2 The Diffusion Equation

In this chapter, we will review various solution techniques for the diffusion equation, 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 diffusion equation, including most of the topics of this text, but they require more background with regard to the physics of mixing processes, which will be addressed in later chapters.

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. In environmental applications, these “solvents” are the solutes, and water or air is usually the solvent. In fact, when neither water nor air is the solvent, the general term nonaqueous phase liquid is applied. A nonaqueous phase liquid is defined as a liquid that is not water, which could be composed of any number of compounds.

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

\[
\frac{\text{Flux rate}}{\text{IN}} - \frac{\text{Flux rate}}{\text{OUT}} + \frac{\text{Source rate}}{\text{}} - \frac{\text{Sink rate}}{\text{}} = \frac{\text{Accumulation rate}}{\text{}}
\]  

(2.1)

Now that we have our mass conservation equation, we must decide 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 Figure 2.1. The general control volume, given in Figure 2.1a, is used for descriptive purposes, to maintain generality. It is rare that we actually work with something that approximates such a contorted control volume. The control volumes that are used in practice are given in Figure 2.1b–d. For the environmental applications of chemical transport, the rectangular control
A. DEVELOPMENT OF THE DIFFUSION EQUATION

Figure 2.1. Common control volumes found in engineering texts and (for the latter three) used in solving the diffusion equation.

volume (Figure 2.1b) has proven to be the most useful. The cylindrical control volume (Figure 2.1c) is used to make pipe or tube flow problems easier to solve, and the spherical control volume (Figure 2.1d) is often helpful when dealing with transport in and around particles 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 onto a plane normal to the light. The $\varphi$ angle measures from the reference axis to the shadow in this plane.

We will use the rectangular control volume for the development of our mass conservation (diffusion) equation.

A. Development of the Diffusion Equation

The diffusion equation will be developed by considering each term in equation (2.1) separately. In addition, the flux terms will be divided into diffusive and convective flux rates.

1. 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.

Let us look at one face of our rectangular control volume (our box) and imagine that we put a tracer on the outside of the box, as shown in Figure 2.2. Initially, the tracer molecules will be distributed uniformly on the outside of the box, with a concentration distribution as shown in Figure 2.2a. However, all of these molecules are vibrating, with inertial movements back and forth. If we look at the tracer
molecules after a certain time, this apparently random motion would have distributed them throughout the box, such that there is no concentration gradient inside or outside the box. This is illustrated in Figure 2.2b.

Then, why is diffusion such a slow process if the molecules are all vibrating and exchanging places? Let us back up and observe the scale of diffusion for the example of liquid water as the solvent. One mole of water is equal to \(6.02 \times 10^{23}\) molecules (Avogadro’s number) and will weigh 18 g. Since 1 g of water occupies roughly 1 cc, we have 18 cc’s of water, which can be represented by a cube that is 2.6 cm on a side. The cube root of \(6 \times 10^{23}\) is approximately \(8 \times 10^7\). Thus, we can visualize one corner of our 2.6 cm cube as being occupied by 80 million molecules. It takes some time for the random motion of these molecules, regardless of how active, to traverse 80 million molecules by a motion that appears random. Diffusion is especially slow in liquids because the molecules are small, compared with the distance traversed, and are relatively close together.

The molecules are generally much farther apart in gases, so the diffusivity of a compound in a gas is significantly larger than in a liquid. We will return to this comparison of diffusion in gases and liquids in Chapter 3.

**Fick’s Law.** Fick’s law is a physically meaningful mathematical description of diffusion that is based on the analogy to heat conduction (Fick, 1855). Let us consider one side of our control volume, normal to the \(x\)-axis, with an area \(A_x\), shown in Figure 2.3. Fick’s law describes the diffusive flux rate as

\[
\text{Diffusive flux rate} = -D \frac{\partial C}{\partial x} A_x
\]

\[
\begin{array}{ccc}
\text{(g/s)} & \text{(m}^2\text{/s)} & \text{(g/m}^4\text{)} & \text{(m}^2\text{)}
\end{array}
\]

\[
(2.2)
\]
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 Figure 2.3. Thus, the diffusive flux rate depends on the diffusion coefficient and the gradient of concentration with distance. In Figure 2.2a there was a greater gradient of tracer molecules than in Figure 2.2b, so there would be a larger chemical flux across the surface of the control volume. The same molecular motion would bring more tracer molecules into the box in Figure 2.2a than in Figure 2.2b, especially when we realize that the diffusive flux is a net flux. Any molecules that come back out of the box, after entering, would count against the diffusive flux into the box.

