CHAPTER 2

Surface Waters

2.1 INTRODUCTION

2.1.1 NATURE OF SURFACE WATERS

Surface waters, including rivers, streams, lakes, and estuaries, were among the first environmental media to receive widespread attention for chemical pollution problems. This attention was due in part to the high visibility and extensive public usage of surface waters, as well as to their historical use as waste receptors. Fish kills, odiferous industrial discharges, sewage, floating refuse, and other obvious signs of pollution mobilized scientific and regulatory communities to study and regulate sources and sinks of pollutants. A major goal of such work was to determine "acceptable" levels of waste loadings to surface waters. For example, estuaries, which are the transitional zones between rivers and the ocean, were at one time regarded as potential pollutant filters. However, research on the very high productivity of these waters, as well as the dependence on them of many sensitive life cycle stages of organisms, has alerted people to the need to maintain these waters in as pristine a condition as possible.

FIGURE 2-1 Bass Brook, a small fast-moving stream in New Britain, Connecticut. Upstream of this location the stream goes over a steep rapids; further downstream, it travels through a floodplain, a broad and flat area of bordering land that becomes part of the river during high water. Downslope flow of water due to gravity distinguishes streams and rivers from lakes. (Photo by H. Hemond.)

Before discussing in detail any of the fate and transport processes occurring in surface waters, the major characteristics of surface waters must be defined. As illustrated in Fig. 2-1, rivers and streams are relatively long, shallow, narrow water bodies characterized by a pronounced horizontal movement of water in the downstream direction. Often the water flow is sufficiently turbulent to erode the stream channel and carry sediment for considerable distances. Due to this movement of sediment, some river channels are constantly shifting in geometry. Compared with rivers, lakes tend to be deeper and wider and are not dominated by a persistent downstream current (Fig. 2-2). Lakes are often vertically *stratified* for part of the year, with two distinct layers of water whose temperatures and chemistries are markedly different. Estuaries (Fig. 2-3), the interfaces between rivers and the ocean, also are often vertically stratified, due to the denser saline seawater sinking beneath the freshwater discharged from the river. Estuaries have tides due to their connection to the ocean, and they tend to be rich in nutrients.

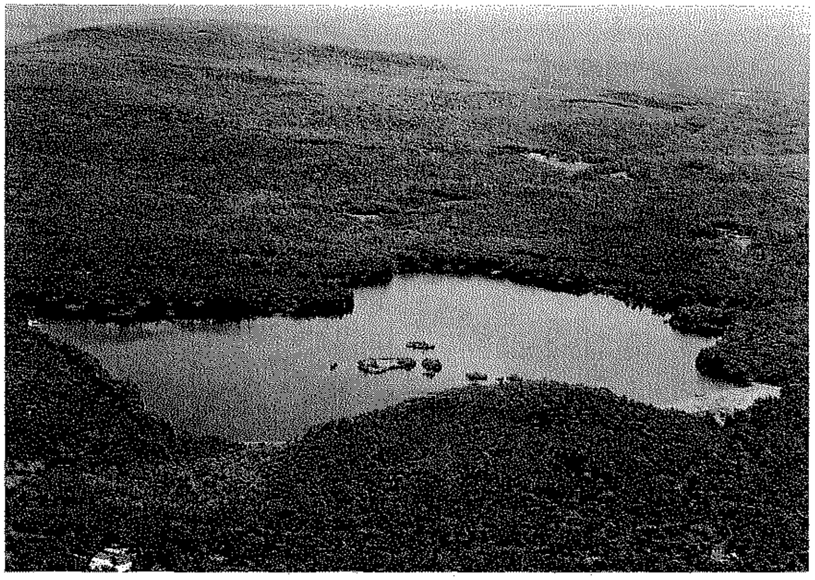


FIGURE 2-2 Bickford Reservoir, a lake in central Massachusetts. Lakes such as this typically stratify during the summer season, but become fully mixed during the spring and fall. Water currents in a lake are mostly wind-driven and vary in velocity. On large lakes, wave action also becomes an important transport factor. (Photo by H. Hemond.)

After a brief description of pollutant sources to surface waters, the physics, biology, and chemistry of surface waters are discussed. The major fate processes for chemicals in surface waters are then presented, including the physical processes of volatilization and sedimentation; the chemical processes of reduction–oxidation reactions, hydrolysis, and photodegradation; and the biological processes of biodegradation and accumulation in aquatic organisms.

