Transport and Fate of Toxicants in the Environment

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27.1 INTRODUCTION

More than 100,000 chemicals are released into the global environment every year through their normal production, use, and disposal. To understand and predict the potential risk that this environmental contamination poses to humans and wildlife, we must couple our knowledge on the toxicity of a chemical to our knowledge on how chemicals enter into and behave in the environment. The simple box model shown in Figure 27.1 illustrates the relationship between a toxicant source, its fate in the environment, its effective exposure or dose, and resulting biological effects. A *prospective* or *predictive* assessment of a chemical hazard would begin by characterizing the source of contamination, modeling the chemical's fate to predict exposure, and using exposure/dose-response functions to predict effects (moving from left to right in Figure 27.1). A common application would be to assess the potential effects of a new waste discharge. A *retrospective* assessment would proceed in the opposite direction starting with some observed effect and reconstructing events to find a probable cause. Assuming that we have reliable dose/exposure-response functions, the key to successful use of this simple relationship is to develop a qualitative description and quantitative model of the sources and fate of toxicants in the environment.

Toxicants are released into the environment in many ways, and they can travel along many pathways during their lifetime. A toxicant present in the environment at a given point in time and space can experience three possible outcomes: it can be *stationary* and add to the toxicant inventory and exposure at that location, it can be *transported* to another location, or it can be *transformed* into another chemical species. Environmental contamination and exposure resulting from the use of a chemical is modified by the transport and transformation of the chemical in the environment. Dilution and degradation can attenuate the source emission, while processes that focus and accumulate the chemical can magnify the source emission. The actual fate of a chemical depends on the chemical's use pattern and physical-chemical properties, combined with the characteristics of the environment to which it is released.

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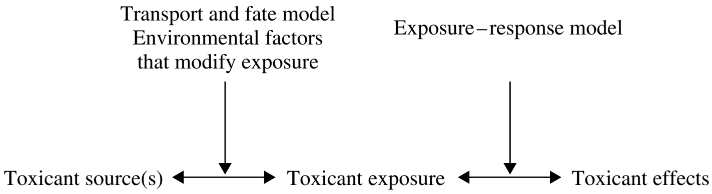


Figure 27.1 Environmental fate model. Such models are used to help determine how the environment modifies exposure resulting from various sources of toxicants.

Conceptually and mathematically, the transport and fate of a toxicant in the environment is very similar to that in a living organism. Toxicants can enter an organism or environmental system by many routes (e.g., dermal, oral, and inhalation versus smoke stack, discharge pipe, or surface runoff). Toxicants are redistributed from their point of entry by fluid dynamics (blood flow vs. water or air movement) and intermedia transport processes such as partitioning (blood-lipid partitioning vs. water-soil partitioning) and complexation (protein binding vs. binding to natural organic matter). Toxicants are transformed in both humans and the environment to other chemicals by reactions such as hydrolysis, oxidation, and reduction. Many enzymatic processes that detoxify and activate chemicals in humans are very similar to microbial biotransformation pathways in the environment.

In fact, physiologically based pharmacokinetic models are similar to environmental fate models. In both cases we divide a complicated system into simpler compartments, estimate the rate of transfer between the compartments, and estimate the rate of transformation within each compartment. The obvious difference is that environmental systems are inherently much more complex because they have more routes of entry, more compartments, more variables (each with a greater range of values), and a lack of control over these variables for systematic study. The discussion that follows is a general overview of the transport and transformation of toxicants in the environment in the context of developing qualitative and quantitative models of these processes.

27.2 SOURCES OF TOXICANTS TO THE ENVIRONMENT

Environmental sources of toxicants can be categorized as either *point sources* or *nonpoint sources* (Figure 27.2). Point sources are discrete discharges of chemicals that are usually identifiable and measurable, such as industrial or municipal effluent outfalls, chemical or petroleum spills and dumps, smokestacks and other stationary atmospheric discharges. Nonpoint sources are more diffuse inputs over large areas with no identifiable single point of entry such as agrochemical (pesticide and fertilizer) runoff, mobile sources emissions (automobiles), atmospheric deposition, desorption or leaching from very large areas (contaminated sediments or mine tailings), and groundwater inflow. Nonpoint sources often include multiple smaller point sources, such as septic tanks or automobiles, that are impractical to consider on an individual basis. Thus the identification and characterization of a source is relative to the environmental compartment or system being considered. For example, there may be dozens of important toxicant sources to a river, each must be considered when assessing the hazards of toxicants to aquatic life in the river or to humans who might drink the water or consume the

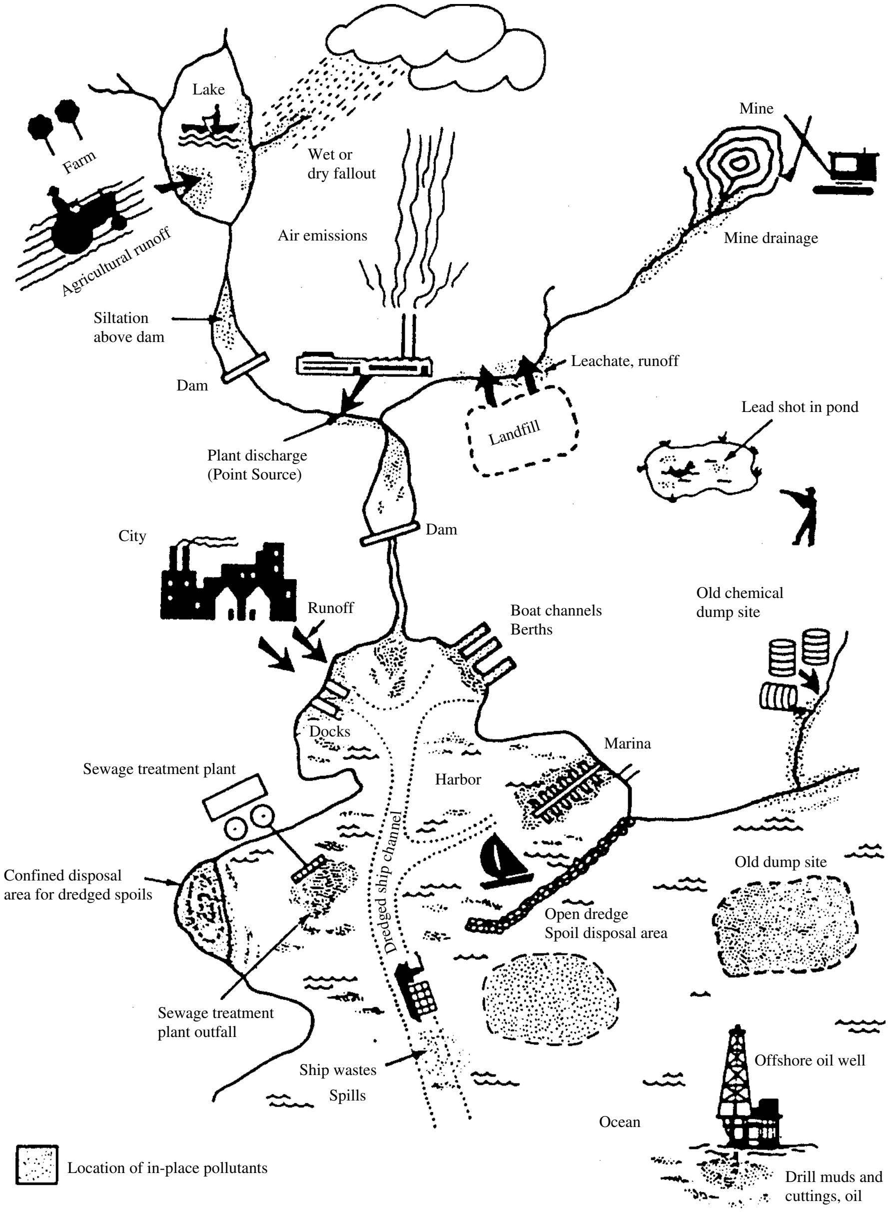


Figure 27.2 Entry of toxicants into environment through many point and nonpoint sources.

fish and shellfish. However, these toxicant sources can be well mixed in the river, resulting in a rather homogeneous and large point source to a downstream lake or estuary (Figure 27.2).

