5. Boundary Exchange: Air-Water and Sediment-Water Interfaces

In the previous chapter we introduced transformation and described both homogeneous and heterogeneous reactions. Now, we would like to look in more detail at heterogeneous reactions and discuss the chemical and physical processes at interfaces that lead to boundary fluxes of chemical species. The two major boundary types in environmental fluid mechanics are the air-water and sediment-water interfaces. Because the processes at both boundaries are very similar, we treat them together in this chapter under the heading of boundary exchange.

This chapter is divided into three main sections. First, the boundary layer in the vicinity of the interface is described, and two common models for treating the boundary dynamics are introduced without specifying what type of boundary is involved. Second, the air-water interface is introduced, and methods are described for treating gas exchange across the interface. As an example, the Streeter-Phelps equation for predicting oxygen concentrations downstream of an organic waste stream is introduced. Third, the sediment-water interface is described, including the complex physical and transformation processes that bring sediment and water into contact, and a short description of the chemistry that occurs at the sediment-water interface is provided.

5.1 Boundary exchange

Under the concept of boundary exchange, we are primarily interested in the transfer of substances that can be dissolved in the water phase. Examples at the air-water interface include chemicals present in both phases (the air and the water), such as oxygen and carbon dioxide, as well as volatile chemicals that off-gas from the water into the atmosphere, where the concentration is negligible, such as mercuric compounds (e.g. $(CH_3)_2Hg$), chlorinated hydrocarbons (e.g. CH_2Cl), and a host of other organic compounds. Examples at the sediment-water interface include metals, salts, nutrients, and organic compounds.

The transfer of these substances at an interface leads to a net mass flux, $\boldsymbol{J}$, which can have diffusive and advective components. Diffusive transfer is often assumed to be controlled by equilibrium chemistry. Advective transfer results from a host of processes, such as the ejection of sea spray from waves or the flow of groundwater. In general, this net mass flux becomes a boundary condition that is imposed on the governing transport equation that is then solved either numerically or analytically.
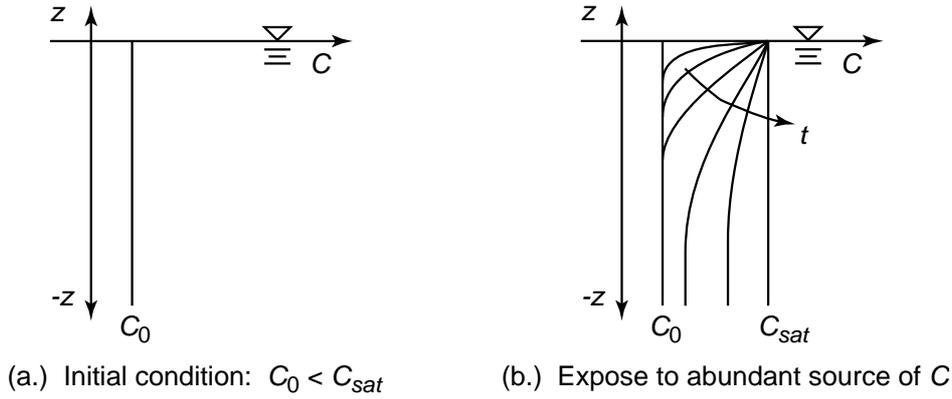
Fig. 5.1. Schematic for the boundary exchange for a dissolving substance into a stagnant water body. Figure (a.) shows the initial condition, and Figure (b.) shows the time-response of the concentration profiles. C_{sat} is the saturation concentration of the dissolving substance.

The challenge in describing boundary exchange is in predicting the magnitude of $\boldsymbol{J}$. Unfortunately, the dynamics that control the magnitude of the exchange flux are often microscopic in nature and must be predicted by sub-models. If we consider the example of sugar dissolving in a cup of tea, we know from experience that the sugar dissolves much faster if we stir the tea than if we let the system remain stagnant. But, if we add sand to a cup of tea and stir for a few years, the sand will still not completely dissolve. Hence, we expect $\boldsymbol{J}$ to depend on the physico-chemical properties of the species in the exchange process, as well as on the hydrodynamic conditions in each phase.

5.1.1 Exchange into a stagnant water body

As a simple introduction, consider a completely stagnant case, where the hydrodynamic effects on transfer are negligible. Figure 5.1 describes such a situation. The initial condition is that a semi-infinite body of water has a uniform initial concentration $C(z,t) = C_0$ that is less than the saturation concentration of the substance, C_{sat}. The surface interface is then instantaneously exposed to an infinite source of the substance. Because the concentration in the water body is below C_{sat}, the substance will want to dissolve into the water until the water body reaches a uniform concentration of C_{sat}. The dissolution reaction is a very fast reaction; hence, the concentration at the surface becomes C_{sat} as soon as the source is applied. However, the movement of C into the water body is limited by diffusion away from the surface. This process is illustrated schematically in Figure 5.1(b.).

To treat this stagnant case quantitatively, consider the governing transport equation and its solution. Because $\partial C/\partial x = \partial C/\partial y = 0$, we can use the one-dimensional equation, and because the fluid is stagnant, we can neglect advection, leaving us with

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}. \tag{5.1}$$

The boundary and initial conditions are:

$$C(-\infty, t) = C_0 \tag{5.2}$$

$$C(0, t) = C_{sat} \tag{5.3}$$

$$C(z, 0) = C_0. \tag{5.4}$$

The solution for this case was found in Section 2.2.2 for the case of $C_0 = 0$. The modified solution for this case is

$$\frac{C(z, t) - C_0}{C_{sat} - C_0} = 1 - \mathrm{erf}\left(\frac{-z}{\sqrt{4Dt}}\right) \tag{5.5}$$

where the minus sign inside the error function is needed since z is negative downward. Recall also that (5.5) is only valid for $z \leq 0$.