2.1.2 SOURCES OF POLLUTANT CHEMICALS TO SURFACE WATERS

Sources of pollutants are commonly divided into two categories: point sources and nonpoint sources. *Point sources* refer to discrete, localized, and often readily measurable discharges of chemicals. Examples of point sources are industrial outfall pipes, untreated storm water discharge pipes, and treated

FIGURE 2-3 The mouth of the Poquonock River in Groton, Connecticut, where it enters the coastal waters of Fishers Island Sound (photo left). Here, a barrier beach (the prominent curving spit of sand) separates the Sound from the estuary; water enters and exits, driven by tides and by river inflow, through the relatively narrow inlet west (photo top) of the barrier. Not all estuaries have such a barrier, but all have a region where saltwater and freshwater come together and mix. This estuary is geometrically complex, with a quilt work of open water, marsh, natural upland, and a region of fill on which the airport (photo top right) is built. (Photo by H. Hemond.)

sewage outfalls. A spill of chemicals, due to an accident on or near a surface water body, can also be regarded as a point source of pollution because the amount and location of the discharge are often well characterized.

Nonpoint sources of pollution are more difficult to measure because they often cover large areas or are a composite of numerous point sources. Examples of nonpoint sources include pesticide and fertilizer runoff from agricultural fields, and urban runoff contaminated with pollutants from automobile emissions. Nonpoint sources may not be directly located next to a surface water body; pollutants may be transported to surface waters by runoff from the land, by groundwater inflow, or by atmospheric transport.

2.2 PHYSICAL TRANSPORT IN SURFACE WATERS

2.2.1 RIVERS

Gravity-Driven Advection

In rivers, water flows downstream by gravity. The velocity of a river is usually measured directly because rivers are generally accessible and satisfactory current-measuring devices exist. Nevertheless, a great deal is known about the factors that control river flow; if river geometry is known, it is possible to determine river velocity without going near the water. One governing principle of river flow is that the gravitational energy gained by the water flowing downslope must either go into frictional energy loss (dissipated as heat) or kinetic energy (energy associated with the water velocity). Two equations are widely used to model the velocity of water in uniform river or stream channels: the Chezy equation and the Manning equation. Both equations relate water velocity to the channel's *hydraulic radius* and slope. The hydraulic radius is the ratio of the cross-sectional area of flowing water to the wetted perimeter (for a rectangular channel, width plus twice the depth). The Chezy equation is

Chezy

$$V = C\sqrt{RS}, \qquad [2\text{-}1]$$

$R = \frac{A_{xs}}{\text{Perim}}$

$S = \text{slope}$

where V is the velocity [L/T], C is the Chezy friction coefficient [$L^{1/2}/T$], R is the hydraulic radius [L], and S is the slope of the water surface (dimensionless). The Manning equation is

$$V = \frac{1.49\, R^{2/3} S^{1/2}}{n}, \qquad [2\text{-}2]$$

Manning's Roughness

TABLE 2-1 Manning Roughness Coefficients (n)[a,b]

Channel characteristics	Value
Smooth concrete	0.012
Ordinary concrete lining	0.013
Vitrified clay	0.015
Straight unlined earth canals in good condition	0.020
Winding natural streams and canals in poor condition—considerable moss growth	0.035
Mountain streams with rocky beds, and rivers with variable sections and some vegetation along banks	0.040–0.050

Increase n = slower flow

[a] Dunne and Leopold (1978).

[b] For use in Eq. [2-2]. Note that in Eq. [2-2], the hydraulic radius must be expressed in units of feet; the resultant velocity has units of feet per second.

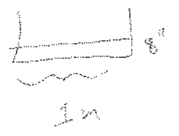
where n is the Manning roughness coefficient, which describes river channel roughness. As commonly tabulated, values of n require that R be expressed in feet; the resultant velocity has units of feet per second.

The coefficients C or n are determined experimentally for different types of channel linings. A tabulation of Manning roughness coefficients is shown in Table 2-1. For further discussion of these two equations, the reader is referred to Henderson (1966), Dunne and Leopold (1978), or Linsley *et al.* (1982).

