11. Reaction and interfacial exchange CONTINUED

11.1 Exchange Across an Air- water Interchange

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

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

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.

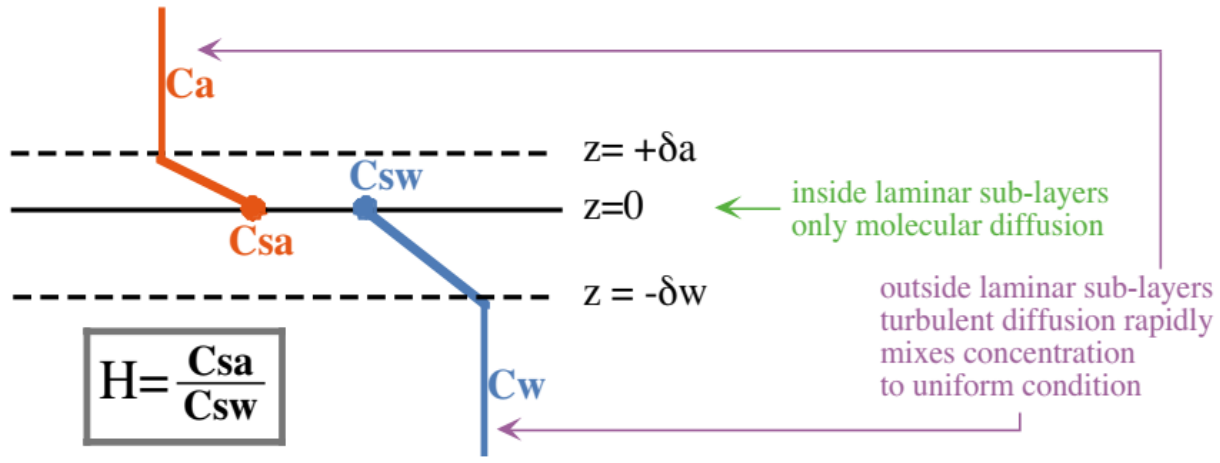


Figure 5. The Thin-Film Model describes the exchange of volatile species across the air-water interface under conditions for which transport is limited by diffusion across the laminar sub-layers. At the surface (z = 0) the aqueous phase (Csw) is in equilibrium with the concentration in air (Csa), such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

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

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

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

	$D[cm^2 s^{-1}]$	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:

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

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,

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

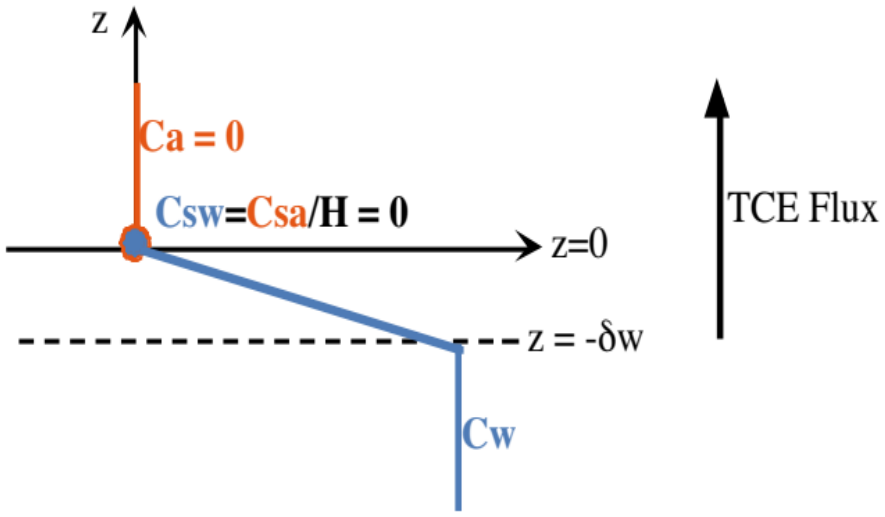


Figure 6. The flux of TCE from lake to atmosphere is controlled by the water-side laminar sub-layer. The air-side laminar sub-layer is negligible so that Csa = Ca. Furthermore, since Csw = Csa/H, Csw = 0 as well.

