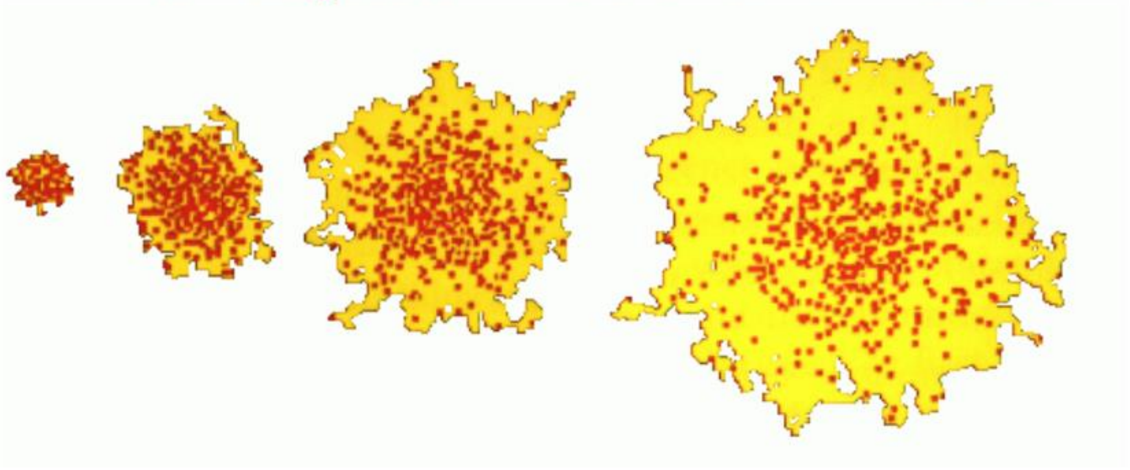
Transport Processes in the Environment

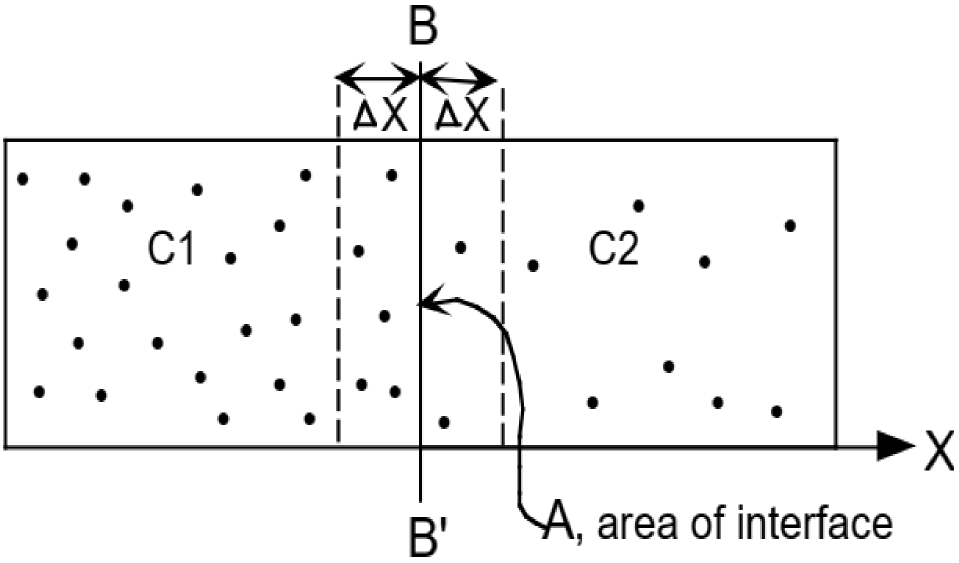
1. Conceptual Model of Diffusion



This section introduces the concept of molecular diffusion based on the random path of molecules. The theory and animation demonstrate how, through Brownian motion, a Gaussian distribution of molecules is obtained from a point release. The diffusion coefficient, D, is introduced as the coefficient in Fick's Law - which states that mass flux is directly proportional to, and in the opposite direction of, the concentration gradient. As noted by Fischer et al. (1979), several environmental dispersion problems can be described by processes that are strongly analogous to molecular diffusion, so it's an incredibly important concept! The example problems test one's knowledge of Fick's Law, the physical meaning of the diffusion coefficient, and the use of the Gaussian distribution to describe concentration profiles.

