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2.6 BIOTRANSFORMATION AND BIODEGRADATION

The primary purpose of the Streeter–Phelps model is to predict dissolved oxygen concentrations in a stream or river based on BOD loadings. In more general terms, the Streeter–Phelps model predicts the impact on the stream of the *biotransformation* of a chemical substance (BOD). Numerous biological processes in surface waters can transform chemicals into other chemicals. The term *biodegradation* is often used to describe the biotransformation of an organic pollutant into other compounds. Although initial transformation products can occasionally be more toxic to humans or aquatic organisms than the original parent compound, eventually successive biological transformations in oxic waters tend to convert organic pollutants into carbon dioxide, water, and mineral salts. The overall process by which organic compounds are converted into simple inorganic compounds is called *mineralization.* Mineralization of organic pollutants often occurs by the same processes that are

involved in the degradation of natural organic matter in ecosystems. The many intermediate biotic transformations of organic pollutants that do not produce purely inorganic compounds represent *partial biodegradation.* Note that inorganic pollutants that contain intrinsically toxic elements, such as mercury and arsenic, may also be transformed from one chemical species to another [e.g., metallic mercury (Hg^0) to the highly toxic monomethyl mercury (CH_3Hg^+)]. Unlike the case with organic contaminants, however, the toxic elements themselves cannot be destroyed.

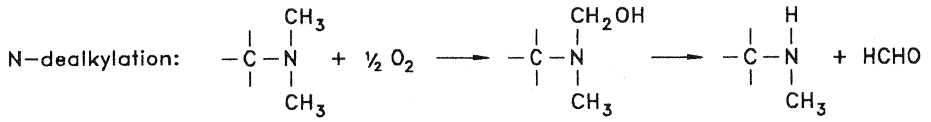
Biotransformation processes are mediated by microorganisms (microbes), especially bacteria and fungi. These two groups are remarkably diverse, although the metabolic capabilities of bacteria as a group tend to be greater; while fungi are aerobic, bacteria are active in both aerobic and anaerobic environments, obtaining energy from a tremendous number of chemicals.

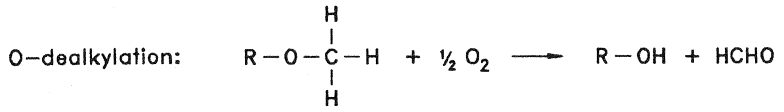
Although the range of chemical transformations of which bacteria and fungi are capable is extensive, a few general principles hold. First, microbes often mediate biotransformations that are energetically favorable. Such reactions result in a net decrease in the Gibbs free energy of the chemical system, and the microbes harvest some of the released energy for their own use. There are important exceptions, such as photosynthesis (in which a cell will use energy obtained elsewhere to force an energetically unfavorable chemical reaction to occur) and *cometabolism* (in which a cell has enzymes that transform a chemical even though the transformation yields no energy to the cell). Often, however, the biodegradation potential of a given compound is related to the free energy changes that can be accomplished by its reaction with other chemicals simultaneously present in the same environment. For example, the energy available from a molecule of sugar is large if oxygen is present, but is much smaller in a system devoid of oxygen.

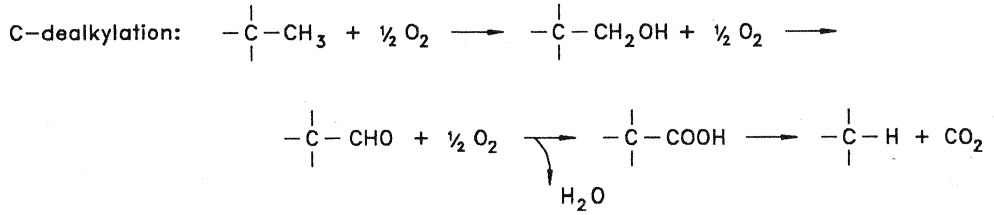
Second, microbial chemical transformations are accomplished by means of *enzymes,* proteins that act as *catalysts.* Catalysts bind with reactants and hold them in such an orientation that they more readily react. The products of the reaction are then released, leaving the catalyst ready to facilitate another transformation. (It is possible for an enzyme to be destroyed if a chemical mimics the proper substrate sufficiently to bind, but fails to react and subsequently release from the enzyme.) Because each enzyme is produced in response to a section of the genetic code (DNA) in the organism and many enzymes are extremely specific, it is possible that some strains of a species of bacteria may accomplish a certain chemical transformation while other individuals cannot. By using modern techniques of molecular biology, scientists can insert specific biotransformation capabilities into bacteria by means of genetic transfer. This procedure is easiest if the genetic material is associated with *plasmids,* which are small circular molecules of DNA that can exist independently within a bacterial cell.

Type of Reaction

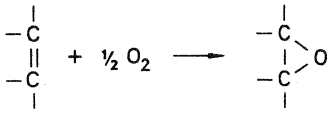
Oxidative Dealkylation



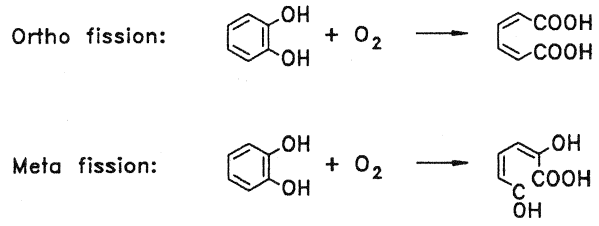




Epoxidation



Aromatic, Non–heterocyclic Ring Cleavage



Only the first step in the degradation pathway is shown

Aromatic Hydroxylation

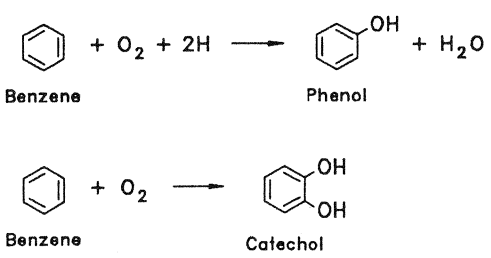


FIGURE 2-24 Several examples of organic compounds biodegraded by *aerobic* microorganisms, and their associated biodegradation reactions. Each of the reactions shown involves the *oxidation* of the organic compound.

2.6.1 Aerobic Biodegradation of Organic Compounds

Although BOD is an aggregate measure of the concentration of biologically degradable material in water, BOD conveys no information about the identities of specific organic compounds or their individual degradation rates. One factor that partially determines the degree to which a particular chemical is readily biodegraded is the extent to which it is a readily usable source of energy for microbes. Most organic pollutants contain carbon in a more reduced state than the (+IV) oxidation state found in carbon dioxide, and oxidation of the organic pollutants to carbon dioxide is often a viable means of aerobic biodegradation. In an aerobic environment, the most energy is usually available from oxidation of the most highly reduced carbon atoms.

Given their enormous variety, biochemical diversity, and rapid growth rates, microbes can oxidize many anthropogenic chemicals, such as hydrocarbon fuels and solvents, as well as the detrital organic material produced by ecosystems. Low-molecular-weight and soluble organic compounds such as alcohols and organic acids are utilized particularly rapidly, perhaps because these classes of compounds also occur naturally in the environment and microorganisms have evolved to degrade them efficiently. The rate of microbial oxidation generally is lower for compounds of high molecular weight, compounds having low water solubilities, and compounds that possess aromatic rings, a large amount of branching, and/or halogen atoms (chlorine, fluorine, bromine, and iodine) in their chemical structure. Figure 2-24 shows typical compound types commonly oxidized by aerobic microorganisms.

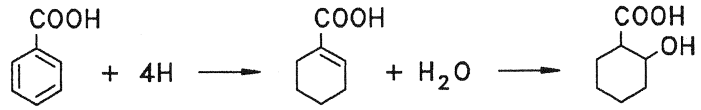
Oxidation also can be promoted by nonbiological processes in the environment. For example, fire brings about the rapid oxidation of chemicals, at elevated temperature, using oxygen from the atmosphere as the electron acceptor. The high temperature obviates the need for the catalytic action provided by organisms in aerobic biodegradation. Although obviously not an issue in most surface waters, fire can oxidize large quantities of organic material in wetlands during times of severe drought. Oxidation also can be promoted by light, as discussed in Section 2.7.1. A few chemicals can be oxidized spontaneously and abiotically: one example is the oxidation of soluble reduced iron (Fe^{2+}) to Fe^{3+} by dissolved oxygen in water at room temperature, a process that is common in iron-rich well waters and is responsible for the brown staining of porcelain and clothes. As another example, chlorophenols ($C_6OHCl_xH_{5-x}$) have been found to be abiotically oxidized at the surface of manganese oxide (MnO_2) particles in water (Ulrich and Stone, 1989).

Type of Reaction

Decarboxylation

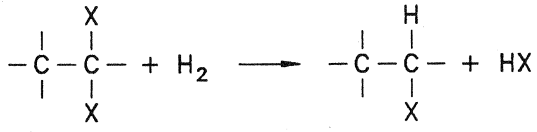
Aromatic Hydroxylation

Anaerobic:

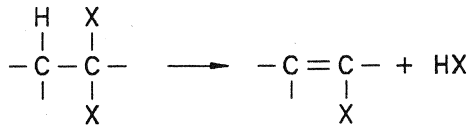


Benzoic acid — Cyclohex-1-ene-1-carboxylate — 1-Hydroxycyclohexane-carboxylate

Reductive dehalogenation



Dehydrrohalogenation



Nitro-reduction

FIGURE 2-25 Several examples of organic compounds biodegraded by *anaerobic* microorganisms and their associated biodegradation reactions occurring in reducing, anaerobic environments. Note that most of these reactions involve the *reduction* of the organic compound.