The rate (units of g/h) at which a toxicant is emitted by a source (*mass emission rate*) can be estimated from the product of the toxicant concentration in the medium (g/m^3) and the flow rate of the medium (m^3/h). This would appear to be relatively simple for point sources, particularly ones that are routinely monitored to meet environmental regulations. However, the measurement of trace concentrations of chemicals in complex effluent matrices is not a trivial task (see Chapter 25). Often the analytical methods prescribed by environmental agencies for monitoring are not sensitive or selective enough to measure important toxicants or their reactive metabolites. Estimating the mass emission rates for nonpoint sources is usually very difficult. For example, the atmospheric deposition of toxicants to a body of water can be highly dependent on both space and time, and high annual loads can result from continuous deposition of trace concentrations that are difficult to measure. The loading of pesticides from an agricultural field to an adjacent body of water also varies with time and space as shown in Figure 27.3 for the herbicide atrazine. Rainfall following the application of atrazine results in drainage ditch loadings more than 100-fold higher than just two weeks following the rain. A much smaller, but longer lasting, increase in atrazine loading occurs at the edge of the field following the rain. Again, we see the need to define the spatial scale of concern when identifying and characterizing a source. If one is concerned with the fate of atrazine within a field, the source is defined by the application rate. If one is concerned with the fate and exposure of atrazine in an adjacent body of water, the source may be defined as the drainage ditch and/or as runoff from the edge of field. In the latter case one either needs to take appropriate measurements in the field or model the transport of atrazine from the field.

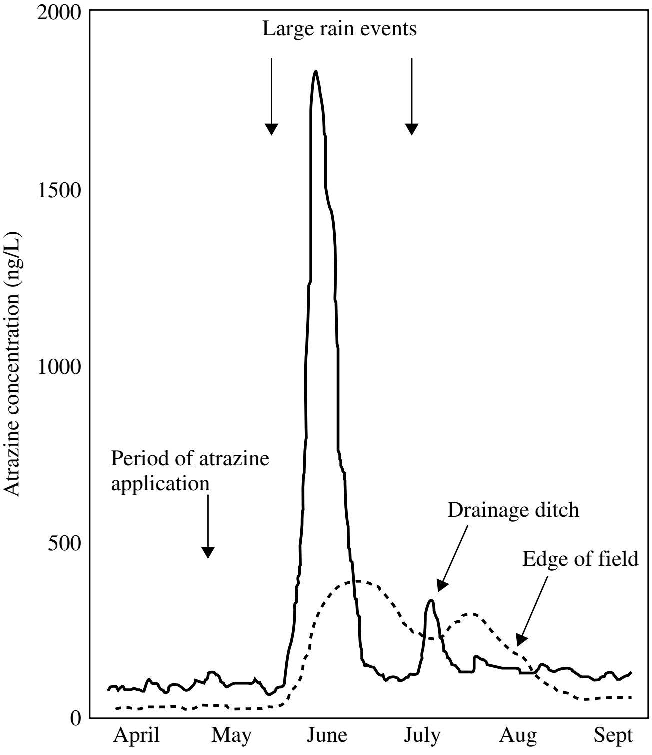


Figure 27.3 Loading of atrazine from an agricultural field to an adjacent body of water. The loading is highly dependent on rainfall and the presence of drainage ditches that collect the chemical and focus its movement in the environment.

27.3 TRANSPORT PROCESSES

Following the release of a toxicant into an environmental compartment, transport processes will determine its spatial and temporal distribution in the environment. The transport medium (or fluid) is usually either air or water, while the toxicant may be in dissolved, gaseous, condensed, or particulate phases. We can categorize physical transport as either *advection* or *diffusion*.

27.3.1 Advection

Advection is the passive movement of a chemical in bulk transport media either within the same medium (intraphase or homogeneous transport) or between different media (interphase or heterogeneous transport). Examples of homogeneous advection include transport of a chemical in air on a windy day or a chemical dissolved in water moving in a flowing stream, in surface runoff (nonpoint source), or in a discharge effluent (point source). Examples of heterogeneous advection include the deposition of a toxicant sorbed to a suspended particle that settles to bottom sediments, atmospheric deposition to soil or water, and even ingestion of contaminated particles or food by an organism (i.e., bioaccumulation). Advection takes place independently from the presence of a chemical; the chemical is simply going along for the ride. Advection is not influenced by diffusion and can transport a chemical either in the same or opposite direction as diffusion. Thus advection is often called *nondiffusive transport.*

Homogeneous Advection. The homogeneous advective transport rate (N, g/h) is simply described in mathematical terms by the product of the chemical concentration in the advecting medium (C, g/m^3) and the flow rate of the medium (G, m^3/h):

$$N = GC.$$

For example, if the flow of water out of a lake is 1000 m^3/h and the concentration of the toxicant is 1 μg/m^3, then the toxicant is being advected from the lake at a rate of 1000 μg/h (or 1 mg/h). The emission rates for many toxicant sources can be calculated in the same way.

As with source emissions, advection of air and water can vary substantially with time and space within a given environmental compartment. Advection in a stream reach might be several orders of magnitude higher during a large rain event compared to a prolonged dry period, while at one point in time, advection within a stagnant pool might be several orders of magnitude lower than a connected stream. Thus, as with source characterization, we must match our estimates of advective transport to the spatial and temporal scales of interest. Again, a good example is the movement of atrazine from an agricultural field (Figure 27.3). Peak flow advective rates that follow the rain might be appropriate for assessing acute toxicity during peak flow periods but not for estimating exposure at other times of the year. Conversely, an annual mean advective rate would underestimate exposure during peak flow but would be more appropriate for assessing chronic toxicity.

In surface waters advective currents often dominate the transport of toxicants, and they can be estimated from hydrodynamic models or current measurements. In many cases advective flow can be approximated by the volume of water exchanged per unit time by assuming conservation of mass and measuring flow into or out of the system. This works only for well mixed systems that have no or only small volumes of stagnant water. In water bodies that experience density stratification (i.e., thermocline) separate advective models or residence times can be used for each water layer. In air, advection also dominates the transport of chemicals, with air currents being driven by pressure gradients. The direction and magnitude of air velocities are recorded continuously in many areas, and daily, seasonal, or annual means can be used to estimate advective air flow.

Advective air and water currents are much smaller in soil systems but still influence the movement of chemicals that reside in soil. Advection of water in the saturated zone is usually solved numerically from hydrodynamic models. Advection of air and water in the unsaturated zone is complicated by the heterogeneity of these soil systems. Models are usually developed for specific soil property classes, and measurements of these soil properties are made at a specific site to determine which soil-model layers to link together.