1. Conceptual Model for Diffusion

Diffusion is defined as the net transport due to random motion. A model for diffusive flux can be constructed from the following simple example. Consider a one-dimensional system with motion in the X direction only. An interface B-B' separates two regions of different concentration, C1 and C2 = particles/volume on the left and right side of the interface, respectively. The motion of each particle is a one-dimensional random walk. In each time interval, Δt, each particle will move a distance $\pm \Delta X$, moving right ($+ \Delta X$) or left ($- \Delta X$) with equal probability.



Within each time step, any particle within a distance ΔX of the interface B-B' has a 50% probability of crossing over that interface. The number of particles with the potential to cross B-B' from left to right (positive mass flux) is (C1 ΔX A), where A is the area of interface B-B'. On average half of these take a positive step and cross the interface in time Δt, such that the flux left to right is (0.5 C1 ΔX A). Similarly, the number of particles crossing right to left in Δt (negative mass flux) will be (0.5 C2 ΔX A). The resulting mass flux, q_X, is

$$(1)\qquad q_X = \frac{0.5\ \Delta X\ A\ (C1 - C2)}{\Delta t}.$$

If C(x) is continuous, then $C2 \approx C1 + \Delta X\ \partial C/\partial x$, and (1) becomes

$$(2)\qquad q_X \approx -\left[\frac{\Delta X^2}{2\Delta t}\right] A\ \frac{\partial C}{\partial x} = -D\ A \frac{\partial C}{\partial x} = [\text{mass}/\text{time}].$$

The coefficient of diffusion, $D \sim (1/2)\Delta X^2/\Delta t$, has units of [length^2 time^{-1}]. The diffusivity of a chemical molecule in a given fluid depends on the ease with which the molecule can move, specifically, how far, ΔX, the molecule can move in a given time interval. The ease of molecular motion, and thus the diffusivity of a particular chemical, will depend on the molecule size and polarity, the type of fluid and the temperature.

Equation (2) is a mathematical expression of **Fick's Law**. Fick's Law states that the flux of solute mass crossing a unit area, A, per unit time, Δt, in a given direction, e.g. x, is proportional to the gradient of concentration in that direction, $\partial C/\partial x$, and is counter-gradient, *i.e.* the net flux is down-gradient. Because the flux in any direction is proportional only to the concentration gradient in that direction, Fick's Law can be directly extended to three-dimensions.

$$(3) \qquad (q_x, q_y, q_z) = \left(-DA_{yz}\frac{\partial C}{\partial x},\ -DA_{xz}\frac{\partial C}{\partial y},\ -DA_{xy}\frac{\partial C}{\partial z}\right).$$

For molecular diffusion the coefficient for diffusion is isotropic, *i.e.* the same in all directions. This is not typically true for turbulent diffusion.

Diffusion from a point source

Consider a cloud of N particles (and total mass M) released at $x = 0$ and $t = 0$. Under the action of molecular diffusion, the cloud will slowly spread. We use the random walk model to predict the distribution of particle (mass) concentration, C(x,t). Note, that if we assume a unit mass per particle, we can conveniently interchange $N = M$. For simplicity we again consider a one-dimensional system, with the same rules of random motion described above, *i.e.* at each time step, Δt, each particle will move either $+\Delta X$ or $-\Delta X$ with equal probability. Over time each particle will move a bit forward and a bit backward. The probable location of an individual particle after many such steps can be predicted with the Central Limit Theorem (see any basic statistics text). Specifically, in the limit of many steps, the probability that a particle will be located between $m\Delta X$ and $(m+1)\Delta X$ approaches a normal distribution with a zero mean and a standard deviation of

