

Excerpts from:

# Chemical Fate and Transport in the Environment

SECOND EDITION

Harold F. Hemond

*Ralph M. Parsons Laboratory  
Department of Civil and Environmental Engineering  
Massachusetts Institute of Technology  
Cambridge, Massachusetts*

Elizabeth J. Fechner-Levy

*Abt Associates, Inc.  
Bethesda, Maryland*

CHAPTER  
**I**

## Basic Concepts

*"Predictions are very difficult  
to make,  
Especially predictions  
about the future."  
— Nicho Bahr*

### 1.1 INTRODUCTION

"By sensible definition any by-product of a chemical operation for which there is no profitable use is a waste. The most convenient, least expensive way of disposing of said waste—up the chimney or down the river—is the best" (Haynes, 1954). This quote, describing once common industrial waste disposal practices, reflects the perception at that time that dispersal of chemical waste into air or water off the factory site meant that the chemical waste was gone for good. For much of the 20th century, many industries freely broadcast chemical waste into the environment as a means of disposal. Other human activities, including use of pesticides and disposal of household waste in landfills, also contributed enormous loads of anthropogenic chemicals to the environment.

Today, however, not only have the ~~gross~~ <sup>pollution</sup> effects of emissions from stacks, pipes, and dumps become evident, but more subtle and less predictable effects of chemical usage and disposal have also manifested themselves. Some lakes, acidified by atmospheric deposition from power plants, smelters, and automobiles, have lost fish populations, while other lakes have burgeoned with unwanted algal growth stimulated by detergent disposal,

septic leachate, and urban and agricultural runoff. Municipal wells have been shut down due to chemical contamination emanating from landfills. Populations of several species of birds of prey have been decimated by pesticides that have become concentrated in their tissues and have adversely affected their reproduction. Humans have been poisoned by polychlorinated biphenyls (PCBs) and by mercury acquired from the environment via the food chain. Even nontoxic, seemingly harmless chlorofluorocarbons (CFCs) from spray cans and refrigerators have threatened the well-being of humans as well as the functioning of ecosystems by creating a hole in Earth's protective ozone shield.

Nevertheless, it is neither possible nor desirable for modern societies to stop all usage or environmental release of chemicals. Even in prehistoric times, tribes of troglodytes roasting hunks of meat over their fires were unknowingly releasing complex mixtures of chemicals into the environment. It is imperative, however, that modern societies understand their environment in sufficient detail so that accurate assessments can be made about the environmental behavior and effects of chemicals that they use. This includes an understanding of both chemical *transport*, referring to processes that move chemicals through the environment, and chemical *fate*, referring to the eventual disposition—either destruction or long-term storage—of chemicals. It then can be hoped that societies will make intelligent, informed decisions that will protect both human health and the environment, while allowing human beings to enjoy the benefits of modern technology.

This book presents the principles that govern the fate and transport of many classes of chemicals in three major environmental media: surface waters, soil and groundwater (the subsurface), and the atmosphere. These several media are treated in one book for three related reasons. First, this is primarily an introductory textbook, and a broad scope is most appropriate to the student who has not specialized in a particular environmental medium. Second, chemicals released into the environment do not respect the boundaries between air, water, and soil any more than they respect political boundaries. Because exchanges among these media are common, modeling a chemical in any single medium is unlikely to be adequate for obtaining a full description of the chemical's fate. Third, a great deal of insight can be gained by comparing and contrasting chemical behavior in surface waters, soil and groundwater, and the atmosphere. For example, although the fact is not immediately apparent in much of the literature, the mathematics describing physical transport in each medium are almost identical; the transport equation that models the mixing of industrial effluent into a river is also useful for describing the movement of contaminants in groundwater or the mixing of air pollutants in the atmosphere. Contrasts are also instructive; for example, the dominant fate process for a chemical in the atmosphere may be photode-

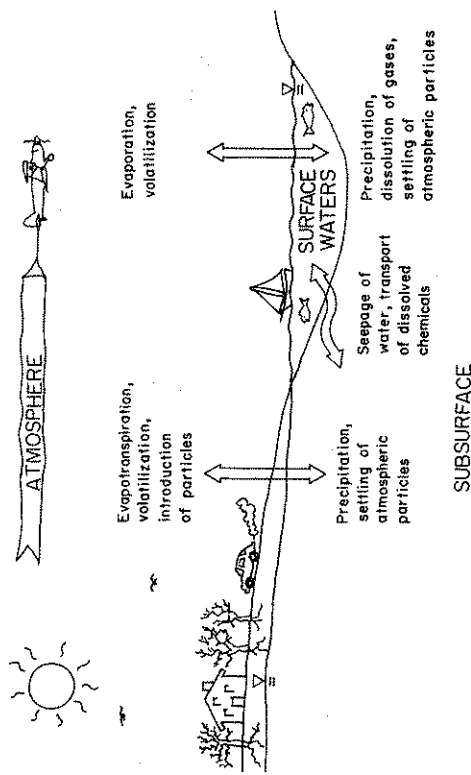


FIGURE 1-1 Three major environmental media: surface waters, the subsurface (soil and groundwater), and the atmosphere. Although each medium has its own distinct characteristics, there are also many similarities among them. Few chemicals are restricted in their movement to only one medium; thus chemical exchanges among the media must be considered. Several very generalized exchange processes between media are shown.

gradation, whereas in the subsurface environment, biodegradation of the chemical may dominate.

Knowledge of the principles underlying the fate and transport of chemicals in the environment allows problems ranging from local to global scales to be defined and analyzed. This first chapter presents fundamental concepts that apply universally to any environmental medium. The subsequent three chapters focus on surface waters, the subsurface environment, and the atmosphere, respectively; see Fig. 1-1 for a diagram of some of the interrelationships among these media. In each chapter, each medium is discussed in terms of its basic physical, chemical, and biological attributes; then the fate and the transport of introduced chemicals are considered.