Heterogeneous Advection. Heterogeneous advective transport involves a secondary phase within the bulk advective phase, such as when a particle in air or water acts as a carrier of a chemical. In many cases we can treat heterogeneous advection the same as homogeneous advection if we know the flow rate of the secondary phase and the concentration of chemical in the secondary phase. In the lake example above, if the volume fraction of suspended particles in the lake water is 10^{-5}, the flow rate of suspended particles is 0.01 m^3/h, and the concentration of the toxicant in the solid particles is 100 mg/m^3, then the advective flow of the toxicant on suspended particles will be 1 mg/h or the same as the homogeneous advection via water. Although the flow rate of particles is much lower than that of water, the concentration of the toxicant is much higher in the suspended particles than dissolved in the water. This is typical of a hydrophobic toxicant such as DDT or benzo[a]pyrene. In soil and sedimentary systems, colloidal particles (often macromolecular detritus) can play a very important role in heterogeneous advective transport because they have greater mobility than larger particles, and they often have greater capacity to sorb many toxicants because of their higher organic carbon content and higher surface area/mass ratio. In highly contaminated sites, organic co-solvents can be present in the water (usually groundwater) and act as a high-capacity and high-efficiency carrier of toxicants through heterogeneous advection in the water.

Unfortunately, the dynamics of heterogeneous transport are rarely simple, particularly over shorter scales of time and space. In addition to advection of particles with flowing water, aqueous phase heterogeneous transport includes particle settling, resuspension, burial in bottom sediments, and mixing of bottom sediments. Particle settling can be an important mechanism for transporting hydrophobic toxicants from the water to the bottom sediments. Modeling this process can be as simple as using an overall mass transfer coefficient or can include rigorous modeling of particles with different size, density, and organic carbon content. Estimates of particle settling are usually obtained through the use of laboratory settling chambers, in situ sediment traps, or by calculation using Stoke's law. Resuspension of bottom sediments occurs when sufficient energy is transferred to the sediment bed from advecting water, internal waves, boats, dredging, fishing, and the movement of sediment dwelling organisms (i.e., bioturbation). Resuspension rates are difficult to measure and often are highly variable in both time and space. Much as the annual runoff of pesticides from an agricultural field may be dominated by a few rain events, annual resuspension rates can be dominated by a major storm, and in smaller areas by a single boat or school of bottom fish. Resuspension rates can be estimated from sediment traps deployed just above the sediment surface or from the difference between particle settling and permanent burial or sedimentation. Sedimentation is the net result of particle settling and resuspension and can be measured using radionuclide dating methods (e.g., ^{210}Pb). Sediment dating itself becomes difficult when there is significant mixing of the surface sediments (e.g., through bioturbation). Thus the heterogeneous transport of toxicants on aqueous particles can be rather complicated, though many aquatic systems have been modeled reasonably well.

Heterogeneous advective transport in air occurs primarily through the absorption of chemicals into falling water droplets (wet deposition) or the sorption of chemicals into solid particles that fall to earth's surface (dry deposition). Under certain conditions both processes can be treated as simple first-order advective transport using a flow rate and concentration in the advecting medium. For example, wet deposition is usually characterized by a washout coefficient that is proportional to rainfall intensity.

27.3.2 Diffusion

Diffusion is the transport of a chemical by random motion due to a state of disequilibrium. For example, diffusion causes the movement of a chemical within a phase (e.g., water) from a location of relatively high concentration to a place of lower concentration until the chemical is homogeneously distributed throughout the phase. Likewise diffusive transport will drive a chemical between media (e.g., water and air) until their equilibrium concentrations are reached and thus the chemical potentials or fugacities are equal in each phase.

Diffusion within a Phase. Diffusional transport within a phase can result from random (thermal) motion of the chemical (molecular diffusion), the random turbulent mixing of the transport medium (turbulent diffusion), or a combination of both. Turbulent diffusion usually dominates the diffusive (but not necessarily the advective) chemical transport in air and water due to the turbulent motions or eddies that are common in nature. In porous media (sediment and soil) the water velocities are typically too low to create eddies, but random mixing still occurs as water tortuously flows around particles. This mechanical diffusion is often called dispersion by hydrologists and dispersion on larger scales, such as when groundwater detours around large areas of less permeable soil, is called macrodispersion. Note, however, that the term dispersion often is used by meteorologists and engineers to describe any turbulent diffusion.

Although different physical mechanisms can cause diffusive mixing, they all cause a net transport of a chemical from areas of higher concentration to areas of lower concentration. All diffusive processes are also referred to as *Fickian* transport because they all can be described mathematically by Fick's first law, which states that the flow (or flux) of a chemical (N, g/h) is proportional to its concentration gradient (dC/dx):

$$N = -DA\left(\frac{dC}{dx}\right),$$

where D is the diffusivity or mass transfer coefficient (m^2/h), A is the area through which the chemical is passing (m^2), C is the concentration of the diffusing chemical (g/m^3), and x is the distance being considered (m). The negative sign is simply the convention that the direction of diffusion is from high to low concentration (diffusion is positive when dC/dx is negative). Note that many scientists and texts define diffusion as an area specific process with units of g/m^2h and thus the area term (A) is not included in the diffusion equation. This is simply an alternative designation that describes transport as a flux density (g/m^2h) rather than as a flow (g/h). In either case the diffusion equation can be integrated numerically and even expressed in three dimensions using vector notation. However, for most environmental situations we usually have no accurate estimate of D or dx, so we combine the two into a one-dimensional mass transfer coefficient (k_M) with units of velocity (m/h). The chemical flux is then the product of this velocity, area, and concentration:

$$N = -k_M AC.$$

Mass transfer coefficients can be estimated from laboratory, mesocosm, and field studies and are widely used in environmental fate models. Mass transfer coefficients can be derived separately for molecular diffusion, turbulent diffusion, and dispersion in porous media, and all three terms can be added to the chemical flux equation. This is usually not necessary because one term often dominates the transport in specific environmental regions. Consider the vertical diffusion of methane gas generated by methanogenic bacteria in deep sediments. Molecular diffusion dominates in the highly compacted and low porosity deeper sediments. Dispersion becomes important as methane approaches the more porous surface sediments. Following methane gas ebulation from the sediment porewater, turbulent diffusion will dominate transport in a well-mixed water column (i.e., not a stagnant pool or beneath a thermocline where molecular diffusion will dominate). At the water surface, eddies tend to be damped and molecular diffusion may again dominate transport. Under stagnant atmospheric conditions (i.e., a temperature inversion) molecular diffusion will continue to dominate but will yield to more rapid mixing when typical turbulent conditions are reached. The magnitude and variability of the transport rate generally increase as the methane moves vertically through the environment, except when very stagnant conditions are encountered in the water or air. Modeling the transport of a chemical in air is particularly difficult because of the high spatial and temporal variability of air movement. Note also that advective processes in water or air usually transport chemicals at a faster rate than either molecular or turbulent diffusion.

