Chapter 20

INTERFACES INVOLVING SOLIDS

Most natural systems are composed of all three types of phase: gas, liquid, and solid. In this respect, the air–water interface discussed in Chapter 19 does not yet exhibit the full range of complexities of transport at boundaries. By including solids in our models, we add a phase that is distinctly different from the fluid phases, gases and liquids. First, transport in solids is slow and may be negligible compared to transport in fluids, and second, sorption in and on solids may significantly retard transport in a combined solid-fluid system.

In Chapters 12 and 17, a common framework was developed for the description of a chemical i occurring in three phases by relating all phase concentrations of i to the total (or bulk) volume (see Box 17.1). These quantities are determined indirectly, since in the field or laboratory the concentrations are measured per volume of a specific phase, e.g., mol per volume of water or air. Furthermore, we have introduced effective diffusivity and bulk diffusivity (Eq. 17-32). The latter serves to describe diffusive transport in terms of spatial bulk distance, rather than in terms of concentration gradients along winding pores, the effect of tortuosity. This framework greatly simplifies our discussion on interfaces between multi-phase compartments. In this chapter, we first deal with two phase systems consisting of water and solids (sediments and water-saturated soil) and then turn to three phase systems such as unsaturated soils.

20.1 The Sediment–Water Interface

The Sediment Surface as an Interface Wall Boundary

We first consider a flat sediment surface in the ocean or a lake (Fig. 20.1). As an initial step, we disregard the effect of a possible boundary layer on the water side of the boundary. At the boundary between the overlying open water (compartment 1, superscript 'op') and the sediment column (compartment 2, superscript 'sc'), diffusivity drops by several orders of magnitude from turbulent (or eddy) diffusion, E_w^{op}, to diffusion in porous medium. According to Section 17.2, such diffusion is similar to molecular diffusivity in water, except for a correction to take into account
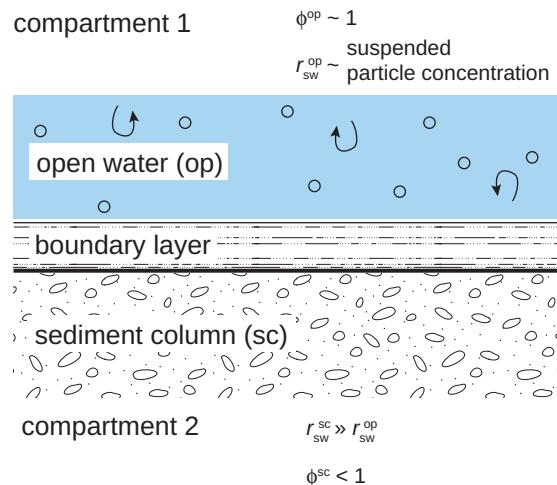
Figure 20.1 The sediment–water interface can be described by a one-sided wall boundary with or without a boundary layer on the water side. It is characterized by a significant drop of diffusivity going from the turbulent open water to the sediment column (sediment bed) and by a large (several orders of magnitudes) increase of the solid-to-water phase ratio, r_{sw}, from water to sediment. In the mathematical framework developed in Chapter 18, the open water is compartment 1, and the sediment column is compartment 2.

compartment 1 $\phi^{op} \sim 1$

$r_{sw}^{op} \sim$ suspended particle concentration

open water (op)

boundary layer

sediment column (sc)

compartment 2 $r_{sw}^{sc} \gg r_{sw}^{op}$

$\phi^{sc} < 1$

the pores (Renkin effect), tortuosity, and sorptive interactions. In Box 17.1 (Eq. 5), we introduced the term effective diffusivity, $D_{i\text{eff}}$, for diffusivity of a sorbing chemical in the porous medium per bulk volume.

Given the sudden drop of diffusivity from turbulent to molecular diffusivity, the sediment surface can be described as a one-sided interface wall boundary (Fig. 18.4). On both sides of the boundary, the chemical i can occur in two phases, as dissolved and as sorbed to solids. Sorption is described by the solid–water distribution coefficients, K_{id}^{op} and K_{id}^{sc}. These coefficients are not necessarily identical. For instance, the relative fraction of organic carbon, an important quantity determining the magnitude of the solid–water distribution coefficient, can differ between suspended material and sediments.

The sediment–water interface is characterized by a sudden change of the solid-to-water phase ratio, r_{sw}, introduced in Chapter 12:

$$r_{\text{sw}} = \rho_s \frac{1 - \phi}{\phi} \tag{12-22}$$

where ρ_s is the density of the solids and ϕ is porosity, the volume fraction occupied by the fluid. In the open water, $r_{\text{sw}}^{\text{op}}$ roughly corresponds to the concentration of suspended solids in the water and is on the order of 10^{-6} kg L^{-1}. Thus, according to Eq. 12-22 the "porosity" of the open water is $\phi^{\text{oc}} \approx 1$. In contrast, by assuming a sediment porosity of $\phi^{\text{oc}} = 0.80$ and a particle density $\rho_s = 2.5$ kg L^{-1}, Eq. 12-22 yields $r_{\text{sw}}^{\text{sc}} = 0.63$ kg L^{-1}. In this case, the concentration of chemical i sorbed on solids in the sediment column is orders of magnitude larger than in the open water, even if the two sorption coefficients are the same.

The sediment surface behaves like the boundary between two matrices, that is, like an interface boundary. The equilibrium concentration ratio of the total concentrations on either side is (Eq. 18-8):

$$R_{i\text{sc/op}} = \frac{C_{it}^{\text{sc}}}{C_{it}^{\text{op}}} \tag{20-1}$$

The ratio of total concentrations, $R_{i\text{sc/op}}$, in a two-phase system (solid/liquid) is (parameters defined in Box 20.1):

$$R_{i\text{sc/op}} = \frac{C_{it}^{\text{sc}}}{C_{it}^{\text{op}}} = \frac{\phi^{\text{sc}} \left(1 + r_{\text{sw}}^{\text{sc}} K_{id}^{\text{sc}}\right)}{\phi^{\text{op}} \left(1 + r_{\text{sw}}^{\text{op}} K_{id}^{\text{op}}\right)} = \frac{\phi^{\text{sc}}/f_{iw}^{\text{sc}}}{\phi^{\text{op}}/f_{iw}^{\text{op}}} \tag{20-2}$$

Since the open water column is virtually pure water ($\phi^{\text{op}} \approx 1$, $r_{\text{sw}}^{\text{op}} \approx 0$) relative to the sediment, Eq. 20-2 can be simplified to:

$$R_{i\text{sc/pure water}} \approx \phi^{\text{sc}}(1 + r_{\text{sw}}^{\text{sc}} K_{id}^{\text{sc}}) = \phi^{\text{sc}}/f_{iw}^{\text{sc}} \quad \text{for} \quad r_{\text{sw}}^{\text{op}} K_{id}^{\text{op}} = 1 \tag{20-3}$$

For chemicals with very large solid–water distribution coefficients, K_{id}^{op}, this approximation may not be valid since f_{iw}^{op} may be smaller than 1. Numerical examples for the size of $R_{i\text{sc/op}}$ are given in Box 20.1. Since $R_{i\text{sc/op}}$ is the ratio of *total* concentrations,

the change of r_{sw} (or of porosity) at the sediment surface causes $R_{isc/op}$ to be different from one even if the chemical does not sorb on particles (see the numerical example in Box 20.1 with $K_{id} = 0$).