$$(4) \qquad \sigma = \sqrt{2Dt},$$

where, as above,

$$(5) \qquad D = (1/2)\Delta X^2/\Delta t.$$

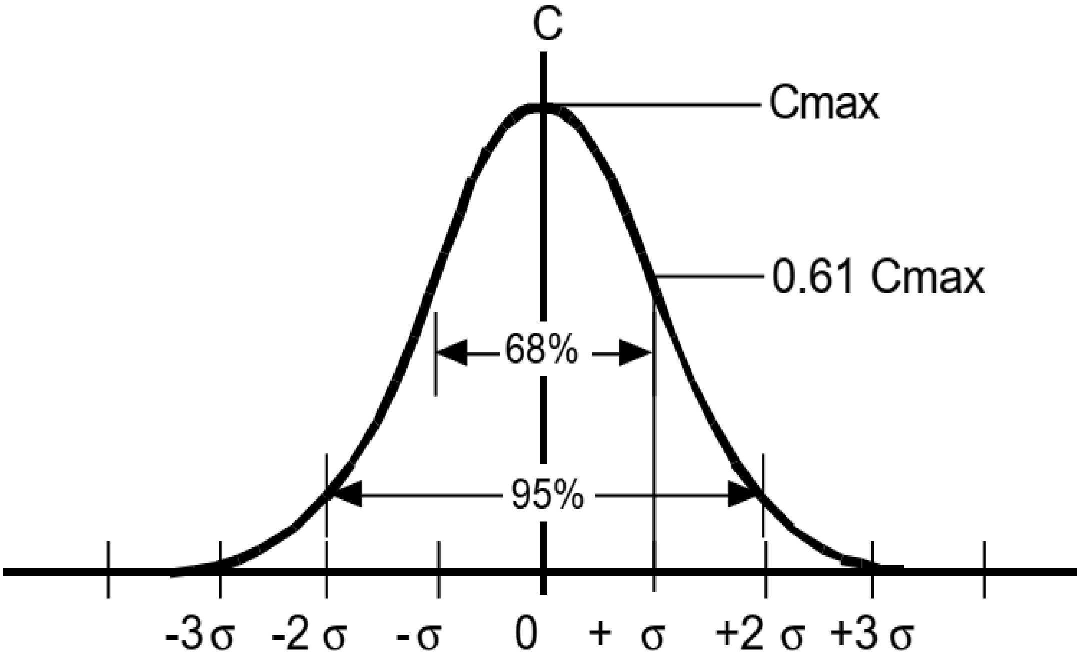
The probability that a particle ends up between x and $x+\Delta X$ is

$$(6) \qquad p(x,t)\Delta X = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{x^2}{2\sigma^2}\right)\Delta X = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{2\sigma^2}\right)\Delta X.$$

Now consider the full cloud of N particles. At any time t, the number of particles between x and $x+\Delta X$ is expected to be $n(x,t) = N\,p(x,t)\Delta X$. Thus, the concentration, C, at position X is $C(x,t) \approx n(x,t)/(A\,\Delta X)$, where A is the constant cross-section of the one-dimensional system. Exchanging M for N, the concentration distribution, C(x,t),

(7) $$C(x,t) = \frac{M}{A\sqrt{4\pi Dt}}\exp(-x^2/4Dt) = [\text{mass} / \text{length}^3]$$

As noted above, this distribution is the normal distribution with zero mean and standard deviation, $\sigma = \sqrt{2Dt}$, which should be familiar to you from any basic statistics course. Briefly, the distribution forms a bell-curve, as shown below. At any time, sixty-eight percent of the total mass (total number of particles) falls within $\pm\sigma$ of the mean position ($x = 0$). Ninety-five percent of the mass falls within $\pm 2\sigma$ of the mean position. And, 99.7% falls within $\pm 3\sigma$ of the mean position. Based on these limits, it has become common to define the extent of a concentration patch based on the contour that includes ninety-five percent of the total mass, i.e. the contour at 2σ from the center. With this convention the length of a diffusing cloud, L, is often taken as $L = 4\sigma$.



It is also useful to note that the concentration level at one standard deviation from the cloud center is 61% of the maximum concentration, *i.e.* $C(x = \pm\sigma) = 0.61$ Cmax, where Cmax is the concentration at the center of the cloud. This value provides a useful way to rapidly define the standard deviation of a particle (species) cloud.

Example of Random Walk Process: See Animation

This animation shows the motion of 500 particles in a one-dimensional random walk with step size $\Delta X = 1$ in time $\Delta t = 1$. At $t = 0$ the particles are located at 0. This random walk animation mimics the effect of Fickian Diffusion. As you watch the animation, consider the following.

Graph of Absolute Particle Location (lower left window).

This graph shows the number of particles located at each position of the x-axis. The number of particles per location is analogous to a concentration.