2. Convective Flux

The convective flux rate into our control volume is simply the chemical mass carried in by convection. If we consider the same box of Figure 2.3, except with a velocity component \( u \) in the \( x \)-direction, the convective flux rate into the box from the left-hand side is

\[
\text{Convective flux rate} = uA_xC \tag{2.4}
\]

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.
3. Rate of Accumulation

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

\[
\text{Rate of accumulation} = \bar{V} \frac{\partial C}{\partial t} \quad (\text{g/s}) \quad (\text{m}^3) \quad (\text{g/m}^3/\text{s})
\]  

(2.5)

where \(\bar{V}\) is the volume of our box.

4. 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 (see Example 5.4). 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

\[
\text{Source – sink rate} = S \quad \bar{V} \quad (\text{g/s}) \quad (\text{g/m}^3/\text{s}) \quad (\text{m}^3)
\]  

(2.6)

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 equation (2.6). These are listed in Table 2.1. The source/sink term could be a combination of two or more of these reactions. For convenience in determining analytical solutions to the diffusion equation, most source/sink terms are approximated as either a first-order or zero-order reaction. This type of application will be demonstrated in Section 2.F.

<table>
<thead>
<tr>
<th>Source/sink name</th>
<th>Equation</th>
<th>Units of constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero order</td>
<td>(S = k_0)</td>
<td>(k_0 = \text{g/m}^2)</td>
</tr>
<tr>
<td>First order</td>
<td>(S = k_1 C)</td>
<td>(k_1 = \text{S}^{-1})</td>
</tr>
<tr>
<td>Second order</td>
<td>(S = k_2 C^2)</td>
<td>(k_2 = \text{m}^3/\text{g} - \text{s})</td>
</tr>
<tr>
<td>Independent variable</td>
<td>(S = k_{li} P^n)</td>
<td>(k_{li} = \text{s}^{-1})</td>
</tr>
<tr>
<td></td>
<td>(S = k_{li} PC^i)</td>
<td>(k_{li} = \text{m}^3/\text{g} - \text{s})</td>
</tr>
<tr>
<td>Monod kinetics(^{\dagger})</td>
<td>(S = \frac{\mu_m C}{k_c + C} P)</td>
<td>(\mu_m = \text{maximum growth rate (s}^{-1})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(k_c = \text{half-saturation coefficient (g/m}^3))</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) If \(P\) is nearly constant, then \(k_{li}\) can be provided as a zero-order term.

\(^{\dagger}\) Often called second order.

\(^{\dagger}\) Common for biologically mediated reactions.
5. Mass Balance on Control Volume

A mass balance on one compound in our box is based on the principle that whatever comes in must do one of three things: (1) be accumulated in the box, (2) flux out of another side, or (3) 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 Figure 2.4. 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 Figure 2.5. Then, the two flux terms in equation (2.1) become

$$\text{Flux rate in} + \text{Difference in flux rate} = \text{Flux rate out} \quad (2.7)$$

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

$$\text{Flux rate out} - \text{Flux rate in} = \text{Gradient in flux rate} \times \text{Distance} \quad (2.8)$$
Equation (2.8) can thus be applied along each spatial component as

\[
\text{Flux rate (out – in)}_x = \frac{\partial}{\partial x} (\text{flux rate}) dx \tag{2.9a}
\]

\[
\text{Flux rate (out – in)}_y = \frac{\partial}{\partial y} (\text{flux rate}) dy \tag{2.9b}
\]

\[
\text{Flux rate (out – in)}_z = \frac{\partial}{\partial z} (\text{flux rate}) dz \tag{2.9c}
\]