Box 20.1   Equilibrium Concentration Ratio at the Sediment–Water Interface

An open water column (op) overlies a sediment column (sc). In both compartments, total concentration per total volume can be evaluated according to the following equations (the superscript α stands for "op" or "sc").

Local sorption equilibrium is assumed everywhere (see Eq. 12-8):

$$K_{id}^{\alpha} = C_{is}^{\alpha}/C_{iw}^{\alpha} \qquad \left[L_w^3\, M_s^{-1} \right] \tag{1}$$

where K_{id} is the solid–water distribution coefficient (e.g., in $L\,kg_{solid}^{-1}$). We use the same subscripts as in Chapter 12 and Box 17.1 to distinguish between the different kinds of concentrations:

C_{iw}^{α}	dissolved concentration per water volume $[ML_w^{-3}]$
C_{is}^{α}	concentration on particles ('particulate') per solid mass $[MM_s^{-1}]$
C_{it}^{α} and C_{id}^{α}	total and dissolved concentration per total volume $[ML_t^{-3}]$
$f_{iw}^{\alpha} = \dfrac{1}{1 + r_{sw}^{\alpha} K_{id}^{\alpha}} = \dfrac{C_{id}^{\alpha}}{C_{it}^{\alpha}}$	fraction of chemical dissolved (Eqs. 12-18)
r_{sw}^{α}	solid-to-water phase ratio (Eq. 12-22), for open water roughly equivalent with concentration of suspended particles
$C_{iw}^{\alpha} = C_{id}^{\alpha}/\phi^{\alpha} = (f_{iw}^{\alpha}/\phi^{\alpha})C_{it}^{\alpha}$	with ϕ = porosity $[L_w^3 L_t^{-3}]$

The total concentration per bulk volume, C_{it}^{α}, can be expressed as a function of C_{iw}^{α}:

$$C_{it}^{\alpha} = C_{iw}^{\alpha} \frac{\phi^{\alpha}}{f_{iw}^{\alpha}} = C_{iw}^{\alpha} \phi^{\alpha} \left[1 + r_{sw}^{\alpha} K_{id}^{\alpha} \right] \tag{2}$$

This equation is valid for every system that consists of a mixture of water and solids. The "continuity condition" of the dissolved concentration per water volume at the boundary between the open water column and the pore water is:

$$C_{iw}^{sc} = C_{iw}^{op} \tag{3}$$

With this condition, the equilibrium concentration ratio at the boundary between the sediment and the water, $R_{isc/op}$, defined in Eq. 20-1 becomes:

$$R_{isc/op} = \frac{C_{it}^{sc}}{C_{it}^{op}} = \frac{\phi^{sc}\left(1 + r_{sw}^{sc}\, K_{id}^{sc}\right)}{\phi^{op}\left(1 + r_{sw}^{op}\, K_{id}^{op}\right)} = \frac{\phi^{sc}/f_{iw}^{sc}}{\phi^{op}/f_{iw}^{op}} \tag{20-2}$$

Numerical Example:

Open water: $r_{sw}^{op} = 10^{-3}$ kg m^{-3} (concentration of suspended solids)

Sediment column: $\rho_s = 2,500$ kg m^{-3}; $\phi^{sc} = 0.80 \Rightarrow r_{sw}^{sc} = 625$ kg m^{-3} (from Eq. 12-12); tortuosity $\tau = 1$

Sorption properties of suspended particles and sediment particles assumed to be equal: $K_{id}^{op} = K_{id}^{sc}$

We consider three chemicals: (1) non-sorbing, (2) weakly sorbing, and (3) strongly sorbing. For simplicity, we assume that the three chemicals have the same bulk diffusivity (Eq. 20-4): $D_{ibulk} = 1 \times 10^{-6}$ cm^2 s^{-1}, but their effective diffusivities are different (see Eq. 20-4).

Calculated Parameters		Chemicals: $K_{id}^{op} = K_{id}^{sc}$ (m^3 kg^{-1})		
		(1) non-sorbing: 0	(2) weakly sorbing: 1	(3) strongly sorbing: 10^3
f_{iw}^{op}		1	1	0.5
f_{iw}^{sc}		1	1.6×10^{-3}	1.6×10^{-6}
$R_{isc/op}$ (Eq. 20-2)		0.80	500	2.5×10^5
$x_{1/2}$ (Eq. 20-8)	$t = 1$ day	0.3 cm	0.01 cm	4×10^{-4} cm
	1 year	6 cm	0.2 cm	7×10^{-3} cm
	10^3 year	200 cm	7 cm	0.2 cm

Now we address the questions of how fast a chemical i penetrates the sediment column from the overlying water and how fast it diffuses back out of it. The sediment–water interface is envisioned as a one-sided wall boundary. The concentration profile in the "wall" (the sediment column) is given by Eq. 18-17, and the integrated flux after time t (t is the exposure time of the sediment surface to a fixed open water concentration, C_{it}^{op}), is given by Eq. 18-18. In this expression, a key parameter is diffusivity in compartment 2 (the sediment column), D_{i2}. Here, the concept of effective diffusivity (see Chapter 17) comes into play. From Box 17.1 (Eq. 5), we arrive at the following substitution law for the diffusivity, D_{i2}:
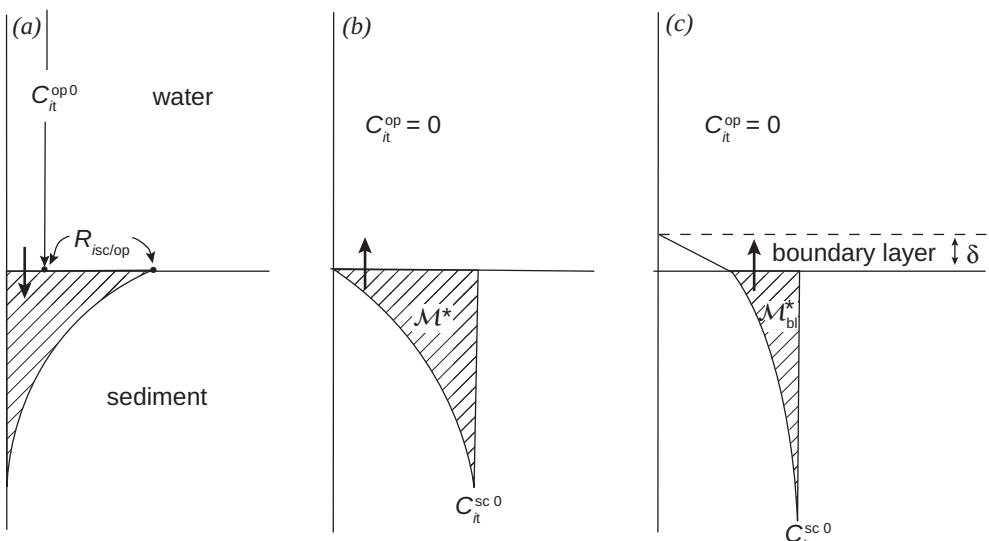
$$D_{i2} \to D_{ieff} = f_{iw}^{sc} D_{ibulk} = \frac{D_{ibulk}}{1 + r_{sw}^{sc} K_{id}} \qquad (20\text{-}4)$$

According to Eq. 17-32, D_{ibulk} is aqueous diffusivity of chemical i in the porous medium corrected for the possible effects of the finite pore space (Renkin effect) and tortuosity, τ:

$$D_{ibulk} = D_{ipm}/\tau^2 \approx D_{iw}/\tau^2 \qquad (20\text{-}5)$$

where it is assumed that the finite pore space is not relevant for molecular diffusivity in a sediment bed ($D_{ipm} \approx D_{iw}$).