## 1.2 CHEMICAL CONCENTRATION

Perhaps the single most important parameter in environmental fate and transport studies is chemical *concentration* ( $C$ ). The concentration of a chemical is a measure of the amount of that chemical in a specific volume or mass of air, water, soil, or other material. Not only is concentration a key quantity in fate

and transport equations; a chemical's concentration in an environmental medium also in part determines the magnitude of its biological effect.

Most laboratory analysis methods measure concentration. The choice of units for concentration depends in part on the medium and in part on the process that is being measured or described. In water, a common expression of concentration is mass of chemical per unit volume of water. Many naturally occurring chemicals in water are present at levels of a few milligrams per liter (mg/liter). The fundamental dimensions associated with such a measurement are [ML<sup>3</sup>]. The letters M, L, and T in square brackets refer to the fundamental dimensions of mass, length, and time, which are discussed further in the Appendix. For clarity in this book, specific units, such as (cm/hr) or (g/m<sup>3</sup>), either are free-standing or are indicated in parentheses, not in square brackets.

Another common unit of concentration in water is *molarity*. Recall that a *mole* of a chemical substance is composed of  $6.02 \times 10^{23}$  atoms or molecules of that substance. Molarity refers to the number of moles per liter of solution and is denoted M, with neither parentheses nor square brackets around it in this book.

A related unit, *normality* (N), refers to the number of *equivalents* of a chemical per liter of water. An equivalent is the amount of a chemical that either possesses, or is capable of transferring in a given reaction, 1 mol of electronic charge. If a chemical has two electronic charge units per molecule, 1 mol of the chemical constitutes two equivalents [e.g., a mole of sulfate (SO<sub>4</sub><sup>2-</sup>) is equal to two equivalents, and a one molar (1-M) solution of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) is two normal (2-N)].

In soil, a chemical's concentration may be measured in units such as milligrams per cubic centimeter (mg/cm<sup>3</sup>). Expressing concentration as mass per unit volume for soil, however, carries the possibility of ambiguity; soils undergo volume changes if they are compressed or expanded. Accordingly, it is often more useful to express soil concentration as mass per unit mass, such as (mg/kg) because the mass of soil does not vary with changes in the degree of compaction of the soil.

For air, which is highly compressible, expression of chemical concentration as mass per volume is even more ambiguous. The volume of a given mass of air changes significantly with changes in pressure and temperature, and thus the chemical concentration, when expressed as mass per volume, also changes. Consider the following situation: if initially there is 1 μg of benzene vapor (C<sub>6</sub>H<sub>6</sub>) per cubic meter of air and the barometric pressure decreases by 5%, the concentration of benzene as expressed in units of mass per volume also decreases by 5%, because the air expands while the mass of benzene remains constant. Expressing the benzene concentration as mass of benzene per mass of air removes all ambiguity because changes in temperature and pressure do not affect the mass of air present.

Ambiguity can also arise when a laboratory reports the concentration of a chemical that can exist in more than one form (*species*) without reference to a particular species. For example, if the concentration of nitrogen in a water sample is reported simply as 5 mg/liter, it is unclear whether 1 liter contains 5 mg of nitrogen atoms (N) or 5 mg of one of the nitrogen species present, such as nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), ammonia (NH<sub>3</sub>), or ammonium (NH<sub>4</sub><sup>+</sup>). In such a situation, clarification from the laboratory performing the measurements must be obtained to understand the actual chemical mass present. Furthermore, if the species associated with a concentration is not known, a conversion from mass to moles is not possible. [Recall that to convert mass to moles, the molecular weight of the species measured must be known; the number of moles is then equal to the mass (in grams) divided by the molecular weight.]

Numerous other options exist for specifying a concentration; common ones are parts per thousand (ppt or ‰), parts per million (ppm), or parts per billion (ppb). For the soil and air cases just mentioned, ppm on a mass basis is numerically equal to milligrams (mg) of chemical per kilogram (kg) of soil or air. Parts per million is also sometimes used on a volume basis. This may be inferred from context or made clear by the term ppm(v); 1 ppm(v) of helium in air would correspond to 1 ml of helium in 1000 liters (1 m<sup>3</sup>) of air. For water, the density of which is approximately 1 g/cm<sup>3</sup>, parts per million corresponds to milligrams of chemical per liter of water (mg/liter) in dilute solutions.

No matter which units are used, however, concentration is the measure of interest for predictions of a chemical's effects on an organism or the environment. Concentration is also critical in one of the most important concepts of environmental fate and transport: the bookkeeping of chemical mass in the environment.

### 1.3 MASS BALANCE AND UNITS

#### 1.3.1 MASS BALANCE AND THE CONTROL VOLUME

Three possible outcomes exist for a chemical present at a specific location in the environment at a particular time: the chemical can remain in that location, can be carried elsewhere by a *transport* process, or can be eliminated through *transformation* into another chemical. This very simple observation is known as *mass balance* or *mass conservation*. Mass balance is a concept around which an analysis of the fate and transport of any environmental chemical can be

organized; mass balance also serves as a check on the completeness of knowledge of a chemical's behavior. If, at a later time in an analysis, the original mass of a chemical cannot be fully accounted for, then there is an incomplete understanding of how transformation and transport processes are affecting that chemical. Accurate late and transport modeling results from an understanding of every process contributing to the mass balance of a chemical.

Implicit in the application of the mass balance concept is the need to choose a *control volume*. A control volume is any closed volume, across whose boundaries we propose to account for all transport of a chemical, and within whose boundaries we propose to account for all the chemical initially present (stored), as well as all processes (*sources or sinks*) that produce or consume the chemical. The *mass balance expression* for any chemical in any control volume during any time interval can be written as

Change in storage of mass = mass transported in - mass transported out  
 + mass produced by sources - mass eliminated by sinks. [1-1a]

The mass balance expression in a control volume can also be written in terms of rates, that is, mass per time [M/T]:

Rate of change in storage of mass = mass transport rate in

- mass transport rate out + mass production rate by sources  
 - mass elimination rate by sinks. [1-1b]

Control volumes are chosen to be convenient and useful. While the choice of a good control volume is somewhat of an art and depends on both the chemicals and the environmental locations that are of interest, the control volume boundaries are almost always chosen to simplify the problem of determining chemical transport into and out of the control volume.

