Chapter 4
Transport in the Environment

John S. Gulliver

Glossary

Adsorption	The process of dissolved chemicals sticking to a solid.
Convection	The movement of a constituent with movement of the fluid.
Desorption	The detachment of a chemical from a solid.
Diffusion	The spreading of fluid constituents through the motion inherent to atoms and molecules.
Diffusion coefficient	A coefficient that describes the tendency of molecules to spread a constituent mass.
Dirac delta	An impulse of a given quantity (mass) that occurs over an infinitely short time or space.
Kinematic viscosity	The fluid viscosity divided by the fluid density, resulting in units that are similar to a diffusion coefficient, or length squared per time.
Laminar flow	Flow that has no turbulent eddies, where the fluid flows in laminas and diffusion creates the mixing of the fluid.
Retardation factor	A divisor that indicates the slowing of chemical movement through a media due to adsorption.
Reynolds number	The ratio of inertial to viscous forces, resulting in a meaningful velocity times a meaningful distance divided by kinematic viscosity.

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Definition of Transport in the Environment

In this section various solution techniques for the convection-diffusion equation are reviewed, which is generally defined as the mass transport equation with diffusive terms. These techniques will be applied to chemical transport solutions in sediments. There are also a number of applications to chemical transport in biofilms. There are many other applications of the convection-diffusion equation, but they require more background with regard to the physics of mixing processes, which will be addressed in later sections of the volume.

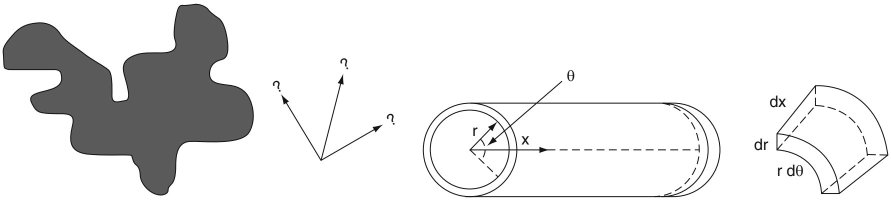
Introduction

What is *mass (or chemical) transport*? It is the transport of a solute (the dissolved chemical) in a solvent (everything else). The solute is the dissolvee and the solvent is the dissolver. There are liquids that are generally classified as solvents because they typically play that role in industry. Some examples would be degreasing and dry-cleaning solvents, such as trichloroethylene (TCE). In environmental applications, these "solvents" are the solutes, and water or air is usually the solvent. In fact, when neither water nor air are the solvents, a general term "nonaqueous phase liquid," or NAPL, is applied. NAPL is defined as a liquid that is not water, which could be composed of any number of compounds.

The substance being transported can either be dissolved (part of the same phase as the solvent) or particulate substances. The diffusion equation will also be discussed by considering mass conservation in a fixed control volume. The mass conservation equation can be written as:

$$\begin{aligned} &Flux\ rate\,IN - Flux\ rate\,OUT + Rate\ of \\ &(Sources - Sinks) = Rate\ of\ Accumulation \end{aligned} \tag{4.1}$$

Now that there is our mass conservation equation, it must be decided which control volume would be the most convenient for our applications. The control volumes used most for this type of mass balance are given in Fig. 4.1. The general control volume, given in Fig. 4.1a, is used for descriptive purposes, to maintain generality. It is rare that one works with something that approximates such a contorted control volume. The control volumes that are used in practice are given in Fig. 4.1b, c, and d. For the environmental applications of chemical transport, the rectangular control volume, Fig. 4.1b, has proven to be the most useful. The cylindrical control volume, Fig. 4.1c, is used to make pipe or tube flow problems easier to solve, and the spherical control volume, Fig. 4.1d, is often helpful when dealing with transport in and around particles

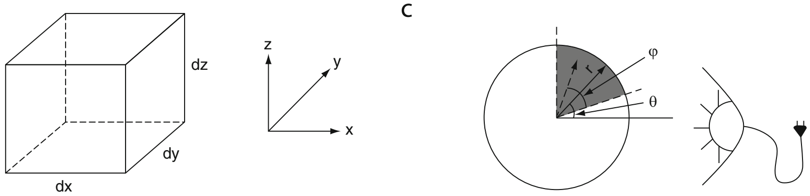


General control volume

a

Cylindrical control volume

c



Rectangular control volume

b

Spherical control volume

d

Fig. 4.1 Common control volumes found in engineering texts and (for the latter three) used in solving the diffusion equation. (From [1])

or drops. For this control volume, it is convenient to imagine a light being shined along the axis, which casts a shadow of the vector on to a plane normal to the light. The φ angle is measured from the reference axis to the shadow in this plane.

A rectangular control volume will be used for the development of our mass conservation (diffusion) equation.

Development of the Diffusion Equation

The diffusion equation will be developed by considering each term in Eq. 4.1 separately. In addition, the flux terms will be divided into diffusive and convective flux rates.

Diffusive Flux Rate

The molecules of a fluid “at rest” are still moving because of their internal energy. They are vibrating. In a solid, the molecules are held in a lattice. In a gas or liquid, they are not, so they move around because of this vibration. Since the molecules are vibrating in all directions, the movement appears to be random. Diffusive fluxes are

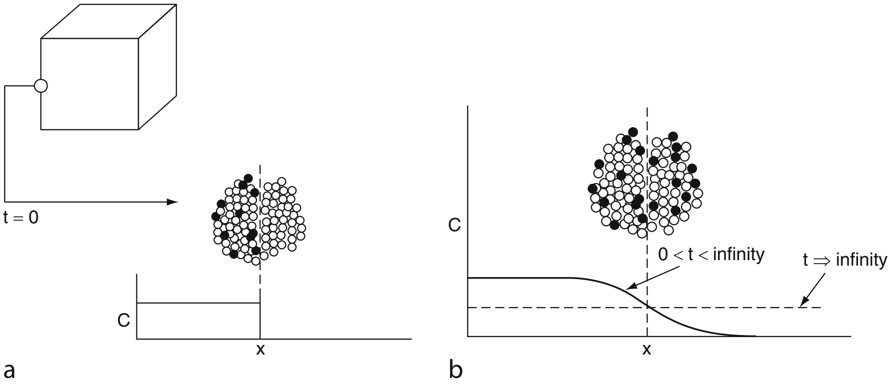


Fig. 4.2 Illustration of net diffusive flux through one side of the rectangular control volume. (From [1])