Figure 20.2 Three situations showing transport across the sediment–water interface. The plots show total (dissolved and sorbed) concentration of chemical i per bulk volume. (a) The sediments are exposed to total concentration $C_{it}^{\text{op } 0}$ in the water. Initially, the concentration of the chemical in the sediments is zero. The flux is from the water into the sediment column. $R_{i\text{sc/op}}$ is the equilibrium concentration ratio at the interface. (b) A sediment column with initial concentration $C_{it}^{\text{sc } 0}$ comes into contact with chemical i-free water. The integrated flux per unit area, $\mathcal{M}^*$ (marked by the hatched area), is from the sediment to the water. (c) As in b, with an additional boundary layer on top of the sediments. The integrated flux, $\mathcal{M}_{\text{bl}}^*$, is reduced compared to case b.

Now, let us evaluate the total effect of sorption in the sediments on the integrated flux per unit area after exposure time, t, from the water to the sediments, $\mathcal{M}_i^*(t)$. We assume that the initial concentration in the sediment is zero (Fig. 20.2a). From Eq. 18-18 and by replacing the variables by the appropriate expressions for this particular situation, we get:

$$\mathcal{M}_i^*(t) = \frac{2}{\sqrt{\pi}} C_{it}^{\text{sc eq}} (D_{i\text{eff}} t)^{1/2} = 1.13 C_{it}^{\text{sc eq}} (D_{i\text{eff}} t)^{1/2} \quad \text{with } C_{it}^{\text{sc eq}} = R_{i\text{sc/op}} C_{it}^{\text{op } 0}$$

(20-6)

where $C_{it}^{\text{op } 0}$ is the initial concentration in the water column, assumed to be constant. By inserting Eqs. 20-2 and 20-4 into Eq. 20-6 and replacing the total concentration in the water column by the corresponding aqueous concentration (Box 20.1), we arrive at:

$$\mathcal{M}_i^*(t) = 1.13 \, C_{iw}^{\text{op } 0} \frac{\phi^{\text{sc}}}{f_{iw}^{\text{sc}}} \left(f_{iw}^{\text{sc}} D_{i\text{bulk}} t \right)^{1/2} = 1.13 C_{iw}^{\text{op } 0} (D_{i\text{bulk}} t)^{1/2} \phi^{\text{sc}} \left(1 + r_{\text{sw}}^{\text{sc}} K_{id}^{\text{sc}} \right)^{1/2}$$

(20-7)

This expression shows that sorption has two opposing effects on the integrated mass exchange. The first one, given by the factor $(f_{iw}^{\text{sc}})^{-1} = (1 + r_{\text{sw}}^{sc} K_{id}^{\text{sc}})$, enhances the exchange, since sorption allows us to accumulate more of the chemical i in a unit bulk volume of the sediments compared to a non-sorbing species. Second, part of the enhancement is reversed by the fact that sorption slows down diffusion in the sediment column by a factor, $(f_{iw}^{\text{sc}})^{+1/2}$. The combination of the two effects still leads to an enhanced mass flux.

The "half-concentration penetration depth", $x_{1/2}$, is (Eqs. 17-11 and 20-4):

$$z_{1/2}^{\text{sc}} = \left(D_{i\text{eff}} t \right)^{1/2} = \left(f_{iw}^{\text{sc}} D_{i\text{bulk}} t \right)^{1/2} = \left(\frac{D_{i\text{bulk}} t}{1 + r_{\text{sw}}^{\text{sc}} K_{id}^{\text{sc}}} \right)^{1/2}$$

(20-8)

Penetration depth increases with time as $t^{1/2}$. In turn, penetration depth is reduced due to sorption and porosity. A numerical example is given in Box 20.1, in which one sees that $x_{1/2}$ for $t = 1000$ years drops from 200 cm for a nonsorbing compound to only 0.2 cm for a strongly sorbing chemical.

We note that by replacing $C_{it}^{sc\ eq}$ in Eq. 20-6 by the concentration difference ($C_{it}^{sc\ eq}$ − $C_{it}^{sc\ 0}$), we can also describe situations where the initial concentration in the sediment column, $C_{it}^{sc\ 0}$, is different than zero. The mass flux may then become negative, indicating a flux in the opposite direction, that is, from the sediment column to the open overlying water (Fig. 20.2b). The penetration depth (Eq. 20-8) then measures the distance in the sediment column from where the chemical i is "eroded" due to the flux to the open water. As an example, the release of PCBs from the polluted sediments in Boston Harbor is discussed in Box 20.2.

### Sediment–Water Interface with a Water-Side Boundary Layer

In the preceding section, the sediment surface is described as a wall boundary. Thereby, we tacitly assumed that the "diffusion wall," that is, the location where diffusivity drops from turbulent conditions in the open water column to molecular diffusion in the sediments, coincides with the interface between the two media. This simplified view of the boundary is not always warranted. As discussed in Chapter 18, the transition from a turbulent to a stagnant medium includes a boundary layer in the former in which diffusivity drops in a characteristic manner ("law of the wall").

Box 20.2   Release of PCBs from the Historically Polluted Sediments of Boston Harbor

The sediments of Boston Harbor (Massachusetts, USA) have long accumulated organic contaminants like polychlorinated biphenyl (PCBs). As a result, investigators like McGroddy (1993) found surface sediment concentrations of compounds like 2,2′,4,5,5′-pentachlorobiphenyl (PCB 101) or 2,2′3,3′4,4′5-heptachlorobiphenyl (PCB 170) near 30 ng g^{-1} dry sediment. In 2000, a major construction effort moved the sewage discharge out of the harbor. Now the question arises, how long will the existing legacy of polluted sediments continue to release undesirable fluxes of these organic chemcials back into the water column?
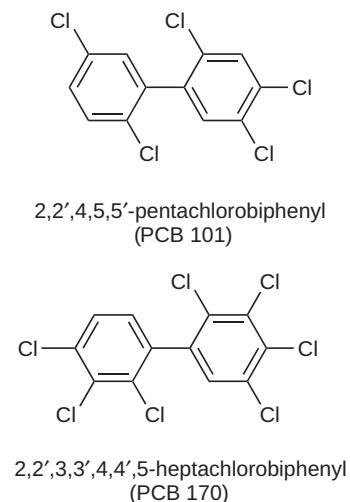
We are interested in deducing what process limits the bed-to-water-column release of such highly sorptive chemicals. Diffusion from the sediments is one possible mechanism to look at, and resuspension of particles and particle–water exchange while the particles are suspended is another. Here, we are interested in the process of pollutant transfer across the sediment–water interface. Particularly, we want to find out how the flux is controlled, by diffusion from within the sediments (as described by the wall boundary model) or by the water-side boundary layer at the sediment surface. In the latter case, the flux would be much smaller than predicted by the wall boundary theory.

