1. Concepts, Definitions, and the Diffusion Equation

Environmental fluid mechanics is the study of fluid mechanical processes that affect the fate and transport of substances through the hydrosphere and atmosphere at the local or regional scale[1] (up to 100 km). In general, the substances of interest are mass, momentum and heat. More specifically, mass can represent any of a wide variety of passive and reactive tracers, such as dissolved oxygen, salinity, heavy metals, nutrients, and many others. Part I of this textbook, "Mass Transfer and Diffusion," discusses the passive process affecting the fate and transport of species in a homogeneous natural environment. Part II, "Stratified Flow and Buoyant Mixing," incorporates the effects of buoyancy and stratification to deal with active mixing problems.

This chapter introduces the concept of mass transfer (transport) and focuses on the physics of diffusion. Because the concept of diffusion is fundamental to this part of the course, we single it out here and derive its mathematical representation from first principles to the solution of the governing partial differential equation. The mathematical rigor of this section is deemed appropriate so that the student gains a fundamental and complete understanding of diffusion and the diffusion equation. This foundation will make the complicated processes discussed in the remaining chapters tractable and will start to build the engineering intuition needed to solve problems in environmental fluid mechanics.

1.1 Concepts and definitions

Stated simply, Environmental Fluid Mechanics is the study of natural processes that change concentrations.

These processes can be categorized into two broad groups: transport and transformation. Transport refers to those processes which move substances through the hydrosphere and atmosphere by physical means. As an analogy to the postal service, transport is the process by which a letter goes from one location to another. The postal truck is the analogy for our fluid, and the letter itself is the analogy for our chemical species. The two primary modes of transport in environmental fluid mechanics are advection (transport associated with the flow of a fluid) and diffusion (transport associated with random motions within a fluid). Transformation refers to those processes that change a substance

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[1] At larger scales we must account for the Earth's rotation through the Coriolis effect, and this is the subject of geophysical fluid dynamics.

of interest into another substance. Keeping with our analogy, transformation is the paper recycling factory that turns our letter into a shoe box. The two primary modes of transformation are physical (transformations caused by physical laws, such as radioactive decay) and chemical (transformations caused by chemical or biological reactions, such as dissolution).

The glossary at the end of this text provides a list of important terms and their definitions in environmental fluid mechanics (with the associated German term).

1.1.1 Expressing Concentration

The fundamental quantity of interest in environmental fluid mechanics is concentration. In common usage, the term concentration expresses a measure of the amount of a substance within a mixture.

Mathematically, the concentration C is the ratio of the mass of a substance M_i to the total volume of a mixture V expressed

$$C = \frac{M_i}{V}. \tag{1.1}$$

The units of concentration are [M/L^3], commonly reported in mg/l, kg/m^3, lb/gal, etc. For one- and two-dimensional problems, concentration can also be expressed as the mass per unit segment length [M/L] or per unit area, [M/L^2].

A related quantity, the mass fraction χ is the ratio of the mass of a substance M_i to the total mass of a mixture M, written

$$\chi = \frac{M_i}{M}. \tag{1.2}$$

Mass fraction is unitless, but is often expressed using mixed units, such as mg/kg, parts per million (ppm), or parts per billion (ppb).

A popular concentration measure used by chemists is the molar concentration θ. Molar concentration is defined as the ratio of the number of moles of a substance N_i to the total volume of the mixture

$$\theta = \frac{N_i}{V}. \tag{1.3}$$

The units of molar concentration are [number of molecules/L^3]; typical examples are mol/l and μmol/l. To work with molar concentration, recall that the atomic weight of an atom is reported in the Periodic Table in units of g/mol and that a mole is $6.022 \cdot 10^{23}$ molecules.

The measure chosen to express concentration is essentially a matter of taste. Always use caution and confirm that the units chosen for concentration are consistent with the equations used to predict fate and transport. A common source of confusion arises from the fact that mass fraction and concentration are often used interchangeably in dilute aqueous systems. This comes about because the density of pure water at 4°C is 1 g/cm^3, making values for concentration in mg/l and mass fraction in ppm identical. Extreme caution should be used in other solutions, as in seawater or the atmosphere, where ppm and mg/l are *not* identical. The conclusion to be drawn is: always check your units!

1.1.2 Dimensional analysis

A very powerful analytical technique that we will use throughout this course is dimensional analysis. The concept behind dimensional analysis is that if we can define the parameters that a process depends on, then we should be able to use these parameters, usually in the form of dimensionless variables, to describe that process at all scales (not just the scales we measure in the laboratory or the field).

Dimensional analysis as a method is based on the Buckingham π-theorem (see e.g. Fischer et al. 1979). Consider a process that can be described by m dimensional variables. This full set of variables contains n different physical dimensions (length, time, mass, temperature, etc.). The Buckingham π-theorem states that there are, then, $m-n$ independent non-dimensional groups that can be formed from these governing variables (Fischer et al. 1979). When forming the dimensionless groups, we try to keep the dependent variable (the one we want to predict) in only one of the dimensionless groups (i.e. try not to repeat the use of the dependent variable).

Once we have the $m - n$ dimensionless variables, the Buckingham π-theorem further tells us that the variables can be related according to

$$\pi_1 = f(\pi_2, \pi_i, ..., \pi_{m-n}) \tag{1.4}$$

where π_i is the ith dimensionless variable. As we will see, this method is a powerful way to find engineering solutions to very complex physical problems.

As an example, consider how we might predict when a fluid flow becomes turbulent. Here, our dependent variable is a quality (turbulent or laminar) and does not have a dimension. The variables it depends on are the velocity u, the flow disturbances, characterized by a typical length scale L, and the fluid properties, as described by its density ρ, temperature T, and viscosity μ. First, we must recognize that ρ and μ are functions of T; thus, all three of these variables cannot be treated as independent. The most compact and traditional approach is to retain ρ and μ in the form of the kinematic viscosity $\nu = \mu/\rho$. Thus, we have $m = 3$ dimensional variables (u, L, and ν) in $n = 2$ physical dimensions (length and time).

The next step is to form the dimensionless group $\pi_1 = f(u, L, \nu)$. This can be done by assuming each variable has a different exponent and writing separate equations for each dimension. That is

$$\pi_1 = u^a L^b \nu^c, \tag{1.5}$$

and we want each dimension to cancel out, giving us two equations

T gives: $0 = -a - c$
L gives: $0 = a + b + 2c.$

From the T-equation, we have $a = -c$, and from the L-equation we get $b = -c$. Since the system is under-defined, we are free to choose the value of c. To get the most simplified form, choose $c = 1$, leaving us with $a = b = -1$. Thus, we have

$$\pi_1 = \frac{\nu}{uL}. \tag{1.6}$$

This non-dimensional combination is just the inverse of the well-known Reynolds number Re; thus, we have shown through dimensional analysis, that the turbulent state of the fluid should depend on the Reynolds number

$$Re = \frac{uL}{\nu}, \tag{1.7}$$

which is a classical result in fluid mechanics.

