WASHINGTON STATE UNIVERSITY

Instructor: Allan Felsot
afelsot@tricity.wsu.edu

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ES/RP 531
Fundamentals of Environmental Toxicology

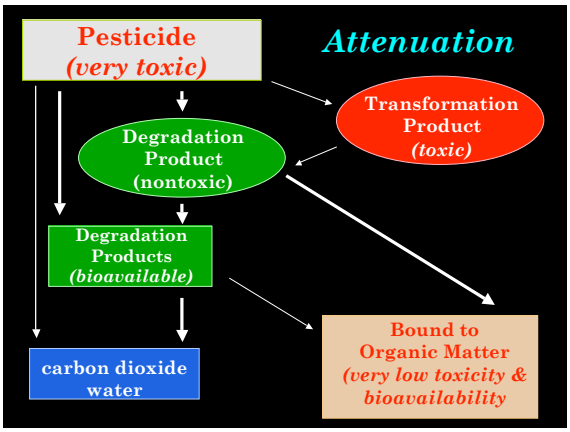
Lecture 22

Abiotic/Biotic Degradation & Transformation

(Environmental Attenuation of Contaminants)

Attenuation Processes

- Transformation of parent molecule to either toxic or nontoxic product forms
- Reduction in concentration
  - **Distinguished from simple dilution or transport out of a specific area by change in molecular structure**



Definitions

- Degradation
  - Decrease in concentration of a contaminant due to nonreversible alteration of chemical structure
- Mineralization
  - Biologically mediated degradation of chemical resulting in release of carbon dioxide
- Persistence
  - Longevity of a contaminant residue in a medium or phase
- Detoxification
  - Degradation resulting in loss of toxicity or biological activity

Definitions

- Transformation
  - Partial change in structure of a contaminant due to biological or nonbiological reaction
  - Transformation product may still retain toxicity
- Bound residue
  - The residue remaining after exhaustive extraction of a soil, water, or plant matrix
  - Covalent incorporation of a transformation product into the natural biochemical matrix

Degradation Products

The degradation process results in changed molecular structure

- **Inactivation (detoxification)**
- **Activation (toxification)**
- **Mineralization (CO_2 & H_2O)**
- **Bound to Organic Matrix**

Reaction Mechanisms

- The processes by which a chemical is degraded
- Divided into two basic mechanisms
  - Phase I (biologically or nonbiologically mediated)
    - ✓ Hydrolysis
    - ✓ Oxidation
    - ✓ Reduction
  - Phase II (biologically mediated)
    - ✓ Conjugation

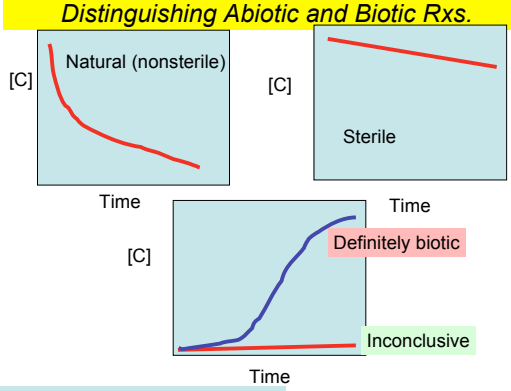
Considerations

- Chemical reactions in the environment occur much slower than dissociation processes in solution
  - For example, deprotonation of an acid (i.e., dissociation of a proton in response to solution pH is faster than a chemical reaction)
  - Thus, we're interested in the rates (kinetics) of the reactions and the mechanisms (what kinds of transformation products)
  - We are also interested in how environmental variables affect rate and mechanisms