In order to answer this question, we estimate the critical time, t_{crit}, defined in Eq. 18-32 and Box 18.2. If the elapsed time since the construction of the offshore sewage pipe is much larger than the critical time, the boundary layer is not relevant anymore for

the size of the flux out of the sediments. If it is much smaller, diffusion is controlled by the boundary layer and not by diffusion within the sediment column.

To evaluate Eq. 18-32 for the sediment–water interface, we can bypass the explicit calculation of the equilibrium distribution ratio between open water and sediment column, $R_{isc/op}$, and directly use the approximation Eq. 20-9. To calculate K_{id}^{sc} from K_{ioc}, we use $f_{oc} = 0.05$ (relative organic carbon content of sediment dry mass) and Eq. 12-11. In order to get the fraction of chemical dissolved, f_{iw}, we use $\phi^{sc} = 0.80$, $\rho_s = 2.5$ g_s cm^{-1}, and Eq. 12-22, assuming $D_{ibulk} \approx D_{iw}$ and $\tau = 1$. The thickness of the benthic boundary layer is estimated as $\delta = 0.01$ cm.

Characteristic Properties of PCBs

2,2′,4,5,5′-pentachlorobiphenyl
(PCB 101)

2,2′,3,3′,4,4′,5-heptachlorobiphenyl
(PCB 170)

	PCB 101	PCB 180
Molar volume, $\bar{V}_i$ $(cm^3\ mol^{-1})$ [a]	194	218
D_{iw} at 15°C $(cm^2\ s^{-1})$ [b]	3.9×10^{-6}	3.7×10^{-6}
$v_{ibl} = D_{iw} / \delta$ $(cm\ s^{-1})$	5.2×10^{-4}	4.8×10^{-4}
$\log K_{iow}$ [c]	6.34	7.18
$\log K_{ioc}$ $(cm^3\ g^{-1}\ oc)$ [d]	5.57	6.32
K_{id}^{sc} $(L\ kg^{-1}) = f_{oc} K_{iocw}$	1.9×10^4	1.0×10^5
$t_{crit} = 2D_{iw} (\phi^{sc}/v_{ibl})^2 (1 + r_{sw}^{sc}K_{id}^{sc})$	4 days	26 days
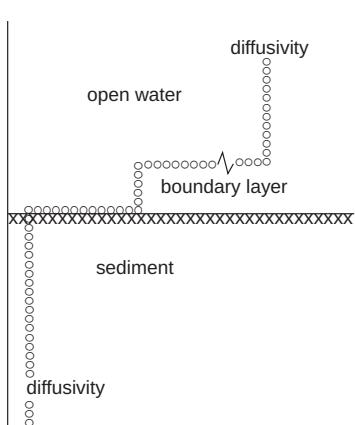
[a] Calculated by the method of Abraham amd McGowan (1987) (see Box 7.2).
[b] Calculated using relation shown in Fig. 17.6a and extrapolated to 15°C by Eq. 17-25.
[c] From Appendix C.
[d] Calculated from expression for PCBs in Table 13.2.
[e] From Eq. 20-9.

The critical time is much smaller than the elapsed time since the sewage pipe has been in operation. However, the result critically depends on the assumed size of the thickness of the benthic boundary layer, δ, a quantity only vaguely known. An increase of δ by a factor of ten causes t_{crit} to grow by a factor of one hundred.

Diffusivity across a sediment–water interface.

In Fig. 18.6, a model is shown where the boundary consists of a combination of a bottleneck boundary (the boundary layer) and a wall boundary whereby the change of diffusivity, $D_i(x)$, and the sudden increase of the equilibrium concentration ratio, R_{i21} (Eq. 18-8), do not coincide. The effect of the additional boundary layer results in a reduction of the integrated exchange flux relative to the situation without a boundary layer. The ratio of the two fluxes (flux with *versus* flux without boundary layer) is called the integrated flux ratio, $\psi(t)$ (Eq. 18-31), where t is normalized time. The integrated flux ratio grows from 0 at $t = 0$ to 1 for $t \rightarrow \infty$ (Fig. 18.7). The critical time, t_{crit}, indicates the threshold below which a boundary layer significantly inhibits the exchange flux. In Box 18.2, orders of magnitudes for t_{crit} are given for the special situation of an interface between a well-mixed waterbody and a porous medium. Critical time can then be approximated by:

$$t_{crit} \approx 2D_{ibulk} \left(\frac{\phi^{sc}}{v_{ibl}}\right)^2 \frac{1}{f_{iw}^{sc}} = 2D_{ibulk} \left(\frac{\phi^{sc}}{v_{ibl}}\right)^2 \left(1 + r_{sw}^{sc}K_{id}^{sc}\right) \qquad (20\text{-}9)$$

where $D_{i\text{bulk}}$ is the diffusivity in the porous medium (see Box 17.1), ϕ^{sc} is porosity of the sediment column, $v_{i\text{bl}}$ is the transfer velocity across the water-side boundary layer (Eq. 18-23), $r_{\text{sw}}^{\text{sc}}$ is the solid-to-water phase ratio in the sediment column, and $K_{i\text{d}}^{\text{sc}}$ is the solid–water distribution coefficient of chemical i.

Large critical times occur for strongly sorbing chemicals or if the boundary exchange velocity is small (little turbulence at the sediment surface). In Box 20.2, we discuss the case of diffusion from a polluted sediment column into the open water and the possible influence of a boundary layer at the sediment surface (Fig. 20.2c).

Bioturbation

So far we have tacitly assumed that in the sediment column the chemical i only move in the pore water, and the fraction that is sorbed on the solid surfaces remains immobile. Although diffusion in or on solids is not zero, it is several orders of magnitude slower than diffusion in fluids (air and water) and, thus, can be neglected. In fact, organisms living in the sediments may move sediment particles around. This mechanism is called bioturbation. The feeding habits of the various organisms living in the sediments may lead to different mixing patterns. For example, some organisms, such as worms, may take up particles at a certain depth in the sediment column and release them again at the sediment surface. This "conveyor belt" action results in a special transport pattern of the chemicals sorbed on these particles called non-local transport. Non-local transport means that the net flux of a chemical does not depend on the local concentration or concentration gradient (as in Fick's law), but is determined by concentration differences over larger distances. In such situations, net transport may be against the gradient, that is, from areas of smaller concentration to areas of larger concentration, an effect that could not be modeled by Fick's law of diffusion.

In other cases, the simultaneous action of different animal species may result in a superposition of different mixing patterns that would be quite complicated to model in detail. Random mixing may again become the simple recipe to describe these patterns, because it is not that far to the usual concept of Fickian diffusion. In fact, many authors who study bioturbation interpret their results with the help of a biodiffusion coefficient, D_{bio}, which they use in Fick's laws. The interested reader is referred to Kristensen et al. (2012) and Majdi et al. (2014).

