

Chapter 18

TRANSPORT AT BOUNDARIES

18.1 The Role of Boundaries in the Environment

18.2 Bottleneck Boundaries

- Simple Bottleneck Boundary
- Simple Bottleneck Boundary at an Interface
- Two-Layer Bottleneck Boundary at an Interface

18.3 Wall Boundaries

- One-Sided Wall Boundary
- Two-Sided Wall Boundary
- Box 18.1 Exchange Flux at a Two-Sided Interface Wall Boundary

18.4 Hybrid Boundaries

- From Wall to Bottleneck Boundary
- Wall Boundary with Boundary Layer
- Box 18.2 Effect of Boundary Layer on Integrated Mass Exchange at Wall Boundary: Estimate of Critical Time t_{crit}

18.5 Questions and Problems

18.6 Bibliography

18.1 The Role of Boundaries in the Environment

Many chemical and biological transformation processes occur at *boundaries*. We use the term *boundary* in a fairly general manner to denote surfaces at which properties of a system change strongly or, as in the case of interfaces, even discontinuously. *Interface boundaries* are characterized by a phase change or by a discontinuity of certain parameters such as chemical composition. Numerous examples of interface boundaries are given in Chapter 5 such as the air–water interface of surface waters (ocean, lakes, or rivers), the sediment–water interface in lakes and oceans, the surface of an oil droplet suspended in air, and the surface of an algal cell or a mineral particle suspended in water.

In the environment, we also frequently deal with non-interface boundaries. They are characterized by property gradients (density, temperature, or concentrations) that are distinctly larger than the gradients in adjacent areas, but not discontinuous. Examples are the tropopause (the boundary between the troposphere and the stratosphere, Fig. 5.1) or the boundary between the warm, less dense surface layer of a lake (epilimnion) and the cold and denser deep-water layer (hypolimnion) called the thermocline (Fig. 5.7). These boundaries are not interfaces in the strict sense, but rather transition zones with a certain spatial extension.

In most cases, *horizontal* non-interface boundaries are the result of a distinct density change in the vertical direction (e.g., tropopause or thermocline). Mixing across such boundaries is by small-scale vertical turbulence or, in cases where the mechanical stirring is very small, by molecular diffusion. In contrast, vertical advection is slow or absent. The situation is very different for a *vertical* non-interface boundary that separates two adjacent environmental compartments like two water bodies linked by a channel (see Fig. 6.7). A prominent example is the Strait of Gibraltar where the highly saline water of the Mediterranean Sea meets with the less saline water of the Atlantic Ocean. Here, horizontal density gradients lead to strong horizontal currents, often in both directions. Transport results from the superposition of diffusion and advection; the physics of the mixing processes are complex and beyond the scope of this book (e.g., Bryden et al., 1994). In the following discussion, we only deal with purely (molecular or turbulent) diffusive boundaries.

Boundaries are distinguished from the interior part of a compartment in two ways: (1) they play a pivotal role in controlling the transport of energy and matter between adjacent compartments, and (2) they may contain sites for special abiotic and biological processes due to the contact of two systems with different chemical and biological composition. Often, the rates of these processes (e.g., acid-base reactions) are much larger than the rate of transport of the reactants to the boundary. If this applies, the reactants at the boundary can be assumed to be at local equilibrium. For other reactions at boundaries, assuming equilibrium may not work because the reactions are slow compared to fluxes to and across the boundary.

From a physical point of view, boundaries are characterized by mixing regimes that are distinctly different from mixing in the adjacent compartments. In essence, every boundary can be considered as being composed of one or several building blocks, but

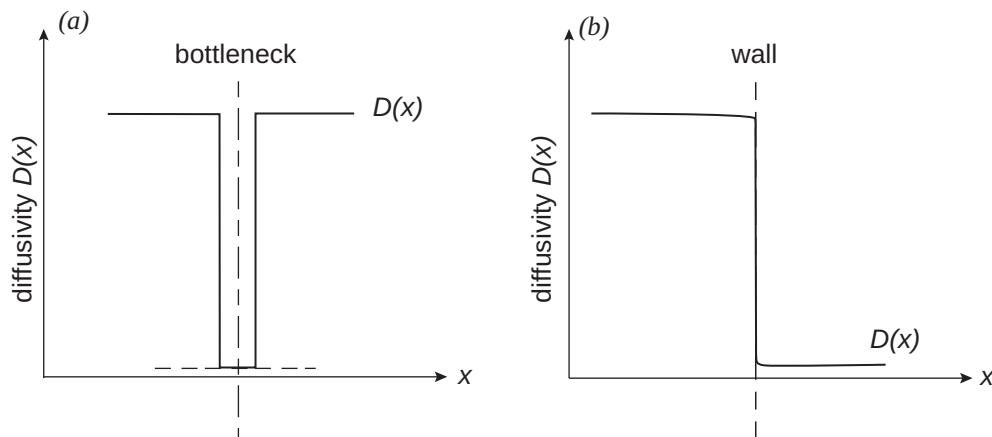


Figure 18.1 Every boundary can be described by one or several building blocks of just two types: (a) a bottleneck boundary in which diffusivity is small compared to positions away from the interface, or (b) a wall boundary in which diffusivity is relatively large on one side of the interface and much smaller on the other side. The diffusivity along the spatial coordinate x perpendicular to the boundary, $D(x)$, is drawn schematically.

just two types of building blocks exist: bottleneck boundaries and wall boundaries. They differ from each other by the diffusivity profile across the boundary, $D(x)$, where x is the spatial coordinate perpendicular to the boundary (Fig. 18.1).

The bottleneck boundary is a layer in which diffusivity is distinctly smaller than in the adjacent compartments. Mass crossing bottleneck boundary must “squeeze” itself through a zone in which transport is slow. It is like a two-lane bridge that separates two sections of a twelve-lane freeway on which cars drive quite fast at all locations away from the bridge.

The wall boundary is characterized by a distinct and sudden change of diffusivity from a volume with large diffusivity (“well-mixed compartment”) to a volume with small diffusivity (“wall”). A wall boundary is like a multi-lane freeway leading into a narrow winding road.

Every real boundary can be considered to consist of one or several “building blocks.” For instance, simple one-layer bottleneck boundaries consist of one bottleneck building block, two- and n -layer bottleneck boundaries consist of two and n bottleneck boundaries, simple and double (two-sided) wall boundaries consist of one or two wall boundary building blocks, and combinations have, for instance, a wall boundary combined with a bottleneck boundary. Although these systematics may look complicated, they have the great advantage that the mathematical description of these boundaries becomes relatively simple, as the following examples show.

The classification of boundaries into just two types is made possible due to the enormous difference in the magnitudes of molecular and turbulent diffusivities (see Figs. 17.5 and 17.6, Table 17.3). In later chapters we learn more about the conditions in which, on one hand, molecular diffusion is relevant and, on the other hand, turbulence overrides the influence of mixing at the molecular level. We discover that as a general principle, transport by turbulence cannot cross *interface boundaries*, although turbulent kinetic energy can as demonstrated by the production of water waves by the wind. Thus, interface boundaries are usually accompanied by distinct changes of diffusivity. Typical examples are discussed in greater detail: (1) the air–water

interface, a bottleneck boundary separating two compartments, air and water, in which transport is by turbulent diffusion, and (2) the sediment–water interface, a wall boundary separating the water column, which is mostly turbulent, and the pore space in which transport is significantly slower than in the overlying water.

18.2 Bottleneck Boundaries

Simple Bottleneck Boundary

A simple bottleneck boundary, as opposed to a double or threefold bottleneck boundary (see following), is characterized by *one* single zone in which diffusivity, D , is significantly smaller than in the bulk part on either side of the boundary. As an example, we consider the thermocline of a lake, that is, the horizontal water layer typically 5 to 20 meters thick that separates the warm and less dense surface water from the cold and denser deep water. In Chapter 5, we learned that the zone in which temperature decreases rather abruptly is characterized by a vertical turbulent diffusion coefficient that is distinctly smaller than turbulent diffusivity above and below the thermocline (see Fig. 5.7). In the case study of Mystery Lake introduced in Chapter 6, we have already made use of the thermocline as a bottleneck boundary (see Fig. 6.2). Another example for a thermocline bottleneck boundary is given in Problem 18.1 that deals with the vertical diffusion of atrazine into the hypolimnion of a lake.