As an example of an environmental pollution problem requiring the choice of a control volume, consider a lake that is receiving industrial effluent from a discharge pipe. To establish a useful volume within which we could describe the fate and transport of chemicals in the effluent, we might choose the entire lake, as shown in Fig. 1-2. The upper boundary of the control volume is then the lake surface; transport across this boundary is described by the general principles that govern chemical transport between water and air. For some *nonvolatile* chemicals (i.e., chemicals that do not rapidly move from a dissolved phase in the water to a gaseous phase in the air), this transport rate is negligible. For many other chemicals, enough knowledge exists to make reasonable estimates of the air/water exchange rate (based on factors such as the volatility of the chemical, the rate of chemical diffusion in water, and the amount of turbulence in the lake). The lower boundary of the control volume

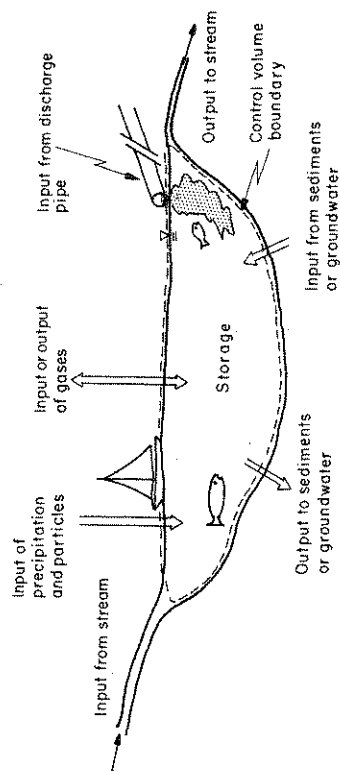


FIGURE 1-2 An example of a control volume that is useful for analyzing chemical behavior in a lake because it facilitates the measurement or estimation of chemical inputs and outputs. Chemicals may enter the control volume via the inflowing stream and the industrial discharge pipe and may leave the control volume across the air-water interface and sediment-water interface as well as via the outflowing stream.

might be chosen to be just above the uppermost layers of lake bottom sediments. Water seeping into or out of the lake sediments is then one transport mechanism by which a dissolved chemical could cross the lower boundary of the control volume. The lake control volume might also receive chemical input from an inflowing stream; the rate at which a chemical enters the lake from the stream could be estimated by multiplying the streamflow by the concentration of the chemical in the stream.

To complete a mass balance on a chemical within the control volume, internal consumption, production, and storage of the chemical also must be quantified. In some cases source and sink strengths can be estimated based on knowledge of chemical and biological composition and physical attributes of the lake. If the lake is well mixed, storage of the chemical in the lake control volume at a given time can be estimated as the product of the chemical concentration in the lake water and the total volume of water in the lake.

Note that the left-hand sides of Eqs. [1-1a] and [1-1b] are zero if storage does not change with time. This is one example of *steady state*, a description that applies to any problem in which quantities do not change with time. (Mathematically, all derivatives with respect to time are zero in steady-state systems.) Steady-state assumptions often simplify the analysis of a problem but should not be invoked when a *transient* (time-varying) situation exists.

If all terms but one are known in the mass balance expressions of Eqs. [1-1a] and [1-1b], the control volume can be used to estimate an otherwise unmeasurable transport, source, or sink term, as shown in Example 1-1.

**EXAMPLE 1-1**

Consider the lake shown in Fig. 1-2. For this example, assume that the discharge pipe releases to the lake small amounts of various alcohols from an industrial fermentation process, and it is desired to estimate the rate at which alcohols are degraded in the lake. One of them, butanol ( $C_4H_9OH$ ), is released to the lake at the rate of 20 kg/day. Butanol is measured in the lake water on several occasions at a concentration of  $10^{-4}$  kg/m<sup>3</sup>; no butanol is detected in the inflowing stream. Average streamflow at the outlet of the lake is measured to be  $3 \times 10^4$  m<sup>3</sup>/day. What is the magnitude of internal sinks of butanol?

By using the mass balance equation of Eq. [1-1b]:

Mass elimination rate by sinks = mass transport rate in

– mass transport rate out + mass production rate by sources

– rate of change in storage of mass.

By assuming no butanol exchange with the atmosphere, this equation can be rewritten more explicitly for the mass balance of butanol:

Internal sink rate = discharge pipe input rate + stream input rate

– stream output rate + internal source rate – rate of change in storage.

By considering the equation term by term:

- The discharge pipe input rate of butanol is 20 kg/day.
- The stream input rate is zero.
- By assuming that the lake is well mixed (i.e., the butanol concentration is the same everywhere in the lake), the stream output rate is  $(3 \times 10^4 \text{ m}^3/\text{day}) \cdot (10^{-4} \text{ kg/m}^3) = 3 \text{ kg/day}$ .
- Assume there are no internal sources of butanol, so the internal source rate is zero.
- Given that the butanol concentration in the lake water seems to be at steady state at  $10^{-4}$  kg/m<sup>3</sup>, the rate of change in storage is zero.

Therefore, the mass balance is

$$\text{Internal sink rate} = 20 \text{ kg/day} + 0 - 3 \text{ kg/day} + 0 - 0 = 17 \text{ kg/day.}$$

The internal sink appears to consume 17 kg of butanol per day, although it is not known by what processes this consumption occurs (e.g., through biodegradation or through consumption by fish). Three other limitations of this mass balance analysis are (1) the calculated internal sink rate may actually be an overestimate because atmospheric exchange is being neglected. There is

probably not much butanol in precipitation, but the assumption of no volatilization (transfer to the air) should be tested and perhaps an atmospheric output rate term added to the mass balance equation (this is discussed in Section 2.3). (2) The well-mixed lake assumption may not be appropriate; the measurements of butanol concentration may not be representative of the butanol concentration in water leaving the lake in the stream outflow. (3) If the lake processes are not at steady state, the rate of change in storage term may be nonzero, thereby affecting the calculated internal sink rate.

