Environmental Engineering Science

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Transport Phenomena

Transport phenomena are encountered in almost every aspect of environmental engineering science. In assessing the environmental impacts of waste discharges, we seek to predict the impact of emissions on contaminant concentrations in nearby air and water. Contaminant transport must be understood to evaluate the effect of wastewater discharge to a river on downstream water quality or the effect of an incinerator on downwind air pollutant levels. In waste treatment technologies, contaminant transport within the control device influences the overall efficiency. In many instruments used to measure environmental contamination, performance depends on the effective transport of contaminants from the sampling point to the detector.

The physical scales of concern for contaminant transport span an enormous range. At the low end, we are interested in phenomena that occur over molecular dimensions, such as the transport of a contaminant into the pore of an adsorbent. At the upper extreme, we consider the transport of air and waterborne contaminants over

global distances. This range of linear dimensions encompasses approximately 15 orders of magnitude. Not surprisingly, some phenomena that are important at one end of the spectrum are irrelevant at the other.

Transport phenomena also are important in other fields of study, notably chemical and mechanical engineering. In these fields, the subject is often subdivided into fluid mechanics, heat transfer, and mass transfer. In environmental engineering, where the focus is on the movement of contaminants in air and water, elements of all three of these branches are considered. The essential ingredients for understanding contaminant transport processes are knowledge of the basic physical phenomena coupled with the analytical tools of engineering mathematics.

Because of the importance of both molecular and particulate impurities in environmental fluids, the dominant transport processes of both molecules and particles will be discussed in this chapter. We consider both the movement of impurities *with* fluids and their movement *relative to* fluids. In Chapter 5, we will explore how the transport mechanisms studied in Chapter 3 and the transport mechanisms explored in this chapter are combined to predict system behavior using mathematical models.

4.A   BASIC CONCEPTS AND MECHANISMS

4.A.1   Contaminant Flux

Transport of both molecules and particles is commonly quantified in terms of *flux density*, or simply *flux*. Flux is a vector quantity, comprising both a magnitude and a direction. The flux vector points in the direction of net contaminant motion, and the magnitude indicates the rate at which the contaminant is moving.

For example, think of an environmental fluid as depicted in Figure 4.A.1. Imagine a small square frame suspended in this fluid and centered at a point of interest. The frame is oriented so that the transport of contaminants through it is maximized. Then the flux vector points in a direction normal to the frame, aligned with the direction of contaminant transport. The magnitude of the flux vector is the net rate of contaminant transport per unit area of the frame. Since the flux can vary from one position to another, the flux at a point represents the net transport through the frame per area in the limit of the frame becoming infinitesimally small. The common units of flux are mass or moles per area per time. We will use the symbol J to represent flux. An arrow is written above J when we wish to emphasize its vector character. Contributions to flux

Figure 4.A.1 Flux, $\vec{J}$, is a vector quantity whose value varies with position (x, y, z). The contaminant flux vector points in the direction of transport, and its magnitude is the quantity transported (usually mass or moles) per area per time.

Table 4.A.1 Dominant Mechanisms That Cause Transport of Molecules and Particles in Environmental Fluids

Transport mechanism	Species[a]	Description	1-D flux[b]
Advection	m, p	Movement with fluid	$J_a = CU$
Gravitational settling	p	Transport induced by gravity	$J_g = Cv_t$
Molecular diffusion or Brownian motion[c]	m, p	Transport caused by random thermal motion	$J_d = -D\dfrac{dC}{dx}$
Turbulent diffusion	m, p	Transport caused by apparently random fluid velocity fluctuations in turbulent flow	$J_t = -\varepsilon_t \dfrac{dC}{dx}$
Shear-flow dispersion	m, p	Transport caused by nonuniform fluid flow with position	$J_s = -\varepsilon_s \dfrac{dC}{dx}$
Hydrodynamic dispersion (porous media)	m, p	Transport caused by nonuniform flow through porous material	$J_h = -\varepsilon_h \dfrac{dC}{dx}$
Electrostatic drift[d]	m, p[e]	Movement of charged species in an electric field	$J_e = Cv_e$
Inertial drift	p	Transport associated with acceleration of a fluid	$J_f = Cv_f$

[a] m = molecule, p = particle.

[b] C = species concentration, U = fluid velocity, v_t = settling velocity, D = molecular or Brownian diffusivity, ε_t = turbulent diffusivity, ε_s = shear-flow dispersivity, ε_h = dispersion coefficient, v_e = electrostatic drift velocity, v_f = inertial drift velocity, J = flux.

[c] Molecular diffusion and Brownian motion apply to molecules and particles, respectively; both occur from the same fundamental process.

[d] See §7.C.

[e] Electrostatic drift applies to charged species only.

may be caused by several mechanisms (Table 4.A.1). A major thrust of this chapter is to explore the basic physical mechanisms that cause contaminant flux.

4.A.2   Advection

Advection is the transport of material caused by the net flow of the fluid in which that material is suspended. Whenever a fluid is in motion, all contaminants in the fluid, including both molecules and particles, are advected along with the fluid.

Figure 4.A.2 shows how an advective flux can be evaluated. Consider a fluid flowing through a tube with a uniform velocity. Assume that the fluid contains a uniform concentration, C, of some contaminant. Focus on the amount of contaminant in a slice of fluid of thickness ΔL. As shown in the upper part of the diagram, at time t, the leading edge of the slice has just reached position x. At some later time, $t + \Delta t$ (see the lower part of the diagram), the trailing edge of the slice passes position x.

The advective flux vector for this contaminant points along the axis of the tube, in the same direction as the velocity vector. The magnitude of the flux vector at position x is obtained by dividing the amount of contaminant that passes position x by the cross-sectional area of the tube (A) and by the time interval required (Δt). The amount of contaminant that passes position x is the contaminant concentration (C) times the volume of the depicted slice ($\Delta L \times A$). Note that the time interval (Δt) is equal to the thickness of the slice divided by the fluid velocity ($\Delta L/U$). So, for this case, the advective flux magnitude, J_a, is the quantity of contaminant passing position x per area
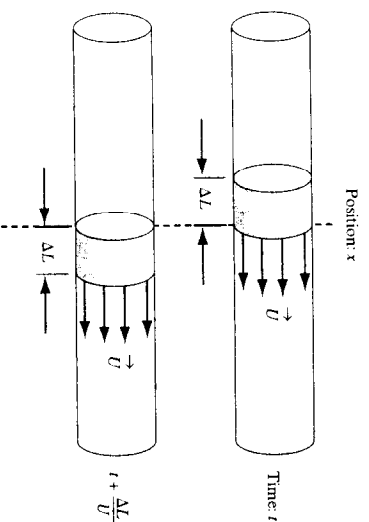
Figure 4.A.2 Advective flux of contaminant through a tube. The two pictures represent the same tube at two points in time, t and $t + \Delta t$, where $\Delta t = \Delta L/U$.

per time:

$$J_a = \frac{C \times \Delta L \times A}{A(\Delta L/U)} = CU \quad (4.A.1)$$

In general, the three-dimensional advective flux vector is the product of the contaminant concentration and the fluid velocity:

$$\vec{J}_a(x, y, z) = C(x, y, z) \times \vec{U}(x, y, z) \quad (4.A.2)$$

4.A.3 Molecular Diffusion

The molecules in air and water are constantly moving. If it could be viewed at a molecular scale, this movement would appear random and chaotic. Molecular movement in gases is particularly frenzied. In air at ordinary environmental conditions, a typical molecule, moving at a speed of ~400 m s^{-1}, collides with other molecules on the order of 10 billion times per second. Each collision involves an exchange of momentum between the participants, causing them to change direction and speed. Every cubic centimeter of air has a phenomenally large number of molecules (~25 million trillion at $T = 298$ K and $P = 1$ atm) participating in this dance. In water, where the molecules are packed a thousand times more densely, molecular motion is less frenetic, but still extremely energetic.

Although the molecular-scale motion seems hopelessly disordered, the macroscopic effects are well understood and predictable. Qualitatively, the random motion of fluid molecules causes a net movement of species from regions of high concentration to regions of low concentration. This phenomenon is known as *molecular diffusion*. The rate of movement depends on the concentration difference, with larger differences leading to higher rates of transport. The rate also varies according to how far the species must travel from high to low concentration: The longer the distance, the lower the flux. The rate of transport varies according to the molecular properties of the species, particularly size and mass, with larger size and larger mass resulting in slower transport. The properties of the fluid itself play a key role: Molecular diffusion

is much slower in water than in air because of the much closer packing density of water molecules.

Our discussion is restricted to conditions in which the diffusing species is present at a low mole fraction ($\ll 1$), referred to as the *infinite dilution* condition. In most environmental engineering applications, this assumption is appropriate. At high concentrations, diffusion can cause significant net flow of the bulk fluid (Bird et al., 1960; Cussler, 1984).

Fick's Law

To better understand diffusion, it is useful to think about a specific physical system, such as the one depicted in Figure 4.A.3. A glass bulb at 25 °C contains a liquid with a moderate vapor pressure, such as ethylbenzene (1280 Pa at 25 °C; see Table 3.B.1). The bulb is open to the air through a thin cylindrical glass tube. Ethylbenzene molecules evaporate from the liquid, maintaining a partial pressure in the gas phase of the bulb equal to the saturation vapor pressure. Because of their random motion, the ethylbenzene molecules gradually migrate through the tube and escape into the open air. After a short transient period, the net rate of transport of ethylbenzene molecules through the tube will reach a steady value that will be maintained as long as there is liquid ethylbenzene in the bulb. The escape rate of ethylbenzene from the tube varies in inverse proportion to tube length, in proportion to the cross-sectional area of the tube, and in proportion to the partial pressure of the species in the bulb. These characteristics can be expressed quantitatively by the relationship

$$J_d \propto -\frac{\Delta C}{\Delta x} \quad (4.A.3)$$

where J_d is the diffusive flux density (moles per cross-sectional area of the tube per time), ΔC is the change in concentration of ethylbenzene molecules across the tube, and Δx is the tube length. The minus sign appears in this relationship to remind us that the diffusive flux proceeds in the direction of decreasing concentration.

