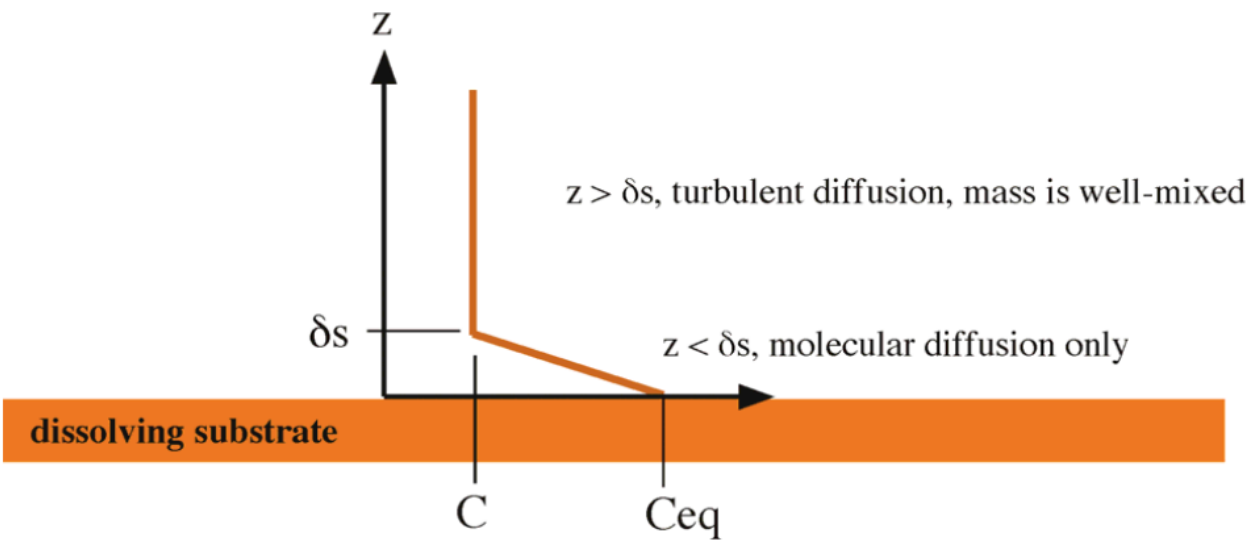
10. Reaction and interfacial exchange



Previously, it has been assumed that the chemical of interest is conservative. Now, we introduce the possibility of the diffusing, dispersing, advecting chemical also undergoing chemical reaction. The manner in which first-order reactions enter the mass-balance equation in 1, 2 and 3-dimensional systems is clearly demonstrated here. Three important environmental reactions, namely (i) dissolution from a bed, (ii) air-water exchange and (iii) partitioning to a solid are all examined in detail.

Sample problems test the user's ability to incorporate reaction into their solutions for cloud concentration, and also to predict the rate of air-water exchange for a variety of chemicals in a variety of flows.

Reaction and exchanges

10.1 Reaction – advection – diffusion Solutions

In this chapter we consider how chemical reactions enter the mass-balance equation as distributed source and sink terms, ±S.

$$\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}+w\frac{\partial C}{\partial z}=\frac{\partial}{\partial x}D_x\frac{\partial C}{\partial x}+\frac{\partial}{\partial y}D_y\frac{\partial C}{\partial y}+\frac{\partial}{\partial z}D_z\frac{\partial C}{\partial z}\pm S$$

Many reactions are modeled as first-order processes for which the rate of loss or gain is proportional to the existing concentration to the first power, *i.e.* $S = kC$, where $k[T^{-1}]$ is called the rate constant. Radioactive decay is a first-order process, with rate constant $k = \ln 2/\lambda$, where λ is the half-life. Biodegradation, the break-down of principally organic chemicals by microbial activity, can be represented as a first-order reaction, as can photodegradation by UV radiation. While the above processes act on chemicals within the fluid domain, processes that remove or add chemicals across the domain boundaries are also sources and sinks. For example, dissolution from a solid boundary is a source to the fluid domain, and sorption onto a solid boundary is a sink. Similarly, exchange across an air-water interface can act as either a source or sink for the fluid domain. If the fluid is well-mixed, these exchanges are modeled through the distributed source/sink term S. If the domain is not well-mixed, then these exchange are modeled through specific boundary conditions set for C or $\partial C/\partial n$, where n is the dimension perpendicular to the interface. Both cases - when the fluid domain is and is not well-mixed - are considered in this chapter. However, before discussing boundary exchange processes, we consider the effect of a generic first-order reaction on instantaneous and continuous point sources.

In the absence of advection and diffusion, the equation of mass conservation reduces to

$$(1) \qquad \frac{\partial C}{\partial t} = \pm kC\,,$$

where the sign + or - indicates a source or a sink, respectively. Given an initial concentration, C_o, the concentration will grow or decay as

$$(2) \qquad C(t) = C_o \exp(\pm kt).$$

Because the reaction is first-order, *i.e.* linear in C, we may integrate (1) over the fluid domain and directly arrive at

$$(3) \qquad \frac{\partial M}{\partial t} = \pm kM\,,$$

and

$$(4) \qquad M(t) = M_o \exp(\pm kt).$$

If the reaction were of higher order, *e.g.* $\partial C/\partial t = K_2 C^2$, the integral of (1) would not give (3). What is convenient about the linear reaction is that (3) and (4) describe the total mass in a system, even as that mass advects and disperses. For example, consider an instantaneous release of mass M at the point (x_o, y_o, z_o) in an unbounded domain with uniform currents, (u, v, w), and homogeneous diffusion coefficients, (D_x, D_y, D_z). The concentration field without reaction was given in equation 6 of Chapter 5, and is repeated here for convenience.