described by Fick's law [9], given in the section by Dr. Cussler on diffusion. For this purpose, let us consider one side of our control volume, normal to the x-axis, with an area A_x, shown in Fig. 4.2. Fick's law describes the diffusive flux rate as:

$$\begin{aligned}&\text{Diffusive flux rate (g/s)}\\&= -\mathrm{D}\,(\mathrm{m}^2/\mathrm{s})\,\frac{\partial C}{\partial x}\,(\mathrm{g}/\mathrm{m}^4)\,A_x(m^2)\end{aligned} \tag{4.2}$$

where C is concentration of the solute (tracer), D is the diffusion coefficient of the solute in the solvent (water), which relates to how fast how and far the tracer molecules are moving to and fro, and $\partial C/\partial x$ is the gradient of concentration with respect to x, or the slope of C with x, as shown in Fig. 4.2. Thus, the diffusive flux rate depends upon the diffusion coefficient and the *gradient* of concentration with distance.

Convective Flux

The convective flux rate into our control volume is simply the chemical mass carried in by convection. If the same box of Fig. 4.2 is considered, except with a velocity component u in the x-direction, the convective flux rate into the box from the left-hand side is:

$$\begin{aligned}&\text{Convective flux rate (g/s)} = \text{Velocity component}\\&\text{normal to surface (m/s)} \times \text{Surface area } (\text{m}^2)\\&\times \text{ Concentration } (\text{g/m}^3)\end{aligned} \tag{4.3}$$

or

$$\text{Convective flux rate} = uA_xC \tag{4.4}$$

where u is the component of velocity in the x-direction and A_x is the surface area normal to the x-axis on that side of the box. All six sides of our box would have a convective flux rate through them, just as they would have a diffusive flux.

Rate of Accumulation

The rate of accumulation is the change of chemical mass per unit time, or:

$$\text{Rate of accumulation (g/s)} = V\!\!\!\!-(\text{m}^3)\frac{\partial C}{\partial t}(\text{g/m}^3/\text{s}) \tag{4.5}$$

where $V\!\!\!\!-$ is the volume of our box.

Source and Sink Rates

The solute chemical can appear or disappear through chemical reaction. In addition, interfacial transfer is often integrated over the control volume and considered as a source or sink throughout the control volume. This type of pseudo-reaction can be of significant help in solving chemical transport problems when averages over a larger control volume, such as cross-sectional mean concentrations, are being computed. For both cases (chemical reactions and pseudo-reactions), the source and sink rates are given as:

$$\text{Source} - \text{sink rate (g/s)} = S\,(\text{g/m}^3/\text{s})V\!\!\!\!-(\text{m}^3) \tag{4.6}$$

where S is the net source/sink rate per unit volume. The particular reactions that a given chemical is likely to undergo will determine the form of S used in Eq. 4.6. These are listed in Table 4.1. The source/sink term could be a combination of two or more of these reactions. For convenience in determining analytical solutions to

Table 4.1 Common source and sink terms used in the convection-diffusion equation

Source/sink name	Equation	Units of constant
Zero order	$S = k_o$	k_o – g/m^3-s
First order	$S = k_1 C$	k_1 = S^{-1}
Second order	$S = k_2 C^2$	k_2-m^3/g-s
Independent variable	$S = k_{1i}\, P^a$	k_{1i} – s^{-1}
	$S = k_{2i}\, PC^b$	k_{2i} – m^3/g-s
Monod kinetics[c]	$S = \frac{\mu_m C}{k_c + C} P$	μ_m = maximum growth rate (s^{-1}) k_c = half-saturation coefficient (g/m^3)

[a] If P is nearly constant, then k_{1i} can be provided as a zero-order term
[b] Often called second order
[c] Common for biologically mediated reactions

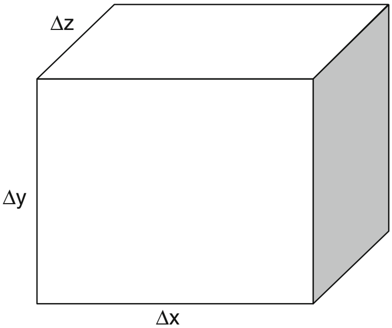


Fig. 4.3 Dimension of the rectangular control volume

the diffusion equation, most source/sink terms are approximated as either a first-order or zero-order reaction.

Mass Balance on Control Volume

A mass balance on one compound in our box is based upon the principle that whatever comes in must do one of three things: be accumulated in the box, flux out of another side, or react in the source/sink terms. If it seems simple, it is.

We will begin by assigning lengths to the sides of our box of dx, dy, and dz, as shown in Fig. 4.3. Then, for simplicity in this mass balance, we will arbitrarily designate the flux as positive in the $+x$-direction, $+y$-direction, and $+z$-direction. The x-direction flux, so designated, is illustrated in Fig. 4.4. Then, the two flux terms in Eq. 4.1 become:

$$\text{Flux rate in} + \text{Difference in flux rate} = \text{Flux rate out} \tag{4.7}$$

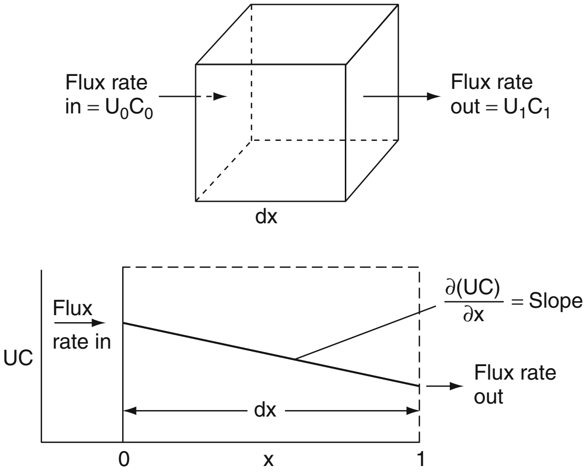


Fig. 4.4 Illustration of the x-component of mass flux rate into and out of the rectangular control volume. (From [1])

or, because a *difference* can be equated to a *gradient times the distance over which the gradient is applied*:

$$\text{Flux rate out} - \text{Flux rate in} = \text{Gradient in flux rate} \times \text{Distance} \tag{4.8}$$

