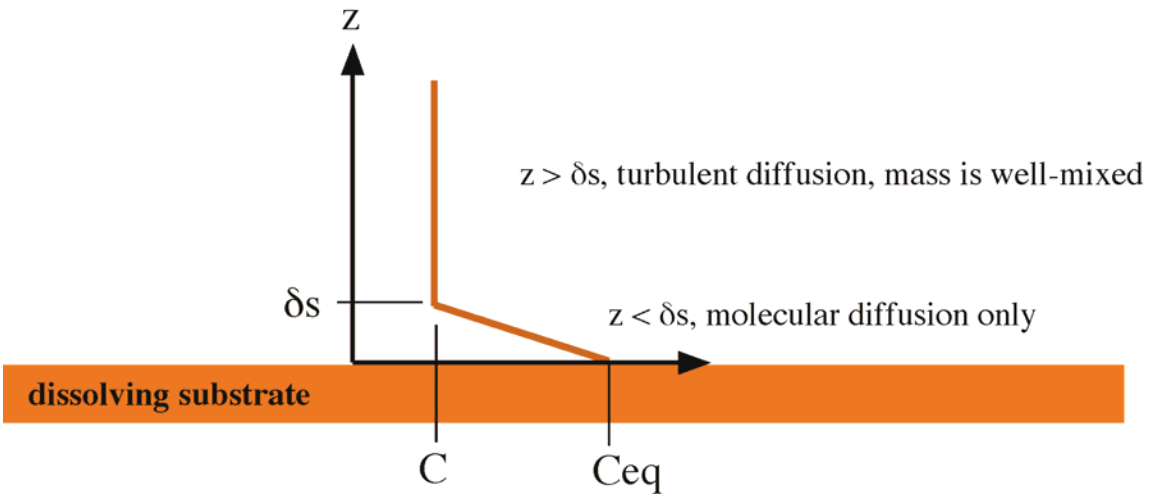

Previously, it has been assumed that the chemical of interest is conservative. Now, we introduce the possibility of the diffusing, dispersing, advecting chemical also undergoing chemical reaction. The manner in which first-order reactions enter the mass-balance equation in 1, 2 and 3-dimensional systems 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.

9. Reactions and Exchanges

9.1 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 = ln2/λ, 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 ∂C/∂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 bondary 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) $$\frac{\partial C}{\partial t} = \pm kC\,,$$

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) $$C(t) = C_O \exp(\pm kt).$$

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

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

and

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

If the reaction were of higher order, *e.g.* $\partial C/\partial t = K_2C^2$, 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

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

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

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

9.2 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.

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

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.

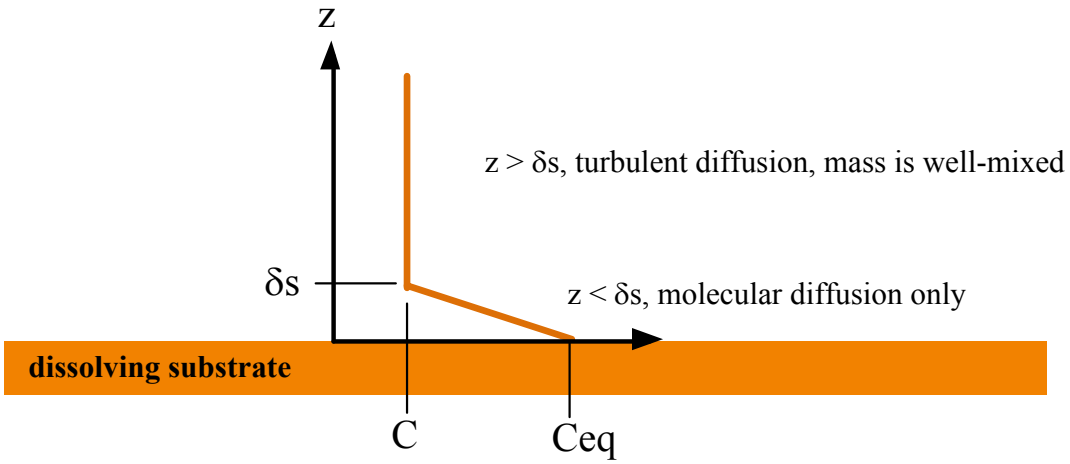

Figure 1. Concentration profile above a dissolving boundary with flux limited by transport across the laminar sub-layer (δs)

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

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 $C << Ceq$, 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).

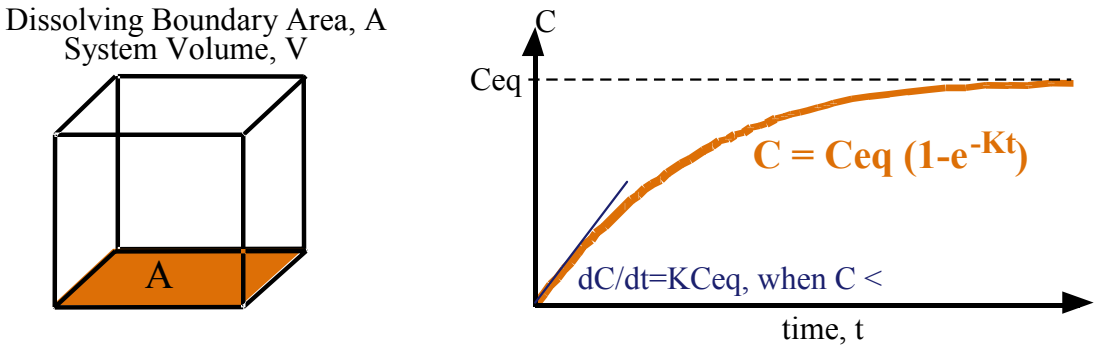

Figure 2. Evolution of concentration with boundary source.

