21 Mathematical Models of Chemical Transport and Fate

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21.1 OBJECTIVES

The objective of this chapter is to describe the role that mathematical models can play in assessing the risks posed by chemicals in the environment. To fully appreciate this role, the ecotoxicologist should understand how these models are formulated, their strengths, weaknesses, and areas of applicability. This chapter first describes the process of model formulation and includes some basic concepts of environmental chemistry. This is followed by an example of a model of chemical fate in an aquatic system. Finally, available models and their application in North America and Europe in assessing risk in an ecological context are described.

The primary aim of the chemical fate and transport modeler is to gather available data on chemical properties, environmental conditions, and rates or quantities of chemical discharges, and then synthesize these data into a comprehensive statement of chemical fate, often as a mass balance. This statement enables the modeler to estimate the amounts and concentrations of a chemical that will be present in each part of the environment, the rates at which the chemical is degraded and transported from place to place, and therefore how long the chemical will reside in the environment in question. Ideally, these concentrations should be compared with available monitoring data to provide assurance that the model is "valid." The calculation, estimation, or prediction of the likely concentrations in various compartments requires a knowledge of the physical–chemical properties of the substance, notably partition coefficients between environmental media and especially parameters such as chemical reactivity, in the form of reaction rate constants or half-lives. It also requires information on prevailing environmental conditions such as hydrology, soil characteristics, and atmospheric processes.

It is important to appreciate that although concentrations in media such as air, water, and fish can be measured, it is usually not possible to measure *fluxes* such as rates of evaporation from water to air or uptake or metabolic degradation in organisms. As a result, monitoring provides only a partial, static "snapshot" of a dynamic system. The modeler's aim is to establish a more complete and quantitative picture of the dynamic behavior of the contaminant in the system. When the chemical's dominant environmental pathways and fate processes are understood quantitatively, a much clearer picture emerges of the behavior of the chemical and the nature of the contamination issue. This information can help to assess the risk of adverse effects, and evaluate actions that may be taken to reduce concentrations, exposures, and effects.

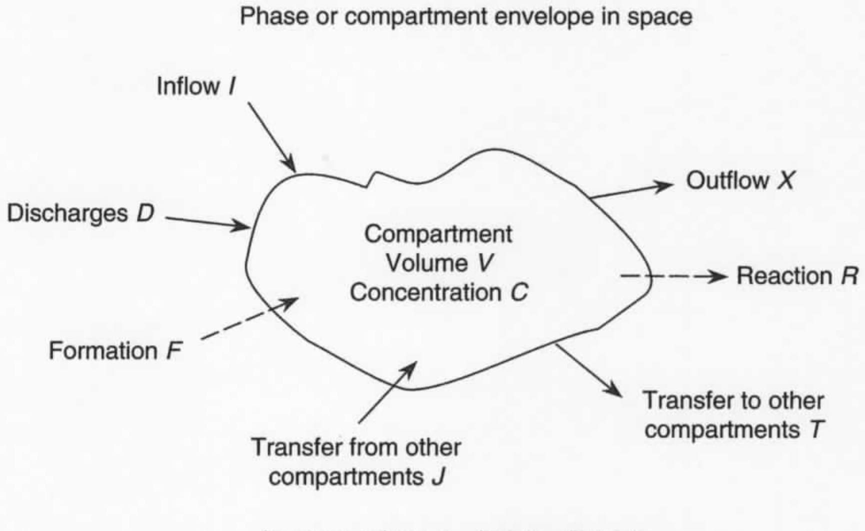
21.2 BASIC MODELING CONCEPTS

The assembly of this quantitative description is frequently referred to as the development of a "mass balance" model. The fundamental concept is illustrated in Figure 21.1 in which a volume in space of the environment is identified as a compartment, and a mass or material balance equation is written for chemical entering and leaving this volume. The volume may be water in a section of a river, a region of the atmosphere, or soil to a depth of 20 cm. It may even be an organism. It must have defined physical boundaries, and preferably be fairly homogenous in conditions within the phase envelope. The mass balance equation states that the inventory change of chemical quantity in the phase envelope (in kg/h) will equal the sum of the input rates to the phase envelope (in kg/h) less the sum of the output rates. The input terms may include flow in air and water, direct discharges, or formation from other chemical compounds. The outputs may include flows such as water from a lake, degrading reactions, and diffusion to other compartments. Antoine Lavoisier, the "Father of Chemistry," is credited with first enunciating this mass balance principle. It is no coincidence that he was also an accountant, as the same principle applies to money entering, leaving, and accumulating in a bank balance. It is now taken as axiomatic that the mass balance equation applies; thus the modeler's task is essentially to develop expressions, equations, or quantities for each term in the mass balance equation.

When assembling this mass balance, the modeler faces a number of decisions that require the exercise of judgment. The "art" of modeling can be viewed as the ability to make the "right" decisions when faced with alternative approaches or strategies. In particular, three aspects of the environmental system being simulated must be recognized and appropriately treated. These involve the nature of the emissions or "loadings" of the chemical and the scale of the system to be addressed.

21.2.1 EMISSIONS OR LOADINGS

Chemicals enter the environment as a result of a wide variety of human activities and in a large number of ways. Some chemicals such as pesticides and biocides are intentionally introduced into the environment. Others are introduced as a result of disposal following



Inventory change = Inputs − Outputs

$$V\,dC/dt = I + D + F + J - X - R - T \text{ kg/h}$$

At steady state when $dC/dt = 0$

$$I + D + F + J = X + R + T \text{ kg/h}$$

FIGURE 21.1 The fundamental concept of a phase envelope or compartment and the corresponding dynamic and steady-state mass balance equations.

usage or production, e.g., pharmaceuticals, veterinary medicines, solvents, surfactants, fuels, and lubricants. Some are inadvertently formed during processes such as combustion, e.g., "dioxins" and polycylic aromatic hydrocarbons. This route or mode of entry into a given environment dictates the most appropriate methods for simulating its environmental fate and subsequent exposure to nontarget organisms. Two characteristics of the emissions are of importance:

1. Does the emission originate from a *point* or *nonpoint* (diffuse) source?
2. Is the emission *steady state* (continuous) or *non-steady-state* (pulse)?

21.2.2 POINT AND NONPOINT SOURCES

As the term suggests, point source loadings are spatially discrete and generally occur as a result of localized human activities such as disposal or accidental releases. In many cases the magnitude of point source loadings is determined by design specifications or can be measured (Chapter 19). In contrast, loadings from nonpoint sources are generally the result of more diffuse processes that occur throughout the environment such as volatilization from soil or water into air, or leaching to groundwater. The magnitude of these loadings into the environment is less easily defined because of dependence upon environmental processes that may themselves require modeling.

21.2.3 STEADY-STATE AND NON-STEADY-STATE SOURCES

Steady-state loadings are (or for pragmatic reasons are considered to be) continuous and constant in rate, whereas non-steady-state loadings are temporally discrete and occur sporadically over time as pulses. Steady-state loadings are often associated with human activities such as continuous production or discharge from industrial or municipal wastewater treatment plants. Examples of non-steady-state loadings include pesticide application or accidental chemical or fuel spills. Depending upon the complexity of the processes involved the scales of loadings can either be directly estimated from observations as in the case of chemical spills, or are themselves simulated, e.g., runoff following pesticide application.

21.2.4 IMPORTANCE OF SCALE

Determining the appropriate spatial and temporal scale is a fundamental component of any exposure and risk assessment (Chapter 6). As models are designed to support exposure and risk assessments at a variety of scales, the selection of an appropriate modeling tool for the task at hand is a vital first step. This is most often dictated by the two considerations discussed earlier that define how discrete loadings are in time and space. The scale at which we view the environment can make these decisions more subtle than one might imagine. Consider, for example, discharges of domestic surfactants from wastewater treatment plants. At the scale of an individual "reach" or "segment" of a river or water body the loadings would be considered point sources. Such loadings may also be investigated at a catchment or watershed scale along with loadings from other wastewater treatment plants. Depending upon the size of the catchment and the number of wastewater treatment plants, these loadings may be considered point sources or, more pragmatically, diffuse (nonpoint) sources. At a regional scale of a state or country involving several catchments because of the ubiquity of such discharges, these loadings are more likely to be considered diffuse sources and simulated accordingly. Examples of modeling approaches that illustrate the importance of scale are illustrated in Table 21.1.

TABLE 21.1
Examples of Modeling Approaches Applied at Different Scales when Simulating Discharges from Wastewater Treatment Plants

Scale of Assessment	Illustrative Modeling Approach	Simulation as Point or Nonpoint Source
Treatment plant	STP (Clark et al. 1995)	Point source
Waterbody "reach" or "segment" (100s of m)	EXAMS (Burns 2002)	Point source
Catchment or watershed ($1\ km^2$ to 1000s of km^2)	GREAT-ER (GREAT-ER Task Force 1997)	Point source
Large lake (e.g., Ontario)	QWASI (Mackay 1989)	Point and nonpoint sources
Regional (1000s of km^2 to 100,000s of km^2)	EUSES (EUSES 1997)	Nonpoint sources

21.3 FORMULATING MASS BALANCE MODELS

There are five steps in formulating a model of the type illustrated in Figure 21.1: defining compartments, quantifying reaction rates, quantifying transport rates, acquiring emission data, and solving the equations describing the overall mass balance to obtain estimates of all chemical concentrations, masses, and fluxes.