From this solution we can derive an expression for the boundary flux at $z = 0$ using Fick's law. Writing the flux law for the stagnant case in one-dimension, we have

$$\begin{aligned} J_z &= uC - D \left.\frac{\partial C}{\partial z}\right|_{z=0} \\ &= -D \left.\frac{\partial C}{\partial z}\right|_{z=0} \end{aligned} \tag{5.6}$$

since $u = 0$. Substituting the solution above, we can compute J_z as

$$J_z(t) = -(C_{sat} - C_0)\sqrt{\frac{D}{\pi t}}. \tag{5.7}$$

We can also compute the characteristic thickness, δ, of the mixing layer, or the concentration boundary layer, over which the concentrations change from C_{sat} to C_0:

$$\delta = \sigma_z = \sqrt{2Dt}. \tag{5.8}$$

Hence, for the stagnant case, the mixing layer grows deeper in time and the boundary flux can be written as

$$J_z = -k_l(C_{sat} - C_0) \tag{5.9}$$

where k_l is the transfer velocity, given in this stagnant case by $k_l = \sqrt{D/(\pi t)}$, with units $[L/T]$.

5.1.2 Exchange into a turbulent water body

When the water body present below (or above) the interface is turbulent, large-scale motion within the fluid body will interact with the mixing layer, defined by the concentration boundary layer δ.

This turbulent motion has two major effects. First, the turbulence in the bulk fluid erodes the boundary layer, thereby, limiting the growth of the layer thickness δ. Since the bulk fluid and interface concentrations C_0 and C_i are independent of δ, this effect will increase the concentration gradient; hence, J_z will be larger than in the stagnant case. Second, the turbulence in the bulk fluid will cause motion within the boundary layer, thereby, increasing the effective diffusivity. Hence, J_z will again be larger than the stagnant case. However, molecular diffusion is still expected to be a rate-limiting process
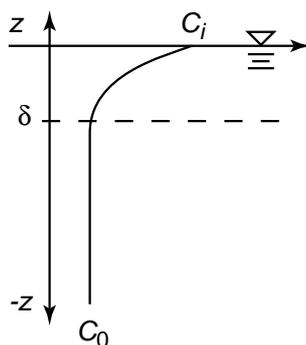
Fig. 5.2. Schematic of the interface exchange for a turbulent water body.

since turbulence (three-dimensional motion) cannot exist directly at the surface. For the case of a large groundwater flux, this last statement may have to be relaxed, but for now we will assume the actual interface is laminar.

These effects of turbulence can be summarized in the following list of expectations regarding the concentration boundary layer for a turbulent flow:

1. We expect an average film thickness, δ. That is, turbulence will prevent δ from growing arbitrarily large.
2. We expect an average boundary layer flux (transfer velocity). This is a consequence of the previous expectation.
3. The transfer rate can be limited on either side of the interface by the chemical or hydrodynamic conditions in that phase.

The following two sections introduce models which seek expressions for k_l that satisfy the three expectations listed above.

5.1.3 Lewis-Whitman model

The simplest type of model is the Lewis-Whitman model, which says that the mixing layer is a constant thickness, δ, which leads to k_l given by

$$k_l = \frac{D}{\delta} \tag{5.10}$$

(refer to Figure 5.2). Note that for this model k_l is linearly proportional to D, as compared to the square-root dependence derived in the stagnant case. Also, the mixing depth δ is a pure function of the hydrodynamic condition. Thus, once one has an expression for δ, the transfer velocity for different substances can be computed using the various respective molecular diffusivities D_m. The weakness of this model is that is does not provide any physical insight into how to predict δ; hence, δ must be determined empirically.

5.1.4 Film-renewal model

The film-renewal model improves on the Lewis-Whitman model by providing a physical mechanism that controls the boundary layer thickness; hence, we can use this mechanism

to formulate a predictive model for δ. In the film renewal model, the boundary layer is allowed to grow as in the stagnant case until at some point the turbulence suddenly replaces the water in the boundary layer, and the mixing layer growth starts over from the beginning. This mixing layer exchange, or film-renewal, occurs periodically with a renewal frequency that is a function of the turbulent characteristics of the flow.

Under the idealized case that the boundary layer grows undisturbed until is it suddenly completely replaced by water from the bulk turbulent flow, the net flux at the boundary can be determined analytically. The governing transport equation and the initial and boundary conditions are exactly the same as in the stagnant case (see (5.1) to (5.4)). The solution is given by (5.5), and the net flux at the boundary is given by (5.7). These solutions are only valid, however, from $t = 0$ to $t = t_r$, the time between renewal events. The mean boundary flux over one cycle can be found easily by taking the time average

$$
\begin{aligned}
\overline{J}_z &= \frac{1}{t_r} \int_t^{t+t_r} J_z(t)dt \\
&= \frac{1}{t_r} \int_t^{t+t_r} -(C_i - C_0)\sqrt{\frac{D}{\pi t}}dt \\
&= -(C_i - C_0)\sqrt{\frac{4D}{\pi t_r}}
\end{aligned}
\tag{5.11}
$$

or, since the renewal frequency, r, is just $1/t_r$,

$$
\overline{J}_z = -(C_i - C_0)\sqrt{\frac{4Dr}{\pi}}.
\tag{5.12}
$$

Thus, the average transfer velocity is independent of time and is given by

$$
k_l = \sqrt{\frac{4Dr}{\pi}}
\tag{5.13}
$$

which leaves us with the need to predict r.