2.6.2 Anaerobic Biodegradation of Organic Compounds

Because the free energy released in respiration decreases as oxygen is depleted and the microbial community shifts to the use of less favorable oxidants such

as $Fe(OH)_3$ and SO_4^{2-}, the tendency for oxidative biodegradation tends to decrease as the ecological redox sequence proceeds and conditions become increasingly reducing. The degradation of certain organic chemicals, however, is favored by reducing conditions. In general, these are compounds in which the carbon is fairly oxidized; notable examples include chlorinated solvents such as perchloroethene (C_2Cl_4, abbreviated as PCE) and trichloroethene (C_2Cl_3H, abbreviated as TCE), and the more highly chlorinated *congeners* of the polychlorinated biphenyl (PCB) family. [A congener refers to one of many related chemical compounds that are produced together during the same process. In the case of PCBs, each congener is a biphenyl molecule containing a certain number and arrangement of added chlorine atoms. There are many commerically marketed products (e.g., Aroclor) containing varying mixtures of PCB congeners.] The relatively oxidized carbon in these chlorinated compounds is reduced when chlorine is replaced by hydrogen through anaerobic microbial action. For example, when TCE is partially dechlorinated to *trans*-1,2-dichloroethene, *cis*-1,2-dichloroethene, or 1,1-dichloroethene (all having the formula $C_2Cl_2H_2$, abbreviated DCE), the carbon is reduced from the (+I) oxidation state to the (0) oxidation state:

$$\tfrac{1}{2}CH_2O + \tfrac{1}{2}H_2O + C_2Cl_3H \longrightarrow C_2Cl_2H_2 + \tfrac{1}{2}CO_2 + Cl^- + H^+. \qquad [2\text{-}70a]$$

The dichloroethene *isomers* (compounds with the same formula but different structures) can be further degraded under reducing conditions into chloroethene (vinyl chloride), and the oxidation state of the carbon is thereby reduced to (−I):

$$\tfrac{1}{2}CH_2O + \tfrac{1}{2}H_2O + C_2H_2Cl_2 \longrightarrow C_2H_3Cl + \tfrac{1}{2}CO_2 + Cl^- + H^+. \qquad [2\text{-}70b]$$

Reductions such as these usually do not completely mineralize a pollutant. Their greatest significance lies in the removal of chlorine or other halogen atoms, rendering the transformed chemical more subject to oxidation if it is ultimately transported back into an aerobic environment. Figure 2-25 shows some types of anaerobically degraded compounds.

2.6.3 Modeling Biodegradation

Kinetics of Microbial Transformations of Chemicals

A simple biodegradation model is one in which microorganisms are in contact with water containing a dissolved organic chemical that serves as the energy substrate. Because chemical uptake into a cell is followed by enzymatic transformation, biodegradation and uptake rates are equivalent in this model. It is

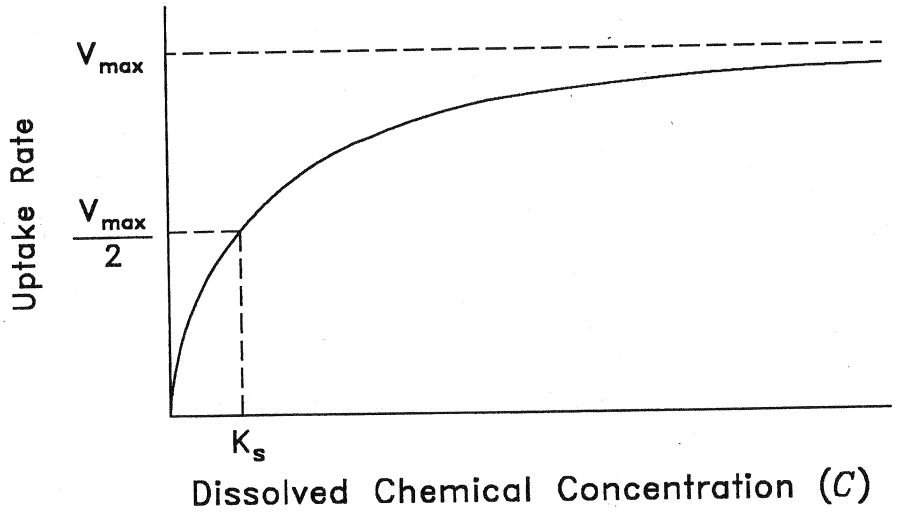


FIGURE 2-26 Microbial uptake rate of a chemical, according to Michaelis–Menten kinetics [see Eq. [2-71a]]. The rate cannot exceed V_{max} no matter how high the chemical concentration becomes. K_s, the half-saturation constant, is the chemical concentration at which uptake equals half of V_{max}. At low concentrations, uptake is nearly proportional to concentration and may be approximated as a first-order process.

customary to model chemical uptake by a cell according to *Michaelis–Menten enzyme kinetics,*

$$V = V_{max} \cdot \frac{C}{C + K_s}, \qquad [2\text{-}71a]$$

where V is the rate of chemical uptake per cell [M/(cell · T)], V_{max} is the maximum possible chemical uptake rate per cell [M/(cell · T)], C is the concentration of dissolved chemical [M/L^3], and K_s is the *half-saturation constant* [M/L^3]. Equation [2-71a] is often written with an S (for substrate concentration) in place of C, the symbol used in this text to represent chemical concentration. The mathematical form of Eq. [2-71a] also appears in other applications; for example, it shows up as the Langmuir isotherm, which is used similarly to the Freundlich isotherm to model certain nonlinear sorption equilibria, as discussed in Section 1.8.3. When K_s equals C, the uptake (and hence transformation) occurs at one-half of its maximum possible rate, V_{max}. When the rate of chemical uptake is plotted against the dissolved chemical concentration, the curve shown in Fig. 2-26 is obtained. Note that V approaches zero when there is no chemical present and reaches a plateau at V_{max} for high concentrations. When K_s is much greater than C (i.e., at low concentrations), the rate of uptake becomes nearly proportional to the chemical

concentration, thereby approximating first-order kinetics,

$$V \approx \left[\frac{V_{max}}{K_s}\right] \cdot C, \qquad [2\text{-}71b]$$

where V is the rate of chemical uptake per cell [M/(cell · T)], V_{max} is the maximum possible chemical uptake rate per cell [M/(cell · T)], C is the concentration of dissolved chemical [M/L^3], and K_s is the half-saturation constant [M/L^3].

When C is much greater than K_s, V approaches independence of C and the rate approximates zero-order kinetics (i.e., there is no dependence on the chemical concentration),

$$V \approx V_{max}, \qquad [2\text{-}71c]$$

where V is the rate of chemical uptake per cell [M/(cell · T)] and V_{max} is the maximum possible chemical uptake rate per cell [M/(cell · T)].

The rate of uptake of the chemical per unit of water is proportional to both

TABLE 2-7 Aerobic Biodegradation Rates Observed in Incubations of River Water Samples[a]

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

[a] Adapted from Lyman *et al.* (1990).
[b] First value is mean for days 0–15; second is for days 20–65.
[c] Dissolved concentrations ranging from 0.2 mg/liter to saturation.

TABLE 2-8 Anaerobic Biodegradation Rates Observed in Soil[a]

Compound	Rate constant (per day)
Carbofuran	0.026
DDT	0.0035
Endrin	0.03
Lindane	0.0046[b]
Pentachlorophenol	0.07[b]
Trifluralin	0.025
Trichloroethene	0.009[c]
1,1-Dichloroethene	0.0063[d]

[a] Rates from die-away studies in soil presented in Lyman *et al.* (1990), unless otherwise noted.
[b] Rates from $^{14}CO_2$ evolution studies in soil presented in Lyman *et al.* (1990).
[c] Rate from die-away studies in soil in Bouwer and McCarty (1983).
[d] Rate from die-away studies in soil in Barrio-Lage *et al.* (1986).

the chemical uptake rate and the cell density,

$$\frac{dC}{dt} = V \cdot X, \qquad [2\text{-}72]$$

where dC/dt is the change in chemical concentration with time [M/(L^3 · T)], V is the rate of chemical uptake per cell [M/(cell · T)], and X is the cell density [cells/L^3].

Thus, the simplest quantitative model for biodegradation in a surface water is one in which the dissolved organic chemical concentration is significantly less than K_s, such that Eq. [2-71b] applies, and cell density X is assumed constant. The change in chemical concentration with time, Eq. [2-72], is then proportional to the chemical concentration, and first-order kinetics may be applied. Many rate constants have been published for surface waters (Table 2-7). Note that V_{max}, K_s, and X are not individually measured; their effects are lumped into a single empirical rate constant. Because degradation rates are highly dependent on the nature and abundance of the microbial population present in the surface water at the time the experiment was

conducted, these values are in no way absolute, but instead provide an approximate indication of some typical rates of aerobic biodegradation in surface waters. Table 2-8 provides some very approximate rates of anaerobic degradation observed for certain specific compounds in soil, and may be applicable to degradation in the sediments of some surface waters.

EXAMPLE 2-17

Spilled benzene (C_6H_6) dissolves into a river flowing at an average velocity of 0.3 m/sec. Will biodegradation significantly decrease the concentration of benzene in the river over a 20-mi reach?

The travel time of the river is

$$\tau = 20 \text{ mi} \cdot \frac{1609 \text{ m}}{1 \text{ mi}} \cdot \frac{\text{sec}}{0.3 \text{ m}} \cdot \frac{1 \text{ hr}}{3600 \text{ sec}} \approx 30 \text{ hr}.$$

From Table 2-7, an approximate aerobic degradation rate for benzene is 0.11/day. By assuming first-order decay,

$$C/C_0 = e^{-kt}.$$

In 30 hr, which is approximately 1.2 days,

$$C/C_0 = e^{-(0.11/\text{day})(1.2 \text{ day})}$$

$$C/C_0 = 0.87.$$

Therefore, over 10% of the benzene may degrade in a 20-mi. reach. Due to the large uncertainty in the aerobic degradation rate estimate, this calculation provides only a crude approximation of the amount of benzene remaining. It is sufficient, however, to indicate that biodegradation may be significant over this reach of river.