In the following discussion, we look at the conditions where bioturbation becomes large enough to influence overall transport in the sediment column. According to the approach taken in Box 17.1, we can write the total flux of chemical i by:

$$F_{i\text{bulk}} = -\phi D_{i\text{bulk}} \frac{\partial C_{i\text{w}}}{\partial x} - D_{\text{bio}} \frac{\partial C_{i\text{t}}}{\partial x} \qquad (20\text{-}10)$$

where D_{bio} is diffusivity due to bioturbation with the usual units of a diffusion coefficient (e.g., cm^2 s^{-1}) and, like turbulent diffusion, does not depend on the chemical. The first term on the right-hand side of Eq. 20-10 describes diffusion in the pore water and only affects the aqueous concentration, $C_{i\text{w}}$; the second term describes transport

due to bioturbation and works on total concentration, that is, in the aqueous and the solid phase. With $C_{iw} = (f_{iw}/\phi)C_{it}$, we get:

$$F_{i\text{bulk}} = -(f_{iw}D_{i\text{bulk}} + D_{\text{bio}})\frac{\partial C_{it}}{\partial x} = -D_{i\text{eff}}\frac{\partial C_{it}}{\partial x} \qquad (20\text{-}11)$$

where the effective diffusivity of the bioturbated sediment is:

$$D_{i\text{eff}} = f_{iw}D_{i\text{bulk}} + D_{\text{bio}} \qquad (20\text{-}12)$$

The contribution of bioturbation reaches the same size as aqueous diffusion or surpasses it if:

$$f_{iw}^{-1} \equiv (1 + r_{\text{sw}}K_{id}) \approx r_{\text{sw}}K_{id} \geq \frac{D_{i\text{bulk}}}{D_{\text{bio}}} \Rightarrow K_{id} \geq \frac{1}{r_{\text{sw}}}\frac{D_{i\text{bulk}}}{D_{\text{bio}}} \qquad (20\text{-}13)$$

Majdi et al. (2014) cite typical values of D_{bio} between 10^{-8} and 10^{-7} cm^2 s^{-1}. With $D_{i\text{bulk}}$ between 10^{-6} and 10^{-5} cm^2 s^{-1} and $r_{\text{sw}} \approx 600$ kg m^{-3}, the critical limit of the solid–water distribution coefficient above which bioturbation becomes important for transport in the sediment column is on the order of:

$$K_{id} \geq (10 \text{ to} 100)\ \text{kg}^{-1}\ \text{m}^3 = (10^4 \text{ to } 10^5)\ \text{L kg}^{-1}$$

This value affects medium to strongly sorbing substances.

20.2   Transport in Unsaturated Soil

We now turn to transport within and at boundaries of systems that include gas, liquid, and solids. The most prominent example is unsaturated soil (see Chapter 5). Again, we use total concentration as the key variable together with the concepts of equilibrium distribution ratio and effective diffusivity.

Effective Diffusivity in Unsaturated Soil

As a special application of the concept of effective diffusivity, we consider the diffusion of a chemical i through unsaturated soil. The situation is slightly more complex than in Box 17.1 since it involves the air-filled pore space as a third medium. To calculate the effective diffusivity, $D_{i\text{eff}}$, of component i, we assume that transport occurs in the two fluid phases, air and water, but not in the solid phase. The total flux per unit bulk cross sectional area is the sum of the fluxes through air and water:

$$\begin{aligned} F_{i\text{bulk t}} &= F_{i\text{bulk a}} + F_{i\text{bulk w}} \\ &= -\theta_g D_{i\text{bulk a}}\frac{\partial C_{ia}}{\partial x} - (\phi - \theta_g)D_{i\text{bulk w}}\frac{\partial C_{iw}}{\partial x} \quad \left[\text{ML}_b^{-2}\text{T}^{-1}\right] \end{aligned} \qquad (20\text{-}14)$$

where ϕ is the total (gaseous and aqueous) porosity, θ_g is the volumetric gas content of the soil ($0 \leq \theta_g \leq \phi \leq 1$), C_{ia} is the gaseous concentration of chemical i per unit air volume, and C_{iw} is the aqueous concentration of chemical i per unit water volume.

The bulk diffusion coefficients in the two phases include the influence of tortuosity, τ. If Knudsen and Renkin effects are neglected, the porous medium diffusivities can be equated to the corresponding molecular diffusion coefficients in air and water (see Eq. 17-32). Adjusting for tortuosity, we have:

$$D_{i\text{bulk a}} = \frac{D_{i\text{soil a}}}{\tau^2} \approx \frac{D_{ia}}{\tau^2} \quad ; \quad D_{i\text{bulk w}} = \frac{D_{i\text{soil w}}}{\tau^2} \approx \frac{D_{iw}}{\tau^2} \tag{20-15}$$

For simplicity, we have assumed that tortuosity through the air-filled and water-filled pores is equal. Of course, this assumption may not hold, especially if the fractions of pore space occupied by either air or water are very different.

If equilibrium phase partitioning of chemical i between the phases is assumed, the fractions of the chemical in air, f_{ia}, and in water, f_{iw}, are calculated by extending the procedure described in Chapter 12 to three phases (see Eqs. 12-16 to 12-18):

$$f_{ia} = \frac{K_{iaw}\theta_g}{K_{iaw}\theta_g + (\phi - \theta_g) + K_{id}\rho_s(1-\phi)} \quad ; \quad f_{iw} = \frac{(\phi - \theta_g)}{K_{iaw}\theta_g + (\phi - \theta_g) + K_{id}\rho_s(1-\phi)} \tag{20-16}$$

where $K_{iaw} = (C_{ia}/C_{iw})_{eq}$ is the nondimensional Henry's law constant (see Eq. 9-15), K_{id} is the solid–water distribution coefficient (Eq. 12-8). C_{ia} and C_{iw} are related to the total concentration per bulk volume, C_{it}, by:

$$C_{ia} = \frac{f_{ia}}{\theta_g}C_{it} \quad ; \quad C_{iw} = \frac{f_{iw}}{(\phi - \theta_g)}C_{it} \tag{20-17}$$

Inserting Eqs. 20-15 to 20-17 into the expression for total flux (Eq. 20-14) yields:

$$F_{i\text{bulk t}} = -\frac{1}{\tau^2}\left(f_{ia}D_{ia} + f_{iw}D_{iw}\right)\frac{\partial C_{it}}{\partial x} = -D_{i\text{eff}}\frac{\partial C_{it}}{\partial x} \tag{20-18}$$

with the effective diffusivity, $D_{i\text{eff}}$:

$$D_{i\text{eff}} = \frac{1}{\tau^2}\left(f_{ia}D_{ia} + f_{iw}D_{iw}\right) = \frac{D_{ia}}{\tau^2}f_{ia}\left(1 + \frac{D_{iw}}{D_{ia}}\frac{1}{K_{iaw}}\frac{(\phi - \theta_g)}{\theta_g}\right) \tag{20-19}$$

On the far right-hand side of Eq. 20-19, the ratio of D's describes the contribution of the flux through the aqueous phase relative to the flux through the gaseous phase. Since D_{iw}/D_{ia} is typically of order 10^{-4} (Section 17.2), aqueous transport is only relevant for substances with small Henry's law coefficients ($K_{iaw} < 10^{-4}$ and smaller), extremely small relative air volumes ($\theta_g/\phi < 10^{-4}$), or a combination of these conditions. An example is given in Box 20.3. The flux ratio (air/water) does not depend on the solid–water distribution coefficient, K_{id}, since both fluid phases (gas, liquid) are equally affected by the molecules that are sorbed to solids. In contrast, because of the factor f_{ia} in Eq. 20-19 the absolute size of $D_{i\text{eff}}$, and thus of the flux, decreases with increasing K_{id}.