A lake can also illustrate a theoretically valid, but not useful, control volume. Consider a control volume that comprised only the northern half of the lake; the southern boundary of the control volume would then be a surface cutting vertically across the entire lake from the water surface to the lake sediments. Measurement of chemical transport across this boundary would be immensely difficult; it would require detailed water flow measurements at an impossibly large number of sites, given that the speed and direction (i.e., the velocity) of water currents in a lake typically vary from place to place and time to time. Such a control volume would not simplify estimates of chemical inputs and outputs.

A little reflection on a variety of other environmental pollution situations suggests any number of relevant control volumes having convenient, useful, and well-defined boundaries. Three typical examples are shown in Fig. 1-3. If

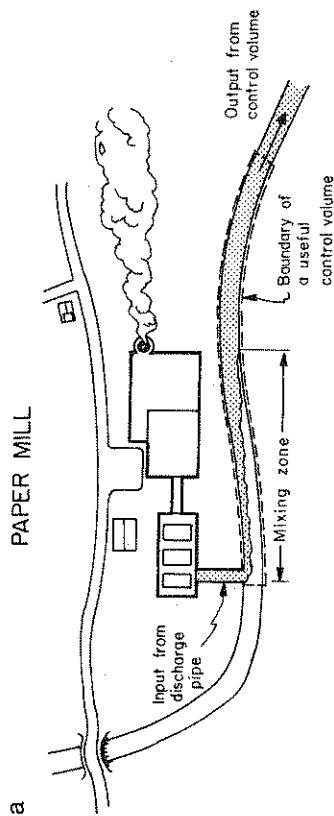


FIGURE 1-3 a Examples of useful control volumes for three principal environmental media. Control volume (a) would be practical if we were studying the various processes that remove a contaminant from a river; the difference between the input and output fluxes would represent internal sinks in the river or volatilization loss to the air (Figure continues).

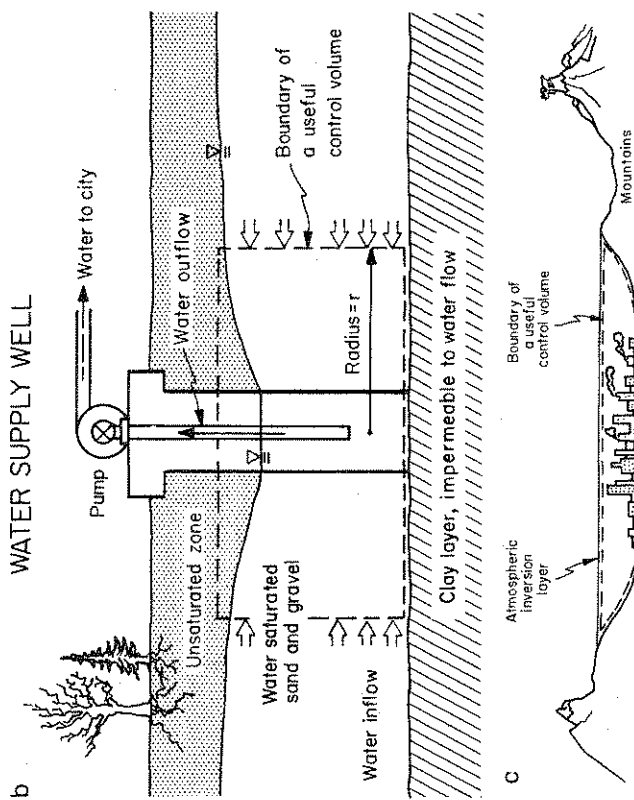


FIGURE 1-3 b-c (Continued) Control volume (b) has water inflow perpendicular to the boundary; by equating an expression for groundwater flow into the control volume to expressions for change in water storage and for the removal of water by the pump, we can derive equations that describe the hydraulic behavior of the well and the movement of chemicals associated with the groundwater. Control volume (c) would be useful when atmospheric conditions, such as an inversion layer, prevent the upward transport of an air pollutant over a city. Knowledge of the air volume into which a pollutant is mixed allows an estimation of the rate of change of the air pollutant concentration (i.e., the rate per unit volume at which the pollutant is being stored in the air), if the rate of pollutant release into the air volume is known.

the fate of river pollution in the vicinity of an industrial outfall is of concern, a specific reach of river beginning just upstream of the outfall and extending downstream to some location where the pollutant has become fully mixed across the river could constitute a good control volume. For analysis of the movement of water to a groundwater well, a cylindrical volume containing a portion of the water-bearing formation from which water is drawn into the well serves as a useful control volume (as illustrated further in Chapter 3). In situations pertaining to urban air quality, an imaginary "bubble" above a city might be a useful control volume to consider, especially if air flow patterns and natural barriers such as hills hinder transport of airborne chemicals across

the wall of the imaginary bubble. Depending on the particulars of a situation, more than one practical control volume may be defined.

### 1.3.2 CONSISTENCY OF UNITS

Anyone working in the environmental sciences must become familiar with the basic physical dimensions and units, many of which are described in the Appendix. A rigorous check for consistency of units is an excellent device for catching errors in expressions used in the modeling of chemical fate and transport. To confirm that an answer has the correct dimensions, one should express units along with each quantity that enters a mathematical expression. Not only does this often give insight into the mathematical expression, but it also highlights missing or superfluous terms that lead to spurious units and erroneous answers. For example, reconsider the lake control volume described in Section 1.3.1. If the rate at which a certain chemical was advected into the lake by the stream (mass per unit time) needed to be determined, the concentration of the chemical in the stream and the average velocity and the cross-sectional area of the stream would be multiplied together. Without containing actual numbers, such a calculation might look like

$$\text{Rate of chemical inflow} = \text{velocity (m/sec)} \cdot \text{area (m}^2\text{)} \cdot \text{concentration (g/m}^3\text{)}.$$

The final units of the answer would be (g/sec) with dimensions of [M/T], entirely appropriate to express the rate of chemical inflow to the lake. Alternatively, if (ft/sec) had been used for river velocity, the units of the answer would have been (g · ft/m · sec), a very good sign that a consistent set of units had not been used in the original expression. If the units for velocity had been omitted, the answer would have had the units of (g/m), which are clearly incorrect, in part because there is no time unit.