21.3.1 DEFINING COMPARTMENTS

Step 1 definines the phase boundaries, envelopes, or compartments. Ideally the volume contained in each compartment or "box" should be well mixed and thus have a fairly homogeneous concentration. The mass of chemical in the compartment can then be expressed simply as the product of this concentration and the compartment volume. Examples are shallow pond water or surface sediments. If a more detailed and complex model is desired, it may be necessary to segment the water column into two: a surface layer and a deep layer. It may be desirable to treat particles in the water column as a separate phase, or they may be lumped into the water column. Obviously the greater the number of compartments, the greater will be the potential fidelity of the model to reality, but as the mathematics becomes more complex, more input data are needed, and the model tends to become more difficult to understand. If it is too complex, it is less likely to be widely used and it may suffer a lack of credibility. Figure 21.2 is a relatively simple, steady-state seven-compartment model of air, aerosols, water, fish, soil, bottom sediments, and suspended sediments, with a chemical (naphthalene) introduced into three compartments. Describing the processes that apply to the chemical as it enters and leaves each of these compartments requires estimations of the rates of 15 processes including rates of sedimentation, runoff from soil, evaporation, reaction, and advective flows.

21.3.2 REACTION RATES

Step 2 defines the various reaction rates experienced by organic chemicals through processes such as biodegradation, hydrolysis, and photolysis. For metals, degradation does not occur, although there may be speciation changes such as ferric to ferrous ion. This may be difficult because temperatures and other conditions such as the density and nature of microbial populations, sunlight intensity, and pH may vary diurnally and seasonally. It is not always clear what average conditions should be used. In some cases a distribution of values may be

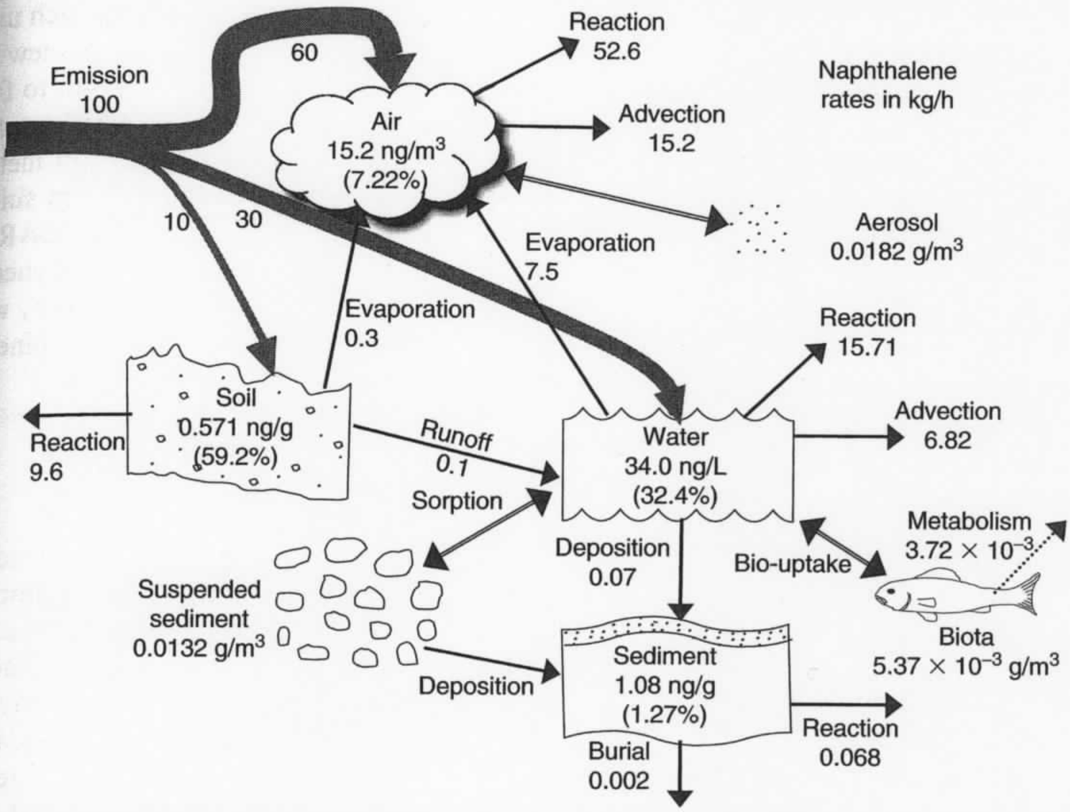


FIGURE 21.2 Illustrative mass balance diagram for the fate of naphthalene in a seven-compartment steady state Level III system. The concentrations and fluxes are obtained by solving the algebraic equations. Double arrows depict assumed equilibrium between compartments.

used. The most scientifically reliable and rigorous data are obtained from bench-scale experiments involving exposure of a chemical in a vessel to a known reactive environment under highly controlled conditions. The challenge is then to translate this physical–chemical information to environmental conditions. Experiments may also be conducted in larger microcosms or mesocosms in which environmental conditions are more closely simulated, but this results in some loss of control over the variables that determine the reaction rate. There is also a loss of reproducibility. It can be difficult to discriminate between the contributions of individual processes such as hydrolysis, evaporation, and biodegradation when all occur simultaneously.

Organic chemicals are usually subject to several competing degradation processes caused by reactive agents in the environment. These agents can be oxidants such as ozone or hydroxyl radicals, sunlight causing photolysis, both directly or indirectly, ionic species such as hydrogen or hydroxyl ions, and microorganisms including bacteria and fungi. Within an organism there may be metabolic conversion. The rate of reaction N is generally expressed as

$$\text{Rate} = N = VCxk_2 \text{ g/h}$$

where V is volume, C is concentration of the chemical, x is concentration of the reactive agent, and k_2 is a second-order rate constant. If environmental conditions are fairly constant, x will also be fairly constant and the terms x and k_2 can be combined as k, a first-order rate constant with units of reciprocal time (e.g., /h), and

$$N = VCk \text{ g/h}$$

The rate constant k is then the fraction of the chemical present that reacts during each unit of time. For example 0.01/h implies that 1% reacts each hour. It is more convenient to view these rate constants as half-lives, i.e., the time required for the amount of concentration to fall to half. This time $t_{\frac{1}{2}}$ can be shown to be $0.693/k$ where 0.693 is the natural logarithm of 2.0. Information on k or $t_{\frac{1}{2}}$ is obtained from laboratory experiments, from estimation methods often referred to as quantitative structure–activity relationships (QSARs) or from suitably interpreted field observations. Boethling and Mackay (2000) review many of these QSARs. Of particular importance are biodegradation rates in water and soil and reactions of the chemical with hydroxyl radicals in the atmosphere. These are often the principal mechanisms by which chemicals degrade. The persistence or longevity of the chemical is largely determined by these rates.

21.3.3 TRANSPORT RATES

Step 3 defines transport rates between the various media. A contaminant may be introduced into a medium such as soil, where it is relatively stable, but when conveyed by evaporation into another medium such as air, it can become subject to a fast degrading reaction. The chemical's lifetime in the environment may then be controlled, not by how fast it reacts in soil, but by how fast it evaporates from the soil to the reactive atmosphere. In the early days of environmental science the prevailing view was that most chemicals tended to remain in the medium into which they were discharged. For example, DDT applied to a soil would remain there indefinitely, subject only to soil degradation processes. It is now clear that most chemicals have the capability of migrating between all environmental media; thus application of DDT to soil will result in appreciable concentrations in the atmosphere that is exposed to that soil. Transport of this contaminated air will result in the contamination of distant areas, as in the case of DDT contamination of Arctic and Antarctic mammals, birds, and fish. Indeed, it was Rachel Carson in *Silent Spring* who first raised concerns about exposure of nontarget organisms to pesticide chemicals as a result of these intermedia transport processes (Carson 1962).

Transport processes can be classified into two general groups. The first is the advective or nondiffusive process (Figure 21.3), in which a chemical is conveyed from one medium to another by virtue of "piggybacking" on "carrier" material, i.e., moving between media for reasons unrelated to the presence of the chemical. Examples are deposition of chemical from the water column to sediment by attachment to depositing particles, and transport from the atmosphere to the soil or water in rainfall, in dust fall, or in wet deposition (dust scavenged from the atmosphere by rain). Ingestion of contaminated food by an organism is also a process of this type. These processes are readily quantified by multiplying the concentration of chemical in the migrating medium by the flow or transport rate of the medium. For example, if rain contains 10 ng/L of polychlorinated biphenyl (PCB) and is falling at a rate of 0.5 m/y, i.e., 0.5 $m^3/m^2/y$, on a region of 5 million m^2, the rain rate will be 2.5×10^6 m^3/y and the transport rate of PCBs will be a product of this rate and the concentration of 10 ng/L (expressed equivalently as 10 μg or 10×10^{-6} g/m^3). The PCB deposition rate will therefore be $2.5 \times 10^6 \times 10 \times 10^{-6}$ or 25 g/y. A calculation similar in principle to this can be done for other intermedia advective processes, including flow in water, air, and on solids, as well as ingestion in food by organisms and uptake by inhalation.