For windy conditions (Table 1), $k = (10^{-5}cm^2s^{-1})/(0.001cm \times 1000cm) = 10^{-5}\ s^{-1}$. 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.

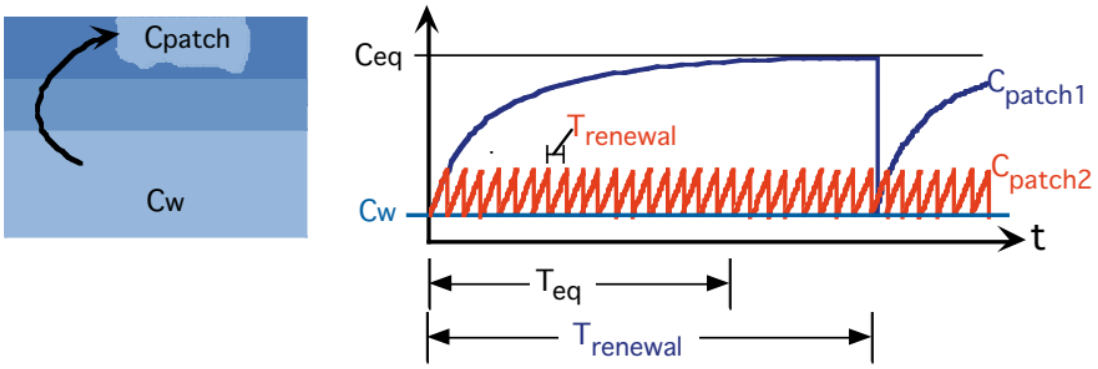


Figure 7. For case 1 (blue curve) the renewal time scale is longer than the equilibrium time-scale. For case 2 (orange curve) the renewal time scale is much shorter than the equilibrium time-scale. Greater flux is achieved in case 2, because the average concentration gradient across the interface (C_{patch}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

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

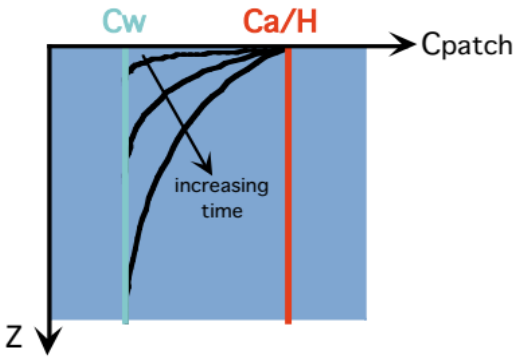


Figure 8. Diffusion of mass into a new patch brought to the surface at t = 0. Before patch arrives at surface (t < 0), C = Cw throughout the patch. For t ≥ 0 the concentration at the patch-air interface (z = 0) is at equilibrium with the air, Ca/H.

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).

$$(37) \quad M \approx \overline{C}\, A\, \delta_c = 0.3 \left[\frac{Ca}{H} - Cw\right] A4\sqrt{D_w T_{renewal}}$$

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

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

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

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

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

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

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

(42) 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.