Diffusion between Phases. The transport of a chemical between phases is sometimes treated as a third category of transport processes or even as a transformation reaction. Interphase or intermedia transport is not a transformation reaction because the chemical is moving only between phases; it is not reacting with anything or changing its chemical structure. Instead, intermedia transport is simply driven by diffusion between two phases. When a chemical reaches an interface such as air–water, particle–water, or (biological) membrane–water, two diffusive regions are created at either side of the interface. The classical description of this process is the Whitman two-film or two-resistance mass transfer theory, where chemicals pass through two stagnant boundary layers by molecular diffusion, while the two bulk phases are assumed to be homogeneously mixed. This allows us to use a first-order function of the concentration gradient in the two phases, where the mass transfer coefficient will depend only on the molecular diffusivity of the chemical in each phase and the thickness of the boundary layers. This is fairly straightforward for transfer at the air–water interface (and often at the membrane–water interface), but not for the particle–water or particle–air interfaces.

Diffusive transport between phases can be described mathematically as the product of the departure from equilibrium and a kinetic term:

$$N = kA(C_1 - C_2K_{12}),$$

where N is the transport rate (g/h), k is a transport rate coefficient (m/h), A is the interfacial area (m^2), C_1 and C_2 are the concentrations in the two phases, and K_{12} is the equilibrium partition coefficient. At equilibrium K_{12} equals C_1/C_2, the term describing the departure from equilibrium $(C_1 - C_2K_{12})$ becomes zero, and thus the net rate of transfer also is zero. The partition coefficients are readily obtained from thermodynamic data and equilibrium partitioning experiments. The transport rate coefficients are usually estimated from the transport rate equation itself by measuring intermedia transport rates (N) under controlled laboratory conditions (temperature, wind and water velocities) at known values of A, C_1, C_2, and K_{12}. These measurements must then be extrapolated to the field, sometimes with great uncertainty. This uncertainty, along with the knowledge that many interfacial regions have reached or are near equilibrium, has led many to simply assume that equilibrium exists at the interface. Thus the net transport rate is zero and the phase distribution of a chemical is simply described by its equilibrium partition coefficient.

27.4 EQUILIBRIUM PARTITIONING

When a small amount of a chemical is added to two immiscible phases and then shaken, the phases will eventually separate and the chemical will partition between the two phases according to its solubility in each phase. The concentration ratio at equilibrium is the partition coefficient:

$$\frac{C_1}{C_2} = K_{12}.$$

In the laboratory, we usually determine K_{12} from the slope of C_1 versus C_2 over a range of concentrations. Partition coefficients can be measured for essentially any two-phase system: air–water, octanol–water, lipid–water, particle–water, and so on. In situ partition coefficients also can be measured where site-specific environmental conditions might influence the equilibrium phase distribution.

27.4.1 Air–Water Partitioning

Air–water partition coefficients ($K_{\text{air-water}}$) are essentially Henry's law constants (H):

$$K_{\text{air-water}} = H = \frac{C_{\text{air}}}{C_{\text{water}}},$$

where H can be expressed in dimensionless form (same units for air and water) or in units of pressure divided by concentration (e.g., Pa m^3/mol). The latter is usually written as

$$H = \frac{P_{\text{air}}}{C_{\text{water}}},$$

where P_{air} is the partial vapor pressure of the chemical. When H is not measured directly, it can be estimated from the ratio of the chemical's vapor pressure and aqueous solubility, although one must be careful about using vapor pressures and solubilities that apply to the same temperature and phase. Chemicals with high Henry's law constants (e.g., alkanes and many chlorinated solvents) have a tendency to escape from water to air and typically have high vapor pressures, low aqueous solubilities, and low boiling points. Chemicals with low Henry's law constants (e.g., alcohols, chlorinated phenols, larger polycyclic aromatic hydrocarbons, lindane, atrazine) tend to have high water solubility and/or very low vapor pressure. Note that some chemicals that are considered to be "nonvolatile," such as DDT, are often assumed to have low Henry's law constants. However, DDT also has a very low water solubility yielding a rather high Henry's law constant. Thus DDT readily partitions into the atmosphere as is now apparent from the global distribution of DDT.

27.4.2 Octanol–Water Partitioning

For many decades chemists have been measuring the octanol–water partition coefficient (K_{OW}) as a descriptor of hydrophobicity or how much a chemical "hates" to be in water. It is now one of the most important and frequently used physicochemical properties in toxicology and environmental chemistry. In fact toxicologists often simply use the symbol P, for partition coefficient, as if no other partition coefficient is important. Strong correlations exist between K_{OW} and many biochemical and toxicological properties. Octanol has a similar carbon:oxygen ratio as lipids, and the K_{OW} correlates particularly well with lipid–water partition coefficients. This has led many to use K_{OW} as a measure of lipophilicity or how much a chemical "loves" lipids. This is really not the case because most chemicals have an equal affinity for octanol and other lipids (within about a factor of ten), but their affinity for water varies by many orders of magnitude. Thus it is largely aqueous solubility which determines K_{OW} not octanol or lipid solubility. We generally express K_{OW} as log K_{OW} because K_{OW} values range from less than one (alcohols) to over one billion (larger alkanes and alkyl benzenes).

27.4.3 Lipid–Water Partitioning

In most cases we can assume that the equilibrium distribution and partitioning of organic chemicals in both mammalian and nonmammalian systems is a function of lipid content in the animal and that the lipid–water partition coefficient (K_{LW}) is equal to K_{OW}. Instances where this is not the case include specific binding sites (e.g., kepone in the liver) and nonequilibrium conditions caused by slow elimination rates of higher level organisms or structured lipid phases that sterically hinder accumulation of very hydrophobic chemicals. For aquatic organisms in constant contact with water, the bioconcentration factor or fish-water partition coefficient (K_{FW}) is simply:

$$K_{\text{FW}} = f_{\text{lipid}} K_{\text{OW}},$$

where f_{lipid} is the mass fraction of lipid in the fish (g lipid/g fish). Several studies have shown this relationship works well for many fish and shellfish species and an aggregate plot of K_{FW} versus K_{OW} for many different fish species yields a slope of 0.048, which is about the average lipid concentration of fish (5%). Again, nonequilibrium conditions will cause deviation from this equation. Such deviations are found at both the top and bottom of the aquatic food chain. Phytoplankton can have higher apparent lipid–water partition coefficients because their large surface area : volume ratios increase the relative importance of surface sorption. Top predators such as marine mammals also have high apparent lipid-water partition coefficients because of very slow elimination rates. Thus the deviations occur not because "there is something wrong with the equation" but because the underlying assumption of equilibrium is not appropriate in these cases.

27.4.4 Particle–Water Partitioning

It has been known for several decades that many chemicals preferentially associate with soil and sediment particles rather than the aqueous phase. The particle–water partition coefficient (K_{P}) describing this phenomenon is

$$K_{\text{P}} = \frac{C_{\text{S}}}{C_{\text{W}}},$$

where C_{S} is the concentration of chemical in the soil or sediment (mg/kg dry weight) and C_{W} is the concentration in water (mg/L). In this form, K_{P} has units of L/kg or reciprocal density. Dimensionless partition coefficients are sometimes used where K_{P} is multiplied by the particle density (in kg/L). It has also been observed, first by pesticide chemists in soil systems and later by environmental engineers and chemists in sewage effluent and sediment systems, that nonionic organic chemicals were primarily associated with the organic carbon phase(s) of particles. A plot of K_{P} versus the mass fraction of organic carbon in the soil (f_{OC}, g/g) is linear with a near-zero intercept yielding the simple relationship

$$K_{\text{P}} = f_{\text{OC}} K_{\text{OC}},$$

where K_{OC} is the organic carbon–water partition coefficient (L/kg). Studies with many chemicals and many sediment/soil systems have demonstrated the utility of this equation when the fraction of organic carbon is about 0.5% or greater. At lower organic carbon fractions, interaction with the mineral phase becomes relatively more important (though highly variable) resulting in a small positive intercept of K_{P} versus f_{OC}. The strongest interaction between organic chemicals and mineral phases appears to be with dry clays. Thus K_{P} will likely change substantially as a function of water content in low organic carbon, clay soils.