EXAMPLE 2-1

A 2-m wide rectangular culvert made of ordinary concrete is constructed to carry storm water flow away from a new housing development. The slope of the culvert is 0.001. After a heavy rainstorm, an 8-in. deep flow of water is measured in the culvert. Assume uniform, steady flow and estimate the velocity of this storm water.

Eq. [2-2] can be used to estimate the water velocity in the culvert. First, estimate the hydraulic radius, in units of feet:



$$R = \frac{\text{width} \cdot \text{depth}}{\text{width} + 2 \cdot \text{depth}}$$

$$= \frac{(2\ \text{m} \cdot 3.281\ \text{ft/m}) \cdot (8\ \text{in.} \cdot 1\ \text{ft/ }12\ \text{in.})}{(2\ \text{m} \cdot 3.281\ \text{ft/m}) + 2 \cdot (8\ \text{in.} \cdot 1\ \text{ft/}12\ \text{in.})}$$

$$= 0.55\ \text{ft.}$$

Then use Table 2-1 to obtain a value of 0.013 for the Manning roughness coefficient for ordinary concrete lining in a channel.

The velocity of the storm water flow can then be estimated from Eq. [2-2] as

$$V(\text{ft/sec}) = \frac{1.49 \cdot (0.55)^{2/3} \cdot (0.001)^{1/2}}{0.013} = 2.4\ \text{ft/sec.}$$

When a mass of a chemical is released at a point in a river, the center of the chemical's mass moves downstream at the average velocity of the river (Fig. 2-4, upper panel). The average amount of time it takes a chemical to travel from an upstream point to a downstream point in a river (i.e., to traverse the length of a given segment, or *reach*, of river) is called the *travel time*, τ, and is expressed as

$$\tau = L/V, \quad \frac{m}{m/s} \qquad [2\text{-}3a]$$

where τ is the travel time [T], L is the length of river reach [L], and V is the average velocity of the river [L/T]. If the river velocity is not uniform along the river, then the travel time must be expressed as an integral,

$$\tau = \int_{x_1}^{x_2} \frac{1}{V(x)}\, dx, \quad \simeq \sum \frac{\Delta x_i}{V_i} = \frac{\Delta x_1}{V_1} + \frac{\Delta x_2}{V_2} + \qquad [2\text{-}3b]$$

where x is the distance along the river [L], points x_1 and x_2 are the endpoints of the reach, and $V(x)$ is the magnitude of the velocity [L/T] of the river at any given point x.

An estimate of travel time is important in many situations. For example, a municipal water supply operator needs to know how long it will take a chemical spilled upriver to reach downstream water intake pipes so that the valves can be closed before the spilled chemical arrives. An estimate of travel time is also necessary when calculating whether processes such as loss to the air (*volatilization*) or bacterial degradation will significantly decrease a chemical concentration along a reach of river.

The total volume of water passing any given point in the river per unit time is called *discharge*. The relationship between discharge and velocity is

$$Q = A \cdot V, \qquad [2\text{-}4]$$

where Q is discharge [L^3/T], A is the cross-sectional area of the river [L^2], and V is the average water velocity [L/T]. Discharge may be measured using a *weir* or a *flume;* these are structures that are built in a river channel and have