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, $R_H = hb/(2h+b) = 25cm$.

Therefore, Re = (20cms^{-1} x 25cm)/(0.01 cm^{2}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 $k = D_mA/(V\,\delta s)$, we must estimate δs. With $u_* \approx 0.1U$, $\delta_s = 5\nu/u_* = 0.025$ cm = 2.5x10^{-4}m. The ratio of volume, V, to bed area, A, is the depth h.

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

From (20), the concentration at x = 100m is then $(8 \times 10^{-6}\ s^{-1})(600gm^{-3})(100m)/(0.2ms^{-1}) = 2.4\ gm^{-3} << 600$, 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. $D_Z\,\partial^2C/\partial z^2$, 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,

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

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

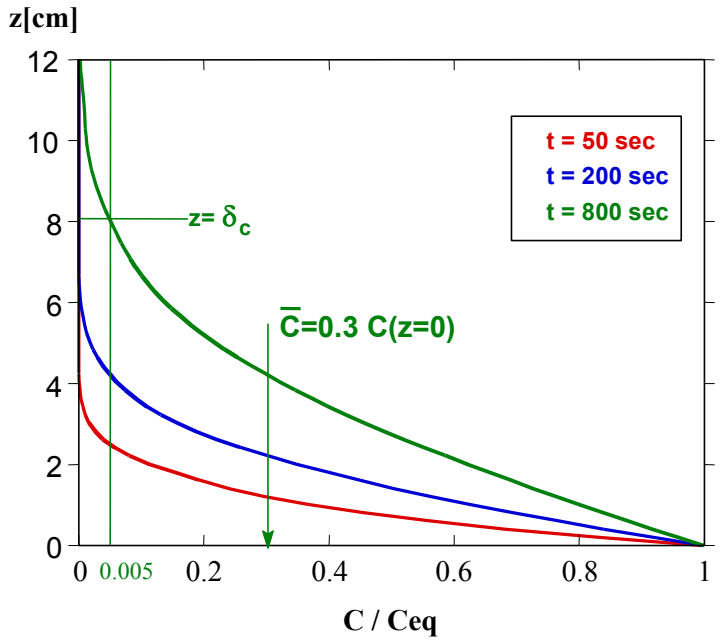

Figure 3. Development of concentration boundary layer above constant concentration boundary. The concentration at the boundary is in equilibrium with the solid phase, C(z=0) = Ceq.

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 $h >> \delta s$, 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.

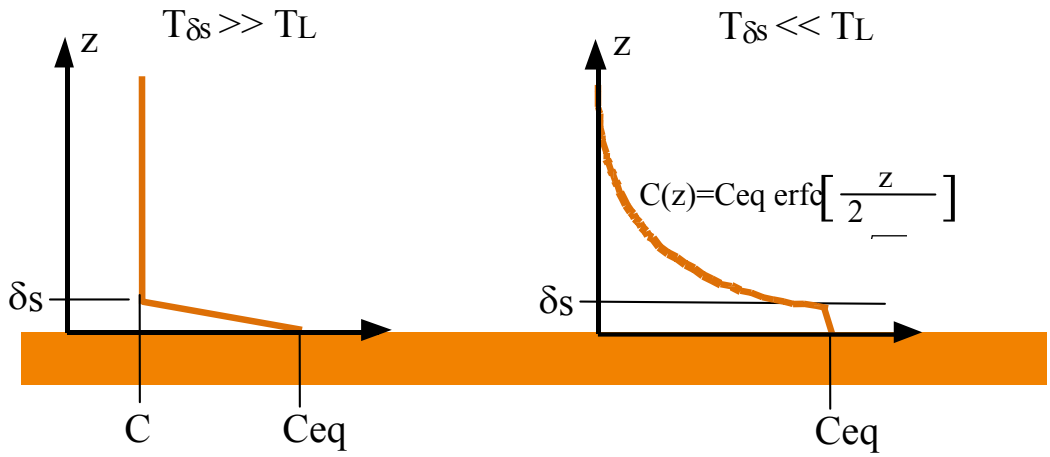

Figure 4. Distribution of concentration near a dissolving boundary for conditions with slow transport across the laminar sub-layer ($T_{\delta s} >> T_L$) and conditions with rapid transport across the laminar sub-layer ($T_{\delta s} << T_L$).

9.3 Exchange Across an Air-Water Interface

Volatile chemicals may partition themselves between water and air phases. At equilibrium, the ratio of these phases is described by a partitioning coefficient called **Henry's Law Constant**. Specifically, Henry's Law Constant, H, is defined as

$$(26) \qquad H = \frac{\text{equilibrium concentration in air [mass/volume air]}}{\text{equilibrium concentration in water[mass / voume water]}}.$$

Thin-Film Model for Air-Water Exchange

The thin-film model is based on the assumption that a laminar sub-layer exists on both sides of the air-water interface. This assumption relies on the following physical ideas and approximations. Because the density difference across the air - water interface is so large, it is approximately true that the turbulence structures in both fluids see the interface as a rigid boundary not as a flexible membrane. This means that on both the air-side and the water-side, the scales of the turbulence diminish approaching the interface, just as if approaching a solid boundary. At small distances from the interface there is a region for which the allowable turbulence scale is too weak to overcome viscous forces, such that no turbulence can exist in this region and the flow is laminar. This laminar sub-layer exists on both sides of the interface. For a chemical to move from the air into the water, or vice versa, it must pass through both an air-side and a water-side laminar sub-layer. If we assume that the transport through these layers controls the overall flux, we can estimate the net mass exchange.