Figure 18.2 gives a schematic view of a simple bottleneck boundary. In real systems, the drop of $D(x)$ to the bottleneck value, D_b , is usually much smoother than shown in Fig. 18.2. In order to describe the flux of a chemical across the boundary, we assume that after some time a steady-state profile is established, that is, no build-up

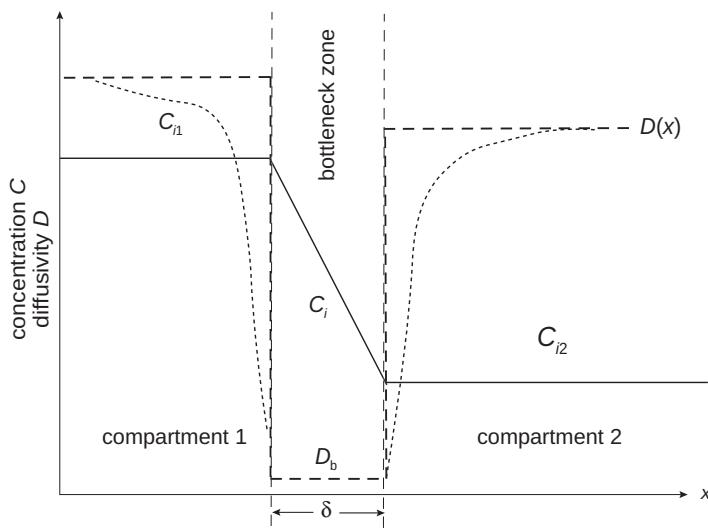


Figure 18.2 Concentration of chemical i , $C_i(x)$, at a simple bottleneck boundary of thickness δ between the compartments 1 and 2. The dashed line is diffusivity $D(x)$, D_b is diffusivity in the bottleneck. As indicated by the dotted line, in reality, the change of $D(x)$ is less abrupt than shown by the dashed line, but the latter helps to simplify the mathematical description of transport through the boundary.

of mass occurs at any position. We conclude from Gauss's theorem (Eq. 6-33) that in a one-dimensional system (only one coordinate x), the flux along x of a *conservative* substance (a substance that is neither produced nor consumed locally) at *steady state*, $F(x)$, must be constant:

$$\left(\frac{\partial C_i}{\partial t} \right)_{\text{transport}} = 0 \Rightarrow -\frac{\partial F_x}{\partial x} = 0 \Rightarrow F_x = \text{constant with } x \quad (18-1)$$

According to Fick's first law (Eq. 6-31), the flux is given by:

$$F_x = -D(x) \frac{dC_i}{dx} = \text{constant} \quad (18-2)$$

where the notation $D(x)$ indicates that the diffusivity depends on x . In other words, the concentration gradient, dC/dx , must be inversely related to $D(x)$.

As an approximation, we assume that (1) the drop of $D(x)$ to the bottleneck value, D_b , occurs discontinuously (dashed line in Fig. 18.2) and (2) diffusivities outside the boundary layer are infinitely large when compared with D_b . The latter means that the concentrations on either side of the bottleneck, C_{i1} and C_{i2} , are constant along the x -axis. Since D_b is assumed constant in the bottleneck, according to Eq. 18-2, the concentration gradient in the bottleneck must also be constant and equal to:

$$\left(\frac{dC_i}{dx} \right)_{\text{bottleneck}} = \frac{C_{i2} - C_{i1}}{\delta} \quad (18-3)$$

where δ is the thickness of the bottleneck. Combining Eqs. 18-2 and 18-3 yields:

$$F_x = -\frac{D_b}{\delta} (C_{i2} - C_{i1}) = -v_b (C_{i2} - C_{i1}) \quad (18-4)$$

The new quantity v_b :

$$v_b = \frac{D_b}{\delta} \quad [\text{LT}^{-1}] \quad (18-5)$$

has the dimension of a velocity and is thus called the (boundary) *exchange or transfer velocity*. The sign of Eq. 18-4 is chosen such that a positive F indicates a flux in the positive x -direction, that is, from compartment 1 to 2. In the example shown in Fig. 18.2, C_{i2} is smaller than C_{i1} , thus F is positive. The flux (or rather the net flux, since random motions always cause back-and-forth exchange fluxes) is directed from the compartment of larger concentration (1) to the compartment of smaller concentration (2).

The mathematical description of the flux across the bottleneck boundary (Eq. 18-4) does not depend on the mechanism responsible for the flux. If the flux is due to molecular motion (as it is the case for interface boundaries), diffusivity at the boundary, D_b , is given by the molecular diffusion coefficient. In this case, different compounds have

different transfer velocities v_b (in fact, we should then use the notation v_{ib}). In contrast, if the flux is due to turbulence, D_b is a turbulent diffusion coefficient and independent of compound i , and we can describe the flux in an alternative way. When we discussed the exchange between two boxes (Fig. 6.6), we introduced the volumetric exchange flux, Q^{ex} , to describe the net transport rate between the boxes with the expression (Eq. 6.16):

$$\mathcal{T}_{i12}^{\text{net}} = Q^{\text{ex}}(C_{i1} - C_{i2}) \quad [\text{MT}^{-1}] \quad (18-6)$$

If the transport rate is normalized by the area perpendicular to the flux, A , we arrive at:

$$F_{i12} = \frac{\mathcal{T}_{i12}^{\text{net}}}{A} = \frac{Q^{\text{ex}}}{A}(C_{i1} - C_{i2}) = -v^{\text{ex}}(C_{i2} - C_{i1}); \quad v^{\text{ex}} = \frac{Q^{\text{ex}}}{A} \quad (18-7)$$

Equation 18-7 has the same form as Eq. 18-4 but expresses the exchange velocity by an exchange flux, Q^{ex} , not by diffusivity, D_b . Both expressions greatly simplify the real processes that occur at boundaries. Which one is more adequate for a specific situation depends on the physical nature of turbulence at the boundary.

Simple Bottleneck Boundary at an Interface

Until now, we have tacitly assumed that the boundary separates two compartments of the same phase, for instance, the water in the epilimnion and in the hypolimnion of a lake. We can intuitively understand why for such situations the net flux across the boundary is zero if the concentrations are equal on either side (Eqs. 18-4 and 18-7). However, how do we treat the situation at an interface boundary, for instance, at the surface of a lake that separates water and air? As discussed in Chapter 7, the equilibrium between two compartments of a different phase, that is, the situation for which the net flux across the boundary is zero, is defined by the equilibrium partition ratio (Box 7.1). For the case of water and air, this ratio is the dimensionless Henry constant, $K_{i\text{aw}}$ (Eq. 9-15). Flux at the air–water interface boundary and the different models used to describe it are discussed in greater detail in Chapter 19.

Also, how about the situation when the chemicals themselves are present in different phases (e.g., dissolved and particulate) in the compartments straddling the boundary? In this case, the overall exchange across the boundary is expressed in terms of the total concentrations on either side of the boundary. According to the nomenclature introduced in Box 7.1, equilibrium at the boundary is then characterized by the equilibrium distribution ratio, R_{i12} , defined by

$$R_{i21} = \left(\frac{C_{i2}}{C_{i1}} \right)_{\text{equilibrium}} \quad (18-8)$$

We use the more general R_{i12} , although in some cases (e.g., air–water interface) R_{i12} may actually be a partition ratio K_{i12} . R_{i21} is the ratio of two concentrations and, thus,

nondimensional, but it may help to distinguish between the volume units of the two phases. For instance, if C_{i1} is concentration in water ($\text{mol m}_{\text{water}}^{-3}$) and C_{i2} concentration in air ($\text{mol m}_{\text{air}}^{-3}$), then R_{i21} has the units ($\text{m}_{\text{water}}^3 \text{ m}_{\text{air}}^{-3}$).

The flux equation (Eq. 18-4) has to be modified such that the flux, F_x , is zero if the distribution ratio in the two compartments is R_{i21} . Thus:

$$F_x = -v_b \left(\frac{C_{i2}}{R_{i21}} - C_{i1} \right) = -v_b (C_{i1}^{\text{eq}} - C_{i1}) \quad \text{with} \quad C_{i1}^{\text{eq}} = \frac{C_{i2}}{R_{i21}} \quad (18-9)$$

We discuss such fluxes in greater detail in Chapter 20.

Two-Layer Bottleneck Boundary at an Interface

By adding another “building block,” we now introduce a two-layer bottleneck boundary with boundary layers on either side of the interface. At the air–water interface, for instance, a boundary layer can exist in air and another in the water (see further discussion in Chapter 19). In both layers, diffusion is molecular, that is, significantly smaller than the eddy diffusivity in the adjacent bulk volumes (see Fig. 18.3a). The concentration “jump” at the position where the two compartments are touching is described by the equilibrium distribution ratio (R_{i21} , Eq. 18-8). This “jump” disappears if the concentration in compartment 2 is expressed by the phase 1-concentration in equilibrium with the local phase 2-concentration, $C_{i1}^{\text{eq}} = C_{i2}/R_{i21}$ (see Fig. 18.3b).