### 1.4 PHYSICAL TRANSPORT OF CHEMICALS

Most physical transport of chemicals in the environment occurs in the fluids air and water. There are primarily two kinds of physical processes by which chemicals are transported in these fluids: bulk movement of fluids from one location to another, and random (or seemingly random) mixing processes within the fluids. Both types of transport processes are implicitly included in the input and output terms of Eqs. [1-1a] and [1-1b]. (Biological transport, such as the swimming of a contaminated fish, is less amenable to analysis by the methods of physics—a fish's agenda depends on feeding and avoiding predators!) The first type of process, *advection*, is due to bulk, large-scale

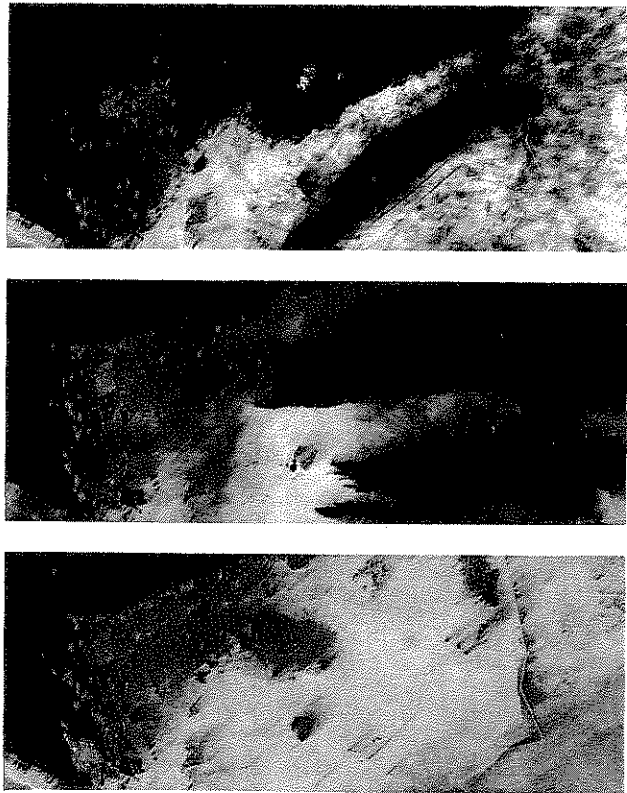


FIGURE 1-4 An example of pollutant advection and diffusion in the atmosphere. Smoke from multiple burning oil wells in Kuwait is carried downwind by advection. At the same time, the plumes of smoke widen because of diffusive transport, one of the major Fickian transport processes. Imagery courtesy of Space Imaging, Thornton, Colorado, USA.

movement of air or water, as seen in blowing wind and flowing streams. Figure 1-4 shows the advective transport of smoke from burning oil wells in Kuwait. (*Convection*, a similar term, often implies vertical advection of air or water resulting from density differences.) A chemical present in air or water is passively carried by this bulk advective movement, resulting in chemical transport.

In the second type of transport process, a chemical moves from one location in the air or water where its concentration is relatively high to another location where its concentration is lower, due to random motion of the chemical molecules (*molecular diffusion*), random motion of the air or water that carries the chemical (*turbulent diffusion*), or a combination of the two. Transport by such random motions, also called *diffusive* transport, is often

modeled as being *Fickian*. Sometimes the motions of the fluid are not entirely random; they have a discernible pattern, but it is too complex to characterize. In this situation, the mass transport process is called *dispersion*, and it is also commonly treated as a Fickian process, even though in some situations it may only approximate true Fickian transport. In a given amount of time, the distances over which mass is carried by Fickian transport (molecular diffusion, turbulent diffusion, and dispersion) are usually not as great as those covered by advection.

### 1.4.1 QUANTIFICATION OF ADVECTIVE TRANSPORT

The bulk motion of fluid is common throughout the environment; this advective motion is described mathematically by the *direction* and the *magnitude* of its velocity. If a chemical is introduced into flowing air or water, the chemical is transported at the same velocity as the fluid. While “spreading” due to Fickian transport may occur at the same time, as described in the next section, the *center of mass* of the chemical moves by advection at the average fluid velocity.

The rate at which a chemical is transported per unit area is often expressed in terms of *flux density*. Flux density is the mass of chemical transported across an imaginary surface of unit area per unit of time (Fig. 1-5) and is often given the symbol  $J$ . Note that the imaginary surface may be one of the boundaries of a control volume. Flux density due to advection is equal to the product of a chemical's concentration in the fluid and the velocity of the air or water,

$$J = CV, \quad [1-2]$$

where  $J$  is the flux density [ $M/L^2T$ ],  $C$  is the chemical concentration [ $M/L^3$ ], and  $V$  is the fluid velocity [ $L/T$ ].