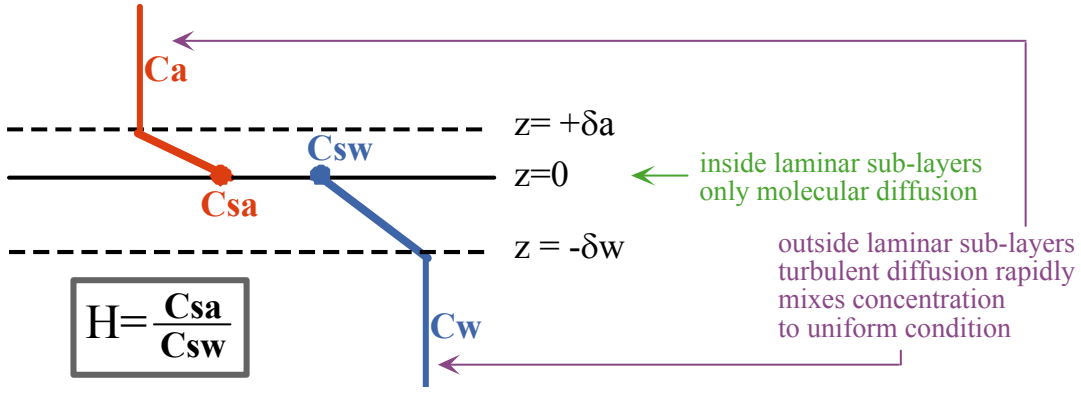

Figure 5. The Thin-Film Model describes the exchange of volatile species across the air-water interface under conditions for which transport is limited by diffusion across the laminar sub-layers. At the surface (z = 0) the aqueous phase (Csw) is in equilibrium with the concentration in air (Csa), such that Csw = Csa/H, where H is the Henry's Law constant.

Consider a volume of water and air in contact over area A. As depicted in Figure 5, a laminar sub-layer exists on both the water side (δw) and the air side (δa) of the interface. Outside the laminar sub-layers turbulent diffusion is sufficient to make the concentrations in the water (Cw) and in the air (Ca) uniform. Within the laminar sub-layers only molecular diffusion is operating, so under steady conditions the concentration profile must be linear (as is true for any diffusive process with constant diffusivity). Finally, we assume that chemical equilibrium exists at the interface (z = 0), such that the dissolved phase concentration at the surface (Csw) is in equilibrium with the air phase concentration at the surface (Csa). Specifically, Csw = Csa/H, where H is the Henry's Law constant. As a final constraint, if we assume that there are no sources or sinks of chemical within the laminar sub-layers, then conservation of mass tells us that the flux through the water-side boundary layer must equal the flux through the air-side boundary layer. This constraint gives us,

$$(27) \qquad \dot{m} = -\,D_a A\left(\left.\frac{\partial C}{\partial z}\right|_{z=0}\right)_a = -\,D_w A\left(\left.\frac{\partial C}{\partial z}\right|_{z=0}\right)_w ,$$

flux through δa flux through δw

where D_a and D_w represent the molecular diffusion in air and water. Using the end-point concentrations to define the gradients in (27),

$$(28) \qquad -D_a A\frac{(Ca - Csa)}{\delta a} \;=\; -D_w A\frac{(Csw - Cw)}{\delta w} .$$

Noting that Csw = Csa/H, we solve for Csa in (28) and use this value in (27) to find,

Flux Across Air-Water Interface based on the Thin Film Model

$$(29) \qquad \dot{m} = \frac{(Cw - Ca/H)\,A}{\frac{\delta w}{D_w} + \frac{\delta a}{H\,D_a}} .$$

We can define two limits of (29). If $\delta w/D_w >> \delta a/(H\,D_a)$, the second term in the denominator of (29) may be dropped, and we arrive at

$$(30) \qquad \text{Water –Side Control [typically, } H >> 0.01\text{]:} \qquad \dot{m} = D_w A\frac{(Cw - Ca/H)}{\delta w} .$$

This limit is referred to as Water-Side Control, because the water-side boundary layer controls the flux through D_w and δw. The air side conditions, both δa and D_a, have no influence over the flux given in (30). At the other limit, $\delta w/D_w << \delta a/(H\, D_a)$, the first term in the denominator of (29) is dropped, and we arrive at,

(31) Air –Side Control [typically, $H << 0.01$]: $$\dot{m} = D_a A \frac{(HCw - Ca)}{\delta a} .$$

In this limit the flux depends only on the air side conditions, through δa and D_a, with no dependence on the water side conditions, specifically D_w and δw. The following table indicates that $\delta w/D_w$ is typically larger than $\delta a/D_a$ by a factor of 100. Then for $\delta w/D_w >> \delta a/(H\, D_a)$, $H >> (\delta a/Da)/(\delta w/Dw) = 0.01$. That is, the flux of a chemical with $H >> 0.01$ is water-side controlled. The flux of a chemical with $H << 0.01$ is air-side controlled.