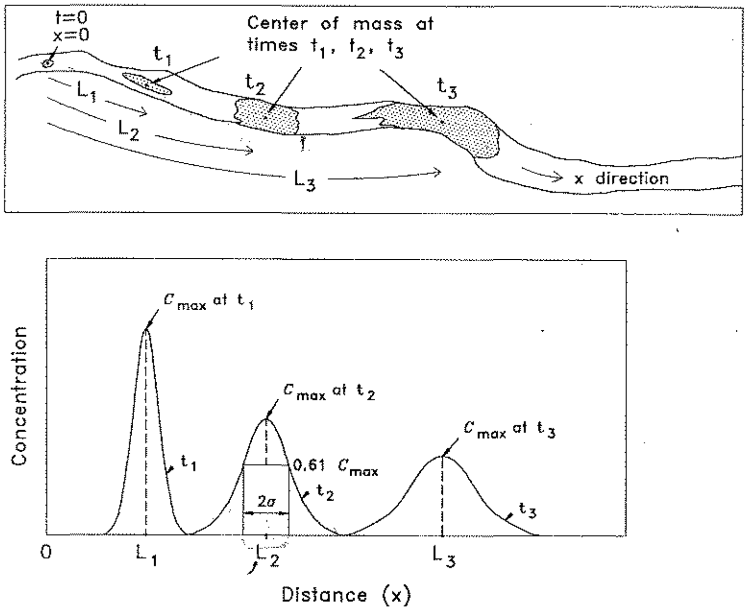


FIGURE 2-4 Transport of a chemical in a river. At time zero, a pulse injection is made at a location defined as distance zero in the river. As shown in the upper panel, at successive times t_1, t_2, and t_3, the chemical has moved farther downstream by advection, and also has spread out lengthwise in the river by mixing processes, which include turbulent diffusion and the dispersion associated with nonuniform velocity across the river cross section. Travel time between two points in the river is defined as the time required for the center of mass of chemical to move from one point to the other. Chemical concentration at any time and distance may be calculated according to Eq. [2-10]. As shown in the lower panel, C_{max}, the peak concentration in the river at any time t, is the maximum value of Eq. [2-10] anywhere in the river at that time. The longitudinal dispersion coefficient may be calculated from the standard deviation of the concentration versus distance plot, Eq. [2-7].

known depth–discharge relationships. Alternatively, discharge may be calculated from stream geometry and velocity measurements made with a current meter. The mass of chemical transported by a river past a given point per unit time is

$$J_{tot} = Q \cdot C, \qquad [2\text{-}5]$$

where J_{tot} is the total flux of chemical [M/T] and C is the average chemical concentration [M/L^3].

Fickian Mixing Processes

A mass of chemical released in a river will spread out as it moves downstream. This spreading is due to dispersion, caused by *velocity shear* within the river, and turbulent diffusion. Velocity shear in a river occurs because different parcels of water have different downstream velocities, depending on their position in a river cross section. Typically, water velocity in a river increases with distance from the river bottom and sides, reaching a maximum near the river center and usually somewhat below the water surface, as shown in Fig. 2-5. Chemical mass dissolved in the midchannel near-surface water will travel downstream more rapidly than mass dissolved in deeper water or in water near the channel sides. The distribution of the chemical mass thus elongates in the direction of flow. Turbulent diffusion is caused by the random motions of water associated with channel irregularities and with the eddies that are caused by velocity shear. A Fickian mixing approach can be used to describe the sum of the mixing due to dispersion and due to turbulent diffusion. The greater the spatial variability in water velocity and the greater the turbulence, the greater will be the mixing.

Mixing in a stream or river can be quantitatively illustrated by instantaneously releasing a mass of chemical uniformly throughout the cross section of a channel; this *pulse injection* is best expressed as mass per cross section of river, [M/L^2]. Ideally, one chooses a *conservative tracer* (i.e., a chemical that does not undergo degradation in the river and is not absorbed to the river channel or suspended particles). The lower panel of Fig. 2-4 shows a chemical concentration in a stream at several different times after a pulse injection. At any instant, the plot of concentration versus distance is "bell-shaped"; ideally, if the mixing is truly Fickian, the curve has the shape of a Gaussian, or *normal*, curve,

$$\phi(x) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-x^2/2\sigma^2}, \qquad [2\text{-}6]$$

where x is the abscissa (x coordinate) of each point on the curve, $\phi(x)$ is the ordinate (y coordinate) of each point on the curve, and σ is the standard deviation of $\phi(x)$ about the origin.

The equation that is used to describe the chemical concentration at various locations has the same mathematical form as Eq. [2-6] because the randomness assumed in Fickian mixing is similar to the randomness that gives rise to the normal curve. For a pulse injection, there is a close relationship between a Fickian mixing, or transport, coefficient D in a given direction, and the standard deviation of the chemical distribution in that direction. D can be