Box 20.3   Effective Diffusivity in Unsaturated Soil: Example of Spilled Gasoline

Soil Properties
$T = 25°C$
40% porosity of which 25%
  is filled with air and 75%
  is filled with water.
$\tau = 2$
Contains 0.1% organic carbon

Gasoline properties
Density: 0.7 g cm^{-3}

Benzene
$M_i = 78.1$ g mol^{-1}
$\bar{V}_i = 72$ cm^3 mol^{-1},
$K_{iaw} = 2.2 \times 10^{-1}$
log $K_{iow} = 2.17 =>$
  log $K_{ioc} = 1.5$

Ethanol
$M_i = 46.1$ g mol^{-1}
$\bar{V}_i = 45$ cm^3 mol^{-1}
$K_{iaw} = 2.1 \times 10^{-4}$
log $K_{iow} = -0.31 =>$
  log $K_{ioc} = 0.38$

An underground fuel storage tank is leaking gasoline below ground such that the hydrocarbon mixture is forming a horizontally extensive lens sitting on a clay layer located several meters below the surface of the unsaturated soil. Depending on their physicochemical properties, the different components of gasoline will migrate to the surface through air-filled pores, water-filled pores, or both. The evaluation of the effective diffusivity serves to identify the dominant pathway and to quantify the flux.

Two components of gasoline are considered: (a) benzene and (b) ethanol. We calculate the effective diffusivity, D_{ieff}, of the two components as well as their flux ratio, that is, the size of the flux through the water relative to the flux through air.

Calculated properties of gasoline components	Benzene	Ethanol
K_{id} (g^{-1} cm^3) (Eq. 12-8)	0.032	0.0024
D_{ia} (cm^2 s^{-1}) (Eq. 17-21a)	0.087	0.12
D_{iw} (cm^2 s^{-1}) (Eq. 17-24a)	0.98×10^{-6}	1.3×10^{-5}
f_{ia} (Box 17.2, Eq. 3)	0.059	6.9×10^{-5}
f_{iw} (Box 17.2, Eq. 3)	0.81	0.99
D_{ieff} (cm^2 s^{-1}) (Box 17.2, Eq. 6)	1.3×10^{-3}	0.25
Flux ratio air/water: $f_{ia} D_{ia} / f_{iw} D_{iw}$	650	0.65

Benzene mostly migrates through the air-filled pores, although it is less than 6% is in the air phase. In contrast, ethanol's air–water partition coefficient, K_{iaw}, is about 10^{-4} times smaller than the value for benzene. For ethanol, migration through the water phase is slightly larger than through air. Effective diffusivity, D_{ieff}, also depends on sorption on solids (but not the flux ratio), but the effect is negligible for ethanol (99% of ethanol is in the aqueous phase) and less than 20% for benzene.

The relative water saturation of the soil has a significant influence on D_{ieff} of the volatile benzene, but it hardly influences the effective diffusivity of ethanol. For saturated soil ($\theta_g = 0$), D_{ieff} drops by nearly a factor of 10^3 to 2.2×10^{-6} cm^2 s^{-1}. In Problem 20.1, you are asked to calculate the absolute size of the diffusive flux of benzene and ethanol from a layer of gasoline sitting on a clay layer.

By using effective diffusivity, Fick's second law for total concentration per bulk volume has the usual form:

$$\frac{\partial C_{it}}{\partial t} = D_{ieff} \frac{\partial^2 C_{it}}{\partial x^2} \quad \text{if} \quad D_{ieff} = \text{constant} \qquad (20\text{-}20)$$

Breakthrough Time

Although the total flux of a chemical per unit bulk area through the porous media is given by the fluxes through the fluid phases, where often the flux through the gas

phase dominates that through the aqueous phase (Eq. 20-14), the front of a chemical plume moves more slowly since the fluid phases have to "drag along" the sorbed phase. Therefore, the effective diffusivity, $D_{i\text{eff}}$ (Eq. 20-19), depends on the solid–water distribution coefficient, K_{id}, through the fractions f_{ia}, and f_{iw}: the larger K_{id}, the smaller $D_{i\text{eff}}$.

The movement of a front of a chemical plume can be estimated by the expression by Einstein and Smoluchowski (Einstein, 1905) (Eq. 6-36) by replacing D by $D_{i\text{eff}}$ and solving for time, the so-called breakthrough time, $t_{\text{breakthrough}}$:

$$t_{\text{breakthrough}} = \frac{d^2}{2D_{i\text{eff}}} \tag{20-21}$$

where d is the distance over which the front moves, for instance the vertical distance from the soil surface to the water table.

In the derivation of Eqs. 20-14 to 20-20, we assume that the chemical i is always at equilibrium in all phases. This means that when we study a pollutant front moving through the soil it is assumed that the solid phase is not preloaded with the pollutant. This assumption may not always be true. For instance, desorption may be slow or incomplete. If a pollution front moves through a preloaded soil, breakthrough time may become significantly smaller.

Transport at the Soil Surface

The soil surface can be described as a one-sided wall boundary (Fig. 18.4) with the atmosphere as the fully mixed compartment 1 and the soil as the "wall," compartment 2. With the formalism developed for the sediment–water interface (see Eq. 20-9), we now add the influence of an atmospheric boundary layer. We assume that transport through the soil is only by molecular diffusion. No assumption on the nature of transport in the atmosphere is necessary; it is just assumed that the atmosphere is always well-mixed. Obviously, this is not always true. For instance, the advective flow of water through the soil during rain may be much more efficient for the downward transport of chemicals than diffusion, especially for chemicals with small Henry's law constants for which transport in the air space is small. In turn, weather-induced changes of air pressure lead to drive flow of air either into or out of the soil. Modeling the combined effect of diffusion and advection was discussed in Section 6.4.

In the following, we restrict the discussion to the case that the initial concentration of the chemical in all phases of the soil is zero. Transport is then always from the atmosphere into the soil. Furthermore, it is assumed that the input of the chemical from the atmosphere only occurs through the gaseous phase and total concentration on the air-side of the air–soil interface is equal to atmospheric concentration: $C_{it}^{\text{atmosphere}} = C_{ia}^{\text{atmosphere}}$ (Fig. 20.3).