Equation 4.8 can thus be applied along each spatial component as:

$$\text{Flux rate (out} - \text{in})_x = \frac{\partial}{\partial x}(\text{flux rate})dx \tag{4.9a}$$

$$\text{Flux rate (out} - \text{in})_y = \frac{\partial}{\partial y}(\text{flux rate})dy \tag{4.9b}$$

$$\text{Flux rate (out} - \text{in})_z = \frac{\partial}{\partial z}(\text{flux rate})dz \tag{4.9c}$$

Convective flux rates. The convective and diffusive flux rates are dealt with separately. They will eventually be separated in the final diffusion equation, and it is convenient to make that break now. The x-component of the convective flux rate is equal to the x-component of velocity times the concentration times the area of our box normal to the x-axis. Therefore, in terms of convective flux rates, Eq. 4.9a becomes:

$$\begin{aligned}\text{Convective flux rate(out} - \text{in})_x &= \frac{\partial}{\partial x}(uCA_x)dx \\ &= \frac{\partial}{\partial x}(uC)dx\,dy\,dz\end{aligned} \tag{4.10a}$$

Because the normal area, $Ax = dy\,dz$, of our box does not change with x, it can be pulled out of the partial with respect to x. This is done in the second part of Eq. 4.10a. The same can be done with the y- and z-components of the convective flux rate:

$$\begin{aligned}\text{Convective flux rate}\,(\text{out} - \text{in})_{\text{y}} &= \frac{\partial}{\partial y}(vCA_y)dy \\ &= \frac{\partial}{\partial y}(vC)\,dx\,dy\,dz\end{aligned} \tag{4.10b}$$

$$\begin{aligned}\text{Convective flux rate}\,(\text{out} - \text{in})\ \text{z} &= \frac{\partial}{\partial y}(wCA_z)dz \\ &= \frac{\partial}{\partial z}(w\,C)dx\,dy\,dz\end{aligned} \tag{4.10c}$$

Finally, adding Eqs. 4.10a, 4.10b, and 4.10c results in the total net convective flux rate.

$$\begin{aligned}&\text{Net convective flux rate} \\ &= \left[\frac{\partial}{\partial x}(u\,C) + \frac{\partial}{\partial y}(vC) + \frac{\partial}{\partial z}(wC)\right]dx\,dy\,dz\end{aligned} \tag{4.11}$$

Diffusive flux rates. For net diffusive flux rate in the x-direction, Eq. 4.9a becomes:

$$\begin{aligned}&\text{Diffusive flux rate(out}-\text{in})_{\text{X}} \\ &= \frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}A_x\right)dx \\ &= \frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}\right)dx\,dy\,dz\end{aligned} \tag{4.12a}$$

The y- and z-directions give a result similar to Eq. 4.12a:

$$\begin{aligned}&\text{Diffusive flux rate}\,(\text{out} - \text{in})_{\text{Y}} \\ &= \frac{\partial}{\partial y}\left(-D\frac{\partial C}{\partial y}A_y\right)dy \\ &= \frac{\partial}{\partial y}\left(-D\frac{\partial C}{\partial y}\right)dx\ \ dy\ \ dz\end{aligned} \tag{4.12b}$$

$$\begin{aligned}&\text{Diffusive flux rate}\,(\text{out} - \text{in})_z \\ &= \frac{\partial}{\partial z}\left(-D\frac{\partial C}{\partial z}A_z\right)dz \\ &= \frac{\partial}{\partial z}\left(-D\frac{\partial C}{\partial z}\right)dx\ \ dy\ \ dz\end{aligned} \tag{4.12c}$$

Finally, Eqs. 4.12a, 4.12b, and 4.12c can be added to write an equation describing the net diffusive flux rate (out–in) out of the control volume:

$$\text{Net diffusive flux rate} = -\left[\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right)\right] dx\,dy\,dz \tag{4.13}$$

The diffusion coefficient is often not a function of distance, such that Eq. 4.13 can be further simplified by putting the constant value diffusion coefficient in front of the partial derivative. However, we will also be substituting turbulent diffusion and dispersion coefficients for D when appropriate to certain applications, and they are not always constant in all directions. We will therefore leave the diffusion coefficient inside the brackets for now.

Control volume mass balance. Now Eqs. 4.1, 4.5, 4.6, 4.11, and 4.13 can be combined into a mass balance on our box for Cartesian coordinates. After dividing by $\forall = dx\,dy\,dz$ and moving the diffusive flux terms to the right-hand side, this mass balance is:

$$\begin{aligned}&\frac{\partial C}{\partial t}+\frac{\partial}{\partial x}(uC)+\frac{\partial}{\partial y}(vC)+\frac{\partial}{\partial z}(wC)\\&=\left[\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right)\right]+S\end{aligned} \tag{4.14}$$

When working with a computational transport code, there is little reason to further simplify Eq. 4.14. One primary objective of this section, however, is to develop approximate analytical solutions to environmental transport problems, and we will normally be assuming that diffusivity is not a function of position, or x, y, and z. The convective transport terms can be expanded with the chain rule of partial differentiation:

$$\frac{\partial}{\partial x}(u\,C) = u\frac{\partial C}{\partial x}+C\frac{\partial u}{\partial x} \tag{4.15a}$$

$$\frac{\partial}{\partial y}(v\,C) = v\frac{\partial C}{\partial y}+C\frac{\partial v}{\partial y} \tag{4.15b}$$

$$\frac{\partial}{\partial z}(w\,C) = w\frac{\partial C}{\partial z}+C\frac{\partial w}{\partial z} \tag{4.15c}$$

This may not seem like much help, because we have expanded three terms into six. However, if the flow is assumed to be incompressible, a derivation given in fluid mechanics texts (the continuity equation) is:

$$\rho\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)=0 \tag{4.16}$$

where ρ is the density of the fluid. Since Eqs. 4.15a, b, and c are added together in the mass balance equation, the incompressible assumption means that the terms on the far right-hand side of these equations will sum to zero, or:

$$\frac{\partial}{\partial x}(uC)+\frac{\partial}{\partial y}(vC)+\frac{\partial}{\partial z}(wC)=u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}+w\frac{\partial C}{\partial z} \tag{4.17}$$

The incompressible flow assumption is most always accurate for water in environmental applications, and is often a good assumption for air. Air flow is close to incompressible as long as the Mach number (flow velocity/speed of sound) is below 0.3. A Mach number of 0.3 corresponds to an air flow velocity of approximately 110 m/s.