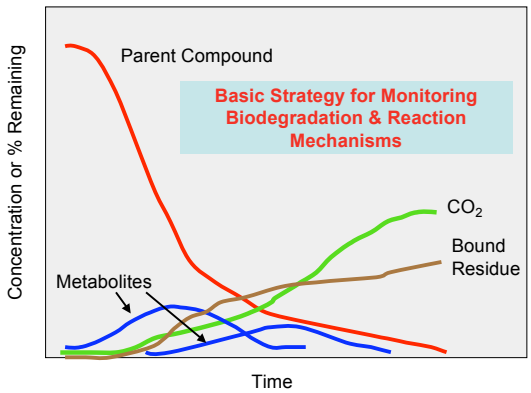
Abiotic vs. Biotic Reactions

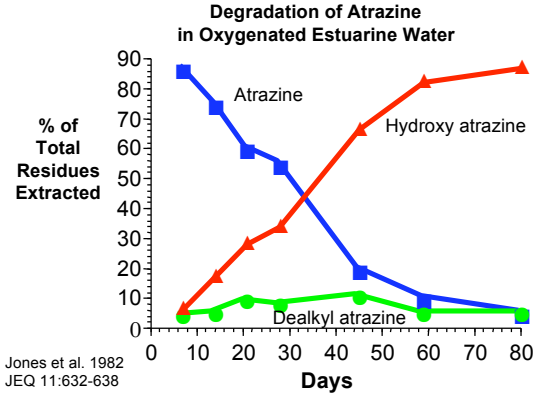
- Location of relevant reaction type
  - Soil & water--abiotic and biotic
  - Plants and animals--biotic only
- End Products
  - Abiotic reactions lead to other organic compounds (or speciation of metals)
  - Biotic reactions lead to other organic compounds and/or carbon dioxide
- Catalysts
  - Abiotic--chemical (metals, water) & photolytic (UV)
  - Biotic--enzymes

Distinguishing Abiotic and Biotic Rxs.



- Sterile vs. nonsterile experiment





Reaction Kinetics

Rate Law=a mathematical function or differential equation describing the turnover rate of a compound as a function of the concentration

Power Rate Law

$$Rate = \frac{-dC}{dT} = kC^n$$

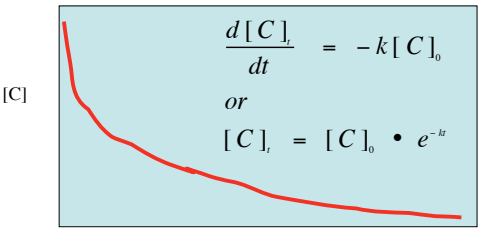
First Order when n = 1

$$\frac{d[C]_t}{dt} = -k[C]_0$$ Differential eq.

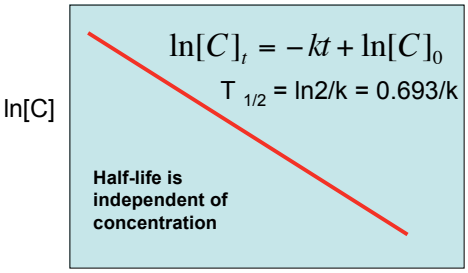
or

$$[C]_t = [C]_0 \bullet e^{-kt}$$ Integrated eq.

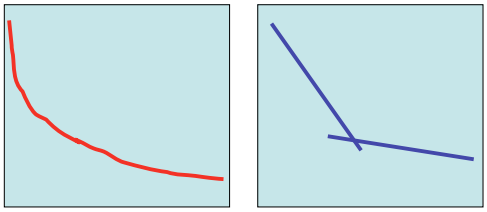
First Order Characterized by Exponential Decrease in Concentration Over Time