The renewal frequency r is a characteristic of the turbulence. Recall that a turbulent flow is a spectrum of eddy sizes, from the integral scale down to the Kolmogorov scale, and is driven, for homogeneous turbulence, by the dissipation rate

$$
\epsilon = \frac{u_I^3}{l_I}
\tag{5.14}
$$

where u_I and l_I are the integral velocity and length scales of the flow, respectively. For a shear flow, the approximations $u_I = u_*$ and $l_I = h$ are generally valid, where u_* is the shear velocity and h is the depth of the shear layer. We can derive two extreme estimates for r: one for the case that the concentration boundary layer is renewed by Kolmogorov-scale eddies (called the small-eddy estimate), and another for the case that the concentration boundary layer is renewed by integral-scale eddies (called the large-eddy estimate).

Small-eddy estimate of r. Since the smallest eddies are dissipated by viscosity ν, an estimate for the Kolmogorov time scale t_K can be written as

$$
t_K = \sqrt{\frac{\nu}{\epsilon}}.
\tag{5.15}
$$

Taking r as $1/t_K$ and substituting approximations for u_I and l_I for a shear flow, we can obtain

$$r = \sqrt{\frac{u_*^3}{h\nu}}. \tag{5.16}$$

If we further substitute the shear velocity as $u_* = \overline{u}\sqrt{f/8}$, where $\overline{u}$ is the mean flow velocity and f is a friction coefficient, then an estimate for k_l can be written as

$$k_l = K\frac{\overline{u}^{3/4}}{h^{1/4}} \tag{5.17}$$

where K is a constant that depends on the fluid properties (i.e. ν) , the physico-chemical properties of the substance (i.e. D), and on the boundary type (i.e. f). For k_l at the air-water interface with units cm/s, K is of order 10^{-1} to 10^0.

Large-eddy estimate of r. The time scale of the largest eddies is given by the integral time scale t_I, which for a shear flow is

$$t_I = \frac{u_*}{h}. \tag{5.18}$$

Taking $r = 1/t_I$, and substituting $u_* = \overline{u}\sqrt{f/8}$ leads the the expression for k_l given by

$$k_l = K\overline{u}^{1/2}h^{1/4} \tag{5.19}$$

where K is another constant which depends on the the physico-chemical properties of the substance (i.e. D), and on the boundary type (i.e. f).

Experimental data are sparse, but tend to agree better with the relationship $k_l \propto \overline{u}^{3/4}$; hence, it is most likely the small-scale eddies that are responsible for the film renewal.

5.2 Air/water interface

At the air-water interface we are primarily concerned with the transfer of gases that can be dissolved in the water. The substance may, or may not, be measurable in the gas phase. Figure 5.3 demonstrates the general case for a substance with measurable concentrations in both the gas and liquid phase. As the figure demonstrates, there is a concentration boundary layer in the vicinity of the water surface for both the phases. Because there cannot be a build-up of concentration at the interface, the flux from the gas into the water, $\dot{m}_a$, must equal the flux at the interface into the water, $\dot{m}_w$. Hence, only one of the phases contains the rate-limiting step.

The rate of transfer at the interface is controlled by the transfer velocity k_l; thus, the rate-limiting phase will have the lowest value of k_l. Consider first the Lewis-Whitman model. The transfer velocity increases as the diffusion coefficient increases and as the concentration boundary layer gets thinner. Both of these conditions are higher in the gas phase than in the liquid phase. The more complex film-renewal model gives the same conclusion: the flux at the interface can be higher in the air than in the water. Therefore,
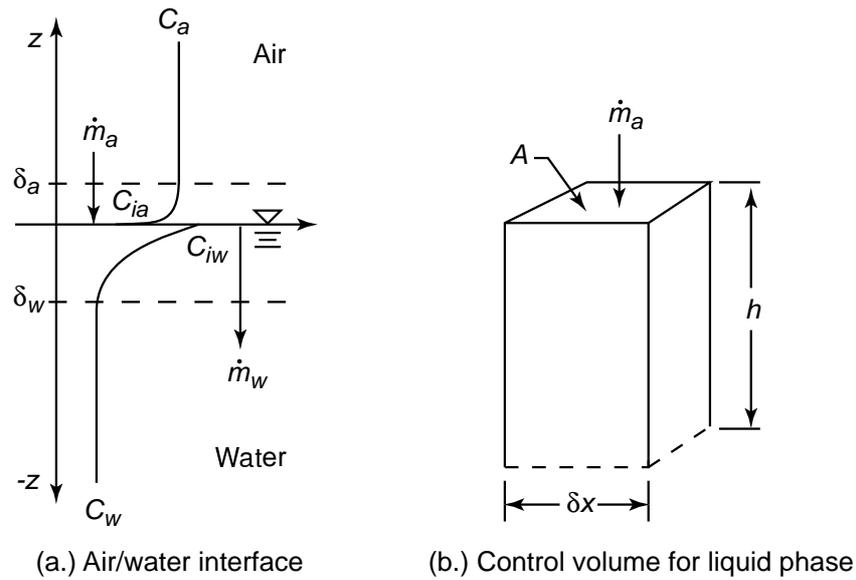
Fig. 5.3. Schematic of the air-water interface for a substance with measurable concentrations in both the air and the water.

we generally assume the substance is immediately available at the gas side of the interface, and we must only consider the concentration boundary layer in the water phase in order to compute the net flux at the boundary.

Because the air-water interface is a moving boundary, two further complications can arise that are not addressed in either of our boundary transfer models. First, wind generates shear directly at the interface. We considered shear at the channel bed as the generation mechanism for turbulence in the film-renewal model. However, shear at the air-water interface generates motion at the interface that can strongly affect (and greatly increase) the transfer velocity from the case of a stagnant wind. These effects are particularly important in the ocean and in lakes. Second, surface waviness, breaking and instabilities, greatly increases gas transfer by disturbing the exchange boundary layer. For example, breaking waves entrain air and carry air bubbles deep into the fluid, that then dissolve as they rise back to the water surface. Such dynamic situations must be handled by more complicated techniques.