The second group is diffusive in nature and the chemical migrates between media because it is in a state of disequilibrium. For example, considering the two-compartment environment also depicted in Figure 21.3, benzene is present in water at a concentration of 1 mg/L and in air at 0.1 mg/L. The physical–chemical properties of benzene, specifically its air/water

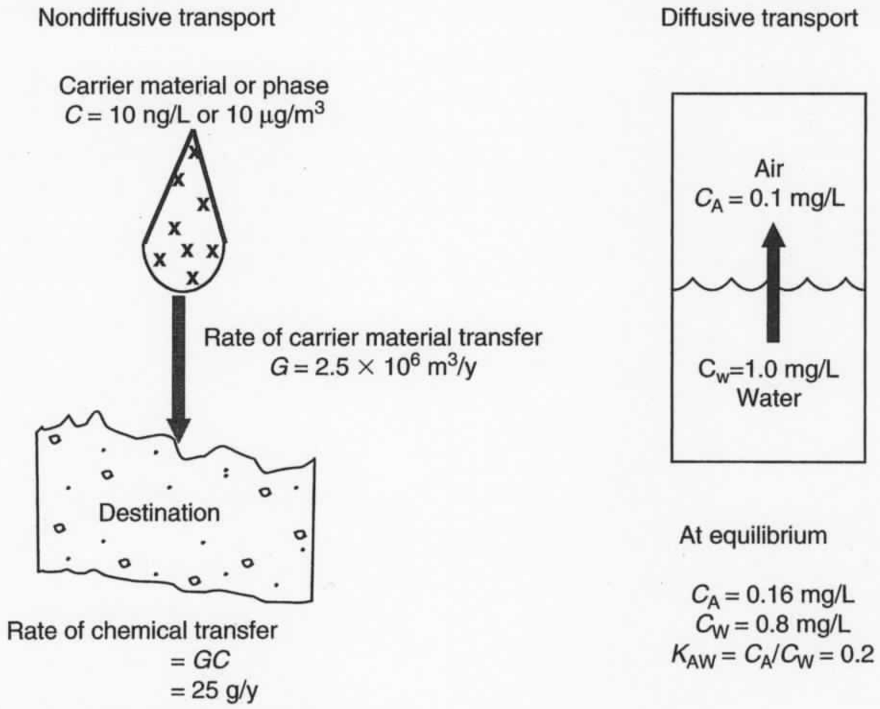


FIGURE 21.3 Intermedia transport processes.

partition coefficient or Henry's law constant, dictate its concentrations when it is in equilibrium. This quantity is determined by benzene's solubility in water and vapor pressure. At equilibrium the ratio of air to water concentrations or the air/water partition coefficient is approximately 0.2 at the prevailing temperature. In this case the air is "undersaturated" with respect to the water. Benzene will thus diffuse from water to air until it establishes concentrations of perhaps 0.8 mg/L in water and 0.16 mg/L in air. From a physical–chemical viewpoint the chemical is striving to achieve a condition of thermodynamic equilibrium, or one in which the benzene has an equal chemical potential or fugacity in both media. It may or may not have time to achieve this equilibrium because of other input and output processes to or from the system, but the direction of diffusive transport is at least clear, and the rate of transport can be calculated.

It must be appreciated that this diffusion process is basically a manifestation of random mixing of benzene throughout the entire system. The benzene in the water does not "know" the concentration in the air, but the rate of loss of benzene from the water compartment to the air is proportional to the concentration of benzene in the water. Thus, that rate of loss will exceed the rate of gain from the air until such time as air and water concentrations adjust to give equal rates of upward and downward transport. It is common to write the equation for net diffusive transport in the following form:

$$N = k_M A(C_1 - C_2 K_{12})$$

where N is the transport rate (g/h), k_M is the transport rate coefficient (m/h) A is the area between the media (m^2), C_1 and C_2, are the concentrations in the two media (g/m^3), and K_{12}, the partition coefficient. At equilibrium, when there is no net transport, K_{12} equals C_1/C_2 or C_1 equals C_2K_{12} and the term $(C_1 - C_2K_{12})$ thus becomes zero. This term is usually referred to as the "driving force" for diffusion or the "departure from equilibrium." Boethling and Mackay (2000) review these partition coefficients and recommend estimation methods.

These diffusive rate calculations can be applied to other combinations of media such as soil and air or water and sediment. The three key quantities are obviously: (i) the intermedia partition coefficients, e.g., K_{12}, which are thermodynamic quantities expressing the equilibrium condition and thus the extent of departure from equilibrium; (ii) a transport rate parameter analogous to k_M, which has the dimensions of velocity and can be viewed as a velocity with which chemical moves from one medium to the other; and (iii) the intermedia area A. A variety of methods are available for measuring, correlating, estimating, and predicting these intermedia transport coefficients. Full accounts are given by Thibodeaux (1996), Mackay (2001), and Schwarzenbach et al. (1993). The quantities involved are generally mass transfer coefficients, molecular diffusion coefficients, diffusion path lengths, or the thickness of boundary layers. Methods for estimating many of these qualities are conveniently reviewed by Lyman et al. (1982). The general experimental approach is to make measurements of intermedia transport rates, N, in controlled conditions in a laboratory in which A, C_1, C_2, and K_{12} are known, and then deduce k_M. It is then correlated with conditions such as turbulence in the atmosphere or water as reflected by wind speed or water current velocity. As it is difficult to make these measurements in the environment, there is often uncertainty that laboratory-to-environment extrapolation is valid.

In some cases the diffusing chemical may pass through two or more layers during its migration from one medium to the other. For example, benzene evaporating from water to the atmosphere must diffuse through near-stagnant boundary layers in the water and in the air. These diffusion processes occur in series and require application of the "two-resistance-in-series" concept, often referred to as the Whitman Two Film or Two Resistance Theory.

21.3.4 EMISSIONS

Step 4 defines the various discharges to the system, which may be from industrial or municipal sources, spills, deliberate applications of chemicals such as pesticides, leaching from groundwater, or use or disposal of consumer products. The total discharge rate, which is also referred to as the "loading rate," is often difficult to determine, at least for large regions in which there are multiple point and nonpoint sources, including deposition from the atmosphere and river flows. Some discharges such as pesticide applications must be treated as dynamic in time and space. The discharge or source term is critically important because it is the magnitude and distribution of the discharge that "drives" the model, establishes the magnitude of the concentrations, and therefore determines the exposure and ultimately the risk of adverse effects.

21.3.5 SOLUTIONS TO THE MASS BALANCE EQUATION

The modeler thus draws on information from a wide variety of sources when estimating rates of emission, transport, and transformation. For each loss process from a compartment, the rate can be expressed directly or as a function of chemical concentration, specifically the product of an estimated rate constant k and C, namely kC. Having defined each rate expression in the mass balance equation in Figure 21.1, the remaining task is to invoke the mass balance principle and solve the equations to obtain the desired concentrations. If there are n compartments there will be n unknown concentrations and n mass balance equations. Solution is then possible. The modeler now has several options.

A simple and valuable approach is to examine the constant or steady-state condition of the system. Often, environmental conditions are close to steady state as a result of long-term, continuous inputs of chemical. The inventory change terms on the left of the equation in Figure 21.1 are set to zero and the mass balance equations take the form of one or more

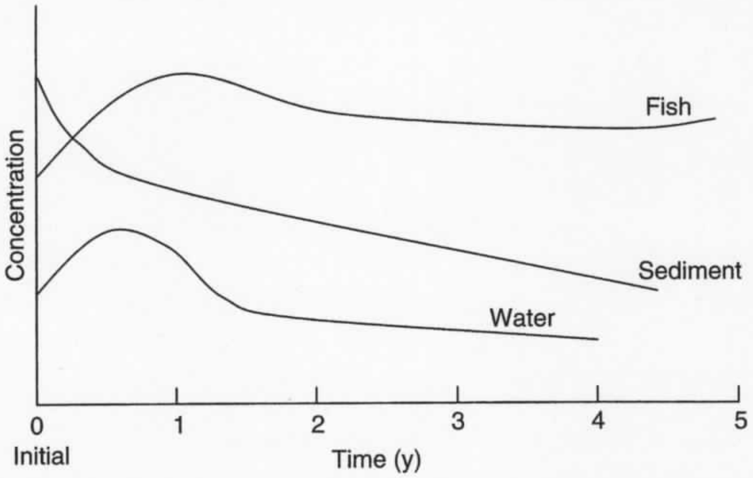


FIGURE 21.4 Illustrative time course of concentration changes in a lake subject to an increase then decrease in chemical input. The curves are obtained by solving the differential equations.

algebraic equations. These equations then express the concentrations that would prevail in the system if the input rate remained constant for a long period of time. Mathematical solution is accomplished by writing the set of algebraic equations and solving either by hand or matrix techniques. This solution, although not necessarily representative of actual conditions, is useful in that it demonstrates which processes and parameters are likely to be most important in determining the chemical's fate, concentration, and hence exposure. The modeler can then strive to establish more accurate values for the critical input parameters. For example, the reaction rate may prove to be so slow that it is relatively unimportant compared to a transport rate by evaporation. Further effort is then justified to obtain a more accurate evaporation transport rate. The quantities in Figure 21.2 were obtained in this way, and show that the important processes are reactions in air, water, and soil, advection from air and water, and evaporation from water.

The second, more rigorous but more demanding approach is to solve the set of differential equations as shown in Figure 21.1. For simple systems, analytical solutions are available, but often numerical integration techniques are used in which the initial or boundary conditions are first established, the change in inventory then deduced for a specified time increment or step, and the new set of concentrations for the system calculated. The equation is applied repeatedly to the new set of conditions. Care is necessary when selecting the time step and method of integration. The output from such a calculation as illustrated in Figure 21.4 is actually the time course of concentration changes in the system as a result of inputs which may be constant or may change with time. The disadvantage of this type of solution is that results are not easily generalizable to other conditions, as each solution is specific to the initial conditions selected, and of course, to the rates of chemical input.