1.2 Diffusion

A fundamental transport process in environmental fluid mechanics is diffusion. Diffusion differs from advection in that it is random in nature (does not necessarily follow a fluid particle). A well-known example is the diffusion of perfume in an empty room. If a bottle of perfume is opened and allowed to evaporate into the air, soon the whole room will be scented. We know also from experience that the scent will be stronger near the source and weaker as we move away, but fragrance molecules will have wondered throughout the room due to random molecular and turbulent motions. Thus, diffusion has two primary properties: it is random in nature, and transport is from regions of high concentration to low concentration, with an equilibrium state of uniform concentration.

1.2.1 Fickian diffusion

We just observed in our perfume example that regions of high concentration tend to spread into regions of low concentration under the action of diffusion. Here, we want to derive a mathematical expression that predicts this spreading-out process, and we will follow an argument presented in Fischer et al. (1979).

   To derive a diffusive flux equation, consider two rows of molecules side-by-side and centered at $x = 0$, as shown in Figure 1.1(a.). Each of these molecules moves about randomly in response to the temperature (in a random process called Brownian motion). Here, for didactic purposes, we will consider only one component of their three-dimensional motion: motion right or left along the x-axis. We further define the mass of particles on the left as M_l, the mass of particles on the right as M_r, and the probability (transfer rate per time) that a particles moves across $x = 0$ as k, with units $[\mathrm{T}^{-1}]$.

   After some time δt an *average* of half of the particles have taken steps to the right and half have taken steps to the left, as depicted through Figure 1.1(b.) and (c.). Looking at the particle histograms also in Figure 1.1, we see that in this random process, maximum concentrations decrease, while the total region containing particles increases (the cloud spreads out).

   Mathematically, the average flux of particles from the left-hand column to the right is kM_l, and the average flux of particles from the right-hand column to the left is $-kM_r$, where the minus sign is used to distinguish direction. Thus, the net flux of particles q_x is
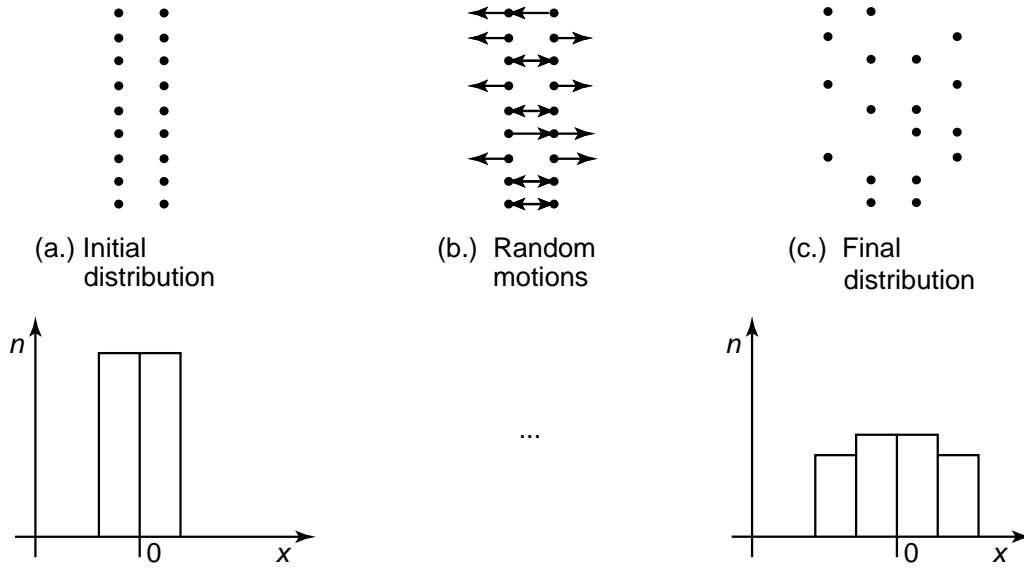
Fig. 1.1. Schematic of the one-dimensional molecular (Brownian) motion of a group of molecules illustrating the Fickian diffusion model. The upper part of the figure shows the particles themselves; the lower part of the figure gives the corresponding histogram of particle location, which is analogous to concentration.

$$q_x = k(M_l - M_r). \tag{1.8}$$

For the one-dimensional case, concentration is mass per unit line segment, and we can write (1.8) in terms of concentrations using

$$C_l = M_l/(\delta x \delta y \delta z) \tag{1.9}$$
$$C_r = M_r/(\delta x \delta y \delta z) \tag{1.10}$$

where δx is the width, δy is the breadth, and δz is the height of each column. Physically, δx is the average step along the x-axis taken by a molecule in the time δt. For the one-dimensional case, we want q_x to represent the flux in the x-direction per unit area perpendicular to x; hence, we will take $\delta y \delta z = 1$. Next, we note that a finite difference approximation for dC/dx is

$$\frac{dC}{dx} = \frac{C_r - C_l}{x_r - x_l}$$
$$= \frac{M_r - M_l}{\delta x(x_r - x_l)}, \tag{1.11}$$

which gives us a second expression for $(M_l - M_r)$, namely,

$$(M_l - M_r) = -\delta x(x_r - x_l)\frac{dC}{dx}. \tag{1.12}$$

Substituting (1.12) into (1.8) yields

$$q_x = -k(\delta x)^2 \frac{dC}{dx}. \tag{1.13}$$

(1.13) contains two unknowns, k and δx. Fischer et al. (1979) argue that since q cannot depend on an arbitrary δx, we must assume that $k(\delta x)^2$ is a constant, which we will

Example Box 1.1:
Diffusive flux at the air-water interface.

The time-average oxygen profile $C(z)$ in the laminar sub-layer at the surface of a lake is

$$C(z) = C_{sat} - (C_{sat} - C_l)\text{erf}\left(\frac{z}{\delta\sqrt{2}}\right)$$

where C_{sat} is the saturation oxygen concentration in the water, C_l is the oxygen concentration in the body of the lake, δ is the concentration boundary layer thickness, and z is defined positive downward. Turbulence in the body of the lake is responsible for keeping δ constant. Find an expression for the total rate of mass flux of oxygen into the lake.

Fick's law tells us that the concentration gradient in the oxygen profile will result in a diffusive flux of oxygen into the lake. Since the concentration is uniform in x and y, we have from (1.14) the diffusive flux

$$q_z = -D\frac{dC}{dz}.$$

The derivative of the concentration gradient is

$$\frac{dC}{dz} = -(C_{sat} - C_l)\frac{d}{dz}\left[\text{erf}\left(\frac{z}{\delta\sqrt{2}}\right)\right]$$

$$= -\frac{2}{\sqrt{\pi}} \cdot \frac{(C_{sat} - C_l)}{\delta\sqrt{2}}e^{-\left(\frac{z}{\delta\sqrt{2}}\right)^2}$$

At the surface of the lake, z is zero and the diffusive flux is

$$q_z = (C_{sat} - C_l)\frac{D\sqrt{2}}{\delta\sqrt{\pi}}.$$

The units of q_z are in $[\text{M}/(\text{L}^2\cdot\text{T})]$. To get the total mass flux rate, we must multiply by a surface area, in this case the surface of the lake A_l. Thus, the total rate of mass flux of oxygen into the lake is

$$\dot{m} = A_l(C_{sat} - C_l)\frac{D\sqrt{2}}{\delta\sqrt{\pi}}.$$

For $C_l < C_{sat}$ the mass flux is positive, indicating flux down, into the lake. More sophisticated models for gas transfer that develop predictive expressions for δ are discussed later in Chapter 5.

call the diffusion coefficient, D. Substituting, we obtain the one-dimensional diffusive flux equation

$$q_x = -D\frac{dC}{dx}. \tag{1.14}$$

It is important to note that diffusive flux is a vector quantity and, since concentration is expressed in units of $[\text{M}/\text{L}^3]$, it has units of $[\text{M}/(\text{L}^2\text{T})]$. To compute the total mass flux rate $\dot{m}$, in units $[\text{M}/\text{T}]$, the diffusive flux must be integrated over a surface area. For the one-dimensional case we would have $\dot{m} = Aq_x$.