Equation 4.14 then becomes

$$\begin{aligned}&\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}+w\frac{\partial C}{\partial z}\\&=D\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right)+S\end{aligned} \tag{4.18}$$

The only assumptions made in developing Eq. 4.18 are (1) that diffusivity does not change with spatial coordinate and (2) incompressible flow. Equation 4.18 will be further simplified in order to develop analytical solutions for mass transport problems. In some cases, all that needs to be done is orient the flow direction so that it corresponds with one of the coordinate axes. There would then be only one convection term.

Adsorption and Desorption in Sediments and Soils

Sorption relates to a compound sticking to the surface of a particle. Adsorption relates to the process of compound attachment to a particle surface, and desorption relates to the process of detachment. Sorption processes will now be reviewed because there are many compounds that are sorptive and subject to spills. Then the solutions of the diffusion equation can be examined as they apply to highly sorptive compounds.

Environmental chemicals are generally classified by the Greek terms hydrophilic (likes water) and hydrophobic (hates water). Water is a polar molecule, in that it has two hydrogen atoms on one side, and an oxygen atom on the other. Solutes with a polarity or charge, therefore, will have water molecules surrounding them with the tendency to have the proper charge of atom adjacent to the solute. Most amides and alcohols are strongly polar, and also soluble in water. These are generally hydrophilic compounds. Other organic compounds with larger molecular weights, especially with aromatic rings, are generally nonpolar and are classified as hydrophobic compounds. It makes sense that these hydrophobic compounds would adsorb to the nonpolar organic material in the sediments or soils. There are handbooks [7] that can be used to estimate the chemical thermodynamics of a water-particle system.

How can sorption be handled in our transport equation? For particles that are not transported with the flow field, like sediments and groundwater flow, we are interested in the water concentrations. The sorbed portion of the compound is not in the solute phase, and should not be considered in the transport equation except when transfer of the compound between the water and particles occur. Adsorption would then be a sink of the compound and desorption would be a source.

Let us assign S_p to be the mass of chemical sorbed to particles per mass of solids contained in our control volume, and C to be the concentration of the compound in solution. Then, the source term in the diffusion equation is equal to the rate of change of mass due to adsorption and desorption per unit volume, or:

$$S = \frac{\rho_b}{\varepsilon} \frac{\partial S_p}{\partial t} \tag{4.19}$$

where ρ_b is the bulk density of the solid (mass of solid/volume of fluid and solid), ε is the porosity of the media (volume of fluid/volume of fluid and solid), and $\partial S_p / \partial t$ is the rate of sorption relative to the mass of solid (mass adsorbed/mass of solid/time). If the sorption rate is negative, desorption is occurring. The units of S in Eq. 4.19 are mass adsorbed/volume of fluid/time. This is similar to the units for the $\partial C / \partial t$ term, which are a change of mass/volume of fluid/time.

The source term in Eq. 4.19 requires a separate differential equation for S_p, which would incorporate the concentration of the compound in solution. There would thus be two equations that need to be solved simultaneously. However, most sorption rates are high, relative to the transport rates in sediments and soil. Thus, *local equilibrium in adsorption and desorption is often a good assumption.* It also simplifies the solution to a transport problem considerably. If that assumption is made, S_p changes in proportion to C alone, or:

$$S_p = S_p(C) \tag{4.20}$$

and

$$\frac{\partial S_p}{\partial t} = \frac{\partial S_p}{\partial C} \frac{\partial C}{\partial t} \tag{4.21}$$

Now, if Eq. 4.21 is substituted into 4.19, we get:

$$S = \frac{\rho_b}{\varepsilon} \frac{\partial S_p}{\partial C} \frac{\partial C}{\partial t} \tag{4.22}$$

The $\partial S_p/\partial C$ term can be found from the equilibrium relationship of Freundlich isotherms, expressed as:

$$S_p = K_d\, C^{\beta} \tag{4.23}$$

where K_d is an equilibrium-partitioning coefficient between the fluid and sorption to the solid and β is a coefficient fit to measured data. Then,

$$\frac{\partial S_p}{\partial C} = \beta\, K_d\, C^{\beta - 1} \tag{4.24}$$

At the lower concentrations normally found in the environment, $\beta = 1$ is a valid assumption. Then Eq. 4.24 becomes

$$\frac{\partial S_p}{\partial C} = K_d\ (\beta = 1) \tag{4.25}$$

Substituting Eq. 4.25 into 4.22 now results in a source term that no longer contains the variable S_p, and keeps the partial differential equation (PDE) of our mass balance linear:

$$S = \frac{\rho_b}{\varepsilon} K_d \frac{\partial C}{\partial t} \tag{4.26}$$

Now, if Eq. 4.26 is substituted into our mass transport Eqs. 4.15a–c for the source term, the result is a PDE where the only dependent variable is C:

$$\begin{aligned} &\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} + w\frac{\partial C}{\partial z} \\ &\quad = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) - \frac{\rho_b}{\varepsilon} K_d \frac{\partial C}{\partial t} \end{aligned} \tag{4.27}$$

or

$$\begin{aligned} &\left(1 + \frac{\rho_b}{\varepsilon} K_d\right) \frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} + w\frac{\partial C}{\partial z} \\ &\quad = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) \end{aligned} \tag{4.28}$$