Measurements of K_{OC} have been taken directly from partitioning experiments in sediment–and soil–water systems over a range of environmental conditions in both the laboratory and the field. Not surprisingly, the K_{OC} values for many organic chemicals are highly correlated with their K_{OW} values. Plots of the two partition coefficients for hundreds of chemicals with widely ranging K_{OW} values yield slopes from about 0.3 to 1, depending on the classes of compounds and the particular methods included. Most fate modelers continue to use a slope of 0.41, which was reported by the first definitive study on the subject in the early 1980s. Thus we now have a means of estimating the partitioning of a chemical between a particle and water by using the K_{OW} and f_{OC}:

$$K_{\mathrm{P}} = f_{\mathrm{OC}} K_{\mathrm{OC}} = f_{\mathrm{OC}}\ 0.41 K_{\mathrm{OW}}.$$

This relationship is commonly used in environmental fate models to predict aqueous concentrations from sediment measurements by substituting the equilibrium expression for K_{P} and rearranging to solve for C_{W}:

$$K_{\mathrm{P}} = \frac{C_{\mathrm{S}}}{C_{\mathrm{W}}} = f_{\mathrm{OC}}\ 0.41 K_{\mathrm{OW}},$$

$$C_{\mathrm{W}} = \frac{C_{\mathrm{S}}}{f_{\mathrm{OC}} 0.41 K_{\mathrm{OW}}}.$$

This last equation forms the basis for the EPA's sediment quality guidelines that are used to assess the potential toxicity of contaminated sediments. The idea is to simply measure C_{S} and f_{OC}, look up K_{OW} in a table, compute the predicted C_{W}, and compare this result to established water quality criteria for the protection of aquatic life or human life (e.g., carcinogenicity risk factors). The use of this simple equilibrium partitioning expression for this purpose is currently the subject of much debate among scientists as well as policy makers.

27.5 TRANSFORMATION PROCESSES

The potential environmental hazard associated with the use of a chemical is directly related to it's persistence in the environment (see Chapter 26), which in turn depends on the rates of chemical transformation reactions. Transformation reactions can be divided into two classes: reversible reactions that involve continuous exchange among chemical states (ionization, complexation) and irreversible reactions that permanently transform a parent chemical into a daughter or reaction product (photolysis, hydrolysis, and many redox reactions). Reversible reactions are usually abiotic, although biological processes can still exert great influence over them (e.g., via production of complexing agents or a change in pH). Irreversible reactions can be abiotic or mediated directly by biota, particularly bacteria.

27.5.1 Reversible Reactions

Ionization. Ionization refers to the dissociation of a neutral chemical into charged species. The most common form of neutral toxicant dissociation is acid-base equilibria. The hypothetical monoprotic acid, HA, will dissociate in water to form the conjugate acid-base pair (H^+, A^-) usually written as

$$\mathrm{HA} + \mathrm{H_2O} = \mathrm{H_3O^+} + \mathrm{A^-}.$$

The equilibrium constant for this reaction, the acidity constant (K_a), is defined by the law of mass action and is given by

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}.$$

For convenience we often express equilibrium constants as the negative logarithm, or pK value. Thus the relative proportion of the neutral and charged species, will be a function of the pKa and solution pH. When the pH is equal to pKa, equal concentrations of the neutral and ionized forms will be present. When pH is less than the pKa, the neutral species will be predominant; when pH is greater than pKa, the ionized species will be in excess. The exact equilibrium distribution can be calculated from the equilibrium expression above and the law of mass conservation.

The fate of a chemical is often a function of the relative abundance of a particular chemical species as well as the total concentration. For example, the neutral chemical might partition into biological lipids or organic carbon in soil to a greater extent than the ionized form. Many acidic toxicants (pentachlorophenol) exhibit higher toxicities to aquatic organisms at lower pH where the neutral species predominates. However, specific ionic interactions will take place only with the ionized species. A classic example of how pH influences the fate and effects of a toxicant is with hydrogen cyanide. The pKa of HCN is about 9 and the toxicity of CN^- is much higher than that of HCN for many aquatic organisms. Thus the discharge of a basic (high pH) industrial effluent containing cyanide would pose a greater hazard to fish than a lower pH effluent (everything else being equal). The effluent could be treated to reduce the pH well below the pKa according to the reaction:

$$\mathrm{CN^- + H^+ = HCN_{(aq)}},$$

thus reducing the hazard to the fish. However, HCN has a rather high Henry's law constant and will partition into the atmosphere:

$$\mathrm{HCN_{(aq)} = HCN_{(air)}}.$$

This may be fine for the fish, but birds in the area and humans working at the industrial plant will now have a much greater exposure to HCN. Thus both the fate and toxicity of a chemical can be influenced by simple ionization reactions.

Precipitation and Dissolution. A special case of ionization is the dissolution of a neutral solid phase into soluble species. For example, the binary solid metal sulfide, CuS, dissolves in water according to

$$\mathrm{CuS(s) + H^+ = Cu^{2+} + HS^-}.$$

The equilibrium constant for this reaction, the solubility product (K_{sp}), is given by

$$K_{sp} = \frac{[\mathrm{Cu^{2+}}][\mathrm{HS^-}]}{[\mathrm{H^+}]}.$$

The solubility product for CuS is very low ($K_{sp} = 10^{-19}$ as written) so that the presence of sulfide in water acts to immobilize Cu (and many other metals) and reduce effective exposure. The formation of metal sulfides is important in anaerobic soil and sediment, stagnant ponds and basins, and many industrial and domestic sewage treatment plants and discharges. Co-precipitation of metals also can be a very important removal process in natural waters. In aerobic systems, the precipitation of hydrous oxides of manganese and iron often incorporate other metals as impurities. In anaerobic systems, the precipitation of iron sulfides can include other metals as well. These co-precipitates are usually not thermodynamically stable, but their conversion to stable mineral phases often takes place on geological time scales.