3-D, Instantaneous, Point Release at (x_o, y_o, z_o) with no reaction

$$(5) C(x,y,z,t) = \frac{M}{(4\pi t)^{3/2}\sqrt{D_x D_y D_z}} \exp\left(-\frac{(x - x_0 - ut)^2}{4D_x t} - \frac{(y - y_0 - vt)^2}{4D_y t} - \frac{(z - z_0 - wt)^2}{4D_z t} \right)$$

If the chemical undergoes a first-order reaction, then the total mass, M, must follow (4). Using (4) in (5), we arrive at the concentration field observed with a first-order reaction:

3-D, Instantaneous, Point Release at (x_o, y_o, z_o) with First-Order Reaction, kC

$$(6)\ C(x,y,z,t) = \frac{M_o \exp(\pm kt)}{(4\pi t)^{3/2}\sqrt{D_x D_y D_z}} \exp\left(-\frac{(x - x_0 - ut)^2}{4D_x t} - \frac{(y - y_0 - vt)^2}{4D_y t} - \frac{(z - z_0 - wt)^2}{4D_z t} \right)$$

Similarly, for two- and one-dimensional systems of length-scale L_y and L_z

2-D, Instantaneous, Point Release at (x_o, y_o) with First-Order Reaction, kC

$$(7)\ C(x,y,t) = \frac{M_o \exp(\pm kt)}{L_z\ 4\pi t\sqrt{D_x D_y}} \exp\left(-\frac{(x - x_o - ut)^2}{4D_x t} - \frac{(y - y_o - vt)^2}{4D_y t} \right).$$

1-D, Instantaneous, Point Release at x_o with First-Order Reaction, kC

$$(8)\ C(x,t) = \frac{M_o \exp(\pm kt)}{L_y L_z\sqrt{4\pi D_x t}} \exp\left(-\frac{(x - x_o - ut)^2}{4D_x t} \right).$$

To find the concentration field downstream of a reacting, continuous, point source, we follow the derivation in Chapter 6 for non-reacting plumes, and incorporate (7) and (8). After steady state has been reached, and for Pe >>1, *3-D, Steady, Continuous Release at (x_o, y_o, z_o) with First-Order Reaction, kC*

$$(9)\qquad C(x,y,z)=\frac{\dot{m}}{4\pi\sqrt{D_yD_z}\left(x-x_o\right)}\exp\left(-\frac{u(y-y_o)^2}{4D_y\left(x-x_o\right)}-\frac{u(z-z_o)^2}{4D_z\left(x-x_o\right)}\right)\exp\left(\pm\frac{k(x-x_o)}{u}\right)$$

2-D, Steady, Continuous Release at (x_o, y_o) with First-Order Reaction, kC

$$(10)\qquad C(x,y)=\frac{\dot{m}/u}{L_z\sqrt{4\pi D_y(x-x_o)/u}}\exp\left(-\frac{u(y-y_o)^2}{4D_y(x-x_o)}\right)\exp\left(\frac{\pm k(x-x_o)}{u}\right)$$

1-D, Steady, Continuous Release at x_o with First-Order Reaction, kC

$$(11)\qquad C(x)=\frac{\dot{m}}{uL_yL_z}\exp\left(\pm\frac{k(x-x_o)}{u}\right)$$

10.2 Dissolving species

Dissolution from a Boundary with Turbulent Flow or Rapid System Mixing.
If a boundary in a fluid system contains a chemical that is soluble in the fluid, then the boundary is a source of that chemical through dissolution. In systems that are stirred by turbulence, the dissolution flux is controlled by the rate of transport across the laminar sub-layer on the solid boundary. Recall that transport across the sub-layer proceeds at the rate of molecular diffusion, which is slower than turbulent diffusion by several orders of magnitude. The figure below depicts the concentration profile that evolves at the boundary of a well-mixed system. The concentration directly at the boundary, $C(z = 0) = Ceq$, is set by chemical equilibrium. That is, at the boundary we assume the dissolved phase is in equilibrium with the solid phase. The rate at which mass is supplied from the boundary to the fluid is set by the rate at which mass diffuses across the laminar sub-layer. That is, transport across the laminar sub-layer is the limiting step. This flux is described by Fick's Law.

$$(12)\qquad \dot{m}[MT^{-1}]\ =\ \text{Flux across }\delta s=\ -D_mA\frac{\partial C}{\partial z}=-D_mA\frac{C-Ceq}{\delta s}$$

Here, A is the area of the dissolving boundary and D_m is the molecular diffusion coefficient of the dissolving substance. To describe how the dissolution flux impacts the concentration in the bulk fluid, C, we consider the equation of mass conservation.