If we divide Eq. 4.28 by the term $(1 + K_d\rho_b/\varepsilon)$, we can see that all convective and diffusive transport is *retarded* by equilibrium adsorption and desorption. Thus, a *retardation factor* is defined:

$$R = \text{retardation factor} = 1 + K_d\rho_b/\varepsilon \tag{4.29}$$

and Eq. 4.28 becomes:

$$\begin{aligned}&\frac{\partial C}{\partial t}+\frac{u}{R}\frac{\partial C}{\partial x}+\frac{v}{R}\frac{\partial C}{\partial y}+\frac{w}{R}\frac{\partial C}{\partial z}\\&=\frac{D}{R}\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right)\end{aligned}\tag{4.30}$$

Equation 4.30 indicates that as long as it can be assumed that the sorption rates are fast compared to our transport rates and the equilibrium partitioning is linearly related to concentration, the retardation factor can utilize and simply convert all of the transport terms through dividing by R. Thus, if there is a spill into the groundwater table that is highly hydrophobic, it would transport through the soil more slowly than one which is hydrophilic. Both the convective and the diffusive flux would be "retarded" for the hydrophobic compound. If both hydrophilic and hydrophobic compounds are contained in the spill, the hydrophilic compound would show up first at a downstream location. The similarity to the manner in which a chromatographic column separates compounds is not fortuitous, because the column is separating compounds through their sorption to the column's media.

Determination of K_d from octanol-water partitioning coefficient. There have been a number of empirical equations developed to determine the water-solid partitioning coefficient, K_d [7]. These are primarily for the many organic chemicals that exist in the environment, usually due to human impacts. Many of them use the octanol-water partitioning coefficient for the compound as an indicator of hydrophobicity. Octanol is a relatively insoluble organic compound. Since most organic compounds tend to adsorb to the organic portion of the particles, a hydrophobic organic compound placed in an octanol-water solution will tend toward the octanol. The ratio of concentration in the octanol over concentration in the water will indicate the degree of the hydrophobicity. It is a straightforward and relatively easy measurement to make, so most organic compounds of interest in the environment have an octanol-water partitioning coefficient that has been measured.

Karikhoff et al. [2] developed a simple empirical equation for equilibrium partitioning of organic compounds that will be used in this text (other equations are given in Lehman et al. [7]):

$$K_d = \beta f K_{ow}\tag{4.31}$$

where K_{ow} is the dimensionless octanol-water partitioning coefficient, f is the fraction of soil that is organic matter (usually from zero in sand to 0.01 in sandy soil to 0.10 in muck), and β is an empirical coefficient, estimated by Karikhoff to be 0.41 cm^3/g. It is generally the organic matter in the medium to which organic compounds adsorb, hence the use of organic fraction.

The other parameters required to compute a retardation coefficient are the bulk density, ρ_b, and the porosity of the media, ε. The bulk density of the water and soil is typically 1.6–2.1 g/cm^3. The porosity of the soil or sediments is typically 0.2–0.4. Thus ρ_b/ε is typically between 4 and 10 g/cm^3.

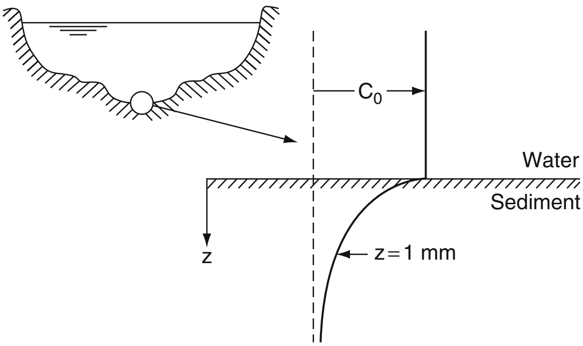


Fig. 4.5 Illustration of dissolved oxygen profile in lake sediments. (From [1])

Example Applications of the Diffusion Equation

The first application of the diffusive is transport of oxygen into lake sediments and the use of oxygen by the bacteria to result in a steady-state oxygen concentration profile.

Example 1: Steady O_2 concentration profile in lake sediments (steady-state solution with a first-order sink) Given a concentration, C_o, in the overlying water, and a first-order sink of oxygen in the sediments, develop an equation to describe the dissolved oxygen concentration profile in the sediments (Fig. 4.5).

Assume:

- Steady: $\frac{\partial}{\partial t} \Rightarrow 0$
- No flow: $u, v, w \Rightarrow 0$
- Small horizontal variation: $\frac{\partial^2 C}{\partial z^2} \gg \frac{\partial^2 C}{\partial x^2}, \frac{\partial^2 C}{\partial y^2}$
- No sorption: $R = 1$ (accurate for O_2 in sediments)
- First-order sink: $S = -kC$, where k is a rate constant

Then, the diffusive mass transport Eqs. 4.15a–c becomes:

$$0 = D\frac{\partial^2 C}{\partial z^2} - kC$$

or, since $C = C(z)$

$$0 = D\frac{d^2 C}{\partial z^2} - kC$$

A solution to this equation requires two boundary conditions because it is a second-order equation. These two are:

B.C.#1: @ $z = 0, C = C_{;0}$
B.C.#2: @ $z \rightarrow \infty, C \Rightarrow 0$

This solution may be achieved by: (1) separating variables and integrating or (2) solving the equation as a second-order, linear ordinary differential equation (ODE). The latter will be used since the solution technique is more general.