The velocities of air and water frequently vary with time, as is evident to anyone who has stood in a gusty wind or swum in a turbulent river. Consequently, any estimate of flux density due to advection by a turbulent fluid flow must involve a time period over which flow variations and corresponding fluctuations of chemical concentration are averaged. Often the fluctuations in time are faster than the instruments for determining velocity and chemical concentration can follow, and the instruments inherently provide averaged values. In other situations, instruments can easily detect and measure the

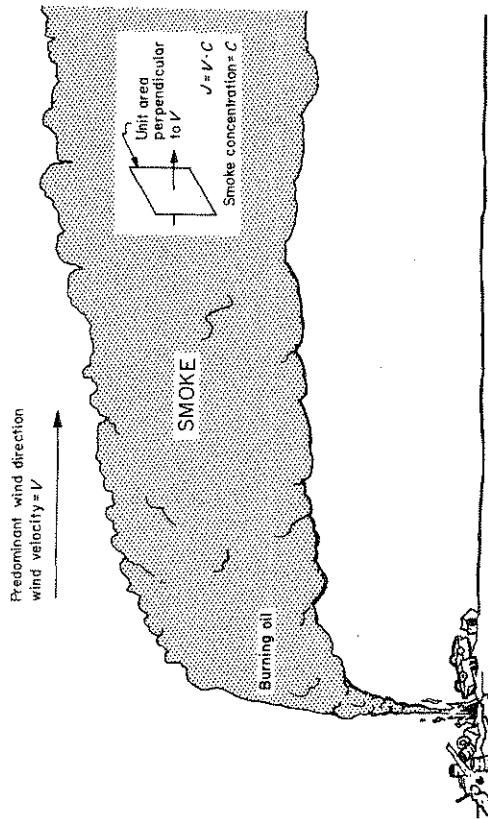


FIGURE 1-5 Advective transport of a smoke plume as shown in Fig. 1-4. The imaginary square frame is oriented perpendicular ( $\perp$ ) to fluid flow and for convenience has an area of one (in whatever units we prefer— $\text{m}^2$ ,  $\text{ft}^2$ , etc.). The flux density of smoke,  $J$ , is the product of the wind velocity  $V$  and the concentration of smoke in the air,  $C$ .

fluctuations, and decisions must be made on how to average the data when reporting the wind or water speed or the associated chemical fluxes.

#### EXAMPLE 1-2

If the salt concentration in a river is 20 mg/liter and the average river velocity is 100 cm/sec, what is the average flux density  $J$  of salt in the downstream direction?

First, convert 20 mg/liter to units consistent with the velocity:

$$C = \frac{20 \text{ mg}}{\text{liter}} \times \frac{1 \text{ liter}}{1000 \text{ cm}^3} = \frac{0.02 \text{ mg}}{\text{cm}^3}$$

Then use Eq. [1-2] to estimate the average flux density of salt:

$$J = 0.02 \text{ mg/cm}^3 \cdot 100 \text{ cm/sec} = 2 \text{ mg/cm}^2 \cdot \text{sec}$$

## 1.4.2 QUANTIFICATION OF FICKIAN TRANSPORT

### Turbulent Diffusion

Turbulent air and water motions contain constantly changing swirls of fluid, known as *eddies*, of many different sizes. One needs only to observe smoke rising from a factory smokestack or to experience gusty winds to appreciate the swirling and billowing that occur in air; in water, turbulence is evident in river rapids and breaking surf. These ubiquitous eddies give rise to another type of mass transport, known as *turbulent* (or *eddy*) *diffusion*. Turbulent diffusion, one of the mass transport processes commonly modeled as Fickian, arises from the random mixing of the air or water by these eddies. This type of mass transport neither augments nor impedes the downwind or downstream advective motion of a chemical. By mixing the chemical in the air or water, however, turbulent diffusion has the net effect of carrying mass in the direction of decreasing chemical concentration. The effects of turbulent diffusion on a mass of chemical are visible in many environmental situations: the spreading of a dye blob injected into a river, the expanding of a puff of smoke from fireworks, and the widening and blurring of condensation trails (contrails) of high altitude jets. Note in Fig. 1-4 that the oil smoke plumes become broader due to Fickian transport as they move downwind from their sources.

Fick's first law is typically used to describe the flux density of mass transport by turbulent diffusion,

$$J = -D(dC/dx) \quad (\text{in one dimension}), \quad [1-3]$$

where  $J$  is the flux density [ $\text{M/L}^2\text{T}$ ],  $D$  is the Fickian mass transport coefficient [ $\text{L}^2/\text{T}$ ],  $C$  is the chemical concentration [ $\text{M/L}^3$ ], and  $x$  is the distance over which a concentration change is being considered [L]. (In simple calculations the minus sign is often omitted if the direction of Fickian transport is clear.)

The parameter  $D$  is usually called a *turbulent* (or *eddy*) *diffusion coefficient* when it arises from fluid turbulence; its value varies enormously from one situation to another, depending on the intensity of turbulence and on whether the environmental medium is air or water. The diagram in Fig. 1-6 shows the Fickian mass flux arising from a concentration gradient in a smoke plume.

Fick's first law can also be expressed in three dimensions using vector notation,

$$\vec{J} = -D\nabla C \quad (\text{in three dimensions}), \quad [1-4]$$

where  $\nabla$  is the gradient operator and  $D$  is assumed to be equal in all directions.



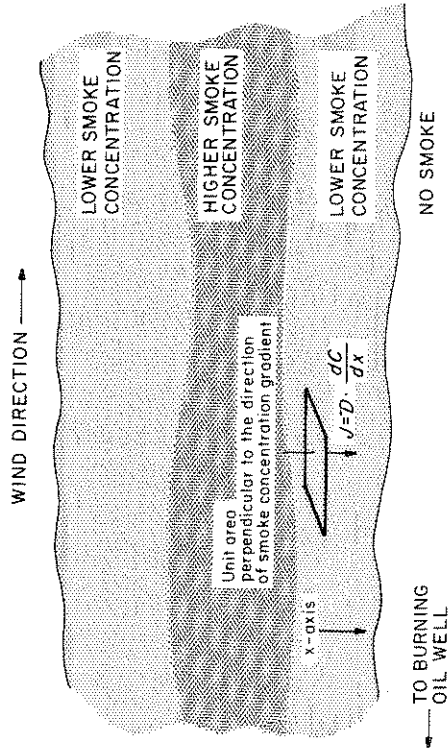


FIGURE 1-6 Fickian transport by turbulent diffusion in a smoke plume as shown in Figure 1-4. As in Figure 1-5, the square frame is of unit area, but in this case is oriented perpendicular to the direction of the concentration gradient (defined as the direction in which the concentration changes the most per unit distance.) In this case the  $x$ -axis is drawn in the direction of the gradient. The flux density,  $J$ , is equal to the concentration gradient,  $dC/dx$ , multiplied by the Fickian transport coefficient  $D$ . (In this situation,  $D$  is called a turbulent or eddy diffusion coefficient, because the major agent of Fickian transport is turbulence.)

