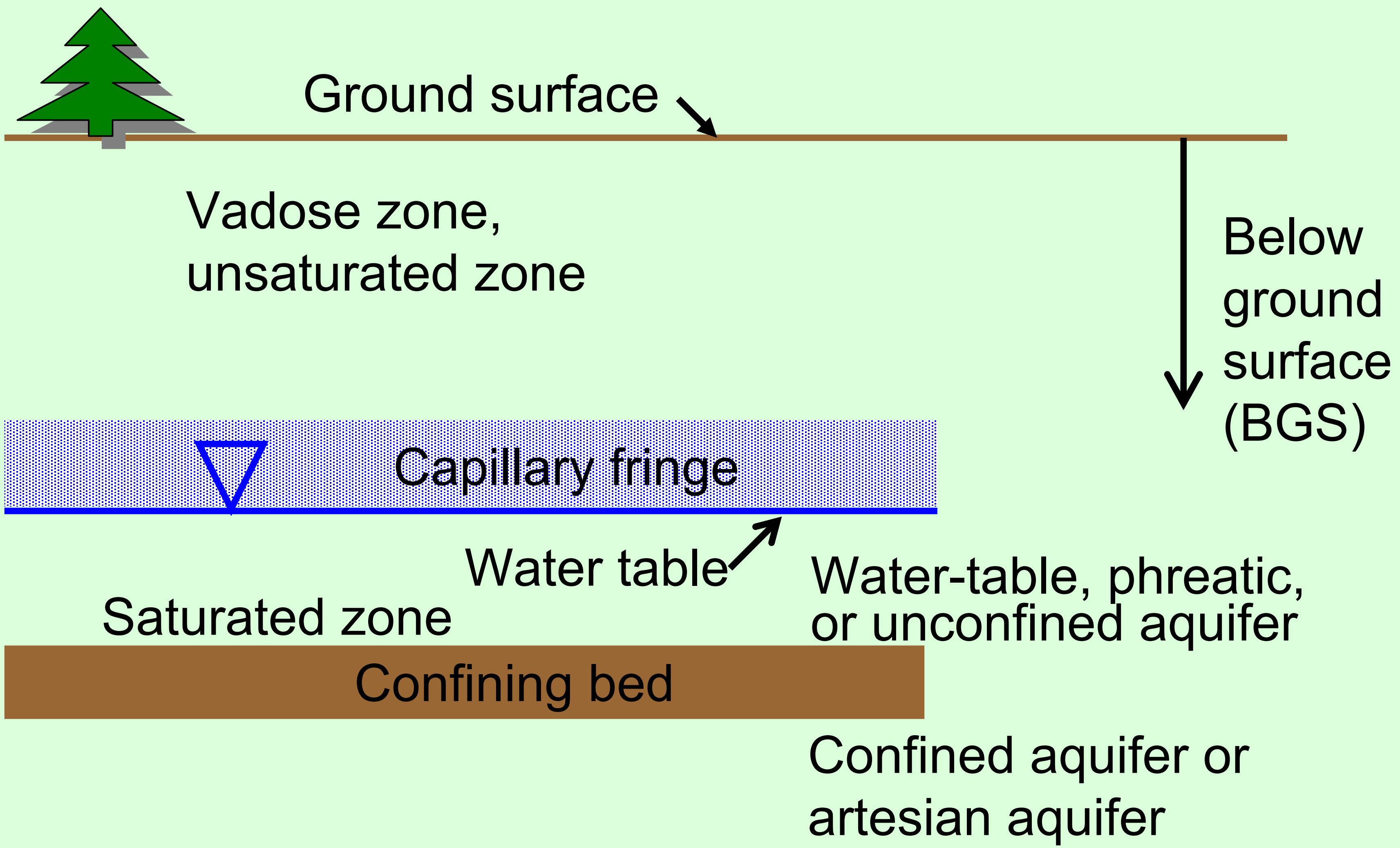
Lecture 3

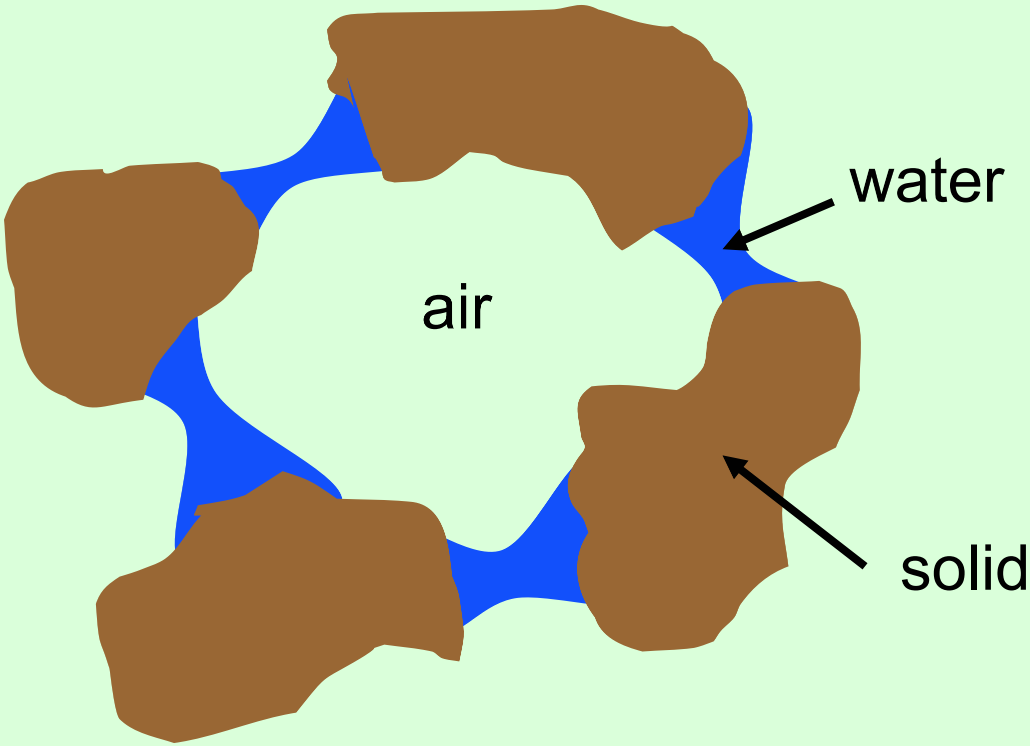
Contaminant Transport Mechanisms and Principles

BASIC DEFINITIONS



Capillary fringe may be >200 cm in fine silt
In capillary fringe water is nearly saturated, but held in tension in soil pores

MICRO VIEW OF UNSATURATED ZONE



Contaminant concentrations:

C_w, mg/L
concentration in water

C_g, mg/L or ppmv
concentration in gas

C_s, gm/kg
concentration in solids

PARTITIONING RELATIONSHIPS

Solid $\leftrightarrow$ water

$$\frac{C_s}{C_w} = K_d = \frac{\text{mg/kg solid}}{\text{mg/L water}}$$

K_d = partition coefficient

Water $\leftrightarrow$ vapor

$$\frac{C_g}{C_w} = H = \frac{\text{mol/m}^3\text{ air}}{\text{mg/m}^3\text{ water}}$$