1. Assign λ to be the $\frac{d}{dz}$ operator. Then, the equation becomes

$$\left(\lambda^2 - \frac{k}{D}\right) C = 0$$

2. Solve for λ

$$\lambda = \pm\sqrt{k/D}$$

3. The solution, developed in texts on solving ordinary differential equations [6], is

$$C = \beta_1 e^{\lambda_1 z} + \beta_2 e^{\lambda_1 z} \quad \lambda_1 = +\sqrt{k/D}$$

$$\lambda_2 = -\sqrt{k/D}$$

4. β_1 and β_2 are determined from boundary conditions

   Apply B.C. #2:

$$C = 0 = \beta_1\, e^{\sqrt{k/D}\infty} + \beta_2\, e^{-\sqrt{k/D}\,\infty}$$

   This is only possible if $\beta_1 = 0$. Apply B.C. #1:

$$C_0 = 0 + \beta_2 e^{-0} = \beta_2$$

   Thus, the solution is:

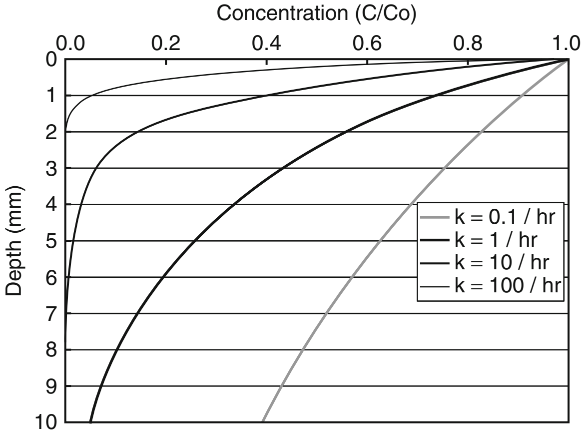
$$C = C_o\ \mathrm{e}^{-\sqrt{k/D}z}$$

which is plotted in Fig. 4.6.

At steady state, the oxygen profile is a balance between diffusion from the sediment surface and bacterial use of oxygen in the sediments. If the sediments are mostly sand, the depth of the layer with oxygen can be 10 cm or more. If the sediments have a substantial organic content (like a mud), the aerobic layer (>0.1 g/m^3 oxygen concentration) can be less than 1 mm.

Example 2: Unsteady dissolution of a highly soluble pollutant **(Herbicides, Pesticides, Ammonia, Alcohols, etc.)** ***into groundwater (unsteady, one-dimensional solution with pulse boundary conditions)*** A tanker truck carrying a highly soluble compound in Mississippi tried to avoid an armadillo at night, ran

Fig. 4.6 Solution to Example 1



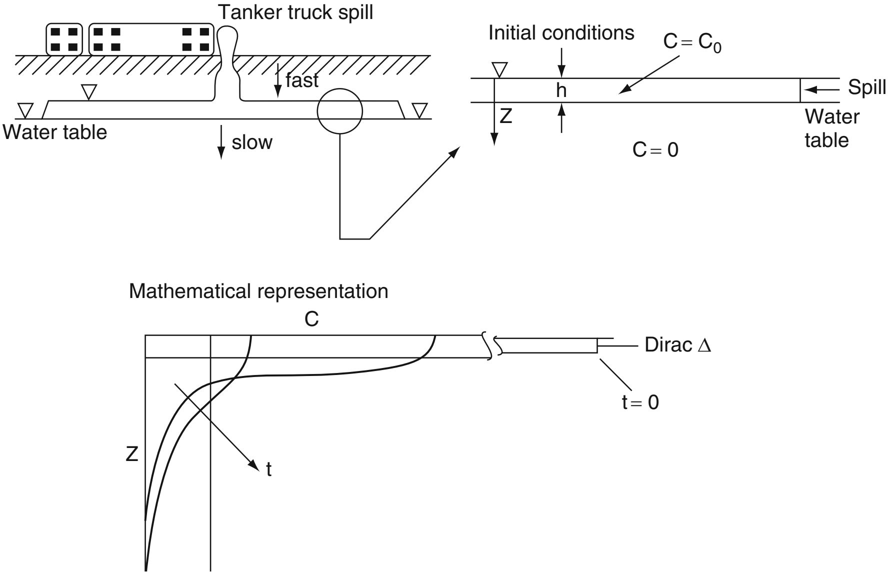


Fig. 4.7 Illustration of the tanker truck spill. (From [1])

off the interstate at a high speed, turned over in the drainage ditch, and spilled a soluble compound. The compound has infiltrated into the ground, and much of it has reached and temporarily spread out over the groundwater table, as illustrated in Fig. 4.7. As part of a spill response team, you need to estimate the groundwater contamination. Predict concentrations over time in the groundwater table.

The mass transport equation for this example is:

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{dy} + w\frac{\partial C}{\partial z}$$
$$= D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) + S$$

Assume:

1. Minimal horizontal variations

$$0 \cong \frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial x^2} \cong \frac{\partial C}{\partial y} \cong \frac{\partial^2 C}{\partial y^2}$$

2. No flow in the vertical direction, $w = 0$
3. No reactions, including adsorption and desorption, such that $S = 0$.

Then with these three assumptions, the governing equation becomes:

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

The initial conditions will be simulated with these boundary conditions:

1. The mass of chemical is assumed to be spread instantaneously across a very thin layer at $t = 0$ (a Dirac delta in z and t). At $z = 0^+$, $t = 0$, the total mass = M and the total surface area is A.
2. At $z \Rightarrow \infty$, $C \Rightarrow 0$.

The above equation, with boundary conditions (1) and (2), has the solution:

$$C = \frac{2M/A}{\sqrt{4\pi Dt}} e^{-z^2/4Dt}$$

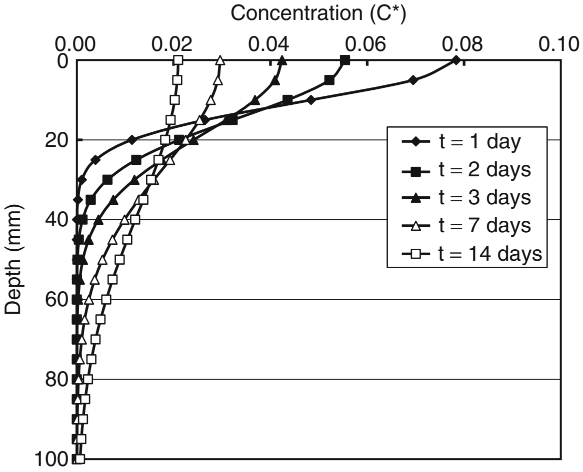
What does the solution look like? The solution can be made dimensionless by assuming that the initial thickness of the spill layer is Δh. Then, a new variable $z = k\,\Delta h$ will be used in assigning:

$$\eta = \frac{\Delta h}{\sqrt{4Dt}}$$

with

$$C^* = \frac{CA\,\Delta h}{2M}$$

Fig. 4.8 Solution to the tanker truck spill illustrating groundwater concentration versus distance at various times. Δh = 2 mm, $D = 6 \times 10^{-4}$ mm^2/s



Substituting these equations into the solution gives:

$$C^* = \frac{\eta}{\sqrt{\pi}} e^{-(k\eta)^2}$$

which is plotted versus depth at various times in Fig. 4.8. The concentration at $z = 0$ decreases as the initial mass is diffused. At low values of time, the concentration at and close to $z = 0$ is strongly dependent upon the Δh chosen. At larger times and deeper depths, however, this dependency decreases, and the solution becomes independent of Δh.