EXAMPLE 2-18

A 1 *M* solution of DCE is accidentally spilled into a stratified lake whose bottom waters are anaerobic. Because the mixture is denser than water, it will tend to sink. Assume the DCE becomes dissolved in the pore waters of the bottom sediments. After 2 months, what compounds would you expect to find in the bottom sediments, and in roughly what ratio?

Equation [2-70b] shows that the anaerobic degradation pathway for DCE is conversion to vinyl chloride. From Table 2-8, a rough estimate of the anaerobic biodegradation rate for DCE in soil is 0.0063/day. Vinyl chloride is very resistant to anaerobic degradation; therefore, its net accumulation is essentially equal to the amount of DCE reduced. By assuming first-order kinetics and 30 days in a month,

$$C = C_0 e^{-kt}$$

$$C/C_0 = e^{-(0.0063/\text{day})(60\ \text{days})}$$

$$C/C_0 = 0.7.$$

A very approximate estimate is that 70% of DCE will remain after 2 months; 30% will have been converted to vinyl chloride.

In the case in which X is constant but C is not significantly less than K_s, Eq. [2-71a] must be used, as shown in the following example.

EXAMPLE 2-19

A *metalimnion* (the transitional layer between the epilimnion and the hypolimnion) contains *methanotrophic* bacteria (bacteria that aerobically oxidize methane) at a cell concentration of 10^5 cells per milliliter. There is adequate oxygen available and the cells have a V_{max} for CH_4 of 10^{-19} mol/(cell · sec) and a half saturation constant, K_s, of 10^{-4} mol/liter. At what rate, R_{CH_4}, is methane degraded if it is present at a concentration of 1.5×10^{-5} M?
By using Eq. [2-71a]:

$$V = 10^{-19}\ \frac{\text{mol}}{\text{cell} \cdot \text{sec}} \cdot \frac{1.5 \times 10^{-5}\ M}{1.5 \times 10^{-5}\ M + 10^{-4}\ M} = 0.13 \times 10^{-19}\ \frac{\text{mol}}{\text{cell} \cdot \text{sec}}.$$

The rate at which CH_4 is degraded is a function of both the CH_4 uptake rate and the population density:

$$R_{CH_4} = \left(0.13 \times 10^{-19}\ \frac{\text{mol}}{\text{cell} \cdot \text{sec}}\right) \cdot \left(\frac{10^5\ \text{cells}}{\text{ml}}\right)$$

$$= 1.3 \times 10^{-15}\ \frac{\text{mol}}{\text{ml} \cdot \text{sec}} \quad \text{or} \quad 1.3 \times 10^{-12}\ \frac{\text{mol}}{\text{liter} \cdot \text{sec}}.$$

The model illustrated in Example 2-19 may also be applied to a flowing stream if the microorganisms are attached to the surfaces of the channel, have a relatively steady cell density, and are exposed to the full chemical concentration in the stream (Kim *et al.*, 1995; Cohen *et al.*, 1995). Microorganisms attached to solid surfaces form *biofilms,* as populations of attached microbes accumulate on top of one another, building up a layer of microbes and extracellular "glue" made of polysaccharide material. Within biofilms, X corresponds to the number of attached microorganisms divided by the volume of the biofilm. A biofilm may also be called a bacterial *slime*, for reasons that are evident to anyone who has tried to cross a stream by walking on the smooth submerged rocks; the slipperiness is due to the biological layers that have accumulated on the rocks. It appears to be advantageous for microbes to remain attached in one place in biofilms and harvest nutrients that are transported to them primarily by advection, instead of being free floating in the water and forced to rely solely on Fickian transport to supply nutrients. Numerous larger scale examples of this attachment strategy also occur; for example, some stream-dwelling insect larvae, such as caddis fly larvae, anchor themselves to rocks and trap small particles of organic detritus for food from the flowing streamwater. Biofilms will be considered in more detail in Chapter 3.

Monod Growth Kinetics

In many situations, the use of a constant cell density in a biodegradation model is not justified. For example, a spill of an easily biodegraded chemical into a surface water may greatly stimulate bacterial growth. *Monod kinetics* allow a model to account for a changing population of microbial cells when cell growth is stimulated by energy released from the biotransformation process. Monod growth kinetics can be inferred from Michaelis–Menten kinetics, together with the assumption that a certain number of new cells grow per unit mass of chemical transformed. The ratio of the number of new cells to the mass of chemical taken up (transformed) is called the *cell yield, y* [cells/M]. The *specific growth rate,* μ [T^{-1}], is the product of the chemical uptake rate, V [M/(cell · T)], and the cell yield. The maximum specific growth rate, μ_{max}, is equal to the product ($V_{max} \cdot y$). The specific growth rate corresponding to a concentration of chemical, C, is therefore,

$$\mu = \mu_{max} \cdot \frac{C}{C + K_s}, \qquad [2\text{-}73]$$

where μ is the specific growth rate [T^{-1}], μ_{max} is the maximum specific growth rate [T^{-1}], C is the concentration of a chemical [M/L^3], and K_s is the

half-saturation constant [M/L^3]. Note that Eq. [2-73], which describes Monod growth kinetics, has the same mathematical form as Eq. [2-71a], which describes Michaelis–Menten enzyme kinetics applied to chemical uptake.

EXAMPLE 2-20

A test tube is filled with water containing bacteria and a chemical that supports cell growth. The chemical concentration is 3×10^{-5} mol/liter and the bacteria have a cell yield of 10^{12} cells/mol. What will be the specific growth rate μ if V_{max} is 10^{-15} mol/(cell · min) and K_s is 5×10^{-5} mol/liter?

The specific growth rate is equal to the product of the chemical uptake rate and the cell yield:

$$\mu = V \cdot y.$$

First, estimate V from Eq. [2-71a]:

$$V = 10^{-15} \frac{\text{mol}}{\text{cell} \cdot \text{min}} \cdot \frac{3 \times 10^{-5}\, M}{(3 \times 10^{-5} + 5 \times 10^{-5})M} = 3.8 \times 10^{-16} \frac{\text{mol}}{\text{cell} \cdot \text{min}}.$$

Then estimate μ as the product of the chemical uptake rate and the cell yield:

$$\mu = 3.8 \times 10^{-16} \frac{\text{mol}}{\text{cell} \cdot \text{min}} \cdot 10^{12} \frac{\text{cell}}{\text{mol}} = 3.8 \times 10^{-4}/\text{min}.$$

Monod kinetics can be used to formulate models that account for both chemical transformations and changes in the microbial population. One such model applies to the *batch culture,* a volume into which a biodegradable, growth-supporting chemical and an initial population of suitable bacteria are introduced. The batch culture could correspond to a chemical spill into a pond, to an industrial process, or even to a vat of brewing beer. Biotransformation is strongly influenced by the increase in cell density, which typically follows three stages (Fig. 2-27). The first stage is the *lag phase,* an interval during which cell growth is much less than predicted by Monod kinetics because the cells are becoming acclimated to the new environment. In the *exponential phase* (assuming C is much greater than K_s), cell density increases according to the equation,

$$X = X_0 e^{\mu t}, \qquad [2\text{-}74]$$

where X is the cell density [cells/L^3] at some time t, X_0 is the initial cell density [cells/L^3], and μ is the specific growth rate [T^{-1}]. If Eq. [2-74] is

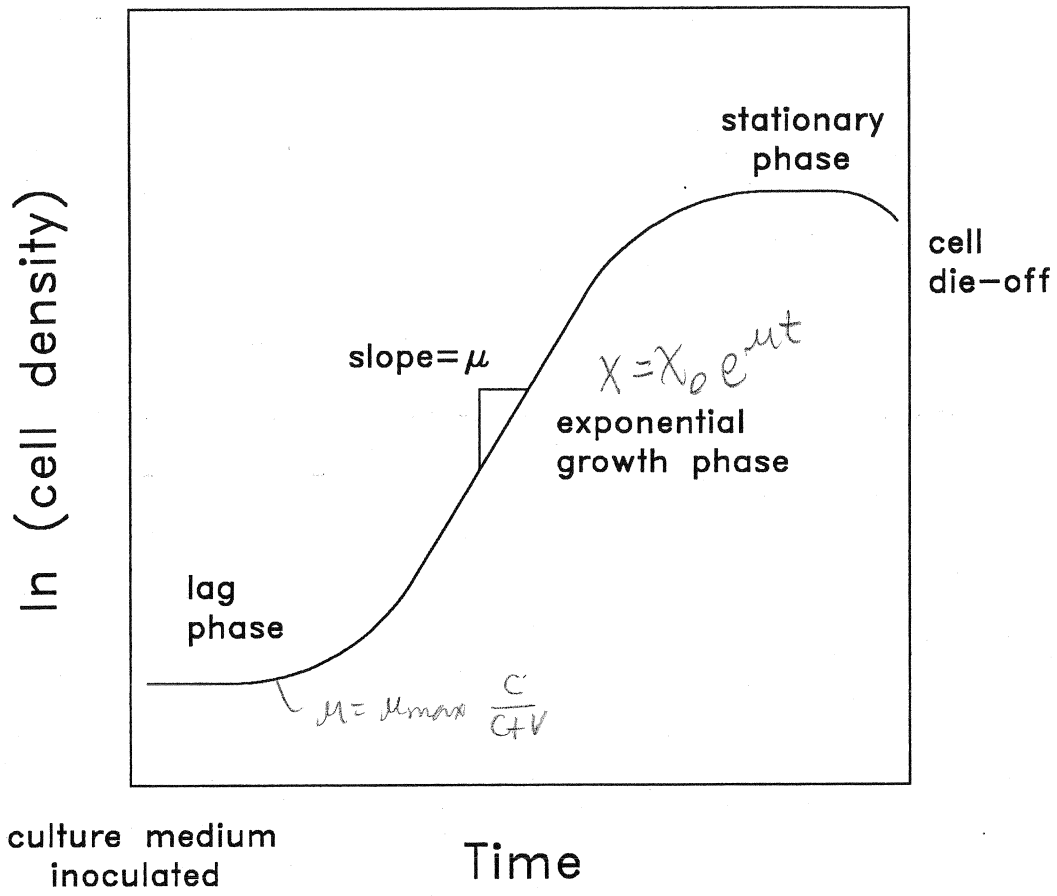


FIGURE 2-27 Cell density versus time in a batch culture. During the lag phase, the cells become acclimated. During the exponential phase, the number of cells increases exponentially as described by Monod growth kinetics, see Eq. [2-73]. During the stationary phase, cell density is constant for some time before the culture declines due to substrate depletion, waste accumulation, and/or excessive cell density.

substituted into Eq. [2-72], it is evident that the chemical degradation rate can increase very rapidly during this phase, with a very large fraction of biodegradation occurring near the end of this phase. As nutrients are depleted and/or excessive cell densities or waste accumulation suppress growth, the cells enter the third stage, a *stationary phase* in which cell density is constant for a period of time prior to decline of the culture.