Generalizing to three dimensions, we can write the diffusive flux vector at a point by adding the other two dimensions, yielding (in various types of notation)

$$\begin{aligned}
\boldsymbol{q} &= -D\left(\frac{\partial C}{\partial x}, \frac{\partial C}{\partial y}, \frac{\partial C}{\partial z}\right) \\
&= -D\nabla C \\
&= -D\frac{\partial C}{\partial x_i}.
\end{aligned} \tag{1.15}$$

Diffusion processes that obey this relationship are called Fickian diffusion, and (1.15) is called Fick's law. To obtain the total mass flux rate we must integrate the normal component of $\boldsymbol{q}$ over a surface area, as in

$$\dot{m} = \iint_A \boldsymbol{q} \cdot \boldsymbol{n} dA \tag{1.16}$$

where $\boldsymbol{n}$ is the unit vector normal to the surface A.

Table 1.1. Molecular diffusion coefficients for typical solutes in water at standard pressure and at two temperatures (20°C and 10°C).[a]

Solute name	Chemical symbol	Diffusion coefficient[b] $(10^{-4}$ cm^2/s$)$	Diffusion coefficient[c] $(10^{-4}$ cm^2/s$)$
hydrogen ion	H^+	0.85	0.70
hydroxide ion	OH^-	0.48	0.37
oxygen	O_2	0.20	0.15
carbon dioxide	CO_2	0.17	0.12
bicarbonate	HCO_3^-	0.11	0.08
carbonate	CO_3^{2-}	0.08	0.06
methane	CH_4	0.16	0.12
ammonium	NH_4^+	0.18	0.14
ammonia	NH_3	0.20	0.15
nitrate	NO_3^-	0.17	0.13
phosphoric acid	H_3PO_4	0.08	0.06
dihydrogen phosphate	$H_2PO_4^-$	0.08	0.06
hydrogen phosphate	HPO_4^{2-}	0.07	0.05
phosphate	PO_4^{3-}	0.05	0.04
hydrogen sulfide	H_2S	0.17	0.13
hydrogen sulfide ion	HS^-	0.16	0.13
sulfate	SO_4^{2-}	0.10	0.07
silica	H_4SiO_4	0.10	0.07
calcium ion	Ca^{2+}	0.07	0.05
magnesium ion	Mg^{2+}	0.06	0.05
iron ion	Fe^{2+}	0.06	0.05
manganese ion	Mn^{2+}	0.06	0.05

[a] Taken from `http://www.talknet.de/~alke.spreckelsen/roger/thermo/difcoef.html`

[b] for water at 20°C with salinity of 0.5 ppt.

[c] for water at 10°C with salinity of 0.5 ppt.

1.2.2 Diffusion coefficients

From the definition $D = k(\delta x)^2$, we see that D has units L^2/T. Since we derived Fick's law for molecules moving in Brownian motion, D is a molecular diffusion coefficient, which we will sometimes call D_m to be specific. The intensity (energy and freedom of motion) of these Brownian motions controls the value of D. Thus, D depends on the phase (solid, liquid or gas), temperature, and molecule size. For dilute solutes in water, D is generally of order $2 \cdot 10^{-9}$ m^2/s; whereas, for dispersed gases in air, D is of order $2 \cdot 10^{-5}$ m^2/s, a difference of 10^4.

Table 1.1 gives a detailed accounting of D for a range of solutes in water with low salinity (0.5 ppt). We see from the table that for a given temperature, D can range over about $\pm 10^1$ in response to molecular size (large molecules have smaller D). The table also shows the sensitivity of D to temperature; for a 10°C change in water temperature, D
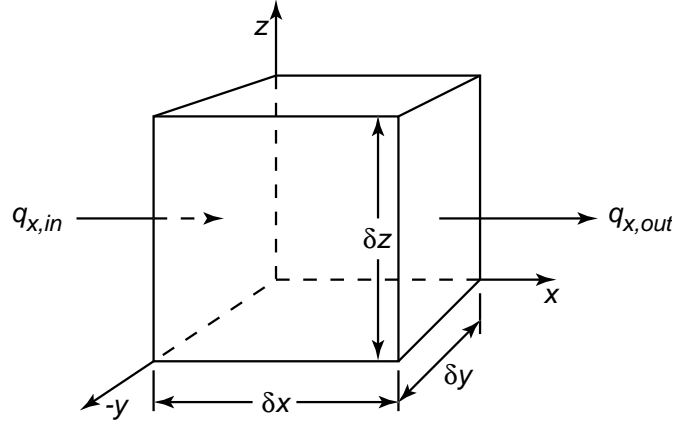
Fig. 1.2. Differential control volume for derivation of the diffusion equation.

can change by a factor of ± 2. These observations can be summarized by the insight that faster and less confined motions result in higher diffusion coefficients.

1.2.3 Diffusion equation

Although Fick's law gives us an expression for the flux of mass due to the process of diffusion, we still require an equation that predicts the change in concentration of the diffusing mass over time at a point. In this section we will see that such an equation can be derived using the law of conservation of mass.

To derive the diffusion equation, consider the control volume (CV) depicted in Figure 1.2. The change in mass M of dissolved tracer in this CV over time is given by the mass conservation law

$$\frac{\partial M}{\partial t} = \sum \dot{m}_{in} - \sum \dot{m}_{out}. \tag{1.17}$$

To compute the diffusive mass fluxes in and out of the CV, we use Fick's law, which for the x-direction gives

$$q_{x,in} = -D \left. \frac{\partial C}{\partial x} \right|_1 \tag{1.18}$$

$$q_{x,out} = -D \left. \frac{\partial C}{\partial x} \right|_2 \tag{1.19}$$

where the locations 1 and 2 are the inflow and outflow faces in the figure. To obtain total mass flux $\dot{m}$ we multiply q_x by the CV surface area $A = \delta y \delta z$. Thus, we can write the net flux in the x-direction as

$$\delta \dot{m}|_x = -D \delta y \delta z \left(\left. \frac{\partial C}{\partial x} \right|_1 - \left. \frac{\partial C}{\partial x} \right|_2 \right) \tag{1.20}$$

which is the x-direction contribution to the right-hand-side of (1.17).