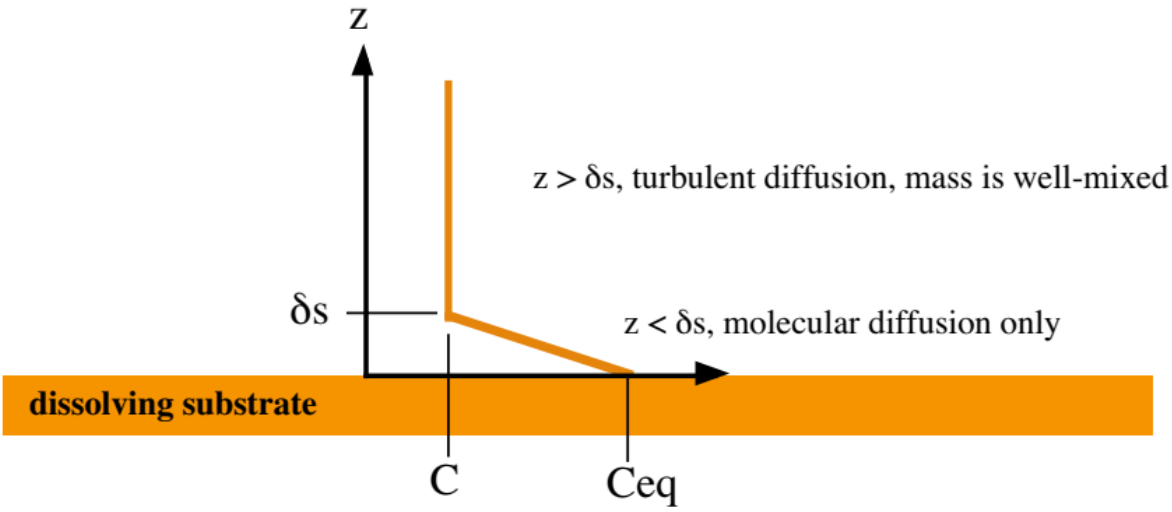


Figure 1. Concentration profile above a dissolving boundary with flux limited by transport across the laminar sub-layer (δs)

$$(13)\qquad \frac{\partial C}{\partial t}+u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}+w\frac{\partial C}{\partial z}=\frac{\partial}{\partial x}D_x\frac{\partial C}{\partial x}+\frac{\partial}{\partial y}D_y\frac{\partial C}{\partial y}+\frac{\partial}{\partial z}D_z\frac{\partial C}{\partial z}\pm S$$

Here, C is the concentration in the bulk fluid at $z > \delta s$. Let's consider a closed system of volume, V, in which the bed contains a soluble chemical. The system is stirred but has no mean currents, so that $u = v = w = 0$. We assume that the system is sufficiently stirred that the concentration is uniform, except within the laminar-sublayer, *i.e.* $\partial/\partial y = \partial/\partial x = \partial/\partial z = 0$ in the bulk of the fluid domain. Conservation of mass for the bulk fluid is then

$$(14)\qquad \frac{\partial C}{\partial t}=+S,$$

If we multiply (14) by the system volume, V, we can replace the source term, SV, by the diffusive flux given in (12).

$$(15)\qquad V\frac{\partial C}{\partial t} = -D_m A\frac{C-Ceq}{\delta s}.$$

Re-arranging, we find the evolution of the bulk-fluid concentration,

$$\frac{\partial C}{\partial t} = -\left[\frac{D_m A}{V\delta s}\right](C-Ceq) = -k(C-Ceq).$$

where $k = D_m A / V\delta s$ is the dissolution rate constant. Thus, for a well-mixed fluid domain, a boundary source can be treated as if distributed over the entire volume, *i.e.* through S, where

$$(16) \qquad S = -\left[\frac{D_m A}{V\delta s}\right](C - Ceq) = -k(C - Ceq)$$

With initial condition, $C(t=0) = 0$,

$$(17) \qquad C = Ceq\,(1 - e^{-kt})$$

When $C \ll Ceq$, then the source in (16) is constant, and C increases linearly,

$$(18) \qquad \frac{\partial C}{\partial t} = kCeq\,,$$

Alternatively, if $Ceq = 0$, *e.g.* an absorbing boundary, then C decreases exponentially, as given by (1) and (2).

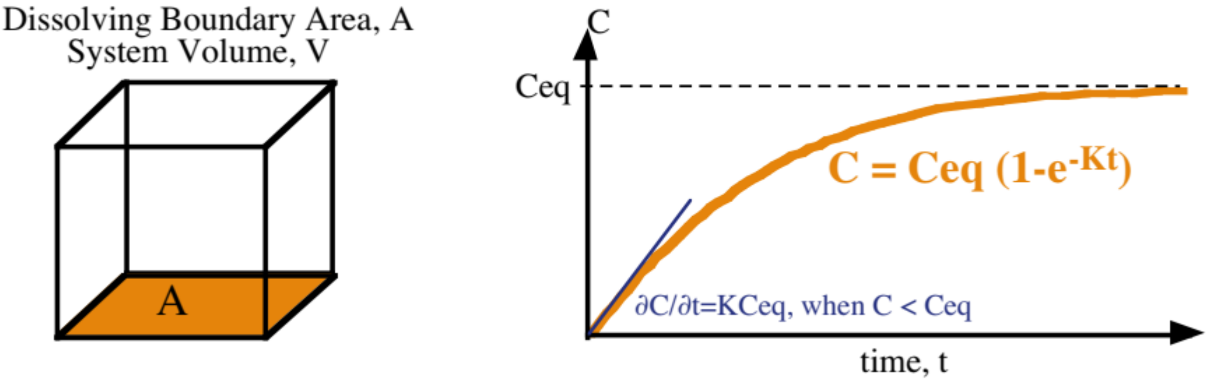


Figure 2. Evolution of concentration with boundary source.

Example: Dissolution from Gypsum Bed

A 100-m section of the stream bed is composed of gypsum from which calcium leaches into the water. The flow speed is U = 20 cm/s, the channel depth is h = 50 cm, and the channel width is b = 100 cm. Estimate the calcium concentration in the water at the end of the gypsum reach. Assume that the stream has no calcium before encountering the gypsum. At equilibrium with the solid phase, the calcium concentration in the water is $600 gm^{-3}$. Assume a calcium molecular diffusivity of $D = 10^{-9} m^2 s^{-1}$.