**Convective Flux Rates.** We will deal with the convective and diffusive flux rates 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, \(u\), times the concentration, \(C\), times the area of our box normal to the \(x\)-axis. Therefore, in terms of convective flux rates, equation (2.9a) becomes

\[
\text{Convective flux rate (out – in)}_x = \frac{\partial}{\partial x} (u C A_x) dx = \frac{\partial}{\partial x} (u C) dx dy dz \tag{2.10a}
\]

Because the normal area, \(A_x = dy dz\), 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 equation (2.10a). The same can be done with the \(y\)- and \(z\)-components of convective flux rate

\[
\text{Convective flux rate (out – in)}_y = \frac{\partial}{\partial y} (v C A_y) dy = \frac{\partial}{\partial y} (v C) dx dy dz \tag{2.10b}
\]

\[
\text{Convective flux rate (out – in)}_z = \frac{\partial}{\partial z} (w C A_z) dz = \frac{\partial}{\partial z} (w C) dx dy dz \tag{2.10c}
\]

Finally, adding equations (2.10a) to (2.10c) results in the total net convective flux rate:

\[
\text{Net convective flux rate} = \left[ \frac{\partial}{\partial x} (u C) + \frac{\partial}{\partial y} (v C) + \frac{\partial}{\partial z} (w C) \right] dx dy dz \tag{2.11}
\]

**Diffusive Flux Rates.** For net diffusive flux rate in the \(x\)-direction, equation (2.9a) becomes

\[
\text{Diffusive flux rate (out – in)}_x = \frac{\partial}{\partial x} \left( -D \frac{\partial C}{\partial x} A_x \right) dx = \frac{\partial}{\partial x} \left( -D \frac{\partial C}{\partial x} \right) dx dy dz \tag{2.12a}
\]

A self-test of understanding flux rates would be to look at Figure 2.3 and write out the diffusive flux rates in the \(y\)- and \(z\)-directions on a separate sheet of paper. The result is similar to equation (2.12a):

\[
\text{Diffusive flux rate (out – in)}_y = \frac{\partial}{\partial y} \left( -D \frac{\partial C}{\partial y} A_y \right) dy = \frac{\partial}{\partial y} \left( -D \frac{\partial C}{\partial y} \right) dx dy dz \tag{2.12b}
\]

\[
\text{Diffusive flux rate (out – in)}_z = \frac{\partial}{\partial z} \left( -D \frac{\partial C}{\partial z} A_z \right) dz = \frac{\partial}{\partial z} \left( -D \frac{\partial C}{\partial z} \right) dx dy dz \tag{2.12c}
\]
Finally, we can add equations (2.12a) to (2.12c) to write an equation describing the net diffusive flux rate (out – in) out of the control volume:

\[
\text{Net diffusive flux rate} = - \left[ \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right) \right] dx \, dy \, dz
\]  
(2.13)

The diffusion coefficient is often not a function of distance, such that equation (2.13) 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. Therefore, we will leave the diffusion coefficient inside the brackets for now.

**Control Volume Mass Balance.** We can now combine equations (2.1), (2.5), (2.6), (2.11), and (2.13) into a mass balance on our box for Cartesian coordinates. After dividing by \( \nabla = dx \, dy \, dz \) and moving the diffusive flux terms to the right-hand side, this mass balance is

\[
\frac{\partial C}{\partial t} + \frac{\partial}{\partial x} (u \, C) + \frac{\partial}{\partial y} (v \, C) + \frac{\partial}{\partial z} (w \, C) = \left[ \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right) \right] + S
\]  
(2.14)

When working with a computational transport code, there is little reason to simplify equation (2.14) further. Our primary task, however, is to develop approximate analytical solutions to environmental transport problems, and we will normally be assuming that diffusion coefficient is not a function of position, or \( x, y, \) and \( z \). We can also expand the convective transport terms with the chain rule of partial differentiation:

\[
\begin{align*}
\frac{\partial}{\partial x} (u \, C) &= u \frac{\partial C}{\partial x} + C \frac{\partial u}{\partial x} \\
\frac{\partial}{\partial y} (v \, C) &= v \frac{\partial C}{\partial y} + C \frac{\partial v}{\partial y} \\
\frac{\partial}{\partial z} (w \, C) &= w \frac{\partial C}{\partial z} + C \frac{\partial w}{\partial z}
\end{align*}
\]  
(2.15a, b, c)

