Environmental Transport and Fate

Chapter 2 – Diffusion Equation Part 1

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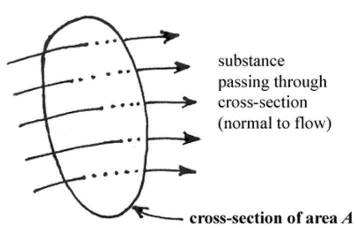
Recall: Flux of a substance



The flux of a substance in a particular direction is defined as the quantity of that substance passing through a section perpendicular to that direction per unit area and per unit time:

$$\text{flux} = q = \frac{\text{amount that passes through cross-section}}{\text{cross-sectional area} \times \text{time duration}} = \frac{m}{A \Delta t}$$

If the amount is a mass, then the flux q is a rate of mass per area per time, and its units are kg/m^2s.

In general, the flux consists of two components:
advection (= passive movement by carrying fluid)
diffusion (= random movement with respect to mean motion of fluid)
due either to molecular agitation
or turbulent fluctuations in fluid flow.

$$q = \text{advection} + \text{diffusion}$$
$$q = c\,u + j$$

For the moment (first part of Chapter 2), we restrict our attention to the diffusive component of the flux. Thus,

$q = j$ only.

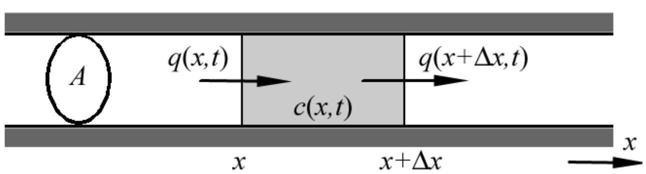
We saw that the diffusive component of the flux can be expressed as

$$j = -D\frac{dc}{dx}$$

in which D is the diffusivity coefficient
and dc/dx is the concentration gradient along the length of the domain.

Mass budget

We now use this form of flux into the mass budget for a short portion [x, $x+\Delta x$] of a one-dimensional domain.



$$V\frac{dc}{dt} = \text{Import} - \text{Export}$$
$$= q(x,t)\ A - q(x+\Delta x,t)\ A$$

Since the volume V of the slice is equal to $A\Delta x$, we can write after division by V:

$$\frac{dc}{dt} = -\frac{q(x+\Delta x,t) - q(x,t)}{\Delta x}$$

And, in the limit of a vanishingly short distance Δx: $\frac{\partial c}{\partial t} = -\frac{\partial q}{\partial x}$

[A switch from total (straight) to partial (curved) derivative is warranted because there are now more than one variable in the derivatives at this stage.]

Putting the pieces together

With the earlier formulation of the diffusive flux $q = -D\frac{\partial c}{\partial x}$ (Fick's first law)

the budget equation $\frac{\partial c}{\partial t} = -\frac{\partial q}{\partial x}$ becomes

$$\frac{\partial c}{\partial t} = +\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$

This equation is the 1D diffusion equation. It is occasionally called Fick's second law.

In many problems, we may consider the diffusivity coefficient D as a constant.
In that case, the equation can be simplified to

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

Remember, however, that in an environmental context D is likely to represent the effect of turbulent fluctuations, which may have spatially varying statistics.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

The preceding equation can hardly be solved in any general way. Each solution depends critically on boundary and initial conditions, specific to the problem at hand.

First and foremost, we need to know how many initial and boundary conditions are necessary so that the problem is neither underspecified or overspecified.

The time derivative is of first order. This demands that we provide one and only one condition in time. Typically, the initial concentration distribution is given:

$$c = c_0(x) \quad \text{at} \quad t = 0$$

The spatial derivative on the right-hand side is of second order and thus calls for two boundary conditions. Typically, any problem will include one boundary condition at each end of the domain (say $x = x_1$ and $x = x_2$). While it would be easier from a mathematical perspective to have the end concentrations imposed, such as

$$c = c_1(t) \quad \text{at} \quad x = x_1$$
$$c = c_2(t) \quad \text{at} \quad x = x_2$$

it is much more typical to encounter flux boundary conditions.