By introducing the proportionality constant, D, this expression can be converted to an equation:

$$J_d = -D\frac{\Delta C}{\Delta x} \quad (4.A.4)$$

The constant, D, is called the *diffusion coefficient*, or *diffusivity*. It is a property of the diffusing species (ethylbenzene in this case), the fluid through which it is diffusing
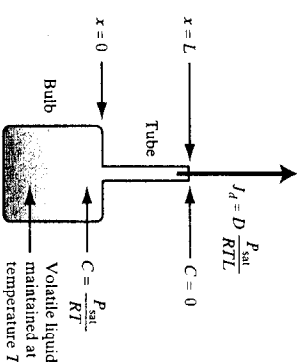

Figure 4.A.3 Apparatus for producing a controlled diffusive flux of a volatile species. P_{sat} is the saturation vapor pressure of the species at temperature T. Provided that the time scale for evaporation and condensation is much more rapid than the time scale for diffusion through the tube, a molar concentration P_{sat}/RT will be attained throughout the bulb. The vapor molecules will diffuse through the tube with a net diffusive flux J_d.

(air), and environmental conditions such as temperature and pressure. The diffusion coefficient has dimensions of length squared per time; typically, D is reported in units of $cm^2 s^{-1}$. For molecules in air, a characteristic diffusivity is $0.1 cm^2 s^{-1}$. In water, molecular diffusivities are on the order of $10^{-5} cm^2 s^{-1}$.

If we treat a fluid as a continuous substance, and take the limit of equation 4.A.4 as the distance Δx becomes infinitesimally small, we can replace $\Delta C/\Delta x$ by the derivative dC/dx and write

$$J_d = -D\frac{dC}{dx} \tag{4.A.5}$$

For applications in three dimensions, the general equation for diffusive flux can be written as follows:

$$\vec{J_d}(x,y,z) = -D\left(\frac{\partial C}{\partial x}, \frac{\partial C}{\partial y}, \frac{\partial C}{\partial z}\right) \tag{4.A.6}$$

In words, equation 4.A.6 states that each component of the flux vector is proportional to the partial derivative of concentration in that coordinate direction, and the proportionality constant is $-D$ for each direction. So diffusive flux occurs in the direction opposite to the concentration gradient at a rate that is proportional to its magnitude. Equations 4.A.5 and 4.A.6 are known as Fick's first law of diffusion, or simply Fick's law. See Exhibit 4.A.1 for more details about the system depicted in Figure 4.A.3.

Significance of Diffusion

Diffusion is a slow transport process. Albert Einstein showed that the characteristic distance a molecule (or a particle) will travel by diffusion in time t is given by

$$x \sim \sqrt{2Dt} \tag{4.A.7}$$

So a gas molecule with a diffusivity of $0.1 cm^2 s^{-1}$ can be expected to move a characteristic distance of 5 mm in a second, 3 cm in a minute, 30 cm in an hour, and 1 m in a day. Molecules in water, with diffusivities lower by a factor of 10^4, will travel only 1 percent as far on these time scales.

Another perspective is gained by comparing the simple form of Fick's law (equation 4.A.4) with the simple advective flux expression (equation 4.A.1). If a species concentration diminishes from C to zero over some distance Δx, then diffusion causes transport at a rate equivalent to advection at a velocity $D/\Delta x$. Given the small values of D for air and especially for water, we see that the effective diffusive velocity is very small except when the concentration changes by a large fractional amount over a very small distance.

Although molecular diffusion is a slow process, it plays a very important role in contaminant transport and fate. Diffusion is particularly important at interfaces, for example between two fluids such as air and water, or at solid-fluid interfaces. There can be no fluid advection at an interface in the direction normal to the surface. So impurities cannot be transported by advection all the way to an interface. Instead, some other transport mechanism must convey the species through a small distance, known as a *boundary layer*, to the interface. For uncharged molecular impurities, diffusion is the dominant mechanism of transport through boundary layers. For ions and particles, diffusion always contributes, although other mechanisms such as electrostatic drift and gravitational settling may also play a role. These details are important because impurities may be removed from a fluid by deposition or other transformation pro-

cesses that occur on surfaces. Often, the rate of transport to the surface governs the overall removal rate.

EXHIBIT 4.A.1 An Application of Diffusion

Let's further explore the behavior of the system depicted in Figure 4.A.3. Devices like this are used to release a volatile substance at a constant rate. By diluting the emissions from the top of the tube with a known flow rate of contaminant-free air, one generates an air stream with a constant, known concentration of the volatile substance. This air stream can be used for instrument calibration among other purposes.

When liquid is first placed into the bulb, some time must elapse before the diffusive flux leaving the tube reaches a steady value. An estimate of this time is obtained by rearranging equation 4.A.7 (substituting $\tau_{diffusion}$ for t and L for x):

$$\tau_{diffusion} \sim \frac{L^2}{2D} \tag{4.A.8}$$

This expression yields an estimate of the time required for a molecule to diffuse through some distance L. It is a good estimate for the characteristic time required to establish a steady concentration profile throughout the tube length. For typical values in a device of this sort, $L \sim 5$ cm and $D \sim 0.1 cm^2 s^{-1}$, so $\tau_{diffusion} \sim 2$ min. With conditions held steady for a time $t \gg \tau_{diffusion}$, the flux will approach a steady value

that will be maintained as long as liquid remains in the bulb.

The characteristic time for the liquid to completely evaporate is obtained as the number of moles of liquid in the bulb divided by the molar rate of escape by diffusion:

$$\tau_{evaporation} \sim \frac{(\rho V/MW)}{J_d A} \tag{4.A.9}$$

where ρ is the liquid density, V is the liquid volume, MW is the molecular weight of the diffusing species, and A is the cross-sectional area of the tube. For the case of ethylbenzene, we can estimate an evaporation time, $\tau_{evaporation} \sim 4 \times 10^7 s \sim 500$ d.

We have assumed the following values for the input data: $\rho V = 1$ g, MW = 106 g mol^{-1}, $J_d = 7.2 \times 10^{-9}$ mol cm^{-2} s^{-1}, $D = 0.07 cm^2 s^{-1}$, $P_{sat} = 1280$ Pa, $R = 8.31 \times 10^6 cm^3$ Pa K^{-1} mol^{-1}, $T = 298$ K, and $L = 5$ cm), and $A = 0.031 cm^2$ (0.2 cm inner tube diameter). For times t that satisfy $\tau_{diffusion} \ll t \ll \tau_{evaporation}$, the diffusive flux from the tube into the air will be constant. During this time interval, the concentration profile within the tube will also be constant, varying linearly with position, x, as shown in Figure 4.A.4.

Species concentration, C

$$\frac{P_{sat}}{RT}$$

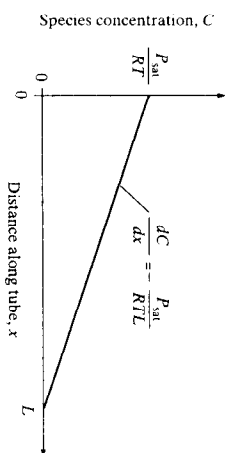$$\frac{dC}{dx} = -\frac{P_{sat}}{RTL}$$

Distance along tube, x — L

Figure 4.A.4 Steady concentration profile within the tube shown in Figure 4.A.3, valid for times t that satisfy $\tau_{diffusion} \ll t \ll \tau_{evaporation}$.

Diffusivity of Molecules in Air

Predictions of diffusive flux depend on the selection of an appropriate diffusion coefficient, D. Measured diffusion coefficients for selected species in air are presented in Table 4.A.2. This table emphasizes species of environmental interest, with air at ordinary environmental temperatures and pressures as the background fluid. Note that there are discrepancies in the data reported from different sources (e.g., ammonia).

Table 4.A.2 Measured Diffusion Coefficients for Species in Air at 1 atm

Species	Formula	T (K)	D (cm² s⁻¹)	Reference[a]
Ammonia	NH_3	273	0.198	Bretsznajder, 1971
		273	0.216	McCabe et al., 1993
Benzene	C_6H_6	273	0.077	McCabe et al., 1993
		298.2	0.096	Cussler, 1984
Carbon dioxide	CO_2	273	0.138	McCabe et al., 1993
		317.2	0.177	Cussler, 1984
Ethanol	C_2H_5OH	273	0.102	McCabe et al., 1993; Cussler, 1984
		313	0.147	Reid et al., 1987 (pressure = 1 bar)
Helium	He	276.2	0.624	Cussler, 1984
Hydrogen	H_2	273	0.611	Cussler, 1984
Methane	CH_4	273	0.196	Cussler, 1984
Methyl alcohol	CH_3OH	273	0.133	Cussler, 1984; McCabe et al., 1993
n-Octane	C_8H_{18}	273	0.051	McCabe et al., 1993
Naphthalene	$C_{10}H_8$	273	0.051	McCabe et al., 1993
		303	0.087	Reid et al., 1987
Oxygen	O_2	273	0.178	McCabe et al., 1993
Toluene	C_7H_8	273	0.071	Cussler, 1984; McCabe et al., 1993
		299.1	0.086	Cussler, 1984
Water	H_2O	273	0.219	Bretsznajder, 1971; McCabe et al., 1993
		289.1	0.282	Cussler, 1984
		298.2	0.260	Cussler, 1984
		312.6	0.277	Cussler, 1984
		313	0.292	Reid et al., 1987

[a]When two sources disagree by less than 5 percent, only one value is listed.

The data in Table 4.A.2 show that the diffusivity of gases in air varies over about an order of magnitude from about 0.05 cm² s⁻¹ for large organic molecules (n-octane and naphthalene) to about 0.6 cm² s⁻¹ for helium and hydrogen. Diffusivities increase with increasing temperature because of the higher kinetic energy of the molecules.

Diffusivities of Molecular Species in Water

Experimental data for selected species in water are presented in Table 4.A.3. These data exhibit a range of about a factor of 5.

4.A.4 Dispersion

Our everyday experience tells us that impurities released into open air or water do not remain confined at high concentration in a small volume for very long. Cooking odors, incense, and cigarette smoke all become detectable throughout an indoor space within minutes of their release. The visible smoke plume from a fire can be seen to spread significantly as it travels downwind. The rate of contaminant spreading is of substantial interest in environmental engineering. And although fundamentally it occurs as a result of advection and diffusion, the rate of spreading is much more rapid than might be inferred from the discussion so far.