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

\[
\rho \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) = 0
\]  
(2.16)

where \( \rho \) is the density of the fluid. Since equations (2.15a) to (2.15c) 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

\[
\frac{\partial}{\partial x} (u \, C) + \frac{\partial}{\partial y} (v \, C) + \frac{\partial}{\partial z} (w \, C) = u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z}
\]  
(2.17)
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 100 m/s.

Equation (2.14) then becomes

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

(2.18)

The only assumptions made in developing equation (2.18) are: (1) that diffusion coefficient does not change with spatial coordinate and (2) incompressible flow. We will further simplify equation (2.18) in developing analytical solutions for mass transport problems. In some cases, all we need to do is orient the flow direction so that it corresponds with one of the coordinate axes. We would then have only one convection term.

6. Cylindrical Control Volume

The cylindrical coordinate system and cylindrical control volume are illustrated in Figure 2.6. There are some differences in the development of a mass balance equation on a cylindrical control volume. Primarily, the \( r d\theta dx \) side of the control volume increases in area as \( r \) increases. For the control volume of Figure 2.6, the area normal to the \( r \)-coordinate would be

\[
A_r = r d\theta dx
\]

(2.19)

which is a function of \( r \), one of the independent variables. Then, analogous to equation (2.12), the convective flux in the \( r \)-direction would be

\[
\text{Convective flux rate (out – in) } = \frac{\partial}{\partial r} \left( v_r C A_r \right) dr = \frac{\partial}{\partial r} \left( v_r C \right) dr d\theta dz
\]

(2.20)

The diffusive flux rates would be treated similarly. The area of the control volume changing with radius is the reason the mass transport equation in cylindrical coordinates, given below – with similar assumptions as equation (2.18) – looks somewhat different than in Cartesian coordinates.

\[
\frac{\partial C}{\partial t} + \frac{v_r}{r} \frac{\partial}{\partial r} \left( r C \right) + \frac{v_{\theta}}{r} \frac{\partial C}{\partial \theta} + v_z \frac{\partial C}{\partial z} = D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial C}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial z^2} \right] + S
\]

(2.21)

Figure 2.6. Cylindrical control volume.
7. Applications of the Diffusion Equation

We will try our hand at applying the diffusion equation to a couple of mass transport problems. The first is the diffusive transport of oxygen into lake sediments and the use of oxygen by the bacteria to result in a steady-state oxygen concentration profile. The second is an unsteady solution of a spill into the groundwater table.

EXAMPLE 2.1: Steady oxygen concentration profile in lake sediments (steady-state solution with a first-order sink)

Given a concentration, $C_0$, 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 (see Figure E2.1.1).

Assume:

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

Then, the diffusive mass transport equation (2.18) becomes

$$0 = D \frac{\partial^2 C}{\partial z^2} - kC$$  \hspace{1cm} (E2.1.1)

or, since $C = C(z)$,

$$0 = D \frac{d^2 C}{dz^2} - kC$$  \hspace{1cm} (E2.1.2)

Figure E2.1.1. Illustration of dissolved oxygen profile in lake sediments.
A solution to equation (E2.1.2) requires two boundary conditions because it is a second-order equation. These boundary conditions are:

1. At \( z = 0, C = C_0 \)
2. At \( z \to \infty, C \to 0 \)

A solution to equation (E2.1.2) may be achieved by (1) separating variables and integrating or (2) solving the equation as a second-order, linear ordinary differential equation. We will use the latter because the solution technique is more general.