5.2.1 General gas transfer

Assuming the rate-limiting step in on the liquid side of the interface, we can now derive a general expression for gas transfer into a well-mixed medium, such as at the surface layer of a lake in summer. We will consider the control volume in Figure 5.3(b.). The conservation of mass equation is

$$\frac{dM}{dt} = \dot{m}_{in} - \dot{m}_{out} \tag{5.20}$$

$$= \dot{m}_w. \tag{5.21}$$

Example Box 5.1:
Volatilization.

As an example, consider the off-gassing of the volatile compound benzyl chloride (CH_2Cl) from a stream with velocity $\overline{u} = 1$ m/s and initial concentration of CH_2Cl of $C_0 = 0.1$ mg/l. The gas transfer coefficient is $K_l = 1 \cdot 10^{-4}$ s^{-1}. Because CH_2Cl is not present in the atmosphere, C_{iw} can be taken as zero. Then (5.23) becomes

$$\frac{C_w}{dt} = -K_l C_w$$

which, after substituting $t = x/\overline{u}$, has solution

$$C_w(x) = C_0 \exp\left(-K_l \frac{x}{\overline{u}}\right).$$

Thus, CH_2Cl concentration decreases exponentially downstream from the source due to volatilization.

To write M as a concentration, we must define the size of the control volume. A common assumption is to use the depth of the well-mixed water body, h, and a non-specified surface area, A. Then, substituting from (5.9)

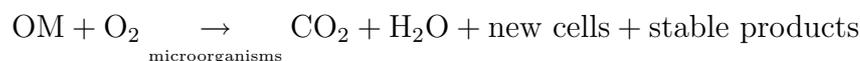$$Ah\frac{C_w}{dt} = Ak_l(C_{iw} - C_w) \tag{5.22}$$

which is rearranged to give

$$\frac{C_w}{dt} = K_l(C_{iw} - C_w) \tag{5.23}$$

where $K_l = k_l/h$ is the gas transfer coefficient with units $[\text{T}^{-1}]$.

5.2.2 Aeration: The Streeter-Phelps equation

A common problem that requires modeling the exchange of oxygen through the air-water interface is that of predicting the oxygen dynamics in a river downstream of a biodegradable waste stream. As the waste is advected downstream, it degrades, thereby consuming oxygen. The oxygen deficit, however, drives the counteracting aeration process, so that the situation is similar to that shown in Figure 5.4.

Biodegradation is a reaction that consumes oxygen. A general biodegradation equation can be written as

$$\text{OM} + \text{O}_2 \quad \underset{\text{microorganisms}}{\longrightarrow} \quad \text{CO}_2 + \text{H}_2\text{O} + \text{new cells} + \text{stable products}$$

where OM stands for organic matter (the biodegradable waste). It can be shown in the laboratory that the consumption of OM is a first-order reaction. Thus, the rate-law for the consumption of OM is given by

$$\frac{d[\text{OM}]}{dt} = -k_d[\text{OM}] \tag{5.24}$$

where k_d is the rate constant for biodegradation. In the classical literature on this subject, the concentration of OM is called the oxygen demand and is given the symbol L. Substituting L for [OM] in the above equation and imposing the initial condition $L(t = 0) = L_0$, the solution for the consumption of oxygen demand becomes

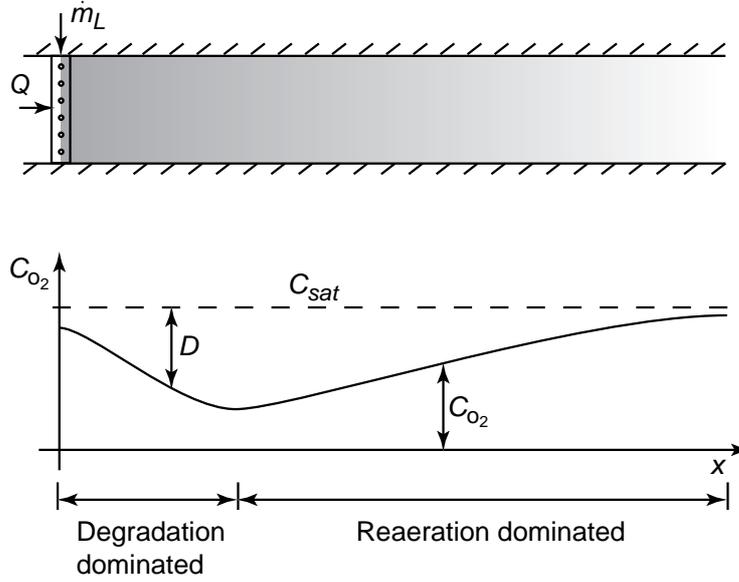$$L(t) = L_0 \exp(-k_d t) \tag{5.25}$$

Fig. 5.4. Schematic of the dissolved oxygen sag curve downstream of a biodegradable waste stream. The upper figure illustrates the receiving stream; the lower diagram shows the downstream dissolved oxygen concentration.

where L_0 is called the ultimate carbonaceous oxygen demand. The word carbonaceous refers to the fact that the oxygen consumption is due to conversion of carbon-based organic matter as opposed to any other chemical reaction that might consume oxygen. Because O_2 is consumed at the same rate as OM, we can write the following relationship:

$$\frac{d[O_2]}{dt} = \frac{d[OM]}{dt}$$
$$= -k_d L_0 \exp(-k_d t). \tag{5.26}$$

If we define the oxygen deficit, $D = ([O_2]_{sat} - [O_2])$, then the production of oxygen deficit is given by

$$\frac{dD}{dt} = k_d L_0 \exp(-k_d t). \tag{5.27}$$

This equation represents a sink term for oxygen due to biodegradation of the waste stream.