Table 4.A.3 Measured Diffusion Coefficients for Species in Water

Species	Formula	T (K)	D (cm² s⁻¹)	Reference[a]
Benzene	C_6H_6	298	1.02×10^{-5}	Cussler, 1984
Hydrogen	H_2	298	3.36×10^{-5}	Bretsznajder, 1971
		298	4.50×10^{-5}	Cussler, 1984
Air		298	2.00×10^{-5}	Cussler, 1984
Methane	CH_4	275	0.85×10^{-5}	Reid et al., 1987
Carbon dioxide	CO_2	298	2.00×10^{-5}	Reid et al., 1987
Methanol	CH_3OH	288	1.26×10^{-5}	Reid et al., 1987
		298	0.84×10^{-5}	Cussler, 1984
Ethanol	C_2H_5OH	288	1.00×10^{-5}	Reid et al., 1987
		298	0.84×10^{-5}	Cussler, 1984
Ethylbenzene	C_8H_{10}	293	0.81×10^{-5}	Reid et al., 1987
Oxygen	O_2	298	2.60×10^{-5}	Bretsznajder, 1971
Vinyl chloride	C_2H_3Cl	298	1.34×10^{-5}	Reid et al., 1987

[a]When two sources disagree by less than 5 percent, only one value is listed.

Uniform, steady advection does not cause pollutant spreading, and we have seen that molecular diffusion is a slow process. Consider the following situation (Cussler, 1984). Imagine that a thin stream of smoke particles is released along the western coast of the United States and is steadily advected at a constant, uniform wind speed of 5 m s⁻¹ to the eastern coast. Assume that particles have a diameter of 0.1 μm. How much spreading of the plume will occur by diffusion during this transcontinental travel? The time required for the wind to travel that distance is ~10⁶ s or 12 d (5000 km ÷ 5 m s⁻¹). In Example 4.B.3 it will be shown that a 0.1 μm particle has a diffusivity in air of 7 × 10⁻⁶ cm² s⁻¹. The plume spread caused by diffusion is estimated to be the characteristic distance traveled due to Brownian motion, which, according to equation 4.A.7, is roughly 4 cm. Clearly, this is not an accurate description! It is entirely contrary to our experience to think that we could even detect a smoke plume at a distance of 5000 km from its source. Yet this example accurately applies the tools and concepts we have introduced. What went wrong?

Our error was made in assuming that the wind speed is uniform and steady. It is a property of most fluid flows, including winds and ocean currents, that they are neither constant nor uniform. When fluid velocity varies with time or position, contaminants in the fluid tend to be transported from high concentration to low concentration. The spreading of contaminants by nonuniform flows is called *dispersion*.* It is not a fundamentally distinct transport process. Instead, dispersion is caused by nonuniform advection and influenced by diffusion.

Figure 4.A.5 illustrates why it is important to incorporate dispersion into the analysis of environmental transport. Pollutants are shown being released from an elevated stack and blowing downwind. The left-hand figures show that in the case of weak dispersion, the plume spreads slowly. Downwind of the source, the peak concentrations remain very high near the plume centerline and the pollutants do not spread rapidly to the ground. On the right, dispersion is strong. The concentrations within the plume are diminished rapidly by dispersion, but the plume reaches the ground much nearer to the source. This trade-off is characteristic of the effect that

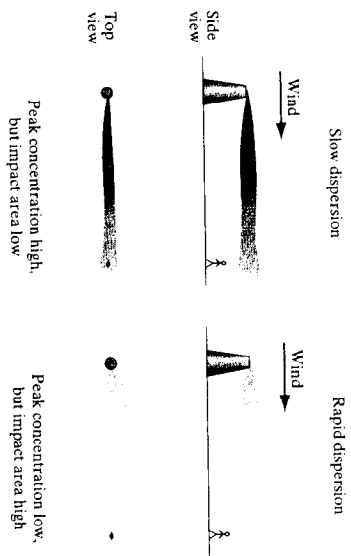*We will use the term *dispersion* to include both shear-flow dispersion and turbulent diffusion.

Side
view

Wind →

Slow dispersion

Peak concentration high,
but impact area low

Wind →

Rapid dispersion

Peak concentration low,
but impact area high

Top
view

Figure 4.A.5 Effect of dispersion on pollutant concentrations downwind of a localized source. If the release rate of pollutants and mean wind speed are the same in the left- and right-hand frames, then the total flow of pollutants is the same in the two cases: Rapid dispersion leads to smaller peak concentrations but a larger impact area.

dispersion has in all environmental settings: High dispersion rates reduce average concentrations at the expense of increasing the area or duration of impact. A common challenge in environmental transport modeling is to predict concentrations in the region downwind or downstream of a pollution source. To make these predictions in the face of dispersion phenomena, we must solve two problems. First, we must have a model that describes pollutant concentration fields in the presence of dispersion. Second, we must be able to determine how the rate of dispersion varies with environmental conditions.

In complex flow fields, it is impossible (or at least impractical) to describe fluid velocity exactly as a function of space and time. Without this information, dispersion cannot be accurately described in terms of the fundamental mechanisms of advection and molecular diffusion. As an alternative, dispersion can be treated as a random process, analogous to molecular diffusion, by applying Fick's first law of diffusion with the molecular diffusion coefficient replaced by a dispersion coefficient. So in one dimension, we would write

$$J_{dispersion} = -\varepsilon \frac{dC}{dx} \qquad (4.A.10)$$

where ε is a *dispersion coefficient*, obtained through a combination of empirical data and theoretical equations.

Although equation 4.A.10 has the same form as Fick's first law, it is important to bear in mind the great distinction between diffusion and dispersion. Diffusivities are properties of the contaminant and the fluid, depending weakly on environmental conditions (such as temperature) but not at all on fluid flows. Dispersion coefficients, on the other hand, are primarily a function of the fluid flow field. Environmental flows are highly variable and very complex. Dispersion in environmental flows is far less well understood than molecular diffusion. One should not expect a high degree of accuracy from any models that must account for dispersion, especially when applied to environmental transport.

Dispersion phenomena arise in all three branches of environmental engineering discussed in this text. Figure 4.A.5 illustrates one of many instances that arise in air quality engineering. In water quality, the impact of wastewater discharges on contaminant concentrations in rivers, lakes, or oceans depend on dispersion. In hazardous waste management, dispersion controls the movement of contaminants in groundwater.

Several types of dispersion phenomena are encountered in environmental engineering. In this section, two common types are introduced: *shear-flow dispersion* and *turbulent diffusion*.

Shear-Flow Dispersion

In a shear flow, the fluid speed varies with position in a direction that is perpendicular to the fluid velocity. If contaminant concentrations in a shear flow vary in the direction of flow, then dispersion will occur, leading to a net transport of contaminants from regions of high concentration to areas of low concentration.

Shear-flow dispersion is generally important when there is a short-term release of contaminants, such as a spill, in environments in which the velocity gradients are large, such as a river, an estuary influenced by tides, or the near-ground atmosphere. Let's consider a relatively simple example: shear-flow dispersion in fully developed laminar flow through a circular tube or pipe (Figure 4.A.6). The velocity profile of the fluid flow is parabolic because of wall friction. At time $t = 0$, some mass, M, of contaminant is injected into the tube at position $x = 0$ and instantaneously mixed laterally so that its concentration is uniform across the tube. We then observe the contaminant as it is advected past some position, L, downstream. The upper frame in the figure shows the initial condition. The lower frame shows the tube at a subsequent time, $t = L/U_0$. At the later time, the contaminant pulse is centered on downstream position $x = L$, but it has been substantially stretched because those molecules that lie close to the centerline of the tube are advected at a higher velocity than those near the wall. At the same time, contaminant molecules positioned near the leading edge of the pulse and near the center of the tube tend to diffuse toward the walls, reducing their average forward velocity. Conversely, contaminant molecules located near the center, increasing their forward velocity. Therefore, surprisingly, the net effect of molecular diffusion is to slow the rate of dispersion, in this case.
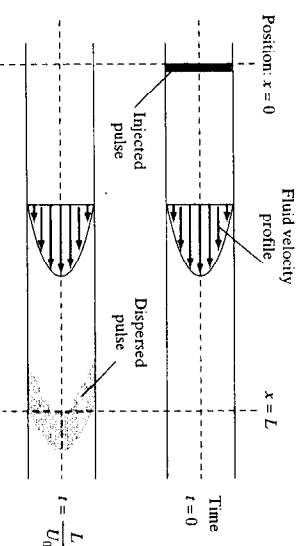
Position: $x = 0$

Fluid velocity
profile

Injected
pulse

$x = L$

Time
$t = 0$

Dispersed
pulse

$t = \frac{L}{U_0}$

Figure 4.A.6 Schematic of a model problem illustrating the effects of shear-flow dispersion.

For the situation depicted in Figure 4.A.6, the contaminant flux in the direction of flow can be described as the sum of two components: (1) advection, which transports the overall pulse through the tube, and (2) shear-flow dispersion, which causes the pulse to become stretched as it travels. The flux in the direction of flow caused by shear-flow dispersion is written as

$$J_s = -\varepsilon_s \frac{dC(x)}{dx}$$ (4.A.11)

where ε_s is the shear-flow dispersivity and $C(x)$ represents the contaminant concentration averaged over a cross-section of the tube at position x.

Shear-flow dispersion is most commonly applied to predict the transport of contaminants in systems in which the flow is confined. In addition to pipe or tube flow, shear-flow dispersion is applied to study pollutant transport in rivers and in estuarine environments influenced by tides.

Turbulent Diffusion

In most systems encountered in environmental engineering, fluid flows are *turbulent* rather than *laminar*. Whereas for laminar flows we can determine the fluid velocity field at each instant and each position, turbulent flows fluctuate in such a manner that predictions are nearly impossible. Instead, we describe turbulent flows in terms of their statistical properties, such as the mean speed and the average size of the fluctuations.

Like molecular diffusion, the apparently random motion that is characteristic of turbulent flows causes a net flux of a contaminant from high to low concentrations. This flux is often described by an equation that is analogous to Fick's law:

$$J_t = -\varepsilon_t \frac{dC}{dx}$$ (4.A.12)

where ε_t is the *turbulent diffusion coefficient* and C now denotes the time-averaged value of concentration. For application in three dimensions, this expression can be generalized to vector form:

$$\vec{J}_t = -\left(\varepsilon_{tx}\frac{\partial C}{\partial x}, \varepsilon_{ty}\frac{\partial C}{\partial y}, \varepsilon_{tz}\frac{\partial C}{\partial z}\right)$$ (4.A.13)

Here ε_{tx}, ε_{ty}, and ε_{tz} represent the *turbulent diffusion coefficients*, or *eddy diffusivities* in the x, y, and z directions, respectively. Typically, for turbulent transport in the atmosphere or in natural waters, the coordinate system is arranged so that x and y lie in the horizontal plane and z is vertical. Vertical eddy diffusivity generally differs from horizontal eddy diffusivity. Usually, though, it is assumed that $\varepsilon_{tx} = \varepsilon_{ty}$.