As in Eq. 18-5, we define:

$$v_{i1} = D_{i1}/\delta_1 \quad ; \quad v_{i2} = D_{i2}/\delta_2 \quad (18-10)$$

with the subscript b (for boundary) replaced for the two boundary layers with $i1$ and $i2$ respectively. The compound subscript i reflects the fact that in the boundary

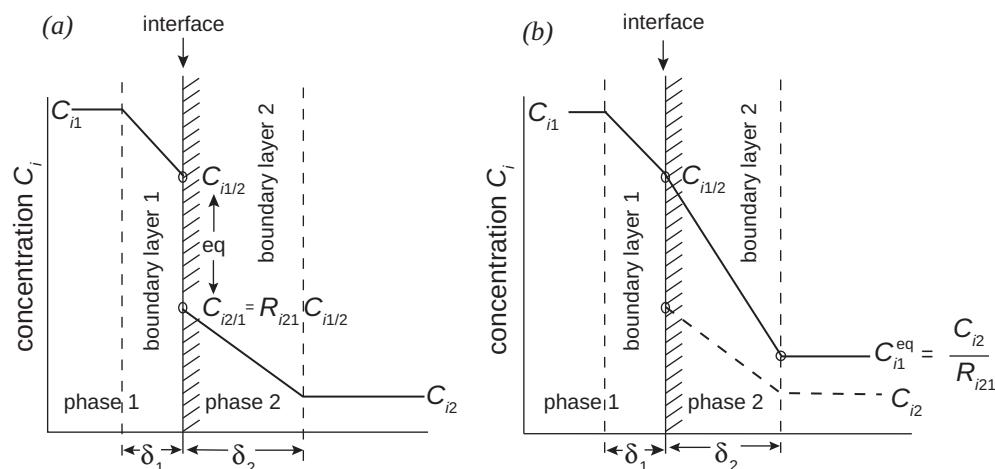


Figure 18.3 Transfer across a two-layer bottleneck boundary at the interface between two phases 1 and 2. (a) “Real” concentrations in both phases. The equilibrium (eq) distribution ratio at the boundary between the two phases is $R_{i21} = (C_{i2/1}/C_{i1/2})$. (b) Concentrations in phase 2 expressed as phase 1-concentration in equilibrium with phase 2. The concentration jump at the interface disappears. The dashed line gives the “real” phase 2-concentration shown in (a).

layers, transport is by molecular diffusion and the transfer velocity is a compound-specific property of the boundary. At the actual interface, the partitioning of molecules between the two phases is assumed to be at equilibrium (Eq. 18-8). Thus, the ratio of the interface concentrations, $C_{i1/2}$ and $C_{i2/1}$, is $R_{i21} = C_{i2/1}/C_{i1/2}$.

To solve for the flux across the entire boundary, we choose phase 1 as the reference phase, which determines the mathematical form of the transfer velocity across the two-layer interface (see Eq. 18-14). One could equally well derive the subsequent equations with phase 2 as the reference phase.

In order to calculate the interface concentrations, $C_{i1/2}$ and $C_{i2/1}$, we assume that the concentration profiles in both boundary layers are at steady state. Thus, the fluxes across the two boundaries, F_{i1} and F_{i2} , must be equal. From Fig. 18.3a, we get:

$$F_{i1} = -v_{i1}(C_{i1/2} - C_{i1}) \quad \text{and} \quad F_{i2} = -v_{i2}(C_{i2} - C_{i2/1}) = -v_{i2}(C_{i2} - R_{i21}C_{i1/2}) \quad (18-11)$$

Since the two fluxes must be equal, we can solve the equations for $C_{i1/2}$:

$$C_{i1/2} = \frac{v_{i1}C_{i1} + v_{i2}C_{i2}}{R_{i21}v_{i2} + v_{i1}} \quad (18-12)$$

By inserting this expression in one of the flux equations (Eq. 18-11) and mathematically rearranging, we get:

$$F_{i1} = F_{i2} = F_{i12} = v_{i12} (C_1 - C_{i1}^{\text{eq}}) \quad \text{with} \quad C_{i1}^{\text{eq}} = \frac{C_{i2}}{R_{i21}} \quad (18-13)$$

The overall transfer velocity from phase 1 to phase 2, v_{i12} , depends on a combination of the two boundary layer velocities:

$$\frac{1}{v_{i12}} = \frac{1}{v_{i1}} + \frac{1}{v_{i2} R_{i21}} \quad (18-14)$$

The inverse of a transfer velocity can be interpreted as a transfer resistance. Then, Eq. 18-14 states that the total resistance of the two-layer bottleneck is the sum of the individual resistances of the two layers. The multiplication of the phase 2-transfer velocity, v_{i2} , by the factor R_{i21} reflects the fact that phase 1 has been chosen as the reference system, and, thus, in Eq. 18-13, both concentrations are expressed in terms of phase 1-concentrations. The concentration in phase 2, C_{i2} , appears in Eq. 18-13 only indirectly by C_{i1}^{eq} , the phase 1-concentration in equilibrium with C_{i2} . By setting $R_{i12} = 1$, Eq. 18-14 can also be used for a two-layer bottleneck boundary *without* phase change, for instance, for a double thermocline.

Let us now discuss Eq. 18-14 for two extreme situations: (1) If $v_{i1} \ll v_{i2} R_{i21}$, then most of the resistance is located in the boundary layer of phase 1. Then:

$$v_{i12} \approx v_{i1} \quad \text{phase 1-controlled transfer} \quad (18-15a)$$

(2) If, conversely, $v_{i1} \gg v_{i2} R_{i21}$, then most of the resistance is located in the boundary layer of phase 2. Then:

$$v_{i12} \approx v_{i2} R_{i21} \quad \text{phase 2-controlled transfer} \quad (18-15b)$$

In some cases (e.g., if transfer is controlled by phase 2), it is more convenient to express the flux in terms of the phase 2-concentration disequilibrium:

$$F_{i12} = v_{i12}^* (C_{i2}^{\text{eq}} - C_{i2}) \quad \text{with} \quad C_{i2}^{\text{eq}} = R_{i21} C_{i1} \quad \text{and} \quad v_{i12}^* = \frac{v_{i12}}{R_{i21}} \quad (18-16)$$

where C_{i2}^{eq} is the phase 2-concentration at equilibrium with the phase 1-concentration, C_{i1} , and v_{i12}^* is the transfer velocity when the concentration difference is expressed by phase 2 concentrations. If the transfer resistance is dominated by phase 2 (see Eq. 18-15b), $v_{i12}^* \sim v_{i2}$.

18.3 Wall Boundaries

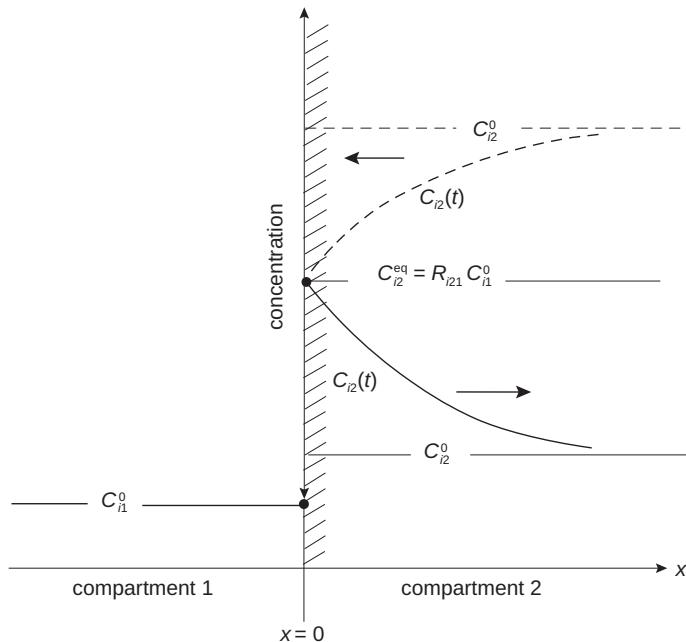
Wall boundaries are defined by an abrupt change of diffusivity, $D(x)$ (Fig. 18.1b). Often, wall boundaries coincide with a phase change, such as an interface boundary. Typically, at a wall boundary, a well-mixed turbulent compartment meets a compartment in which transport is by molecular diffusion. Prominent examples in the environment are the sediment–water interface in lakes and oceans or the surface of a particle suspended in water.

One-Sided Wall Boundary

A one-sided wall boundary refers to a situation where at time $t = 0$, two compartments come into contact, and chemicals start to move across the boundary. Diffusivity in one of the compartments (e.g., compartment 1, as in Fig. 18.4) is fast enough to keep the concentration in that compartment well-mixed while transport in the other compartment to and from the boundary is by finite diffusion. We also assume that the well-mixed compartment is large enough to keep the concentration constant over time, in spite of the flux across the boundary.