21.3.6 COMPLEXITY, VALIDITY, AND CONFIDENCE LIMITS

Modelers strive to obtain models that describe real systems with high fidelity and provide accurate predictions of prevailing concentrations. This can result in complicated models of chemical migration in highly segmented or detailed multimedia environments involving hundreds of transport and transformation processes, and hence input parameters. So many parameters and assumptions may be built into the model that potential users become suspicious that there may be some hidden sensitivity, error, or even a mistake. Mathematically, the problem is that the "fit" involves a multitude of adjustable and poorly quantified parameters; thus the agreement with reality may be largely fortuitous. It may not be obvious which are the most sensitive, fate-controlling parameters. The key processes may be controlled by one or a few expressions or parameters that contain considerable error. Extrapolations to other chemicals or conditions may be unreliable. Frequently, the total rate of loss or "dissipation" of chemicals such as a pesticide is known fairly accurately from field data, and can be modeled accurately, but if it is the sum of several contributing processes such as volatilization and biodegradation, the individual components of this total may not be known accurately. It is important that field tests be designed to give the required process rates and that the model adequately expresses the rates of individual losses as well as the total rate of loss. A strong case can be made that the model should be only as complex as necessary, and should be sufficiently transparent that it is capable of being checked for intuitive reasonableness especially if it is to be widely used by non-modelers. (Chapter 9).

To an experienced environmental scientist the results should be in accord with what is expected from the chemical in question in the specified environment. Often the most useful aspect of the model is that it sorts the multitude of disparate processes into order of importance, and identifies the key processes. A very simple "back of the envelope" model can then be assembled containing only those key processes that can give a satisfactory, approximate simulation.

It is obviously desirable to compare the model results with reality in the form of monitored concentrations, often as a plot of predicted vs. observed values. Some adjustment of parameters may be needed to improve the fit. Some refer to this process of confirming the model to be correct as "validation." Others view "validation" as being too strong a word, as conditions can always be found in which the model is invalid. "Reconciliation", "corroboration" or "evaluation" may be better words. It is important that the modeler expresses all limitations of the model, e.g., it may be inapplicable to ionizing chemicals and it may be invalid at subfreezing temperatures. An expression of confidence limits is also desirable, for example, in the form that 95% of the estimates will be within a factor of 2.5. Such confidence limits or error estimates become very significant when calculated concentrations are to be compared with environmental standards or levels of toxicological concern when assessing risk.

Having set the stage, we now illustrate these concepts by developing and discussing a simple, illustrative model containing a variety of processes.

21.4 ILLUSTRATION OF A SIMPLE MASS BALANCE MODEL

21.4.1 THE SYSTEM BEING MODELED

To illustrate these concepts we treat a simple one-compartment aquatic model. The aim is to establish a mass balance for a specimen chemical in a lake subjected to a continuous direct discharge of chemical. The lake is 10 m deep and has an area of 10^6 m^2, the volume of water then being 10^7 m^3. Water flows into, and out of, this lake at a rate of 1000 m^3/h, the residence time of the water thus being 10,000 h or approximately 14 months. There is inflow of 75 kg/h or 50 L/h of suspended sediment (density 1.5 kg/L), of which 45 kg/h or 30 L/h is deposited on the bottom, and the remaining 30 kg/h or 20 L/h flows out of the system. The bottom (which we ignore here) consists of sediment. Chemical can react in the water column with a half-life of 289 d, i.e. a rate constant of 10^{-4}/h. It evaporates with an overall water–side mass transfer coefficient or diffusion velocity of 0.001 m/h. The chemical (molar mass 100 g/mol) has an air–water equilibrium partition coefficient K_{AW} of 0.01, a dimensionless particle–water partition coefficient K_{PW} of 5450, and a biota–water partition coefficient K_{BW} or bioconcentration factor of 5000. It is noteworthy that partition coefficients can be expressed as above in dimensionless form, e.g. (g/m^3 particle)/(g/m^3 water) or equivalently mg/L in both phases. Often the ratio is expressed as (mg/kg particle)/(mg/L water) and thus has units of L/kg. To convert from this dimensional form to the dimensionless form requires multiplication by the particle density. K_{PW} is thus 5450 (dimensionless) or 3633 L/kg. For biotic phases the density is usually 1.0 kg/L, i.e., equal to that of water; thus the values are numerically equal. The concentration of particles is 30 mg/L or 20 cm^3/m^3 or 20 ppm by volume and that of biota (including fish) is 5 ppm, again by volume. There is a constant chemical discharge of 40 g/h. The chemical is also present in the inflowing water at a concentration of 0.01 mg/L.

The aim of the model is to calculate the steady-state or constant concentration in the system of water, particles, and fish, and all the loss rates. We can undertake this calculation in two equivalent ways: first, a conventional concentration calculation, and second, a fugacity calculation.

21.4.2 CONCENTRATION CALCULATION

We set the total concentration of chemical in the water (including chemical present in particles and fish) as an unknown, C_W g/m^3. The various process rates are calculated in terms of C_W, summed, and equated to the total input rate, then solved for C_W, and finally the various process rates deduced. We use units of g/h for the mass balance calculation. The unknown could also be the dissolved concentration, rather than the total concentration.

21.4.2.1 Chemical Input Rate

The discharge rate is 40 g/h. The inflow rate is the product of 1000 m^3/h and 0.01 g/m^3 (i.e. 0.01 mg/L) or 10 g/h. The total input rate is thus 50 g/h.

21.4.2.2 Partitioning between Water, Particles, and Fish

The total amount in the water is $V_W C_W$, where V_W is the volume of water (10^7 m^3). But this contains 20 ppm by volume of particles, i.e. a volume of $20 \times 10^{-6} \times 10^7$ or 200 m^3, and similarly 5 ppm of biota or 50 m^3. The total quantity in the water is the sum of the quantities dissolved, in particles and in biota, namely:

$$V_W C_W = V_W C_O + V_P C_P + V_B C_B$$

The concentrations C_O, C_P, and C_B refer to dissolved, particulate, and biotic forms, respectively. The volumes are known, the concentration C_P is $K_{PW} C_O$ or 5450 C_O and C_B is $K_{BW} C_O$ or 5000 C_O. Substituting gives:

$$10^7 C_W = 10^7 C_O + 200 \times 5450 C_O + 50 \times 5000 C_O$$

$$10^7 C_W = C_O(10 + 1.09 + 0.25) \times 10^6 = 11.34 \times 10^6 C_O$$

It follows that C_O is $0.882 C_W$, C_P is $4800 C_W$, and C_B is $4400 C_W$, with 88.2% of the chemical being dissolved, 9.6% sorbed to particles, and 2.2% bioconcentrated in biota. Note that we used dimensionless partition coefficients K_{PW} and K_{BW}, i.e., ratios of (mg/L)/(mg/L). If the dimensional form is used, the volume of 200 m^3 is replaced by the mass of 300,000 kg and K_{PW} is 3633 L/kg; thus the amount is $300{,}000 \times 3633 C_O/1000$ or again 1.09×10^6 g. The 1000 converts L to m^3.

21.4.2.3 Outflow in Water

As the outflow rate is 1000 m^3/h, the outflow rate of dissolved chemical must be $1000C_O$ g/h or $882C_W$ g/h.

21.4.2.4 Outflow in Particles

In addition, there is outflow of 20 L/h (0.02 m^3/h) of particles containing $5450C_O$ g/m^3 of sorbed chemical, namely $109C_O$ g/h or $96C_W$ g/h, as C_O is $0.882C_W$. We assume that biota remain in the lake, but their outflow could be included if desired.

21.4.2.5 Reaction

The reaction rate is the product of water volume, concentration, and rate constant: $10^7 C_W \times 10^{-4}$ or $1000C_W$ g/h. Note that we assume all chemicals in the system to be subject to the reaction. Different rate constants could be defined for dissolved, sorbed, and biotic forms.

21.4.2.6 Deposition to Sediment

The concentration on the particles is $5450C_O$ or $4800C_W$ g/m^3 particle. As the particle deposition rate is 30 L/h or 0.03 m^3/h, the chemical deposition rate will be $4800 \times 0.03C_W$ or $144C_W$ g/h.

21.4.2.7 Evaporation

The evaporation rate is the product of the mass transfer coefficient (0.001 m/h), the water area (10^6 m^2), and the concentration dissolved in water: $0.001 \times 10^6 \times 0.882C_W$ or $882C_W$. We assume that the air contains no chemical to create a "back pressure" causing diffusion from air to water. If this were the case, it would be included as another input term.

21.4.2.8 Combined Loss Processes

Combining the process rates, we apply the mass balance principle and assert that at steady-state conditions the sum of these loss rates will equal the total input rate of 50 g/h, hence:

$$50 = 882C_W + 96C_W + 1000C_W + 144C_W + 882C_W = 3004C_W$$

thus:

$$C_W = 50/3004 = 0.0166 \text{ g/m}^3 \text{or mg/L}$$

The dissolved concentration is thus 0.0146 g/m^3, that on the particles is 5450 times this or 80 g/m^3 particle, and as the particle density is 1.5 g/cm^3, approximately 53 mg/kg. This is also 0.0016 g/m^3 water. The concentration in biota will be 73 g/m^3 or mg/kg biota and is equivalent to 0.0004 g/m^3 water.