To continue we must find a method to evaluate $\partial C/\partial x$ at point 2. For this, we use linear Taylor series expansion, an important tool for linearly approximating functions. The general form of Taylor series expansion is

$$f(x) = f(x_0) + \left.\frac{\partial f}{\partial x}\right|_{x_0} \delta x + \text{HOT}s, \tag{1.21}$$

where HOTs stands for "higher order terms." Substituting $\partial C/\partial x$ for $f(x)$ in the Taylor series expansion yields

$$\left.\frac{\partial C}{\partial x}\right|_2 = \left.\frac{\partial C}{\partial x}\right|_1 + \frac{\partial}{\partial x}\left(\left.\frac{\partial C}{\partial x}\right|_1\right) \delta x + HOTs. \tag{1.22}$$

For linear Taylor series expansion, we ignore the HOTs. Substituting this expression into the net flux equation (1.20) and dropping the subscript 1, gives

$$\left.\delta\dot{m}\right|_x = D\delta y\delta z\frac{\partial^2 C}{\partial x^2}\delta x. \tag{1.23}$$

Similarly, in the y- and z-directions, the net fluxes through the control volume are

$$\left.\delta\dot{m}\right|_y = D\delta x\delta z\frac{\partial^2 C}{\partial y^2}\delta y \tag{1.24}$$

$$\left.\delta\dot{m}\right|_z = D\delta x\delta y\frac{\partial^2 C}{\partial z^2}\delta z. \tag{1.25}$$

Before substituting these results into (1.17), we also convert M to concentration by recognizing $M = C\delta x\delta y\delta z$. After substitution of the concentration C and net fluxes $\delta\dot{m}$ into (1.17), we obtain the three-dimensional diffusion equation (in various types of notation)

$$\begin{aligned}\frac{\partial C}{\partial t} &= D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right)\\ &= D\nabla^2 C\\ &= D\frac{\partial C}{\partial x_i^2},\end{aligned} \tag{1.26}$$

which is a fundamental equation in environmental fluid mechanics. For the last line in (1.26), we have used the Einsteinian notation of repeated indices as a short-hand for the ∇^2 operator.

1.2.4 One-dimensional diffusion equation

In the one-dimensional case, concentration gradients in the y- and z-direction are zero, and we have the one-dimensional diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}. \tag{1.27}$$

We pause here to consider (1.27) and to point out a few key observations. First, (1.27) is first-order in time. Thus, we must supply and impose one initial condition for its solution, and its solutions will be unsteady, or transient, meaning they will vary with time. To
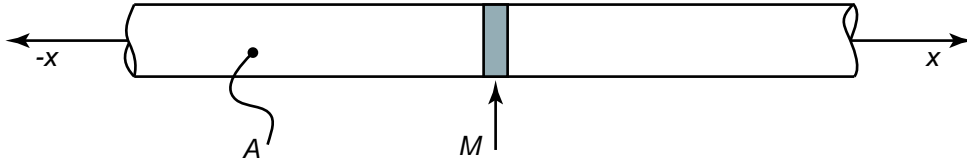
Fig. 1.3. Definitions sketch for one-dimensional pure diffusion in an infinite pipe.

solve for the steady, invariant solution of (1.27), we must set $\partial C/\partial t = 0$ and we no longer require an initial condition; the steady form of (1.27) is the well-known Laplace equation. Second, (1.27) is second-order in space. Thus, we can impose two boundary conditions, and its solution will vary in space. Third, the form of (1.27) is exactly the same as the heat equation, where D is replaced by the heat transfer coefficient κ. This observation agrees well with our intuition since we know that heat conducts (diffuses) away from hot sources toward cold regions (just as concentration diffuses from high concentration toward low concentration). This observation is also useful since many solutions to the heat equation are already known.

1.3 Similarity solution to the one-dimensional diffusion equation

Because (1.26) is of such fundamental importance in environmental fluid mechanics, we demonstrate here one of its solutions for the one-dimensional case in detail. There are multiple methods that can be used to solve (1.26), but we will follow the methodology of Fischer et al. (1979) and choose the so-called similarity method in order to demonstrate the usefulness of dimensional analysis as presented in Section 1.1.2.

Consider the one-dimensional problem of a narrow, infinite pipe (radius a) as depicted in Figure 1.3. A mass of tracer M is injected uniformly across the cross-section of area $A = \pi a^2$ at the point $x = 0$ at time $t = 0$. The initial width of the tracer is infinitesimally small. We seek a solution for the spread of tracer in time due to molecular diffusion alone.

As this is a one-dimensional ($\partial C/\partial y = 0$ and $\partial C/\partial z = 0$) unsteady diffusion problem, (1.27) is the governing equation, and we require two boundary conditions and an initial condition. As boundary conditions, we impose that the concentration at $\pm\infty$ remain zero

$$C(\pm\infty, t) = 0. \tag{1.28}$$

The initial condition is that the dye tracer is injected uniformly across the cross-section over an infinitesimally small width in the x-direction. To specify such an initial condition, we use the Dirac delta function

$$C(x, 0) = (M/A)\delta(x) \tag{1.29}$$

where $\delta(x)$ is zero everywhere accept at $x = 0$, where it is infinite, but the integral of the delta function from $-\infty$ to ∞ is 1. Thus, the total injected mass is given by

Table 1.2. Dimensional variables for one-dimensional pipe diffusion.

	Variable	Dimensions
dependent variable	C	M/L^3
independent variables	M/A	M/L^2
	D	L^2/T
	x	L
	t	T

$$M = \int_V C(x,t)dV \tag{1.30}$$

$$= \int_{-\infty}^{\infty} \int_0^a (M/A)\delta(x)2\pi r dr dx. \tag{1.31}$$

To use dimensional analysis, we must consider all the parameters that control the solution. Table 1.2 summarizes the dependent and independent variables for our problem. There are $m = 5$ parameters and $n = 3$ dimensions; thus, we can form two dimensionless groups

$$\pi_1 = \frac{C}{M/(A\sqrt{Dt})} \tag{1.32}$$

$$\pi_2 = \frac{x}{\sqrt{Dt}} \tag{1.33}$$

From dimensional analysis we have that $\pi_1 = f(\pi_2)$, which implies for the solution of C

$$C = \frac{M}{A\sqrt{Dt}} f\left(\frac{x}{\sqrt{Dt}}\right) \tag{1.34}$$

where f is a yet-unknown function with argument π_2. (1.34) is called a similarity solution because C has the same shape in x at all times t (see also Example Box 1.3). Now we need to find f in order to know what that shape is. Before we find the solution formally, compare (1.34) with the actual solution given by (1.53). Through this comparison, we see that dimensional analysis can go a long way toward finding solutions to physical problems.

The function f can be found in two primary ways. First, experiments can be conducted and then a smooth curve can be fit to the data using the coordinates π_1 and π_2. Second, (1.34) can be used as the solution to a differential equation and f solved for analytically. This is what we will do here. The power of a similarity solution is that it turns a partial differential equation (PDE) into an ordinary differential equation (ODE), which is the goal of any solution method for PDEs.