A second type of culture described by Monod kinetics is the *continuous culture,* in which a chemical is constantly fed into a vessel and both microbial cells and the chemical are constantly lost from the vessel at a given rate. This culture is often called a *chemostat* when operated under steady-state conditions. Like the batch culture, a continuous culture may be a useful model of certain environmental systems, such as lakes receiving continuous discharges of pollutants. Continuous cultures are common in industrial processes as

well, including many wastewater treatment processes, in which the large-scale, well-mixed culture vessel is often called a *continuously stirred tank reactor* (CSTR). In a chemostat, the growth rate μ of the cells must equal or exceed the reciprocal of the hydraulic residence time, or X will decline and the system will suffer *washout,* after which no further biodegradation will occur. For further discussion of batch and continuous cultures the reader is referred to Brock and Madigan (1991).

The models discussed here are all simplifications of the real world, in which numerous factors influence microbial populations, which in turn comprise a mixture of numerous microbial strains having a great range of growth and uptake parameters. However, even the most complex computer-based models that attempt to predict biodegradation rates are usually based on the uptake and growth expressions described here, and may be recognized as variations of batch, continuous, or biofilm models. (Biofilm models, although they are also applicable to rivers and streams, will be discussed further in Chapter 3.)

2.6.4 Bioconcentration and Bioaccumulation in Aquatic Organisms

Aquatic biota not only degrade pollutant chemicals but also may accumulate them. If aquatic organisms accumulate chemicals only from the water, the process is called *bioconcentration;* if they accumulate chemicals from both water and food, the process is called *bioaccumulation.* In surface waters, bioconcentration and bioaccumulation are of particular concern in relatively large aquatic organisms that may be ingested by humans or by other nonaquatic organisms, such as birds or bears. A current example of the detrimental effects of bioaccumulation is the occurrence of mercury poisoning among natives of the Hudson Bay area of Canada due to hydroelectric development. This poisoning is a result of the release of mercury from flooded soils, its transformation into methylmercury (CH_3Hg^+), and its subsequent bioaccumulation in fish that are consumed by people. The near extinction of many birds of prey, which resulted from reproductive failure caused by the accumulation of DDT pesticide residues from fish, is another, historical example of the effects of bioaccumulation.

In surface waters, the *bioconcentration factor* (BCF) is the ratio of a chemical's concentration in an organism to the chemical's aqueous concentration. BCF is often expressed in units of liter per kilogram (i.e., the ratio of mg of chemical per kg of organism to mg of chemical per liter of water). The BCF

may be merely an observed ratio, or it may be the prediction of a *partitioning model.*

Partitioning models are founded on the assumptions that pollutant chemicals partition, in a more or less passive fashion, between water and aquatic organisms and that chemical equilibrium exists between the organisms and the aquatic environment. Such assumptions are most justifiable in the case of hydrophobic chemicals that are more rapidly exchanged between an organism and the water than they are excreted or metabolized by the organism. An organism such as a fish is in effect modeled as a bag of oil and tissue water; the chemical partitions between the bag's contents and the surrounding water according to its hydrophobicity (as reflected by its K_{ow} or the reciprocal of its water solubility) and the percentage of fish that is oil and fat (the lipid content). Exchange is facilitated by a large surface to volume ratio (as is found in smaller organisms) and by organs that facilitate exchange between the organism and water, such as the gills of fish. Several empirical formulae for establishing BCF on the basis of partitioning are shown in Table 2-9 (see also Hawker and Connell, 1989). Although partitioning models are very simple, some are reasonably successful in appropriate circumstances (Fig. 2-28).

TABLE 2-9 Regression Equations for Estimating BCF for Fish

Equation[a]	N[b]	r^2[c]	Species used
$\log BCF = 0.76 \log K_{ow} - 0.23$	84	0.823	Fathead minnow Bluegill sunfish Rainbow trout Mosquitofish
$\log BCF = \log K_{ow} - 1.32$[d]	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
$\log BCF = 3.41 - 0.508 \log S$[e] ($S$ in μM)	7	0.93	Rainbow trout
$\log BCF = 1.119 \log K_{oc} - 1.579$	13	0.757	Various

[a] Adapted from Lyman *et al.* (1990) unless otherwise noted. BCF, bioconcentration factor; K_{ow}, octanol–water partition coefficient; S, water solubility; K_{oc}, organic carbon–water partition coefficient.

[b] N = number of chemicals used to obtain regression equation.

[c] r^2 = correlation coefficient for regression equation.

[d] Mackay (1982).

[e] Chiou *et al.* (1977).

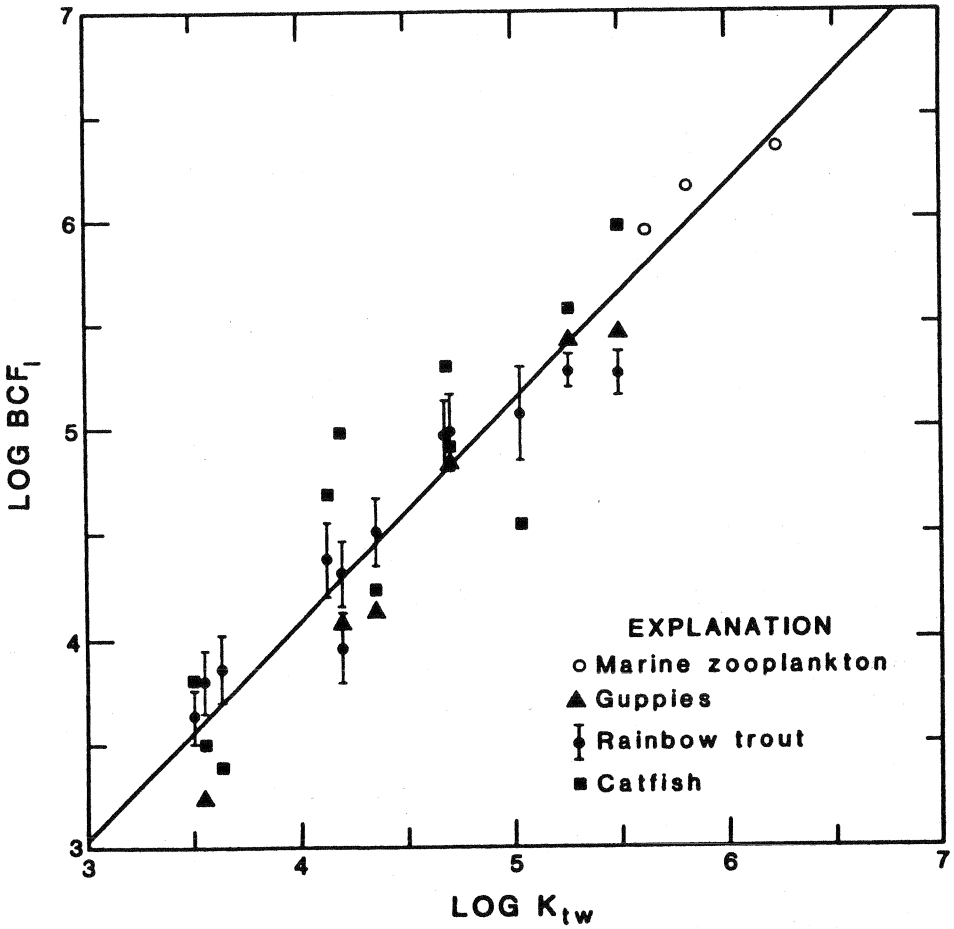


FIGURE 2-28 Correlation of the measured, lipid-normalized bioconcentration factor (BCF) with the triolene–water partition coefficient (K_{tw}) for a suite of 16 nonpolar compounds. (The partition coefficient K_{tw} is similar to K_{ow}.) Note that the overall correlation is very strong, but any single prediction of BCF from K_{tw} may be in error by half a log unit (a factor of three) [Smith *et al.* (1988). Reproduced with permission of Springer-Verlag New York, Inc.].

It is important to note that partitioning models *do not imply* that an increase in chemical concentration occurs as one moves up a food chain; in fact, partitioning models predict that the concentration of a chemical in an organism is not dependent on what the organism eats. Partitioning models are not appropriate for terrestrial ecosystems; for those ecosystems, models for chemical accumulation must be based on the food chain (i.e., bioaccumulation).