The structure of the turbulence at the transition from a fully turbulent fluid to a non-fluid medium has been extensively studied both theoretically and experimentally. As it turns out, the spatial variation of turbulence and diffusivity, known as the *law of the wall*, is gradual (e.g., William and Elder, 1989). Environmental examples of such a transition occur at the turbulent wind field above land or ocean (known as the planetary boundary layer) or the mixing regime above the sediments of lakes and oceans (benthic boundary layer), further discussed in Chapter 19. In the following, diffusivity, $D(x)$, at the boundary is approximated by a sudden (discontinuous)

Figure 18.4 Interface wall boundary with constant concentration in compartment 1 ($x < 0$), C_{i1}^0 , and initial concentration in compartment 2 ($x > 0$), C_{i2}^0 . At the boundary ($x = 0$), the two systems are assumed to be at equilibrium described by the equilibrium distribution ratio $C_{i2}^{\text{eq}} = R_{i21} C_{i1}^0$. In compartment 2, two different initial concentrations are shown: If $C_{i2}^0 < C_{i2}^{\text{eq}}$, the flux is into the wall, if $C_{i2}^0 > C_{i2}^{\text{eq}}$ (dashed lines), the flux is out of the wall. The black arrows indicate the flux direction.



change. More refined models that include the spatial variation of diffusivity near the boundary are not discussed.

Figure 18.4 depicts the concentration profile across an interface wall boundary. Here, the well-mixed compartment 1 (with large diffusivity) is in contact with the slowly mixing compartment 2 (the “wall”). At the interface, the concentrations in the two phases are related by an equilibrium distribution ratio, R_{i21} (Eq. 18-8). The concentration in compartment 1, C_{i1}^0 , is assumed to be constant with time. C_{i2}^0 is the initial concentration in compartment 2. Transport across the boundary starts at time $t = 0$.

The mathematics of diffusion at a flat wall boundary has been derived in Section 17.1 (see Fig. 17.3). We can extend the concentration profile in compartment 2 (Eq. 17-13) to the case of an interface boundary by replacing C_{i1}^0 by $C_{i1}^0 R_{i21}$, the boundary value in compartment 2 in equilibrium with C_{i1}^0 :

$$C_{i2}(x, t) = C_{i2}^0 + (R_{i21} C_{i1}^0 - C_{i2}^0) \operatorname{erfc} \left(\frac{x}{2(D_{i2} t)^{1/2}} \right) \quad \text{for } x \geq 0 \quad (18-17)$$

where D_{i2} is the diffusivity of compound i in compartment 2. Here, the diffusivity in compartment 1 is not relevant; it is assumed to be large enough to keep compartment 1 well-mixed.

As in Eq. 18-16, we replace $R_{i21} C_{i1}^0$ by C_{i2}^{eq} , the compartment 2-concentration at equilibrium with compartment 1-concentration, C_{i1} . By analogy to Eq. 17-12, the

integrated flux per unit area from compartment 1 to compartment 2 at elapsed time t , $\mathcal{M}_{i12}^*(t)$, is:

$$\begin{aligned}\mathcal{M}_{i12}^*(t) &= (C_{i2}^{\text{eq}} - C_{i2}^0) \int_0^\infty \operatorname{erfc} \left(\frac{x}{2(D_{i2}t)^{1/2}} \right) dx \\ &= \frac{2}{\sqrt{\pi}} (C_{i2}^{\text{eq}} - C_{i2}^0) (D_{i2}t)^{1/2} \quad \text{with } C_{i2}^{\text{eq}} = R_{i21} C_{i1}^0\end{aligned}\quad (18-18)$$

The integrated mass flux increases as the square root of the elapsed time, t , and is unlimited since compartment 2 is assumed to be infinitely large. As a consequence, equilibrium between the two compartments cannot be reached within a finite time.

The instantaneous flux, F_{i12} , at the boundary is given by the time derivative of Eq. 18-18:

$$F_{i12}(t) = \frac{d\mathcal{M}_{i12}^*}{dt} = \left(\frac{D_{i2}}{\pi t} \right)^{1/2} (C_{i2}^{\text{eq}} - C_{i2}^0) = v_{i12}^*(t) (C_{i2}^{\text{eq}} - C_{i2}^0) \quad [\text{ML}^{-2}\text{T}^{-1}] \quad (18-19)$$

where v_{i12}^* (and not v_{i12}) appears in Eq. 18-19 since the concentration disequilibrium between the two compartments is expressed in terms of the concentrations in compartment 2 (see Eq. 18-16). In contrast to the bottleneck boundary, the exchange velocity, $v_{i12}^*(t)$, depends on elapsed time, t :

$$v_{i12}^*(t) = \frac{F_{i12}(t)}{(C_{i2}^{\text{eq}} - C_{i2}^0)} = \left(\frac{D_{i2}}{\pi t} \right)^{1/2} \quad (18.20a)$$

Correspondingly, the exchange velocity for the compartment 1-concentrations is:

$$v_{i12}(t) = \frac{F_{i12}}{(C_{i1}^0 - C_{i1}^{\text{eq}})} = R_{i21} v_{i12}^* = R_{i21} \left(\frac{D_{i2}}{\pi t} \right)^{1/2} \quad (18.20b)$$

$F_{i12}(t)$ approaches zero as $t \rightarrow \infty$. If $C_{i2}^0 > C_{i2}^{\text{eq}}$ or $C_{i1}^{\text{eq}} > C_{i1}^0$, the flux is directed in the negative x -direction and describes the loss from compartment 2 to compartment 1.

Two-Sided Wall Boundary

The two-sided wall boundary refers to a situation where at time $t = 0$, two compartments come into contact and mixing is slow in both compartments. Due to the exchange flux, concentration gradients develop on both sides of the boundary. This situation was analyzed in Chapter 17. The concentration profile across the boundary is a symmetric curve crossing the boundary halfway between the initial concentration gap, $\Delta C_i = C_{i1}^0 - C_{i2}^0$ (Eq. 17-15 and Fig. 17.4a).

As shown in Fig. 17.4b, if the diffusivities are not equal in the two compartments, the boundary concentration, C_{ib} , moves away from the symmetric position at $\Delta C_i/2$ toward the initial concentration of that compartment that has the larger

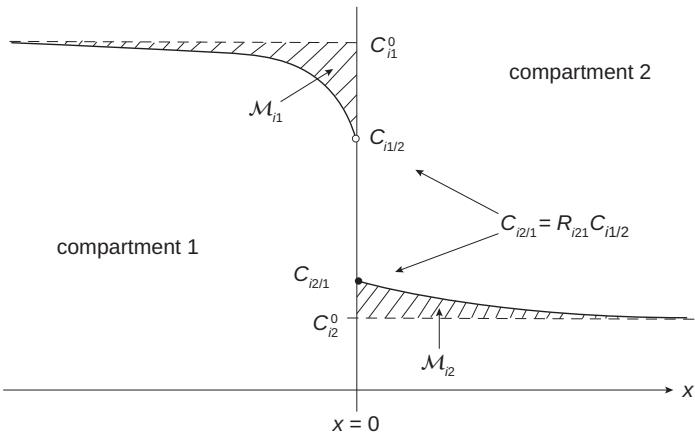


Figure 18.5 Two-sided interface wall boundary with different compartment diffusivities and, thus, different penetration depths. C_{i1}^0 and C_{i2}^0 are initial concentrations. The boundary concentrations on either side of the interface, $C_{i2/1}$ and $C_{i1/2}$, are determined by the equilibrium distribution ratio, $R_{i21} = C_{i2/1}/C_{i1/2}$, and by the condition that the integrated fluxes, M_{i1} and M_{i2} , must be equal at all times.

diffusivity. Eq. 17-17 gives the position of C_{ib} as a function of the diffusivity ratio, $\varphi = (D_{i2}/D_{i1})^{1/2}$. In the case shown in Fig. 17.4b, diffusivity in compartment 1 is larger than in compartment 2, thus, C_{ib} is larger than the symmetry point at $\Delta C/2$. The figure also shows the larger penetration distance of diffusive transport in compartment 1 relative to compartment 2.