Complexation and Chemical Speciation. Natural systems contain many chemicals that undergo ionic or covalent interactions with toxicants to change toxicant speciation and chemical speciation can have a profound effect on both fate and toxicity. Again, in the case of copper, inorganic ions (Cl^-, OH^-) and organic detritus (humic acids, peptides) will react with dissolved Cu^{2+} to form various metal-ligand complexes. Molecular diffusivities of complexed copper will be lower than uncomplexed (hydrated) copper and will generally decrease with the size and number of ligands. The toxicity of free, uncomplexed Cu^{2+} to many aquatic organisms is much higher than Cu^{2+} that is complexed to chelating agents such as EDTA or glutathione. Many transition metal toxicants, such as Cu, Pb, Cd, and Hg, have high binding constants with compounds that contain amine, sulfhydryl, and carboxylic acid groups. These groups are quite common in natural organic matter. Even inorganic complexes of OH^- and Cl^- reduce Cu^{2+} toxicity. In systems where a mineral phase is controlling Cu^{2+} solubility, the addition of these complexing agents will shift the solubility equilibrium according to LeChatelier's principle as shown here for CuS and OH^-, Cl^-, and GSH (glutathione):

$$\begin{aligned} &\mathrm{CuS(s)} + \mathrm{H^+} = \mathrm{Cu^{2+}} + \mathrm{HS^-}, && K_{\mathrm{sp}}, \\ &\mathrm{Cu^{2+}} + \mathrm{OH^-} = \mathrm{CuOH^+}, && K_{\mathrm{CuOH}}, \\ &\mathrm{Cu^{2+}} + \mathrm{Cl^-} = \mathrm{CuCl^+}, && K_{\mathrm{CuCl}}, \\ &\mathrm{Cu^{2+}} + \mathrm{GSH} = \mathrm{CuGS^+} + \mathrm{H^+}, && K_{\mathrm{CuGS}}. \end{aligned}$$

Each successive complexation reaction "leaches" Cu^{2+} from the solid mineral phase, thereby increasing the total copper in the water but not affecting the concentration of (or exposure to) Cu^{2+}. These equilibria can be combined into one reaction:

$$\begin{aligned} 4\mathrm{CuS(s)} + 3\mathrm{H^+} + \mathrm{OH^-} + \mathrm{Cl^-} + \mathrm{GSH} = {} & \mathrm{Cu^{2+}} + 4\mathrm{HS^-} \\ & + \mathrm{CuOH^+} + \mathrm{CuCl^+} + \mathrm{CuGS^+}, \end{aligned}$$

and the overall equilibrium constant derived as shown:

$$\begin{aligned} K_{\mathrm{overall}} &= (4)K_{\mathrm{sp}} \times K_{\mathrm{CuOH}} \times K_{\mathrm{CuCl}} \times K_{\mathrm{CuGS}} \\ &= [\mathrm{Cu^{2+}}]\ [\mathrm{CuOH^+}]\ [\mathrm{CuCl^+}]\ [\mathrm{CuGS^+}]\ [\mathrm{HS^-}]^4/[\mathrm{H^+}]^3\ [\mathrm{OH^-}]\ [\mathrm{Cl^-}]\ [\mathrm{GS^-}]. \end{aligned}$$

A series of simultaneous equations can be derived for these reactions to compute the concentration of individual copper species, and the total concentration of copper, $[\mathrm{Cu}]_\mathrm{T}$, would be given by

$$[\mathrm{Cu}]_\mathrm{T} = [\mathrm{Cu^{2+}}] + [\mathrm{CuOH^+}] + [\mathrm{CuCl^+}] + [\mathrm{CuGS^+}].$$

Thus the total copper added to a toxicity test or measured as the exposure (e.g., by atomic absorption spectroscopy) may be much greater than that which is available to an organism to induce toxicological effects.

Literally hundreds of complex equilibria like this can be combined to model what happens to metals in aqueous systems. Numerous speciation models exist for this application that include all of the necessary equilibrium constants. Several of these models include surface complexation reactions that take place at the particle–water interface. Unlike the partitioning of hydrophobic organic contaminants into organic carbon, metals actually form ionic and covalent bonds with surface ligands such as sulfhydryl groups on metal sulfides and oxide groups on the hydrous oxides of manganese and iron. Metals also can be biotransformed to more toxic species (e.g., conversion of elemental mercury to methyl-mercury by anaerobic bacteria), less toxic species (oxidation of tributyl tin to elemental tin), or temporarily immobilized (e.g., via microbial reduction of sulfate to sulfide, which then precipitates as an insoluble metal sulfide mineral).

27.5.2 Irreversible Reactions

The reversible transformation reactions discussed above alter the fate and toxicity of chemicals, but they do not irreversibly change the structure or properties of the chemical. An acid can be neutralized to its conjugate base, and vice versa. Copper can precipitate as a metal sulfide, dissolve and from a complex with numerous ligands, and later re-precipitate as a metal sulfide. Irreversible transformation reactions alter the structure and properties of a chemical forever.

Hydrolysis. Hydrolysis is the cleavage of organic molecules by reaction with water with a net displacement of a leaving group (X) with OH^-:

$$RX + H_2O = ROH + HX.$$

Hydrolysis is part of the larger class of chemical reactions called nucleophilic displacement reactions in which a nucleophile (electron-rich species with an unshared pair of electrons) attacks an electrophile (electron deficient), cleaving one covalent bond to form a new one. Hydrolysis is usually associated with surface waters but also takes place in the atmosphere (fogs and clouds), groundwater, at the particle–water interface of soils and sediments, and in living organisms.

Hydrolysis can proceed through numerous mechanisms via attack by H_2O (neutral hydrolysis) or by acid (H^+) or base (OH^-) catalysis. Acid and base catalyzed reactions proceed via alternative mechanisms that require less energy than neutral hydrolysis. The combined hydrolysis rate term is a sum of these three constituent reactions and is given by

$$\frac{d[\mathrm{RX}]}{dt} = k_{\mathrm{obs}}[\mathrm{RX}] = k_{\mathrm{a}}[\mathrm{H}^+][\mathrm{RX}] + k_{\mathrm{n}}[\mathrm{RX}] + k_{\mathrm{b}}[\mathrm{OH}^-][\mathrm{RX}],$$

where [RX] is the concentration of the hydrolyzable chemical, k_{obs} is the macroscopic observed hydrolysis rate constant, and k_{a}, k_{n}, and k_{b} are the rate constants for the acid-catalyzed, neutral, and base-catalyzed hydrolysis. If we assume that the hydrolysis can be approximated by first-order kinetics with respect to RX (which is usually true), the rate term is reduced to

$$k_{\mathrm{obs}} = k_{\mathrm{a}}[\mathrm{H}^+] + k_{\mathrm{n}} + k_{\mathrm{b}}[\mathrm{OH}^-].$$

Neutral hydrolysis is dependent only on water which is present in excess, so k_{n} is a simple pseudo-first-order rate constant (with units t^{-1}). The acid- and base-catalyzed hydrolysis depend on the molar quantities of $[H^+]$ and $[OH^-]$, respectively, so k_a and k_b have units of $M^{-1}t^{-1}$.

The observed or apparent hydrolysis half-life at a fixed pH is then given by

$$t_{1/2} = \frac{\ln 2}{k_{obs}}.$$

Compilations of hydrolysis half-lives at pH and temperature ranges encountered in nature can be found in many sources. Reported hydrolysis half-lives for organic compounds at pH 7 and 298 K range at least 13 orders of magnitude. Many esters hydrolyze within hours or days, whereas some organic chemicals will never hydrolyze. For halogenated methanes, which are common groundwater contaminants, half-lives range from about 1 year for CH_3Cl to about 7000 years for CCl_4. The half-lives of halomethanes follows the strength of the carbon-halogen bond with half-lives decreasing in the order $F > Cl > Br$. Small structural changes can dramatically alter hydrolysis rates. An example is the difference between tetrachloroethane ($Cl_2HC–CHCl_2$) and tetrachloroethene ($Cl_2C{=}CCl_2$) which have hydrolysis half-lives of about 0.5 year and 10^9 years, respectively. In this case the hydrolysis rate is affected by the C–Cl bond strength and the steric bulk at the site of nucleophilic substitution.