Linearization of First-Order Function

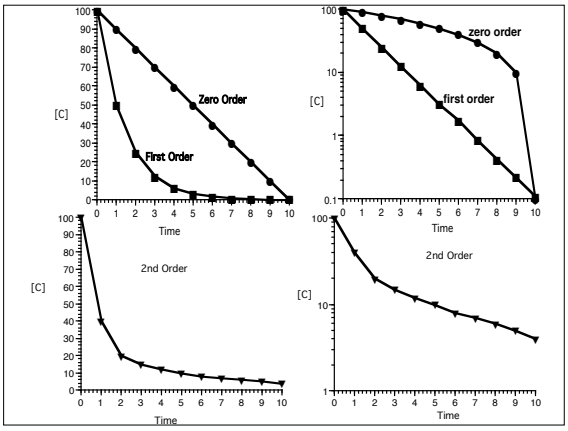


Pseudo-First Order Reaction



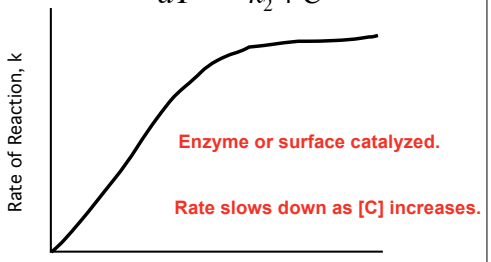
Reaction Kinetics

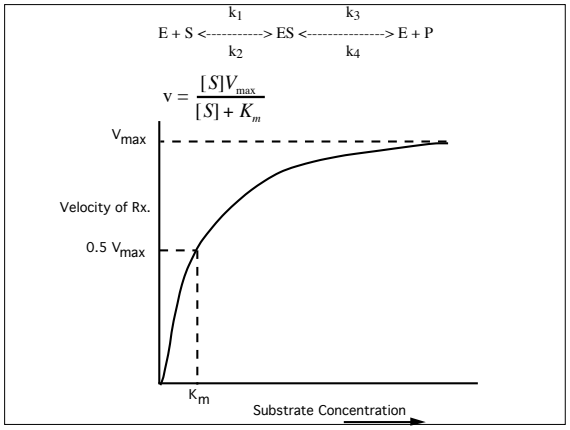
- First Order
- Zero Order
  - Disappearance of compound is independent of concentration
- Second Order
  - A second species involved in the disappearance is rate limiting
  - For ex., hydrolysis reaction where base is limited in concentration
    - ✓Can be reduced to pseudo-first order by considering that one of the reactants (for ex., water) is at a much larger concentration then the other reactant and therefore not rate limiting)