In Box 18.1, we discuss the general case of a two-sided interface wall boundary, characterized by the equilibrium distribution ratio, R_{i21} , with different diffusivities on either side of the boundary, D_{i1} and D_{i2} , and initial concentration, C_{i1}^0 and C_{i2}^0 (Fig. 18.5). If expressed in terms of the compartment 1-concentrations, the exchange velocity at the boundary from compartment 1 to compartment 2 is (Box 18.1, Eq. 4a):

$$F_{i12} = (C_1^0 - C_1^{eq}) v_{i12}(t) \quad \text{with} \quad C_1^{eq} = \frac{C_2^0}{R_{i21}} \quad (18-21)$$

$$v_{i12}(t) = \left(\frac{1}{\pi t} \right)^{1/2} \frac{R_{i21} \sqrt{D_{i1} D_{i2}}}{\sqrt{D_{i1}} + R_{i21} \sqrt{D_{i2}}} = \left(\frac{1}{\pi t} \right)^{1/2} \left(\frac{1}{\sqrt{D_{i1}}} + \frac{1}{R_{i21} \sqrt{D_{i2}}} \right)^{-1}$$

This expression can be reduced to simpler situations previously discussed. For instance, if $D_{i1} \gg D_{i2}$, we get the one-sided wall boundary exchange velocity (Eq. 18-20b) where compartment 2 represents the wall and compartment 1 the well-mixed compartment.

All these expressions for bottleneck and wall boundaries have been derived without any assumptions on the nature of the concentration variable, diffusivity, and equilibrium distribution ratio. The concentration can be a single-phase value (aqueous, gaseous, or solid) or a composite of them (e.g., total concentration per bulk volume). Depending on the nature of the concentration variable, diffusivities may relate to turbulent diffusion, single-phase molecular diffusion, or a weighted average of diffusivities, in case the concentration is a composite of different phases. Applications of the developed expressions follow in Chapters 19 (air–water exchange) and Chapter 20 (sediment–water exchange).

Box 18.1 Exchange Flux at a Two-Sided Interface Wall Boundary

We consider the case of the two-sided interface wall boundary between compartments 1 and 2, with equilibrium distribution ratio, R_{i21} , diffusivities, D_{i1} and D_{i2} , and initial concentrations, C_{i1}^0 and C_{i2}^0 (Fig. 18.5). The concentration profiles in the compartments are:

$$\begin{aligned} \text{compartment 1: } x \leq 0, \quad C_{i1}(x, t) &= 2C_{i1/2} - C_{i1}^0 + (C_{i1}^0 - C_{i1/2}) \operatorname{erfc} \left(\frac{x}{2(D_1 t)^{1/2}} \right) \\ \text{compartment 2: } x \geq 0, \quad C_{i2}(x, t) &= C_{i2}^0 + (C_{i2/1} - C_{i2}^0) \operatorname{erfc} \left(\frac{x}{2(D_2 t)^{1/2}} \right) \end{aligned} \quad (1)$$

The special values of the complement error function, $\operatorname{erfc}(-\infty) = 2$, $\operatorname{erfc}(0) = 1$, and $\operatorname{erfc}(+\infty) = 0$ (Appendix A2) help to confirm that C_{i1} and C_{i2} adopt the same values at the interface and at $x \rightarrow \pm\infty$, as shown in Fig. 18.5.

The concentrations at the interface, $C_{i1/2}$ and $C_{i2/1}$, are determined by the equilibrium distribution ratio ($C_{i2/1}/C_{i1/2} = R_{i21}$) and by the condition that the fluxes on either side of the boundary (Eq. 18-19) must be equal at any time, t , yielding:

$$C_{i1/2} = \frac{C_1^0 + \varphi C_2^0}{1 + R_{i21}\varphi}; C_{i2/1} = R_{i21}C_{i1/2} \quad \text{where} \quad \varphi = \left(\frac{D_{i2}}{D_{i1}} \right)^{1/2} \quad (2)$$

The exchange flux is:

$$\begin{aligned} F_{i12}(t) &= \left(\frac{D_{i1}}{\pi t} \right)^{1/2} \left(C_1^0 - \frac{C_2^0}{R_{i21}} \right) \frac{R_{i21}\varphi}{1 + R_{i21}\varphi} \\ &= \left(\frac{1}{\pi t} \right)^{1/2} (C_1^0 - C_1^{\text{eq}}) \frac{R_{i21}\varphi}{\sqrt{D_{i1}} + R_{i21}\sqrt{D_{i2}}} \quad \text{where} \quad C_1^{\text{eq}} = \frac{C_2^0}{R_{i21}} \end{aligned} \quad (3)$$

As for the one-sided wall boundary (Eqs. 18-20), the exchange velocity can either be expressed in terms of the compartment 1-concentrations:

$$F_{i12} = (C_1^0 - C_1^{\text{eq}}) v_{i12}(t) \quad \text{with} \quad v_{i12}(t) = \left(\frac{1}{\pi t} \right)^{1/2} \left(\frac{1}{\sqrt{D_{i1}}} + \frac{1}{R_{i21}\sqrt{D_{i2}}} \right)^{-1} \quad (4a)$$

or the compartment 2-concentrations:

$$F_{i12} = (C_2^{\text{eq}} - C_2^0) v_{i12}^*(t) \quad \text{with} \quad v_{i12}^*(t) = \frac{v_{i12}(t)}{R_{i21}} = \left(\frac{1}{\pi t} \right)^{1/2} \left(\frac{R_{i21}}{\sqrt{D_{i1}}} + \frac{1}{\sqrt{D_{i2}}} \right)^{-1}; C_2^{\text{eq}} = R_{i21}C_1^0 \quad (4b)$$

For $D_{i1} \gg D_{i2}$ and $R_{i21} = 1$, Eq. (4b) converges to the one-sided exchange velocity (Eq. 18-20).

18.4 Hybrid Boundaries

From Wall to Bottleneck Boundary

While a distinction between two “pure” types of boundaries, bottleneck and wall, is extremely helpful for mathematical modeling of boundary fluxes, we should not forget that transitions between the two types can occur. Whenever a new boundary is formed and diffusive exchange begins (e.g., at the water surface of the ocean when strong winds move water parcels from the deeper parts of the water column to the surface and back again), it takes some time until a steady-state concentration profile at the boundary is established. In fact, every newly formed boundary first acts as a wall boundary. If the boundary is characterized by a low diffusivity layer of finite thickness (boundary layer), after some time, the concentration profile across the layer assumes a steady state, and a bottleneck boundary is formed. In contrast, if the low diffusivity zone is infinite in thickness, the boundary keeps its wall-like characteristics.

For a bottleneck boundary of thickness δ and diffusivity D_b , the time-to-steady-state, t_{ss} , can be estimated from the Einstein-Smoluchowski law (Eq. 6-36) to be of the order of:

$$t_{ss} = \frac{\delta^2}{2D_b} \quad (18-22)$$

As an example, we calculate t_{ss} for the thermocline of a small lake with $\delta = 4$ m and $D_b = 0.04 \text{ cm}^2 \text{ s}^{-1} = 0.35 \text{ m}^2 \text{ d}^{-1}$ (see Problem 18.1). Thus, $t_{ss} \sim 23$ d.

Wall Boundary with Boundary Layer

In Chapter 20, the sediment surface in lakes and oceans are described as a one-sided interface wall boundary. A phase change occurs between a pure liquid phase (water) to a conglomerate of water and solids. Since chemicals can sorb to solids, the total concentration of the chemicals per unit bulk volume can undergo a sudden change at the interface that is described by an equilibrium distribution ratio R_{i21} . When the flux equation for an interface wall boundary was derived in Section 18.4, it was tacitly assumed that the “diffusion wall,” that is, the location where diffusivity drops abruptly, coincides with the interface between the two phases. Closer inspection shows that this assumption is not always valid. The transition from a turbulent to a stagnant media actually includes a boundary layer in the former in which diffusivity changes in a characteristic manner (law of the wall). In a still simplified manner, we can describe the zone of reduced diffusivity by a boundary layer that lies between the fully turbulent, homogeneously mixed compartment 1 and the interface to the “wall” compartment 2 (Fig. 18.6). Then, the boundary consists of a combination of a bottleneck boundary (the boundary layer) and a wall boundary whereby the change of diffusivity, $D(x)$, and the sudden increase of the equilibrium distribution ratio, R_{i21} (Eq. 18-8), do not coincide. Here, we develop the necessary mathematical tools to describe such a combined bottleneck/wall boundary. The application of the model follows in Chapter 20.