1. Assign \( \lambda \) to be the \( \frac{d}{dz} \) operator. Then, equation (E2.1.2) becomes

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

(E2.1.3)

2. Solve for \( \lambda \)

\[
\lambda = \pm \sqrt{\frac{k}{D}}
\]

3. The solution, developed in texts on solving ordinary differential equations (Kreysig, 1982), is

\[
C = \beta_1 e^{\lambda_1 z} + \beta_2 e^{\lambda_2 z}
\]

\[
\lambda_1 = +\sqrt{\frac{k}{D}}
\]

\[
\lambda_2 = -\sqrt{\frac{k}{D}}
\]

(E2.1.4)

4. \( \beta_1 \) and \( \beta_2 \) are determined from boundary conditions:

Apply boundary condition 2 to equation (E2.1.4):

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

This is only possible if \( \beta_1 = 0 \). Apply boundary condition 1 to equation (E2.1.4):

\[
C_0 = 0 + \beta_2 e^0 = \beta_2
\]

Thus, the solution is

\[
C = C_0 e^{\sqrt{k/D} z}
\]

(E2.1.5)

which is plotted in Figure E2.1.2.

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/m³ oxygen concentration) can be less than 1 mm in depth.
Figure E2.1.2. Solution (equation (E2.1.5)) to Example 2.1. for oxygen concentration in lake sediments with first-order sink.

**EXAMPLE 2.2: 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 off the interstate at a high speed, turned over in the drainage

![Diagram of tanker truck spill and groundwater](image)

Figure E2.2.1. Illustration of the tanker truck spill.
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 part of a spill response team, you need to estimate the groundwater contamination. Predict concentrations over time in the groundwater table. (See Figure E2.2.1.)

The mass transport equation for this example is

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

(E2.2.1)

Assume:

1. Minimal horizontal variations

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

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, equation (E2.2.1) becomes

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

(E2.2.2)

We will simulate the initial conditions 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 \( z \to \infty, C \to 0 \)

Equation (E2.2.2), with boundary conditions 1 and 2, has the solution

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

(E2.2.3)

For the solution of boundary conditions with a Dirac delta, it is easier to provide the solution and then prove that it works. We will do that now.

Equation (E2.2.3) is the correct solution if it solves equation (E2.2.2) and meets the boundary conditions. Let's test it:

a) Boundary condition 2:

At \( z \to \infty \quad e^{-z^2/4Dt} \to 0 \quad \therefore C \to 0 \)

Boundary condition 2 is satisfied by equation (E2.2.3).

b) Boundary condition 1:

$$M = A \int_0^\infty C \, dz = A \int_0^\infty \frac{2M/A}{\sqrt{4 \pi D t}} e^{-z^2/4Dt} \, dz$$

(E2.2.4)
Equation (E2.2.4) looks like the probability integral with the limits given from 0 to \(\infty\). The probability integral is

\[
\int_0^\infty e^{-\xi^2} d\xi = \frac{\sqrt{\pi}}{2}
\]

Now assign \(\xi = \frac{z}{\sqrt{4Dt}}\); then, \(d\xi = \frac{dz}{\sqrt{4Dt}}\) or \(dz = \sqrt{4Dt} \, d\xi\)

and equation (E2.2.4) becomes

\[
M = \frac{2M}{\sqrt{\pi}} \int_0^\infty e^{-\xi^2} d\xi = \frac{2M \sqrt{\pi}}{2} = M
\]

Boundary condition 1 is satisfied by the solution:

c) Finally, let us substitute equation (E2.2.3) into (E2.2.2) to see if the solution satisfies our governing equation:

i. \[
\frac{\partial C}{\partial t} = -\frac{1}{2} \frac{2M/A}{\sqrt{4\pi Dt}} e^{-\frac{z^2}{4Dt}} + \frac{2M/A}{\sqrt{4\pi Dt}} \left( \frac{z^2}{4Dt^2} \right) e^{-\frac{z^2}{4Dt}}
\]

or

\[
\frac{\partial C}{\partial t} = -\frac{M/A}{\sqrt{4\pi Dt^3}} \left( 1 - \frac{z^2}{2Dt} \right) e^{-\frac{z^2}{4Dt}} \quad (E2.2.5)
\]