Bioaccumulation can be estimated by a *kinetic model.* In kinetic models (sometimes called *physiological models* or *physiologically based pharmacokinetic models*), consideration is given to the dynamics of ingestion, internal transport, storage, metabolic transformation, and excretion processes that occur in each type of organism for each type of chemical. In kinetic models,

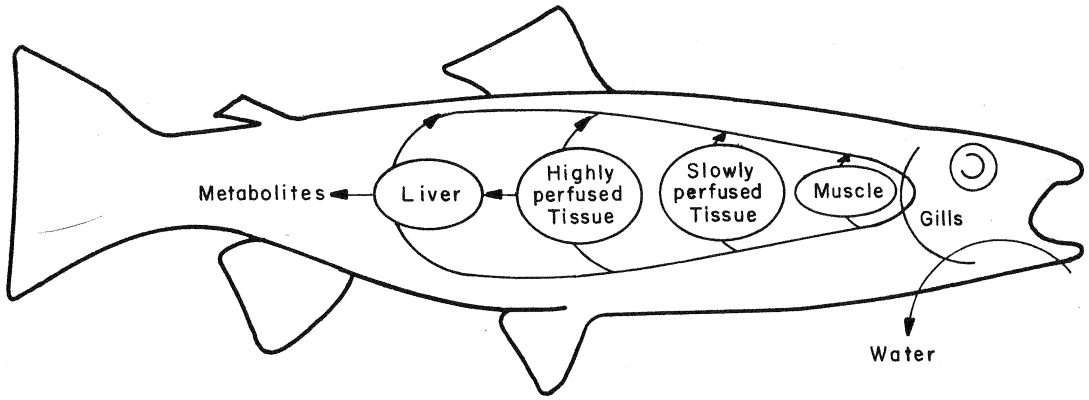


FIGURE 2-29 Schematic representation of a physiologically based kinetic model for bioaccumulation of a chemical that is absorbed through the gills, transported by blood flow, stored in various body tissues, and metabolized by the liver. Such a model requires much more detailed information on the fish than does a partitioning model; however, it may be necessary to use this more complex approach for chemicals that are metabolized or excreted by the fish more rapidly than they are exchanged with the water [adapted from Barron (1990). Reprinted with permission. © 1990 American Chemical Society].

organisms in a surface water ecosystem may ingest food containing a particular chemical and absorb the chemical from the water. The ingested and absorbed chemical is subject both to elimination through excretion and to metabolic transformation to other chemicals (often, in higher organisms, the liver carries out oxidative transformations catalyzed by cytochrome P450 enzymes; Fig. 2-29). Kinetic models can be reasonably accurate representations of what actually occurs in an organism, even a large and complex one. Kinetic models do, however, require considerable information on the uptake, transformation, storage, and excretion processes. The amount of data required to parameterize kinetic models becomes enormous when a whole ecosystem is considered, because an understanding of chemical accumulation by organisms high on the food chain requires understanding each lower step in the food chain, all the way down to the lowest trophic level at which chemicals become incorporated into organisms. For a detailed description of a bioaccumulation model for nonmetabolized organic chemicals, the reader is referred to Barber *et al.*, 1991.

EXAMPLE 2-21

A catfish metabolizes and/or excretes 2,4′,5-trichlorinated biphenyl (a PCB congener) with a hypothetical first-order rate constant of 0.021/day. How long will it take for fish from a contaminated stream, on being placed in clean

water, to undergo *depuration* (cleansing of pollutants) if the levels of the biphenyl exceed safe levels by a factor of three (i.e., how long will it take for them to become "safe")?

First-order kinetics are suggested by the problem statement:

$$C = C_0 e^{-kt}$$

$$\tfrac{1}{3} = e^{-(0.021/\text{day})(t\ \text{days})}$$

$$-1.1 = -0.021\ t$$

$$t = 52\ \text{days}.$$

Note also that knowledge of the nature of the compound into which the biphenyl is being metabolized and the nature of other PCB congeners present is necessary before concluding that the fish are "clean" and safe for consumption!

2.7 ABIOTIC CHEMICAL TRANSFORMATIONS

2.7.1 DEGRADATION OF CHEMICALS BY LIGHT

Nature of Light

Light is a form of electromagnetic radiation, in which energy is transmitted through space by the interaction of electric and magnetic fields. Light can be described both in terms of particles and in terms of waves; different effects are better described by one or the other model. In surface waters, light penetrates to depths of at least several meters in all but the most darkly colored or turbid waters; numerous light-driven reactions can lead to the *photodegradation* of organic chemicals.

Light is characterized in part by its *wavelength* distribution. Visible light consists of radiation having wavelengths (λ) ranging from approximately 400 to 700 nm. The distribution of wavelengths in extraterrestrial solar radiation occupies a much wider range, from approximately 100 nm to greater than 3000 nm (Fig. 2-30). Some of these wavelengths are absorbed strongly as the radiation passes through Earth's atmosphere (as discussed more fully in Section 4.7); the amount of energy remaining in wavelengths less than 290 nm is small by the time the light reaches Earth's surface. All electromagnetic radiation travels at a constant speed, c, of 3.0×10^8 m/sec in free space. Thus,

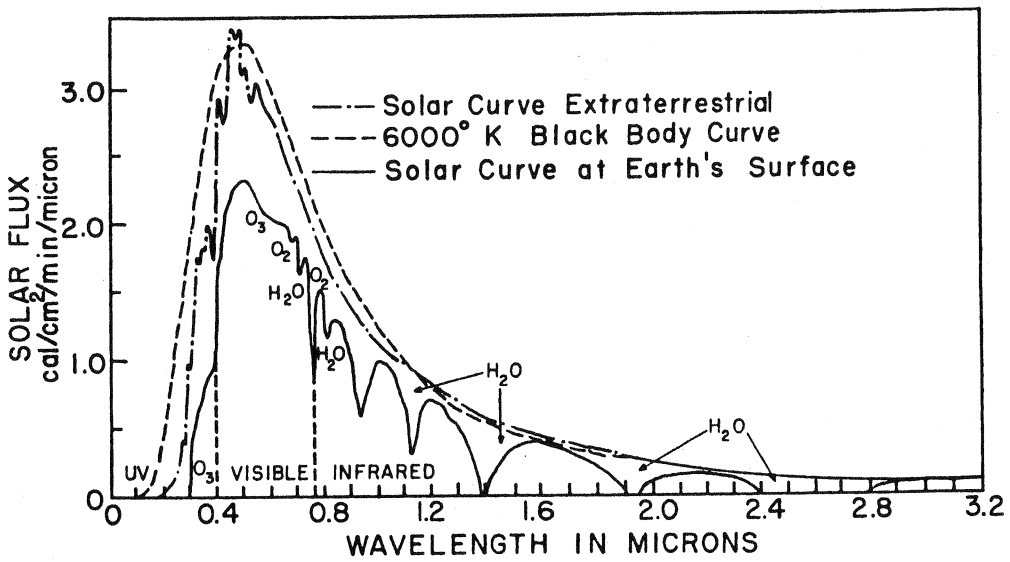


FIGURE 2-30 Spectrum of solar radiation received at Earth's surface (solid line) and at the outer edge of the atmosphere (dashed and dotted line). Radiation from the Sun approximates radiation from a surface having an emissivity of one (blackbody) at 6000 K (dashed line); see also Section 4.7.1. Note that significant amounts of radiation are absorbed by the atmosphere, and that this absorption is concentrated in discrete regions of the spectrum, a result of wavelength-specific absorption by gases and vapors. Absorption by water vapor, oxygen (O_2), and ozone (O_3) are shown here. Note also the large amount of energy that lies outside the visible range [Gates (1962)].

the *frequency*, ν, of light of a given wavelength is

$$\nu = c/\lambda = 3 \times 10^8/\lambda \text{ sec}^{-1}, \qquad [2\text{-}75]$$

when λ is expressed in meters. When applied to electromagnetic radiation, the unit sec^{-1} is called the *hertz* (Hz).

Other aspects of the effects of light are best described by invoking its particle nature. Each quantum of light, called a *photon*, possesses an energy equal to E,

$$E = h \cdot \nu, \qquad [2\text{-}76]$$

where h is Plank's constant, 6.6×10^{-34} J · sec. Note that the shorter the wavelength becomes, the higher the energy per photon becomes. Each individual photon of light at the blue end of the visible spectrum (λ = 400 nm) has an energy of 5.0×10^{-19} J, while each photon at the red end of the visible spectrum (λ = 700 nm) has an energy of 2.8×10^{-19} J.

Light Distribution in Surface Waters

The actual distribution of light in water is complex, affected not only by the light's wavelength composition and *intensity* (intensity can be thought of as

the number of photons hitting a unit surface per unit time) but by the angle at which light enters the water (*angle of incidence*) and the optical properties of the water itself. Light intensity decreases with depth in water due to absorbance by the water and by substances in it. The extent of absorbance varies with the concentrations and types of substances dissolved in the water, such as dissolved humic substances, and with the concentration of suspended particles in the water [turbidity or *total suspended solids* (TSS)]. Humic substances include humic and fulvic acids, which are formed during the degradation of natural organic material (see also Section 2.4.1). Humic substances are of high molecular weight [on the order of 500 to 10,000 *daltons* (Da); a dalton is approximately the mass of a hydrogen atom], contain aromatic rings, and are at least somewhat resistant to further biodegradation. As an approximation, light intensity in a surface water body is typically modeled based on Beer's law. Beer's law, as applied to water, states that the absorbance (fraction of light absorbed) in traveling a path is equal to the product of chemical concentration, the chemical's molar absorptivity, and the path length. Absorptivity varies with wavelength; however, for practical purposes in surface waters where the mixture of absorbing chemicals often has a broad collective absorbance spectrum, an approximate overall *extinction coefficient* that is not wavelength dependent is often used. Light intensity is then modeled by

$$I = I_0 e^{-\eta z}, \qquad [2\text{-}77]$$

where I is the light intensity at a given depth z in the water expressed either as number of micromoles of photons per unit area per unit time [microeinsteins/($m^2 \cdot$ sec)], or power per unit area (watts/m^2), I_0 is the light intensity at the water surface, and η is an experimentally measured extinction coefficient [L^{-1}].