To help visualize the impact of turbulence on pollutant dispersion, ignite something that will generate a visible smoke plume, such as a cigarette or some incense. Place the smoldering object indoors in still air with lighting that permits good observation of the plume. (For example, position a high-intensity desk lamp on the opposite side of the plume from you, but just out of your line of sight, and direct the light at the plume.) If the air is sufficiently still so that the buoyancy of the plume controls its motion, you will see the plume rise in a steady, narrow stream for a distance on the order of 10–30 cm, then buckle, and finally break up into turbulent eddies. The flow in the lower portion of the plume is laminar, and the flow in the upper portion is turbulent. If you now imagine that the concentration of smoke particles is to be determined on a
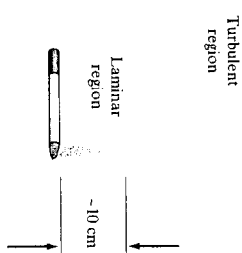
Turbulent region

Laminar region

~10 cm

Figure 4.A.7 Schematic representation of time-averaged smoke plume rising from a smoldering cigarette in still air.

time-averaged basis, over a minute or so, you should arrive at a picture like the one shown in Figure 4.A.7. The broadening of the plume in the turbulent region is a direct consequence of turbulent air motion. The mean fluid flow is still upward, but there are fluctuating horizontal components of the flow that cause rapid pollutant dispersion in the horizontal direction. For environmental engineering applications, this is a key property of turbulence: In unbounded flow, turbulent diffusion controls the transport of pollutants in directions normal to the mean flow.

Figure 4.A.8 depicts a plume spreading from a point source discharging either to water or to air. A horizontal slice through the center of the plume is shown from above, and the mean fluid velocity is oriented from left to right. The coordinates are oriented so that x is aligned with the mean velocity and y represents the horizontal distance from the plume centerline. The origin is positioned at the source.

Assume that the rate of pollutant discharge is constant and the mean fluid velocity is independent of position and time. Then Figure 4.A.8 represents the average conditions over some period such as an hour. On this basis, the plume spreads fairly smoothly and symmetrically from the source. The coordinate axes at right show the time-averaged concentration profile plotted against y at some distance away from the source. The peak concentration occurs at $y = 0$ and gradually approaches zero as the distance from the centerline increases. The spreading of the plume in the y-direction is controlled by turbulent diffusion.

A practical challenge in the use of equation 4.A.13 is to determine the turbulent diffusivities. These parameters vary not only with flow conditions, but also with position and direction. For example, turbulent diffusivities diminish to zero at rigid fluid boundaries, because the fluid velocity itself goes to zero. Correlations exist for
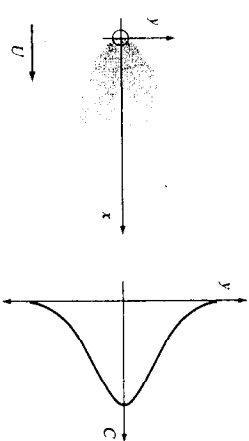
U

y

x

y

C

Figure 4.A.8 Plume spreading from a point source. The pollutant discharge rate is constant and the mean fluid velocity is steady and uniform, but the flow is turbulent.

predicting turbulent diffusivities, but these should be used cautiously, as the supporting experimental data are limited.

Turbulent diffusivities are higher in rivers than in regular channels because the irregularities in the river channel create additional irregularities in the flow, which tend to enhance mixing. Turbulent diffusivities in rivers are an order of magnitude smaller than longitudinal (shear-flow) dispersion coefficients. Consequently, studies of transport and mixing in rivers typically account for transport across the flow by turbulent diffusion and along the flow by advection and shear-flow dispersion. Vertical transport is assumed to occur very rapidly, since most rivers are much wider than deep.

In the atmosphere, turbulent diffusion is especially important in the vertical direction. Most pollutants are emitted near the ground, and the rate and extent of vertical turbulent diffusion strongly influences ground-level concentrations. Atmospheric stability, as will be discussed in §7.D, has a very strong influence on turbulent diffusivities, especially in the vertical direction. In unstable conditions, which are characterized by strong heating of the ground by the sun, vertical velocity fluctuations are strong and turbulent diffusivities are high.

Typical turbulent diffusivity values for both rivers and the atmosphere exceed by many orders of magnitude molecular diffusivities of contaminants. This observation reinforces the point that pollutant dispersion away from fluid boundaries is controlled by a combination of shear-flow dispersion and turbulent diffusion, and not by molecular or Brownian motion.

SKIP 'PARTICLE MOTION', PICK UP AGAIN ON P.182

182 Chapter 4 Transport Phenomena

4.C MASS TRANSFER AT FLUID BOUNDARIES

Several important phenomena occur at the boundaries of fluids. The rate of contaminant transport to and from these boundaries may have a strong influence on contaminant concentration. This influence occurs in both natural and engineered systems. Contaminants can enter or leave a fluid at a boundary, and they may also undergo chemical transformations there. The boundaries of interest include air-water interfaces as well as boundaries between either air or water and (a) soil, (b) other solid surfaces, or (c) nonaqueous liquids such as fuels and solvents.

There is a close relationship between the transport phenomena explored in this section and the transformation processes involving phase change discussed in §3.B. In fact, the distinction between transport and transformation is somewhat blurred here. The kinetics of phase change processes depend, in general, both on the rate of transport to or from the fluid boundary and the kinetics of the transformation processes. Transport and transformation processes occur serially, so the slower process governs the overall rate.

Transport across air-water interfaces is of particular interest in environmental engineering. Several treatment technologies involve transferring pollutants from one phase

to the other. For example, scrubbers remove acid gases such as sulfur dioxide and hydrochloric acid from waste air streams by transferring them to water, where they can easily be neutralized. Air strippers remove volatile organic compounds from water. Once the organic molecules are transferred to the gas phase, they can be more easily captured by sorption or destroyed by oxidation processes. In nature, air-water exchanges are also important. The transfer of oxygen from air to water supports aquatic life. The ultimate fate of many air pollutants involves transfer to cloud or rainwater followed by deposition to the earth's surface. The uptake of carbon dioxide by the oceans plays a key role in moderating the impact of fossil fuel combustion on climate.

Transport to a fluid boundary may occur by a variety of mechanisms. Diffusion is always present and often is the rate-limiting process because, at rigid boundaries, flow velocities diminish to zero. Advection usually plays a role in controlling the thickness of the layer through which diffusion must occur. For particles, gravitational settling, electrostatic drift, inertial drift, and other mechanisms may dominate transport near boundaries.

For engineering analysis of transport processes at fluid boundaries, we seek a description that captures the overall effects, that does not violate central principles such as mass conservation, and that is practical to apply. We will employ models that link flux to concentrations and may include an empirical parameter. In the case of turbulent diffusion, we used an equation inspired by Fick's law of diffusion, and the empirical parameter was turbulent diffusivity. For mass transfer at boundaries, similarly inspired flux equations will be written that incorporate a mass-transfer coefficient as the empirical parameter.

4.C.1 Mass-Transfer Coefficient

The net rate of mass flux between a fluid and its boundary is commonly expressed in this form:

$$J_b = k_m(C - C_i) \qquad (4.C.1)$$

Here J_b is the net flux to the boundary (amount of species per area per time). When J_b is greater than zero, the flux is directed from the boundary to the fluid. The concentration terms C and C_i, respectively, represent the species concentration in the bulk fluid far from the boundary and the species concentration in the fluid immediately adjacent to the boundary. The other parameter in this equation, k_m, is known as a *mass-transfer coefficient*. The mass-transfer coefficient commonly has units of velocity (length per time).

Figure 4.C.1 shows a simple system for which a mass-transfer coefficient can be directly derived. A glass cylinder is partly filled with a pure volatile liquid (with a sat-
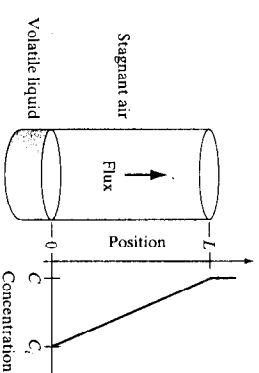
Stagnant air
Flux
Volatile liquid
Position
Concentration
0   L C_i C

Figure 4.C.1 A simple system in which a mass-transfer coefficient can be directly determined.

uration vapor pressure $\ll 1$ atm). The remainder of the cylinder contains stagnant air. Molecules of the liquid evaporate, diffuse through the cylinder, and escape from the open top into the free air. Provided that diffusion is not too rapid, the gas-phase concentration of the diffusing species at the liquid–gas interface will be determined directly as $P_{sat}/(RT)$, where P_{sat} is the equilibrium vapor pressure of the liquid. Assume that the concentration at the top of the cylinder is maintained at some value, C, determined by processes occurring in the open air. After an initial transient period, during which the gas-phase concentration profiles may change, a steady-state linear profile will be established, as depicted in Figure 4.C.1. The diffusive flux through the tube, J_d, is given by Fick's law as

$$J_d = D\frac{C_i - C}{L} \qquad (4.C.2)$$

The net transport rate from the air to the liquid is equal to the negative of the diffusive flux. J_d. Comparing equation 4.C.2 with equation 4.C.1, we see that the mass-transfer coefficient for this system is

$$k_m = \frac{D}{L} \qquad (4.C.3)$$

This is a general result, provided that the concentration profile is steady: For pure diffusion through a stagnant layer, the mass-transfer coefficient is given by the diffusivity divided by the thickness of the layer.

A second case is illustrated in Figure 4.C.2. Particles are suspended in a fluid above a horizontal boundary. The fluid is motionless, the particle concentration is uniform, and the particles migrate only because of gravitational settling. All particles are assumed to have the same setting velocity, v_t. The concentration of particles in the fluid at the interface is taken to be zero. This may seem peculiar, since the particles accumulate on the bottom boundary. However, once the particles strike the boundary, they are no longer suspended in the fluid, and so it is reasonable to assign $C_i = 0$. The gravitational flux to the surface. J_g, is then given by
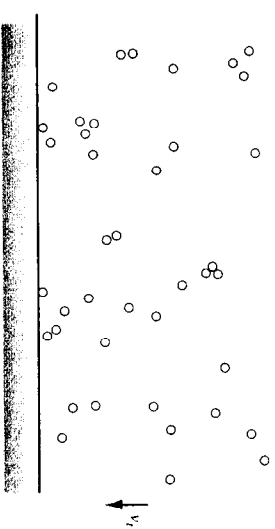
$$J_g = v_t C \qquad (4.C.4)$$

Figure 4.C.2 In a uniform suspension of monodisperse particles settling through a stagnant fluid onto a horizontal surface, the mass-transfer coefficient is equal to the settling velocity.