At the same time the waste is being degraded the river is being aerated by exchange at the air-water interface. The mass flux of oxygen, $\dot{m}_{O_2}$, is derived from the boundary exchange flux in (5.9)

$$\dot{m}_{O_2} = -A k_r ([O_2]_{sat} - [O_2])$$
$$= -A k_r D \tag{5.28}$$

where k_r is the river aeration transfer velocity for oxygen and the negative sign indicates a flux of oxygen goes into the river.

We can now use the control volume in Figure 5.3(b.) to derive the oxygen balance downstream of the waste source. If we make the one-dimensional assumption and move

our control volume with the mean flow velocity in the river, then the mass balance for our control volume is

$$\frac{dM_{O_2}}{dt} = \dot{m}_{O_2} - S \tag{5.29}$$

where S is a sink term representing the biodegradation process. Taking the width of the river as W and the depth as h, we can write the equation for the concentration of O_2 as

$$W\delta x h \frac{d[O_2]}{dt} = \dot{m}_{O_2} - S$$
$$= W\delta x k_r([O_2]_{sat} - [O_2]) - W\delta x h R_{O_2} \tag{5.30}$$

where R_{O_2} is the reaction rate law for the consumption of O_2. Rewriting this equation for the oxygen deficit D, we have

$$\frac{dD}{dt} = R_D - K_r D \tag{5.31}$$

where R_D is the rate law for the production of D and $K_r = k_r/h$ is the oxygen transfer coefficient. Substituting (5.27) R_D, we obtain the inhomogeneous ordinary differential equation

$$\frac{dD}{dt} = k_d L_0 \exp(-k_d t) - K_r D \tag{5.32}$$

subject to the initial condition $D(t = 0) = D_0$, which is the initial oxygen deficit just upstream of the point where the waste stream is introduced. The solution to this equation is the classic Streeter-Phelps equation:

$$D(t) = \frac{k_d L_0}{K_r - k_d}(\exp(-k_d t) - \exp(-K_r t)) + D_0 \exp(-K_r t). \tag{5.33}$$

The derivation of this solution is given in Appendix C.

5.3 Sediment/water interface

Unlike the air-water interface, where the interface is generally confined to an abrupt transition at the water surface, the sediment-water interface is very difficult to define and is controlled by a number of complicated physical and chemical processes. The real difficulty of the sediment-water interface lies in the multi-phase (dispersive) nature of the interface. At an individual sediment grain, the interface may be clearly defined. However, since we cannot treat every sediment grain individually, a continuum description of the system is necessary. Two important quantities are used to describe dispersed systems. The porosity, n, is the volume of water contained in a unit volume of mixture

$$n = \frac{V_w}{V}. \tag{5.34}$$

This parameter can vary widely, but is generally between 0.1 and 0.9 within a porous media (groundwater system) and is 0.99 and higher within the water column (suspended sediment system). For suspended sediments, the second parameter is also important: the

Example Box 5.2:
Dissolved-oxygen sag curve.

As an example of the application of the Streeter-Phelps equation, consider the following waste stream. A wastewater treatment plant discharges an oxygen demanding waste stream at a rate of $\dot{m} = 295$ g/s of BOD (biochemical oxygen demand) into a stream $h = 3$ m deep, $W = 30$ m wide, and with a flow rate $Q = 27$ m^3/s. The waste stream is introduced through a longitudinal diffuser so that the we can assume complete lateral and vertical mixing at the source. The initial concentration of BOD in the river L_0 is then

$$L_0 = \frac{\dot{m}}{Q}$$
$$= \frac{295}{27}$$
$$= 10.9 \text{ mg/l}.$$

Based on regular experiments conducted by the facility operator, the decay rate of the waste is known to be $k_d = 0.2$ day^{-1}.

A rule of thumb often used for computing the aeration rate is

$$K_r = \frac{3.9\overline{u}^{1/2}}{h^{3/2}}$$

where K_r is in day^{-1}, $\overline{u}$ is the mean stream velocity in m/s, and h is the depth in m. For this stream $K_r = 0.4$ day^{-1}. The initial oxygen deficit was measured to be $D_0 = 1.5$ mg/l (the saturation oxygen concentration is 9.1 mg/l). The plot below shows the solution (5.33) for the oxygen concentration ($[O_2]_{sat} - D$) downstream of the mixing zone. The critical time to reach the minimum oxygen concentration is

$$t_c = \frac{1}{K_r - k_d} \ln \left[\frac{K_r}{k_d} \left(1 - \frac{D_0(K_r - k_d)}{k_d L_0} \right) \right]$$

which for this case is 2.67 days, or 69 km. This example illustrates how slow the aeration process can be in the absence of aeration devices, such as cascades and water falls.