Flux boundary conditions are:

$$-D\frac{\partial c}{\partial x} = q_1(t) \quad \text{at} \quad x = x_1$$
$$-D\frac{\partial c}{\partial x} = q_2(t) \quad \text{at} \quad x = x_2$$

A common situation is that of an impermeable boundary.
In that case, there cannot be any flux across the boundary,
and there is no concentration gradient at that boundary:

$$\frac{\partial c}{\partial x} = 0 \qquad \text{at an impermeable boundary}$$

Mixed conditions (e.g., concentration given at one end of the domain and flux specified at the other) are possible.

Prototypical 1D solution

The diffusion equation is a linear one, and a solution can, therefore, be obtained by adding several other solutions. An elementary solution ('building block') that is particularly useful is the solution to an instantaneous, localized release in an infinite domain initially free of the substance.

Mathematically, the problem is stated as follows:

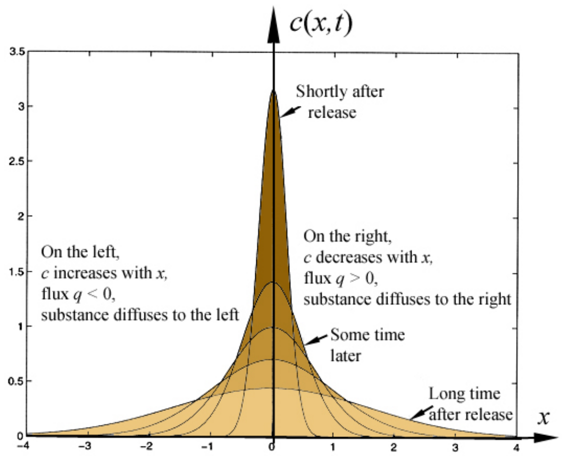
- Infinite domain: $-\infty < x < +\infty$
- D = constant
- No initial concentration, except for a localized release: $c(x) = M\,\delta(x)$ at $t = 0$
- Since the substance will take an infinite time to reach the infinitely far ends of the domain, we impose:

$$\lim_{x\to-\infty} c = \lim_{x\to+\infty} c = 0$$

at finite times ($t < \infty$).

In the above, M is the total mass of the substance released per unit cross-sectional area, and $\delta(x)$ is the Dirac function [$\delta(x) = 0$ for $x \neq 0$, $\delta(x) = +\infty$ at $x = 0$, with area under the infinitely tall and infinitely narrow peak being unity].

We expect the substance to spread gradually from its location of release and the concentration distribution therefore to look like this:



After some rather lengthy mathematics (see written notes), we find that the solution is:

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

We note that this solution already meets the boundary conditions (vanishing concentrations far away on both sides). The initial condition is also met away from $x = 0$, because when $t = 0$, the exponent is $-\infty$ and the exponential vanishes.

Conservation of the total amount of the substance is what sets the front coefficient. It requires that

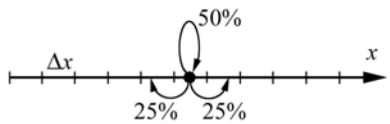
$$\int_{-\infty}^{+\infty} c(x,t)\, dx = \int_{-\infty}^{+\infty} c_0(x,t)\, dx = M$$

And one can show that the above solution satisfies this requirement.

Random-walk analogy

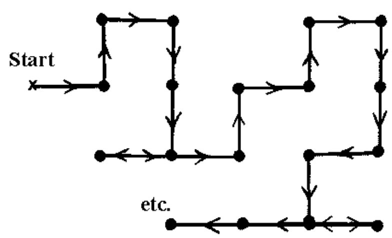
Random-walk process

Take a one-dimensional domain (1D axis), divide it in a series of boxes of identical lengths Δx ('bins'), and place one particle in one of the bins. Imagine now that this particle is endowed with a mechanism that makes it jump randomly every time interval, Δt, according to the following rules:



- There is a 25% chance that the particle will hop one bin to the left,
- There is a 25% chance that it will hop one bin to the right, and
- There is a 50% chance that it will remain in the same bin.