The similarity solution (1.34) is really just a coordinate transformation. We will call our new similarity variable $\eta = x/\sqrt{Dt}$. To substitute (1.34) into the diffusion equation, we will need the two derivatives

$$\frac{\partial \eta}{\partial t} = -\frac{\eta}{2t} \tag{1.35}$$

$$\frac{\partial \eta}{\partial x} = \frac{1}{\sqrt{Dt}}. \tag{1.36}$$

We first use the chain rule to compute $\partial C/\partial t$ as follows

$$\begin{aligned}
\frac{\partial C}{\partial t} &= \frac{\partial}{\partial t}\left[\frac{M}{A\sqrt{Dt}}f(\eta)\right] \\
&= \frac{\partial}{\partial t}\left[\frac{M}{A\sqrt{Dt}}\right]f(\eta) + \frac{M}{A\sqrt{Dt}}\frac{\partial f}{\partial \eta}\frac{\partial \eta}{\partial t} \\
&= \frac{M}{A\sqrt{Dt}}\left(-\frac{1}{2}\right)\frac{1}{t}f(\eta) + \frac{M}{A\sqrt{Dt}}\frac{\partial f}{\partial \eta}\left(-\frac{\eta}{2t}\right) \\
&= -\frac{M}{2At\sqrt{Dt}}\left(f + \eta\frac{\partial f}{\partial \eta}\right).
\end{aligned} \tag{1.37}$$

Similarly, we use the chain rule to compute $\partial^2 C/\partial x^2$ as follows

$$\begin{aligned}
\frac{\partial^2 C}{\partial x^2} &= \frac{\partial}{\partial x}\left[\frac{\partial}{\partial x}\left(\frac{M}{A\sqrt{Dt}}f(\eta)\right)\right] \\
&= \frac{\partial}{\partial x}\left[\frac{M}{A\sqrt{Dt}}\frac{\partial \eta}{\partial x}\frac{\partial f}{\partial \eta}\right] \\
&= \frac{M}{ADt\sqrt{Dt}}\frac{\partial^2 f}{\partial \eta^2}.
\end{aligned} \tag{1.38}$$

Upon substituting these two results into the diffusion equation, we obtain the ordinary differential equation in η

$$\frac{d^2 f}{d\eta^2} + \frac{1}{2}\left(f + \eta\frac{df}{d\eta}\right) = 0. \tag{1.39}$$

To solve (1.39), we should also convert the boundary and initial conditions to two new constraints on f. As we will see shortly, both boundary conditions and the initial condition can be satisfied through a single condition on f. The other constraint (remember that second order equations require two constrains) is taken from the conservation of mass, given by (1.30). Substituting $dx = d\eta\sqrt{Dt}$ into (1.30) and simplifying, we obtain

$$\int_{-\infty}^{\infty} f(\eta)d\eta = 1. \tag{1.40}$$

Solving (1.39) requires a couple of integrations. First, we rearrange the equation using the identity

$$\frac{d(f\eta)}{d\eta} = f + \eta\frac{df}{d\eta}, \tag{1.41}$$

which gives us

$$\frac{d}{d\eta}\left[\frac{df}{d\eta} + \frac{1}{2}f\eta\right] = 0. \tag{1.42}$$

Integrating once leaves us with

$$\frac{df}{d\eta} + \frac{1}{2}f\eta = C_0. \tag{1.43}$$

It can be shown that choosing $C_0 = 0$ satisfies both boundary conditions and the initial condition (see Appendix A for more details).

With $C_0 = 0$ we have a homogeneous ordinary differential equation whose solution can readily be found. Moving the second term to the right hand side we have

$$\frac{df}{d\eta} = -\frac{1}{2}f\eta. \tag{1.44}$$

The solution is found by collecting the f- and η-terms on separate sides of the equation

$$\frac{df}{f} = -\frac{1}{2}\eta d\eta. \tag{1.45}$$

Integrating both sides gives

$$\ln(f) = -\frac{1}{2}\frac{\eta^2}{2} + C_1 \tag{1.46}$$

which after taking the exponential of both sides gives

$$f = C_1 \exp\left(-\frac{\eta^2}{4}\right). \tag{1.47}$$

To find C_1 we must use the remaining constraint given in (1.40)

$$\int_{-\infty}^{\infty} C_1 \exp\left(-\frac{\eta^2}{4}\right) d\eta = 1. \tag{1.48}$$

To solve this integral, we should use integral tables; therefore, we have to make one more change of variables to remove the 1/4 from the exponential. Thus, we introduce ζ such that

$$\zeta^2 = \frac{1}{4}\eta^2 \tag{1.49}$$

$$2d\zeta = d\eta. \tag{1.50}$$

Substituting this coordinate transformation and solving for C_1 leaves

$$C_1 = \frac{1}{2\int_{-\infty}^{\infty} \exp(-\zeta^2)d\zeta}. \tag{1.51}$$

After looking up the integral in a table, we obtain $C_1 = 1/(2\sqrt{\pi})$. Thus,

$$f(\eta) = \frac{1}{2\sqrt{\pi}} \exp\left(\frac{\eta^2}{4}\right). \tag{1.52}$$

Replacing f in our similarity solution (1.34) gives

$$C(x,t) = \frac{M}{A\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{1.53}$$

which is a classic result in environmental fluid mechanics, and an equation that will be used thoroughly throughout this text. Generalizing to three dimensions, Fischer et al. (1979) give the the solution

$$C(x,y,z,t) = \frac{M}{4\pi t\sqrt{4\pi D_x D_y D_z t}} \exp\left(-\frac{x^2}{4D_x t} - \frac{y^2}{4D_y t} - \frac{z^2}{4D_z t}\right) \tag{1.54}$$

which they derive using the separation of variables method.

Example Box 1.2:
Maximum concentrations.

For the three-dimensional instantaneous point-source solution given in (1.54), find an expression for the maximum concentration. Where is the maximum concentration located?

The classical approach for finding maxima of functions is to look for zero-points in the derivative of the function. For many concentration distributions, it is easier to take a qualitative look at the functional form of the equation. The instantaneous point-source solution has the form

$$C(\boldsymbol{x}, t) = C_1(t) \exp(-|f(\boldsymbol{x}, t)|).$$

$C_1(t)$ is an amplification factor independent of space. The exponential function has a negative argument, which means it is maximum when the argument is zero. Hence, the maximum concentration is

$$C_{max}(t) = C_1(t).$$

Applying this result to (1.54) gives

$$C_{max}(t) = \frac{M}{4\pi t \sqrt{4\pi D_x D_y D_z t}}.$$

The maximum concentration occurs at the point where the exponential is zero. In this case $\boldsymbol{x}(C_{max}) = (0, 0, 0)$.