By inserting the appropriate variables into Eq. 18-18, the integrated flux per unit area is:

$$\mathcal{M}_i^*(t) = \frac{2}{\sqrt{\pi}} C_{it}^{\text{soil eq}} (D_{i\text{eff}} t)^{1/2} \approx C_{it}^{\text{soil eq}} (D_{i\text{eff}} t)^{1/2} \tag{20-22}$$
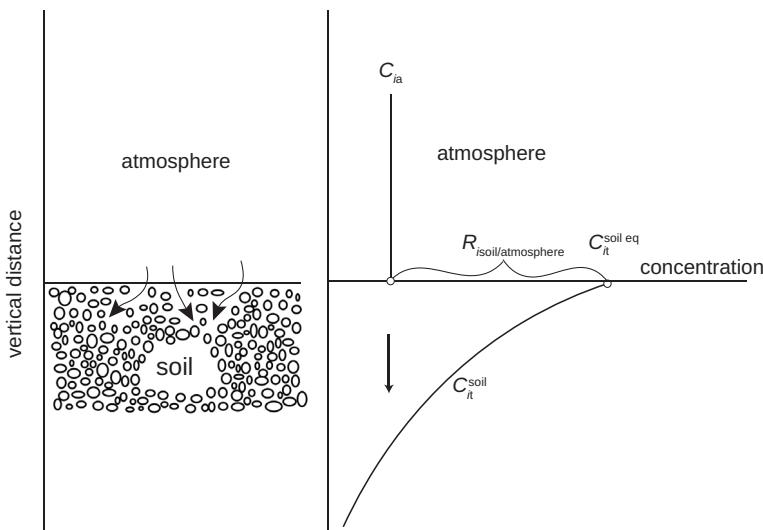
Figure 20.3 Transfer of a chemical from the atmosphere into unsaturated soil (see Eq. 20-25).

where $D_{i\text{eff}}$ is the effective diffusivity in the soil (Eq. 20-19). In order to calculate the total concentration in the soil in equilibrium with the atmospheric concentration, $C_{it}^{\text{soil eq}}$, we have to take into account that at the soil surface the gaseous concentration should be the same on both sides of the interface: $C_{ia}^{\text{soil eq}} = C_{ia}^{\text{atmosphere}}$. Then from Henry's law, we get $C_{iw}^{\text{soil eq}} = C_{ia}^{\text{atmosphere}}/K_{iaw}$. Finally, from Eq. 20-17 we get:

$$C_{it}^{\text{soil eq}} = \frac{(\phi - \theta_g)}{f_{iw}} C_{iw}^{\text{soil eq}} = \frac{(\phi - \theta_g)}{f_{iw}K_{iaw}} C_{ia}^{\text{atmosphere}} \tag{20-23}$$

Inserting Eq. 20-23 into 20-22 yields:

$$\mathcal{M}_i^*(t) \approx \frac{(\phi - \theta_g)}{f_{iw}K_{iaw}}(D_{i\text{eff}}t)^{1/2}C_{ia}^{\text{atmosphere}} \tag{20-24}$$

Using Eq. 20-16, the integrated flux into the soil can also be written as:

$$\mathcal{M}_i^*(t) \approx \left[K_{iaw}\theta_g + (\phi - \theta_g) + K_{id}\rho_s(1 - \phi)\right](D_{i\text{eff}}t)^{1/2}\frac{C_{ia}^{\text{atmosphere}}}{K_{iaw}} \tag{20-25}$$

To summarize, the flux into the soil is proportional to $C_{ia}^{\text{atmosphere}}$ and depends on the sorption properties of the chemical (K_{id}^{soil}), on its Henry's law coefficient (K_{iaw}), and on the physical characteristics of the soil, primarily ϕ and θ_g.

20.3   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.

Q 20.1

Regarding the movement of a chemical, in what respect is the solid phase different than fluid phases (gas and liquid).

Q 20.2

Sediments are formed by the settling of suspended particles. Explain why the solid–water distribution coefficients in the water and the sediments, K_{id}^{op} and K_{id}^{sc}, can be different nevertheless.

Q 20.3

Explain why for non-sorbing chemicals ($K_{id}^{sc} = 0$) the equilibrium concentration ratio between water and sediment is not 1.

Q 20.4

Explain the difference between D_{ibulk} and diffusivity in a porous medium, D_{ipm}.

Q 20.5

Sorption on particles has two opposing effects on the exchange flux of a chemical between the sediment and the water. What are these effects and which one is stronger? What is the influence of sorption on penetration depth?

Q 20.6

The critical time, t_{crit}, measures the influence of a possible boundary layer on the exchange flux at a one-sided wall boundary. Explain how v_{bl} and D_{ieff} influence the critical time.

Q 20.7

What do we mean with the term "non-local transport?" Explain how bioturbation could result in non-local transport.

Q 20.8

What is the effective diffusivity as compared to the diffusion coefficients in water and air, D_{iw} and D_{ia}, as discussed in Chapter 17?

Q 20.9

Which factors (properties of the chemical and of the sediment bed) enhance transport through the aqueous phase relative to transport through the gas phase?

Q 20.10

Explain why in unsaturated soil the porous medium diffusion model developed in Chapter 17 may not be adequate to assess the flux between the atmosphere and the soil.

Problems

P 20.1 *Evaluating the Steady-State Flux of Benzene and Ethanol through the Soil from Spilled Gasoline*

In Box 20.3, we analyzed the transport of two components of gasoline, benzene and ethanol, from a horizontal lens of spilled gasoline through the unsaturated soil to the surface. The gasoline contains 1% of benzene and 10% of ethanol by mass. Assume the average molar mass of gasoline is 100 g mol^{-1}. The vapor pressures of benzene and ethanol at 25°C, p_{iL}^*, are 0.13 bar and 0.077 bar (Appendix C). Assume an activity coefficient in gasoline, $\gamma_{i\ell}$, of 1 for benzene and 10 for ethanol. The gasoline sits on a clay layer 3 m below the soil surface, has a total volume of 4000 L, is spread over an area of about 1000 m^3, and is 0.01 m thick.

Use the information given in Box 20.3 to calculate the upward flux of the two components (g m^{-2}d^{-1}) at steady state. Estimate the time needed to establish a vertical steady-state concentration profile through the soil. Assume that the benzene and ethanol concentrations in the atmosphere are zero. Estimate the time until 10% of each chemical has left the ground.

P 20.2 *The Effect of Bioturbation on Transport in Unsaturated Soils*

In Box 20.3, the effective diffusivity in unsaturated soil for gasoline components was calculated. How would the result be affected by bioturbation in the soil? Describe bioturbation by $D_b = 10^{-6}$ cm^2 s^{-1}? How would the answer change with $D_b = 10^{-3}$ cm^2 s^{-1}?

P 20.3 *Atmospheric Inputs of Organic Contaminants to Surface Soils*

A variety of organic compounds are commonly present in the lower atmosphere. As one example, Warneke et al. (2001) found benzene averaged 440 pptv at a site in the Netherlands. You wonder if this benzene gets into the surface soils (a) carried by rain and (b) by diffusing from the air into the soil.

For the conditions listed, calculate the input of benzene to the soil (mol m^{-2}), first by rain out and then by diffusion from air into the soil, for a period of 1 month. For this problem, neglect transformations that would degrade benzene in the air or the soil and assume:

- the air concentration of benzene remains constant,

- the episodic rain events do not change the water content of the soil (Note: the water content of 10% by volume implies that the soil solid surfaces are not dry and so one can neglect sorption to mineral surfaces as discussed in Chapter 11),

- falling rain drops come to equilibrium with the benzene vapor in the air, and

- the soil is initially devoid of benzene.
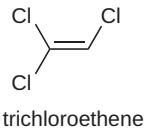
Hint: See Section 20.2 and do not forget that some chemical properties depend on temperature.