This is the 1D version of the more general 2D random walk, commonly referred to as the *drunkard's path*: Late into the night, an inebriated fellow leaves a bar and has no recollection of where he is and where he is going; every second or so, he makes a step forward, backward (he turns completely around), leftward or rightward, making a random path that may look like that displayed in the figure below.



The question is:

Where is this drunkard expected to be after *m* steps?

Because of the random nature of the problem, the answer can only be in terms of probabilities. We thus define

$$p(n\Delta x,\ m\Delta t)$$

as the probability that the particle is in bin number n at time $t = m\ \Delta t$.

We can calculate the probability at one time step based on the previous time step: At time $(m + 1)\ \Delta t$, the probability that the particle is in bin n is equal to the probability that it was already there [$p(n\Delta x,\ m\Delta t)$] times the probability that it stayed there (50%), plus the probability that it was one bin to the left [$p((n\text{-}1)\Delta x,\ m\Delta t)$] times the probability that it jumped to the right (25%), plus the probability that it was one bin to the right [$p((n+1)\Delta x,\ m\Delta t)$] times the probability that it jumped to the left (25%). Mathematically, we have:

$$p[n\Delta x,(m+1)\Delta t] = \frac{1}{2}\ p(n\Delta x, m\Delta t) + \frac{1}{4}\ p[(n-1)\Delta x, m\Delta t] + \frac{1}{4}\ p[(n+1)\Delta x, m\Delta t]$$

And, the initial condition is:

$$p(0,0) = 1$$
$$p(n\Delta x, 0) = 0 \quad \text{for} \quad n \neq 0$$

The solution to this discretized system is:

n=	-5	-4	-3	-2	-1	0	+1	+2	+3	+4	+5
m=0						1.000					
m=1					0.250	0.500	0.250				
m=2				0.063	0.250	0.375	0.250	0.063			
m=3			0.016	0.094	0.234	0.313	0.234	0.094	0.016		
m=4		0.004	0.031	0.109	0.219	0.273	0.219	0.109	0.031	0.004	
m=5	0.0010	0.010	0.044	0.117	0.205	0.246	0.205	0.117	0.044	0.010	0.0010
m=6	0.0029	0.016	0.054	0.121	0.193	0.226	0.193	0.121	0.054	0.016	0.0029

Note the spreading over time and the thinning of the fringes.

To compare with the continuous solution obtained from the diffusion equation, we sample the continuous solution at $x = n\Delta x$ and $t = m\Delta t$:

$$c(n\Delta x, m\Delta t) = \frac{M}{\sqrt{4\pi Dm\Delta t}} \exp\left(-\frac{(n\Delta x)^2}{4Dm\Delta t} \right)$$

Then, let us set $(\Delta x)^2$ equal to $4D\Delta t$ to clean up the exponent:

$$c(n\Delta x, m\Delta t) = \frac{M}{\sqrt{\pi m}\ \Delta x} \exp\left(-\frac{n^2}{m} \right)$$

Finally, let us set the front coefficient to match the probability value at (n = 0 , m=5):

$$c(n\Delta x, m\Delta t) = 0.246\sqrt{\frac{5}{m}} \exp\left(-\frac{n^2}{m} \right)$$

The c values thus calculated compare quite favorably to the probabilities of the random-walk process, at least for the larger times.

