Biological Transformations

- Oxidation - very slow unless photochemical
- Hydrolysis - often - slow

But these are other reactions can be 100, - 1000, of times faster with biological catalysis, (Up to 10^9x or more!)

- Biodegradation: Oxidation of an organic compound that leads to breakdown, and, which typically yields some metabolic energy to the organism.

- Mineralization: Complete degradation to CO_2 & H_2O (minerals, NO_3 & PO_4, etc)

- Biotransformation: Any microbially mediated change in a compound. (E.g., non-oxidative, or that yield no energy to microbe)

- Primary Substrate Utilization: Microbe uses compound as main source of energy.
  Example: Hexane oxidation in a gasoline spill.

- Secondary Substrate Utilization: Microbe uses something else to support growth, but also uses the compound.
  Example: Oxidation of alkylbenzene sulfonates (detergent) in sewage.

- Co-Metabolism: Microbe cannot use the compound as sole carbon (energy) source, regardless of concentration but will degrade compound in the presence of other substrates.
  Example: Breakdown of DDT or chlorinated solvents when other "food" available.

Knowing which of these is taking place helps predict the fate of compound or to plan a remediation.
Steps in Biodegradation:

(Affects rates, products, our model(s), etc.)

Transport to Cell:

- Film diffusion of cell surface
- Film diffusion of surface
- Intraparticle diffusion
- Transport in solution
- 

Is compound mostly dissolved or adsorbed?

- Are microbes free-swimming or in colonies or in coatings on surfaces ("Schmutzdecke")

And what about co-substrate transport?

- E.g., how will O₂ get to the cell?
- Are co-metabolized compounds soluble or only sparingly available?

Uptake by the Cell:

- Nonpolar cmpds (esp. very hydrophobic) may passively partition into cell
- Ionic cmpds usually can't permeate cell mem passively \( \Rightarrow \) active uptake via surface proteins or other uptake sites

May be a rate-limiting step in some situations.

Enzyme Synthesis/Activity:

- Constitutive enzymes: Always there, ready to go but may need to produce more

- Enzyme induction: Not there until the genes are "switched on" for synthesis.

- Enzyme derepression: Existing enzymes are enabled to do the catalysis.
Ex: Decarboxylation or 3-chlorobenzensulfinate

Requires these species:
- Decarboxylation
- 3-chlorobenzensulfinate

Sometimes required for transformation:
- Cooperation groups of different species
- Consortia of microorganisms

Ecology (Cont'd)

Role of Microbial Ecology

Chlorinated

Salts

Very Stable in Oxidative Conditions

Rigid Electrotransformation

(Cont'd Phenol)

Very Stable under anoxic conditions

Oxidative Conditions

Ex: Hydrocarbons: Rigid degradation under

(Anoxic Conditions)

Aerobic vs. Anaerobic Organisms

- Main Factors: Oxygen or NO Oxidation
- IS chemical or co-contamination toxic?
- Salinity
- pH
- Temperature, etc.

Are chemical conditions favorable?

What organisms are present? In what proportions?
MODELING DEGRADATION

TRANSPORT LIMITED:
- Diffusion out of particles
- Diffusion into cells or biofilm

**Fick's Law**  
\[ J_a = -D_m \frac{\partial C}{\partial x} \]

- Need effective diffusivity of the medium.

- Need effective diffusional distance.
  Film thickness? Effect of mixing?
  Membrane thickness? Biofilm thickness?
  Particle average radius?

Frequently we just reduce to empirical expression, often first order:

\[ \frac{dC}{dt} = J_{A_{surf}} = k_e [C] \]

**EMPIRICAL MASS TRANSFER**

\[ k_e = \frac{\text{mass transferred}}{\text{area} \times \text{time}} \]


BIOCHEMICAL RATE EXPRESSIONS

- Abundant cell population.
- Enzymes already induced
- Abundant primary substrate

(Contaminant is secondary substrate or co-metabolized)

**Expect 1st ORDER DECAY**
(Depends only on Conc. of contaminant assuming other conditions met)

\[ \frac{dC}{dt} = -k C \]

where \( C \) must be valid

**EX:**

CELLS GROWN ON QUINOLINE: [00]

\[ \text{CELLS} \times 10^6 \]

\[ \text{CELLS/L} \]

\[ 10^9 \]

\[ 10^8 \]

\[ 10^7 \]

\[ 10^6 \]

\[ 10^5 \]

\[ 1.47 \times 10^{10} \text{ cells/L} \]

**EX:**

BENZOF(quinoline)

\[ \text{CELS/L} \]

\[ (\mu \text{mol/L}) \]

\[ 6 \]

\[ 4 \]

\[ 2 \]

\[ 0 \]

\[ 1 \]

\[ 2 \]

\[ 3 \]

\[ 4 \]

\[ 5 \]

\[ 0 \]

\[ 1 \]

\[ 2 \]

\[ 3 \]

\[ 4 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 8 \]

**Smith et al., 1978**

Adapted to similar compound

Loss of added BENZO(F)QUINOLINE

\[ [00] \]
CAND TREAT DATA AS 1<sup>st</sup> or 2<sup>nd</sup> ORDER

1<sup>st</sup> ORDER:  
- Cell number is constant  
- B(t)Q disappears

\[
\frac{d[B(t)Q]}{dt} = -k_{obs} [B(t)Q]
\]

\[k_{obs} = 0.5 \text{hr}^{-1}\]

Would be good model for controlled reactor (e.g., treatment) or very stable nat. environment.

2<sup>nd</sup> ORDER:  
- When cell # varies

\[
\frac{d[B(t)Q]}{dt} = -k_{b0} [\text{cells}][B(t)Q]
\]

\[k_{b0} = 3.6 \times 10^{-11} \text{ L cell}^{-1} \text{ hr}^{-1}\]

**Note:** In either model we are assuming conc. of B(t)Q is LESS THAN the HALF-SAT'N constant of the enzyme system. Often OK. Here OK because B(t)Q is II<sup>°</sup> substic \(
\text{B(t)Q}
\)

MONOD GROWTH KINETICS

14.15 Timecourses for cell numbers and p-cresol concentrations in a batch culture (Smith et al., 1978).

- When substrate does NOT limit growth: \( \mu = \mu_{max} \)

\[
\mu_{max} = \frac{\ln \frac{B(t)}{B_{0}}}{t_{0}-t_{r}} \] (slope)

\[
\frac{B(t)}{B_{0}} = 0.100 = 0.6 \text{ hr}^{-1}
\]

- After ~10 hr, cresol declines exponentially while cells keep growing exponentially, so can get Y/EB

\[
Y = \frac{d[B]}{d[R]} \text{ mol cresol} = \frac{4R}{B} = \frac{B_{10-20}^\text{min} \times B_{10-20}}{R_{10-20}^\text{min} 
\}
\]

\[
Y = 2 \times 10^{14} \text{ cell/mol cresol} \times 0.5 \times 10^{6} \text{ cells/g cell mass} = 100 \text{ g cells}
\]