It is interesting to note that the solution is very similar to a Gaussian probability distribution, with the following relationship for $P(z)$:

$$P(z) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(z-z_m)^2/2\sigma^2}$$

where z_m is the depth of the maximum concentration (or the center of concentration mass).

Comparing the probability distribution and the solution to this problem, we can see that:

$$2\sigma^2 \Leftrightarrow 4Dt$$

or:

$$D = \sigma^2/2t$$

Note that if we measure σ, we can determine D.

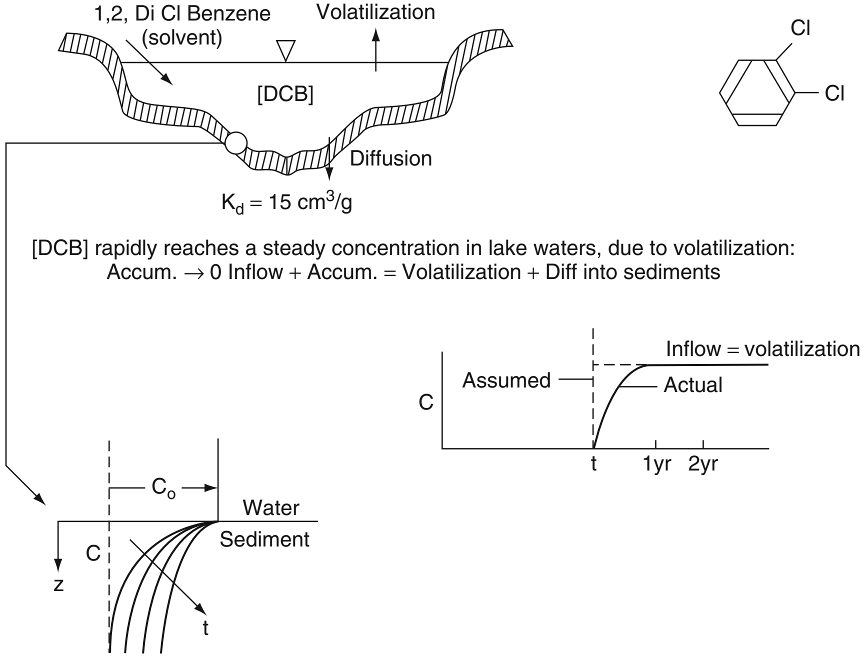


Fig. 4.9 Illustration of concentration front moving down into the sediments of a lake. (From [1])

Example 3*: *Dichlorobenzene concentration in lake sediments due to a plating facility discharge (solution to a concentration front) Sometimes the boundary conditions can be approximated as a step in concentration. This difference in boundary conditions changes the solution from one which is related to pulse boundaries (known mass release) to one resulting from a concentration front with a known concentration at one boundary.

For many years, a plating facility for a telecommunications company let their rinse waters flow into an adjacent lake. The compounds used in their rinse included dichlorobenzene, which is a semi-volatile compound that also has a fairly high tendency to adsorb to organic compounds in the sediments. Within a few years of the plating facility opening, the dichlorobenzene concentration reached a steady-state value in the lake waters as illustrated in Fig. 4.9. Estimate the buildup of dichlorobenzene in the sediments during the 50 years since the facility opened until it stopped discharging its untreated waste water.

Assumptions:

1. Biodegradation is small. ∴ S ⇒ 0 except for sorption.
2. Variation in *x* and *y* are small

$$\frac{\partial^2 C}{\partial x^2}, \frac{\partial^2 C}{\partial y^2} \ll \frac{\partial^2 C}{\partial z^2}$$

3. No flow in sediments under lake: $u = v = w = 0$
4. $D \cong 6 \times 10^{-10}\ \mathrm{m^2/s}$
5. $$\frac{\rho_b}{\varepsilon} = 6.3 \ \Rightarrow \ R = 1 + \frac{\rho_b}{\varepsilon} K_d = 96$$

Then the diffusion equation for the sediments becomes:

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

with boundary conditions:

(a) $t > 0$, $z = 0$; $C = C_0$
(b) t = 0, z $\neq$ 0; C = 0

There are three known techniques to solve this governing equation:

Laplace transforms, Fourier transforms, and change of variables, which incorporates both luck and skill. We will use change of variables:

Assign $\eta = \frac{z}{\sqrt{4Dt/R}}$

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \eta}\frac{\partial \eta}{\partial t} = \frac{-1}{4}\frac{z}{\sqrt{Dt/Rt}}\frac{\partial C}{\partial \eta} = \frac{-\eta}{2t}\frac{\partial C}{\partial \eta}$$

$$\frac{\partial C}{\partial z} = \frac{\partial C}{\partial \eta}\frac{\partial \eta}{\partial z} = \frac{1}{2\sqrt{Dt/R}}\frac{\partial C}{\partial \eta}$$

$$\frac{\partial^2 C}{\partial z^2} = \frac{\partial}{\partial \eta}\left(\frac{\partial C}{\partial z}\right)\frac{\partial \eta}{\partial z} = \frac{R}{4Dt}\frac{\partial^2 C}{\partial \eta^2}$$