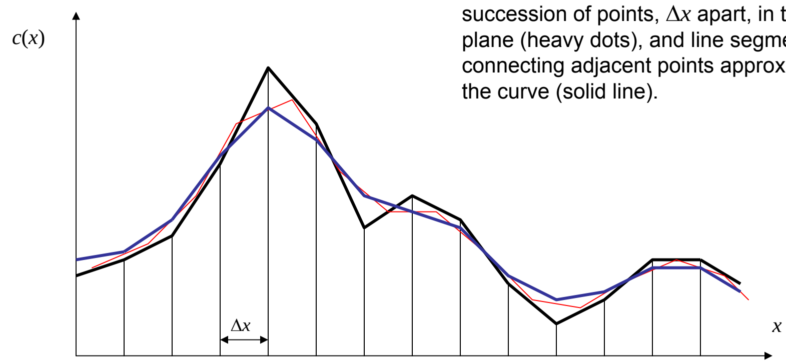
n=	-5	-4	-3	-2	-1	0	+1	+2	+3	+4	+5
m=0	*p* values					1.000					
m=1					0.250	0.500	0.250				
m=2				0.063	0.250	0.375	0.250	0.063			
m=3			0.016	0.094	0.234	0.313	0.234	0.094	0.016		
m=4		0.004	0.031	0.109	0.219	0.273	0.219	0.109	0.031	0.004	
m=5	0.0010	0.010	0.044	0.117	0.205	0.246	0.205	0.117	0.044	0.010	0.0010
m=6	0.0029	0.016	0.054	0.121	0.193	0.226	0.193	0.121	0.054	0.016	0.0029

n=	-5	-4	-3	-2	-1	0	+1	+2	+3	+4	+5
m=0	*c* values					∞				= anchor between both representations	
m=1					0.202	0.550	0.202				
m=2				0.053	0.236	0.389	0.236	0.053			
m=3			0.016	0.084	0.228	0.318	0.228	0.084	0.016		
m=4		0.005	0.029	0.101	0.214	0.275	0.214	0.101	0.029	0.005	
m=5	0.0017	0.010	0.041	0.111	0.201	0.246	0.201	0.111	0.041	0.010	0.0017
m=6	0.0035	0.016	0.050	0.115	0.190	0.225	0.190	0.115	0.050	0.016	0.0035

We conclude that the random-walk and diffusion are similar processes (Einstein, 1905).

A graphical iteration

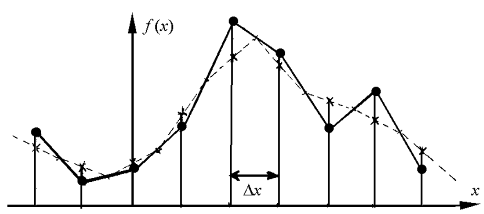
(An old pencil-and-paper method predating computers or even slide rules!)



A curve $c(x)$ is given graphically as a succession of points, Δx apart, in the (x, c) plane (heavy dots), and line segments connecting adjacent points approximate the curve (solid line).

The following graphical constructions are then made:
1. Join the midpoints of adjacent line segments (red lines),
2. At each location, move the function value to the level of the red line (purple lines),
3. Repeat these steps again and again.

The obvious result of this manipulation is the cutting of spikes, filling of valleys and overall smoothing of the curve.



At every cycle of this procedure, we effectively replace the current value of the function by a new value, which is the average of the averages of the neighboring values. Thus,

$$\text{new } f(x) = \frac{1}{2}\left[\frac{f(x-\Delta x)+f(x)}{2}+\frac{f(x)+f(x+\Delta x)}{2}\right]$$

$$= \frac{1}{4} f(x-\Delta x) + \frac{1}{2} f(x) + \frac{1}{4} f(x+\Delta x)$$

In other words, we are performing a (¼, ½, ¼) running average, which is the same as following the random walk.

We conclude:

Diffusion, random-walk and curve smoothing are all similar.
Diffusion ≡ random walk → diffusion spreads.
Diffusion ≡ curve smoothing → diffusion smoothes.