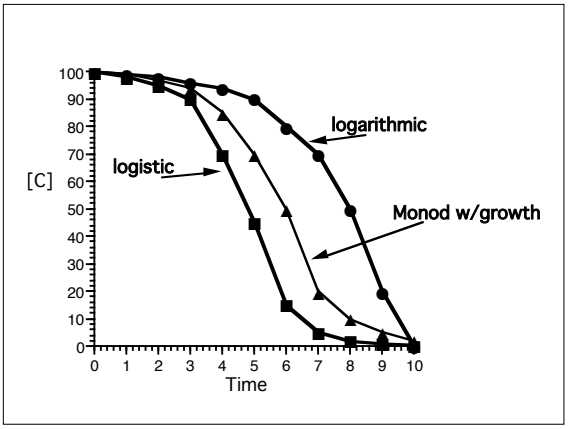


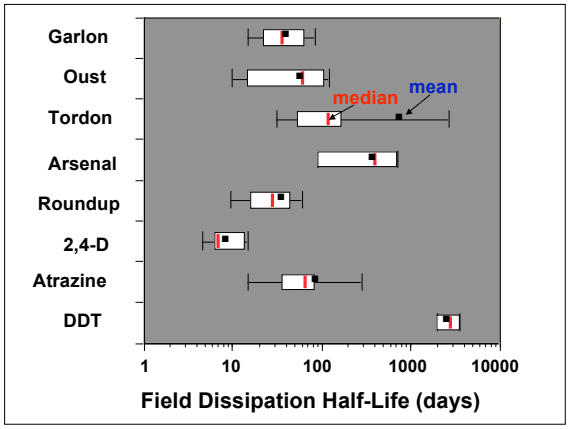
Hyperbolic Kinetics

$$Rate = \frac{-dC}{dT} = \frac{k_1 C}{k_2 + C}$$







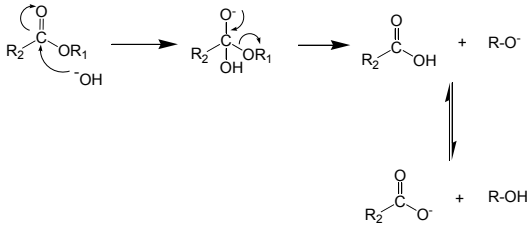


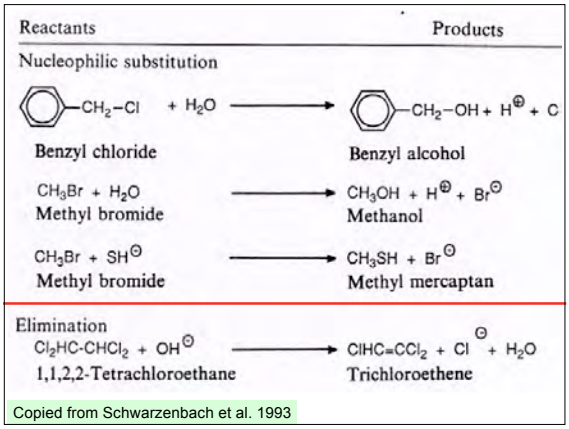
Hydrolysis Reactions

- Nucleophilic substitutions
  - Proton, water, or hyroxyl is nucleophile
  - Attracted to electron deficient atom
- pH dependent
- Abiotic
- Products same as for biotic rxs.

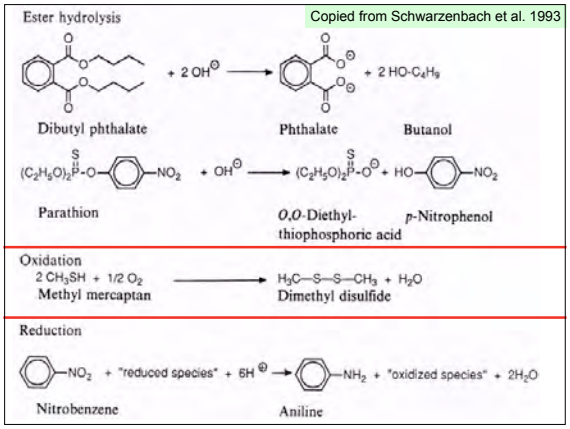
Typical Hydrolysis Reaction

(Nucleophilic Substitution)





Copied from Schwarzenbach et al. 1993



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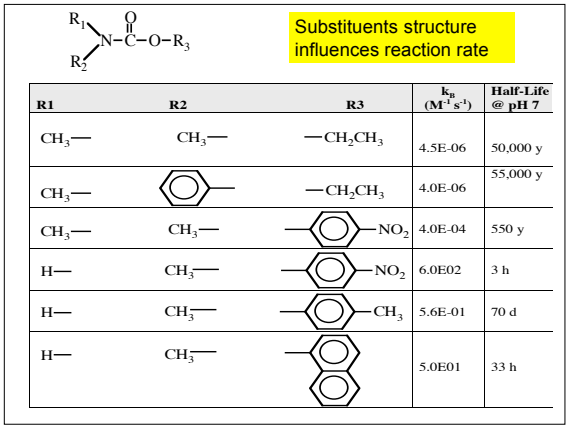
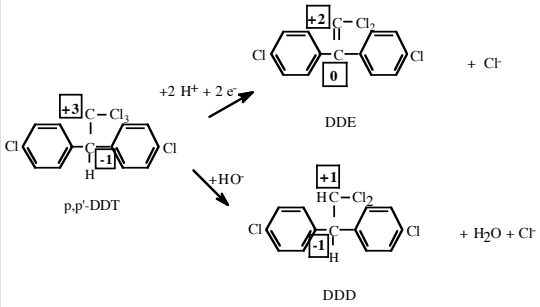


Substituents structure influences reaction rate

R1	R2	R3	k_B ($M^{-1}s^{-1}$)	Half-Life @ pH 7
CH_3—	CH_3—	—CH_2CH_3	4.5E-06	50,000 y
CH_3—		—CH_2CH_3	4.0E-06	55,000 y
CH_3—	CH_3—		4.0E-04	550 y
H—	CH_3—		6.0E02	3 h
H—	CH_3—		5.6E-01	70 d
H—	CH_3—		5.0E01	33 h

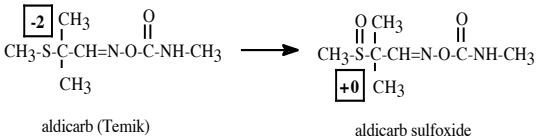
Reductions

- Transfer of electrons to acceptor molecule (REDOX rxs.)