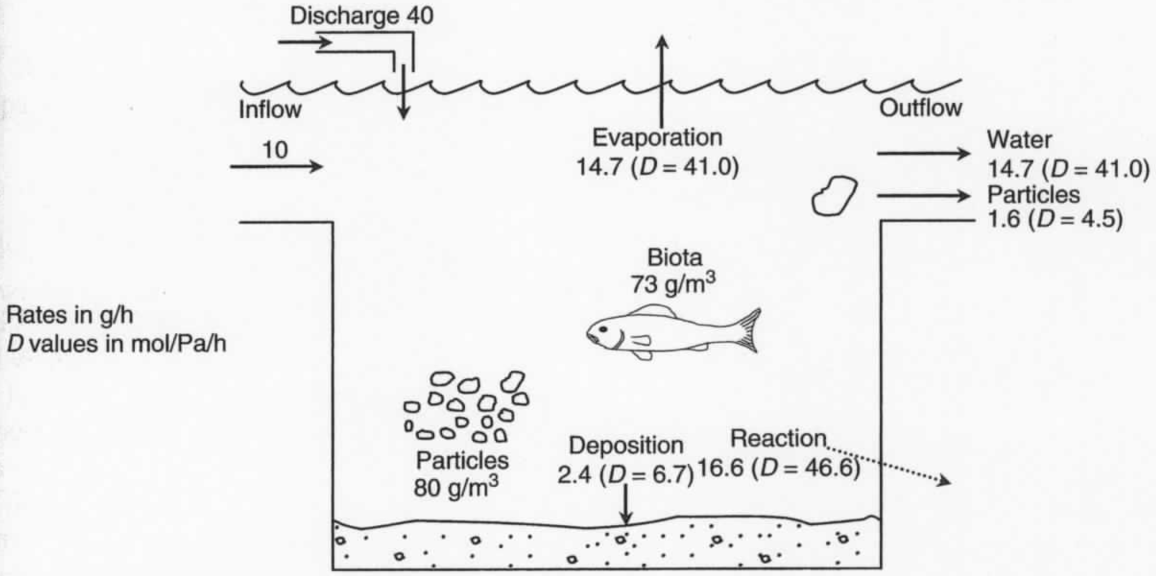
The process rates are thus:

Outflow in water	14.7 g/h	29%
Outflow in particles	1.6 g/h	3%
Reaction	16.6 g/h	34%
Deposition	2.4 g/h	5%
Evaporation	14.7 g/h	29%

These values total to the input of 50 g/h, thus satisfying the mass balance. The relative importance of the loss processes is immediately obvious. Figure 21.5 depicts this mass balance. There is now a clear and complete picture of the chemical's fate including concentrations, masses, and fluxes. The model thus provides the additional information about fluxes, whereas a monitoring program can only give concentrations.

21.4.3 FUGACITY CALCULATION

An alternative approach, which yields the same answer, is to use fugacity as the descriptor of chemical quantity rather than concentration. In this approach, partitioning of chemical between phases is expressed in terms of the equilibrium criterion of fugacity. Fugacity f can be considered the partial pressure of the chemical with units of pressure (Pa) and is a surrogate for concentration. It is related to concentration C mol/m^3 through a fugacity capacity or Z value, i.e., C is equated to Zf. These Z values are calculated from estimated or measured partition coefficients or indirectly from a chemical's physical properties of molecular weight, vapor pressure, solubility, and octanol/water partition coefficient, as well as environmental properties such as density and fraction organic content of the phases present. Full details are given by Mackay (2001). In this case, definition of Z values for the specimen chemical starts in the air phase where Z_A is $1/RT$ or 4.1×10^{-4} mol/m^3 Pa where R is the gas constant (8.314 Pa m^3/mol K) and T is absolute temperature (298 K). As a partition coefficient K_{12} is the ratio of Z values Z_1/Z_2, the Z for water can be calculated as Z_A/K_{AW} or 4.1×10^{-2}, for particles Z_P as $K_{PW}Z_W$ or 223, and for fish Z_B is $K_{BW}Z_W$ or 205.



Dissolved chemical	0.0146 g/m^3 water
Chemical on particles	0.0016 g/m^3 water
Chemical in biota	0.0004 g/m^3 water
Total	0.0166 g/m^3 water

Fugacity in water = 3.57×10^{-3} Pa

FIGURE 21.5 Steady-state mass balance of a chemical in a lake as described in the example in the text.

The total Z value for water, particles, and biota is the sum of these Z values, weighted in proportion of their volume fractions:

$$Z_{WT} = Z_W + 20 \times 10^{-6} Z_P + 5 \times 10^{-6} Z_B \text{ or } 4.65 \times 10^{-2} \text{mol/m}^3\text{Pa}.$$

Diffusive transfer between air and water, air and soil, and water and sediment is again estimated from mass transfer coefficients, interfacial areas, diffusivities, and path length. Nondiffusive processes include air and water advection, wet and dry atmospheric deposition, leaching from groundwater, sediment deposition, burial and resuspension, and runoff from soil, and are estimated from flow rate, Z value, and fugacity. In each case the rate parameter is expressed as a "D value" such that the rate is the product of D and fugacity. Degradation in each compartment or subcompartment is included by means of a rate constant, again expressed as a D value.

The mass balance calculation can be repeated in fugacity format by first calculating Z values, then D values, then equating input and output rates as before. It is preferable to express rates in units of mol/h when doing fugacity calculations.

The D values (in units of mol/Pa·h) and fluxes (mol/h) are shown in Table 21.2.

The overall mass balance is then expressed in terms of the unknown fugacity of the chemical in the water f_W. The input rate of 50 g/h is also 0.5 mol/h. Equating inputs to outputs gives:

$$0.5 = f_W D_1 + f_W D_2 + f_W D_3 + f_W D_4 + f_W D_5 = f_W \; 139.8$$

thus $f_W = 3.58 \times 10^{-3}$ Pa

$$C_O = Z_W f_W = 1.46 \times 10^{-4} \text{ mol/m}^3 \text{ or } 0.0146 \text{ g/m}^3$$

$$C_P = Z_P f_W = 0.80 \text{ mol/m}^3 \text{ or } 80 \text{ g/m}^3$$

$$C_B = Z_B f_w = 0.73 \text{ mol/m}^3 \text{ or } 73 \text{ g/m}^3 \text{ or } 73 \text{ mg/kg}$$

The individual rates are Df and are identical to those calculated earlier. The D values give a useful and direct expression of the relative importance of each process as all are expressed in identical units.

TABLE 21.2
D Values and Fluxes

				Flux D_f (mol/h)
Outflow in water	$D_1 = G_w Z_w$	$= 1000 \times 4.1 \times 10^{-2}$	$= 41.0$	0.147
Outflow in particles	$D_2 = G_p Z_p$	$= 0.02 \times 223$	$= 4.5$	0.016
Reaction	$D_3 = V Z_{wt} K$	$= 10^7 \times 4.66 \times 10^{-2} \times 10^{-4}$	$= 46.6$	0.167
Deposition	$D_4 = G_D Z_p$	$= 0.03 \times 223$	$= 6.7$	0.024
Evaporation	$D_5 = K_M A Z_w$	$= 0.001 \times 10^6 \times 4.1 \times 10^{-2}$	$= 41.0$	0.147
		Total	$= 139.8$	0.500

21.4.4 DISCUSSION

The model provides invaluable information on the status and fate of the chemical in this lake system. Obviously it is desirable to measure concentrations in particles, water, and biota to determine if the model assertions are correct. If, as is likely, discrepancies are observed, the model assumptions can be reexamined to test if some process has not been included, or if the assumed parameters are correct in magnitude. When reconciliation is successful, the environmental scientist is in the satisfying position of being able to claim that the system is well understood. It is then possible to explore the effect of various changes in inputs to the system.

For example, if the discharge were eliminated, the water, particle, and biotic concentrations would eventually fall to one-fifth of the values calculated above because the input would now be 10 g/h instead of 50 g/h. The biota would now contain 14 mg/kg instead of 73 mg/kg. To achieve an ecologically based "target" of, for example, 5 mg/kg would require reduction of the input rate to about 3 g/h. The nature and magnitude of interventions necessary to achieve a desired environmental quality in the ecosystem can thus be estimated.

It may be judged that to protect the resident aquatic species from risk of adverse effects requires a dissolved concentration in water of less than 0.001 g/m^3 or mg/L. To achieve this target requires that the total inputs be reduced to 3.4 g/h.

Another issue is how long it will take for such measures to become effective. This requires solution of the differential mass balance equation, which in this case is

$$V_W \mathrm{d}C_W/\mathrm{d}t = \text{input rate} - \text{output rate} \quad \text{or} \quad V_W \mathrm{d}C_W/\mathrm{d}t = 50 - 3004 C_W$$

dividing by V_W of 10^7 m^3 gives

$$\mathrm{d}C_W/\mathrm{d}t = 50 \times 10^{-7} - 3004 \times 10^{-7} C_W = A - BC_W$$

If the initial water concentration is C_{WO} at time t of zero, this equation can be solved by separation of variables to give

$$C_W = C_{WF} - (C_{WF} - C_{WO}) \exp(-Bt)$$

where C_{WF} is the final value of C_W at t of infinity, and is A/B. C_W thus changes from C_{WO} to C_{WF} with a rate constant of B or a half-time of $0.693/B$ h. Here B is 3004×10^{-7}/h; thus the half-time is 2300 h or 96 d. The actual time course of the changing concentrations can be calculated.