Comparing this result with equation 4.C.1, we see that for this case the mass-transfer coefficient is equal to the particle settling velocity:

$$k_m = v_t \qquad (4.C.5)$$

This too is a general result. Whenever contaminant transport to a surface occurs solely because of a net migration velocity, the mass-transfer coefficient is equal to that velocity.

These examples yield exact expressions for the mass-transfer coefficient. However, in most applications, the use of a mass-transfer coefficient is a simplified description of what is a very complicated set of processes. Therefore, a high degree of precision should not be expected in problems involving mass transfer at boundaries.

Applying equation 4.C.1 wisely requires a sound understanding of the meaning of each of the four variables. First, let's consider the concentration at the interface, C_i. In many cases, C_i can be taken to be zero. This is appropriate when a transformation process that is fast and irreversible occurs at the boundary. Particle deposition by settling is one example where C_i is zero. When a particle strikes a surface with a low incident velocity, it adheres essentially immediately. Chemical transformations can also produce an interface concentration of zero if transport, rather than surface-reaction kinetics, is the rate-limiting step. In some cases, such as that shown in Figure 4.C.1, the interface concentration can be determined by assuming local equilibrium at the boundary.

An important issue arises concerning the species concentration in bulk fluid, C. Where should it be determined? The issue is easily resolved when the fluid is well mixed outside of a thin boundary layer (see Figure 4.C.3). Then C is the concentration anywhere outside the boundary layer. However, some circumstances arise in environmental engineering in which species concentrations vary strongly with position throughout the fluid. In such cases, the use of a mass-transfer coefficient may yield no more than a rough approximation of the mass-transfer rate at surfaces.

A complication arises when the fluid boundary occurs at a surface that has a complex texture. If J_b represents the quantity of contaminant transferred *per area* per time, how do we define the area? Typically, the flux to rough surfaces is determined on the basis of a superficial or apparent area. In other cases, rather than determining the interface area and the mass-transfer coefficient separately, their product is determined and the mass-transfer equation is rewritten in terms of total net transfer of species (flux times area) rather than in terms of flux.

The final issue to address is how an appropriate mass-transfer coefficient is determined for a given situation. There are two main approaches, and both are widely used. For systems with fairly regular geometries, the mass-transfer coefficient is calculated using existing correlations based on theory or experimental data. Some of these correlations are presented below. A second approach, commonly used for more complex systems, is to calculate mass-transfer coefficients based on experiments conducted in laboratory or field settings.

Film Theory

The simplest model system that includes fluid flow divides the fluid into two layers. Adjacent to the surface is a stagnant layer, or film, through which species must diffuse. The concentration profile within the film is assumed to be linear, corresponding to steady diffusive flux. In the second layer, the fluid is well mixed and the species concentration is uniform everywhere.
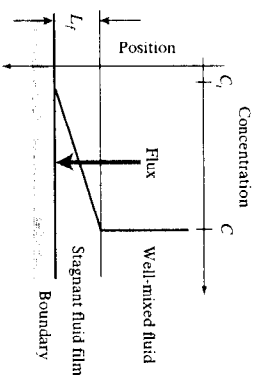
Figure 4.C.3 Schematic of mass transfer to a surface according to film theory.

Mass transfer from the fluid to a surface, according to film theory, is depicted in Figure 4.C.3. This situation is almost identical to that depicted in Figure 4.C.1, and so, in analogy with equation 4.C.3, it should be clear that the mass-transfer coefficient for this case is

$$k_m = \frac{D}{L_f} \qquad (4.C.6)$$

where L_f is the film thickness. Film theory suggests that for given flow conditions, the mass-transfer coefficient should scale in direct proportion to species diffusivity ($k_m \propto D$). Experiments consistently demonstrate that, in systems with fluid flow, the mass-transfer coefficient flow increases in proportion to D^α, with $\alpha < 1$. The key weakness of film theory is its dependence on a specific value of the film thickness, L_f. In most circumstances, there is no practical way to determine L_f that is independent of a measurement of mass transfer (or heat transfer) to a surface. Furthermore, the effective thickness of the film through which species must diffuse varies with species diffusivity: A higher diffusion coefficient results in a larger film thickness. Still, although not entirely accurate, film theory provides a helpful conceptual picture of interfacial mass transfer.

Penetration Theory

Recall (equation 4.A.8) that the characteristic time required for a steady-state concentration profile to be established by diffusion is given by $L^2(2D)^{-1}$ where L is the distance over which diffusion occurs. In film theory, the boundary must be in contact with the fluid for a minimum time of $\tau \sim L_f^2(2D)^{-1}$ for the concentration profile to approach the constant-slope condition depicted in Figure 4.C.3. In some circumstances, the contact time between a boundary and a fluid is not long enough for film theory to apply. A second conceptual model, known as penetration theory, has been developed to address this case.

The model is based on transient diffusion in one dimension. At time $t = 0$, the concentration in the fluid is assumed to be uniform everywhere except at the position of the boundary, where it is C_f. Then diffusion to the surface begins and a boundary layer begins to grow (Figure 4.C.4). Fluid motion affects the contact time between the fluid and the boundary.

Analysis of time-dependent diffusion to a flat surface yields the following expression for the mass-transfer coefficient:

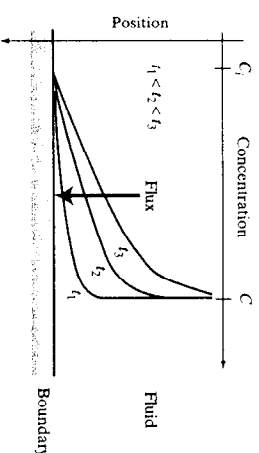$$k_m(t) = \left[\frac{D}{\pi t}\right]^{1/2} \qquad \text{instantaneous} \qquad (4.C.7)$$

Figure 4.C.4 Schematic of mass transfer to a surface according to penetration theory.

This is the instantaneous mass-transfer coefficient at time t. Because the distance through which species must diffuse increases with time, k_m decreases as t increases. If the contact period is maintained for some interval t^*, the time-averaged mass-transfer coefficient is obtained by integration:

$$k_m = \frac{1}{t^*}\int_0^{t^*} k_m(t)\,dt = 2\left[\frac{D}{\pi t^*}\right]^{1/2} \qquad \text{average} \qquad (4.C.8)$$

From equation 4.C.8, we see that penetration theory predicts that the mass-transfer coefficient should increase in proportion to the square root of species diffusivity. By contrast, we have just seen that film theory predicts that the mass-transfer coefficient is proportional to diffusivity. The reason for the difference lies in the assumptions about the distance through which species must diffuse. In film theory, the film thickness is assumed to be constant and so is independent of D. In penetration theory, the diffusion distance increases with time, and the rate of growth depends on species diffusivity.

Boundary-Layer Theory: Laminar Flow along a Flat Surface

Transport from moving fluids to boundaries is caused by simultaneous advection and diffusion, with advection being stronger far from the boundary and diffusion dominating adjacent to the boundary. Film and penetration theories simplify the analysis by decoupling advection from diffusion. Boundary-layer theory can predict mass-transfer coefficients for simple flows and geometries while simultaneously accounting for the effects of both transport mechanisms.

Let's consider the case of laminar fluid flow at velocity U, parallel to a flat surface (see Figure 4.C.5). The species concentration is C_f at the surface and is C far from the surface. Within the boundary layer there is a concentration gradient, which gives rise to diffusion toward the surface. There are also advective velocity components in
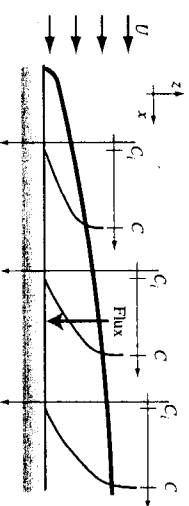

Figure 4.C.5 Schematic of mass transfer to a surface according to boundary-layer theory for the case of a flat surface parallel to a uniform, laminar fluid flow.

LINEAR DRIVING FORCE MODEL

the x-direction (relatively strong) and the z-direction (relatively weak) that affect the concentration profile. The characteristic thickness of the boundary layer for a contaminant species is the distance from the surface over which the concentration increases to approximately C. As shown in Figure 4.C.5, the boundary-layer thickness grows with increasing distance downstream of the leading edge. The thickness of this boundary layer at any x-position is a function of species diffusivity, with higher diffusivity causing a thicker boundary layer. For any given species, a thicker boundary layer means slower mass transfer to the surface. Because of species loss at the surface, the boundary-layer thickness grows with downstream distance and the rate of mass transfer correspondingly decreases.

This problem is analyzed using equations that describe the conservation of fluid mass, momentum, and species in the boundary layer (Cussler, 1984; Bejan, 1984). The result is a mass-transfer coefficient calculated at a specific position x downstream of the leading edge of the surface:

$$k_m(x) = 0.323\left(\frac{U}{x}\right)^{1/2} \nu^{-1/6} D^{2/3} \qquad \text{local} \tag{4.C.9}$$

where ν is the kinematic fluid viscosity. (Recall that $\nu = \mu/\rho$, where μ is the dynamic fluid viscosity and ρ is the fluid density.) The overall mass-transfer coefficient to the surface is obtained by averaging over the length of the surface:

$$k_m = \frac{1}{L}\int_0^L k_m(x)\,dx = 0.646\left(\frac{U}{L}\right)^{1/2} \nu^{-1/6} D^{2/3} \qquad \text{average} \tag{4.C.10}$$

Equation 4.C.10 gives the average mass-transfer coefficient for this flow system for a surface from the leading edge to a distance L downstream. Note that the mass-transfer coefficient, k_m, varies with the diffusion coefficient raised to the 2/3 power. It is generally true that when advection and diffusion are combined, the mass-transfer coefficient increases with diffusivity raised to some power between 0.5 (penetration theory) and 1 (film theory).