Answer.
First, check if the flow is turbulent. From Chapter 7, the flow is turbulent if the Reynolds number based on the hydraulic radius, R_H, is above 3000. Here, $R_H = hb/(2h+b) = 25\text{cm}$. Therefore, $Re = (20\text{cms}^{-1} \times 25\text{cm})/(0.01\ \text{cm}^2\text{s}^{-1}) = 50{,}000$. So, the channel flow is turbulent, and we expect that the concentration will be well-mixed over the cross-section, *i.e.* $\partial C/\partial z = \partial C/\partial y = 0$. If the Peclet (Pe) number is >>1, we can neglect longitudinal dispersion relative to advection. We estimate longitudinal dispersion as $K_X = 5.9u_*h$, using the approximate relation $u_* = 0.1U$. For reach length L = 100 m, the Peclet number is $Pe = UL/K_x = UL/(0.59Uh) \approx 330 >> 1$. Finally, we assume steady-state conditions, $\partial C/\partial t = 0$. Conservation of mass then simplifies to $u\ \partial C/\partial x = S$. If throughout the reach $C << Ceq$, we can use (18) to describe the calcium source, *i.e.* $S = kCeq$, such that,

$$(19) \qquad u\frac{\partial C}{\partial x} = kCeq\ .$$

Defining x = 0 at the beginning of the gypsum, C (x=0) = 0, as given, and

$$(20) \qquad C(x) = (k\ Ceq\ /\ U\ )\ x.$$

To evaluate the rate constant $k = D_m A/(V\ \delta s)$, we must estimate δs. With $u_* \approx 0.1U$, $\delta_s = 5\nu/u_* = 0.025\ \text{cm} = 2.5\text{x}10^{-4}\text{m}$. The ratio of volume, V, to bed area, A, is the depth h.

$k = D_m/(h\ \delta s) = (10^{-9}\ \text{m}^{-2}\text{s}^{-1})/(0.5\text{m} \times 2.5 \times 10^{-4}\text{m}) = 8 \times 10^{-6}\ \text{s}^{-1}$.

From (20), the concentration at x = 100m is then $(8 \times 10^{-6}\ \text{s}^{-1})(600\text{gm}^{-3})(100\text{m})/(0.2\text{ms}^{-1}) = 2.4\ \text{gm}^{-3} << 600$, confirming our assumption $C << C_{eq}$.

Dissolution from a Boundary with Laminar Flow or Slow System Mixing
If mixing conditions are weak, the concentration field outside the laminar sub-layer will not be uniform, and the gradient terms, *e.g.* $\partial C/\partial z$, will not drop out of the transport equation as occurred in the well-mixed system described above. Furthermore, if the entire fluid domain is laminar, there is no discrete laminar sub-layer. In these cases the flux is controlled by the rate of diffusion throughout the domain. The boundary source is accounted for by the diffusive flux term, e.g. $D_Z\ \partial^2 C/\partial z^2$, rather than being represented through the distributed source term, S, as was done in the well-mixed system above. Here S = 0.

Consider again a discrete volume of fluid, V, in contact with a dissolving boundary area, A. At the boundary the concentration is set by chemical equilibrium, such that C(z=0) = Ceq. If the source is never depleted, Ceq is constant over time. In addition, if the bed has uniform chemical composition, then $Ceq \neq f(x,y)$, and we expect $C \neq f(x,y)$ throughout the fluid. For simplicity we neglect advection (u = v = w = 0). The bed source is accounted for by the boundary condition, C(z=0) = Ceq. The conservation of mass equation,

(21) $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2},$$

with the boundary conditions;

$C = 0$, for all z, at $t < 0$
$C = Ceq$ at $z = 0$ for $t \geq 0$;

has the solution

(22) $$C(z,t) = Ceq\ \mathrm{erfc}\left(\frac{z}{2\sqrt{Dt}}\right).$$

The complementary error function (erfc) was described in Chapter 6. The evolution of C(z) given by (22) is depicted below. As time progresses, the mass-containing region near the boundary grows. By convention we define the limits of this concentration boundary layer, $z = \delta_c$, at the height for which $C/Ceq = 0.005$. From (22), and the erfc table, this occurs at $z/(2\sqrt{(Dt)}) = 2$, or

Concentration Boundary Layer above a Constant Concentration Source

(23) $$\delta_c = 4\sqrt{Dt}.$$

In the graph below the boundary layer height is indicated for t = 800 s. It is useful to note that the mean concentration within the concentration boundary layer is

(24) $$\bar{C} = \frac{Ceq}{\delta_c}\int_{z=0}^{z=\delta_c} \mathrm{erfc}\left(\frac{z}{2\sqrt{Dt}}\right)dz \approx 0.3Ceq.$$