In Eq. [1-4] the vector notation indicates that the direction of flux is in the direction of the steepest change in concentration with distance (the direction of the gradient vector), assuming that  $D$  is equal in all directions. For illustrative purposes, this book works mostly with the one-dimensional form of Fick's first law—Eq. [1-3]; in practice, many environmental situations also can be modeled in one dimension. Note that in the most general case, not only may  $D$  be *anisotropic* (i.e., not equal in all directions), but also  $D$  may vary with time and location.

### Dispersion

Turbulent diffusion is an important mode of chemical transport in both surface water and air. In the subsurface environment, groundwater flow normally lacks the eddy effects that characterize surface water and air movements because typical groundwater velocities are so much lower. Nevertheless, groundwater must take myriad detours as it moves from one point to another, traveling over, under, and around soil particles, as shown in Fig. 1-7. These random detours cause mixing, thus the net transport of a chemical from

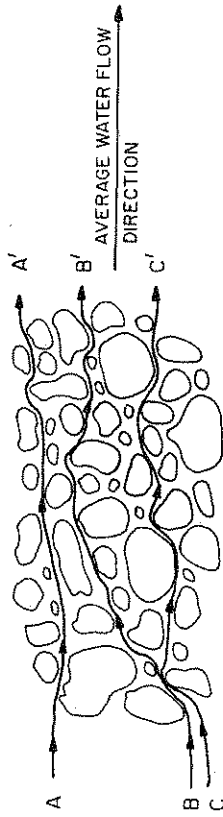


FIGURE 1-7 Fickian transport by dispersion as water flows through a porous medium such as a soil. Seemingly random variations in the velocity of different parcels of water are caused by the tortuous and variable routes water must follow. This situation contrasts with that of Fig. 1-6, in which turbulence is responsible for the random variability of fluid paths. In this case as well as in the previous one, Fickian mass transport is driven by the concentration gradient and can be described by Fick's first law. The mass transport effect arising from dispersion can be further visualized in Fig. 3-17. There, a mass initially present in a narrow slice in a column of porous media is transported by mechanical dispersion in such a way as to form a wider but less concentrated slice. At the same time, the center of mass also is transported longitudinally in the direction of water flow.

regions of higher concentration to regions of lower concentration. Despite the different physical mechanism causing the mixing, the net mass transport is entirely analogous to that of turbulent diffusion.

As in the case of turbulent diffusion, the chemical flux is often expressed by Fick's first law, as shown in Eqs. [1-3] and [1-4], but in this case  $D$  is called a *mechanical dispersion coefficient*. Dispersion also occurs at much larger scales than that of soil particles; for example, groundwater may detour around regions of relatively less permeable soil that are many cubic meters in volume. At this scale, the process is called *macrodispersion*.

### Molecular Diffusion

The Fickian mass transport processes discussed so far involve parcels of fluid taking irregular paths, due to either turbulence or obstructions, in such a complex manner that the individual eddies and obstructions cannot be tracked. Even if a fluid is entirely quiescent and without obstructions, however, chemicals will still move from regions of higher concentration to regions of lower concentration, due to the ceaseless random movement (*thermal motion*) of molecules. This type of mixing is called *molecular diffusion* and is also described by Fick's first law, but for a given chemical gradient it usually results in lower flux densities than those of the other Fickian mass transport processes. In this case,  $D$  in Eqs. [1-3] and [1-4] is called a *molecular diffusion*

*coefficient*. Unlike the coefficients for the previous two examples of Fickian transport, molecular diffusion coefficients can be estimated for a particular situation without much site-specific data, because they depend primarily on the size of the molecules that are diffusing. At environmental temperatures, most chemicals exhibit a molecular diffusion coefficient in air of about  $0.2 \text{ cm}^2/\text{sec}$ , and in water of about  $10^{-5} \text{ cm}^2/\text{sec}$ . Molecular diffusion increases in magnitude at higher temperatures and for smaller molecules or particles (which, at any given temperature, have higher average speeds than larger molecules or particles). Molecular diffusion sets the lower limit on the amount of Fickian mixing that can be expected in a fluid. The total Fickian transport coefficient equals the sum of the contributing Fickian coefficients due to molecular diffusion, turbulent diffusion, and mechanical dispersion.

#### EXAMPLE 1-3

Gasoline-contaminated groundwater has been transported under a residential dwelling from a nearby gasoline station. Two meters beneath the  $100 \text{ m}^2$  dirt floor of the residential basement, the concentration of hydrocarbon vapors in the soil air is 25 ppm on a mass/mass basis. Estimate the flux density of gasoline vapor and the daily rate of vapor inflow transported into the basement by molecular diffusion. Assume an approximate diffusion coefficient of  $10^{-2} \text{ cm}^2/\text{sec}$  for gasoline vapor in the soil (this value includes a correction for the presence of soil grains, as discussed in Chapter 3). Also assume the basement is well ventilated, so that the gasoline vapor concentration in the basement is much less than 25 ppm. Air density is approximately  $1.2 \text{ g/liter}$  at 1 atm pressure and  $20^\circ\text{C}$  (Weast, 1990).

Diffusion calculations require that concentration be expressed as mass per unit volume. To express the concentration of vapor as mass per unit volume, consider that 25 ppm is the same as 25 g per million grams of air. Given that  $1000 \text{ cm}^3$  of air has a mass of about 1.2 g at 1 atm pressure, the concentration of gasoline vapor 2 m below the dirt floor can be expressed as

$$C = 25 \text{ g}/10^6 \text{ g air} \cdot 1.2 \text{ g air}/1000 \text{ cm}^3 \text{ air} = 3 \times 10^{-8} \text{ g/cm}^3.$$

Treating this as a one-dimensional problem, the upward concentration gradient of vapor is approximately

$$dC/dz = (3 \times 10^{-8} \text{ g/cm}^3)/200 \text{ cm} = 1.5 \times 10^{-10} \text{ g/cm}^4.$$

The flux density, by Fick's first law in Eq. [1-3], is

$$J = -DdC/dz = (10^{-2} \text{ cm}^2/\text{sec}) \cdot (1.5 \times 10^{-10} \text{ g/cm}^4) \\ = 1.5 \times 10^{-12} \text{ g/cm}^2 \text{ sec}.$$

(Note informal treatment of the minus sign.)