Table 1. Typical Orders of Magnitude for Molecular Diffusion and Sub-Layer Thickness

	$D[cm^2s^{-1}]$	δ[cm] no wind	δ[cm] high wind	δ/D [s cm^{-1}] no wind	δ/D [s cm^{-1}] high wind
water-side	10^{-5}	10^{-2}	10^{-3}	1000	100
air-side	10^{-1}	1	0.1	10	1

Example. Flux of TCE from lake to atmosphere.
A lake of depth h = 10m and surface area, A, is polluted with the solvent TCE at a uniform concentration, Cw = 1 ppb [µg/l]. TCE is volatile so that it is slowly removed from the lake by a flux to the atmosphere. The Henry's Law constant for TCE is H = 0.4. Assume that strong, steady winds keep the lake well-mixed and rapidly remove the TCE that enters the atmosphere. Estimate the time for the TCE concentration in the lake to be reduced to 0.05 ppb.

Answer. Since we assume that the lake is well-mixed, $\partial C/\partial x = \partial C/\partial y = \partial C/\partial z = 0$. We will also assume there are no currents (u = v = w = 0). If we assume that there are no inflows or outflows of water volume, then the only sink for TCE is the atmosphere. With $H = 0.4 >> 0.01$, the flux of TCE is controlled by the water-side laminar sub-layer and can be modeled with (30). The evolution of chemical in the lake is then described by the following conservation of mass equation:

(32) $$\frac{\partial M}{\partial t} = Ah\frac{\partial Cw}{\partial t} = - D_w A \frac{(Cw - Ca/H)}{\delta w}$$

Note that although the flux from the lake to the atmosphere is positive, *i.e.* directed upward, the flux results in a loss from the lake volume, and so appears as a sink in (32).

If steady winds carry away all TCE that enters the atmosphere, the air concentration remains at zero, Ca = 0. Then, (32) reduces to,

$$(33) \qquad \frac{\partial Cw}{\partial t} = - \frac{D_w}{h \delta w} Cw \ .$$

This is a first-order reaction, with rate constant

$$(34) \qquad k = (D_w / h\, \delta w).$$

With initial concentration Cw = Cwo, the concentration in the lake evolves as,

$$(35) \qquad Cw(t) = Cwo \exp\left(- \frac{D_w}{h\ \delta w} t \right) = Cwo \exp(-kt) \, .$$

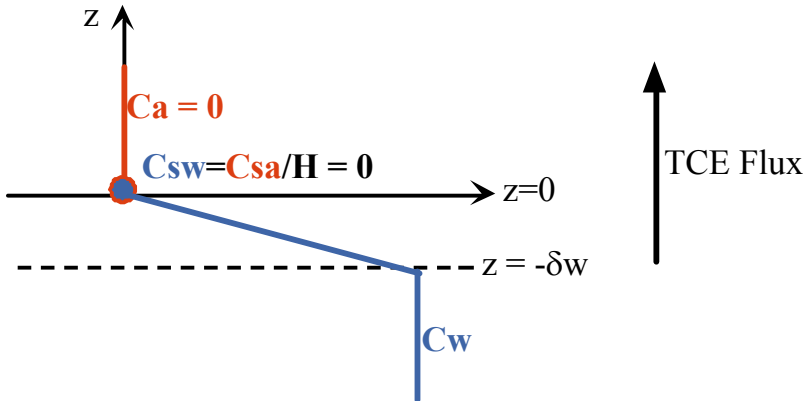

Figure 6. The flux of TCE from lake to atmosphere is controlled by the water-side laminar sub-layer. The air-side laminar sub-layer is negligible so that Csa = Ca. Furthermore, since Csw = Csa/H, Csw = 0 as well.

For windy conditions (Table 1), $k = (10^{-5} cm^2 s^{-1})/(0.001cm \times 1000cm) = 10^{-5}\ s^{-1}$. The time required for Cw to reach 0.05 ppb, or 0.05 Cwo is $t = 3/k = 3 \times 10^5$ s = 3.4 days. Given this time-scale, we will now assess the assumption that the concentration within the body of the lake remains uniform. For this to be true, the time-scale for vertical transport in the lake must be much shorter than the time-scale of the flux (T_{flux} = 3.4 days). If this is not so, then TCE will be depleted from the surface waters more rapidly than it is supplied from the lower waters through vertical mixing, and vertical gradients in concentration will develop in the lake. In fact, the vertical mixing time-scale, T_{mix}, would need to be at least an order of magnitude smaller than T_{flux} for the vertical transport within the lake to not limit the flux to the atmosphere. It is unlikely that a lake of 10-m depth would consistently mix over depth with time-scale $T_{mix} \leq 0.34$ days. So, we expect that the loss of TCE to the atmosphere will be somewhat limited by the rate of vertical transport within the lake. With this in mind, the estimate T_{flux} = 3.4 days is a lower limit for the time required to removed 95% of the TCE from the entire lake.

Surface Renewal Model for Air-Water Exchange

For the thin film model the laminar sub-layers in the air and water maintain their fluid identity over time, *i.e*. the fluid within these layers is assumed to be stagnant relative to the rest of the fluid domain. While this model is reasonable when the turbulence in the bulk of the fluid is weak, the stagnant film assumption breaks down under vigorous turbulence. Firstly, as the strength of the turbulence increases, the laminar sub-layer is diminished, and at some point becomes negligible. Secondly, vigorous turbulent eddies can carry parcels of fluid from the bulk fluid directly to the interface, breaking through the laminar sub-layer. When new patches of fluid arrive at the air-water interface they have the concentration of the bulk fluid. After they arrive at the interface, the patch immediately begins to move toward equilibrium with the concentration on the other side of the interface. Once the patch has reached equilibrium, flux across the interface in the area of the patch will cease. With this model the net flux across the interface depends on the frequency with which the layer of water adjacent to the interface is renewed.