4.C.2 Transport across the Air–Water Interface

In environmental engineering applications, the rate of transport of a molecular species across an air-water interface is described by an expression similar to equation 4.C.1:

$$J_{gi} = k_{gi}(C_s - C) \tag{4.C.11}$$

where J_{gi} is the net flux of a species from the gas phase to the liquid phase (mass per interfacial area per time), k_{gi} is a mass-transfer coefficient (length per time), C is the concentration of the species in the bulk liquid phase, and C_s is the saturation (or equilibrium) concentration of the species in the liquid phase that corresponds to the given partial pressure of the species in the gas phase. Typically, C_s is obtained from Henry's law (see §3.B.2). When C_s exceeds the current aqueous concentration, $J_{gi} > 0$ and net transfer occurs from the gas to the liquid. Conversely, when the water is supersaturated with respect to the gas phase, $C > C_s$, so $J_{gi} < 0$, and equation 4.C.11 predicts a net rate of volatilization.

In general, the mass-transfer coefficient k_{gi} depends on fluid flow near the interface and on species diffusivity in both air and water. The film model introduced in the previous section can be extended to a two-film model, as depicted in Figure 4.C.6, with the air-water interface as the boundary. In this model, stagnant film layers exist
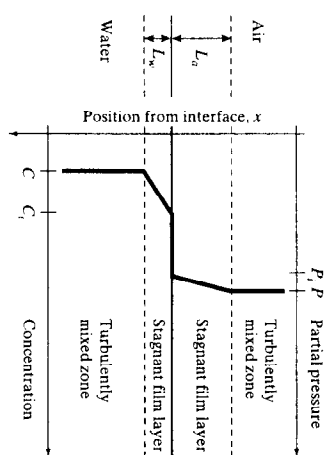
Figure 4.C.6 Schematic of the two-film model for estimating mass transport across an air-water interface.

on either side of the boundary through which species transport occurs only by molecular diffusion. Outside of its stagnant film layer, each fluid is well mixed. Immediately adjacent to the interface, the partial pressure in the gas phase, P_i, is assumed to be in equilibrium with the aqueous concentration, C_i, as described by Henry's law. As in the film model, the concentration profiles in the stagnant film layers are assumed to be linear. Also, because of mass conservation, the flux through the air layer must be equal to the flux through the water layer.

Applying Fick's law, we can write the gas-side flux (from air to the interface) as

$$J_{gi} = D_a \frac{(P - P_i)/RT}{L_a} \tag{4.C.12}$$

where D_a is the species diffusivity through air and L_a is the thickness of the stagnant film layer in the air. Likewise, the liquid-side flux (from the interface into the water) is

$$J_{gi} = D_w \frac{C_i - C}{L_w} \tag{4.C.13}$$

where D_w is the species diffusivity in water and L_w is the film-layer thickness in the water. Since we don't know either P_i or C_i, we would like to eliminate these parameters from the expressions. So far, we have two equations but three unknowns (J_{gi}, C_i, and P_i).

The third equation comes from the equilibrium relationship at the interface:

$$C_i = K_H P_i \tag{4.C.14}$$

where K_H is the Henry's law constant for the species (see Table 3.B.2). Now, we can use algebra to derive an expression for flux that is in the form of equation 4.C.11. Use equation 4.C.14 to replace P_i with C_i/K_H in equation 4.C.12. Then equate the right-hand sides of equations 4.C.12 and 4.C.13 and solve for C_i to obtain

$$C_i = \frac{\alpha C_s + C}{1 + \alpha} \tag{4.C.15}$$

where

$$\alpha = \frac{D_a L_w}{D_w L_a K_H RT} \tag{4.C.16}$$

and

$$C_s = K_H P \tag{4.C.17}$$

Next substitute for C_i from equation 4.C.15 into equation 4.C.13. After some algebraic manipulation, one arrives at equation 4.C.11, where

$$k_{gl} = \frac{D_w}{L_w}\left(\frac{\alpha}{1+\alpha}\right) = \frac{1}{\dfrac{L_w}{D_w} + \dfrac{L_a}{D_a}K_H RT}$$

(4.C.18)

The film thicknesses, L_w and L_a, cannot be measured. So for practical application, we rewrite equation 4.C.18 in this form:

$$\frac{1}{k_{gl}} = \frac{1}{k_l} + \frac{K_H RT}{k_g}$$

(4.C.19)

where k_l and k_g are the respective mass-transfer coefficients through the liquid and gas boundary layers near the interface, each corresponding to the diffusivity divided by the film thickness (D_w/L_w and D_a/L_a, respectively), as in equation 4.C.6. The factor K_H appears with k_g in this expression because k_g is used with the aqueous concentrations to determine the flux (equation 4.C.11). The factor RT is needed to convert partial pressure to molar concentration, since we write Henry's law in a way that relates aqueous molar concentration to gaseous partial pressure.

Equations 4.C.11 and 4.C.19 are together sometimes called the *two-resistance model for interfacial mass transfer*. Since species must be transported through fluid on both sides of the interface, the total resistance (k_{gl}^{-1}) is the sum of the resistance in the liquid side of the interface (k_l^{-1}) plus the resistance on the gas side ($K_H RT k_g^{-1}$).

From equation 4.C.19 we see that the relative sizes of the gas and liquid resistances vary according to the Henry's law constant, K_H. The diffusion coefficients, D, of molecular species in a given fluid vary by about one order of magnitude (§4.A.3). The film resistance terms k_l and k_g are expected to vary by no more than D to the first power (§4.C.1). The Henry's law constant, on the other hand, varies by at least eight orders of magnitude among species of interest in environmental engineering (see Table 3.B.2). Therefore, even for fixed flow conditions, the interfacial mass-transfer coefficient, k_{gl}, may vary greatly from one species to another according to the value of the Henry's law constant. This point is illustrated in Figure 4.C.7.

Liss and Slater (1974) reviewed available information on the mass transfer of species between the oceans and the atmosphere and concluded that liquid-side and gas-side mass-transfer coefficients of $k_l = 0.2$ m h^{-1} and $k_g = 30$ m h^{-1} apply for average meteorological and ocean current conditions. These coefficients are suggested to be approximately correct for species with molecular weights between 15 and 65 g/mol. Figure 4.C.7 shows how the overall mass-transfer coefficient varies with the Henry's law constant for molecular species exchange between the atmosphere and the seas. For sparingly soluble gases such as oxygen ($K_H = 0.0014$ M atm^{-1}), the resistance lies entirely on the liquid side and an overall average mass-transfer coefficient of approximately $k_{gl} = 0.2$ m/h applies. On the other hand, the resistance for a highly soluble species such as formaldehyde ($K_H = 6300$ M atm^{-1}) lies entirely on the gas side.

The liquid-side and gas-side mass-transfer coefficients can be combined with values of species diffusivities to estimate effective film thicknesses: $L_a \sim D_a k_g^{-1} \sim 2$ mm and $L_w \sim D_w k_l^{-1} \sim 20$ μm. We see from these estimates that diffusive transport over very small length scales controls the overall rate of interfacial mass transfer. The time scales required for steady-state concentration profiles to be achieved in gas and liquid films of this size are approximately $\tau_g \sim L_a^2(2D_a)^{-1} \sim 0.1$ s and $\tau_l \sim L_w^2(2D_w)^{-1} \sim 0.2$ s.
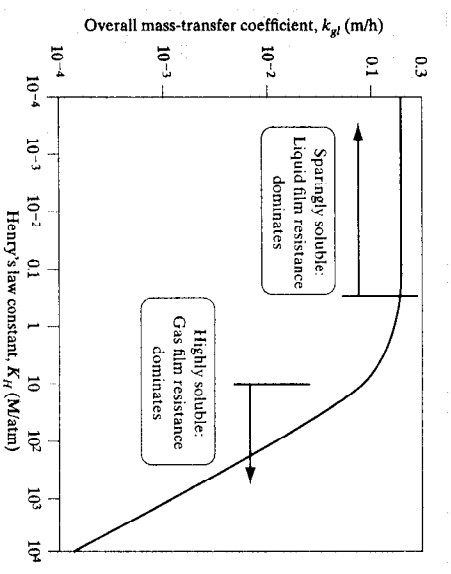
Figure 4.C.7 Dependence of the overall mass-transfer coefficient on the Henry's law constant for average conditions in large bodies of water. The curve traces equation 4.C.19 with $k_l = 0.2$ m h^{-1}, $k_g = 30$ m h^{-1}, and $T = 293$ K (Liss and Slater, 1974).

For natural bodies of water, the following expressions can be applied to estimate gas-side and liquid-side mass-transfer coefficients in relation to environmental and species conditions (Schwarzenbach et al., 1993). For the gas-phase mass-transfer coefficient,

$$k_g = \left[\frac{D_a}{0.26 \text{ cm}^2 \text{ s}^{-1}}\right]^{2/3}(7U_{10} + 11)$$

(4.C.20)

For oceans, lakes, and other slowly flowing waters,

$$k_l = \left[\frac{D_w}{2.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}}\right]^{0.57}(0.0014U_{10}^2 + 0.014)$$

(4.C.21)

For rivers,

$$k_l = 0.18\left[\frac{D_w}{2.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}}\right]^{0.57}\left(\frac{U_w}{d_w}\right)^{1/2}$$

(4.C.22)

In these expressions, U_{10} is the mean wind speed measured at 10 m above the water surface (units are m/s). The term U_w is the mean water velocity in the river (m/s). The mean stream depth is d_w (m). The equations are written so that k_g and k_l have units of m/h. Example 4.C.1 illustrates how these equations are used.

In general, for interfacial transfer of molecular species in any air-water flow system, the overall mass-transfer coefficient for any species can be determined by making measurements of k_{gl} for a minimum of two species with known Henry's law constants, provided one is sparingly soluble and the other is highly soluble. From these measurements, one can determine the values of k_l and k_g. Then the overall mass-transfer coefficient for any other species can be estimated using equation 4.C.19.

EXAMPLE 4.C.1 *Mass-Transfer Coefficient for Oxygen in a River*

In Nebraska, the Missouri River has a mean depth of 2.7 m and flows at a mean velocity of 1.75 m/s (Fischer et al. 1979). Assume that the wind speed at 10 m is 4 m/s. Estimate the overall mass-transfer coefficient for oxygen (O_2) from the atmosphere to the river.

SOLUTION The diffusion coefficient of O_2 in water is $D_w = 2.6 \times 10^{-5}$ cm^2 s^{-1} (Table 4.A.3). From equation 4.C.22, the liquid-side mass-transfer coefficient is estimated to be $k_l = 0.14$ m/h. The diffusion coefficient for O_2 in air is $D_a = 0.178$ cm^2 s^{-1} (Table 4.A.2). From equation 4.C.20, the gas-side mass-transfer coefficient is estimated to be $k_g = 30$ m/h. The Henry's law constant for oxygen is $K_H = 0.0014$ M atm^{-1} (Table 3.B.2). With $R = 0.0821$ atm K^{-1} M^{-1} and $T = 293$ K, we predict from equation 4.C.19 that $k_{el} = 0.14$ m/h. As expected for a sparingly soluble gas such as oxygen, mass transfer through water adjacent to the interfacial boundary controls the overall rate of the process.