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

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

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

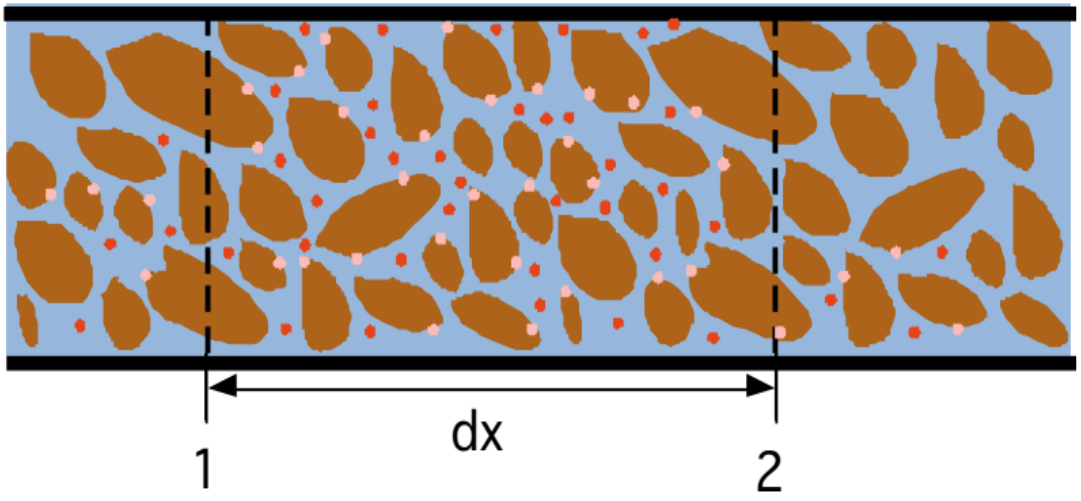


Figure 9. Boundaries at 1 and 2 define a one-dimensional, sub-surface control volume with cross-sectional area A. The soil matrix is shown in brown and the groundwater in blue. The chemical mass is partitioned between the water phase (red dots) and the solid phase (pink dots). At equilibrium the ratio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

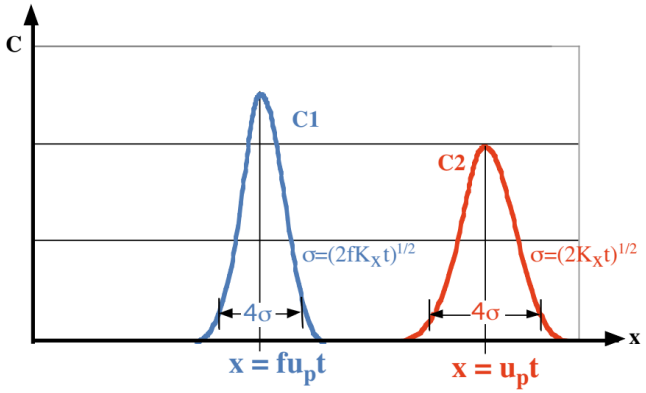


Figure 10. The same mass, M, of two different chemicals is released instantaneously into a one-dimensional groundwater system. The chemicals are released at x = 0. The soil porosity, n = 0.4. Chemical 1 does partition to solid phase. Chemical 2 does not partition to solid phase. The mobile fraction of 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			

EXERCISES WITH SOLUTIONS

Problem 1

You have identified a point source of TCE that is contaminating a small stream. The stream is h=20 cm deep, b=80 cm wide and flows at U = 10 cm/s. At the source (x = 0) the TCE mixes quickly across the channel depth and width with the resulting initial concentration, $C(x=0)=C_o=10$ ppb. You wish to determine if there are additional sources of TCE to the river. Because TCE is volatile and the concentration in the atmosphere is negligible, you know there is a flux of TCE from the river to the atmosphere. The Henry's Law constant for TCE is $H_{TCE} = 0.42$, indicating that the flux is water-side controlled. Because of the flux to the atmosphere, you expect the TCE concentration to decline downstream. Indeed, 2 km downstream of the known source $C_{2km} = 5$ ppb. To determine the rate of water-air exchange for the TCE you inject and measure the concentration of Propane [$H_{propane} = 0.42$] along the stream. From this study you find that $K_{propane} = 1.5 \times 10^{-4}\ s^{-1}$. The molecular diffusion coefficients for TCE and Propane in water are $D_{w,\,TCE} = 0.75 \times 10^{-5}\ cm^2s^{-1}$ and $D_{w,\,Propane} = 1.3 \times 10^{-5}\ cm^2s^{-1}$.

Determine if additional sources of TCE exist along the reach x = 0 to 2 km.