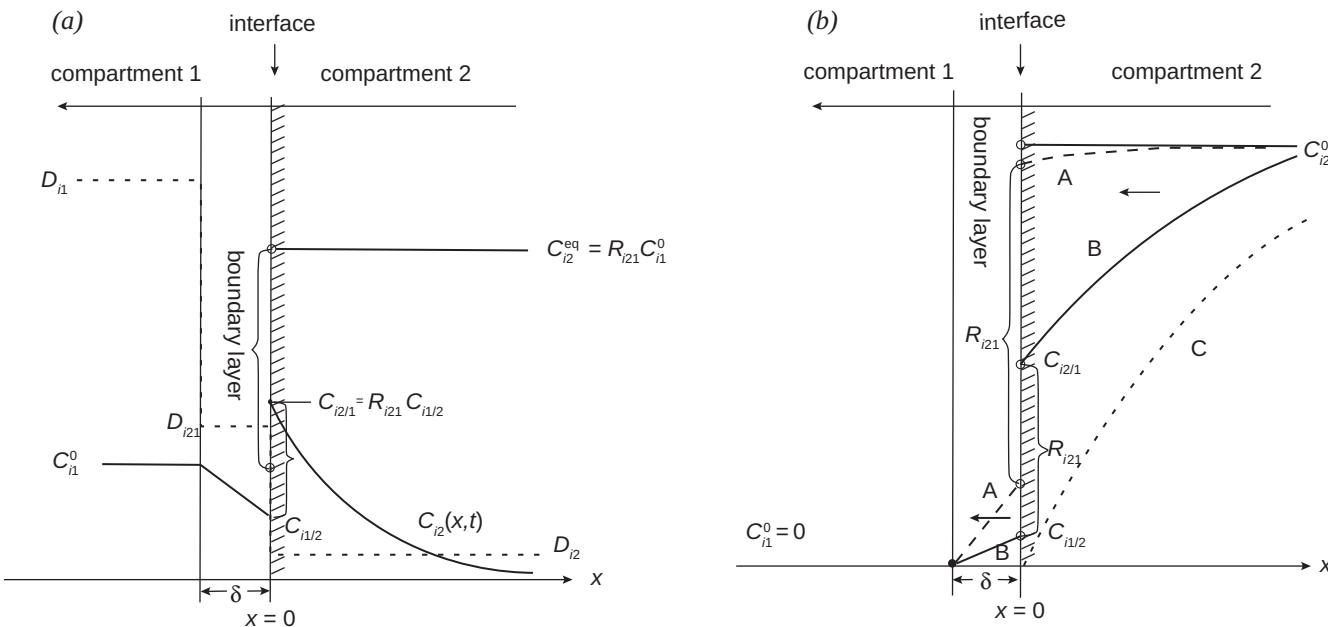


Figure 18.6 (a) Concentration profile across a wall boundary between different phases with a boundary layer of thickness, δ , on the left side of the interface (compartment 1). Diffusivities are D_{i1} in the completely mixed compartment 1, D_{ibl} in the boundary layer, and D_{i2} in the diffusive compartment 2 (dotted line). The concentration in compartment 1, C_{i1}^0 , is assumed to be constant with space and time, and the initial concentration in compartment 2 is zero: $C_{i2}^0 = 0$. C_{i2}^{eq} is the concentration that is attained in compartment 2 once complete equilibrium with the constant concentration in compartment 1 has been reached. The concentrations at the interface, $C_{i1/2}$ and $C_{i2/1}$, are time-dependent and related by Eq. 18-8. (b) As (a), but with different initial conditions. The concentration in compartment 1 is zero, $C_{i1}^0 = 0$, that is, diffusion is directed from compartment 2 to compartment 1. Three concentration profiles are shown (t_{crit} is defined in Eq. 18-32). A: $t \ll t_{crit}$, boundary layer significantly reduces the flux out of compartment 2; B: t about t_{crit} ; and C: $t \gg t_{crit}$ (boundary layer has no influence on flux). The case discussed in Box 20.2 (diffusion of PCBs out of sediments) corresponds to (b).

The concentration in the homogeneous compartment 1, C_{i1}^0 , is assumed to be constant with time. The initial concentration in compartment 2 is C_{i2}^0 . Although in reality diffusivity gradually drops from the interior part of compartment 1 to the interface, we approximate the transition zone by a boundary layer of thickness, δ , with constant diffusivity, D_{ibl} . At time $t = 0$, the two systems come into contact, and mass exchange across the boundary is initiated.

As in the case of the two-layer bottleneck boundary (Fig. 18.5), we assume that the concentrations at either side of the interface, $C_{i1/2}$ and $C_{i2/1}$, are at equilibrium and are related by the equilibrium distribution ratio, $R_{i21} = C_{i2/1}/C_{i1/2}$ (Eq. 18-8). We assume that the diffusing chemical i is conservative (nonreactive) on a time scale characterizing the migration of the molecules across the boundary. Then, the flux on either side of the boundary must be equal. Moving left from the interface in Fig. 18.6a, transport across the boundary layer of compartment 1 is (Eq. 18-4):

$$F_{ibl} = -\frac{D_{ibl}}{\delta} (C_{i1/2} - C_{i1}^0) = -v_{ibl} (C_{i1/2} - C_{i1}^0) \quad (18-23)$$

where $v_{ibl} = D_{ibl}/\delta$ is the boundary layer transfer velocity and the sign of F_{ibl} has been chosen as usual (positive flux points into the positive x -direction). In turn, the

flux into compartment 2 is (Eq. 18-19):

$$F_{i2} = \left(\frac{1}{\pi}\right)^{1/2} \left(\frac{D_{i2}}{t}\right)^{1/2} (C_{i2/1} - C_{i2}^0) = \left(\frac{1}{\pi}\right)^{1/2} \left(\frac{D_{i2}}{t}\right)^{1/2} (R_{i21}C_{i1/2} - C_{i2}^0) \quad (18-24)$$

Since at any time the two fluxes must be equal ($F_{ibl} = F_{i2}$), we can solve Eqs. 18-23 and 18-24 for $C_{i1/2}$:

$$C_{i1/2}(t) = \frac{\tau^{1/2}C_{i1}^0 + C_{i1}^{\text{eq}}}{1 + \tau^{1/2}} \quad \text{with} \quad C_{i1}^{\text{eq}} = \frac{C_{i2}^0}{R_{i21}} \quad (18-25)$$

According the notation introduced earlier, C_{i1}^{eq} is the concentration in compartment 1 in equilibrium with the initial concentration in compartment 2, C_{i2}^0 . We have introduced the normalized (non-dimensional) time, τ :

$$\tau = \left(\frac{\pi}{D_{i2}}\right) \left(\frac{v_{ibl}}{R_{i21}}\right)^2 t \quad (18-26)$$

Now, we insert Eq. 18-25 into one of the flux equations, for instance, into Eq. 18-23:

$$F_{ibl}(t) = v_{ibl} \frac{C_{i1}^0 - C_{i1}^{\text{eq}}}{1 + \tau^{1/2}} \quad (18-27)$$

The flux across the boundary approaches the following asymptotic values:

$$F_{ibl}(t) \cong \begin{cases} v_{ibl} (C_{i1}^0 - C_{i1}^{\text{eq}}) & \text{for } \tau \text{ or } t \rightarrow 0 \\ v_{ibl} \tau^{-1/2} (C_{i1}^0 - C_{i1}^{\text{eq}}) = (C_{i2}^{\text{eq}} - C_{i2}^0) \left(\frac{D_{i2}}{\pi t}\right)^{1/2} & \text{for } \tau \text{ or } t \rightarrow \infty \end{cases} \quad (18-28)$$

In this equation, we recognize expressions that by now have become familiar to us. During the initial phase of the exchange process (τ or t small), the flux at the interface looks like a bottleneck boundary in compartment 1 with transfer velocity v_{ibl} (Eq. 18-4). As time goes by, the interface looks more and more like a wall boundary. Eventually, the concentration gradient across the boundary layer becomes zero ($C_{i1/2} \sim C_{i1}^0$, see Eq. 18-25), and the flux takes the form of Eq. 18-19.

We are now interested in how the boundary layer affects the integrated flux across the boundary, $M_i^*(t)$, relative to the situation without a boundary layer. For no boundary layer, we use Eq. 18-18:

$$M_{i0}^* = 2 \left(\frac{D_{i2}t}{\pi}\right)^{1/2} (C_{i2}^{\text{eq}} - C_{i2}^0) \quad \text{without boundary layer} \quad (18-29)$$

Analogously, we calculate the integrated flux for the situation with a boundary layer by integrating the flux, $F_{ibl}(t)$, given by Eq. 18-27 from time 0 to time t :

$$\mathcal{M}_{ibl}^* = \int_0^t F_{ibl}(t') dt' = \mathcal{M}_{i0}^* \left[1 - \frac{\ln(1 + \boldsymbol{t}^{1/2})}{\boldsymbol{t}^{1/2}} \right] \quad \text{with boundary layer} \quad (18-30)$$

We define the integrated flux ratio, ψ , as the integrated flux *with* a boundary layer, \mathcal{M}_{ibl}^* , divided by the flux *without* a boundary layer, \mathcal{M}_{i0}^* . It is convenient to express ψ as a function of the normalized time, \boldsymbol{t} :

$$\psi(\boldsymbol{t}) \equiv \frac{\mathcal{M}_{ibl}^*}{\mathcal{M}_{i0}^*} = 1 - \frac{\ln(1 + \boldsymbol{t}^{1/2})}{\boldsymbol{t}^{1/2}} \quad \text{with} \quad \boldsymbol{t} = \left(\frac{\pi}{D_{i2}} \right) \left(\frac{v_{ibl}}{R_{i21}} \right)^2 t \quad (18-31)$$

The integrated flux ratio grows from zero at $\boldsymbol{t} = 0$ to 1 for $\boldsymbol{t} \rightarrow \infty$ (Fig. 18.7). It reaches 1/2 at $\boldsymbol{t} = 6.3$. We can choose this \boldsymbol{t} -value to define a critical time, t_{crit} , below which the integrated mass flux is significantly reduced by the boundary layer. From Eq. 18-26, we get:

$$t_{crit} = \frac{6.3}{\pi} D_{i2} \left(\frac{R_{i21}}{v_{ibl}} \right)^2 \approx 2D_{i2} \left(\frac{R_{i21}}{v_{ibl}} \right)^2 \quad (18-32)$$

For $t > t_{crit}$, the influence of the boundary layer on the flux is less than 50%. In turn, for $t \ll t_{crit}$, the boundary layer may reduce the flux by several orders of magnitude.