Dissolved oxygen concentration downstream of pollutant discharge
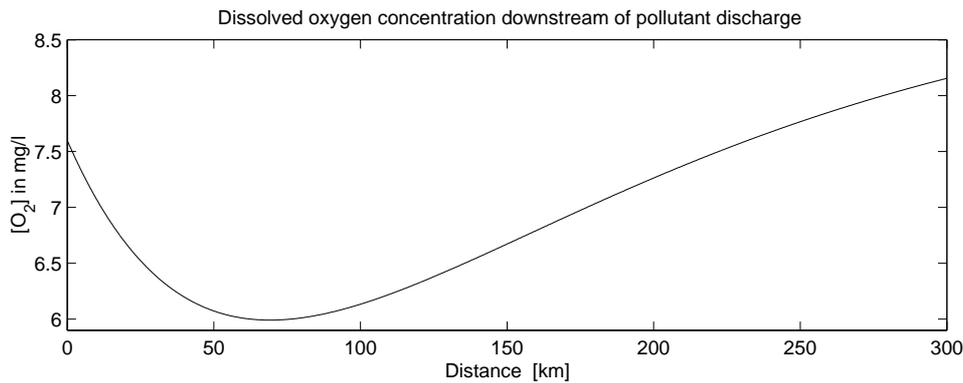
slip velocity, or settling velocity, u_s. The settling velocity is generally taken as the terminal fall velocity of the sediment in a quiescent system. The porous media/water column interface can then be defined as the point where n becomes small enough that u_s goes to zero due to contact with other sediment particles, forming a (relatively) fixed matrix.

As shown in Figure 5.5 many processes lead to the transport of chemical species in the water column and through the sediment bed. These processes are organized in the figure into two categories. On the left are physical processes that do not involve chemical transformation; on the right are chemical and biological processes.

The physical processes are responsible for transport. Within the water column, chemicals can move with either the solid or liquid phase. Of the transport processes listed in the figure, we have already discussed advection and diffusion (both turbulent and molecular) in detail. The other transport processes in the water column (which are specific to the sediment phase) are:
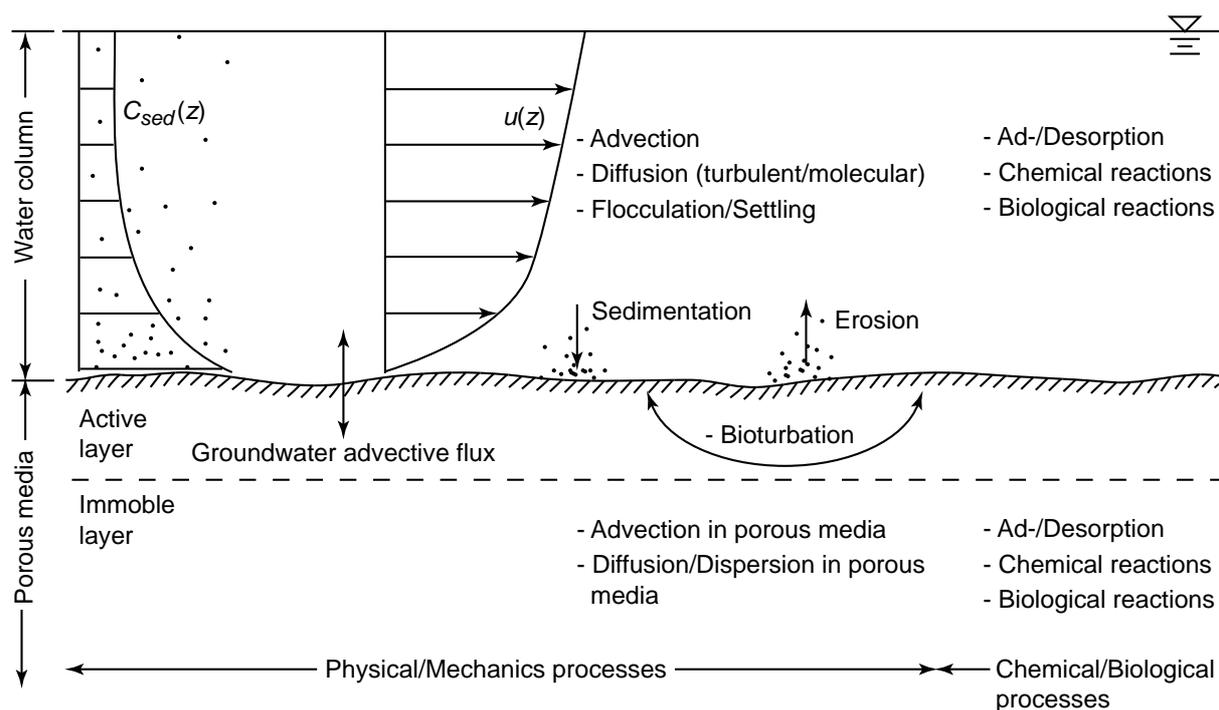
Fig. 5.5. Schematic of processes occurring at the sediment-water interface, in the water column and in the sediment bed (porous media).

- **Flocculation and settling**: flocculation is the sticking together of several sediment particles to form larger particles. Settling is the downward fall of sediment particles due to their negative buoyancy. Accept for very small particles (colloids), sediment particles always have a negative vertical velocity component relative to the water column motion.
- **Sedimentation**: sedimentation is the process whereby sediment is lost from the water column and gained by the sediment bed. This occurs once the settling sediment particles reach the channel, lake or ocean bottom and rejoin the sediment bed.
- **Erosion**: erosion is the process by which sediment is lost from the sediment bed and entrained into the water column.

Within the sediment bed, or porous media, further transport processes are at work. For species in the liquid phase, the processes of advection, diffusion, and dispersion are active throughout the porous media. For the sediment particles, physical transport occurs only in the upper active layer due to the process of bioturbation:

- **Bioturbation**: bioturbation is the name given to the mixing of sediment caused by animals living in the sediment (mostly worms). These animals move sediment as they dig. Two important classes of worms mix the sediment differently. In the one case, sediment is eaten at the base of the active layer and moved up to the surface. In the other case, sediment is removed from the surface and carried down to the bottom of the active layer. The net movement of sediment is often modeled by an enhanced diffusion process, where we use bioturbation diffusion coefficients.

