BIOLOGICAL TRANSFORMATIONS

- Oxidation - Very slow unless photochemical
- Hydrolysis - often ~ slow

But these and other rxns 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 spi
  microbes use [illegible] substance for energy

- **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.

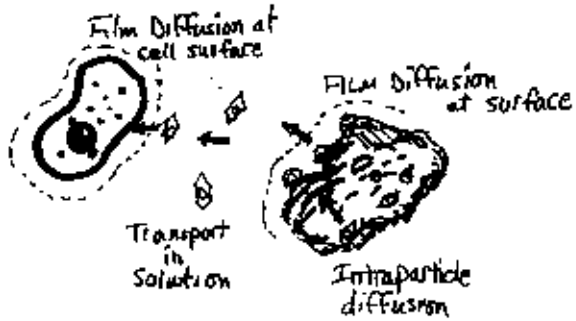
  EXAMPLE: Breakdown of DDT or chlorinated solvents when other "food" available.

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



- 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

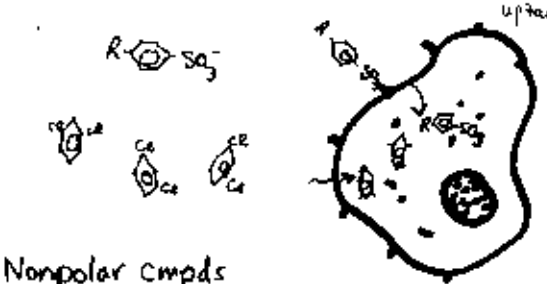
E.g., how will O_2 get to the cell?

Are co-metabolized cmpds soluble or only sparingly available?

UPTAKE BY THE CELL

another possible limitation

active uptake may be slower than passive uptake



- Nonpolar cmpds (esp. very hydrophobic) may PASSIVELY PARTITION INTO CELL
- Ionic cmpds usually can't permeate cell mem passively. ⇒ 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

fairly quick

very slow process (mutation)

ROLE OF MICROBIAL ECOLOGY

- What organisms are present? In what proportions?
- Are chemical conditions favorable?
  - SALINITY
  - pH
  - Temperature, etc
- Is chemical OR co-contaminants TOXIC?
- MAJOR FACTOR: Oxygen or No Oxygen?

AEROBIC vs. ANAEROBIC ORGANISMS

(OXIC vs ANOXIC CONDITIONS)

Ex: **Hydrocarbons**: Rapid degradation under Oxic conditions.

(OPPOSITE BEHAVIOR) ↕

Very stable under anoxia.

Chlorinated Solvents: Rapid biotransformation under ANOXIC conditions.

Very stable in oxic conditions.

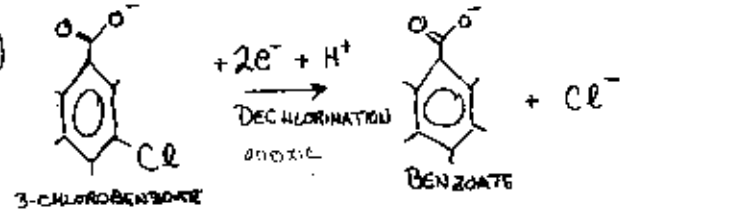
ECOLOGY (Cont'd)

CONSORTIA OF MICROBES

"Cooperating" groups of different specie sometimes required for transformations.

EX: DEGRADATION OF 3-CHLOROBENZOATE (herbicide) REQUIRES THREE SPECIES:

(I.)



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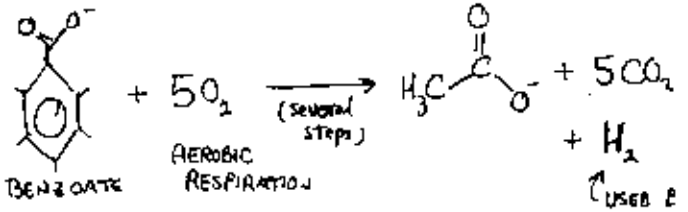

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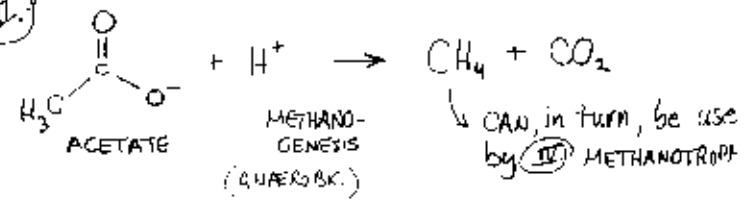


MODELING DEGRADATION

TRANSPORT LIMITED:

Ex: ▽ Diffusion out of particles
▽ Diffusion into cells or biofilm

Fick's Law $J_A^x = -D_{AB}\frac{\partial c}{\partial x}$

- Need effective diffusivity of the medium.
  "A" in water? Or, "A" in "organic matter"
  Or "A" in membrane?