We can apply this same analysis to other concentration distributions as well. For example, consider the error function concentration distribution

$$C(x, t) = \frac{C_0}{2} \left(1 - \mathrm{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right).$$

The error function ranges over $[-1, 1]$ as its argument ranges from $[-\infty, \infty]$. The maximum concentration occurs when $\mathrm{erf}(\cdot) = -1$, and gives,

$$C_{max}(t) = C_0.$$

C_{max} occurs when the argument of the error function is $-\infty$. At $t = 0$, the maximum concentration occurs for all points $x < 0$, and for $t > 0$, the maximum concentration occurs only at $x = -\infty$.
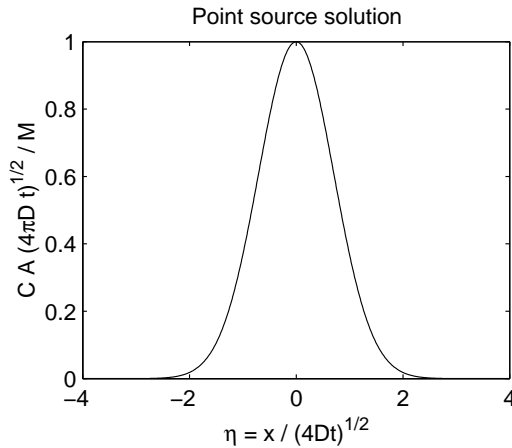

Fig. 1.4. Self-similarity solution for one-dimensional diffusion of an instantaneous point source in an infinite domain.

1.3.1 Interpretation of the similarity solution

Figure 1.4 shows the one-dimensional solution (1.53) in non-dimensional space. Comparing (1.53) with the Gaussian probability distribution reveals that (1.53) is the normal bell-shaped curve with a standard deviation σ, of width

$$\sigma^2 = 2Dt. \tag{1.55}$$

The concept of self similarity is now also evident: the concentration profile shape is always Gaussian. By plotting in non-dimensional space, the profiles also collapse into a single profile; thus, profiles for all times $t > 0$ are given by the result in the figure.

The Gaussian distribution can also be used to predict how much tracer is within a certain region. Looking at Figure 1.4 it appears that most of the tracer is between -2 and 2. Gaussian probability tables, available in any statistics book, can help make this observation more quantitative. Within $\pm\sigma$, 64.2% of the tracer is found and between $\pm 2\sigma$, 95.4% of the tracer is found. As an engineering rule-of-thumb, we will say that a diffusing tracer is distributed over a region of width 4σ, that is, $\pm 2\sigma$.

Example Box 1.3:
Profile shape and self similarity.

For the one-dimensional, instantaneous point-source solution, show that the ratio C/C_{max} can be written as a function of the single parameter α defined such that $x = \alpha\sigma$. How might this be used to estimate the diffusion coefficient from concentration profile data?

From the previous example, we know that $C_{max} = M/\sqrt{4\pi Dt}$, and we can re-write (1.53) as

$$\frac{C(x,t)}{C_{max}(t)} = \exp\left(-\frac{x^2}{4Dt}\right).$$

We now substitute $\sigma = \sqrt{2Dt}$ and $x = \alpha\sigma$ to obtain

$$\frac{C}{C_{max}} = \exp\left(-\alpha^2/2\right).$$

Here, α is a parameter that specifies the point to calculate C based on the number of standard deviations the point is away from the center of mass. This illustrates very clearly the notion of self similarity: regardless of the time t, the amount of mass M, or the value of D, the ratio C/C_{max} is always the same value at the same position αx.

This relationship is very helpful for calculating diffusion coefficients. Often, we do not know the value of M. We can, however, always normalize a concentration profile measured at a given time t by $C_{max}(t)$. Then we pick a value of α, say 1.0. We know from the relationship above that $C/C_{max} = 0.61$ at $x = \sigma$. Next, find the locations where $C/C_{max} = 0.61$ in the experimental profile and use them to measure σ. We then use the relationship $\sigma = \sqrt{2Dt}$ and the value of t to estimate D.

1.4 Application: Diffusion in a lake

With a solid background now in diffusion, consider the following example adapted from Nepf (1995).

As shown in Figures 1.5 and 1.6, a small alpine lake is mildly stratified, with a thermocline (region of steepest density gradient) at 3 m depth, and is contaminated by arsenic. Determine the magnitude and direction of the diffusive flux of arsenic through the thermocline (cross-sectional area at the thermocline is $A = 2 \cdot 10^4$ m^2) and discuss the nature of the arsenic source. The molecular diffusion coefficient is $D_m = 1 \cdot 10^{-10}$ m^2/s.

Molecular diffusion. To compute the molecular diffusive flux through the thermocline, we use the one-dimensional version of Fick's law, given above in (1.14)

$$q_z = -D_m\frac{\partial C}{\partial z}. \tag{1.56}$$

We calculate the concentration gradient at $z = 3$ from the concentration profile using a finite difference approximation. Substituting the appropriate values, we have
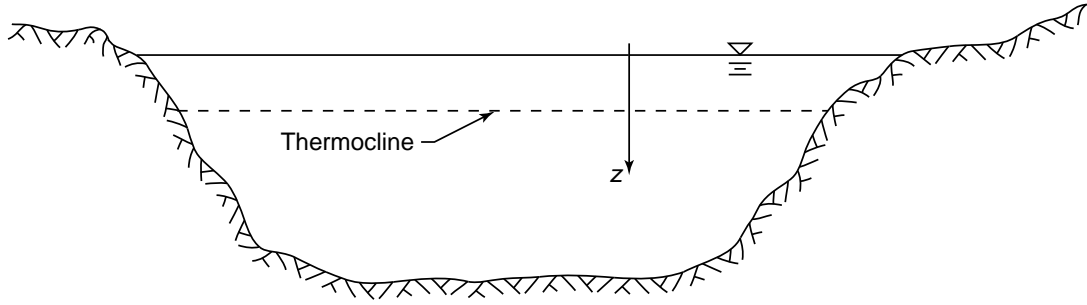
$$q_z = -D_m\frac{\partial C}{\partial z}$$

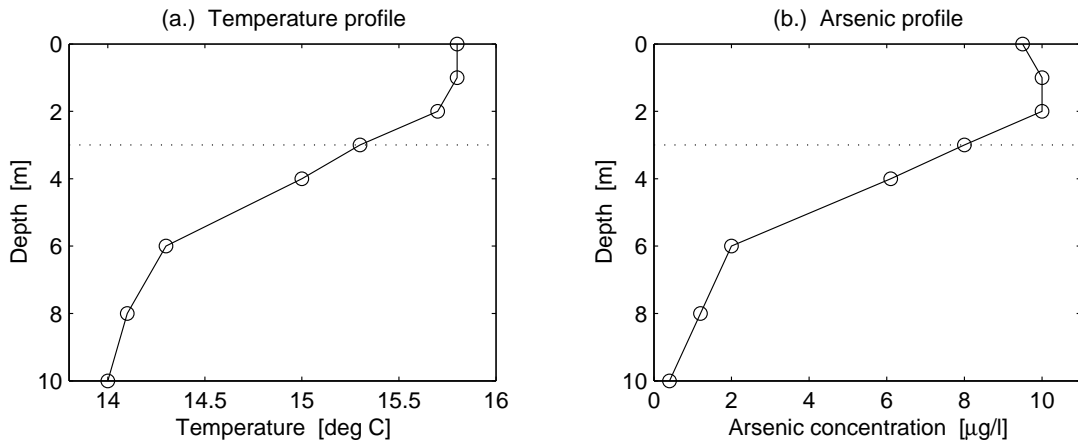**Fig. 1.5.** Schematic of a stratified alpine lake.