Spreading

Spreading induced by diffusion implies that the spatial extent of contamination grows with time. For practical purposes, we wish therefore to quantify this spreading, *viz.* to have an answer to the question:

How wide is the zone affected by the contaminant?

We easily conceive that the quantity that tells us how wide is a diffusing patch of contamination should be a function of time. However, what should be its precise definition is not trivial. Indeed, the prototypical solution

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

exhibits spreading over time but does not yield a specific width because c is nonzero all the way to infinity, starting immediately after the moment of release. [This instantaneous infinitely wide effect is obviously unrealistic and is attributed to the mathematical simplification of a continuum medium.] Therefore, looking for the edges of the concentration distribution does not yield an answer. We need to do something else.

To determine objectively the width of a pollutant patch, we then resort to integral quantities. Let us explore a few of them.

A first integral is the area under the curve:

$$\int_{-\infty}^{+\infty} c \, dx = M = \text{constant}$$

giving the total amount of substance; this tells nothing about the width of the patch.

A second integral is formed by inserting the coordinate x, to inject the notion of distance,

$$\int_{-\infty}^{+\infty} xc \, dx = 0$$

which vanishes by symmetry; this tells us where the mean position of the patch is ($\bar{x} = 0$ for this solution) but still nothing about the width.

A third integral is

$$\int_{-\infty}^{+\infty} (x-\bar{x})^2 c \, dx = 0$$

$$\int_{-\infty}^{+\infty} (x-\overline{x})^2 c\, dx > 0$$

is a function of time, positive and always nonzero.

Because $(x-\overline{x})^2$ represents the squared distance to the mean position, the above integral says something about the average distance to the center of the patch and therefore holds information about the patch width.

The time evolution of this width should then provide information about the rate of spreading.

For convenience, we define the normalized quantity

$$\sigma^2 = \frac{1}{M}\int_{-\infty}^{+\infty} (x-\overline{x})^2 c\, dx = 0$$

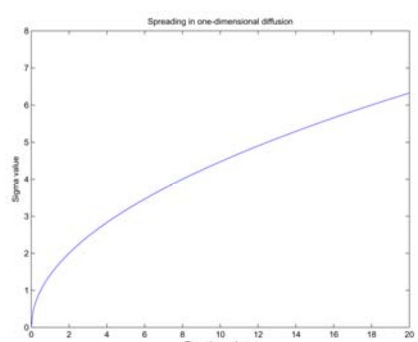
in which

$$M = \int_{-\infty}^{+\infty} c\, dx \qquad \text{and} \qquad \overline{x} = \frac{1}{M}\int_{-\infty}^{+\infty} xc\, dx$$

For the prototypical solution above, calculations yield

$$\begin{aligned}\sigma^2 &= \frac{1}{M}\int_{-\infty}^{+\infty} x^2 \frac{M}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) dx \\ &= \frac{4Dt}{\sqrt{\pi}} \underbrace{\int_{-\infty}^{+\infty} \zeta^2 e^{-\zeta^2} d\zeta}_{=\frac{\sqrt{\pi}}{2}} \qquad \text{with} \quad \zeta = \frac{x}{\sqrt{4Dt}} \\ &= 2Dt\end{aligned}$$

Thus, $\sigma = \sqrt{2Dt}$

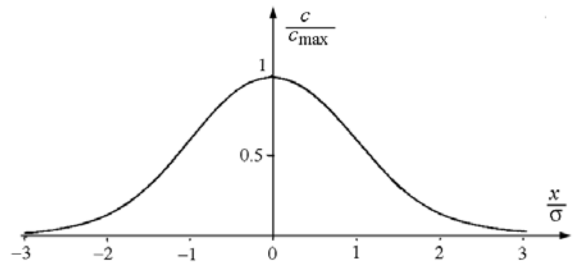


We immediately note that the distance σ grows in time, but as the square root of time rather than time itself. Thus, the spreading goes on with time, never stopping but gradually slowing down.