Then the daily rate of vapor flow into the house is

$$(1.5 \times 10^{-12} \text{ g/cm}^2 \text{ sec}) \cdot (10^6 \text{ cm}^2) \cdot (3600 \text{ sec/hr}) \cdot (24 \text{ hr/day}) \\ = 0.13 \text{ g/day}.$$

This flux is probably not enough to worry about from a flammability perspective because the house is well ventilated.

### 1.5 MASS BALANCE IN AN INFINITELY SMALL CONTROL VOLUME: THE ADVECTION-DISPERSION-REACTION EQUATION

So far, the concept of mass conservation has been applied to large, easily measurable control volumes such as lakes. Mass conservation also can be usefully expressed in an infinitesimal control volume, mathematically considered to be a point. Conservation of mass is expressed in such a volume with the *advection-dispersion-reaction equation*. This equation states that the rate of change of chemical storage at any point in space,  $dC/dt$ , equals the sum of both the rates of chemical input and output by physical means and the rate of net internal production (sources minus sinks). The inputs and outputs that occur by physical means (advection and Fickian transport) are expressed in terms of the fluid velocity ( $V$ ), the diffusion/dispersion coefficient ( $D$ ), and the chemical concentration gradient in the fluid ( $dC/dx$ ). The input or output associated with internal sources or sinks of the chemical is represented by  $r$ . In one dimension, the equation for a fixed point is

$$\frac{dC}{dt} = -V \cdot \frac{dC}{dx} + \frac{d}{dx} \left( D \cdot \frac{dC}{dx} \right) + r. \quad [1-5]$$

The only difference between Eqs. [1-5] and [1-1a] and [1-1b] is that, because the control volume is of an unspecified, arbitrarily small size, each term is expressed as mass per unit time *per unit volume*. Thus, the leftmost term,  $dC/dt$ , represents the rate at which a chemical's concentration (storage per unit time) changes at a fixed point in a flowing fluid. The concentration

can change if there is a different concentration elsewhere in the flowing fluid and this different concentration is carried by advection to the fixed point of interest; this process corresponds to the term  $V \cdot dC/dx$ . The concentration can also change by Fickian transport if there is a spatially varying concentration gradient in the fluid; this process corresponds to the term  $d/dx(D \cdot dC/dx)$ . Changes in the concentration also can occur if a source or sink process, such as a chemical or biological reaction, is introducing or removing the compound of interest ( $r$ ).

Equation [1-5] is pertinent to a one-dimensional system, such as a long, narrow tube full of water, where significant variations in concentration may be assumed to occur only along the length of the tube. In a three-dimensional situation, the advection-dispersion-reaction equation can be represented most succinctly using vector notation, where  $\nabla$  is the divergence operator:

$$\frac{dC}{dt} = -\vec{V} \cdot \nabla C + \nabla \cdot D(\nabla C) + r \quad [1-6]$$

Note that the transport terms (the second and third terms) in Eq. [1-6] are the three-dimensional counterparts of the corresponding terms in Eq. [1-5]. As in Eq. [1-4],  $D$  is assumed equal in all directions. In many cases, this assumption is an oversimplification; the value of  $D$  in the direction of flow can be very different than the value perpendicular to flow (i.e.,  $D$  may be anisotropic). Furthermore,  $D$  may vary with location (i.e., be inhomogeneous), or vary with time. Often, a larger value of  $D$  may become applicable as the scale of the problem increases.

Although the forms of the mass conservation equation shown in Eqs. [1-5] and [1-6] may not appear to be directly applicable to large-scale environmental situations, they actually are very powerful tools. These equations can be integrated to yield mathematical solutions to chemical distributions in many physical systems. Given information on the inflow rates and chemical concentrations at the boundaries of a control volume, the chemical concentrations throughout the control volume may be determined by invoking solutions to Eqs. [1-5] and [1-6].

## 1.6 BASIC ENVIRONMENTAL CHEMISTRY

Now that the transport and storage terms of Eqs. [1-1a] and [1-1b] have been discussed, consider the source and sink terms. These correspond to the introduction or removal of a chemical due to either chemical reactions or transfer to another phase (e.g., volatilization of a chemical from water to air). Chemical reactions, which may occur spontaneously (abiotically) or be biologically

mediated, result in the transformation of one chemical substance into another. Chemical substances can be uncharged atoms or molecules, ions (electrically charged atoms or aggregations of atoms), or free radicals (highly reactive atoms or aggregations of atoms having an unpaired valence electron). The degradation of pollutant chemicals is a subset of all possible chemical reactions occurring in the environment.

By definition, chemical reactions involve the formation or breakage of chemical bonds between atoms. Chemical bonds hold atoms together in a variety of ways. Bond types include *covalent bonds*, in which electrons are shared between atoms; *ionic bonds*, in which the bonding force arises from electric charges of opposite sign on adjacent atoms; and *hydrogen bonds*, in which the somewhat positively charged hydrogen atom at one end of a molecule loosely bonds with a somewhat negatively charged atom of another molecule. Other forces, such as *Van der Waals forces*, which cause weak mutual attractions between all molecules, can also contribute to bonding. A chemical bond may have characteristics of more than one idealized type of bonding. For further discussions on chemical reactions, the reader is referred to texts such as Petrucci (1989), Radel and Navidi (1990), and Shriver *et al.* (1994) for inorganic chemicals; and to Roberts and Caserio (1977), McMurry (1992), and Streitwieser *et al.* (1992) for organic chemicals.