Oxidations

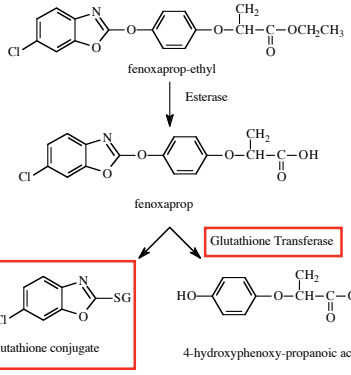
- Removal of electrons from carbon or heteroatom



aldicarb (Temik)

aldicarb sulfoxide

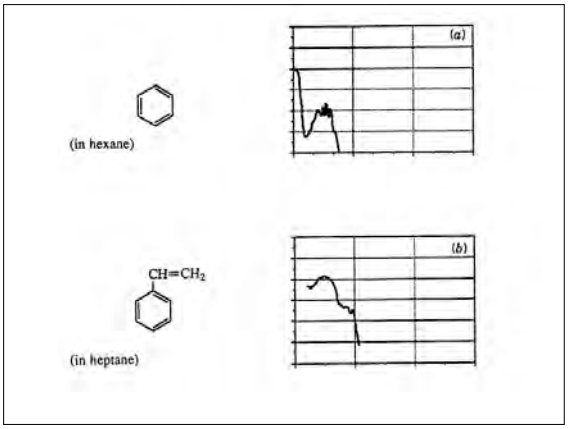
Conjugation

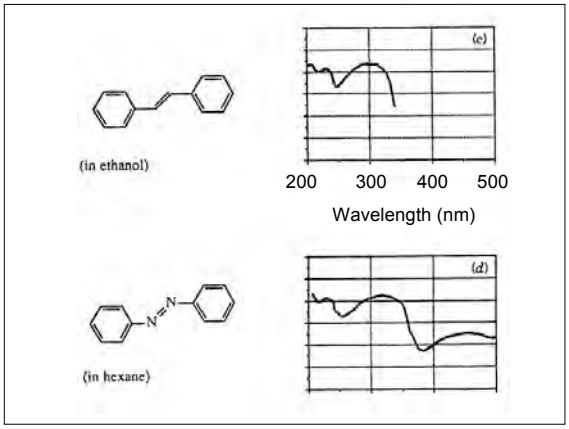


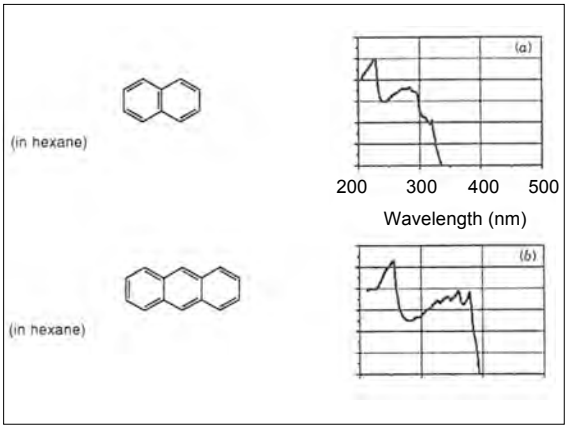
Photolysis

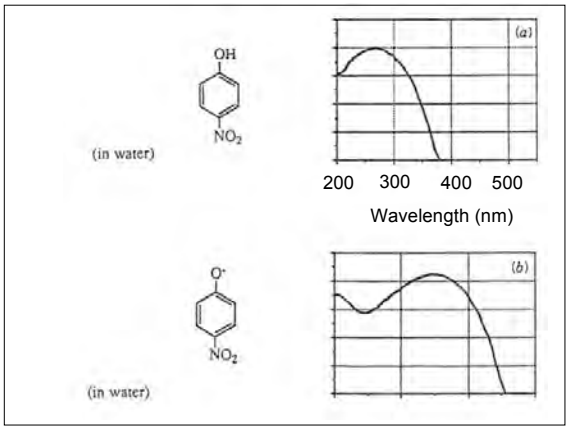
Bond	Bond Energy (kJ mol^{-1})	Wavelength (nm)
O-H	465	257
H-H	436	274
C-H	415	288
N-H	390	307
C-O	360	332
C-C	348	344
C-Cl	339	353
Cl-Cl	243	492
Br-Br	193	630
O-O	146	820

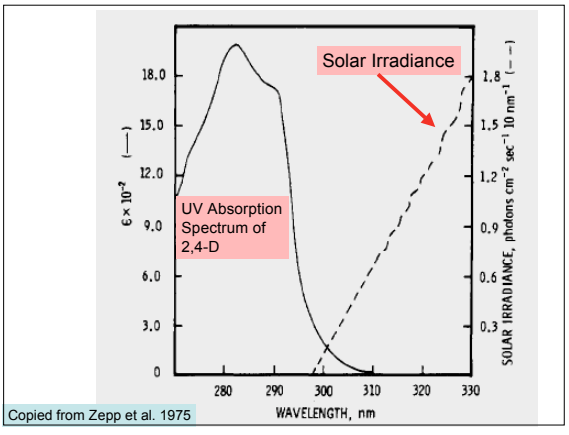