Fig. 1.6. Profiles of temperature and arsenic concentration in an alpine lake. The dotted line at 3 m indicates the location of the thermocline (region of highest density gradient).

$$= -(1 \cdot 10^{-10}) \frac{(10 - 6.1)}{(2 - 4)} \cdot \frac{1000 \text{ l}}{1 \text{ m}^3}$$

$$= +1.95 \cdot 10^{-7} \; \mu\text{g}/(\text{m}^2 \cdot \text{s}) \tag{1.57}$$

where the plus sign indicates that the flux is downward. The total mass flux is obtained by multiplying over the area: $\dot{m} = A q_z = 0.0039 \; \mu\text{g/s}$.

Turbulent diffusion. As we pointed out in the discussion on diffusion coefficients, faster random motions lead to larger diffusion coefficients. As we will see in Chapter 3, turbulence also causes a kind of random motion that behaves asymptotically like Fickian diffusion. Because the turbulent motions are much larger than molecular motions, turbulent diffusion coefficients are much larger than molecular diffusion coefficients.

Sources of turbulence at the thermocline of a small lake can include surface inflows, wind stirring, boundary mixing, convection currents, and others. Based on studies in this lake, a turbulent diffusion coefficient can be taken as $D_t = 1.5 \cdot 10^{-6}$ m^2/s. Since turbulent diffusion obeys the same Fickian flux law, then the turbulent diffusive flux $q_{z,t}$ can be related to the molecular diffusive flux $q_{z,t} = q_z$ by the equation

$$q_{z,t} = q_{z,m} \frac{D_t}{D_m} \tag{1.58}$$

$$= +2.93 \cdot 10^{-3} \ \mu\text{g}/(\text{m}^2 \cdot \text{s}). \tag{1.59}$$

Hence, we see that turbulent diffusive transport is much greater than molecular diffusion. As a warning, however, if the concentration gradients are very high and the turbulence is low, molecular diffusion can become surprisingly significant!

Implications. Here, we have shown that the concentration gradient results in a net diffusive flux of arsenic into the hypolimnion (region below the thermocline). Assuming no other transport processes are at work, we can conclude that the arsenic source is at the surface. If the diffusive transport continues, the hypolimnion concentrations will increase. The next chapter considers how the situation might change if we include another type of transport: advection.

Summary

This chapter introduced the subject of environmental fluid mechanics and focused on the important transport process of diffusion. Fick's law was derived to represent the mass flux (transport) due to diffusion, and Fick's law was used to derive the diffusion equation, which is used to predict the time-evolution of a concentration field in space due to diffusive transport. A similarity method was used through the aid of dimensional analysis to find a one-dimensional solution to the diffusion equation for an instantaneous point source. As illustrated through an example, diffusive transport results when concentration gradients exist and plays an important role in predicting the concentrations of contaminants as they move through the environment.

Exercises

1.1 Definitions. Write a short, qualitative definition of the following terms:

Concentration.	Partial differential equation.
Mass fraction.	Standard deviation.
Density.	Chemical fate.
Diffusion.	Chemical transport.
Brownian motion.	Transport equation.
Instantaneous point source.	Fick's law.
Similarity method.	

1.2 Concentrations in water. A student adds 1.00 mg of pure Rhodamine WT (a common fluorescent tracer used in field experiments) to 1.000 l of water at 20°C. Assuming the solution is dilute so that we can neglect the equation of state of the solution, compute the concentration of the Rhodamine WT mixture in the units of mg/l, mg/kg, ppm, and ppb.

1.3 Concentration in air. Air consists of 21% oxygen. For air with a density of 1.4 kg/m^3, compute the concentration of oxygen in the units of mg/l, mg/kg, mol/l, and ppm.

1.4 Instantaneous point source. Consider the pipe section depicted in Figure 1.3. A student injects 5 ml of 20% Rhodamine-WT solution (specific gravity 1.15) instantaneously and uniformly over the pipe cross-section ($A = 0.8$ cm^3) at the point $x = 0$ and the time $t = 0$. The pipe is filled with stagnant water. Assume the molecular diffusion coefficient is $D_m = 0.13 \cdot 10^{-4}$ cm^2/s.

- What is the concentration at $x = 0$ at the time $t = 0$?
- What is the standard deviation of the concentration distribution 1 s after injection?
- Plot the maximum concentration in the pipe, $C_{max}(t)$, as a function of time over the interval $t = [0, 24 \text{ h}]$.
- How long does it take until the concentration over the region $x = \pm 1$ m can be treated as uniform? Define a uniform concentration distribution as one where the minimum concentration within a region is no less than 95% of the maximum concentration within that same region.

1.5 Advection versus diffusion. Rivers can often be approximated as advection dominated (downstream transport due to currents is much faster than diffusive transport) or diffusion dominated (diffusive transport is much faster than downstream transport due to currents). This property is described by a non-dimensional parameter (called the Peclet number) $Pe = f(u, D, x)$, where u is the stream velocity, D is the diffusion coefficient, and x is the distance downstream to the point of interest. Using dimensional analysis, find the form of Pe such that $Pe \ll 1$ is advection dominated and $Pe \gg 1$ is diffusion dominated. For a stream with $u = 0.3$ m/s and $D = 0.05$ m^2/s, where are diffusion and advection equally important?

1.6 Maximum concentrations. Referring to Figure 1.4, we note that the maximum concentration in space is always found at the center of the distribution ($x = 0$). For a point at $x = r$, however, the maximum concentration over time occurs at one specific time t_{max}. Using (1.53) find an equation for the time t_{max} at which the maximum concentration occurs at the point $x = r$.

1.7 Diffusion in a river. The Rhein river can be approximated as having a uniform depth ($h = 5$ m), width ($B = 300$ m) and mean flow velocity ($u = 0.7$ m/s). Under these conditions, 100 kg of tracer is injected as a point source (the injection is evenly distributed transversely over the cross-section). The cloud is expected to diffuse laterally as a one-dimensional point source in a moving coordinate system, moving at the mean stream velocity. The river has an enhanced mixing coefficient of $D = 10$ m^2/s. How long does it take the cloud to reach a point $x = 15000$ m downstream? What is the maximum concentration that passes the point x? How wide is the cloud (take the cloud width as 4σ) when it passes this point?

Table 1.3. Measured concentration and time for a point source diffusing in three-dimensions for problem number 18.

Time (days)	Concentration (μg/cm^3 $\pm$0.03)
0.5	0.02
1.0	0.50
1.5	2.08
2.0	3.66
2.5	4.81
3.0	5.50
3.5	5.80
4.0	5.91
4.5	5.81
5.0	5.70
5.5	5.54
6.0	5.28
6.5	5.05
7.0	4.87
7.5	4.65
8.0	4.40
8.5	4.24
9.0	4.00
9.5	3.84
10.0	3.66

1.8 Measuring diffusion coefficients 1. A chemist is trying to calculate the diffusion coefficient for a new chemical. In his experiments, he measured the concentration as a function of time at a point 5 cm away from a virtual point source diffusing in three dimensions. Select a set of coordinates such that, when plotting the data in Table 1.3, D is the slope of a best-fit line through the data. Based on this coordinate transformation, what is more important to measure precisely, concentration or time? What recommendation would you give to this scientist to improve the accuracy of his estimate for the diffusion coefficient?

