## "Biological, Photolysis and Hydrolysis Reactions in Surface Waters"

### Module 2: Surface Waters, Lecture 6

*Chemical Fate and Transport in the Environment*, 2nd edition. H.F. Hemond and E.J. Fechner-Levy. Academic Press. London. 2000.

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### 2.6.1 Aerobic Biodegradation of Organic Compounds

- BOD is an aggregate measure of the concentration of biologically degradable material in water, but it conveys no information about the specific organic compounds or their individual degradation rates.
- Most organic pollutants contain carbon in a more reduced state than the (+IV) oxidation state found in carbon dioxide and the oxidation of organic compounds to carbon dioxide is often a viable means of aerobic degradation.
- Microbes (due to their great abundance, variety and rapid growth rates) can oxidize many anthropogenic chemicals (such as hydrocarbon fuels and solvents) as well as detrital organ material produced by ecosystems.
- Low molecular weight and soluble organic compounds, such as alcohols and organic acids, are utilized by microbes particularly rapidly (because they also occur naturally and microbes have evolved?)
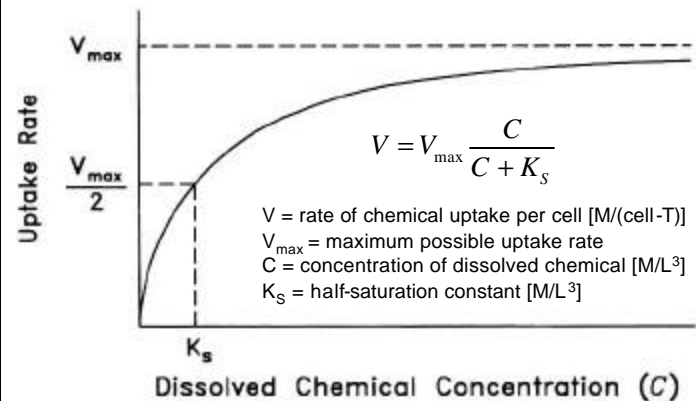
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### 2.6.2 Anaerobic Degradation of Organic Compounds

Example of dichloroethene isomer degraded under reducing conditions into chloroethene (vinyl chloride); with oxidation state of carbon reduced to (-1):

$$\frac{1}{2}CH_2O + \frac{1}{2}H_2O + C_2H_2Cl_2 \rightarrow C_2H_3Cl + \frac{1}{2}CO_2 + Cl^- + H^+$$
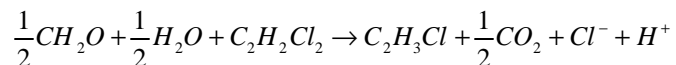
These reductions usually do not result in complete mineralization of a pollutant. They can remove chlorine and other halogen atoms, making the compound more subject to oxidation if the transported into an aerobic environment.

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### 2.6.3 Modeling Biodegradation (Michaelis-Menton Kinetics):



$$V = V_{max}\frac{C}{C + K_S}$$

V = rate of chemical uptake per cell [M/(cell-T)]
$V_{max}$ = maximum possible uptake rate
C = concentration of dissolved chemical [M/L$^3$]
$K_S$ = half-saturation constant [M/L$^3$]

V approaches zero when there is no chemical present and V reaches a plateau at $V_{max}$ for high concentrations.

When $K_S$ is much greater than C (at low concentrations), the rate of uptake becomes nearly proportional to the chemical concentration:

$$V \approx \left[ \frac{V_{max}}{K_S} \right] C$$

When C is much greater than $K_S$, V approaches independence of C and the rate approximates zero-order kinetics:

$$V \approx V_{max}$$

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Aerobic Biodegradation Rates Observed in Incubations of River Water Samples

| Compound | Rate constant (per day) |
|---|---|
| Anthracene | 0.007–0.055[b] |
| Atrazine (N-phosphorylated) | 0.22 |
| Benz[a]anthracene | None observed |
| Benzene | 0.11 |
| Benzo[a]pyrene | None observed |
| Chlorobenzene | 0.0045 |
| Glucose | 0.24 |
| Mirex | None observed |
| Nitrilotriacetate (NTA) | 0.05–0.23[c] |
| Parathion | <0.00016 |
| Phenol | 0.079 |
| 2,4,5-T | 0.001 |
| 1,4,5-Trichlorophenoxyacetic acid | 0.0005 |

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## Example Problem 2-17

Spilled benzene ($C_6H_6$) dissolves in a river flowing at 0.3 m/sec. How much will biodegradation decrease the concentration of the benzene in the river over a 20 mile reach?

Travel time in river:

$$t = 20mi \bullet \frac{1609\,m}{1mi} \bullet \frac{\sec}{0.3m} \bullet \frac{1hr}{3600\sec} \approx 30hr$$

The aerobic degradation rate for benzene is about 0.11/day. Assuming first-order decay and a travel time of 1.2 days:

$$C/C_o = e^{-kt} = e^{-(0.11/day)(1.2\,day)} = 0.87$$

Therefore, about 13% of the benzene will degrade in this reach (but there is large uncertainty in this estimate).