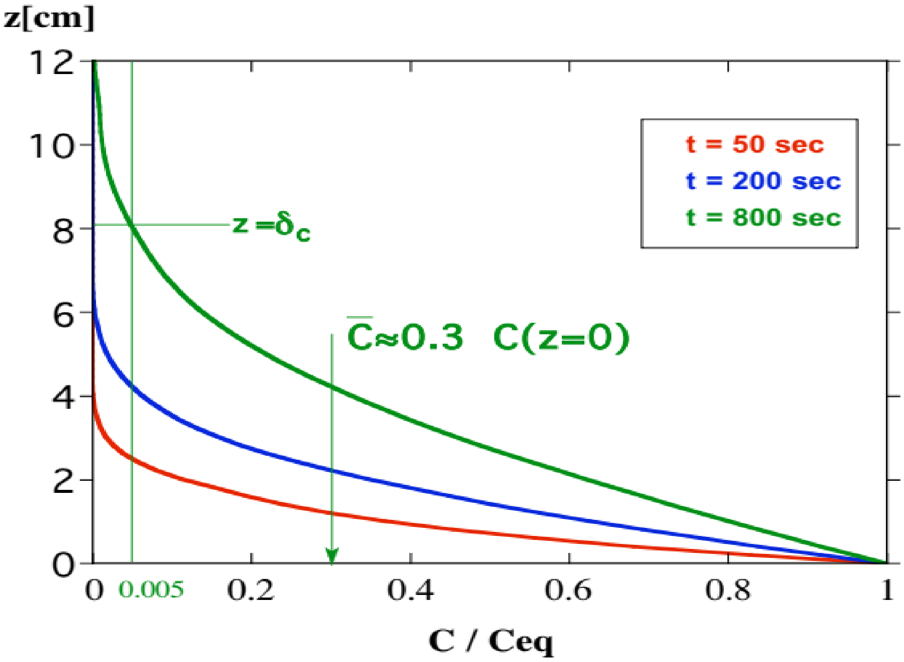


Figure 3. Development of concentration boundary layer above constant concentration boundary. The concentration at the boundary is in equilibrium with the solid phase, C(z=0) = Ceq.

Selecting a Dissolution Model

If the flow field is laminar, there is no laminar sub-layer, and only the second model will apply. If the flow is not laminar, then scale-analysis will determine which of the above models fits a given system. One must compare the time-scale for transport across the laminar sub-layer, $T_{\delta s}$, to the time-scale for transport over the fluid domain outside the laminar sub-layer, T_L, where L is the domain length-scale perpendicular to the dissolving boundary (=h, in this case). In the laminar sub-layer transport is controlled by molecular diffusion, D. Above the laminar sub-layer transport is controlled by turbulent diffusion, D_t. If h >> δs, the ratio $T_{\delta s}/T_L$ is

$$(25) \qquad \frac{T_{\delta s}}{T_L} = \frac{\delta_s^{2}/D}{h^{2}/D_t} = \frac{\text{time to diffuse across } \delta_s}{\text{time to mix across h}}.$$

If $T_{\delta s}/T_L >> 1$, chemical is delivered to the bulk fluid very slowly compared to the rate at which it is mixed to uniform concentration within the bulk fluid. Under this condition the concentration is uniform outside the laminar sub-layer, and the first model will apply (Figure 1). Alternatively, if $T_{\delta s}/T_L << 1$, the chemical is delivered relatively quickly from the dissolving substrate and through the laminar sub-layer, but once in the bulk fluid it takes a long time to mix over depth. In this case, concentration in the bulk fluid is not uniform, but follows an erfc distribution, as shown in Figure 3.

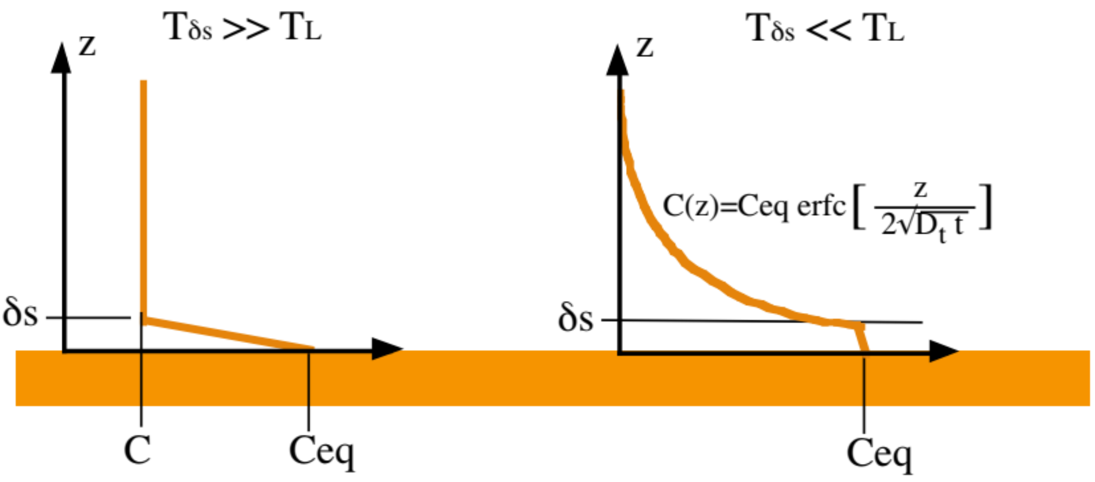


Figure 4. Distribution of concentration near a dissolving boundary for conditions with slow transport across the laminar sub-layer ($T_{\delta s} >> T_L$) and conditions with rapid transport across the laminar sub-layer ($T_{\delta s} << T_L$).