1) Over time how does the peak particle number, N, (concentration, C) change under the influence of random particle motion (diffusion)?
2) Over time how does the gradient in particle number (concentration), i.e. dN/dx (dC/dx) change under the influence of random particle motion (diffusion)?
3) What is the sign of the particle number (concentration) gradient (dN/dx) for $x > 0$? Consider the animation of individual particle motion (uppermost window). For $x > 0$, is the net particle flux positive (to the right) or negative (to the left)? Is the direction of flux up-gradient of down-gradient? Is the relationship between the direction of flux and the concentration gradient consistent with Fick's Law (equation 3)?
4) Estimate the diffusion coefficient, D, using equation (4) above, and the values of σ given in the upper left corner of this graph. You can pause the animation. How does the realized value of D compare with the theoretical value given in equation (5). Note that no specific units are given here, such that D will simply have unit L^2T^{-1}, where L is an arbitrary length unit and T is the arbitrary time unit.

Graph of Particle Location in Terms of σ.

This graph plots the distribution of particle location with the position normalized by the standard deviation, σ. The solid curve is the Gaussian distribution.

5) Note that at early time (first few time steps) the real distribution of particles does not approximate a Gaussian distribution very well. This is because the Gaussian distribution is only valid after a sufficient number of steps (Central Limit Theorem). Use the animation to estimate how many steps are required for the distribution to consistently fit the Gaussian distribution.

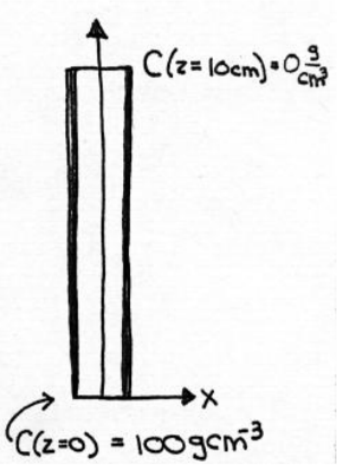
Key Aspects of Diffusion

(1) Diffusion is the net flux due to random motion.
(2) Diffusive flux is proportional but opposite in sign to the gradient of concentration.
(3) Diffusion acts to dilute concentration and reduce gradients of concentration.

CLASS EXERCISES (WITH SOLUTIONS)

Problem 1

A circular tube is filled with still water. The concentration at each end of the tube is maintained at a constant value. Estimate the magnitude and direction of mass flux through the tube. The cross-section is $A = 1\,cm^2$, and diffusion is molecular, $D = 10^{-5}\,cm^2 g^{-1}$.

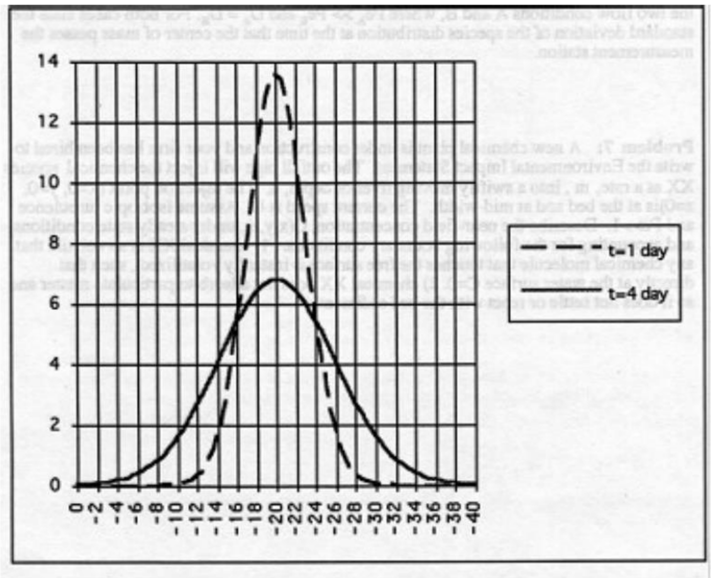


Problem 2

Based on the conceptual model for diffusion, how might molecular diffusivity, D, change with temperature and molecule size?

Problem 3

As part of a water quality study, you have been asked to access the diffusion of a new fluorescent dye. To accomplish this, you do a dye study in a laboratory tank (h = 40 cm). You release 100g of 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 the figure below; the x-axis represents depth and the y-axis represents the reading on your fluorometer.