As an example, we'll consider oxygen, whose flux is water-side limited ($H_{O2} = 26$), so that we need only consider surface renewal on the water side. Let's say that, on average, the layer of water adjacent to the surface is completely renewed in a time-scale $T_{renewal}$. In addition, when a new patch of fluid arrives at the surface, it requires a time-scale T_{eq} to equilibrate with the atmosphere. Two scenarios are possible. If $T_{renewal} < T_{eq}$, then the fluid adjacent to the interface will never reach equilibrium. If $T_{renewal} > T_{eq}$, then the fluid adjacent to the interface regularly reaches equilibrium, and when it does flux across the interface stops. These two cases are compared in Figure 7. Since the flux increases linearly with the concentration difference ($C_{patch} - Ceq$), the greatest flux occurs when the average value of this difference is maximized. As shown in Figure 7, short $T_{renewal}$, associated with vigorous turbulence, maintains the greatest concentration difference and thus the greatest flux across the interface.

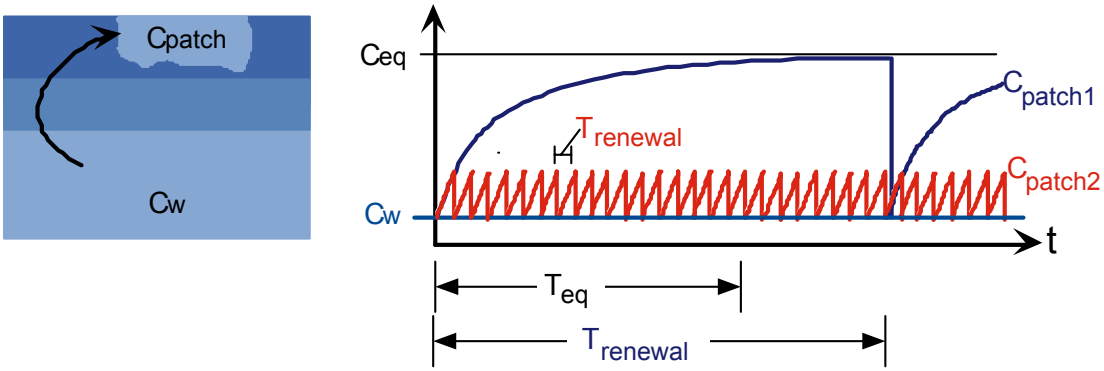

Figure 7. For case 1 (blue curve) the renewal time scale is longer than the equilibrium time-scale. For case 2 (orange curve) the renewal time scale is much shorter than the equilibrium time-scale. Greater flux is achieved in case 2, because the average concentration gradient across the interface ($C_{patch} - Ceq$) is larger.

To estimate the flux based on the surface renewal model, consider a single patch of fluid brought to the surface at time t = 0 and contacting area A of the interface. Before touching the surface (t<0) the concentration in the patch is Cw. As soon as the patch touches the surface, the fluid directly at the interface (z = 0) immediately equilibrates with the atmosphere, such that for $t \geq 0$, $C(z = 0) = Ceq = Csa/H$. This constant concentration boundary condition is similar to that below (21). Adapting the solution given in (22) for the case described here, letting z be positive downward for convenience, and remembering that for water-side control Csa = Ca, the concentration in the patch is

$$(36) \qquad C(z,t) = \left[\frac{Ca}{H} - Cw\right] \operatorname{erfc}\left(\frac{z}{2\sqrt{D_w t}}\right).$$

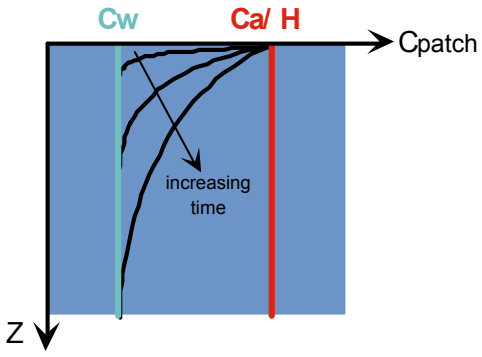

Figure 8. Diffusion of mass into a new patch brought to the surface at t = 0. Before patch arrives at surface (t < 0), C = Cw throughout the patch. For $t \geq 0$ the concentration at the patch-air interface (z = 0) is at equilibrium with the air, Ca/H.

Flux into this patch will proceed until a new patch replaces it at $t = T_{renewal}$. At that time the concentration front will have penetrated to $z = \delta_c = 4\sqrt{D_w T_{renewal}}$. The total mass that enters the patch in time $T_{renewal}$ can be estimated using (23) and (24).

$$(37) \qquad M \approx \overline{C}\, A\, \delta_c = 0.3 \left[\frac{Ca}{H} - Cw\right] A 4\sqrt{D_w T_{renewal}}$$

The net flux is then $\dot{m} = M / T_{renewal}$, or

$$(38) \qquad \dot{m} \approx A\left[\frac{Ca}{H} - Cw\right]\sqrt{\frac{D_w}{T_{renewal}}} \qquad \textit{Surface Renewal Model, Water-Side Control}$$

Consistent with Figure 7, the flux increases as $T_{renewal}$ decreases.