- 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:

$$\frac{dC}{dt} = JA_{surf} = K_e[C]$$

$K_e = AD_{AB}^{eff}/\Delta x^{eff}$

EMPIRICAL MASS TRANSFER COEFFICIENT

BIOCHEMICAL RATE EXPRESSIONS

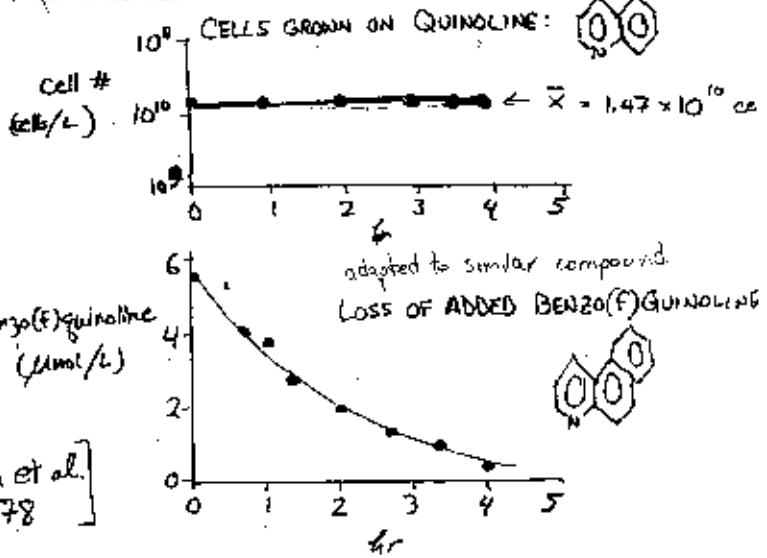
Ex.
- Abundant cell population.
- Enzymes already induced
- Abundant primary substrate
  (contaminant is secondary substrate or co-metabolized)

Expect 1st ORDER DECAY

(Depends only on Conc. of contaminant assuming other conditions met)

where might it be valid

Ex:



[Smith et al. 1978]

CAN TREAT DATA AS 1ST or 2ND ORDER

- **1ST ORDER:** – Cell number is constant
  – B(f)Q disappears

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

$k_{obs} = 0.5\ hr^{-1}$

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

- **2ND ORDER:** – When cell # varies

$$\frac{d[B(f)Q]}{dt} = -k_{bio}[cells][B(f)Q]$$

$k_{bio} = 3.6 \times 10^{-11}\ L \cdot cell^{-1} \cdot h^{-1}$

NOTE: In either model we are assuming Conc. of B(f)Q is LESS THAN the HALF-SAT'N CONSTANT of the enzyme system.
Often OK. Here OK because B(f)Q is $\frac{1}{3}$ II° substrate

MONOD GROWTH KINETICS

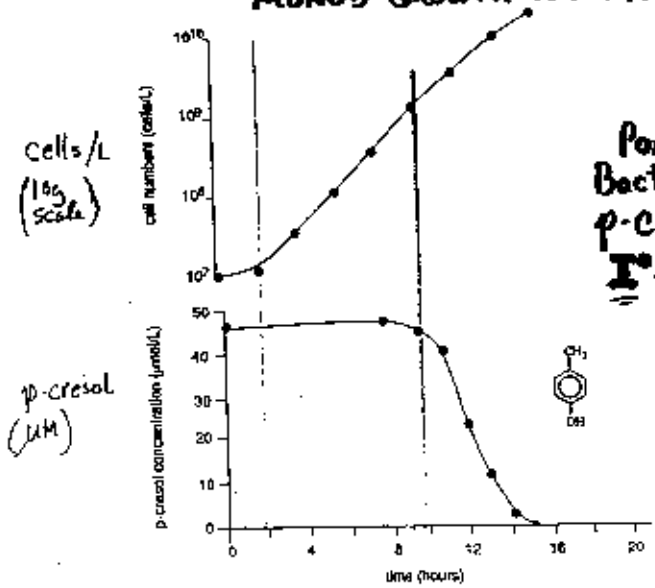


Figure 14.15 Timecourses for cell numbers and p-cresol concentrations in a batch culture experiment (Smith et al., 1978).

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

$$\mu_{max} = \ln \frac{B(t_2)}{B(t_1)} / [t_2 - t_1] \quad \text{(SLOPE)} \simeq \frac{\ln 100}{8\ h} = 0.6\ h^{-1}$$

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

$$Y = \frac{d[B]}{d[RH]} = \frac{d[B]/dt}{d[RH]/dt} = \frac{\Delta B}{\Delta RH} = \frac{B_{48} - B_{10}}{RH_{48} - RH_{10}} \simeq \frac{(9.4E9) - (.2E9)}{(4.4E-6) - (0.3E-6)} \frac{cell}{M}$$

$Y \simeq 2 \times 10^{14}$ cell/mol-cresol $\left[\text{typical cell mass } \sim 0.5 \times 10^{-12}\ g/cell\right] \Rightarrow \sim \frac{100\ g\text{-cells}}{100\ g\text{-cresol}}$