (which depends on what?), photosynthesis, aeration, and benthic oxygen demand (O<sub>2</sub> consumption by the bottom sediment).

# Streeter-Phelps Model for Mass Balances of O<sub>2</sub> and BOD in a River or Stream

- Allows estimation of the DO sag as a function of distance from injection.
- Assume a stream initially saturated with O<sub>2</sub> that receives a point source BOD.
- BOD decays typically at first order rate constant  $-K_{\text{BOD}}$  of 0.2/day.
- - So if  $\tau$  = travel time than  $\text{BOD} = \text{BOD}_0 e^{-K_{\text{BOD}}\tau}$
- Remember to use mass balance in calculations so that  $\text{Rate of O}_2 \text{ inflow} - \text{Rate of O}_2 \text{ outflow} + \text{rate of O}_2 \text{ reaeration} - \text{rate of O}_2 \text{ consumption by BOD} = 0$
- Can calculate the travel time maximum at which DO is minimum after a point source release by using formula 2-68

# Biotransformation and Biodegradation

- Biotransformation – the changing of either organic or inorganic pollutants from one chemical species to another. This term is often used instead of biodegradation but this is not really correct because a transformation may not necessarily be degradation. One instance of this is elemental Hg given off by coal fired power plants and incinerators. The elemental Hg falls to water and can be transformed into methylmercury by the methylating action of bacteria. Methylmercury is highly toxic and is quite persistent in the environment.
- Biodegradation – describes the biotransformation-of an organic pollutant. Transformations in oxic water tend to favor less toxic offspring compounds. The term **mineralization** is used to denote the process where the organic compound is converted into inorganic compounds generally mineral salts, CO<sub>2</sub> and water.
- Partial Biodegradation – refers to intermediate biotic transformations that are not only inorganic in nature. For instance, benzene is degraded by aerobic microorganisms via aromatic hydroxylation to phenol and water. Phenol is an intermediate in a chain of biodegradation.
- Biotransformation and degradation are mediated via fungi (aerobic) and bacteria (aerobic and/or anaerobic). The microbes generally harvest energy from the transformation.
- Transformations are performed by microbes using enzymes which act as catalytic agents for the reaction-Bacteria can be changed genetically to transform organic pollutants by insertion of plasmids into their cells-plasmids are small circular molecules of DNA