Problem 2

A small pond is h = 1 m deep with a surface area A. Three chemicals are spilled into the pond and rapidly mixed over the volume. The chemicals are the pesticide Lindane (w/ Henry's Law constant $H_L = 2.2 \times 10^{-5}$), the solvent Toluene ($H_T = 0.28$), and Napthalene ($H_N = 0.04$). Assume that mixing is sufficient to maintain a uniform concentration of each chemical within the bulk of the lake volume, i.e. below the laminar sub-layer at the surface.

Molecular diffusivity in air, $D_a = 10^{-5}\ m^2s^{-1}$ for all chemicals

Molecular diffusivity in water, $D_w = 10^{-9}\ m^2s^{-1}$ for all chemicals

Turbulent diffusivity in water, $D_{tw} = 10^{-3}\ m^2s^{-1}$

Waterside laminar sub-layer, $\delta_w = 100\ \mu m$

Airside laminar sub-layer, $\delta_a = 10$ mm

a) Sketch the profile of C (z) for each chemical. Indicate the concentration at z = 0, the air-water interface; at $z = -\delta_w$; at $z < -\delta_w$; and at $z = +\delta_a$. Assume that the atmosphere is a perfect sink for each chemical, such that $C_a = 0$ for $z > +\delta_a$.

b) Write an equation for the mass flux at the air-water interface for each chemical.

c) For each chemical determine the time at which only 5% of the original mass remains.

d) For which chemicals is the assumption of a uniform concentration within the bulk fluid appropriate?

Problem 3

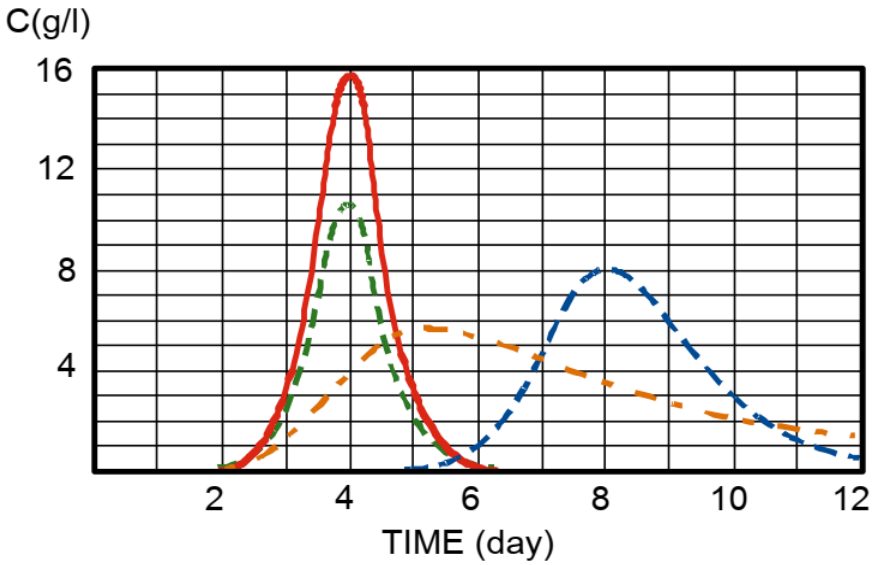
A mixture containing an equal mass of four chemicals is released as a pulse into a groundwater aquifer. The concentration of each chemical is measured in the pore water at a monitoring well located 8-m from the injection. Match the following descriptions to the correct curves.

Chemical 1 is a conservative tracer that does not react or degrade.

Chemical 2 does not adsorb to the grains, but is degraded by microbes living in the aquifer. What is the rate of degradation, K_d [day^{-1}]?

Chemical 3 readily adsorbs to organic material. The rate of adsorption/desorption is so rapid that the water/organic matter partitioning is always at equilibrium. What fraction of this chemical is associated with the pore water, *i.e.* is in the mobile phase?

Chemical 4 adsorbs to organic material, but at a rate that is much slower than that of chemical 3, such that the solid/water partitioning is never at equilibrium. What is the order of magnitude of the rate constant describing the adsorption/desorption reaction?