Question 1

Estimate the diffusion coefficient of the dye, D, based on the evolution of the dye cloud.

Question 2

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

Problem 4

An infinitely long cylinder with a diameter of 10 cm is filled with a stationary fluid. A mass input ($M = 0.1\, g\, CO_2$) is introduced instantaneously at $t = 0$ and uniformly at the center of the tube ($x = 0$). Find the time for the CO_2 to reach a concentration (mass fraction) of 1 ppm at $x = 50\, cm$ for

i) Molecular diffusion in air.

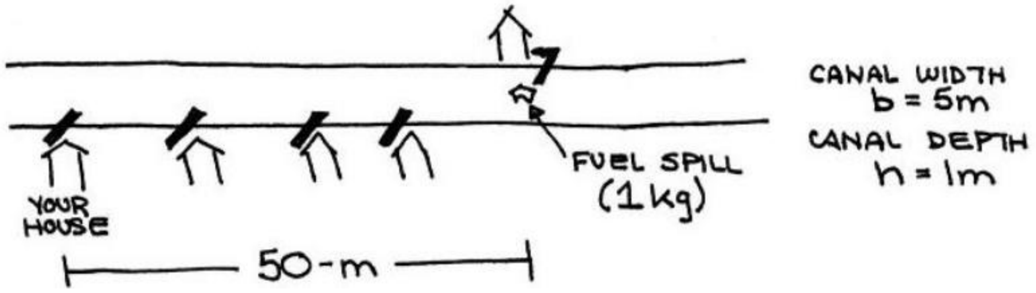
ii) Molecular diffusion in water.

Note:

(a) *the densities of air and of water are 1.23 and 1000* kg/m^3 *respectively*

(b) *the diffusion coefficient of gaseous carbon dioxide is* $0.14\, cm^2/s$ *in air and* $1.71 \times 10^{-5}\, g/cm^3$ *in water*

Problem 5



You own a house and dock along a long boat canal. One day your neighbor has a small fuel spill. Due to the boat traffice, the diffusivity in the canal is quite high, $D = 0.01\, m^2/s$. The current in the canal is negligible, such that the fuel is transported to your house by diffusion only. Assume the fuel mixes rapidly across the width and depth.

A) How long does it take for the spilled fuel to reach your house?

B) For the time found in A), what is the concentration at your house?

C) What is the maximum concentration at your house?

CLASS EXERCISES SOLUTIONS

Solution 1

From Fick's Law (Eq 3 in Chap 1)

$$q_z = -DA\frac{\partial C}{\partial Z} \approx -DA\frac{C\,(z=10\,cm) - C\,(z=0\,cm)}{(10-0)\ cm}$$

$$= -\left(10^{-5}\,cm^2 s^{-1}\right)\left(1\,cm^2\right)\left(\frac{0-100\,gcm^{-3}}{10\,cm}\right)$$

$$= +10^{-4}\,g/s$$

"+" z-direction is upward

Solution 2

Temperature:

As temperature of the fluid increases, the water molecules move about more vigorously. The collision of water molecules with molecules of the diffusing species causes the species molecules to move about as well. As the strength and number of collisions increase with temperature, the mean distance (Δx) moved per time (Δt) increases. Therefore, based on the random walk model, we expect D to increase with temperature. $D \sim \frac{\Delta x^2}{\Delta t}$.

Molecule size:

Bigger molecules will be less easily moved by collisions from surrounding water molecules, especially if species molecule is much bigger than water molecule, and $\therefore$ will experience multiple, simultaneous, uncoordinated collisions. Thus, the mean step size, Δx, per time is smaller for bigger molecules. And we expect $D \sim \frac{\Delta x^2}{\Delta t}$ to be smaller too.

Solution 3

Question 1

t(day)	t(sec)	C_{max}	$0.6\,C_{max}$	$\sigma(cm)$
1	86400	13.5	8.1	3.0
4	345600	6.8	4.1	6.0

Assuming you released the dye in a very thin horizontal layer, such that initially $\sigma = 0$, then:

$$\sigma = \sqrt{2Dt} \Rightarrow D = \frac{\sigma^2}{2t}$$

Thus, our two estimates of D are:

$$D_1 = (3.0\,cm)^2\,/2\,(86400\,s) = 5.2 \times 10^{-5}\,cm^2 s^{-1}.$$

and

$$D_2 = (6.0\,cm)^2\,/2\,(345600\,s) = 5.2 \times 10^{-5}\,cm^2 s^{-1}.$$

Therefore, the estimated diffusion coefficient of the dye is $\mathbf{5.2 \times 10^{-5}\,cm^2 s^{-1}}$.