Whether a reactions will take place depends on the probability that a given compound absorbs a specific wavelength of light or on the probability that the excited molecular species undergoes a particular reaction.



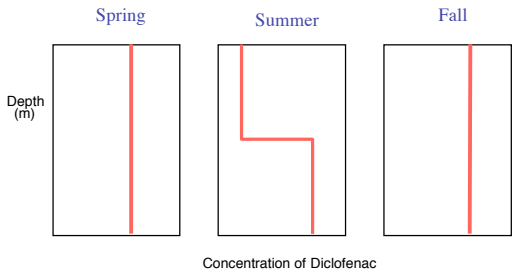






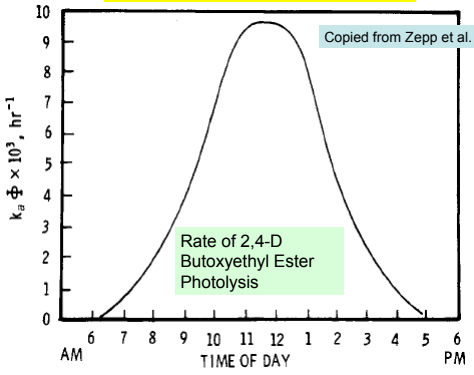


Distribution of Diclofenac, a pharmaceutical, in a lake



Thermal Influence on Potential for Photolysis: Lake Turnover & Stratification

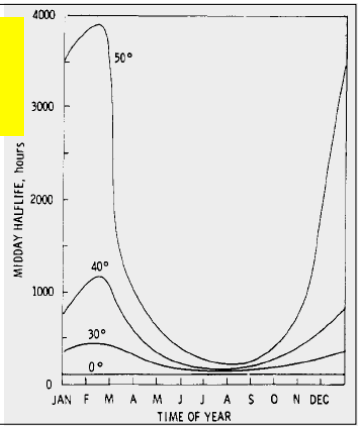
Time of Day Affects Photolysis Rate



Copied from Zepp et al. 1975

Rate of 2,4-D Butoxyethyl Ester Photolysis

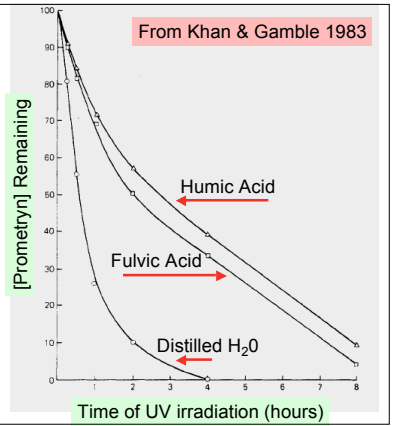
Dependence of 2,4-D Butoxyethyl Ester Photolysis Half-Life on Season & Northern Latitude