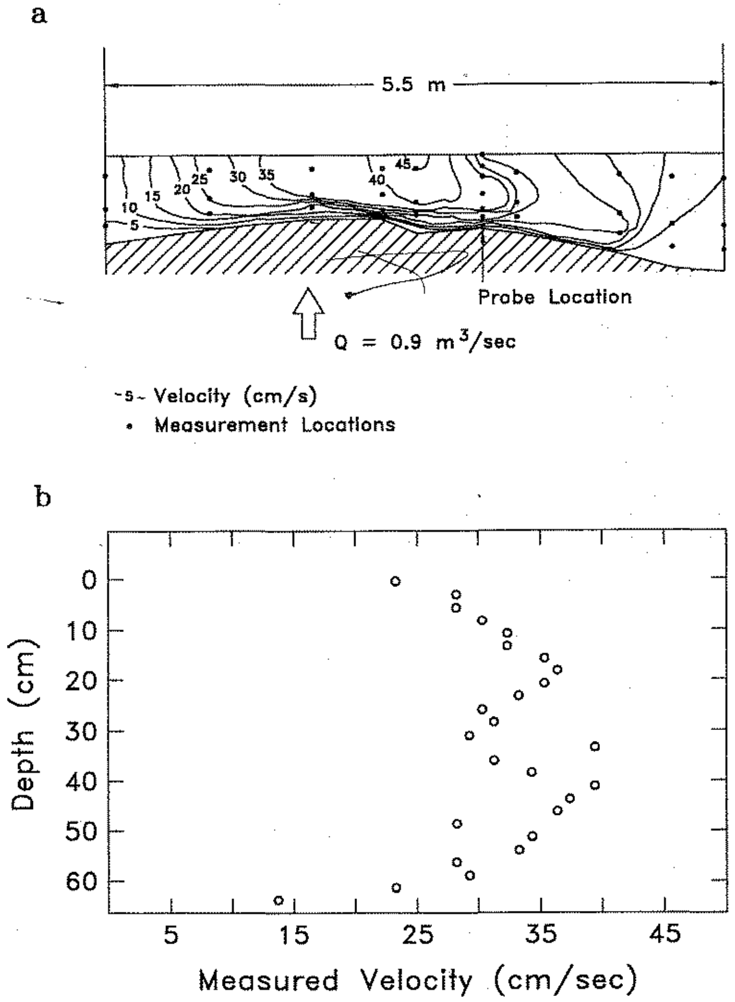


FIGURE 2-5 (a) Velocity distribution across a channel cross section in the Aberjona River in Woburn, Massachusetts. A nonuniform velocity distribution results in longitudinal dispersion of chemicals carried by the river. (b) Vertical velocity profile in the Aberjona River at the probe location. Velocity is highest at an intermediate depth, lower at the surface due to air resistance, and zero at the channel bottom [data from Solo-Gabriele (1995)].

$\sigma^2 = 2Dt$

$\sigma = \sqrt{2Dt}$

calculated from the following equation,

$$D = \sigma^2/2\,t, \qquad [2\text{-}7]$$

where σ^2 is the spatial variance (the square of the standard deviation) of the chemical distribution [L^2], and t is the time since the pulse injection of the chemical was made. σ increases with time, but the tracer maintains the shape of a Gaussian distribution about its center of mass.

When Eq. [2-7] is solved for σ in the direction of river flow (the longitudinal direction), and then σ is substituted into Eq. [2-6], the resulting equation still describes a Gaussian curve,

$$\phi(x, t) = \frac{1}{\sqrt{2D_L t}\,\sqrt{2\pi}}\, e^{-x^2/2\cdot 2D_L t}, \qquad [2\text{-}8]$$

where D_L is the longitudinal dispersion coefficient [L^2/T]. Given that the center of mass of the cloud of tracer is moving downstream at velocity V, the distance x must be replaced by $(x - Vt)$ in Eq. [2.8]:

$$\phi(x, t) = \frac{1}{\sqrt{2D_L t}\,\sqrt{2\pi}}\, e^{-(x-Vt)^2/2\cdot 2\,D_L t}. \qquad [2\text{-}9]$$

To obtain an expression for chemical concentration in the river, the chemical mass M injected into the river must be taken into account. In Eq. [2-9], the area under the curve is unity, whereas for a conservative tracer, the area under a curve of concentration versus distance must equal M, the initial chemical mass injected into the river per unit area of cross section. Thus, Eq. [2-9], when multiplied by M, yields Eq. [2-10], which gives the concentration of a conservative tracer at any time t after injection and any distance x downstream:

$$C(x, t) = \frac{M}{\sqrt{4\pi D_L t}}\, e^{-(x-Vt)^2/(4\,D_L t)}, \qquad [2\text{-}10]$$

where C is the concentration of chemical [M/L^3], M is the mass of chemical injected per cross-sectional area of river [M/L^2], x is the distance downstream of injection location [L], V is the river velocity [L/T], t is the time elapsed since injection [T], and D_L is the longitudinal Fickian mixing coefficient [L^2/T]. Eq. [2-10] is also a solution, given this particular set of conditions, to the advection–dispersion–reaction equation shown in Eq. [1-5].