EXERCISES WITH SOLUTIONS

Problem 1

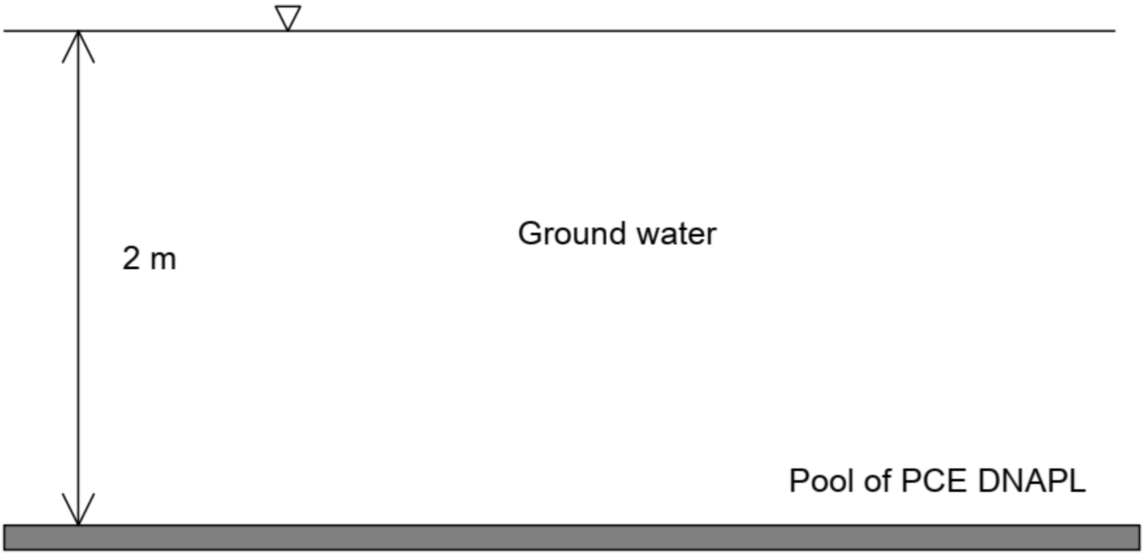
A smokestack of height H = 20 m releases two gases, dichlorodifluoromethane (Freon 12) and trichloroethene (TCE), each at a rate of 5 kg/min. Freon 12 is conservative. TCE undergoes first-order degradation in the atmosphere at a rate of $k_{TCE} = 0.1\ \text{day}^{-1}$, producing the highly toxic chemical phosgene ($C(=O)Cl_2$). Assume that the wind blows steadily and uniformly at 5 m/s in the positive x direction. The atmospheric turbulence is homogeneous but anisotropic, with the vertical diffusivity, $D_Z = 0.1\ m^2s^{-1}$, smaller than the horizontal diffusivities, $D_X = D_Y = 1\ m^2s^{-1}$. For both gases the ground acts as a no-flux boundary. Find the maximum concentration of Freon and TCE 10-km downwind of the stack.

Problem 2

A small channel is h = 5 cm deep and b = 10 cm wide. It carries flow at $U = 10\ cms^{-1}$. The stream-wise coordinate is x. The vertical coordinate is z, with z = 0 at the bed and positive upward. A continuous source of dye is injected at a rate of $\dot{m} = 1\ gs^{-1}$ at mid-depth and mid-width, and at x = 0. Assume that the channel has no dye upstream of the injection point. The bed of the channel is a perfect absorber for the dye, such that the concentration of dye in equilibrium with the bed is zero, and thus $C(z=0) = 0$. The molecular diffusivity for the dye is $D = 10^{-5}\ cm^2s^{-1}$. What is the maximum concentration in the channel 20 m downstream of the source?

Problem 3

Dense non-aqueous phase liquids (DNAPLs) are liquids that are heavier than water and have very low solubility in water. Typical DNAPLs include chlorinated solvents like the dry-cleaning fluid perchloroethylene (PCE), also called tetrachloroethylene or tetrachloroethene. When a DNAPL enters an aquifer it will sink under gravity until it encounters a layer of low permeability, such as clay. It then spreads into a thin layer. Consider the pool of PCE depicted below which was created at time t = 0. For t < 0 the PCE concentration in the aquifer is zero. For t > 0, PCE slowly diffuses into the water above. The coefficient of diffusion is $D = 4.4 \times 10^{-9}\ m^2s^{-1}$. The ground water is stagnant and the aquifer is 2 meters thick above the DNAPL. PCE has a solubility in water of 150 mg/L. The Maximum Contaminant Level (MCL) for PCE in drinking water is 5 ppb. When will the concentration of PCE throughout the aquifer be above the MCL?



EXERCISE - SOLUTIONS

Answer 1

For a continuously operating smokestack and steady climatic conditions, we can assume a steady concentration field, *i.e.* $\partial C/\partial t = 0$. The wind is given as $u = 5$ m/s, implying $v = w = 0$. We are told to assume a uniform wind, *i.e.* no shear, so we neglect shear-dispersion. For the length-scale of interest, $L_X = 10{,}000$m, the Peclet number is $(5\text{m/s})(10{,}000\text{m})/(1\text{m}^2/\text{s}) = 50{,}000 >>> 1$. With this high value of Pe, the longitudinal diffusion term is negligible relative to longitudinal advection, and we drop it. With the above assumptions, the transport equation

$$\text{(a)}\quad \frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} + w\frac{\partial C}{\partial z} = \frac{\partial}{\partial x}D_x\frac{\partial C}{\partial x} + \frac{\partial}{\partial y}D_y\frac{\partial C}{\partial y} + \frac{\partial}{\partial z}D_z\frac{\partial C}{\partial z} \pm S,$$

becomes

$$\text{(b)}\quad u\frac{\partial C}{\partial x} = D_y\frac{\partial^2 C}{\partial y^2} + D_z\frac{\partial^2 C}{\partial z^2} - S,$$

with $S = 0$ for Freon and $S = k_{TCE}C$ for the TCE.

For a continuous release $\dot{m} = 5$ kg/min $= 83$ gs^{-1} at $(x,y,z) = (0, 0, H)$, the solution to (b) is

$$\text{(c)}\quad C(x,y,z) = \frac{\dot{m}}{4\pi\sqrt{D_y D_z}\,x}\exp\left(-\frac{uy^2}{4D_y x} - \frac{u(z-H)^2}{4D_z x}\right)\exp\left(-\frac{kx}{u}\right),$$

where k = 0 for Freon and $k = k_{TCE}$ for the TCE. To account for the no-flux boundary we add a positive image source at (x,y,z) = (0, 0, -H).