Question 2

We must consider the boundaries of the tank when the cloud width (4σ) is 40 cm. That is, when:

$$4\,(2Dt)^{1/2} = 40\,cm$$

(i.e. when $Dt = 50\,cm^2$)

Using our value of D above, the boundaries of the tank become important when

$$t = 50\,cm^2/5.2 \times 10^{-5}\,cm^2 s^{-1} = 9.6 \times 10^5\,s = 11.1\,days.$$

Solution 4

(i) **Air**

The concentration we are interested in is given by:

$$\frac{C}{\rho_{air}} = 1\,ppm \Rightarrow C = \frac{1.23\,kgm^{-3}}{10^6} = 1.23 \times 10^{-9}\,gcm^{-3}$$

The normal distribution of concentration is:

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

Therefore, for a mass fraction of 1 ppm,

$$1.23 \times 10^{-9} = \frac{9.599 \times 10^{-4}}{\sqrt{t}} exp\left(-\frac{4.464 \times 10^{3}}{t}\right) \Rightarrow exp\left(\frac{4.464 \times 10^{3}}{t}\right) = \frac{7.804 \times 10^{4}}{\sqrt{t}}$$

Solving this equation by trial and error gives us the solution that $C = 1\,ppm$ at $x = 50\,cm$ when **t = 423 s**.

(ii) **Water**

Following the same solution method,

$$\frac{C}{\rho_{water}} = 1\,ppm \Rightarrow C = \frac{1000\,kgm^{-3}}{10^{6}} = 1.00 \times 10^{-6}\,gcm^{-3}$$

Therefore, for a mass fraction of 1 ppm,

$$1.00{\times}10^{-6}\,gcm^{-3} = \frac{0.1\,g}{\left(\pi\,(5\,cm)^{2}\right)\sqrt{4\pi\,(1.71 \times 10^{-5}\,cm^{2}s^{-1})\,t}} exp\left(-\frac{(50\,cm)^{2}}{4\,(1.71 \times 10^{-5}\,cm^{2}s^{-1})\,t}\right)$$

With t in seconds, the dimensions cancel, and we are left with:

$$1.00 \times 10^{-6} = \frac{8.686 \times 10^{-2}}{\sqrt{t}} exp\left(-\frac{3.655 \times 10^{7}}{t}\right) \Rightarrow exp\left(\frac{3.655 \times 10^{7}}{t}\right) = \frac{8.686 \times 10^{4}}{\sqrt{t}}$$

Solving this equation by trial and error gives us the solution that C = 1 ppm at x = 50 cm when $\mathbf{t = 1.12 \times 10^{7}\,s}$(= **130 days**), much longer than when the fluid is air.

Solution 5

A) To answer this question, you must define the edge of the diffusing patch of fuel. By convention, this is typically taken as $\pm 2\sigma$ from the center of the patch. By this definition, the edge of the fuel patch will reach your house

$$\text{when } 2\sigma = 50\,m$$
$$\text{or } 2\sqrt{2Dt} = 50\,m.$$

Solving for $t = 31,250\,s = 8.7\,hr$.

B) At the above time (31, 250 s), the concentration at your house is, from EQ. 7,

$$
\begin{aligned}
C(x=-2\sigma, t=31250\,s) &= \frac{M}{A\sqrt{4\pi D t}} exp\left\{-\frac{(-2\sigma)^2}{2\sigma^2}\right\} \\
&= \frac{1\,kg}{(5\,m\cdot 1\,m)\sqrt{4\pi(0.01\,m^2/s)(31250\,s)}} exp\{-2\} \\
&= 4.3\times 10^{-4}\,kgm^{-3} = 0.43\,gm^{-3}
\end{aligned}
$$

C) The maximum concentration at $x = -50\,m$ can be found by setting $\frac{\partial}{\partial t}[C(x=-50\,m, t)] = 0$. As this is a difficult derivative, a graphical solution is easier and more instructive.