Then the governing equation becomes:

$$\frac{-\eta}{2t}\frac{\partial C}{\partial \eta} + \frac{D}{R}\left(\frac{R}{4Dt}\frac{\partial^2 C}{\partial \eta^2}\right) = 0$$

or

$$\frac{d^2 C}{d\eta^2} + 2\eta\frac{dC}{d\eta} = 0 \tag{4.32}$$

This equation may be written as: $\frac{dC'}{d\eta} + 2\eta C' = 0$

where $C' = \frac{\mathrm{dC}}{d\eta}$ or

$$\frac{1}{C'}\,dC' = -2\eta\,d\eta$$

We can integrate this:

$$\ell n\, C' = -\eta^2 + \beta_o$$

or

$$C' = e^{\beta o}\, e^{-\eta^2} = \beta_1\, e^{-\eta^2}$$

Now integrate again:

$$C = \beta_1 \int_0^{\eta} e^{-\eta^2} d\eta + \beta_2 \;\Rightarrow\; \beta_1 \int_0^{\eta} e^{-\phi^2} d\phi + \beta_2$$

Now, note that the error function is given as:

$$erf\,(\eta) = \frac{2}{\sqrt{\pi}} \int_0^{\eta} e^{-\phi^2} d\phi$$

and the complementary error function is erfc(η) = 1−erf(η). Values of the error function and complimentary error function for various values of η may be found in an Internet search. The error function is designed such that erf(∞) = 1, erfc(∞) = 0, erf(0) = 0, and erfc(0) = 1. The solution may therefore be written as:

$$C = \beta_1\, erf\,(\eta) + \beta_2$$

Now we need to determine our boundary conditions in terms of η:

1. $t > 0$, $z = 0$, $\eta = 0$, $C = C_0$
2. $t = 0$, $z = 0$, $\eta = \infty$, $C = 0$

Checking other boundary conditions:
$t \rightarrow \infty$, $\eta \Rightarrow 0$, $C = C_0$
$z \rightarrow \infty$, $\eta \Rightarrow \infty$, $C = 0$

Now, at $\eta = 0$, $C = C_0$, thus:

$$C_0 = \beta_1 0 + \beta_2$$

or

$$\beta_2 = C_0$$

At $\eta = \infty$, $C = 0$

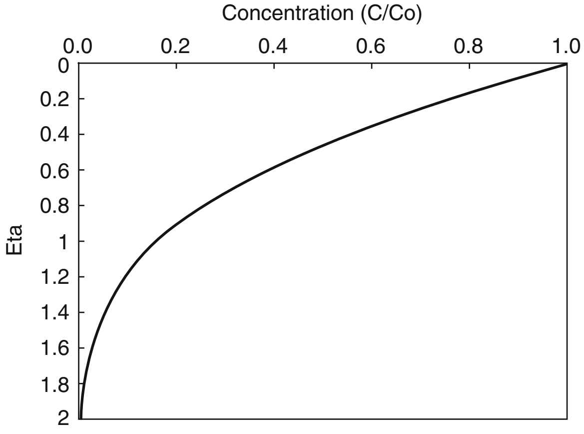


Fig. 4.10 Illustration of the effect of the change of variables used in Example 3. Eta = η

Table 4.2 Penetration of dichlorobenzene into the sediment over time

Time, z	1 year, C/C_0	4 years, C/C_0	10 years, C/C_0	50 years, C/C_0
1 mm	0.96	0.98	0.988	0.994
1 cm	0.62	0.803	0.87	0.94
10 cm	0	0.015	0.11	0.48
20 cm	0	0	0.01	0.16
30 cm	0	0	0	0.03
100 cm	0	0	0	0

$$0 = \beta_1 1 + C_0$$

or

$$\beta_1 = -C_0$$

Then, our solution is:

$$C = C_0\left(1 - erf\left(\frac{z}{\sqrt{4\,Dt/R}}\right)\right) = C_0\,erfc(\eta) \tag{4.33}$$

which is illustrated in Fig. 4.10.

We will now apply Eq. 4.33 to estimate the dichlorobenzene penetration versus time from spillage. The results are given in Table 4.2, which gives the interstitial dichlorobenzene concentrations.

The total concentration (TDCB(z)) includes compound adsorbed to the sediments.

$$TDCB(z) = C(z) + (1 - \varepsilon)\rho_s S$$

where ε = porosity

$1-\varepsilon$ = % by volume sediment $\cong 0.6$
ρ_s = density of sediment $\cong 2.5\ \mathrm{g/cm^3}$
S = concentration of sorbed compound (g DCB/g sediment)

Since $S = K_d\, C_1$, the above equation becomes:

$$\begin{aligned} TDCB(z) &= C(z)(1 + (1-\varepsilon)\,\rho_s K_d) \\ &= C(z)(1 + 0.6(2.5\ \mathrm{g/cm^3})(15\ \mathrm{cm^3/g}) \end{aligned}$$

or

$$TDCB = 23.5\, C(z)$$

Thus, the total dichlorobenzene per volume of sediment and water would be 23.5 times the concentrations given in Table 4.2.

Conclusion

The purpose of this section of the volume is to introduce the reader to the equations and mathematics used in developing approximate solutions (due to simplified boundary conditions) to convection-diffusion processes. One may say that, with computational capabilities, there is no longer any need to develop these approximate solutions. However, these approximate solutions are useful in the following manners:

1. A quick, back of the envelope solution is always much quicker and more reliable than a computational solution. Computational solutions require substantial time to develop and are often wrong until they are fully vetted.
2. A computational solution always requires vetting, which means that a computational solution is compared to an analytical solution, hopefully in a similar condition with simplified boundary conditions. This means that some analytical solution is always needed, and as close to the real simulation as possible, to make sure that the computational solution is doing what the user desires.
3. Developing analytical solutions are an excellent means of getting a feel for solutions to the convection-diffusion equations. It is a knowledge-building practice that is difficult to surpass.

Note that the examples given in this section do not include any with convection. That is because convection in the environment most always includes either turbulence (surface waters and the atmosphere) or dispersion (groundwater). These will be dealt with in other sections.

Future Directions

Most of the future directions with regard to transport in the environment (without turbulent transport) will involve transport across interfaces, such as the air–water and solid–fluid interfaces. While research has been conducted on describing the predominant transport mechanisms for these two cases (McCready et al. [8], [3–5]), there is more to be done. An especially vexing problem is transport in the vadose zone of soils (unsaturated zone). The multiplicity of three interfaces, air, water, and soil, and the heterogeneities in the soil make this a complex problem to handle in a deterministic manner. However, meaningful relationships for an effective diffusion coefficient still need to be developed.

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