Copied from Zepp et al. 1975

Effect of Humic Materials on Photolysis Rate

From Khan & Gamble 1983



Photodegradation Is Faster in Dirty Water

- Malathion photolysis in distilled water (pH 6) in presence of light
  - $T_{1/2}$ = 990 hours
- Malathion photolysis in Suwannee River water (a lot of humic material)
  - $T_{1/2}$ = 16 hours

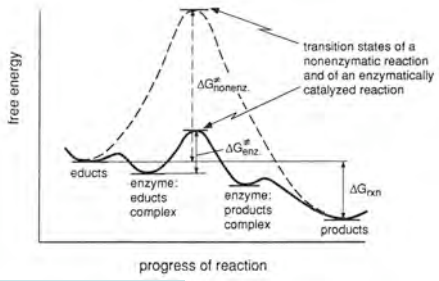
Photodegradation is only effective in soil when a chemical is at the soil surface

Biochemical Ecology of Biodegradation

- End products represent
  - Mineralizations
  - Transformations
- Biochemical reactions involve catalysis by enzymes

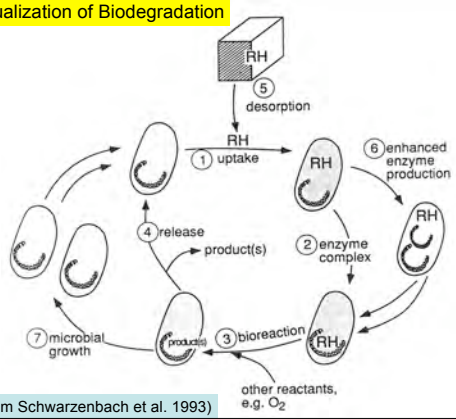
Biodegradation

- Catalysis by enzymes



(Copied from Schwarzenbach et al. 1993)

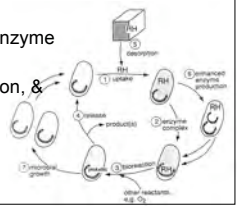
Conceptualization of Biodegradation



(Copied from Schwarzenbach et al. 1993)

Conceptualization of Biodegradation

1. Bacterial cell containing enzymes takes up chemical
2. Chemical binds to suitable enzyme
3. Enzyme-chemical complex reacts, producing transformation products
4. Products released from enzyme
5. Sorption in soil may influence processes above
6. Production of new or additional enzyme capacity (induction, activation)
7. Growth of total microbial population, & thus biodegradation capacity

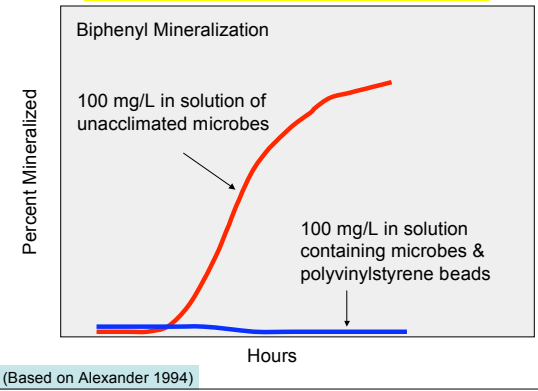


Rate of Biodegradation

(Considerations Beyond Enzyme-Substrate Interactions)

- Rate of delivery of substrate molecules to the microbial cells
- Rate of diffusion of substrate across intervening media
- Rate of uptake by microbial cells
- Biochemical effects
  - Enzyme induction
  - De-repression of enzyme
  - Mutation
  - Constitutive enzyme
  - Adaptation

Effect of Sorption on Biodegradation Processes



(Based on Alexander 1994)