The apparent rate of hydrolysis and the relative abundance of reaction products is often a function of pH because alternative reaction pathways are preferred at different pH. In the case of halogenated hydrocarbons, base-catalyzed hydrolysis will result in elimination reactions while neutral hydrolysis will take place via nucleophilic displacement reactions. An example of the pH dependence of hydrolysis is illustrated by the base-catalyzed hydrolysis of the structurally similar insecticides DDT and methoxychlor. Under a common range of natural pH (5 to 8) the hydrolysis rate of methoxychlor is invariant while the hydrolysis of DDT is about 15-fold faster at pH 8 compared to pH 5. Only at higher pH (>8) does the hydrolysis rate of methoxychlor increase. In addition the major product of DDT hydrolysis throughout this pH range is the same (DDE), while the methoxychlor hydrolysis product shifts from the alcohol at pH 5–8 (nucleophilic substitution) to the dehydrochlorinated DMDE at pH > 8 (elimination). This illustrates the necessity to conduct detailed mechanistic experiments as a function of pH for hydrolytic reactions.

Photolysis. Photolysis of a chemical can proceed either by direct absorption of light (direct photolysis) or by reaction with another chemical species that has been produced or excited by light (indirect photolysis). In either case photochemical transformations such as bond cleavage, isomerization, intramolecular rearrangement, and various intermolecular reactions can result. Photolysis can take place wherever sufficient light energy exists, including the atmosphere (in the gas phase and in aerosols and fog/cloud droplets), surface waters (in the dissolved phase or at the particle–water interface), and in the terrestrial environment (on plant and soil/mineral surfaces).

Photolysis dominates the fate of many chemicals in the atmosphere because of the high solar irradiance. Near the earth's surface, chromophores such as nitrogen oxides, carbonyls, and aromatic hydrocarbons play a large role in contaminant fate in urban areas. In the stratosphere, light is absorbed by ozone, oxygen, organohalogens, and hydrocarbons with global environmental implications. The rate of photolysis in surface waters depends on light intensity at the air–water interface, the transmittance through this interface, and the attenuation through the water column. Open ocean waters ("blue water") can transmit blue light to depths of 150 m while highly eutrophic or turbid waters might absorb all light within 1 cm of the surface.

Oxidation-Reduction Reactions. Although many redox reactions are reversible, they are included here because many of the redox reactions that influence the fate of toxicants are irreversible on the temporal and spatial scales that are important to toxicity.

Oxidation is simply defined as a loss of electrons. Oxidizing agents are electrophiles and thus gain electrons upon reaction. Oxidations can result in the increase in the oxidation state of the chemical as in the oxidation of metals or oxidation can incorporate oxygen into the molecule. Typical organic chemical oxidative reactions include dealkylation, epoxidation, aromatic ring cleavage, and hydroxylation. The term autooxidation, or weathering, is commonly used to describe the general oxidative degradation of a chemical (or chemical mixture, e.g., petroleum) upon exposure to air. Chemicals can react abiotically in both water and air with oxygen, ozone, peroxides, free radicals, and singlet oxygen. The last two are common intermediate reactants in indirect photolysis. Mineral surfaces are known to catalyze many oxidative reactions. Clays and oxides of silicon, aluminum, iron, and manganese can provide surface active sites that increase rates of oxidation. There are a variety of complex mechanisms associated with this catalysis, so it is difficult to predict the catalytic activity of soils and sediment in nature.

Reduction of a chemical species takes place when an electron donor (reductant) transfers electrons to an electron acceptor (oxidant). Organic chemicals typically act as the oxidant, while abiotic reductants include sulfide minerals, reduced metals or sulfur compounds, and natural organic matter. There are also extracellular biochemical reducing agents such as porphyrins, corrinoids, and metal-containing coenzymes. Most of these reducing agents are present only in anaerobic environments where anaerobic bacteria are themselves busy reducing chemicals. Thus it is usually very difficult to distinguish biotic and abiotic reductive processes in nature. Well-controlled, sterile laboratory studies are required to measure abiotic rates of reduction. These studies indicate that many abiotic reductive transformations could be important in the environment, including dehalogenation, dealkylation, and the reduction of quinones, nitrosamines, azoaromatics, nitroaromatics, and sulfoxides. Functional groups that are resistant to reduction include aldehydes, ketones, carboxylic acids (and esters), amides, alkenes, and aromatic hydrocarbons.

Biotransformations. As we have seen throughout much of this textbook, vertebrates have developed the capacity to transform many toxicants into other chemicals, sometimes detoxifying the chemical and sometimes activating it. The same or similar biochemical processes that hydrolyze, oxidize, and reduce toxicants in vertebrates also take place in many lower organisms. In particular, bacteria, protozoans, and fungi provide a significant capacity to biotransform toxicants in the environment. Although many vertebrates can metabolize toxicants faster than these lower forms of life, the aggregate capacity of vertebrates to biotransform toxicants (based on total biomass and exposure) is insignificant to the overall fate of a toxicant in the environment. In this section we use the term *biotransformation* to include all forms of direct biological transformation reactions.

Biotransformations follow a complex series of chemical reactions that are enzymatically mediated and are usually irreversible reactions that are energetically favorable, resulting in a decrease in the Gibbs free energy of the system. Thus the potential for biotransformation of a chemical depends on the reduction in free energy that results from reacting the chemical with other chemicals in its environment (e.g., oxygen). As with inorganic catalysts, microbes simply use enzymes to lower the activation energy of the reaction and increase the rate of the transformation. Each successive chemical reaction further degrades the chemical, eventually mineralizing it to inorganic compounds (CO_2, H_2O, inorganic salts) and continuing the carbon and hydrologic cycles on earth.

Usually microbial growth is stimulated because the microbes capture the energy released from the biotransformation reaction. As the microbial population expands, overall biotransformation rates increase, even though the rate for each individual microbe may be constant or even decrease. This complicates the modeling and prediction of biotransformation rates in nature. When the toxicant concentrations (and potential energy) are small relative to other substrates or when the microbes cannot efficiently capture the energy from the biotransformation, microbial growth is not stimulated but biotransformation often still proceeds inadvertently through cometabolism.

Biotransformation can be modeled using simple Michaelis-Menten enzyme kinetics, Monod microbial growth kinetics, or more complex numerical models that incorporate various environmental parameters, and even the formation of microbial mats or slime, which affects diffusion of the chemical and nutrients to the microbial population. Microbial ecology involves a complex web of interaction among numerous environmental processes and parameters. The viability of microbial populations and the rates of biotransformation depend on many factors such as genetic adaptation, moisture, nutrients, oxygen, pH, and temperature. Although a single factor may limit biotransformation rates at a particular time and location, we cannot generalize about what limits biotransformation rates in the environment. Biotransformation rates often increase with temperature (according to the Arrhenius law) within the optimum range that supports the microbes, but many exceptions exist for certain organisms and chemicals. The availability of oxygen and various nutrients (C, N, P, Fe, Si) often limits microbial growth, but the limiting nutrient often changes with space (e.g., downriver) and time (seasonally and even diurnally).