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## Example Problem 2-18

A 1 M solution of DCE is accidentally spilled into a stratified lake whose bottom waters are anaerobic. The DCE will sink due to its density being greater than the water, and will dissolve in the sediment pore waters. After 2 months, what compounds would be expected to be found in the sediments, and in roughly what ratio?

The anaerobic degradation pathway for DCE is conversion to vinyl chloride:

$$\frac{1}{2}CH_2O + \frac{1}{2}H_2O + C_2H_2Cl_2 \rightarrow C_2H_3Cl + \frac{1}{2}CO_2 + Cl^- + H^+$$
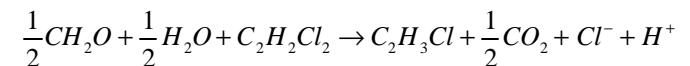
The estimated biodegradation rate for DCE in soil is 0.0063/day. Assuming a 60 day period and first-order kinetics:

$$C = C_o e^{-kt}$$

$$C/C_o = e^{-kt} = e^{-(0.0063/day)(60 days)} = 0.7$$

Therefore, about 70% of the DCE will remain in the bottom sediments after 2 months, and 30% will be converted to vinyl chloride.

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## 2.6.4 Bioconcentration and Bioaccumulation in Aquatic Organisms

**Regression Equations for Estimating BCF for Fish**

| Equation | N | $r^2$ | Species used |
|---|---|---|---|
| log BCF = 0.76 log $K_{ow}$ − 0.23 | 84 | 0.823 | Fathead minnow Bluegill sunfish Rainbow trout Mosquitofish |
| log BCF = log $K_{ow}$ − 1.32 | 44 | 0.95 | Various |
| log BCF = 2.791 − 0.564 log S (S in ppm) | 36 | 0.49 | Brook trout Rainbow trout Bluegill sunfish Fathead minnow Carp |
| log BCF = 3.41 − 0.508 log S (S in μM) | 7 | 0.93 | Rainbow trout |
| log BCF = 1.119 log $K_{ow}$ − 1.579 | 13 | 0.757 | Various |

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($K_{TW}$ is the triolene-water partition coefficient and Is similar to $K_{OW}$)

EXPLANATION
o Marine zooplankton
▲ Guppies
⫯ Rainbow trout
■ Catfish

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## Example Problem 2-21

A catfish metabolizes and/or excretes 2,4',5-trichlorinated biphenyl (a PCB congener) with an assumed first-order rate constant of 0.021/day. How long will it take the fish from a contaminated stream, after being placed in a clean system, to undergo depuration, if the levels if the catfish exceeds safe levels by a factor of 3?

$$C = C_o e^{-kt}$$
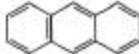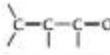
$$\frac{1}{3} = e^{-(0.021/day)(t)}$$

$$-1.1 = -0.21t$$

$$t = 52 \, days$$
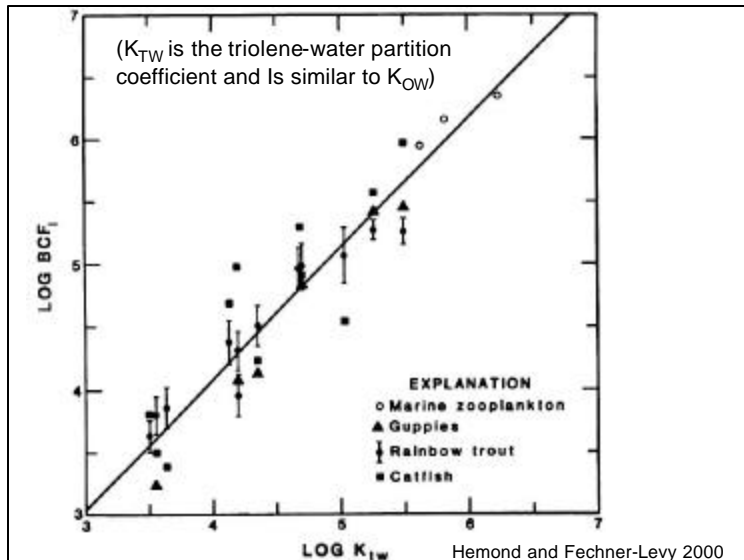
## Photodegradation

- Common examples of photodegradation include: fading of colors and dyes, degradation of tire rubber exposed to sunlight, plastic sheeting decomposition, etc.
- Photodegradation depends on both the intensity and wavelength spectrum of the light.
- A greater amount of energy is possessed by photons at shorter wavelengths. UV is therefore particularly effective in degrading many materials.
- If the energy per photon is sufficient to break a specific bond or otherwise induce a chemical reaction, then increased intensity will cause the chemical reaction to proceed at a faster rate.
- If the energy required to initiate a reaction is greater than the energy per photon for light of a given wavelength, then the light will not break the chemical bond, regardless of its intensity.