(d)
$$C(x,y,z) = \frac{\dot{m}}{4\pi\sqrt{D_y D_z}\,x}\left[\underbrace{\exp\left(-\frac{uy^2}{4D_y x}-\frac{u(z-H)^2}{4D_z x}\right)\exp\left(-\frac{kx}{u}\right)}_{\text{real source}}+\underbrace{\exp\left(-\frac{uy^2}{4D_y x}-\frac{u(z+H)^2}{4D_z x}\right)\exp\left(-\frac{kx}{u}\right)}_{\text{image source}}\right]$$

In any transverse dimension for which the plume is unbounded (here the y-direction), the maximum concentration is at the centerline of the plume (here y = 0). The vertical coordinate, however, is bounded by a no-flux boundary at the ground, z = 0. Once the plume reaches the ground, concentration will build up at the no-flux boundary. Because the upper edge of the plume is not bounded, the vertical concentration field will eventually become asymmetric with the maximum concentration at the ground. We estimate the distance at which this will occur using the time-scale for the edge of the plume (the 2σ contour) to reach the ground,

(e) $$T_{2\sigma} = H^2/(8D_Z) = (20\text{m})^2 / (8 \times 0.1\ \text{m}^2\text{s}^{-1}) = 500\ \text{s}.$$

Thus, for $x \gg u\,T_{2\sigma} = 2500$ m, which includes the point of interest, we expect the maximum concentration to be at the ground. Therefore, the maximum concentration at x = 10,000 m will be $C_{max} = C\ (x = 10000\ \text{m}, y = 0, z = 0)$. Evaluating (d) for Freon and TCE we find,

FREON:

$$C_{max} = \frac{83\text{gs}^{-1}}{2\pi\sqrt{(1\text{m}^2\text{s}^{-1})(0.1\text{m}^2\text{s}^{-1})}\ 10{,}000\text{m}}\exp\left(-\frac{5\text{ms}^{-1}(20\text{m})^2}{4(0.1\text{m}^2\text{s}^{-1})10{,}000\text{m}}\right) = 2.5\ \text{mg m}^{-3}$$

TCE:

$$C_{max} = \frac{83\text{gs}^{-1}}{2\pi\sqrt{(1\text{m}^2\text{s}^{-1})(0.1\text{m}^2\text{s}^{-1})}\ 10{,}000\text{m}}\exp\left(-\frac{5\text{ms}^{-1}(20\text{m})^2}{4(0.1\text{m}^2\text{s}^{-1})10{,}000\text{m}}\right)\exp\left(-\frac{10000\text{m}}{5\text{ms}^{-1}}(0.1\text{d}^{-1})(\text{d}/86400\text{s})\right)$$

$$= 2.5\ \text{mgm}^{-3} \times 0.998 \approx 2.5\ \text{mgm}^{-3},$$

Very little degradation of TCE occurs over the 10,000m distance.

Answer 2

A perfectly absorbing boundary can be treated like a dissolving boundary with $C_{eq} = 0$. The boundary is a sink rather than a source, otherwise the process of exchange between the bed and the water column is the same. Here, dye is injected as a continuous point source and the evolving plume experiences a sink at the absorbing boundary. If the system has fast mixing, then we can assume that $\partial C/\partial z = \partial C/\partial y = 0$ and use the fast-mixing model for bed-exchange. Then the effects of the boundary sink are modeled as a distributed sink S. For steady-state conditions and Pe >> 1, the transport equation

$$\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}+w\frac{\partial C}{\partial z}=\frac{\partial}{\partial x}K_x\frac{\partial C}{\partial x}+\frac{\partial}{\partial y}D_y\frac{\partial C}{\partial y}+\frac{\partial}{\partial z}D_z\frac{\partial C}{\partial z}\pm S,$$

will reduce to,

(1) $$u\frac{\partial C}{\partial x}=-S.$$

However, if the dye mixes slowly over the cross-section, we cannot assume $\partial C/\partial z = \partial C/\partial y = 0$ in the channel. Under these conditions we would use the solution for a 3-D, steady, continuous release (equation 8, chapter 6), with positive image sources to account for the no-flux side-boundaries, and a negative image source to account for the perfectly absorbing bed.

Before proceeding with (1), we must check all the assumptions. First, we will determine if the flow is turbulent, and if it is we will estimate turbulent diffusivities. The hydraulic radius is (5cm x 10cm)/ (10cm + (2 x 5 cm)) = 2.5 cm. The Reynolds number based on hydraulic radius is, $Re_H = (10cms^{-1}x2.5cm)/(0.01\ cm^2s^{-1}) = 2500$, which indicates the flow is likely to be turbulent. Next to each boundary there is a laminar sub-layer with thickness, $\delta_s = 5\ \nu/u_*$. The friction velocity is estimated as $u_* \approx 0.1U = 1\ cms^{-1}$. This gives $\delta_s = 0.05$ cm.

Now, we estimate the coefficients of turbulent diffusion using the empirical relations for a straight channel given in Table 1 of Chapter 7.

$$D_{t,x} = 0.45\ u_*h = 2.3\ cm^2s^{-1}$$

$$D_{t,y} = 0.15\ u_*h = 0.75\ cm^2s^{-1}$$

$$D_{t,z} = 0.067\ u_*\ h = 0.34\ cm^2s^{-1}$$

Confirm Fast-Mixing Bed Exchange Model

To determine if the system will follow a fast-mixing or slow-mixing model of bed-exchange, we compare the time scale required for the channel to mix vertically with the time scale for diffusive flux to cross the laminar sub-layer.

$$\frac{T_{\delta s}}{T_L}=\frac{\delta_s^{\,2}/D}{h^2/D_t}=\frac{(0.05cm)^2(0.34cm^2s^{-1})}{(5cm)^2(10^{-5}cm^2s^{-1})}=3.4$$

To be very confident that the fast-mixing model is appropriate, we require that $T_{\delta s}$ is an order of magnitude greater than T_L. Here the time scales only differ by a factor of three. However, the system is closer to the fast-mixing model then the slow-mixing model, so we proceed with that assumption.