Through the combination of all these transport processes, chemical species move in and out of the water column and the porous media.

Through transformation processes, chemical species move in and out of the solid and liquid phases and, also, change to other species. We have already discussed chemical and biological transformation reactions. These reactions occur both in the water column and in the porous media. They can also occur in either the liquid phase, the solid phase or at the interface. Processes at the sediment interface are particularly important for the transport of chemicals through these multi-phase systems:

- **Adsorption/desorption**: the chemical processes of adsorption and desorption control the distribution of certain chemicals between the solid and liquid phases. Due to complex chemical/physical processes, some molecules have an affinity for sticking to the solid phase (often due to electrical charge interaction). That is, some molecules would rather stick to a sediment particle than remain dissolved in the surrounding fluid. The behavior of most organic compounds and heavy metals is controlled by sorption chemistry.

Because sorption is a dominant process occurring at the sediment-water interface, it is discussed in more detail at the end of this section.

As discussed in Gschwend (1987), the processes at the sediment-water interface (at the bottom of a lake or channel) depend on the energetic state of the water body. Beginning with laminar conditions (as in a deep lake) and progressing to increasingly energetic, turbulent conditions (as in reservoirs, estuaries, and streams), the progression is as follows. With no motion, exchange occurs due to direct sorption exchange and diffusion of dissolved species from the pore water. Next, the system begins to flow, allowing the advective and dispersive flux of groundwater flow. Bioturbation, which may always be present, adds energy by actively mixing the sediments. As the water column begins to flow, sediments can be pushed along the top layer of sediments in a process called bed-load transport. Finally, with an energetic water column, erosion begins, sediment is carried up into the water column, and suspended transport (advection of sediment in the water column) becomes important. Hence, the transport of species associated with sediment is a complex problem dependent on the chemistry of the species and the mobility of the sediment.

5.3.1 Adsorption/desorption in disperse aqueous systems

Ignoring the complex problems that lead to the transport of sediment, we focus in this section on the exchange at the solid/liquid interface of a mixed solution of suspended sediment particles in a dispersed (large n) system. An important process controlling the distribution of many toxins in sediment-laden solutions is adsorption/desorption. Defined above, this process causes a large fraction of the sorbing compound to attach to the sediment particles. Hence, sorption controls the concentration of dissolved contaminant, and causes much of the contaminant to be transported with the sediment.

Figure 5.6 illustrates the situation. Sorbing compounds include most polar and non-polar organic compounds and heavy metal ions. To describe the situation quantitatively,
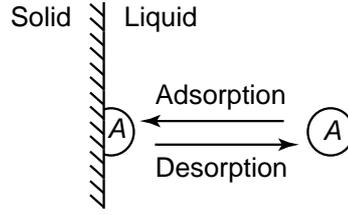
Fig. 5.6. Schematic of the adsorption/desorption process for the molecule A.

we define two concentrations. First, the concentration of substance A that is dissolved in solution is designated C and is defined as

$$C = \frac{M_{\text{dissolved}}}{V_w} \tag{5.35}$$

having normal concentration units. Second, the non-dimensional sorbed-fraction concentration, C_s^*, is defined as

$$C_s^* = \frac{M_{\text{adsorbed}}/V_w}{M_{\text{sediment}}/V_w}$$
$$= \frac{M_{\text{adsorbed}}}{M_{\text{sediment}}}. \tag{5.36}$$

These equations are valid only for highly dispersed systems, where $nV \approx V$.

Because sorption kinetics are very fast, we can usually assume that equilibrium exists between the adsorbed and desorbed fractions. Based on experiments, the following simple type of equilibrium relationship has been proposed:

$$C_s^* = \frac{\Gamma C}{K + C} \tag{5.37}$$

which is called the Langmuir equation. The coefficient K is a constant with units of concentration; the coefficient Γ is a non-dimensional constant, called the Langmuir isotherm, which gives the asymptotic value of C_s^* as C becomes large. Figure 5.7 plots the Langmuir equation for $\Gamma = 1$ and $K = 1$. For most toxins in the environment, $C \ll K$, and we can simplify the Langmuir equation to

$$C_s^* = \mathcal{P}C \tag{5.38}$$

where $\mathcal{P}$ is the partition coefficient with units [L^3/M]. Typical values of $\mathcal{P}$ are between 10^3 to 10^6 l/kg.

In order to avoid the confusion caused by C_s^* being non-dimensional, a dimensional concentration of adsorbed contaminant is convenient to define. From the density of the sediment ρ_s and the porosity, the dimensional adsorbed concentration is

$$C_s = C_s^* \rho_s \left(\frac{1-n}{n}\right)$$
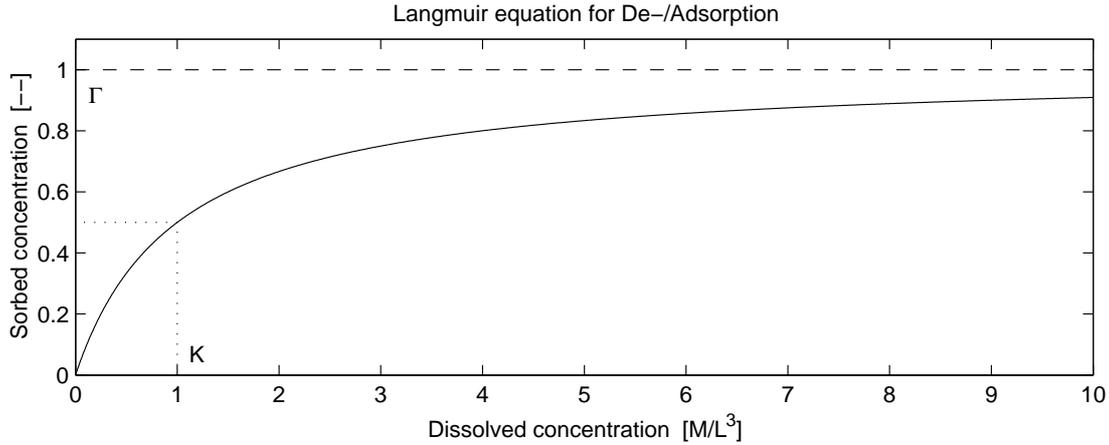$$= K_D C \tag{5.39}$$