1.9 Measuring diffusion coefficients 2.[1] As part of a water quality study, you have been asked to assess the diffusion of a new fluorescent dye. To accomplish this, you do a dye study in a laboratory tank (depth $h = 40$ cm). You release the dye at a depth of 20 cm (spread evenly over the area of the tank) and monitor its development over time. Vertical profiles of dye concentration in the tank are shown in Figure 1.7; the x-axis represents the reading on your fluorometer and the y-axis represents the depth.

- Estimate the molecular diffusion coefficient of the dye, D_m, based on the evolution of the dye cloud.
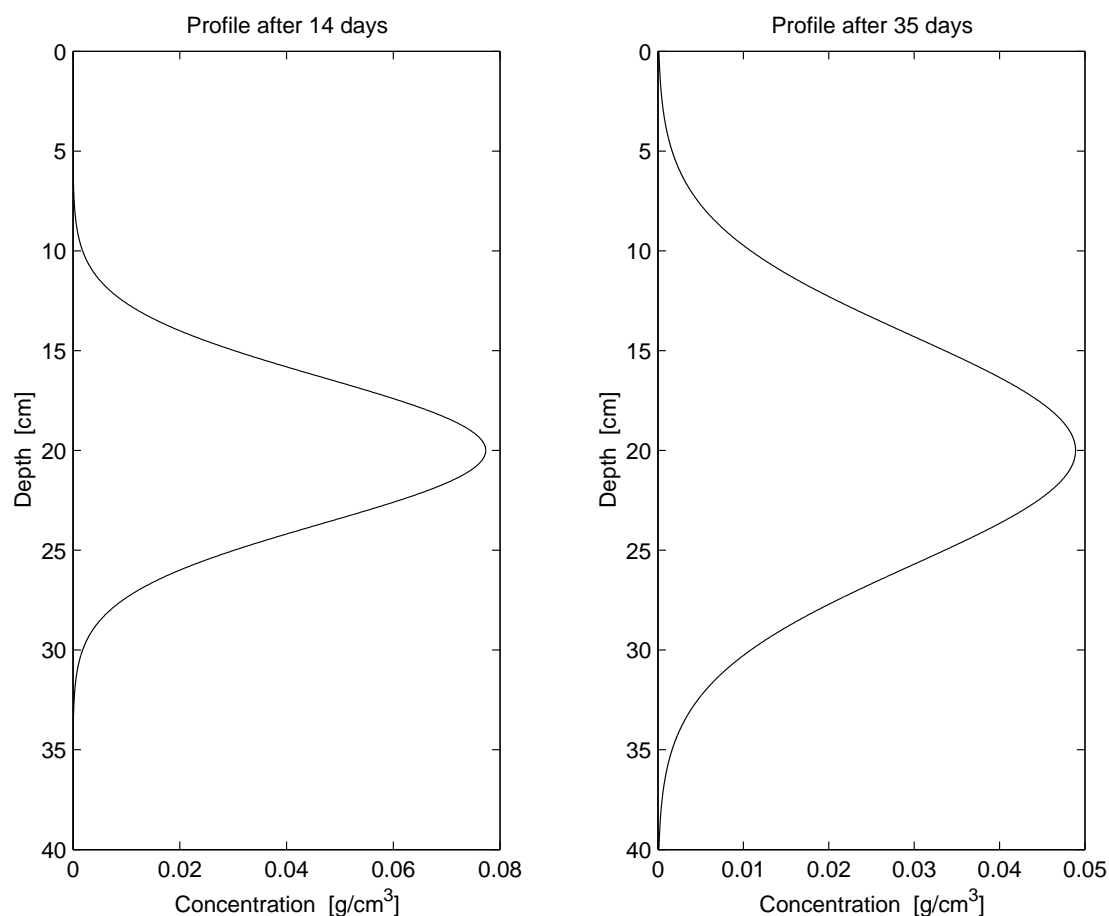
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[1] This problem is adapted from Nepf (1995).

Fig. 1.7. Concentration profiles of fluorescent dye for two different measurement times. Refer to problem number 1.9.

- Predict at what time the vertical distribution of the dye will be affected by the boundaries of the tank.

1.10 Radiative heaters. A student heats his apartment (surface area $A_r = 32$ m^2 and ceiling height $h = 3$ m) with a radiative heater. The heater has a total surface area of $A_h = 0.8$ m^2; the thickness of the heater wall separating the heater fluid from the outside air is $\delta x = 3$ mm (refer to Figure 1.8). The conduction of heat through the heater wall is given by the diffusion equation

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T \tag{1.60}$$

where T is the temperature in °C and $\kappa = 1.1 \cdot 10^{-2}$ kcal/(s°Cm) is the thermal conductivity of the metal for the heater wall. The heat flux $\boldsymbol{q}$ through the heater wall is given by

$$\boldsymbol{q} = -\kappa \nabla T. \tag{1.61}$$

Recall that 1 kcal = 4184 J and 1 Watt = 1 J/s.

- The conduction of heat normal to the heater wall can be treated as one-dimensional. Write (1.60) and (1.61) for the steady-state, one-dimensional case.
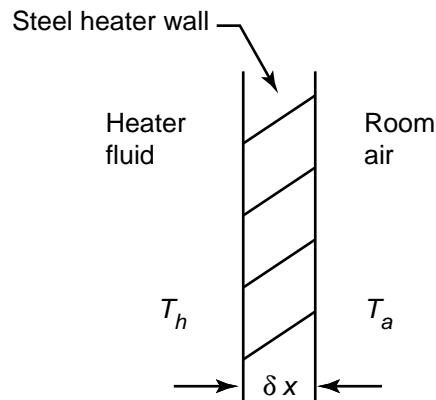
Fig. 1.8. Definitions sketch for one-dimensional thermal conduction for the heater wall in problem number 1.10.

- Solve (1.60) for the steady-state, one-dimensional temperature profile through the heater wall with boundary conditions $T(0) = T_h$ and $T(\delta x) = T_r$ (refer to Figure 1.8).
- The water in the heater and the air in the room move past the heater wall such that $T_h = 85°C$ and $T_r = 35°C$. Compute the heat flux from (1.61) using the steady-state, one-dimensional solution just obtained.
- How many 300 Watt lamps are required to equal the heat output of the heater assuming 100% efficiency?
- Assume the specific heat capacity of the air is $c_v = 0.172$ kcal/(kg·K) and the density is $\rho_a = 1.4$ kg/m³. How much heat is required to raise the temperature of the apartment by 5°C?
- Given the heat output of the heater and the heat needed to heat the room, how might you explain that the student is able to keep the heater turned on all the time?