EXERCISE – SOLUTIONS

Answer 1

Since Propane and TCE are both water-side controlled [H >> 0.01], from Chapter 9 we expect the rate constants describing their exchange with the atmosphere to have the following ratios:

Thin-Film Model, Water-Side Control

$$\frac{K_{TCE}}{K_{Propane}} = \frac{D_{wTCE}}{D_{wPropane}}$$

Surface Renewal Model, Water-Side Control

$$\frac{K_{TCE}}{K_{Propane}} = \sqrt{\frac{D_{wTCE}}{D_{wPropane}}}.$$

The channel Reynolds number based on hydraulic radius is Re_{RH}=13,000, indicating that the flow is turbulent. As described in the text, empirical evidence suggests that the surface renewal model is more appropriate for turbulent flows. Using this model, K_{TCE} = 1.1 x 10^{-4} s^{-1}.

Given that the atmospheric concentration of TCE is negligible, the flux of TCE to the atmosphere can be represented by the first-order sink, $S = -K_{TCE}C$, in the mass balance equation for the stream. As a first guess, we assume that this is the only source/sink of TCE along the stream. Assume that the cross-section has uniform concentration, *i.e.* with rapid mixing, $\partial C/\partial y = \partial C/\partial z = 0$. Assume the system is at steady-state ($\partial C/\partial t = 0$). Then, the mass balance equation is $u\partial C/\partial x = -K_{TCE}C$. With an upstream boundary condition, $C = C_o$ = 10 ppb at x = 0, the concentration downstream of the source will be

$C(x) = C_o \exp(-K_{TCE}x/u)$.

Evaluating this at x = 2000m,

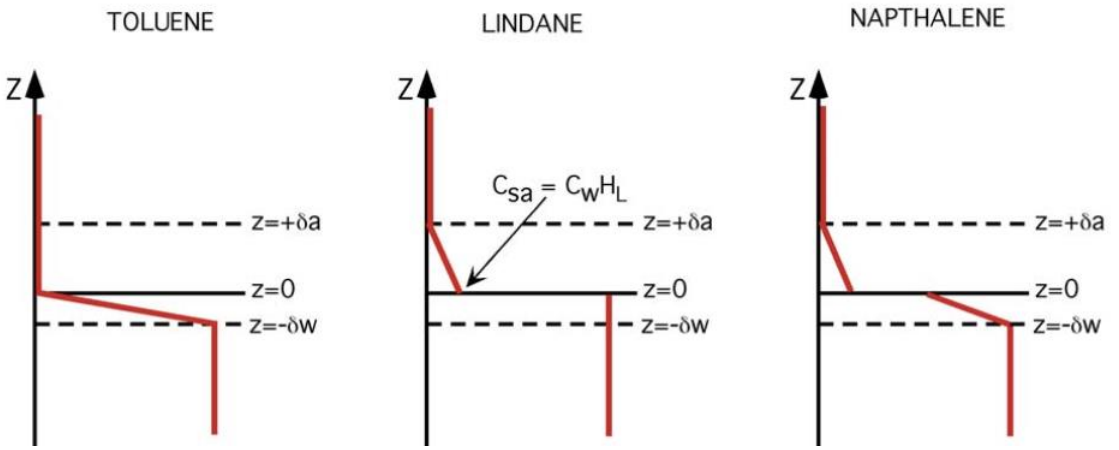
$C(x = 2km) = 10ppb \exp(-(1.1 \times 10^{-4}\ s^{-1})(2000m)/(0.1ms^{-1})) = 1.1$ ppb.

The estimated concentration is much less than the measured concentration at this position (C = 5 ppb). This suggests that there is another source of TCE between x = 0 and 2 km.

Answer 2

Toluene [$H_T = 0.28 >> 0.01$] is waterside controlled
Lindane [$H_L = 2.2 \times 10^{-5} << 0.01$] is airside controlled
Napthalene [$H_N = 0.04 \approx 0.01$] is controlled by both air and water side conditions.