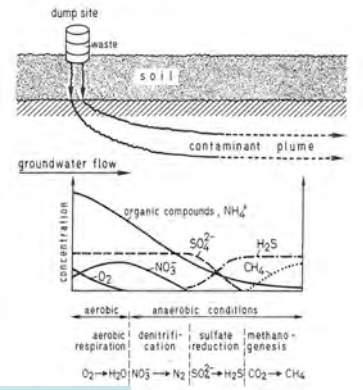
Anaerobic Biodegradation

•Alternative electron acceptors (ie., alternative to O_2)

•Methanogenesis (CO_2; methane)

•Sulfate Reduction (SO_4; hydrogen sulfate)

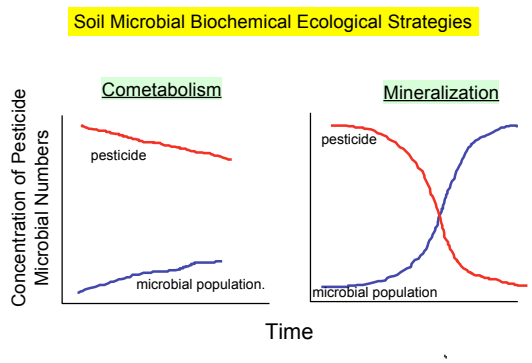
•Denitrification (Nitrate; N_2)

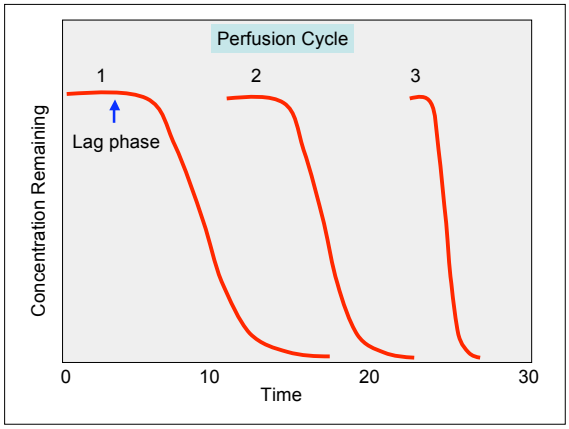


(Copied from Schwarzenbach et al. 1993)

Microbial Biochemical Ecological Strategies

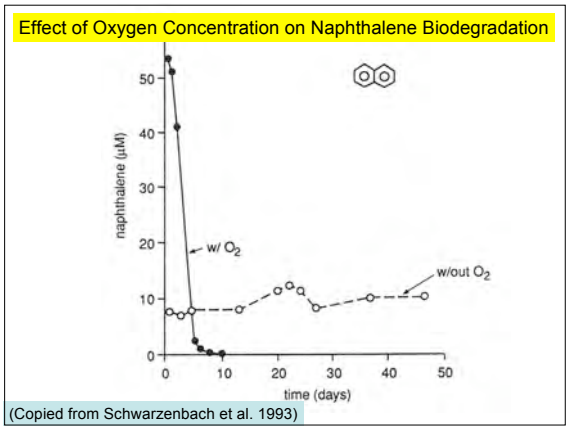
- Mineralization
- Cometabolism
- Consortia
- Plasmid exchange





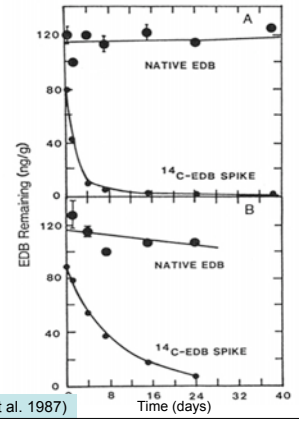
Factors Influencing Degradation

- Concentration of chemical
- Temperature
- Moisture
- Sunlight
- Soil type and characteristics (texture, pH, OC)
- Nutrients
- Product formulation ingredients
- Other chemicals and previous exposures
- Aging of residues



(Copied from Schwarzenbach et al. 1993)

Effect of Contaminant Aging



(Copied from Steinberg et al. 1987)