ii. \[
\frac{\partial C}{\partial z} = \frac{-2z}{4Dt} \frac{M/A}{\sqrt{4\pi Dt}} e^{-\frac{z^2}{4Dt}} = \frac{-z}{Dt\sqrt{4\pi}} \frac{M/A}{\sqrt{4\pi Dt}} e^{-\frac{z^2}{4Dt}}
\]

and

iii. \[
\frac{\partial^2 C}{\partial z^2} = \frac{\partial}{\partial z} \left( \frac{\partial C}{\partial z} \right) = -\frac{M/A}{\sqrt{4\pi Dt^3}} \left( \frac{1}{D} - \frac{z^2}{2D^2t} \right) e^{-\frac{z^2}{4Dt}} \quad (E2.2.6)
\]

Plug equations (E2.2.5) and (E2.2.6) into equation (E2.2.2)

\[
-\frac{M/A}{\sqrt{4\pi Dt^3}} \left( 1 - \frac{z^2}{2Dt} \right) e^{-\frac{z^2}{4Dt}} = D \left[ -\frac{M/A}{\sqrt{4\pi Dt^3}} \left( \frac{1}{D} - \frac{z^2}{2D^2t} \right) e^{-\frac{z^2}{4Dt}} \right]
\]

The solution – equation (E2.2.3) – works!

To repeat: equation (E2.2.3) is a solution to the diffusion equation, and we have shown that it meets the boundary conditions. It is therefore a solution to our problem as we have formulated it. This may seem like a fairly extensive example for one solution. However, we can use equation (E2.2.3) as a basis for an entire set of Dirac delta solutions that can model instantaneous spills. Thus, equation (E2.2.3) is a building block for many of the solutions we will model.
The solution to equation (E2.2.3) is plotted versus depth at various times in Figure E2.2.2. The solution can also be made dimensionless by assuming that the initial thickness of the spill layer is \( \Delta h \). Then, a new variable \( z = k \Delta h \) will be used in assigning

\[
\eta = \frac{\Delta h}{\sqrt{4Dt}} \quad \text{(E2.2.7)}
\]

with

\[
C^* = \frac{CA\Delta h}{2M} \quad \text{(E2.2.8)}
\]

Substituting equation (E2.2.7) and (E2.2.8) into equation (E2.2.3) gives

\[
C^* = \frac{\eta}{\sqrt{\pi}} e^{-(k\eta)^2} \quad \text{(E2.2.9)}
\]

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 on the \( \Delta h \) chosen. At larger times and deeper depths, however, this dependency decreases, and the solution becomes independent of \( \Delta h \).

It is interesting to note that the solution given as equation is very similar to a Gaussian probability distribution (given in Figure (E2.2.3)), with the following relationship for \( P(z) \):

\[
P(z) = \frac{1}{\sigma \sqrt{2\pi}} e^{-(z-\omega_0)^2/2\sigma^2} \quad \text{(E2.2.10)}
\]
where $z_m$ is the depth of the maximum concentration (or the center of concentration mass).

Comparing equations (E2.2.3) and (E2.2.7), we can see that

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

or

$$D = \sigma^2 2t$$  \hspace{1cm} (E2.2.11)

Note that if we measure $\sigma$, we can determine $D$. The following equations can be used to determine $\sigma$ (and thus $D$) from measurements:

Centroid of concentration distribution, $z_m$ (for our problem $\bar{z} = 0$):

$$z_m = \frac{\int_{-\infty}^{\infty} zC \, dz}{\int_{-\infty}^{\infty} C \, dz} \approx \frac{\sum (z - z_m)C/\Delta z}{\sum C \Delta z}$$  \hspace{1cm} (E2.2.12)

Variance of distribution, $\sigma^2$:

$$\sigma^2 = \frac{\int_{-\infty}^{\infty} (z - z_m)^2 C \, dz}{\int_{-\infty}^{\infty} C \, dz} \approx \frac{\sum (z - z_m)^2C/\Delta z}{\sum C \Delta z}$$  \hspace{1cm} (E2.2.13)

Substituting $\sigma$ from equation (E2.2.13) into equation (E2.2.11) will give an estimate of $D$. 