It is interesting to compare this flux with that predicted by the thin film model.

$$\dot{m} = D_w A \frac{(Cw - Ca/H)}{\delta w} \qquad \textit{Thin-Film Model, Water-Side Control}$$

Both models suggest that the flux is linearly dependent on the difference between the water concentration (Cw) and the equilibrium concentration (Ca/H). Also, both models suggest that the flux is dependent on flow conditions through the parameters $T_{renewal}$ and δw. These parameters decrease with increasing levels of turbulence, so both models predict an increase in flux with increasing turbulence strength. However, the models indicate different dependence on molecular diffusion. Field observations suggest a range of dependence, D_w^n, with n = 0.5 to 1. That the empirical exponent falls between those indicated by the models suggests that the flux is dependent on some combination of the two models. In general the surface renewal model is considered more appropriate for swiftly moving water (or turbulent flow), such as rivers, and the thin-film model is considered more appropriate for stagnant or quiet waters, such as lakes, and of course laminar flow conditins. Finally, if the concentration in the atmosphere is negligible, Ca ≈ 0, then both the Thin-Film and Surface Renewal Models reduce to first-order reactions, $\partial Cw/\partial t = k\, Cw$, with the following rate constants,

Thin-Film Model, Water-Side Control, Ca = 0, h = water depth

$$(39) \qquad k\ [s^{-1}] = \frac{D_w}{h\ \delta w}$$

Surface Renewal Model, Water-Side Control, Ca = 0, h = water depth

$$(40) \qquad k\ [s^{-1}] = \frac{\sqrt{D_w / T_{renewal}}}{h}.$$

To apply (39) or (40) one must estimate the physical parameter δw or $T_{renewal}$. Prediction of either parameter can be difficult in the field, requiring a careful characterization of turbulence structure, which depends on flow speed, bed roughness, channel non-uniformity, and the presence and strength of waves. However, since these parameters are associated with the physical aspects of the flow, they must be the same for all chemicals. So, if one knows the exchange rate for one chemical that is water-side controlled, and thus dependent on δw or $T_{renewal}$, then one can use (39) or (40) to estimate it for a different chemical in the *same system* and *under the same flow conditions*. For example, if I know the exchange rate for chemical B, k_B, with molecular diffusion, Dw_B, then I can estimate the exchange rate for chemical C, k_C, with molecular diffusion, Dw_C.

$$(41) \qquad \text{Thin-Film Model, Water-Side Control: } \frac{k_B}{k_C} = \frac{D_{wB}}{D_{wC}}$$

$$(42) \qquad \text{Surface Renewal Model, Water-Side Control: } \frac{k_B}{k_C} = \sqrt{\frac{D_{wB}}{D_{wC}}}.$$

A similar analogy will hold between two chemicals that are both air-side controlled, with all physical parameters then referring to the air-side, i.e. D_a, $T_{renewal}$, δa.

9.4 Partitioning to a Solid

In the previous section we considered how chemical partitioning between air and water phases affects transport. In this section we consider how partitioning between solid and water phases, a process called sorption and desorption, affects transport. There are two types of sorption. In *adsorption* the chemical sticks to the surface of the solid. In *absorption*, the chemical enters into the matrix of the solid, *i.e.* diffusing into the solid volume. The fraction of chemical that will sorb onto the solid phase is described by a partitioning coefficient, K_d. Like the Henry's Law constant, the solid/water phase partitioning coefficient describes the ratio of concentrations in each phase *in equilibrium*.

$$(43)\quad K_d = \frac{\text{concentration associated with solid [mass chemical/mass solid]}}{\text{concentration in water[mass / volume water]}}$$

K_d is typically reported in the units, $\frac{\text{mg / mg - solid}}{\text{mg / liter}}$.

In general, if a chemical can partition to a stationary solid phase, such as the soil matrix in groundwater flow or the channel walls in surface flow, then its transport will be slowed relative to chemicals that do not partition to the boundary. This is true for both advective and dispersive transport. To demonstrate this, consider sub-surface flow through soil directed along the x-axis. For simplicity, we assume uniform conditions in the cross-stream direction, *i.e.* $\partial/\partial y = \partial/\partial z = 0$. We define a control volume of length dx and cross-sectional area A, as shown in Figure 9. The soil has porosity, n, and the mean pore velocity is u_P. The conservation of mass for this control volume is,

$$(44)\quad \frac{\partial M}{\partial t} = \left[u_p C_w An\right]_1 - \left[u_p C_w An\right]_2 + \left[-K_x \frac{\partial C_w}{\partial x} An\right]_1 - \left[-K_x \frac{\partial C_w}{\partial x} An\right]_2,$$

advection in advection out dispersion at 1 dispersion at 2

with K_X the dispersion coefficient. Note that only the water-phase concentration, C_W, is included in the flux terms of (44), because only mass in the water-phase is advected and dispersed by the fluid motion. The solid-phase concentration, C_S, is immobile. If the time-scale for the chemical to partition between the two phases is negligible, then we may assume that the chemical is everywhere and always at equilibrium, so that

$$(45)\quad K_d \left[\frac{\text{mg / mg - solid}}{\text{mg / liter}}\right] = \frac{C_s}{C_w}.$$