Confirm well-mixed conditions ($\partial C/\partial y = \partial C/\partial z = 0$) for plume evolution.
To use (1) to describe plume evolution, we must confirm that the plume rapidly mixes over the channel cross-section. We need to find the distance from the source at which the plume is uniform in y and z. These distances are,

$$X_{mix,y} = b^2 u / (4 D_{t,y}) = (10\text{cm} \times 10\text{cm} \times 10 \text{ cm}^2\text{s}^{-1}) / (4 \times 0.75 \text{ cm}^2\text{s}^{-1}) = 333 \text{ cm}$$

$$X_{mix,z} = h^2 u / (4 D_{t,z}) = (5\text{cm} \times 5\text{cm} \times 10 \text{ cm}^2\text{s}^{-1}) / (4 \times 0.34 \text{ cm}^2\text{s}^{-1}) = 183 \text{ cm}.$$

This indicates that for distances greater than 333 cm from the source, the plume will be uniform in y and z. We are interested in the position x = 2000 cm, so we can model the concentration as if it originated from a one-dimensional source at x = 0. That is, we can assume $\partial C/\partial y = \partial C/\partial z = 0$.

Confirm assumption of Pe >>1
If $Pe = UL_x/K_x >> 1$, we can neglect longitudinal dispersion relative to longitudinal advection. The relevant length-scale is the distance at which we want to predict the concentration, L = 2000 cm. The longitudinal dispersion is $K_X = 5.9u_*h = 30 \text{ cm}^2\text{s}^{-1}$. Then, $Pe = (10 \text{ cms}^{-1} \times 2000 \text{ cm})/(30 \text{ cm}^2\text{s}^{-1}) = 666 >> 1$. So, this assumption is confirmed.

We have confirmed the assumptions that led to (1). Now, we can replace the sink term, S, in (1) with the form given in equation (16) in Chapter 9. That is,

$$(2) \qquad S = -\left[\frac{D_m A}{V\delta s}\right](C - Ceq) = -k(C - Ceq).$$

With V/A = h, we estimate the bed-exchange rate constant $k=10^{-5} \text{ cm}^2\text{s}^{-1}/(5\text{cm} \times 0.05\text{cm}) = 4 \times 10^{-5} \text{ s}^{-1}$. In this system $C_{eq} = 0$, such that (1) becomes

$$(3) \qquad u\frac{\partial C}{\partial x} = -kC$$

As shown in Chapter (6), leading to and including equation 13, the initial concentration at the source will be $C(x = 0) = \dot{m}/ubh$. With this initial condition, the solution to (3) is.

(4) $$C(x) = \frac{\dot{m}}{ubh}\exp\left(-\frac{kx}{u}\right)$$

Note, a generic form of equation (4) was also given for a 1-D, steady, continuous release with first-order reaction in equation (11) of chapter 9.

Using (4) we find the concentration at x = 2000 cm to be,

$$C(x = 2000\text{ cm}) = \frac{1\text{gs}^{-1}}{(10\text{cms}^{-1})(10\text{cm})(5\text{cm})}\exp\left(-\frac{(4\text{x}10^{-5}\text{s}^{-1})(2000\text{cm})}{10\text{cms}^{-1}}\right) = 0.00198\text{gcm}^{3}$$

In fact, the boundary sink does not make a significant contribution between x = 0 and 2000 cm, as the initial concentration is 0.002 gcm^{-3}. Barely 1 percent of the dye has been lost to the bed.

Answer 3

We are interested in the vertical diffusion of PCE from its source at z = 0 upward into the aquifer. The groundwater is given to be stagnant, so that u = v = w = 0. In addition, all groundwater is laminar, so we will use the laminar (slow mixing) model of dissolution. That is, the boundary source is modeled by a fixed concentration boundary condition. We assume that the DNAPL pool is large in lateral extent and uniform in concentration, so that the lateral gradients of PCE are negligible ($\partial C/\partial x = \partial C/\partial y = 0$). No additional sources or sinks are named, so that S = 0. The system cannot be in steady state, because there is a source at the lower boundary and no sink, so that $\partial M/\partial t > 0$ within the aquifer. Directly at the boundary, z = 0, the concentration is assumed to be at the solubility concentration, $C_o = 150\text{ mgl}^{-1} = 150$ ppm. We assume that the total PCE in the DNAPL pool is sufficiently large that C_O remains constants, even as PCE dissolves out of the pool. With these assumptions we may write the transport equation and boundary conditions,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2},$$

$C = 0$, for all z, at $t < 0$

$C = C_o = 150$ ppm at $z = 0$ for $t \geq 0$.

The PCE concentration profile evolves according to,

$$C(z,t) = C_o\,\text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right).$$

The maximum concentration in the aquifer will be at the source ($z = 0$) and the minimum concentration at $z = 2\text{m}$, until a uniform concentration is reached throughout the aquifer. Thus, to find $C > 5$ ppb throughout the aquifer, we need only find when $C(z=2\text{ m}) = 5$ ppb. From the above equation, we need to find when

$$\operatorname{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) = \frac{0.005}{150} = 0.000033.$$

Interpolating from the table at the end of chapter 9,

$$\operatorname{erfc}(2.94) \approx 0.000033$$

$$\frac{2\text{m}}{2\sqrt{\left(4.4\text{ x}10^{-9}\text{m}^2\text{s}^{-1}\right)t}} = 2.94$$

$$t = 2.6\text{ x }10^{7}\text{ s} = 304\text{ days}$$