In reality, the red and infrared wavelengths are preferentially absorbed, even in pure water, and the blue-violet–ultraviolet wavelengths are also selectively attenuated if the water contains appreciable concentrations of dissolved organic material. Thus, the midspectrum green and yellow wavelengths often penetrate most deeply into a surface water. In addition to neglecting the wavelength composition of light, Eq. [2-77] does not explicitly consider the angles at which the light travels through the water; this direction is not vertical for all of the photons. The greater attenuation that occurs with depth for light traveling nonvertical paths is accounted for in the empirical extinction coefficient.

The extinction coefficient η may be calculated from measurements of I made by a light meter. The Secchi disk is another time-honored device for estimating light penetration in a lake. In 1865, P. A. Secchi developed this method, which was subsequently used aboard the papal yacht, S. S. L'immacolata Concezione. The Secchi disk is about 20 cm in diameter, col-

ored all white or white with two 90 degree sectors painted black. Suspended horizontally on a line, it is lowered into the water until it cannot be seen, and the depth of its disappearance is recorded. It is then raised and the depth of its reappearance recorded. The average of the two depths is an approximation of the depth above which 90 to 95% of the light initially entering the lake is absorbed.

EXAMPLE 2-22

What is the light intensity at 1-m depth in a lake, given an intensity of 3000 microeinsteins (μE)/(m^2 · sec) just beneath the lake's surface and an extinction coefficient of 0.6/m? If an aquatic plant has a light *compensation point* (the light intensity at which respiration rate equals photosynthetic rate) of 150 μE/(m^2 · sec), what is the maximum depth at which the plant may be expected to grow?

To estimate the light intensity at 1-m depth, use Eq. [2-77]:

$$I = \frac{3000\ \mu\text{E}}{\text{m}^2 \cdot \text{sec}}\, e^{-(0.6/\text{m}\cdot 1\ \text{m})} = \frac{1650\ \mu\text{E}}{\text{m}^2 \cdot \text{sec}}.$$

To calculate the maximum depth at which the plant can grow, use Eq. [2-77] and solve for z:

$$z = \frac{-1}{\eta} \cdot \ln\left(\frac{I}{I_0}\right) = \frac{-1}{0.6/\text{m}} \cdot \ln\left(\frac{150\ \mu\text{E/m}^2 \cdot \text{sec}}{3000\ \mu\text{E/m}^2 \cdot \text{sec}}\right) = 5\ \text{m}.$$

The plant should be able to barely survive at 5 m below the water surface.

Photodegradation

Everyday examples of photochemical degradation by sunlight are common; they include the fading of colors and dyes of objects exposed to the sun, and the embrittlement and cracking of plastic objects left outdoors. In surface waters, photodegradation of chemicals depends on both the intensity and wavelength spectrum of light. If the energy per photon is sufficient to break a specific chemical bond or otherwise induce a chemical reaction, then increased light 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 that light will not break the chemical bond, regardless of its intensity. Due to the greater amount of energy

possessed by photons at shorter wavelengths, ultraviolet light is particularly effective in degrading many materials. Often, photodegradation is called *photolysis,* in reference to the breaking of chemical bonds by light.

For light to cause chemical reactions, its energy must first be transferred to the chemical system (i.e., the light must be *absorbed*). Evidence for absorption of light by natural waters is often visible to the human eye. The color of a lake or river, as seen from above the surface, is due in part to selective absorption of certain wavelengths. To a diver, the phenomenon of light extinction in a surface water, discussed previously, is clearly evident. When light is absorbed by an atom or a molecule, it may cause movement of an electron from a *nonexcited* or *ground* state, to a higher energy level or *excited* state. According to quantum theory, only a finite number of energy levels are available. Prior to photoexcitation, most species are in the *singlet* state (i.e., for each electron of one spin, there is an electron with opposite spin). (O_2 is an exception; in the ground state it has two electrons with unpaired spins, making it a *triplet.*) Initial photoexcitation of most atoms or molecules is usually to a more energetic singlet state; photoexcitation of O_2 often causes transition from a triplet state to a singlet state. The excited atom or molecule may then lose its energy by one of several processes:

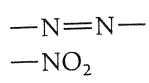
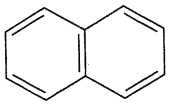
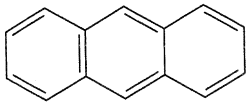
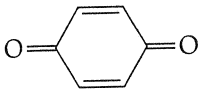
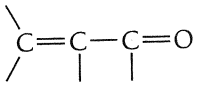
1. The energy may be lost as heat in the process of *internal conversion.*
2. The electron may lose energy by electromagnetic radiation as it returns to ground state, in the process of *fluorescence.*
3. The electron may undergo *intersystem crossing* into a *triplet* state; to go between a singlet and a triplet state, the spin of an electron is reversed. The triplet state is usually longer lived than the original excited state, and may decay radiatively to ground state in the process of *phosphorescence.*
4. The energy may initiate a chemical reaction within the molecule, in the process of *direct photodegradation.* Common examples are the *photodissociation* of H_2O_2 into $OH\cdot$ or Cl_2 into $Cl\cdot$.
5. The energy may be transferred to another molecule.

The probability that the initial excited state will decay via any given pathway is called the *quantum yield* for that pathway.

Because direct photodegradation (process 4) can only occur in chemicals that are capable of absorbing light energy, it often occurs in compounds that have light-absorbing double bonds between carbon atoms, as in alkenes or aromatic rings, although other structures also can absorb photons (Table 2-10). Note that absorption is strongly wavelength dependent. First-order photodegradation rate constants or half-lives for many compounds have been empirically determined (Table 2-11; see also Marcheterre *et al.,* 1988). Often such tabulated rates are measured under natural daylight; consequently, al-

photolysis

TABLE 2-10 Several Chemical Structures That Absorb Light at Wavelengths Greater than 290 nm[a]

Group	λ_{max} (nm)	Molar absorptivity (liter/(mol·cm))
	295	10
	460	Weak
	347 278	15 10
	311 270	250 5000
	360	6000
	440 300	20 1000
	330	20

[a]Lyman *et al.* (1990).

though they are environmentally relevant, they do not reveal wavelength dependency. Photodegradation in daylight may be due primarily to the blue or ultraviolet fraction of the spectrum because of the higher energies associated with shorter wavelengths.

Even those chemicals that do not themselves absorb photons of light can be degraded in the environment through *indirect photodegradation.* One process of indirect photodegradation is *sensitized photodegradation,* which may occur when other, light-absorbing molecules in the water, such as plant pigments or humic substances, absorb photons and subsequently transfer energy, sometimes in association with electrons or hydrogen ions, to the chemical of interest (process 5 cited previously). The light-absorbing molecules serve as *chromophores.* Natural chromophores are often made of humic substances (Faust and Hoigné, 1987), although certain metal oxides, such as titanium dioxide (TiO_2) particles, are also known to serve as effective inter-

TABLE 2-11 Half-Lives for Disappearance via Direct Photolysis in Aqueous Media[a]

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

[a] Adapted from Lyman *et al.* (1990).
[b] Wavelength(s) at which photolysis rate was measured. S, sunlight.

mediates in photodegradation. Most natural chromophores are not specifically identified as to their origin and chemical structure and therefore are sometimes called *unknown photoreactive chromophores* (UPC).

Indirect photodegradation can also occur when highly reactive (usually oxygen-containing) species are formed photochemically, and subsequently attack and degrade chemical compounds. One of the most important species is the *hydroxyl radical*, $OH\cdot$, which can be formed by several processes. In one process, a chromophore absorbs light and reacts with water to form hydrogen peroxide (H_2O_2). H_2O_2 in turn breaks into two hydroxyl radicals on absorption of a photon of sufficient energy ($\lambda < 335$ nm). H_2O_2 can also react with Fe^{2+} to form Fe^{3+}, OH^-, and $OH\cdot$ in the *Fenton reaction*. $OH\cdot$ can also be

formed by the photolysis of the nitrate ion (NO_3^-). $OH\cdot$ is present at levels of about 10^{-17} M in many illuminated surface waters. It is an exceedingly powerful oxidant in both air and water, capable of causing the degradation of many organic compounds. Another reactive species, *singlet oxygen* ($^1O_2$), is formed by the interaction of light with a chromophore and dissolved oxygen (Haag and Hoigné, 1986). A variety of other indirect photolysis possibilities exist, as shown in Table 2-12. For further information on photodegradation, the reader is referred to Lyman *et al.* (1990), Stumm and Morgan (1996), Mill (1989), Schwarzenbach *et al.* (1993), and Malkin (1992).

EXAMPLE 2-23

Benzo[*a*]pyrene, or B[*a*]p, a polycyclic aromatic hydrocarbon, is measured in a facility's wastewater lagoon 2.5 hr after a release at a concentration of 3 μg/liter. If direct photodegradation is the only degradation process occurring, what was the initial concentration of B[*a*]p in the lagoon?

From Table 2-10, it is evident that polycyclic aromatic hydrocarbons such as B[*a*]p are likely to directly photodegrade because double bonds in aromatic rings can absorb light. Indirect degradation of B[*a*]p can also occur via attack by $^1O_2$.

From Table 2-11, an approximate half-life for B[*a*]p due to direct photodegradation is 1 hr. From Eq. [1-20], the corresponding first-order decay constant is 0.69/hr. Then using Eq. [1-19]:

$$C_0 = C_t \cdot e^{kt}$$

$$C_0 = (3\ \mu\text{g/liter}) \cdot e^{(0.69/\text{hr})\cdot 2.5\ \text{hr}}$$

$$C_0 = 17\ \mu\text{g/liter}.$$

Therefore, the initial concentration of B[*a*]p in the lagoon was approximately 17 μg/liter.