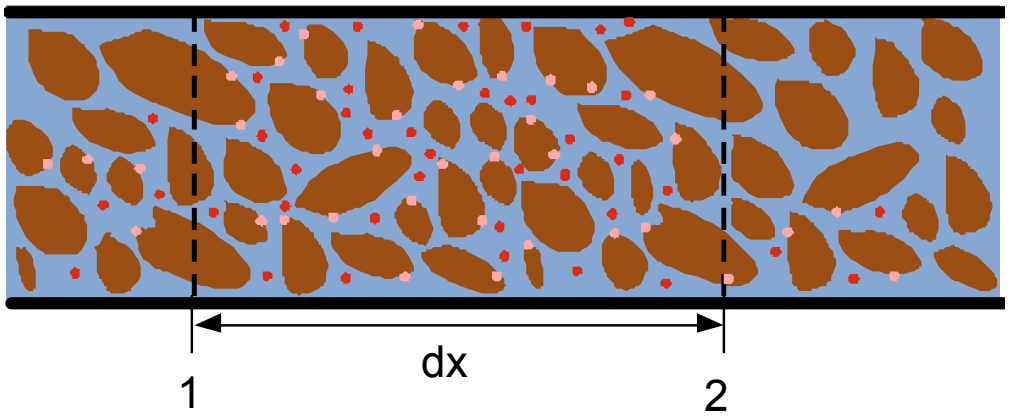

Figure 9. Boundaries at 1 and 2 define a one-dimensional, sub-surface control volume with cross-sectional area A. The soil matrix is shown in brown and the groundwater in blue. The chemical mass is partitioned between the water phase (red dots) and the solid phase (pink dots). At equilibrium the ratio of concentrations in the solid phase (C_s) and water phase (C_w) is given by the partition coefficient, $K_d = C_s/C_w$.

If C_w and $\partial Cw/\partial x$ are a continuous function in x, we can approximate, $C_{W2} = C_{W1} + (\partial C_W/\partial x)\, dx$, and $\partial C_W/\partial x|_2 = \partial C_W/\partial x|_1 + (\partial^2 C_W/\partial x^2)\, dx$. Then, (44) becomes,

$$(46) \qquad \frac{\partial M}{\partial t} = -u_p An \frac{\partial C_w}{\partial x} dx + K_x An \frac{\partial^2 C_w}{\partial x^2} dx .$$

The total mass, M, includes both the solid and water phase components. Defining the bulk density of the soil matrix as ρ_B = mass of solid matrix per unit volume, V = Adx, then the total mass in the control volume can be written,

$$(47) \qquad M = C_W\, n\, V + \rho_B V\, C_S .$$

We define a total concentration,

$$(48) \qquad C = M / V .$$

Combining (45), (47) and (48) we can write

$$(49) \qquad C_w = \frac{C}{\left(n + \rho_B K_d\right)} .$$

Using (49) in (46), and assuming that the porosity, n, and bulk density, ρ_B, are not functions of x, then

$$(50) \qquad \frac{\partial M}{\partial t} = V\frac{\partial C}{\partial t} = -u_p A\left[\frac{n}{n+\rho_B K_d}\right]\frac{\partial C}{\partial x} dx + K_x A\left[\frac{n}{n+\rho_B K_d}\right]\frac{\partial^2 C}{\partial x^2} dx .$$

Eliminating V = A dx from both sides, we are left with,

$$(51) \qquad \frac{\partial C}{\partial t} = - f u_p \frac{\partial C}{\partial x} + f K_x \frac{\partial^2 C}{\partial x^2},$$

in which f represents the fraction of total mass that is in the water phase. Because only this mass is mobile, f is called the mobile fraction, and f is defined in (50) as,

$$(52) \qquad \text{Mobile Fraction, } f = \frac{n}{n + \rho_B K_d}.$$

The inverse of the mobile fraction is called the retardation factor, $R = f^{-1}$. Using this nomenclature, (51) is written as,

$$(53) \qquad \frac{\partial C}{\partial t} = - \frac{u_p}{R} \frac{\partial C}{\partial x} + \frac{K_x}{R} \frac{\partial^2 C}{\partial x^2}.$$

From either (51) or (53) one quickly recognizes the impact of partitioning to transport. Specifically, both the velocity (u_P) and the dispersion (K_X) are modified by the coefficient $f = R^{-1}$. If f = 1, all chemical is in the water phase, and we recover the one-dimensional transport equation for non-partitioning species. If f < 1, *i.e*. some fraction of the mass is associated with the immobile solid phase, the net advection and the net dispersion is reduced by the factor f. This effect is best demonstrated by comparing the transport of two chemicals, one which partitions and one which does not. For an instantaneous release of mass M at x = 0, the concentration field downstream is,

Chemical 1: Partitioning [f < 1]

$$C1(x,t) = \frac{M}{A\sqrt{4\pi f K_x t}} \exp(-(x - f u_p t)^2 / 4 f K_x t).$$

Chemical 2: Non-Partitioning [f = 1]

$$C2(x,t) = \frac{M}{A\sqrt{4\pi K_x t}} \exp(-(x - u_p t)^2 / 4 K_x t)$$

Remember that C1 and C2 represent a total concentration, C, as defined in (48). In each case, the concentration in the water phase is given by (49), or simply $C_w = (f/n)\, C$. The spatial distribution of C is shown for each release in Figure 10. At time t after the release, the partitioning chemical has traveled less distance, x1 < x2, and has undergone less longitudinal spreading, $\sigma 1 < \sigma 2$, then the chemical that does not partition.