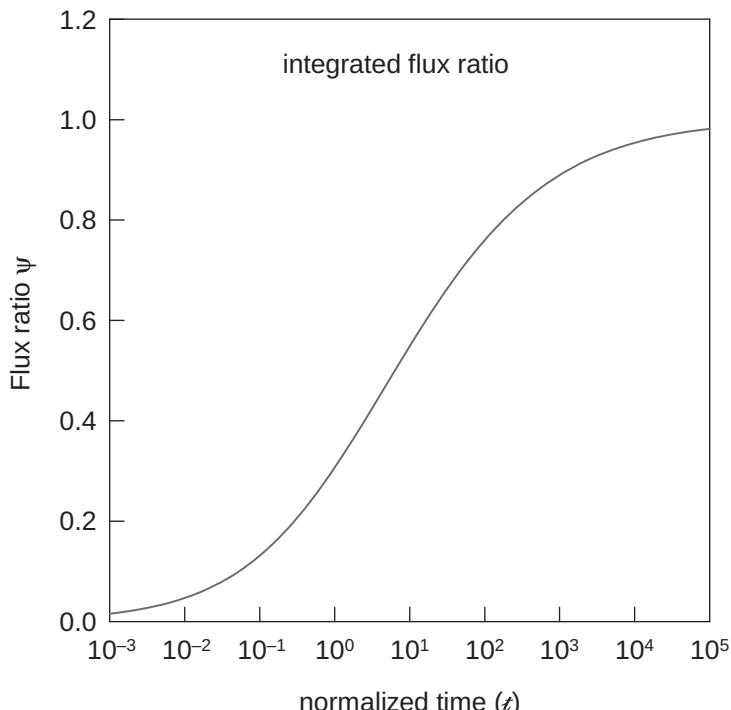


Figure 18.7 The influence of a boundary layer on the integrated flux at a wall boundary expressed by the integrated flux ratio, ψ (Eq. 18-31), the ratio of the flux with and without boundary layer. ψ depends on elapsed time, plotted here as the normalized time, \boldsymbol{t} (Eq. 18-26), and ψ reaches 0.5 at $\boldsymbol{t} = 6.3$ ($\log \boldsymbol{t} = 0.8$).

Equation 18-32 helps us to identify those situations for which the reduction of the integrated flux by a boundary layer may be relevant. Such situations are characterized by a combination of the boundary layer's properties on one hand and the diffusive compartment on the other. Large critical times result from (1) small boundary layer exchange velocities, v_{ibl} , that in turn result from large layer thicknesses, δ , see Eq. 18-23, and from (2) large diffusivities in compartment 2, D_{i2} , combined with an equilibrium distribution ratio, R_{i21} , that favors compartment 2. The latter case enhances the potential flux in compartment 2 so that the boundary layer may more easily become the factor that controls the overall flux.

In Box 18.2, ranges of critical times, t_{crit} , are calculated for two types of wall boundaries for which diffusive boundary layers may be important. Case A is a gas–liquid interface, described here between air and water, but any other gases and liquids would show a similar picture. The gas is the mixed compartment 1 that is connected to a liquid by a gaseous boundary layer. Here, R_{i21} is an inverse nondimensional Henry's law coefficient (Eq. 9-15). The range of estimated critical times, t_{crit} , indicates that the influence of the boundary layer is only relevant for nonvolatile substances. A more detailed discussion can be found in Chapter 19.

Case B depicts the boundary between an open water column (compartment 1) and a porous medium (compartment 2). Here, R_{i21} measures the strength of sorption of a chemical in the porous media. Further examples are given in Chapter 20 (Eq. 20-9 and Box 20.2). Critical time, t_{crit} , has to be compared to the time, t_{ss} , needed to establish a steady-state concentration profile across the boundary layer (Eq. 18-22): $t_{ss} \sim \delta^2/(2D_{ibl}) = D_{ibl}/(2v_{ibl}^2)$. For strongly sorbing chemicals ($f_{iw}^{sc} \ll 1$), t_{ss} is much smaller than t_{crit} and thus not relevant for the integrated flux ratio. For non-sorbing chemicals, t_{ss} and t_{crit} are of a similar magnitude, but then the influence of the boundary layer is not important anyway.

Box 18.2 Effect of Boundary Layer on Integrated Mass Exchange at Wall Boundary: Estimate of Critical Time t_{crit}

Critical time, t_{crit} (Eq. 18-32), is estimated for two types of wall boundaries.

A. Boundary between a well-mixed gas (compartment 1) and a stagnant liquid (compartment 2)

Typical values: Transfer velocity across gaseous boundary layer, $v_{ibl} = 0.1$ to 1 cm s^{-1} (Eq. 19-17).

R_{i21} is nondimensional liquid-gas partition coefficient. For water, it is the inverse nondimensional Henry's law coefficient, K_{iaw} (Eq. 9-15), $R_{i21} = R_{iwa} \approx 10^{-1}$ to 10^5 .

D_{i2} is molecular diffusivity in liquids with typical size $10^{-5}\text{ cm}^2\text{ s}^{-1}$ (Fig. 17.6).

Thus:

$$t_{crit}(\text{s}) \approx 2 \times 10^{-5} \text{ cm}^2\text{ s}^{-1} \left(\frac{R_i \text{ liquid air}}{v_{ibl} (\text{cm s}^{-1})} \right)^2 \quad (1)$$

Solving for critical time, t_{crit} (s), for typical values of $R_{i\text{wa}}$ and $v_{i\text{bl}}$:

$R_{i\text{wa}} = (K_{i\text{aw}})^{-1}$	$v_{i\text{bl}} = 0.1 \text{ cm s}^{-1}$	$v_{i\text{bl}} = 1 \text{ cm s}^{-1}$
10^{-1} (volatile)	$2 \times 10^{-5} \text{ s}$	$2 \times 10^{-7} \text{ s}$
10^2	20 s	0.2 s
10^5 (nonvolatile)	$2 \times 10^7 \text{ s} (\sim 7 \text{ months})$	$2 \times 10^5 \text{ s} (\sim 2 \text{ d})$

B. Boundary between well-mixed water (compartment 1) and porous media (compartment 2)

Typical values: If D_{i1} is the typical molecular diffusion coefficient in water, then $D_{i\text{w}} \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Fig. 17.6).

If $v_{i\text{bl}}$ is calculated with $\delta = 1 \text{ cm}$, the typical boundary layer thickness at the solid–water interface, then $v_{i\text{bl}} = D_{i\text{w}}/\delta \approx 10^{-5}$ to $10^{-3} \text{ cm s}^{-1}$.

The equilibrium distribution ratio of total concentration at the sediment column (sc)–overlying open water (op) interface, $R_{i21} = R_{i\text{sc op}}$, is approximated by $\phi_{iw}^{\text{sc}}/f_{iw}^{\text{sc}}$ (see Chapter 20, Eq. 20-3). f_{iw}^{sc} is the aqueous fraction of chemical i in the sediment, and ϕ^{sc} is porosity. Depending on the strength of sorption, values are between 1 (no sorption) and 10^5 (strong sorption).