4.D   TRANSPORT IN POROUS MEDIA

Porous materials are solids that contain distributed void spaces. Permeable porous materials contain an interconnected network of voids or pores that permit bulk flow of fluid through the material. Soil is a common example of a permeable porous material. Usually, the pores are highly variable in shape and size, resulting in complex flow channels.

Environmental engineers study the movement of fluids and contaminants through porous media for several reasons. Many treatment technologies for removing pollutants from water and air entail passing the fluid through a porous material. In municipal treatment plants, for example, drinking water is passed through sand filters to remove small, suspended particles. Drinking water is also sometimes treated by passing a fluid through a porous material. Much attention in hazardous waste management focuses on characterizing contaminant migration in subsurface soils, either to predict the threat to water quality or to evaluate a treatment strategy.

The aim of this section is to provide an introduction to transport in porous media, emphasizing the movement of water and air and the contaminants dissolved or suspended within these fluids. The behavior of nonaqueous-phase liquids in subsurface environments is also important in environmental engineering, but the complexities that must be addressed render it beyond the scope of this book. Application of the ideas introduced here for filtering contaminants from water are discussed in Chapter 6. Groundwater contamination is addressed in Chapter 8.

Before proceeding, we must define some basic terms and concepts that arise when dealing with transport through porous materials. One quantitative descriptor of a porous material is its *porosity*, here given the symbol ϕ and defined as

$$\phi = \frac{\text{pore volume}}{\text{total volume}} \qquad (4.D.1)$$

The pores may contain both air and water (and, in general, other fluids). We define the *air-filled porosity*, ϕ_a, and the *water-filled porosity*, ϕ_w, in analogy with equation 4.D.1, but with the numerator replaced by the pore volume filled with air or water, respectively. If the air and water are the only fluids contained in the pores, the porosities must satisfy this relationship:

$$\phi = \phi_w + \phi_a \qquad (4.D.2)$$

A porous material is *saturated* with a particular fluid if that fluid entirely fills the pores. So, for example, a medium is saturated with water if $\phi_w = \phi$.

Most porous materials encountered in environmental engineering are granular or fibrous. Granular materials, such as soils, typically have porosities in the range 0.3–0.7. The porosities of fibrous materials are usually higher, sometimes as high as 0.99. These materials may have two distinct classes of pores, those that are external to the grains or fibers and those that are internal. Bulk fluid flow occurs only in the external pores, but contaminants can migrate by diffusion into the internal pores and interact with the solid surfaces there. This characteristic is especially important for porous sorbents, such as activated carbon, which have large internal porosities and enormous internal surface areas. However, in this section, we will emphasize fluid and contaminant behavior in the pores that are external to grains and fibers.

Two densities are commonly defined for a porous solid. The *solids density*, ρ_s, represents the mass of solid per volume of solid (often including internal pores). The *bulk density*, ρ_b, represents the mass of solid per total volume. These measures are related by the total porosity:

$$\rho_b = \rho_s (1 - \phi) \qquad (4.D.3)$$

The solids density of soil grains is fairly constant at ~2.65 g cm^{-3}. Given a range of porosities of 0.3–0.7, the bulk density would be in the range 0.8–1.9 g cm^{-3}. Soil bulk density varies with grain size, but the dependence is not strong. In soil, as in any granular material, porosity tends to be higher when grain sizes are distributed over a narrow range. With a broad distribution of grain sizes, smaller grains can fill the pores created by larger grains, reducing overall porosity.

Porosity is an area characteristic as well as a volume characteristic of granular materials. Imagine a plane slicing through a porous material. The *area porosity* is the ratio of the area of the plane that intersects pores to the total area that intersects the porous material. Conveniently, if pores are randomly distributed and the number of pores in a plane is large, then the area porosity is equal to the porosity measured on a volume basis. This conclusion is reached by considering a porous material as a collection of infinitesimally thin slices. The volume porosity of the whole is the average of the porosities of the individual slices. If these slices include a random distribution of a large number of pores, then the porosity of each slice will be close to the mean for all slices.

4.D.1   Fluid Flow through Porous Media

During the middle of the nineteenth century, Henri Darcy, a French engineer who was interested in the development of groundwater resources, studied the hydraulics of water flow through a sand column using an apparatus like that shown in Figure 4.D.1. With experiments conducted under steady flow conditions, he found that the following relationship described his results:

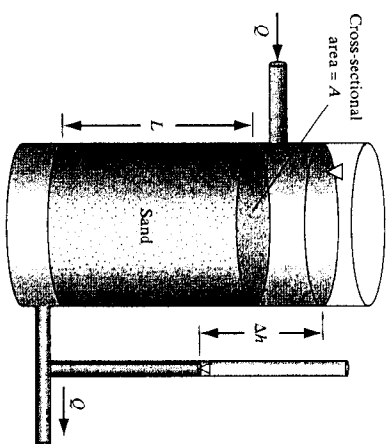$$Q = KA \frac{\Delta h}{L} \qquad (4.D.4)$$

Figure 4.D.1 Apparatus similar to that used by Darcy to study the hydraulics of water flow through sand.

where Q is the volumetric flow rate (m^3 s^{-1}), Δh is the change in fluid head from the inlet to the outlet of the column (m), A is the cross-sectional area of the column (m^2), and L is the length of the column (m). The parameter K, which has units of velocity, was constant for a given sand but varied from one sand sample to another, increasing with increasing grain size.

This relationship has been generalized and is now commonly known as *Darcy's law*. For water flow in one dimension through a water-saturated material, Darcy's law can be written as

$$U = -K \frac{dh}{dl} \qquad (4.D.5)$$

where U is called the *Darcy velocity*, *filtration velocity*, or *superficial flow velocity*; K is called the *hydraulic conductivity*; and dh/dl is the rate of change of pressure head with distance. In relation to Darcy's experiment, U represents Q/A, and the hydraulic gradient, dh/dl, replaces $\Delta h/L$. The filtration velocity (U) should not be confused with the local velocity of water through the pores. Rather, it represents the average volumetric flow of water per unit *total* cross-sectional area of the porous material. Since solids occupy some area, and since water can flow only through pores, the average local velocity of water in the pores must be higher than the filtration velocity. The minus sign in Darcy's law, like the minus sign in Fick's law, reminds us that water flows from high to low pressure head, just as molecules diffuse from high to low concentration. Since head has units of length, dh/dl is dimensionless, and so the hydraulic conductivity must have the same units as U, velocity.

Another form of Darcy's law applies to porous media saturated with any fluid:

$$U = -\frac{k}{\mu} \frac{dP}{dl} \qquad (4.D.6)$$

where k is called the *intrinsic permeability*, or simply *permeability*, of the porous material; μ is the viscosity of the fluid; and dP/dl is the derivative of dynamic pressure with respect to distance. This form of Darcy's law assumes that the fluid is incompressible, which, for air, would mean that the pressure drop across the medium must be much smaller than the inlet pressure.

The hydraulic conductivity in Darcy's law (equation 4.D.5) depends primarily on two properties of the system: the viscosity of the fluid and the size of the pores. Fluids

that are more viscous flow more slowly, and materials with smaller pores permit less flow. The second form of Darcy's law (equation 4.D.6) separates these two properties. The intrinsic permeability is a function only of the porous material and does not depend on the fluid properties.

Given the units of viscosity (e.g., kg m^{-1} s^{-1}), pressure derivative (kg m^{-2} s^{-2}), and velocity (m s^{-1}), we see that permeability has units of length squared. For a porous medium made up of uniform spherical grains, the permeability increases approximately in proportion to the square of the grain diameter.

The dynamic pressure (P) in equation 4.D.6 is the difference between the total pressure and the hydrostatic pressure. In the absence of motion, fluid pressure must increase with depth to support the mass of the fluid suspended above it against the acceleration of gravity. This hydrostatic change in pressure with height does not induce flow.

The difference between the two forms of Darcy's law lies primarily in the coefficients K and k. By noting that head loss corresponds to dynamic pressure drop according to $\rho_w g \Delta h = \Delta P$, where ρ_w is the density of water and g is gravitational acceleration, we can show that the hydraulic conductivity is related to the intrinsic permeability by

$$K = \frac{k \rho_w g}{\mu_w} \qquad (4.D.7)$$

where μ_w is the dynamic viscosity of water.

Intrinsic permeability, k, may be expressed in ordinary area units such as m^2. However, the permeabilities of ordinary materials are so low that a special unit, the darcy, has been defined for permeability, with 1 darcy = 0.987×10^{-12} m^2. Figure 4.D.2 shows representative permeabilities and hydraulic conductivities of soils. Note the enormous range of values between homogeneous clays and coarse sand or gravel.
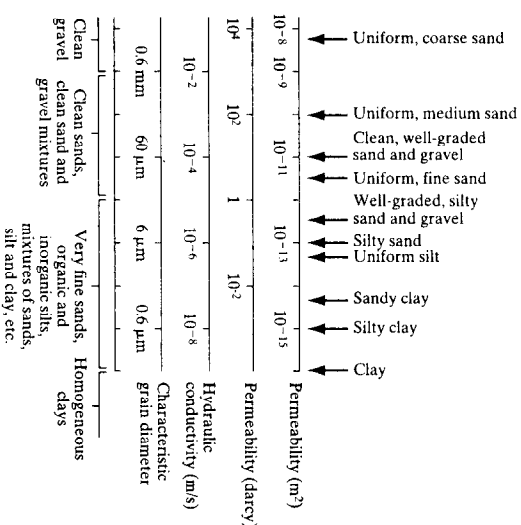

Figure 4.D.2 Permeability and hydraulic conductivity scales, indicating representative values for soils and gravel (Terzaghi and Peck, 1967; Tuma and Abdel-Hady, 1973). Characteristic grain diameters are computed from the Carman-Kozeny equation (4.D.8), assuming $\phi = 0.5$.
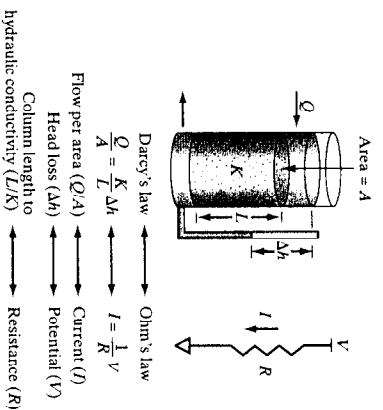
Darcy's law	Ohm's law
$\dfrac{Q}{A} = \dfrac{K}{L}\,\Delta h$	$I = \dfrac{1}{R}\,V$
Flow per area (Q/A)	Current (I)
Head loss (Δh)	Potential (V)
Column length to hydraulic conductivity (L/K)	Resistance (R)

Figure 4.D.3 The analogy between Darcy's law and Ohm's law.