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Several Chemical Structures That Absorb Light at Wavelengths Greater than 290 nm

| Group | $\lambda_{max}$ (nm) | Molar absorptivity (liter/(mol·cm)) |
|---|---|---|
| C=O (aldehyde, ketone) | 295 | 10 |
| C=S | 460 | Weak |
| —N=N— | 347 | 15 |
| —NO₂ | 278 | 10 |
| | 311 | 250 |
| | 270 | 5000 |
| | 360 | 6000 |
| O= =O | 440 | 20 |
| | 300 | 1000 |
| C—C—C=O | 330 | 20 |

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Half-Lives for Disappearance via Direct Photolysis in Aqueous Media

| Compound | λ (nm) | $t_{1/2}$ |
|---|---|---|
| **Pesticides** | | |
| Carbaryl | 5 | 50 hr |
| 2,4-D, butoxyethyl ester | 5 | 12 days |
| 2,4-D, methyl ester | 5 | 62 days |
| DDE | 5 | 22 hr (calc) |
| Malathion | 5 | 15 hr |
| Methoxychlor | 5 | 29 days |
| Methyl parathion | 5 | 30 days |
| Mirex | 5 | 1 year |
| N-Nitrosoatrazine | 5 | 0.22 hr (calc) |
| Parathion | 5 | 10 days (calc) |
| | 5 | 9.2 days |
| Sevin | 5 | 11 days |
| **Polycyclic aromatic hydrocarbons (PAHs)** | | |
| Anthracene | 366 | 0.75 hr |
| Benz[a]anthracene | 5 | 3.3 hr |
| Benzo[a]pyrene | 5 | 1 hr |
| Chrysene | 313 | 4.4 hr |
| Fluoranthene | 313 | 21 hr |
| Naphthalene | 313 | 70 hr |
| Phenanthrene | 313 | 8.4 hr |
| Pyrene | 313, 366 | 0.68 hr |
| **Miscellaneous** | | |
| Benzo[f]quinoline | 5 | 1 hr |
| p-Cresol | 5 | 35 days |
| Dibenzothiophene | 5 | 4–8 hr |
| Quinoline | 5 | 5–21 days |

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### Example Problem 2-23

Benzo[a]pyrene, a polycyclic aromatic hydrocarbon, is measured at 3µg/L, 2.5 hours after release from a wastewater lagoon. If direct photodegradation is the only degradation process occurring, what was the initial concentration when discharged?

PAHs are likely to directly photodegrade because the double bonds in the aromatic rings can absorb light (indirect degradation can also occur by oxidation). The approx. half-life of this compound is 0.69/hr.
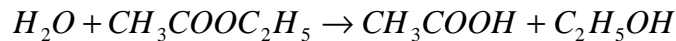
The initial concentration was therefore about:

$$C_o = C_t e^{kt}$$

$$C_o = (3\,mg/L) \bullet e^{(0.69/hr)(2.5hr)} = 17\,mg/L$$

## 2.7.2 Degradation of Chemicals by Water

- Hydrolysis means the breaking of water.
- The net result of hydrolysis is that both a pollutant molecule and a water molecule are split, and the two water molecule fragments join to the two pollutant fragments to form new chemicals.
- An example is the conversion of esters into an organic acid and an alcohol; such as the following example for ethyl acetate hydrolyzing to acetic acid and ethanol:
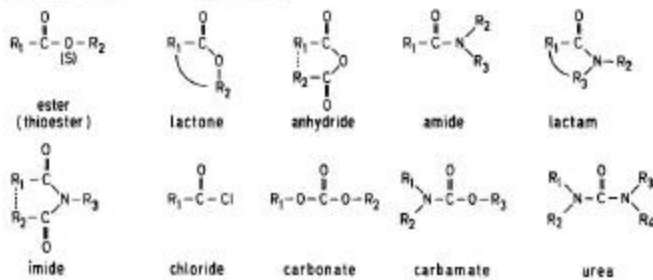
$$H_2O + CH_3COOC_2H_5 \rightarrow CH_3COOH + C_2H_5OH$$

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Several Examples of Light-Driven Chemical Processes Occurring in Surface Waters

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Hydrolysis Rates for Some Esters and Six Ester Analogs

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## Example Problem 2-24

Ethyl acetate is spilled at an industrial site and runs into a pond. The resulting concentration is 20 μg/L. Assuming the water pH is 6 and hydrolysis is the only degradation process, what is the half-life of the ethyl acetate, given the following ?

$k_a$ – 1.1x10$^{-4}$/(M-sec)
$k_n$' = 1.5x10$^{-10}$/sec
$k_b$ = 1.1x10$^{-1}$/(M-sec)

Using equation 2-85 for combining the separate hydrolysis rates:

$$k_T^{'} = [1.5x10^{-10} + (1.1x10^{-1})(10^{-8}) + (1.1x10^{-4})(10^{-6})]/\sec$$

$$k_T^{'} = 1.4x10^{-9}/\sec = 0.043/year$$

$$t_{1/2} = \frac{0.693}{k} = 16\, years$$