If the chemical of interest undergoes first-order decay during transport downstream, the righthand side of Eq. [2-10] can be multiplied by the factor e^{-kt}, where k is a first-order rate constant for chemical transformation and removal processes [T^{-1}]:

$$C(x, t) = \frac{M}{\sqrt{4\pi D_L t}} e^{-(x-Vt)^2/(4D_L t)} \cdot e^{-kt}. \qquad [2\text{-}11]$$

At any given time t, the maximum concentration of the chemical ($C_{\max}$) is found at a distance downstream of the injection point (x) equal to the product of the time elapsed since injection (t) and the average river velocity (V). At this location, the quantity ($x - Vt$) in Eq. [2-10] equals zero, and thus

$$C_{\max} = \frac{M}{\sqrt{4\pi D_L t}} e^{-kt}. \qquad [2\text{-}12]$$

It follows from the properties of the normal distribution that the portion of the river lying within one standard deviation (σ) upstream or downstream on either side of the point of maximum chemical concentration includes 68% of the chemical mass in the river. It also follows that the chemical concentration one standard deviation from the point of maximum concentration equals the maximum concentration multiplied by 0.61 (see Fig. 2-4, lower panel).

The preceding discussion assumed that a chemical is injected into a river or stream uniformly across a river cross section. In fact, spills and other inputs are rarely introduced uniformly across a channel, and a certain distance must be traveled before a chemical concentration becomes uniform across the channel. For a chemical released at a river bank, the length L of this *transverse mixing zone* can be roughly estimated by equating the lateral standard deviation (σ_t) of the chemical's concentration distribution to the width of the river,

$$\sigma_t = \sqrt{2D_t t} \approx w, \qquad [2\text{-}13]$$

where D_t is the transverse Fickian mixing coefficient [L^2/T], t is the time since the chemical was released, and w is the width of the river [L]. Combining Eq. [2-3a] with Eq. [2-13] results in the estimate of the length of the transverse mixing zone,

$2D_t t = w^2$

$t = \frac{L}{V} = \frac{w^2}{2D_t} \Rightarrow$

$$L \approx \frac{w^2 V}{2D_t}, \qquad [2\text{-}14]$$

where V is the average velocity [L/T].

Estimation of Fickian Transport Coefficients from Tracer Experiments

In the case of mixing primarily due to turbulent diffusion and dispersion, the Fickian transport coefficients are essentially independent of the chemical, so that the values of D determined from tracer experiments can be applied to other chemicals of interest in the same river. Two types of commonly used tracers are salts, such as sodium chloride (NaCl), and fluorescent dyes, such as rhodamine, which can be measured at very low concentrations.

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1159

For example, to estimate D_L, a pulse of tracer is injected into a river and the longitudinal distribution of the tracer is measured as the river carries it past a downstream location. The spatial standard deviation of tracer and the travel time are determined from tracer concentration data, and D_L is computed using Eq. [2-7].

Travel time and the longitudinal Fickian transport coefficient can also be evaluated from a *continuous injection* experiment, in which injection of tracer is initiated at time $t = 0$ and continues until steady-state conditions are reached downstream. This type of experiment is discussed for groundwater in Section 3.2.5; the equation describing concentrations resulting from a continuous injection in a river is identical to Eq. [3-18]. The equivalent equation presented in Fig. 3-19 could also be used, but with 100% porosity. In fact, equations such as Eq. [2-10] that describe advective and Fickian transport are surprisingly general. Although applied here to rivers and streams, they can be used to describe transport and evaluate Fickian mixing coefficients in many environmental situations, including groundwater and air.

EXAMPLE 2-2

The t_2 profile of Fig. 2-4 was measured 5 hr after a pulse injection of dye. What is the average river velocity if the maximum concentration is occurring 1025 m down the river from the pulse injection at this time? Estimate the longitudinal dispersion coefficient for this river if the standard deviation in the longitudinal direction, σ_L, is approximately 350 m when the chemical has traveled a distance of 1975 m to L_3.