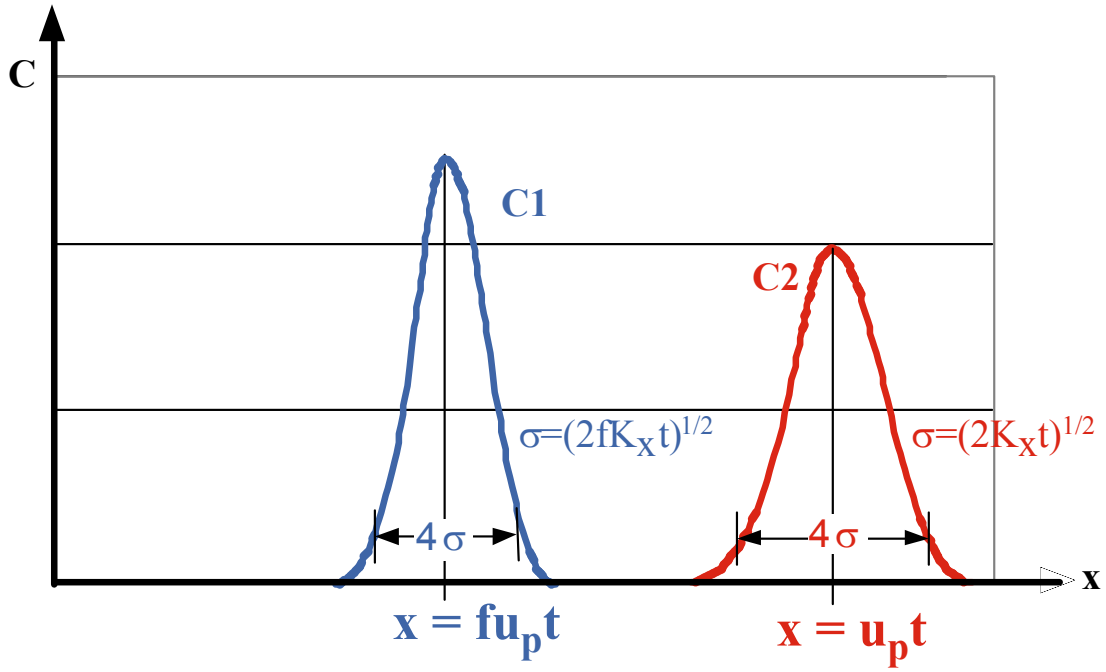

Figure 10. The same mass, M, of two different chemicals is released instantaneously into a one-dimensional groundwater system. The chemicals are released at x = 0. The soil porosity, n = 0.4. Chemical 1 does partition to solid phase. Chemical 2 does not partition to solid phase. The mobile fraction of chemical 1 is f = 0.5. The figure shows the distribution of total concentration, C1 and C2, at time t after the release. The partitioning chemical (C1) has traveled less distance and has spread (σ) over a smaller longitudinal extent then the non-partitioning chemical (C2).

As a final point, let us examine the assumption that the dissolved and sorbed phases are always in equilibrium. Consider a chemical cloud migrating through the subsurface. The length scale of the cloud in the streamwise direction is 4σ, *e.g.* as in Figure 10. If the mean pore velocity is u_P, the time-scale for the cloud to advect one cloud length is $T_U = 4\sigma/u_P$. T_U represents the duration of time that any part of the soil matrix is exposed to the chemical cloud. Suppose the chemical can sorb to the soil matrix and does so with reaction rate, k[s^{-1}]. If $k^{-1} << T_U$, then the duration of exposure to each dissolved phase concentration will be long compared to the time-scale for sorption/desorption to occur, and the sorbed phase can easily remain in equilibrium with the local dissolved phase concentration. Under these conditions, the retardation model described above will apply. If, however, $k^{-1} >> T_U$, the time-scale for sorption/desorption to occur is long compared to the duration of dissolved phase exposure, and the sorbed phase will not be in equilibrium with the dissolved phase concentration. Sorbed chemical will remain sorbed (and thus stationary) long after the dissolved phase cloud has passed. Because the sorbed phase is delayed relative to the dissolved phase, slow sorption processes ($k^{-1} >> T_U$) increase the longitudinal dispersion of the cloud, as depicted in Figure 5 of Chapter 8.

VALUES OF THE ERROR FUNCTION, erf(x), AND COMPLEMENTARY ERROR FUNCTION, erfc(x), FOR POSITIVE VALUES OF x.

x	erf(x)	erfc(x)	x	erf(x)	erfc(x)
0	0	1.0	1.1	0.880205	0.119795
0.05	0.056372	0.943628	1.2	0.910314	0.089686
0.1	0.112463	0.887537	1.3	0.934008	0.065992
0.15	0.167996	0.832004	1.4	0.952285	0.047715
0.2	0.222703	0.777297	1.5	0.966105	0.033895
0.25	0.276326	0.723674	1.6	0.976348	0.023652
0.3	0.328627	0.671373	1.7	0.983790	0.016210
0.35	0.379382	0.620618	1.8	0.989091	0.010909
0.4	0.428392	0.571608	1.9	0.992790	0.007210
0.45	0.475482	0.524518	2.0	0.995322	0.004678
0.5	0.520500	0.479500	2.1	0.997021	0.002979
0.55	0.563323	0.436677	2.2	0.998137	0.001863
0.6	0.603856	0.396144	2.3	0.998857	0.001143
0.65	0.642029	0.357971	2.4	0.999311	0.000689
0.7	0.677801	0.322199	2.5	0.999593	0.000407
0.75	0.711156	0.288844	2.6	0.999764	0.000236
0.8	0.742101	0.257899	2.7	0.999866	0.000134
0.85	0.770668	0.229332	2.8	0.999925	0.000075
0.9	0.796908	0.203092	2.9	0.999959	0.000041
0.95	0.820891	0.179109	3.0	0.999978	0.000022
1.0	0.842701	0.157299			