In reality, the biota, especially fish, would respond more slowly because of the delay in bio-uptake or release, but the important finding is that within a year the system would be well on its way to a new steady-state condition. In fugacity terms, the equivalent of the rate constant B is the sum of the $D/V_W Z_{WT}$ terms and each individual process contributing to this overall rate constant is $D/V_W Z_{WT}$. It is thus apparent that water outflow, evaporation, and reaction have about equal equivalent influences on the rate or time of response, while deposition and particle outflow are relatively unimportant. Such information can be of considerable value when deciding on interventions to improve environmental quality and reduce risk.

It is possible to include a sediment compartment or another water compartment to provide more details. Figure 21.4 presented earlier illustrated the possible time-course of changing concentrations in such a system. If birds are exposed to chemical from fish consumption, it may be necessary to develop a separate bioconcentration or food chain model. The nature and detail of the modeling activity can be tailored to the exposure assessment needs. An example of a more complex aquatic model of PCBs in Lake Ontario has been given by Mackay (1989).

21.5 CHEMICALS OF CONCERN AND MODELS SIMULATING THEIR BEHAVIOR

More than 20 million chemicals have been identified by the Chemical Abstracts System of the American Chemical Society. Of these perhaps 100,000 are used in commercial quantities. Many are relatively innocuous inorganic substances but many are organic or contain "toxic" metals such as mercury or chromium. These chemicals find a wide variety of applications including pesticides, solvents, detergents, polymers, fuels, and medicinal products. They vary enormously in properties such as relative partitioning between environmental media and in degradability. Many are ionic and thus speciate between protonated and ionic forms depending on prevailing pH conditions. The web sites of most regulatory agencies provide lists of chemicals that are of concern to them, and handbooks such as those of Mackay et al. (2006) and Verschueren (1996) have compilations of chemicals and their properties. Models are available to simulate or predict the behavior of many of these chemicals, but extreme care is necessary to ensure that the model selected is appropriate and does not contain inherent assumptions that invalidate its application. For example, many models cannot treat ionizing substances.

In this section we describe some of the available environmental fate models that can be used for exposure estimation as part of risk assessment. No attempt is made to provide a comprehensive list, so this section should be viewed as merely a glimpse into the world of models. Many regulatory agencies such as the US Environmental Protection Agency (US EPA) publish lists of acceptable or recommended models. Examples of useful sources are listed in Table 21.3. References are given in this section to enable the reader to pursue the details of these models as desired.

21.5.1 GENERAL MULTIMEDIA MODELS

These models seek to simulate or predict the behavior of chemicals in a "multimedia" environment similar to that of Figure 21.2, consisting of air, water, soil, sediment, and biotic

TABLE 21.3
Useful Sources of Information on Models and Chemical Properties

Models and Modeling		Chemical Properties and Estimation Methods	
Jorgensen et al.	1996	Mackay et al.	2006
Mackay	2001	Baum	1997
Cowan et al.	1995a	Reinhard and Drefahl	1999
Turner	1994	Boethling and Mackay	2000
Thibodeaux	1996	Jorgensen et al.	1998
Clark	1996	Schwarzenbach et al.	1993
Nirmalakhandan	2002	Lyman	1982
DiToro	2001	Reid et al.	1987
Linders	2001	Fogg and Sangster	2003
Paquin et al.	2002	Howard and Meylan	1997

Websites
www.syrres.com/esc/on syracuse research corp.2003
www.epa.gov/crem
www.utsc.utoronto.ca/~wania
www.trentu.ca/cemc
www.rem.sfu.ca/toxicology

compartments such as vegetation, mammals, birds, fish, and other aquatic organisms. Each compartment is usually treated as a well-mixed "box" of material, homogeneous in composition. Subcompartments can be included such as aerosols in air and particles in water. The compartments are connected, with the chemical of interest having the opportunity of moving between them by processes of advection, diffusion, deposition, resuspension, and food intake. The models may contain segmented compartments such as different soil layers or soil types, e.g., agricultural and industrial. Steady-state and dynamic versions can be compiled.

Their primary value is their ability to describe how nonpoint sources of chemical will behave, the likely magnitudes of concentration in different media, the key transport and transformation processes, and the overall persistence or residence time of the substance. They are not suitable for accurate determination of concentrations on a local scale close to point discharges.

The applications of such models and a comparison of three such models are described in a monograph by Cowan et al. (1995b). The models can treat a range of complexity expressed as "levels."

21.5.1.1 Level I

Level I calculations describe a situation in which a fixed quantity of chemical is allowed to come to thermodynamic equilibrium within a closed and defined environment. There is no resistance to chemical migration between environmental phases, and each phase is considered to be homogeneous and well mixed. This calculation provides a general impression of the environmental media into which a chemical is likely to partition based principally on physical–chemical properties such as vapor pressure, octanol–water partition coefficient, and solubility in water.

21.5.1.2 Level II

Level II calculations describe a situation in which the chemical is continuously discharged at a constant rate and reaches both steady-state and equilibrium conditions at which the emissions are balanced by advective and degradation losses. Degradation half-lives must now be supplied. New information obtained includes the overall environmental persistence of a chemical and the relative importance of chemical degradation processes.

21.5.1.3 Level III

Level III calculations are the most useful for risk assessment. They introduce resistance to chemical migration between environmental compartments. The chemical is continuously discharged at a constant rate to one or more of the environmental compartments (e.g. air, water, soil, and sediment) and achieves a steady-state but nonequilibrium condition. Each compartment has a unique equilibrium status or fugacity. Additional input parameters that characterize the environment are required to calculate transfer rates between environmental media. The Level III calculation shows, as illustrated in Figure 21.2, the dependence of overall environmental fate on media of release, i.e., "mode of entry," and highlights the key intermedia transport pathways (e.g., air–water or air–soil exchange).

21.5.1.4 Level IV

Level IV unsteady-state (or dynamic) models can also be formulated to analyze short-term (e.g., seasonal) effects on environmental concentrations, or to determine the effect of changing chemical emissions over a period of years or decades. Figure 21.4 illustrates typical output of this level.

21.5.1.5 Fugacity Models

A series of fugacity-based models have been developed in the last two decades at the University of Toronto and Trent University by Mackay and coworkers. They are available from the Trent University Canadian Environmental Modelling Centre web site (www.trentu.ca/cemc).

The equilibrium criterion (EQC) evaluative model includes Level I through Level III and deduces the fate of a variety of specified chemicals in an evaluative environment of fixed properties (Mackay et al. 1996a–c). The aim is to provide a "benchmark" environmental fate profile for a chemical that can be compared with the fates of other chemicals in the same model world. The RAIDAR model of Arnot et al. (2006) extends the EQC model to include a natural and agricultural food web resulting in ecological and human exposure and risk.

21.5.1.6 CalTOX Model

The CalTOX model was originally developed by McKone (1993a) to describe the fate of chemicals in California, especially substances released from waste sites. It has a more detailed treatment of soil layers and is Level III in structure. Human exposure is also estimated.

21.5.1.7 Simplebox Model

The Simplebox model from the Netherlands is incorporated into the European Union System for the Evaluation of Substances (EUSES) assessment process (EUSES 1997). It is Level III in structure but has a nested configuration, with a small local region contained in a larger national region, which in turn is contained in a continental scale region. The EUSES program also calculates human exposure at these three scales.

21.5.1.8 Regional, Continental, and Global-Scale Models

Fugacity- and concentration-based models can be parameterized to simulate a region or a set of connected regions, states, or nations. Examples of such applications include the ChemCAN model for Canada (Webster et al. 2004), the ChemFrance model (Devillers and Bintien 1995), the BETR North American model (MacLeod et al. 2001), the BETR World model (Toose et al. 2004), and the GloboPOP model (Wania 2003), which treats the entire planet and is used to assess long-range global fate and transport.

21.5.2 MODELS SPECIFIC TO ENVIRONMENTAL MEDIA

With increased specialization in environmental science and regulatory demands for more accurate and site-specific models, clusters of media-specific models have evolved which treat in more detail the atmosphere, water bodies (lakes, rivers, estuaries) and their underlying sediments, groundwater, soils, urban and indoor conditions, sewage treatment plants, and various organisms (including humans). The handbook by Jorgensen et al. (1996) lists many such models. Most national regulatory agencies have lists of "acceptable" models. Here we only briefly outline the general features of each cluster.

21.5.2.1 Plume Models in General

For the flowing media of air and water, it is frequently necessary to calculate the concentration of a chemical in a "plume" downwind or downstream of the discharge point. In its simplest form a dilution model can be applied in which the concentration in the flowing medium is E/G g/m^3, where E is the emission rate (g/h) and G is the flow rate (m^3/h). This is appropriate for narrow rivers in which mixing is rapid both vertically and horizontally from side to side. For wider rivers, estuaries, groundwater, and in the atmosphere the plume is not constrained and it expands vertically and horizontally. It is then necessary to calculate the changing plume dimensions. Essentially the flow term G increases and the concentration falls by dilution and diffusion. A common approach is to assume a Gaussian distribution of concentrations vertically and horizontally over the plume cross section. The distance parameters equivalent to the standard deviation of the distribution can be estimated from empirical correlations. The distribution of concentrations can be calculated from the maximum on the center line to the "edges" of the plume. Obviously, constraints may apply at surfaces such as the ground or river bottom, restricting diffusion. It is also possible to include an expression for degradation of the chemical as is done in river "die away" models, and for other loss processes such as deposition.