The average velocity is

$$V = \frac{L_2}{t_2} = \frac{1025 \text{ m}}{5 \text{ hr}} = 205 \text{ m/hr}.$$

To estimate the dispersion coefficient, consider the concentration profile at time t_3; the peak of the profile ($C_{\max}$) occurs at approximately 1975 m, and the standard deviation is roughly 350 m. Assuming the average river velocity is 205 m/hr, the travel time to L_3, using Eq. [2-3a], is

$$\tau_3 = \frac{L_3}{V} = \frac{1975 \text{ m}}{205 \text{ m/hr}} = 9.6 \text{ hr}.$$

The longitudinal dispersion coefficient D_L can then be estimated from Eq. [2-7]:

$$D_L = \sigma_L^2/2\tau = (350 \text{ m})^2/(2 \cdot 9.6 \text{ hr}) \simeq 6400 \text{ m}^2\text{/hr}.$$

Estimation of Fickian Transport Coefficients from Flow Data

In the absence of experimental tracer data, it is also possible to estimate Fickian transport coefficients from stream channel geometry and stream discharge (Fischer *et al.*, 1979). A substantial amount of work has been done on the problem of estimating both longitudinal dispersion coefficients and transverse diffusion coefficients (commonly called transverse dispersion coefficients) for rivers. The distinction between transverse (or lateral) mixing and longitudinal mixing is that transverse mixing occurs only by turbulence (there is by definition no lateral advection in a river), whereas longitudinal mixing is caused in part by turbulence, but is usually dominated by dispersion. The result is that different formulations have arisen for estimating Fickian transport in each direction.

As previously discussed, turbulence is caused in part by velocity shear due to a nonuniform velocity profile. In a river, a *shear velocity*, which is related to the shear force per unit area exerted by the water flow on the river channel, can be estimated (Fischer *et al.*, 1979) as

$$u^* = \sqrt{gdS}, \qquad [2\text{-}15]$$

where u^* is the shear velocity [L/T], g is the acceleration due to gravity [L/T^2], d is the stream depth [L], and S is the channel slope (dimensionless). (Strictly speaking, the hydraulic radius R should be used instead of d, but most rivers are wide compared with their depth, so that the hydraulic radius is approximately equal to the depth.)

A fairly good correlation (within a factor of two) has been reported between u^* and the transverse dispersion coefficient, D_t:

$$D_t \approx 0.15 \cdot d \cdot u^* \text{ for straight channels,} \qquad [2\text{-}16a]$$

$$D_t \approx 0.6 \cdot d \cdot u^* \text{ for typical natural channels.} \qquad [2\text{-}16b]$$

Table 2-2 shows a range of reported D_t for straight, sinuous, and meandering natural channels.

In the case of longitudinal dispersion coefficients, D_L, the stream velocity and width become important predictors; the following equation typically predicts D_L within a factor of four (Fischer *et al.*, 1979),

$$D_L = \frac{0.011 \cdot V^2 \cdot w^2}{d \cdot u^*}, \qquad [2\text{-}17]$$

where D_L is the longitudinal dispersion coefficient [L^2/T], V is the average velocity [L/T], w is the width of the channel [L], d is the stream depth [L], and u^* is the shear velocity [L/T]. Typical values of D_L range from 0.05 to 0.3 m^2/sec for small streams (Genereux, 1991) to greater than 1000 m^2/sec for large rivers such as the Rhine (Wanner *et al.*, 1989). Table 2-3 presents a range of reported D_L at particular locations and times for several rivers.

TABLE 2-2 Reported Transverse Dispersion Coefficients[a]

River type/river	Transverse dispersion coefficients (m^2/sec)	Discharge during dispersion measurement (m^3/sec)
Straight channels		
Atrisco	0.010	7.4
South	0.0047	1.5
Athabasca	0.093	776
Bends		
Missouri	1.1	1900[b]
Beaver	0.043	20.5
Mississippi	0.1	92–120
Meandering		
Missouri	0.12	966
Danube	0.038	1030
Rea	0.0014	0.30
Orinoco	3.1	47,000
MacKenzie	0.67	15,000[b]

[a] Rutherford (1994).
[b] Estimated based on height, width, and velocity.