Fig. 5.7. Langmuir equation for de-/adsorption with $\Gamma = 1$ and $K = 1$. Note that C_s^* is $1/2$ at $C = K$.

where K_D is a non-dimensional distribution coefficient. It is important to note that $\mathcal{P}$ is a purely physico-chemical parameter; whereas, K_D also depends on the sediment concentration and physical characteristics (through the porosity and density, respectively).

Example Box 5.3:
Naphthalene partitioning.

Consider the partitioning of the organic toxin naphthalene, the smallest of the polynuclear aromatic hydrocarbons (PAHs). We wish to find the fraction of dissolved to adsorbed naphthalene, f_d. Using (5.38), this fraction is given by

$$f_d = \frac{C}{C + C_s}$$
$$= \frac{1}{1 + \rho_s \left(\frac{1-n}{n}\right)\mathcal{P}}.$$

For naphthalene $\mathcal{P} = 10^3$ l/kg. Typical sediment has a density of 2600 kg/m^3. For a mixture with $n = 0.99$, $f_d = 4\%$.

We can see that f_d is always large for low concentrations C by looking at the range of expected K_D. From above

$$K_D = \rho_s \left(\frac{1-n}{n}\right)\mathcal{P}.$$

Making the following order-or-magnitude estimates

$$\rho_s = 10^3$$
$$(1-n)/n = 10^{-3}$$
$$\mathcal{P} = 10^3 \text{ to } 10^6$$

K_D ranges from 10^3 to 10^6; f_d ranges from 10^{-3} to 10^{-6}. Therefore, we can assume that a large fraction of the contaminant is present in the sorbed state.

If we manage to eliminate the source of a toxic contaminant that is also sorbed to the sediments, then the sediment bed itself will start to release its sediment load into the water column water, creating a new source (see Exercise 5.3). Unfortunately, because f_d is so large, the sediment load is large, and it takes a long time before the water column is free from this sediment source of the contaminant.

Summary

This chapter introduced the processes that result in boundary exchange of chemical species. The general issue in describing boundary exchange is in determining the net boundary flux $\boldsymbol{J}$. Once that flux is know, boundary exchange becomes a boundary condition on the governing transport equation. The solution for $\boldsymbol{J}$ in a stagnant water body

was used to develop two descriptions of exchange in turbulent water bodies. The Lewis-Whitman model, the simplest model, assumes the concentration boundary layer between phases has a constant depth. The film-renewal model assumes that turbulence constantly refreshes the fluid in the concentration boundary layer, and that the renewal rate derives from turbulent eddy characteristics. The exchange at the air-water interface was discussed in more detail, with examples for volatile chemicals and oxygen aeration. The sediment-water interface was described qualitatively, and the sorption chemistry at the sediment water interface was described in more detail.

Exercises

5.1 BOD test. To determine the biodegradation rate coefficient of a particular waste, the waste is placed in solution in a closed bottle, where the oxygen concentration in monitored over time. Table 5.1 gives the results of a typical test. Based on all the data in the table, estimate the value of the rate coefficient, k_d.

5.2 PCB contamination. An industrial plant releases PCBs (polychlorinated biphenols) through a diffuser into a river. The river moves swiftly, with a modest sediment load. PCB is volatile (will off-gas into the atmosphere) and can be adsorbed by the sediment in the river. Describe the network of complex interactions that must be investigated to predict the fate of PCBs from this disposal source.

5.3 Sediment source of phosphorus. Phosphorus, in the form of phosphate (PO_4^{3-}), is often a limiting nutrient for algae production in lakes. Because the uncontrolled growth of algae is undesirable, the discharge of phosphorus into the environment should be minimized (this is why you cannot buy laundry detergent any more that contains phosphorus). The U.S. Environmental Protection Agency recommends a limit of 0.05 mg/l PO_4^{3-} for streams that flow into freshwater lakes.

An old chemical plant recently shut off their phosphorus discharge; however, high concentrations of phosphorus are still being measured downstream of the chemical plant. After further investigation, the following facts were collected:

- The concentration of phosphate in the stream water upstream of the plant is $C_0 = 0.003$ mg/l.
- The sediments in the stream are saturated with sorbed phosphorus for a distance of 2 km downstream of the plant.
- The phosphate concentration at the sediment bed is kept constant by desorption at a value of $C_b = 0.1$ mg/l.
- The design conditions in the stream are $h = 2$ m deep and $u = 0.2$ m/s.
- The phosphate transfer velocity at the sediment bed is given approximately by the relationship (film-renewal model):

$$k_l = 0.002 \frac{u^{3/4}}{h^{1/4}} \text{ in m/s.} \tag{5.40}$$

Table 5.1. Measurements of time and oxygen concentration for a BOD test. (Data taken from Nepf (1995))

Time [days]	$[O_2]$ [mg/l]
0	9.00
2	5.21
4	3.81
6	3.30
8	3.11
10	3.04
12	3.01
14	3.01
16	3.00
18	3.00
20	3.00

What is the concentration of phosphate in the stream just after passing the region of contaminated sediments? If the stream carries a suspended sediment load, how would that affect the concentration of phosphate in the stream?