2.7.2 Degradation of Chemicals by Water

Hydrolysis

Even in the absence of microorganisms or light, some chemical pollutants undergo degradation in water due to a variety of abiotic reactions, including

TABLE 2-12 Several Examples of Light-Driven Chemical Processes Occurring in Surface Waters[a]

Environment	Substrates	Products	Probable mechanisms	Likely effects
Freshwaters	Natural organic chromophores and pigments, $C\cdot$	$C\cdot + HO_2$ or $C\cdot + AH\cdot$	H atom transfer to O_2 or A	
		$C^+ + \cdot O_2^-$	Electron transfer to O_2	Numerous
		$C + O_2$	Energy transfer to O_2	
		HOOH	$\cdot O_2^-$ disproportionation; other?	
	NO_2^-	$\cdot NO + \cdot OH$	Direct photolysis	Changes N speciation
	$R\cdot$	$ROO\cdot$	O_2 addition	Oxidizes organic radicals
	Fe(III)–organic complex	$Fe(II) + CO_2$	Uncertain; consumes O_2	Oxidation of organics; reduction of O_2
	Fe(III)–organic–PO_4 complex	$Fe(II) + PO_4$	Unknown	Dissolution of colloidal Fe; bioavailability of P
Polluted waters				
Oil spills	RH, ArH, R_2S	$R{=}O$, RCO_2^-, ArOH, R_2SO	Free radicals; direct photolysis; singlet oxygen	Changes spreading emulsification and toxicity of oil
Herbicides	2,4-D	Oxidation, reduction, hydrolysis products	Direct photolysis	Complex
Pesticides	Disulfoton	Disulfoton sulfoxide	Singlet oxygen	Product more soluble and toxic in some tests
Preservatives	Pentachlorophenol (PCP)	Phenols, quinones, acids, CO_2, Cl^-	Initiated by direct photolysis of PCP	Complex
Domestic waste	Fe(III)–NTA	Fe(II) + amine + CO_2 + CH_2O	Charge transfer to metal	Degrades NTA; induces Fe(II) autooxidation

[a]Adapted from Zafiriou *et al.* (1984).

hydrolysis reactions. Hydrolysis literally means 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. Often hydrolysis is catalyzed by H^+ or OH^-. If either H^+ or OH^- is involved in the rate-limiting step of the overall process of hydrolysis, the hydrolysis reaction rate will be sensitive to the pH of the water. Other abiotic reactions include elimination reactions and nucleophilic substitutions; for further discussion of these reaction types, the reader is referred to Schwarzenbach *et al.* (1993).

Types of Compounds Undergoing Hydrolysis

The members of two classes of common pollutant chemicals are likely to undergo hydrolysis. One class includes the alkyl halides, which are straight-chain or branched hydrocarbons in which one or more hydrogen atoms have been replaced by a chlorine, fluorine, bromine, or iodine atom. Using "X" to represent a halogen atom and "R" to represent the hydrocarbon group, the overall hydrolysis reaction can be written

$$H_2O + R{-}X \longrightarrow R{-}OH + H^+ + X^-. \qquad [2\text{-}78]$$

In this reaction, an alkyl halide has been converted to an alcohol, the halogen has been released as a negatively charged halide ion, and a hydrogen ion has been released. The alcohol, in turn, is highly biodegradable. Although alcohols are frequently the products of alkyl halide hydrolysis, other products may be formed instead. For example, chloroform ($CHCl_3$) can hydrolyze to formic acid (HCOOH) and hydrochloric acid (HCl).

A second class of compounds that may undergo hydrolysis includes *esters* and ester analogs. An ester is a compound containing a modified carboxylic acid group (—COOH), in which the acidic hydrogen atom has been replaced by some other organic functional group. For example, if the acidic hydrogen atom of acetic acid (CH_3COOH) is replaced by an ethyl group (C_2H_5), the result is ethyl acetate ($CH_3COOC_2H_5$), an ester.

Hydrolysis converts esters into the "parent" organic acid and an alcohol. Therefore, continuing the example, ethyl acetate hydrolyzes to acetic acid and ethanol:

$$H_2O + CH_3COOC_2H_5 \longrightarrow CH_3COOH + C_2H_5OH. \qquad [2\text{-}79]$$

The hydrolysis reaction as written in the preceding equations is the overall reaction. Many steps are involved in a hydrolysis reaction, and a number of intermediate chemical species are formed. The reader is referred to Schwarzenbach *et al.* (1993) and Tinsley (1979) for a discussion of the actual reaction pathways.

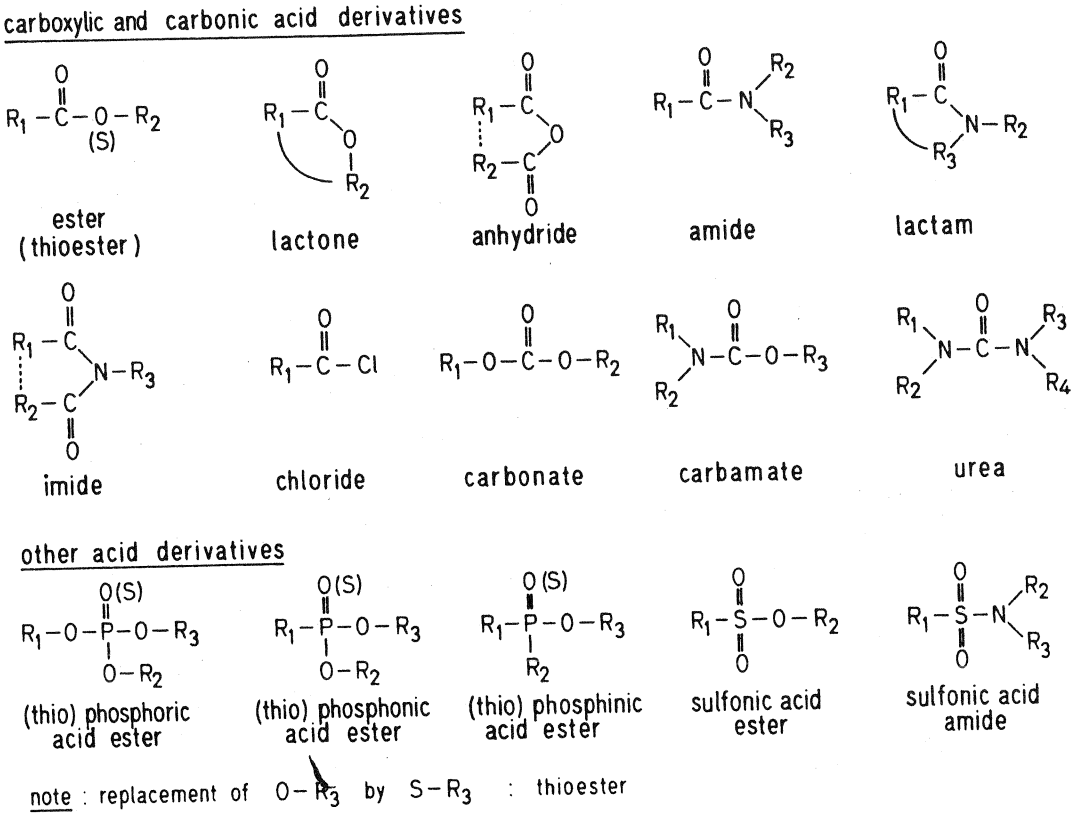


FIGURE 2-31 A variety of esters and ester analogs that tend to degrade by hydrolysis. [From *Environmental Organic Chemistry*, by R. P. Schwarzenbach, P. M. Gschwend, and D. M. Imboden. Copyright © 1993, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.].

Hydrolysis can also occur in *ester analogs*, chemicals having ester-like structures. These chemicals include compounds in which the oxygen of the "parent" carboxylic acid can be thought of as being replaced by another electronegative element, such as sulfur or nitrogen. If the oxygen atom of the ester linkage is replaced by a nitrogen atom, the compound is called an amide or a substituted amide; if it is replaced by a sulfur atom, it is called a thioester. Some of these compounds are shown in Fig. 2-31, along with other compounds such as carbamates, phosphoric acid esters, and thiophosphoric acid esters, which also may undergo hydrolysis. Many current pesticides have ester-like structures to shorten their environmental lifetime and thereby to help limit their impact on ecosystems and their residues in the human food supply.

Rates of Hydrolysis Reactions

As discussed in Section 1.6.6, at any given temperature the rate of a reaction between two different chemicals depends not only on the chemicals involved,

but also on their concentrations. Concentration affects the probability that, over any given time interval, a molecule of one reactant will collide with a molecule of the other reactant, thereby allowing the reaction to proceed. For a hydrolysis reaction that involves the direct action of the neutral species H_2O on an alkyl halide, ester, or ester analog molecule, the two concentrations of interest are the concentration of H_2O and the concentration of the ester. Because the concentration of H_2O is essentially constant in any dilute solution (approximately 55.4 *M*), the rate of this hydrolysis reaction varies only with changes in the concentration of the ester,

$$dC/dt = -k_{H_2O} \cdot C \cdot [H_2O] \qquad [2\text{-}80a]$$

or

$$dC/dt = -k'_n \cdot C, \qquad [2\text{-}80b]$$

where C is the concentration of the hydrolyzable compound [M/L^3], k'_n is the pseudo-first-order neutral rate constant [T^{-1}], and t is time [T]. Eq. [2-80b] is an example of pseudo-first-order kinetics because the constant k'_n is actually a product of a reactant concentration [H_2O] that is nearly constant and an intrinsic rate constant k_{H_2O}. If the initial concentration of the hydrolyzable compound is C_0 and there are no other sources or sinks of the compound, the familiar exponential solution is obtained:

$$C_t = C_0 e^{-k'_n \cdot t}. \qquad [2\text{-}81]$$

In the case where the hydrolysis rate is controlled by a reaction step involving the hydroxide ion OH^- (*base-catalyzed hydrolysis*), the expression for the change in chemical concentration is

$$dC/dt = -k_b \cdot C \cdot [OH^-], \qquad [2\text{-}82]$$

where [OH^-] is the concentration of hydroxide ions and k_b is the rate constant for the base-catalyzed hydrolysis reaction [$T^{-1} \cdot L^3 \cdot M^{-1}$].