The next question is by which numerical factor (such as 4, 1/2, or whatever) should this σ be multiplied to yield a practical definition of the patch width.

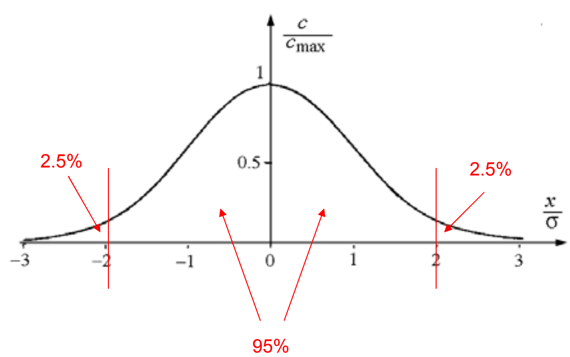
The $c(x,t)$ distribution at any given time obeys the so-called Gaussian (or 'bell') curve. Normalizing distance x by σ and concentration c by its maximum, central value $c_{\max} = \frac{M}{\sqrt{4\pi Dt}}$ the function becomes

$$\frac{c}{c_{\max}} = \exp\left[-\frac{1}{2}\left(\frac{x}{\sigma}\right)^2\right]$$



which contains no parameter. Graphically, the curve is universal.

It is the so-called Gaussian 'bell' curve encountered in probability and statistics.



The region $-2\sigma < x < +2\sigma$ contains 95% of the pollutant, which is about most of it.

We can then say that the overall width of the region over which the pollutant is spread is

$$\text{width} = 4\sigma = 4\sqrt{2Dt} = 5.66\sqrt{Dt}$$

We call this the "4-sigma" rule.

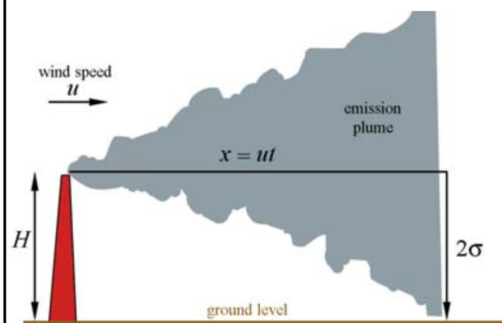
A remark

There are occasions when one should distinguish between

4σ – the full width, and

2σ – the spreading distance from the location of release.

Take for example a smokestack plume.



A pertinent question is:

By which distance does the ground level become affected?

The answer is: where the underside of the plume begins to touch the ground, that is, where $2\sigma = H$, the height of the stack.

$$2\sigma = H \quad \rightarrow \quad 2\sqrt{2Dt} = H, \quad x = ut \quad \rightarrow \quad x = \frac{uH^2}{8D}$$

An example

A tank aboard a barge traveling along the Chicago Ship Canal suddenly collapses, releasing its benzene content (C_6H_6, density = 0.879 g/cm^3), of which 100 liters find their way quickly to the water. The rest of the benzene remains contained on the barge. Assuming rapid mixing across the canal section (8.07 m deep and 48.8 m wide) and estimating the turbulent diffusion coefficient at 3.0 m^2/s, what are the concentrations of benzene 2, 6, 12 and 24 hours after the accident, at the site of the spill and 300 m away?