(a) Sketch the profile of C (z) for each chemical



b) Write an equation for the mass flux at the air-water interface for each chemical.
c) For each chemical determine the time at which only 5% of the original mass remains.

TOLUENE	LINDANE	NAPTHALENE
$\dot{m} = D_w A \frac{C_w}{\delta_w}$	$\dot{m} = D_a A \frac{C_w H_L}{\delta_a}$	$\dot{m} = A \frac{C_w}{[(\delta_w / D_w) + \delta_a / (H_N D_a)]}$
$\frac{\partial C_w}{\partial t} = -\left[\frac{D_w}{\delta_w h}\right] C_w$	$\frac{\partial C_w}{\partial t} = -\left[\frac{D_a H_L}{\delta_a h}\right] C_w$	$\frac{\partial C_w}{\partial t} = -\frac{C_w / h}{(\delta_w / D_w) + \delta_a / (H_N D_a)}$
$C_w(t) = C_o \exp\left(-\frac{D_w}{\delta_w h} t\right)$	$C_w(t) = C_o \exp\left(-\frac{D_a H_L}{\delta_a h} t\right)$	$C_w = C_o \exp\left(-\frac{t}{\left[\frac{\delta_w}{D_w} + \frac{\delta_a}{H_N D_a}\right] h}\right)$
$T_{5\%} = \frac{3\delta_w h}{D_w} = 3 \times 10^5 s$	$T_{5\%} = 3\frac{\delta_a h}{D_a H_L} = 1.4 \times 10^8 s$	$T_{5\%} = 3h\left[\frac{\delta_w}{D_w} + \frac{\delta_a}{H_N D_a}\right]$ $= 3.8 \times 10^5 s$

d) For which chemicals is the assumption of a uniform concentration within the bulk fluid appropriate?
The mixing time is, $T_D = h^2/(4D_t) = (1m)^2/(4x0.001\ m^2s^{-1}) = 250$ s. For every chemical $T_D << T_{5\%}$, so the assumption of well-mixed conditions in the lake are appropriate for each chemical.

Answer 3

Chemical 1 is a conservative tracer that does not react or degrade.
The peak of the non-adsorbing, non-degrading chemical will arrive soonest and with the highest concentration. This corresponds to the red curve. From the peak arrival time we can estimate the velocity, u = 8m/4day = 2 md^{-1}.

Chemical 2 does not adsorb, but is degraded by microbes living in the aquifer.
This chemical does not adsorb, and so has no retardation. Its peak will arrive with that of chemical 1, but with a diminished concentration. This corresponds to the green curve. Specifically, C2(t) = C1(t) exp(-kt). Using the peak values at $T_{1,2}$ = 4 days, $C2_{peak}$ /$C1_{peak}$ = (10.5/15.8) = exp(-kt), from which

$$k2 = -\ln(C2/C1)/t = -\ln(10.5/15.8) / (4\ days) = 0.1\ d^{-1}.$$

Both Chemical 3 and 4 adsorb to the soil matrix, and so experience some retardation, as seen in the orange and blue curves. However, Chemical 4 has a slow adsorption process, and so will not be in equilibrium. Slow sorption leads to additional dispersion. This is consistent with the orange curve. Chemical 3 therefor corresponds to the blue curve.

Chemical 3 adsorbs rapidly and the partitioning is always at equilibrium.
Blue Curve. The transport of this plume is slowed because at any time only the fraction f of the mass is in the dissolved phase and subject to fluid transport. Specifically, the plume advects at the speed fu rather than u. We can estimate f by comparing the peak arrival time with that of the non-adsorbing chemical. Specifically, $T_{1,2}$ = L/u and T_3 = L/(fu), so that f = $T_{1,2}$ / T_3 = 4 d / 8 d = 0.5.

Chemical 4 adsorbs so that the partitioning is not at equilibrium.
From the discussion above, this corresponds to the orange curve. The rate of sorption/desorption must be slow compared to the transport time scales. Using the observed transport scale, $k4^{-1} >> 5$ d, or $k4 << 0.2\ d^{-1}$.