D_{i2} is effective diffusivity in pore water of chemical i (see Chapter 17). It depends on pore size, tortuosity, and the strength of sorption as expressed by f_{iw}^{sc} , the fraction of the chemical in the sediments that is dissolved in water. Its order of magnitude can be estimated by $f_{iw}^{\text{sc}}D_{i\text{bulk}}$ (see Box 17.1, Eq. 5), where $D_{i\text{bulk}} \approx 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

$$t_{\text{crit}} = 2f_{iw}^{\text{sc}}D_{i\text{bulk}} \left(\frac{\phi^{\text{sc}}}{f_{iw}^{\text{sc}}v_{i\text{bl}}} \right)^2 \approx 2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \left(\frac{\phi^{\text{sc}}}{v_{i\text{bl}}} \right)^2 \frac{1}{f_{iw}^{\text{sc}}} \quad (2)$$

Solving for the critical time, t_{crit} (order of magnitude), at $\phi^{\text{sc}} = 0.8$ and typical values of f_{iw}^{sc} and $v_{i\text{bl}}$:

f_{iw}^{sc}	$v_{i\text{bl}} = 10^{-3} \text{ cm s}^{-1}$	$v_{i\text{bl}} = 10^{-5} \text{ cm s}^{-1}$
1 (nonsorbing)	1 s	10^4 s (3 h)
10^{-3}	10^3 s (20 min)	10^7 s (100 d)
10^{-6} (strongly sorbing)	10^6 s (10 d)	$10^{10} \text{ s (300 yr)}$

18.5 Questions and Problems

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

Questions

Q 18.1

Explain the difference between a boundary and an interface. Give examples of both.

Q 18.2

The flux across a bottleneck boundary can be expressed either in terms of Fick's first law or by a transfer velocity. Explain how the two models are related.

Q 18.3

Assume that the concentration on either side of a boundary, C_A and C_B , remain constant with time. If you calculate the flux across the boundary, either as bottleneck boundary flux or as wall boundary flux, how do these fluxes evolve as a function of time in each model? Give a qualitative answer.

Q 18.4

Why must there be a zone at an interface boundary where transport occurs by only molecular diffusion?

Q 18.5

Explain the conditions by which the concentrations on either side of an interface wall boundary, where the two phases meet, are determined.

Q 18.6

What is the concentration at a two-sided interface wall boundary with equal diffusivity in both compartments? What happens to the boundary concentration if in compartment 2 diffusivity significantly drops relative to diffusivity in compartment 1? Give a qualitative answer.

Q 18.7

How does a boundary layer influence the flux at a one-sided wall boundary? Which properties of the involved systems favor the influence of a boundary layer on the flux? What happens with the effect of the boundary layer after a very long time?

Q 18.8

Give characteristic physical and chemical properties that distinguish a boundary from the interior of an environmental compartment.

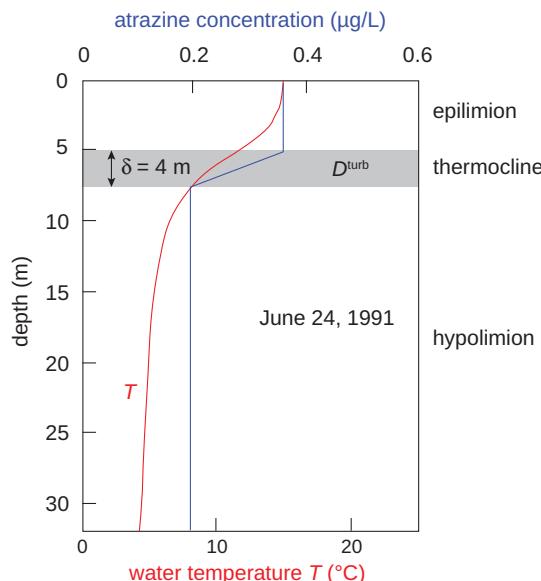
Problems

P 18.1 Downward Transport of Atrazine across the Thermocline of a Lake

Imboden and Emerson (1978) found that the coefficient of vertical turbulent diffusion in early summer, D^{turb} , in the thermocline of Greifensee, Switzerland is between 0.01 and $0.04 \text{ cm}^2 \text{ s}^{-1}$. Use the upper limit of this range and apply the bottleneck boundary model to calculate the vertical flux of atrazine across the thermocline of Greifensee from the atrazine profile shown below.

Lake characteristics

Volume of hypolimnion (V_H)	$1 \times 10^8 \text{ m}^3$
Lake area at thermocline (A_{th})	$7.5 \times 10^6 \text{ m}^2$

**P 18.2 The Thermocline of a Lake as a Two-Layer Bottleneck Boundary**

In Problem 18.1, you calculated the vertical exchange of water across the thermocline in a lake by assuming that transport between the epilimnion and hypolimnion is controlled by a bottleneck layer with thickness $\delta = 4 \text{ m}$. From experimental data, the vertical diffusivity was estimated to lie between 0.01 and $0.04 \text{ cm}^2 \text{ s}^{-1}$. Closer inspection of the temperature profiles suggest that it would be more adequate to subdivide the bottleneck boundary in two or more sublayers, each with its own diffusivity.

You are interested in the question whether such a refinement of the model would have a significant influence on the total exchange velocity, v_{tot} . Therefore, you calculate v_{tot} in two different ways. First, you assume there is *one* bottleneck boundary with an average diffusivity of $0.025 \text{ cm}^2 \text{ s}^{-1}$. Second, you divide the bottleneck into two layers, each 2 m thick. In the upper layer, diffusivity shall be $0.01 \text{ cm}^2 \text{ s}^{-1}$, in the lower, $0.4 \text{ cm}^2 \text{ s}^{-1}$. Compare the results.

P 18.3* Three-Layer Bottleneck Model

(a) Derive a general expression for the total exchange velocity, v_{tot} , across an interface composed of three bottleneck boundaries. As an example, consider the air–water exchange for the case that the water surface is covered by a thin organic surface layer. Define the water phase as compartment 1 and use it as the reference system. Then, the organic layer is compartment 2, and the air is compartment 3. The transfer velocities in these systems are v_{i1} , v_{i2} , and v_{i3} . The chemical equilibrium ratio between the three phases is defined by K_{i21} and K_{i31} . With these ratios, K_{i23} is indirectly defined as well.

(b) Apply the model developed in (a) to assess the influence of an organic surface layer (osl) (thickness $\delta_{\text{osl}} = 0.1 \text{ cm}$) on the overall air–water exchange of a chemical. Use the following information (the origin of some of the values will become clearer in Chapter 19 that deals in greater detail with air–water exchange models): $v_{iw} = 1 \times 10^{-3} \text{ cm s}^{-1}$, $v_{ia} = 1 \text{ cm s}^{-1}$. The molecular diffusion coefficient in the organic

layer is $D_{iosl} = 0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The subscripts stand for w = water, a = air, osl = organic surface layer. Consider first compounds with a nondimensional Henry coefficient $K_{iaw} < 10^{-3}$ and determine the range of K_{ioslw} for which the organic surface layer has an influence on the overall transfer velocity v_{tot} . Second, make the same analysis for compounds with $K_{iaw} > 10^{-3}$.

P 18.4* Bottleneck Boundary Around a Spherical Structure

We consider a spherical compartment with radius r (e.g., particle suspended in water, air bubble in water, or water droplet in air) surrounded by a fluid (e.g., water or air). We define the fluid as compartment 1 (f) and the sphere as compartment 2 (s). The sphere is surrounded by a fluid-side concentric boundary layer of thickness δ . It can be shown that the exchange flux per unit area and time of a chemical i , F_i , (defined positive if directed from the sphere to the surrounding fluid) can be described by (e.g., Schwarzenbach et al., 2003):

$$F_i = -v_{isph} \left(C_{if} - \frac{C_{is}}{R_{isf}} \right) = \frac{D_{ibl}}{\delta_{eff}} \left(C_{if} - \frac{C_{is}}{R_{isf}} \right) \quad \text{with} \quad \frac{1}{\delta_{eff}} = \left(\frac{1}{r} + \frac{1}{\delta} \right) \quad (18-33)$$

where v_{sph} is the exchange velocity across the spherical boundary layer, D_{bl} is diffusivity of chemical i in the boundary layer, R_{isf} is the equilibrium distribution ratio of chemical i between the sphere and the fluid, r is the sphere radius, and δ and δ_{eff} are the real and the effective boundary layer thickness.

- (a) How is this equation related to the flat bottleneck flux and under what condition does the spherical shape of the boundary become irrelevant?
- (b) Use Eq. 18-33 to derive an equation for the temporal change of the concentration of chemical i in the sphere, C_{is} , and solve the equation by assuming that the sphere radius r does not change while taking up chemical i , that is, that the chemical i represents only a minor component of the sphere.

18.6 Bibliography

- Bryden, H. L.; Candela, J.; Kinder, T. H., Exchange through the Strait of Gibraltar. *Prog. Oceanogr.* **1994**, 33(3), 201–248.
- Imboden, D. M.; Emerson, S., Natural radon and phosphorus as limnologic tracers: Horizontal and vertical eddy diffusion in Greifensee. *Limnol. Oceanogr.* **1978**, 23(1), 77–90.
- Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., Transport through boundaries. In *Environmental Organic Chemistry*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, **2002**; pp 833–885.