Fluid flow through a sand column is analogous to electrical current flow through a resistor. Figure 4.D.3 makes the comparison, showing that the ratio of the column length to hydraulic conductivity acts like a "resistor" to fluid flow driven by a loss in pressure head.

A widely used expression that relates permeability to grain size is known as the Carman-Kozeny equation. It was derived by analyzing flow through porous media in analogy to flow through a bundle of small capillaries, but with varying size and orientation (Dullien, 1979), giving

$$k = \frac{\phi^3 d_g^2}{180(1 - \phi)^2} \qquad (4.D.8)$$

where d_g is the grain diameter. For grains that are not spherical, d_g is replaced by $\psi\, d_{eq}$ where ψ is known as the *sphericity* of the grain and d_{eq} is the *equivalent diameter*. The sphericity is the ratio of the surface area of a sphere with the same volume as the grain to the (external) surface area of the grain. Sphericities of materials used in granular bed filters typically range from 0.45 to 0.8 (Cleasby, 1990). The equivalent diameter is that which produces a sphere with the same volume as the grain. Example 4.D.1 shows how the Carman-Kozeny relationship is used.

EXAMPLE 4.D.1 *Hydraulics for a Granular Activated Carbon Filter*

A filter of granular activated carbon is used for treating drinking water. It has the following characteristics, which are typical for municipal water treatment (Cleasby, 1990; Snoeyink, 1990). Estimate the permeability and the head loss.

$d_{eq} = 1$ mm	Equivalent grain diameter
$\psi = 0.75$	Sphericity
$\phi = 0.5$	Porosity
$L = 1$ m	Bed depth
$U = 3$ m h^{-1}	Filtration velocity

SOLUTION Substitution into equation 4.D.8 yields an estimate of the permeability:

$$k = \frac{0.5^3(0.75 \times 1 \times 10^{-3}\,\text{m})^2}{180(1 - 0.5)^2} = 1.6 \times 10^{-9}\,\text{m}^2$$

EXAMPLE 4.D.1 *Hydraulics for a Granular Activated Carbon Filter (continued)*

From equation 4.D.7, the hydraulic conductivity is

$$K = \frac{1.6 \times 10^{-9}\,\text{m}^2 \times 1000\,\text{kg m}^{-3} \times 9.8\,\text{m s}^{-2}}{0.001\,\text{kg m}^{-1}\,\text{s}^{-1}} = 0.015\,\text{m s}^{-1}$$

The head loss is determined from equation 4.D.5:

$$\Delta h = L\frac{dh}{dl} = -L\frac{U}{K}$$

$$= -1\,\text{m} \times \frac{3\,\text{m h}^{-1}}{0.015\,\text{m s}^{-1}} \times \frac{1\,\text{h}}{3600\,\text{s}} = -0.06\,\text{m}$$

The head loss in this case is about 6 cm.

4.D.2 Contaminant Transport in Porous Media

All of the mechanisms that cause contaminant transport in bulk fluids also act on contaminants suspended in fluids in porous media. Contaminants are advected with the fluid flow. Molecules diffuse within the fluid through the pores. Particles settle and undergo Brownian motion. Contaminants sorb onto and within porous media grains. Chemical or biological reactions may cause generation or decay of contaminants. If both air and water are present in the pores, contaminants can partition between the two fluids and migrate within both. Additional transport mechanisms arise, such as surface diffusion, but discussion of these is beyond the scope of this text.

Because of the large surface area of solids in contact with the fluid, contaminant-surface interactions may assume a particularly important role in transport through porous media. Particles may contact and adhere to the solid grains or fibers. Molecular contaminants may sorb onto the solid surface and may undergo chemical reactions there. Our attention in this section is focused mainly on transport mechanisms that do not involve pollutant-surface interactions. The modeling of sorption and transformation reactions in porous media is discussed in §5.B, and applications of particle deposition in porous filters are described in §6.C.2 and §7.C.1.

Diffusion

Molecular diffusion through porous materials affects the migration of gases through soils. In groundwater, diffusion is slow (recall that molecular diffusivities in water are 10,000 times smaller than in air) and therefore of little importance. In treatment technologies, transport is generally dominated by advection because of the need to treat fluids quickly.

In this discussion, we will emphasize gas-phase diffusion. Fick's law relates diffusive flux through a porous medium to the concentration gradient, but requires some clarification and adjustment because of the presence of the solids. For molecular diffusion through a porous solid, Fick's law is written in one dimension as

$$J_d = -D_e\frac{dC}{dx} \qquad (4.D.9)$$

For three-dimensional transport applications, Fick's law can be written in vector form:

$$\vec{J_d} = -D_e\left(\frac{\partial C}{\partial x}, \frac{\partial C}{\partial y}, \frac{\partial C}{\partial z}\right) \qquad (4.D.10)$$

Here J_d representing diffusive flux through the porous medium, gives the quantity of contaminant transported per total area (not just pore area) per time. The parameter D_e is an effective diffusion coefficient, and C is the species concentration in the pores (per pore volume, not per total volume). These equations have the same form as Fick's law for bulk fluids (equations 4.A.5–6), but each of the parameters has an altered meaning.

The effective diffusion coefficient through a porous material is smaller than the corresponding ordinary diffusion coefficient for the given contaminant/fluid combination. For gas molecules in a granular material, such as soil, the following expression is widely used to estimate the effective diffusivity (Millington, 1959):

$$D_e = D\frac{\phi_a^{10/3}}{\phi^2} \qquad (4.D.11)$$

In vadose-zone soils (i.e., above the groundwater table), typical values of air-filled and total porosity are $\phi_a = 0.2$ and $\phi = 0.4$. According to equation 4.D.11, the effective diffusivity would be reduced to $0.03D$ in this case. For air-saturated pores, equation 4.D.11 reduces to

$$D_e = D\phi_a^{4/3} \qquad \phi_a = \phi \qquad (4.D.12)$$

So with a typical value for dry soil of $\phi_a = 0.4$, $D_e = 0.3D$.

An alternative expression, applied in the case of water- or air-saturated pores, uses an empirical correction factor, the *tortuosity*, T, which accounts for (a) the reduced area through which diffusion can occur and (b) the longer average path a molecule must travel to move a certain distance through the pores. The effective diffusivity is related to the tortuosity by

$$D_e = \frac{D}{T} \qquad (4.D.13)$$

Typical values of tortuosity are in the range 2 to 6 (Cussler, 1984), yielding effective diffusivities that are approximately consistent with predictions based on 4.D.12.

Hydrodynamic Dispersion

Hydrodynamic dispersion in porous media is similar to the shear-flow dispersion that occurs in pipes and rivers, as discussed in §4.A.4. The dispersion of a nonreactive groundwater contaminant, or *conserved tracer*, is depicted in Figure 4.D.4. At some time t_1, contamination occurs in the groundwater, as shown in the left-hand portion of the figure. The groundwater flows with a uniform filtration velocity, U, in the +x-direction. At some later time, t_2, the center of mass of contamination has been transported downstream to position x_2, given by

$$x_2 = x_1 + (t_2 - t_1)U \qquad (4.D.14)$$

In words, the center of mass of contamination moves at the same speed as the fluid. However, the areal extent of contaminated groundwater increases, and typically this increase is much greater than can be explained by molecular diffusion alone. Because
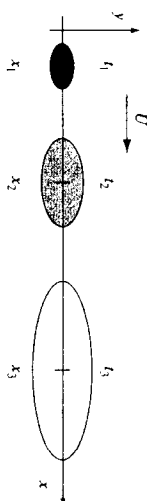
Figure 4.D.4 Transport and dispersion of a fixed quantity of a nonreactive groundwater contaminant. The figure schematically shows the areal extent of contamination at three instants in time, with $t_3 > t_2 > t_1$. The center of mass of contamination is advected in the x-direction at a rate given by the mean velocity, U. Hydrodynamic dispersion causes the contamination to spread more rapidly in the direction of flow than in the transverse direction.

the local velocity through the soil pores is not uniform, some of the contamination travels at an average speed greater than U, while other contaminant molecules travel more slowly than U. There is also some spreading in the y-direction, although the mean velocity in that direction is zero. Since the contaminant is conserved, the greater areal extent of contamination is offset by a lower average concentration. The same characteristics prevail in the interval from t_2 to t_3.

This spreading is not caused by turbulence; it occurs even if the grain Reynolds number is much less than 1, so that the flow is stable and laminar. It is observed to occur in uniform sand columns in the laboratory, although it can be much stronger in the field if the soil contains zones of higher and lower permeability than the average.

Fundamentally, this spreading is caused by the variation of fluid velocities within the pores. At the grain surfaces, the velocities diminish to zero. In the center of a channel between two grains, the local velocity may be much higher than the volume average. Individual contaminant molecules experience independent velocity histories. When averaged over all contaminant molecules, the rate of advection matches that of the fluid, but some individual molecules may travel significantly faster or slower than the mean, causing plume dispersion.

The contaminant flux in the direction of flow caused by hydrodynamic dispersion in porous media is described by an expression analogous to Fick's law in one dimension:

$$J_h = -\varepsilon_h \frac{\partial C}{\partial x} \qquad (4.D.15)$$

where ε_h is the *dispersion coefficient* and x is the direction of flow. In this expression, the dispersion coefficient includes molecular diffusion as a limiting condition:

$$\varepsilon_h = D_e + \varepsilon U \qquad (4.D.16)$$

Here ε is a characteristic of the porous medium called the *dispersivity* (units of length). As defined above, U is the filtration velocity and D_e is the effective diffusivity. So, the flux J_h represents the sum of transport due to molecular diffusion and due to dispersion caused by nonuniform fluid flow. As with molecular diffusion alone, this flux represents the net rate of contaminant movement per unit total cross-sectional area. Similar expressions could be written for the flux components in the transverse direction, but these would require different dispersion coefficients, since it is observed that transverse dispersion is weaker than longitudinal dispersion.