To solve this problem, we first determine the mass of benzene that was spilled. Since the density of benzene is 0.879 g/cm^3 = 0.879 kg/L, this mass *m* is:

$$m = \text{mass} = \text{density} \times \text{volume} = 0.879\ \text{kg/L} \times 100\ \text{L} = 87.9\ \text{kg}$$

Over the cross-section of the canal, we have

$$M = \frac{\text{mass}}{\text{cross} - \text{sectional area}} = \frac{m}{A} = \frac{87.9\ \text{kg}}{(8.07\ \text{m})(48.8\ \text{m})} = 0.2232\ \frac{\text{kg}}{\text{m}^2}$$

The concentration at the location of the spill (x = 0) is given by

$$c_{spill}(t) = c(0,t) = c_{\max}(t) = \frac{M}{\sqrt{4\pi Dt}}$$

$$= \frac{0.0364\ \text{kg/m}^3}{\sqrt{t(\text{in sec})}} = \frac{0.606\ \text{mg/L}}{\sqrt{t(\text{in hrs})}}$$

Time since spill	Concentration at spill
2 hours	0.428 mg/L
6 hours	0.247 mg/L
12 hours	0.175 mg/L
24 hours	0.124 mg/L

The peak concentration decreases over time. This can be expected since diffusion spreads the pollutant away from the point of release.

At a distance x = 300 m away, the concentration is obtained from the full formula

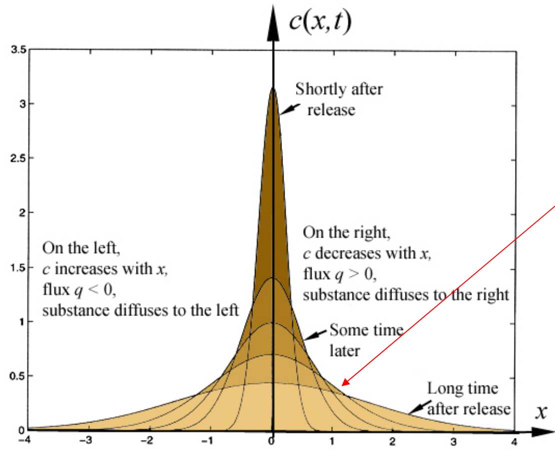
$$c(x,t) = \frac{M}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

with $$\frac{x^2}{4Dt} = \frac{(300\ \text{m})^2}{4\,(3.0\ \text{m}^2/\text{s})\ t} = \frac{2.083}{t\ (\text{in hrs})}$$

Thus $$c(300\ \text{m},t) = \frac{0.606\ \text{mg/L}}{\sqrt{t\ (\text{in hrs})}} \exp\left(-\frac{2.083}{t\ (\text{in hrs})}\right)$$

Time since spill	Concentration 300 m away
2 hours	0.151 mg/L
6 hours	0.175 mg/L
12 hours	0.147 mg/L
24 hours	0.113 mg/L

Note how the concentration at 300 m first increases (because it takes time for the benzene to diffuse over that distance) and then decreases (because further diffusion leads to dilution).



Observe how, at some distance from the peak, the concentration first increases and then decreases.

We can actually calculate the exact time at which the concentration reaches its maximum and what that maximum is.

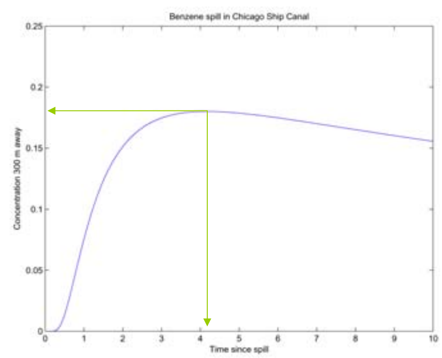
Setting to zero the time derivative of solution, we obtain the time t_{max} of the maximum concentration for any distance x from the release location:

$$t_{\max} = \frac{x^2}{2D}$$

Substitution in the solution then yields the maximum concentration:

$$c_{\max}(x) = c\left(x, t = \frac{x^2}{2D}\right) = \frac{M}{\sqrt{2\pi}\ x}\exp\left(-\frac{1}{2}\right)$$

$$= 0.2420\,\frac{M}{x}$$



In the case of the benzene spill in the Chicago Ship Canal, with M = 0.2232 kg/m^2 and x = 300 m:

c_{max} = 0.180 mg/L at t_{max} = 4 hrs 10 min.