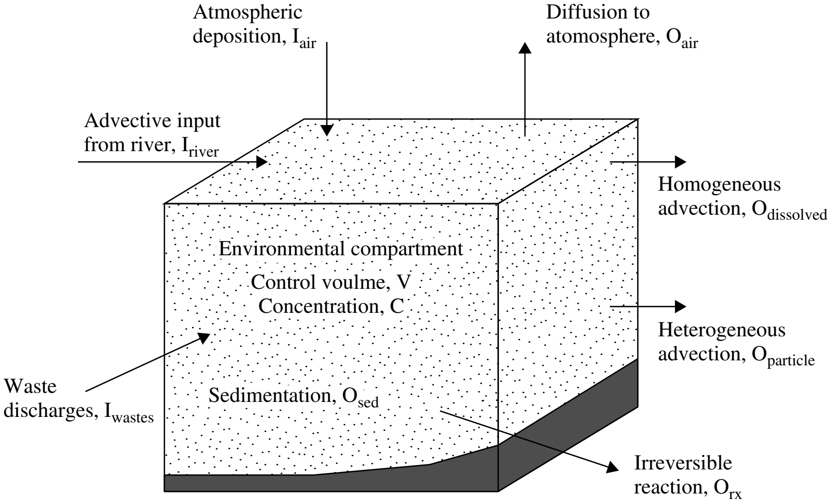
Long-term exposure of microbial populations to certain toxicants often is necessary for adaptation of enzymatic systems capable of degrading those toxicants. This was the case with the Exxon Valdez oil spill in Alaska in 1989. Natural microbial populations in Prince William Sound, Alaska, had developed enzyme systems that oxidize petroleum hydrocarbons because of long-term exposure to natural oil seeps and to hydrocarbons that leached from the pine forests in the area. Growth of these natural microbial populations was nutrient limited during the summer. Thus the application of nutrient formulations to the rocky beaches of Prince William Sound stimulated microbial growth and helped to degrade the spilled oil.

In terrestrial systems with high nutrient and oxygen content, low moisture and high organic carbon can control biotransformation by limiting microbial growth and the availability of the toxicant to the microbes. For example, biotransformation rates of certain pesticides have been shown to vary two orders of magnitude in two separate agricultural fields that were both well aerated and nutrient rich, but spanned the common range of moisture and organic carbon content.

27.6 ENVIRONMENTAL FATE MODELS

The discussion above provides a brief qualitative introduction to the transport and fate of chemicals in the environment. The goal of most fate chemists and engineers is to translate this qualitative picture into a conceptual model and ultimately into a quantitative description that can be used to predict or reconstruct the fate of a chemical in the environment (Figure 27.1). This quantitative description usually takes the form of a mass balance model. The idea is to compartmentalize the environment into defined units (control volumes) and to write a mathematical expression for the mass balance within the compartment. As with pharmacokinetic models, transfer between compartments can be included as the complexity of the model increases. There is a great deal of subjectivity to assembling a mass balance model. However, each decision to include or exclude a process or compartment is based on one or more assumptions—most of which can be tested at some level. Over time the applicability of various assumptions for particular chemicals and environmental conditions become known and model standardization becomes possible.

The construction of a mass balance model follows the general outline of this chapter. First, one defines the spatial and temporal scales to be considered and establishes the environmental compartments or control volumes. Second, the source emissions are identified and quantified. Third, the mathematical expressions for advective and diffusive transport processes are written. And last, chemical transformation processes are quantified. This model-building process is illustrated in Figure 27.4. In this example we simply equate the change in chemical inventory (total mass in the system) with the difference between chemical inputs and outputs to the system. The inputs could include numerous point and nonpoint sources or could be a single estimate of total chemical load to the system. The outputs include all of the loss mechanisms: transport



Inventory change = inputs (I) – outputs (O)

$$Vdc/dt = (I_{air} + I_{river} + I_{wastes}) - (O_{air} + O_{sed} + O_{dissolved} + O_{particle} + O_{rx})$$

at steady state, $dc/dt = 0$ and $(I_{air} + I_{river} + I_{wastes}) = (O_{air} + O_{sed} + O_{dissolved} + O_{particle} + O_{rx})$

Figure 27.4 A simple chemical mass balance model.

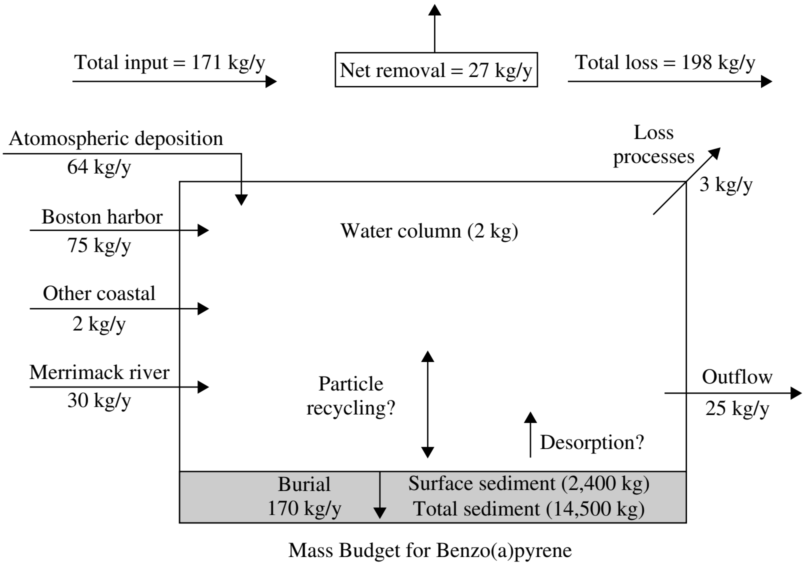


Figure 27.5 Information provided by a chemical mass balance model. The annual mass budget of benzo[*a*]pyrene in Massachusetts Bay is shown.

out of the compartment and irreversible transformation reactions. If steady state can be assumed (i.e., the chemical's concentration in the compartment is not changing over the time scale of the model), the inventory change is zero and we are left with a simple mass balance equation to solve. Unsteady-state conditions would require a numerical solution to the differential equations.

There are many tricks and shortcuts to this process. For example, rather than compiling all of the transformation rate equations (or conducting the actual kinetic experiments yourself), there are many sources of typical chemical half-lives based on pseudo-first-order rate expressions. It is usually prudent to begin with these "best estimates" of half-lives in air, water, soil, and sediment and perform a sensitivity analysis with the model to determine which processes are most important. One can return to the most important processes to assess whether more detailed rate expressions are necessary. An illustration of this mass balance approach is given in Figure 27.5 for benzo[*a*]pyrene. This approach allows a first-order evaluation of how chemicals enter the environment, what happens to them in the environment, and what the exposure concentrations will be in various environmental media. Thus the chemical mass balance provides information relevant to toxicant exposure to both humans and wildlife.

SUGGESTED READING

Hemond, H. F., and E. J. Fechner. *Chemical Fate and Transport in the Environment*. New York: Academic Press, 1994.

Mackay, D., W. Y. Shiu, and K. C. Ma. *Physical-Chemical Properties and Environmental Fate and Degradation Handbook*. CRCnetBASE 2000 CR-ROM. Boca Raton, FL: CRC Press, 2000.

Mackay, D. *Multimedia Environmental Models: The Fugacity Approach*, 2nd ed. Boca Raton, FL: Lewis Publishers, 2001.

Rand, G. M., ed. *Fundamentals of Aquatic Toxicology: Part II Environmental Fate*. Washington, DC: Taylor and Francis, 1995.

Schnoor, J. L. *Environmental Modeling: Fate and Transport of Pollutants in Water, Air, and Soil*. New York: Wiley, 1996.

Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden. *Environmental Organic Chemistry*, 2nd ed. New York: Wiley, 2002.