

# **Lecture 6.b., Aerobic and Anaerobic Biodegradation of Organic Compounds, Modeling Biodegradation and Bioconcentration and Accumulation in Aquatic Organisms**

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# Aerobic Biodegradation of Organic Compounds

## Biodegradation and BOD Relationship

- BOD is an overall measure of the concentration of biologically degradable material
- BOD gives us no information about the specificity of organic compounds in the mixture or their degradation rates
- In aerobic degradation the most energy comes from oxidation of carbon that is in its most reduced state (refer to Peterson Notes-Oxidation-reduction for the non-chemical skeptic).

# Microbial Oxidation of Anthropogenic Compounds

- Tremendous variety of microorganisms that have the ability to use pollutants such as alcohols, fuels and solvents as well as natural organic detritus as a source of energy.
- Microorganisms can be configured to help humans in the event of fuel spills etc.
- Microbial oxidation of more soluble and low molecular weight hydrocarbons occurs quickly (like alcohols and organic acids).
- The rate of microbial degradation decreases for contaminants with;
  - Increasing molecular weight.
  - Lower solubility in water.
  - Increasing number of aromatic rings.
  - Increasing numbers of branches.
  - The number of halogen atoms in their make-up (chlorine, fluorine, bromide etc.)
- If there were a train derailment on the Allegheny River and equal masses of Cyclohexane, Dichloroethane, Acetic Acid and PCB (Aroclor 1260) were spilled into the river-in what order would you expect aerobic microbial biodegradation to remove the contaminant? What compounds would you expect might only be partially degraded or have no significant degradation?

# Anaerobic Microbial Degradation of Anthropogenic Compounds

- As DO is depleted microorganisms shift to using other oxidants such as  $\text{SO}_4$  (-2 oxidation state) and ecological conditions increasingly become reducing.
- The degradation of some organic contaminants occurs more readily in reducing environments. These contaminants -
  - Have more oxidized carbon (remember this does not refer to oxygen but the oxidation state of the key carbon atoms).
  - Are reduced meaning that they go from a more positive oxidation number to lower oxidation number.
- See figure 2-25 on page 146 of text.

# Modeling Biodegradation

## Kinetic Model

- Assumptions
  - Microorganisms are in contact with the water at all times.
  - Water contains a dissolved organic compound that serves as an energy source.
  - Biodegradation rate is same as uptake rate, so there is sufficient enzyme to continually catalyze the reaction.

# Michaelis-Menten Enzyme Kinetics

- $V = V_{max} \frac{C}{C + K_s}$  -Where  $V$  is the rate of chemical uptake per cell in mass per cell-Time,  $V_{max}$  is the maximum chemical uptake per cell.  $C$  is the concentration of the contaminant in water in mass per cubic Liter, and  $K_s$  is the half saturation constant also in mass per cubic Liter
- Rate of Uptake vs. Chemical Concentration is plotted in Figure 2-26.
- When  $C = K_s$  then  $V$  is  $\frac{1}{2}$  of  $V_{max}$  also when  $K_s$  is much greater than  $C$  then uptake is proportional to concentration and obeys first order kinetics-Formula 2-71b.
- If  $C$  is far greater than  $K_s$  then uptake approaches independence of  $C$ -zero order kinetics so that  $V$  is approximately equal to  $V_{max}$ .
- Rate of uptake of a contaminant from water is proportional to both the rate of chemical uptake per cell and the cell density.

# **Bioconcentration and Accumulation in Aquatic Organisms**

- Bioconcentration – The process of aquatic organisms accumulating chemicals from water only.
- Bioaccumulation - The process of aquatic organisms accumulating chemicals from both water and food.

# Bioconcentration Factor- (BCF)

- **Bioconcentration Factor- (BCF)** – The ratio of the concentration of a chemical in an organism to the concentration of that chemical in seawater, freshwater or brackish water.
- Therefore-  
$$\frac{\text{mg of chemical/kg of organism}}{\text{mg of chemical in solution/Liter}} = \text{Liter/kg}$$
- BCF can be an observed ratio or be the prediction of a partitioning model.

# Partitioning Models

## Assumptions

- Pollutant chemicals partition in passive way between water and the organism.
- Chemical equilibrium exists between chemicals concentrations in the water and the organism.

These assumptions are most valid for lipophilic (hydrophobic) chemicals- they are more rapidly exchanged between the water and organism than they are excreted or biodegraded by the organism.

## Fish Model- Fish is a bag of oil and tissue water.

- Chemical partitions between the bag and surrounding water according to:
  - $K_{ow}$  which is the reciprocal of the chemicals water solubility.
  - The lipid content of the fish.
- Table 2.9 in Hemond and Fechner-Levy presents a number of formulas for determining BCF.
- Such as----  $\log BCF = 2.791 - 0.564 \log S$  where S is Water Solubility of chemical in ppm. This formula has been determined using Brook and Rainbow Trout, Sunfish, Flathead Minnow and Carp
- Review Figure 2-28----BCF- remember that the log BCF are highly correlated with  $\log K_{ow}$  but that a single prediction can be off by a factor of three so averages using a number of formulas for each species provides more accuracy.
- Kinetic Models that depend on the dynamics of intake, storage, metabolic transformation and excretion of specific chemicals in specific organisms can be used to estimate **bioaccumulation**.

# Depuration

- Use a first order kinetic model to estimate the depuration (cleansing) or partial removal of a contaminant from a fish given a specific contaminant concentration so
- $C = C_0 e^{-kt}$  Where  $C$  is the concentration at any time  $t$ ,  $C_0$  is the initial concentration,  $k$  is the first order rate constant (depuration-essentially analogous to decay) and  $t$  is the time.