21.5.2.2 Atmospheric Models

Numerous air dispersion models with general or limited geographic applicability have been developed with the objective of deducing ground level concentrations and exposures from stack emissions. Most texts or handbooks on air pollution contain full descriptions of the basic principles underlying such models. The workbook by Turner (1994) is an excellent starting point.

The general approach is to first define the emission rate or strength of one or more sources in units such as kg/h. The emission may be continuous or as an intermittent "puff." As most discharges to the atmosphere are from stacks, it is usually necessary to deduce a plume rise height, yielding an estimate of the effective height at which contaminant is released. The chemical then blows downwind and disperses horizontally and vertically, diluting steadily at a rate controlled by the prevailing meteorology. A "map" of concentrations as a function of position can then be assembled. The equations employ standard deviation terms in the Gaussian distribution equation and are functions of wind speed and atmospheric stability. Ground-level concentrations downwind of the source are of most interest, as these control human and terrestrial ecosystem exposure.

Models range from simple application of Gaussian dispersion equation to complex, multisource models containing allowance for depositing particles and topographic features of the terrain. The use of such models is often written into legislations or regulations as a means of determining acceptable stack emission rates that will result in specified acceptable ground-level concentrations. Among these the Industrial Source Complex (ISC3) Dispersion Models of the US EPA and the commercial CALPUFF model are notable.

21.5.2.3 Aquatic Models

Water quality modeling is a highly developed subject with models being available for ponds, lakes, rivers, entire river basins, and estuaries. The approach is usually to segment the water into a number of connected "boxes" or to apply plume dispersion equations. Biotic components may be included to calculate concentrations in planktonic organisms, invertebrates, and fish. Models such as the WASP series, AQUATOX, and EXAMS are available from US EPA web sites (www.epa.gov/epahome/models). The QWASI model described early in the chapter is available from the Trent University web site cited earlier. Paquin et al. (2003) provide an

TABLE 21.4
Models of Aquatic Systems

Model	Scope	Reference
EXAMS	Exposure analysis modeling system, OSEPA	Ambrose 1997
WASTOX	Water quality analysis simulation of toxics	Connolly and Winford 1984
WASP4	Water quality analysis simulation program	Ambrose 1988
QWASI	Quantitative water–air sediment interaction fugacity model for lakes	Mackay et al. 1983; Mackay 2002
ROUT	GIS model applied to US rivers	Wang et al. 2000
GREAT-ER	European GIS river basin model	Feijtel et al. 1997, Boeije (1999)
DITORO	Sediment water exchange	DiToro 2000
SIMPLETREAT	Simpletreat (sewage treatment)	Stuijs 1996
STP	Sewage treatment plant	Clarke et al. 1995
TOXSWA	Edge of field systems	Adriaanse 1996, 1997

up-to-date listing of these models, especially for metals. Table 21.4 lists some of these models including wastewater treatment plant models.

Integral to these models are sediment compartments that often contain most of the chemical mass in the aquatic system. DiToro (2001) describes a number of such models. For metals there is usually a need to describe chemical speciation as a function of pH and the presence of other ions and dissolved organic matter. Speciation models are reviewed by Paquin et al. (2003).

Sophisticated river and river basin models have been developed in Europe and the United States to assess the fate of chemicals such as detergents or drugs that may be used domestically and are discharged to sewer and municipal treatment systems. They may incorporate GIS software to enhance the presentation of the results. An example is the GREAT-ER model (1997).

There is also a need to evaluate behavior in small, edge-of-field water bodies associated with agricultural uses of chemicals. One example of such a model is TOXSWA (Adriaanse 1996, 1997) developed for regulatory evaluations in the Netherlands and recently adopted as a standard regulatory tool for broader European evaluations under Directive 91/414/EEC.

21.5.2.4 Soil Models

The commonest application of soil models is to pesticides applied agriculturally. They are used for both scientific and regulatory purposes, primarily to provide an assessment of risk of leaching to groundwater, field drainage systems or runoff to surface waters. They may also be used to support more complex risk assessments for key terrestrial taxa such as soil invertebrates, birds and mammals. In principle, the aim is usually to quantify rates of degradation, leaching, runoff, and evaporation under the dynamic conditions following pesticide application. Models used in this context are described later in the section on pesticides. Also of concern is the fate of chemicals applied in sludge amendments to soil and of veterinary pharmaceuticals.

21.5.2.5 Fish Uptake and Food Chain Models

Because of the importance of the human and ecological exposure route resulting from fish consumption, considerable effort has been devoted to estimating chemical concentrations in fish. Contaminants may enter fish through the gills (bioconcentration) and, especially in the case of hydrophobic chemicals, by way of food (biomagnification). These models are

TABLE 21.5
Bioaccumulation Models

Name	Scope	Reference
GOBAS	Model of fish and food webs	Gobas 1993, 2003
AQUATOX	Aquatic fate toxicity model	Park 1998
FGETS	Food and Gill Exchange of Toxic Substance	Barber et al. 1991
BASS	Bioaccumulation and Aquatic System Simulator	Barber.craig@epamail.epa.gov
FISH	Fugacity model of fish	Mackay 2001
FOODWEB	Fugacity model of aquatic foodweb	Campfens and Mackay 1997
THOMANN	Model of fish and foodweb	Thomann and Connolly 1984
TOXSWA	Small-scale aquatic systems model	Adriaanse 1996, 1997
PEARL	Ricardian hydrology leaching model	Boesten and van der Linden 2001; Leistra et al. 2001
GeoPEARL	Spatially indexed hydrology leaching model	Tiktak et al. 2002, 2003, 2004

reviewed by Paquin et al. (2003), Gobas and Morrison (2000), and Mackay and Fraser (2000). Table 21.5 lists some of these models.

21.5.2.6 Miscellaneous Models

Models are also available for describing the fate of chemical and oil spills, contaminants in groundwater, in vegetation, in urban areas, in indoor environments, for remediation purposes and for processes within organisms (e.g. physiologically based pharmacokinetic (PBPK) models).

21.5.3 MODELS SPECIFIC TO CHEMICAL CLASSES

The models described above have been categorized according to the impacted environment such as air, water, or soil. In recognition of the need to regulate specific classes of chemical substances such as pesticides, the industrial and regulatory communities have developed a series of models that address the need for ecological and human risk assessment in the context defined by the nature of these substances and the way they are used. To illustrate this, we discuss models for only three classes of substances: agricultural pesticides, veterinary medicines, and biocides.

21.5.3.1 Agricultural Pesticides

This group of chemicals consists of fungicides, herbicides, and insecticides that are designed to eliminate or restrict the growth or infection of fungal, weed, or insect pests. For regulatory purposes, the scale of assessment is often the field or edge-of-field scale. Modeling may be carried out to assess the scale of exposure in soil, vegetation, surface water, sediment, groundwater, and air, although for ecological risk assessment the first four compartments are usually of primary interest. Table 21.6 lists some of these models recommended for use for various processes at a screening level, focusing on (primary) processes in the soil and (secondary) processes in the environment. Linders (2001) has compiled a valuable set of papers on these models.

Exposure experienced by soil organisms may be direct, following application "in crop," or indirect, typically as a result of spray drift. Two general exposure estimation methods are

TABLE 21.6
Pesticide Fate Models

Name	Scope	Reference
PELMO	Pesticide fate in soils	Klein et al. 2000
PRZM	Pesticide root zone model	Carsel et al. 2003; Mullins et al. 1993
SoilFug	Fugacity model of pesticide fate in soil	Di Guardo et al. 1994
MACRO	Model of pesticide fate in soils	Jarvis et al. 1994, 1995, 1996, 1998
GENEEC	Generic estimated environmental concentration based on PRZM	Parker et al. 1995
AGDRIFT	Model of pesticide drift	Spray Drift Task Force 1997

employed: models that simulate spray drift, and "look-up" tables that have been created from observations or models. In the United States horizontal transport and deposition field research has been used to support models such as AGDRIFT developed by the Spray Drift Task Force (Spray Drift Task Force 1997). In the European Union (EU) spray drift losses are most often assessed through use of "look-up" tables that condense the results of a large number of field-based horizontal deposition studies (Ganzelmeier et al. 1995; Rautmann et al. 2001). Within the EU regulatory arena it is necessary to assess "off-crop" impacts to nontarget arthropods. At present the spray drift tables discussed earlier are used within the ESCORT scheme (ESCORT 2001) to generate estimates of exposure on off-crop vegetation. It is, however, recognized that horizontal deposition estimates may give a poor representation of a combination of horizontal deposition and vertical interception by vegetation (Tones et al. 2001). "... interception by vegetation (Tomes et al. 2001)." ... Assessment of spray drift is just one example where a wide range of modelling approaches are available. Although such diversity is a healthy scientific state-of-affairs, this has led to regulatory uncertainty and confusion, e.g., "which model should be used as a basis for the regulatory assessment?" Within the European Union the need for standardisation of modelling frameworks to facilitate regulatory assessment of pesticides under Directive 91/414/EEC led to the establishment of a number of Working Groups under an initiative known as FOCUS. Regulatory and technical experts have reviewed modelling techniques and prepared shortlists of models recommended to support regulatory submissions, accompanying scenarios and supporting guidance on conduct and reporting of such assessments.

Loadings to surface waters for agricultural pesticides may occur as a result of a number of processes, the most important being drift, drainage, and runoff. Simulation models in use by industry and regulators in line with FOCUS guidance are listed below.