Recall that if pH is known, [OH^-] can be directly calculated from the mass action expression for the ionization of water (see Section 1.6.3):

$$[OH^-] = 10^{-14}/[H^+]. \qquad [2\text{-}83]$$

It can be seen from Eqs. [2-82] and [2-83] that pH exerts a strong effect on base-catalyzed hydrolysis. For example, hydrolysis would be 1 million times faster at a pH of 10 than at a pH of 4. As long as pH is known and constant, however, the rate constant k_b can be combined with the concentration of hydroxide ions, resulting in a pseudo-first-order conditional rate constant k'_b

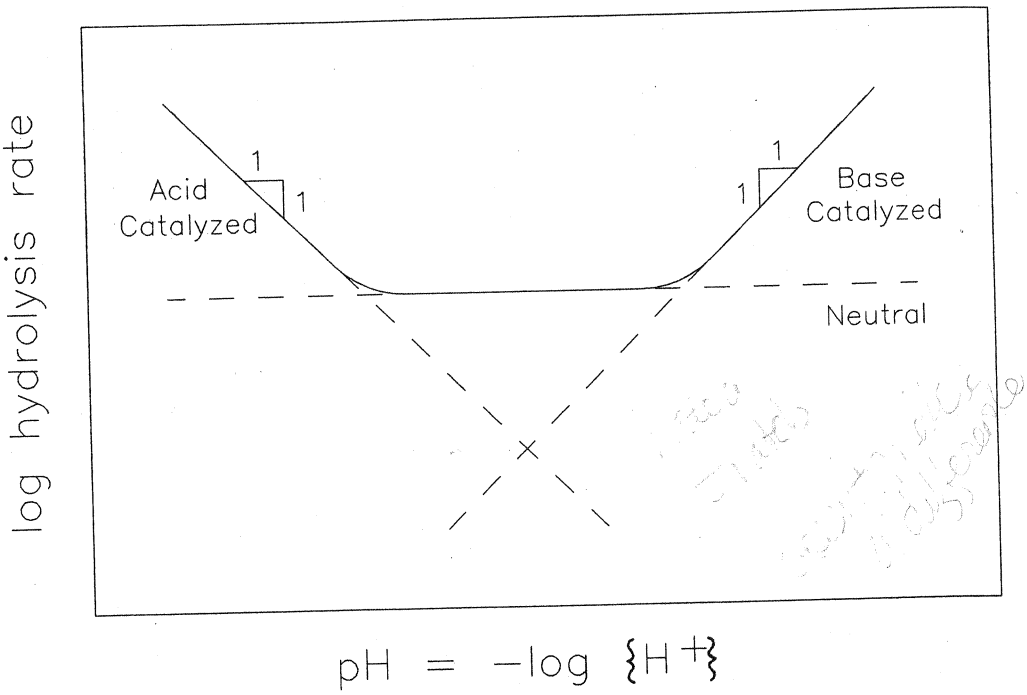


FIGURE 2-32 Effect of pH on hydrolysis rate. The graph shows, in dashed lines, the rate of each hydrolysis process (acid-catalyzed, neutral, and base-catalyzed) as it varies with pH. Because reaction rates are proportional to $[H^+]$ and $[OH^-]$ for the acid-catalyzed and base-catalyzed reactions, respectively, the slopes of the log (rate) versus pH lines for acid-catalyzed and base-catalyzed hydrolysis are -1 and $+1$, respectively.

that is valid only for that particular pH:

$$k'_b = k_b \cdot [OH^-]. \qquad [2\text{-}84]$$

A parallel treatment applies for hydrolysis when reaction with the hydrogen ion is rate controlling *(acid-catalyzed hydrolysis)*. In this case, $k'_a = k_a \cdot [H^+]$. Pseudo-first-order rate constants, such as k'_a and k'_b, can only be used as first-order rate constants as long as the pH is constant.

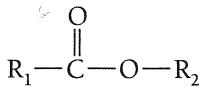
Hydrolysis by all three mechanisms can occur simultaneously and independently for some classes of compounds such as esters (Fig. 2-32); therefore, it is possible to define an overall conditional pseudo-first-order rate constant k'_T,

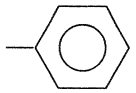
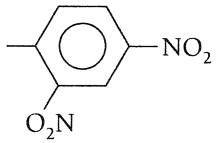
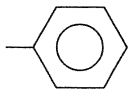
$$k'_T = k'_n + k'_b + k'_a = k'_n + k_b \cdot [OH^-] + k_a \cdot [H^+]. \qquad [2\text{-}85]$$

Hydrolysis rate constants are tabulated for many chemicals; a few are listed in Table 2-13. In certain environments, hydrolysis can be accelerated by microbial catalysis.

TABLE 2-13 Hydrolysis Rates for Some Esters and Six Ester Analogs[a]

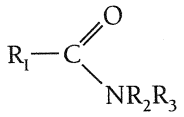
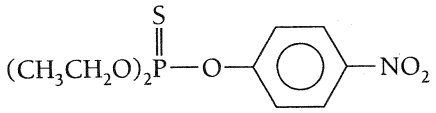
Compound



R_1	R_2	k_a ($M^{-1}sec^{-1}$)	k'_n (sec^{-1})	k_b ($M^{-1}sec^{-1}$)	$t_{1/2}$ (pH 7)
CH_3—	—CH_2CH_3	1.1×10^{-4}	1.5×10^{-10}	1.1×10^{-1}	2 years
CH_3—	—$C(CH_3)_3$	1.3×10^{-4}		1.5×10^{-3}	140 years
CH_3—	—$CH{=}CH_2$	1.4×10^{-4}	1.1×10^{-7}	1.0×10^{1}	7 days
CH_3—		7.8×10^{-5}	6.6×10^{-8}	1.4×10^{0}	38 days
CH_3—			1.1×10^{-5}	9.4×10^{1}	10 hr
CH_2Cl—	—CH_3	8.5×10^{-5}	2.1×10^{-7}	1.4×10^{2}	14 hr
$CHCl_2$—	—CH_3	2.3×10^{-4}	1.5×10^{-5}	2.8×10^{3}	40 min
$CHCl_2$—			1.8×10^{-3}	1.3×10^{4}	4 min

(*continues*)

TABLE 2-13 (*continued*)

Compound						
						
R_1	R_2	R_3	k_a ($M^{-1}sec^{-1}$)	k_n' (sec^{-1})	k_b ($M^{-1}sec^{-1}$)	$t_{1/2}$ (pH 7)
CH_3—	—H	—H	8.4×10^{-6}		4.7×10^{-5}	4000 years
CH_2Cl—	—H	—H	1.1×10^{-5}		1.5×10^{-1}	1.5 years
CH_3—	—CH_3	—H	3.2×10^{-7}		5.5×10^{-6}	40,000 years
CH_3—	—CH_3	—CH_3	5.2×10^{-7}		1.1×10^{-5}	20,000 years
Parathion				8.3×10^{-8}	5.7×10^{-2}	89 days
Disulfoton[b]				1.4×10^{-7}	2.0×10^{-3}	57 days

[a] Adapted from Schwarzenbach *et al.* (1993). All rates at 25°C except where otherwise noted.
[b] Rate measured at 20°C.

EXAMPLE 2-24

Ethyl acetate is spilled at an industrial site and runs into a pond, where it accumulates to a concentration of approximately 20 ppb. Assuming the water pH is 6 and hydrolysis is the only degradation process acting to diminish the concentration, what is the half-life of ethyl acetate?

From Table 2-13, $k_a = 1.1 \times 10^{-4}/(M \cdot \text{sec})$, $k'_n = 1.5 \times 10^{-10}/\text{sec}$, and $k_b = 1.1 \times 10^{-1}/(M \cdot \text{sec})$.

The overall rate constant from Eq. [2-85] is

$$k'_T = [1.5 \times 10^{-10} + (1.1 \times 10^{-1})(10^{-8}) + (1.1 \times 10^{-4})(10^{-6})]/\text{sec}$$

$$k'_T = 1.4 \times 10^{-9}/\text{sec} \quad \text{or} \quad 0.043/\text{year}$$

Use Eq. [1-20] to obtain:

$$t_{1/2} = 0.693/k_T = 16 \text{ years.}$$

2.8 CONCLUSION

Despite their enormous variability, surface waters share many common features, including an interface with the atmosphere, a sediment layer capable of both retaining and releasing chemicals, active communities of living organisms, and the presence of sunlight. Through knowledge of these and other aspects of surface waters, it is possible to make reasonable judgments about the expected behavior of individual chemicals in specific surface water ecosystems.

In the following chapter, the subsurface environment is discussed. In many respects the subsurface environment is radically different from rivers, lakes, and estuaries; yet, numerous analogies with surface waters can be drawn. Readers are urged to make their own comparisons between these two media, as an aid to fully appreciating the fundamental physical, chemical, and biological processes that govern the fate and transport of chemicals in each medium.

EXERCISES

2 - 1. On August 10, 1992, at 1535, a pulse injection of food-grade table salt (sodium chloride, NaCl) was made at a point on an experimental stream in the Bickford watershed (see Fig. 2-2) in central Massachusetts. The molarity of chloride as a function of time was measured at "site 1" 20 m downstream.