Conditions
Average air temperature: 8°C
Rain rate: 80 cm/year
Rain pH: 6
Soil porosity: 40%
Air-filled soil porosity: 30%
Water filled soil porosity: 10%
Soil tortuosity: 2
Soil minerals: 88% quartz (SiO$_2$)
5% illite
3% goethite
4% organic matter

P 20.4 *Potential for Exposure to TCE in Groundwater at the Ground Surface*

You hear that the groundwater beneath your house is contaminated with a carcinogen, trichloroethene (TCE). The mean aqueous concentration of TCE in the groundwater was measured to be 250 mg L^{-1}. The water table is located 4 m below the soil surface. The groundwater temperature is 10°C.

Cl, Cl, Cl

trichloroethene

$M_i = 131.4$ g mol^{-1}
Density $= 1.46$ g cm^{-3}
$T_m = -73°C$
$T_b = 121°C$
$\bar{V}_{McGowan} = 71$ cm^3 mol^{-1}

(a) Estimate TCE's effective diffusivity (cm^2 s^{-1}) in the unsaturated zone at 10°C. The porosity is 0.3 and the pore spaces are half full of water throughout the unsaturated zone. Assume that, due to sorption of TCE to the soil, only 5% of the compound is present in the gas phase ($f_{ia} = 0.05$).

(b) Calculate the vertical diffusive flux of TCE at steady-state (mg m^{-2} d^{-1}) from the top of the groundwater table through the unsaturated zone into the atmosphere.

(c) Estimate the time (days) to reach a steady-state for the diffusive flux. In case you are astonished by the result (very large time), you may reconsider the assumption that transport of TCE occurs by diffusion only. Given the fact that diffusion is very slow, what kind of other mechanism may become important and overrule diffusion?

Unsaturated zone characteristics
Depth below ground surface: 4 m
Temperature: 10°C
Porosity, ϕ: 0.3
Moisture content: 50% of porosity
Tortuosity through air-filled porosity, τ: 10
Aqueous TCE concentration: 250 mg L^{-1}

P 20.5* *Equilibration Time of Passive Polyethylene Samplers*
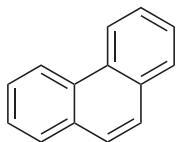
Low-density polyethylene (PE) sheets are widely used to measure trace organic compounds in natural waters. Tcaciuc et al. (2015) have studied the dynamics of the uptake of organic compounds. They developed a mathematical model consisting of an aqueous boundary layer of thickness δ_w and a PE sheet of thickness $2\delta_s$ (s = sheet) and compared it to experiments in the laboratory. In order to vary the thickness of the boundary layer, they stirred the water with different intensities. By comparing the experimental data with the model calculation, they determined δ_w, a quantity that is not directly measurable. Depending on the stirring intensity, they found δ_w between 100 and 300 μm. Use $\delta_w = 100$ μm for the following calculations.

(a) We are interested in the question whether the aqueous boundary layer is controlling the uptake dynamics of a chemical by the PE sheet. As a first attempt, you want to calculate (i) the time needed to establish a steady-state profile in the aqueous boundary layer; and (ii) the critical time t_{crit} below which the uptake is slowed down by the boundary layer (see Eq. 18-32). Use the characteristic properties of the three chemicals, phenanthrene, PCB 18, and PCB 153 listed as follows.
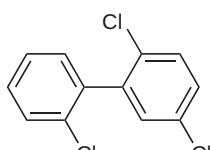
(b) Since t_{crit} may turn out to be extremely large (in fact, so large that the passive sampler would be unsuitable for obtaining reproducible results), you ask yourself whether

the theory developed in Chapter 18 is indeed applicable to the case of the passive sampler given the fact that the sheet is very thin. Use $2\delta_s = 50\ \mu m$ and explain the problem with Eq. 18-32.
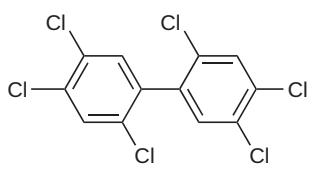
Hint: Calculate the diffusion time in the PE sheet.

(c) As an alternative to the approach of question (a), describe the PE sheet as a well mixed box separated from the water by an aqueous boundary layer with thickness δ_w and calculate the time until the sheet is 95% saturated with the chemical i. Assume that the concentration in the water remains constant.

In Chapter 28, the diffusion of the chemical into the PE sheet is analyzed with a more refined model.

phenanthrene

2,2',5-trichlorobiphenyl
(PCB 18)

2,2′,4,4′,5,5′-hexachlorobiphenyl
(PCB 153)

Properties of the Phenanthrene, PCB 18, and PCB 153

	Phenanthrene	PCB 18 2,2′,5- trichlorobiphenyl	PCB 153 2,2′,4,4′,5,5′- hexachlorobiphenyl
molar volume $\bar{V}_i$ $(cm^3\ mol^{-1})\ ^a$	145	169	206
$D_{iw}\ (cm^2\ s^{-1})\ ^b$	6.3×10^{-6}	5.7×10^{-6}	5.0×10^{-6}
$D_{iPE}\ (cm^2\ s^{-1})\ ^c$	3.6×10^{-9}	1.4×10^{-9}	4.3×10^{-10}
$K_{iPEw}\ (-)\ ^c$	1.4×10^4	7.2×10^4	5.7×10^6

^{a} Calculated by the method of Abraham and McGowan (1987), see Box 7.2.
^{b} From molar volume and Fig. 17.6.
^{c} From Lohmann (2012).

20.4　**Bibliography**

Abraham, M. H.; McGowan, J. C., The use of characteristic volumes to measure cavity terms in reversed phase lquid chromatography. *Chromatographia* **1987**, *23*(4), 243–246.

Einstein, A., Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. *Annalen der Physik* **1905**, *322*(8), 549–560.

Kristensen, E.; Penha-Lopes, G.; Delefosse, M.; Valdemarsen, T.; Quintana, C. O.; Banta, G. T., What is bioturbation? The need for a precise definition for fauna in aquatic sciences. *Mar. Ecol.-Prog. Ser.* **2012**, *446*, 285–302.

Lohmann, R., Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environ. Sci. Technol.* **2012**, *46*(2), 606–618.

Majdi, N.; Bardon, L.; Gilbert, F., Quantification of sediment reworking by the Asiatic clam Corbicula fluminea Muller, 1774. *Hydrobiologia* **2014**, *732*(1), 85–92.

McGroddy, S. E., *Sediment-Pore Water Partitioning of PAHS and PCBs in Boston Harbor*, MA. University of Massachusetts, Boston, 1993.

Tcaciuc, A. P.; Apell, J. N.; Gschwend, P. M., Modeling the transport of organic chemicals between polyethylene passive samplers and water in finite and infinite bath conditions. *Environ. Toxicol. Chem.* **2015**, *34*(12), 2739–2749.

Warneke, C.; van der Veen, C.; Luxembourg, S.; de Gouw, J. A.; Kok, A., Measurements of benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: calibration, humidity dependence, and field intercomparison. *Int. J. Mass Spectrom.* **2001**, *207*(3), 167–182.