- Drift: Drift curves incorporated into the FOCUS SWASH based upon look-up tables and aspects of AGDRIFT (Spray Drift Task Force 1997)
- Drainage: MACRO, a Ricardian soil leaching model with macropore transport capability (Jarvis 1994, 1995, 1998; Jarvis et al. 1996)
- Runoff: PRZM, a capacity-based soil leaching and transport model with runoff simulation based upon the Universal Soil Loss Equation (Mullins et al. 1993; Carsell et al. 2003)

In addition to the need to assess loadings into surface water from these processes, it is also essential to consider the subsequent fate and behavior of chemicals within the receiving waters using aquatic models of the types outlined earlier. In the scheme established by FOCUS the loadings from each relevant process provide direct input for the TOXSWA model (Adriaanse 1996, 1997; Beltman and Adriaanse 1999a,b). TOXSWA is capable of simulating loadings from point source or distributed over a defined length of the water body. The simulated water body system is two dimensional and consists of two subsystems: a water layer containing suspended solids and a sediment layer whose properties (porosity, organic matter content, and bulk density) vary with depth. Within the version used to evaluate aquatic exposure for national registration in the Netherlands it is also possible to include partitioning interactions with macrophytes.

Within the United States assessments generally focus upon drift and runoff. In common with the regulatory assessment scheme in the EU, initial stages of exposure assessment are carried out with a set of conservative assumptions regarding loadings (generic estimated exposure concentration (GENEEC); Parker et al. 1995). Where appropriate, more sophisticated mechanistic modeling is then carried out employing models such as AGDRIFT and the PRZM runoff model already discussed. As outlined earlier, upon entry into surface waters it is necessary to consider the fate and behavior. Although various tools are available for this task, the most commonly used regulatory tool is the EXAMS modeling system developed (as in the case of PRZM and GENEEC) by the US EPA Office of Pesticide Programs.

21.5.3.2 Veterinary Medicines

This group of chemicals is of interest because they represent an "emerging" issue. Assessment and modeling procedures are still in the early stages of development. The two most significant classes from the perspective of scale of ecological exposure and risk are livestock and fish treatments.

Because livestock veterinary medicines are often repeatedly administered as whole herd treatments within intensive production systems, there are concerns surrounding the impact of potentially large quantities of active substance or active metabolites within excreta that are then applied to land, either directly in the case of pasture animals or indirectly in the case of spreading of manure or slurry produced by housed animals. Risk assessment concerns include impact on soil-dwelling organisms (such as microorganisms, earthworms, and any succeeding crops) and any subsequent exposure to aquatic organisms following runoff or drain discharge. There is increasing concern surrounding potential impacts on dung fauna and grassland invertebrate species following administration of veterinary medicines with insecticidal properties. In the United Kingdom a modeling system (VetPEC) developed for the Veterinary Medicines Directorate has provided a more complete mechanistic scheme for considering fate and behavior of veterinary medicines and their exposure in soil, groundwater, and surface waters following excretion.

Fish treatments (either freshwater or marine farmed fish) generally involve vaccines, "in-feed" treatments, and "bath" treatments. Depending upon the method of administration, these medicines enter the environment as pseudo-pulse doses (short-term administration) or pseudo-steady-state (long-term, chronic treatments). To assist with regulation of such formulations and agricultural practices, models are being developed as site-specific evaluation tools. Ultimately such models will require the capability of simulating partitioning of residues between organic matter (waste food, feces, suspended organic matter) and water.

There is still much work to be done to improve chemical fate representations in veterinary models. Sophisticated hydrological models including particle-tracking methods exist for simulating seabed deposition of treated fish feed and faeces (e.g., DEPOMOD, Cromey, 2002) but representation of chemical fate and behaviour remains generally very limited and is surprisingly inconsistent with the sophistication of other environmental process algorithms.

21.5.3.3 Biocides

This group of chemicals has been defined as chemicals or microorganisms, mixtures of either, or both, intended to control unwanted organisms such as animals, insects, bacteria, viruses, and fungi. Biocides present a unique set of risk assessment challenges as they are characterized by:

- Intentional introductions into the environment
- Both "point" and "nonpoint" introductions into the nontarget environment
- Diverse usage, disposal, and environmental release scenarios
- They are deliberately designed to be highly toxic

The range of product types covered by the Biocides Directive (98/8/EC) in the EU includes disinfectants and sanitizers used in drinking water, in public areas, and for veterinary purposes, preservatives used to protect wood, polymers, masonry and film, slimicides, molluscicides, rodenticides, antifoulants used on vessels, and even embalming fluids. In the United States, biocides are assessed under the auspices of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) along with agricultural pesticides.

These Emission Scenario Documents have been developed for most biocides to provide a necessarily simplistic approach to exposure assessment based upon scenarios and conservative default assumptions of loadings and transport processes. Most calculations are simple enough to be carried out without computer models. Nonetheless, when simplistic exposure assessments suggest that exposure and risk may be unacceptable, more sophisticated modeling can be carried out to replace crude default assumptions, and thereby refine the risk assessment. Some of the modeling approaches discussed for other chemicals such as pesticides and veterinary medicines can be employed here.

21.5.3.4 Metals

Metals present a set of challenges that differ fundamentally from those posed by organic substances. Although the basic principles of mass balance modeling are identical, there has tended to be a disciplinary separation into those who study and model metals from those who address organics, and indeed from those concerned with radionuclides. Several key differences in focus are noteworthy.

Although organic molecules such as benzene are subject to degradation to carbon dioxide and water, metals are totally persistent. They may change from oxide to sulfide to carbonate, they can adopt different ionic forms such as ferrous and ferric ions, but the element is conserved. In this respect, metals are easier to model because the mass of the element does not change.

Metals ionize, and therefore their state and behavior in the environment is dictated, at least in part, by the prevailing acidity and redox conditions. This complicates the expressions describing transport in the environment including uptake by organisms. It is a much more severe problem for metals than for organics. As a result, considerable effort has been devoted to building chemical equilibrium models for aquatic systems, the most established being the MINEQL and MINTEQ series by Westall et al. (1976) which are available from the US EPA. These models predict speciation, adsorption, and precipitation of metal ions as a function of the presence of other cations and anions including natural organic matter.

To a first approximation, organic molecules partition into organic matter such as humic and fulvic acids and lipids in organisms by a solution or solvent mechanism. Because of this behavior, the octanol–water partition coefficient K_{OW} is effective for describing partitioning of a wide variety of organic substances to natural organic matter in soils, sediments, and aerosol particles as well as lipids in organisms. There is no analog for K_{OW} for metals. Partitioning tends to be highly specific to the metal in question and transport through membranes is often active in nature using ion-specific protein "pumps." Models have been developed describing metal partitioning to natural organic matter, the most notable being the Windermere Humic Acid Model (WHAM) of Tipping (1994).

The primary focus of metal models is the aquatic environment of water, sediments, and their resident biota. Only in rare cases such as mercury is transport to air important. The review by Paquin et al. (2003) provides a full account of fate, bioaccumulation, and toxicity models.

For both metals and organics the concept of bioavailability has proved crucial. This asserts that only a fraction of the total substance present is "available" to exert toxic effects. This fraction may range from 99% to 0.1%. For organics the fugacity approach automatically treats this issue. In the example given earlier, of the chemical in the water column only 88% is in free molecular form and thus "available." For metals the equivalent approach is the Free Ion Activity Model (FIAM) developed by Morel (1983). Campbell (1995) has discussed in detail the strengths and weaknesses of this model.

In summary, although metals differ from organics in many significant respects, these differences are more in process emphasis than of a fundamental nature. The same general modeling principles apply to both.

21.6 CONCLUDING THOUGHTS ON SELECTING AND APPLYING MODELS

Faced with the need to conduct an ecological risk assessment for a specific environment and specific chemicals, the assessor must evaluate how a model can assist the process and, indeed, if modeling is justified. If the risk arises from exposure to chemical substances that are of anthropogenic origin and there is a possibility that discharges can be reduced, it is likely that a model which relates discharge quantities to exposure concentrations will be useful. The extent of discharge reduction and the time response of the system can be estimated. For "new" situations in which a discharge is planned or expected it can be invaluable to forecast concentrations, even approximately. Many past "mistakes" such as the widespread contamination by PCBs could have been prevented if models had been applied prior to discharge.

In general, when an ecosystem is subject to a source of chemical and the properties and discharge rate of that chemical are known, even approximately, it is likely that a model will be useful for predicting concentrations or reconciling monitored concentrations. The model framework can then be used to determine the factors that control concentrations and exposures and to explore the implications of changing discharge rates. It should be noted that modeling can be relatively fast and inexpensive compared to ecological field investigations and chemical monitoring campaigns. As a tool, a model can then add considerable value to these conventional investigative tools.

Another problem facing the risk assessor is which model to use. Environmental situations vary considerably in nature and models are often specific to certain classes of chemical. The best strategy is to explain the nature of the situation to a modeler and seek advice on the preferred approach. An "off-the-shelf" model may be adequate, or a customized model may be required. The strengths and weaknesses of the model may not become apparent until it is actually applied. A valuable practice is to proceed from simplicity to complexity. The simplest available model is applied first, then its inadequacies are assessed with a view to introducing greater complexities only where they are most needed. This is essentially the principle expressed in Ockham's Razor that can be stated colloquially, in this context, as: "Don't make the model more complex than is dictated by the ecological risk assessment task being addressed."