H = Henry's Law constant

HENRY'S LAW CONSTANT

H has dimensions: atm m^3 / mol

H' is dimensionless

H' = H/RT

R = gas constant = 8.20575×10^{-5} atm m^3/mol °K

T = temperature in °K

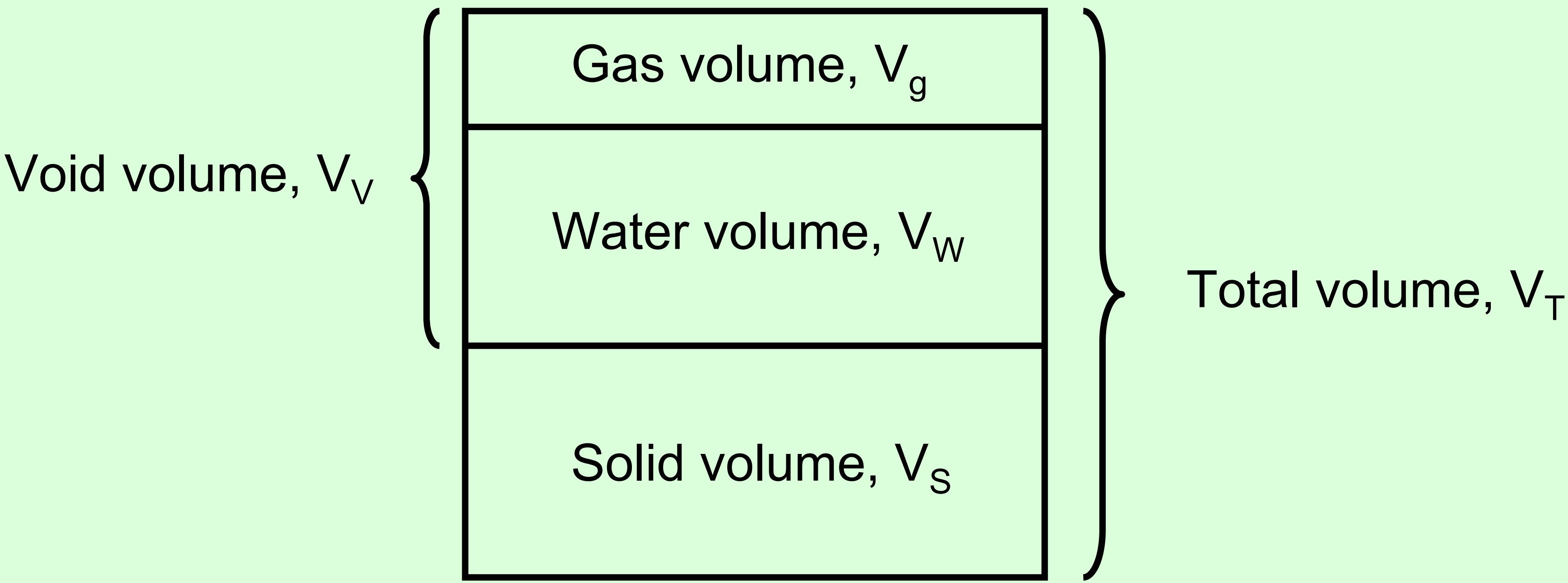
NOTE ON SOIL GAS CONCENTRATION

Soil gas is usually reported as:

ppmv = parts per million by volume

$$\mathbf{C_g\ (ppmv)} = \frac{\mathbf{C_g\ (mg/L)} \times \mathbf{24{,}000\ mL/mole}}{\mathbf{molecular\ weight\ g/mole}}$$

VOLUME REPRESENTATION



VOLUME-RELATED PROPERTIES

Bulk density $= \rho_b = \dfrac{\text{mass of solids}}{\text{total volume}}$

Porosity $= n = \theta = V_V/V_T$

Volumetric water content or
water-filled porosity $= \theta_W = V_W/V_T$

Saturation $= S = V_W/V_V$

Gas-filled porosity $= \theta_g$ (or θ_a) $= V_g/V_T$

$\theta_W + \theta_g = n$

CONTAMINANT CONCENTRATION IN SOIL

Total mass in unit volume of soil:

$$C_T = \rho_b\, C_s \;+\; \theta_w\, C_W \;+\; \theta_g\, C_g$$

If soil is saturated, $\theta_g = 0$ and $\theta_W = n$

$$C_T = \rho_b\, C_s \;+\; n\, C_W$$

NOMENCLATURE FOR DARCY'S LAW

$Q = K\,i\,A$

K = hydraulic conductivity

i = hydraulic gradient = dh/dL

A = cross-sectional area

Velocity of ground-water movement

$u = Q / n A = q / n = K i / n$ = average linear velocity

$n A$ = area through which ground water flows

$q = Q / A$ = Darcy seepage velocity = Specific discharge

For transport, n is n_e, effective porosity

ADVECTIVE FLUX

Flowing ground water carries any dissolved material with it → Advective Flux

$J_A = n\,u\,C$ mass / area / time

= mass flux through unit cross section due to ground-water advection

n is needed since no flow except in pores

DIFFUSIVE FLUX

Movement of mass by molecular diffusion (Brownian motion) – proportional to concentration gradient

$$\mathbf{J_D} = -\mathbf{D_O}\frac{\partial \mathbf{C}}{\partial \mathbf{x}}$$

in surface water !!!

D_O is molecular diffusion coefficient [L^2/T]

DIFFUSIVE FLUX

In porous medium, geometry imposes constraints:

$$J_D = -\tau \ D_O \, n \frac{\partial C}{\partial x} = -D^* n \frac{\partial C}{\partial x}$$

τ = tortuosity factor

D^* = effective diffusion coefficient

Factor n must be included since diffusion is only in pores

TORTUOSITY

Solute must travel a tortuous path, winding through pores and around solid grains

Common empirical expression: $$\tau = \left(\frac{L}{L_e}\right)^2$$

L = straight-line distance

L_e = actual (effective) path

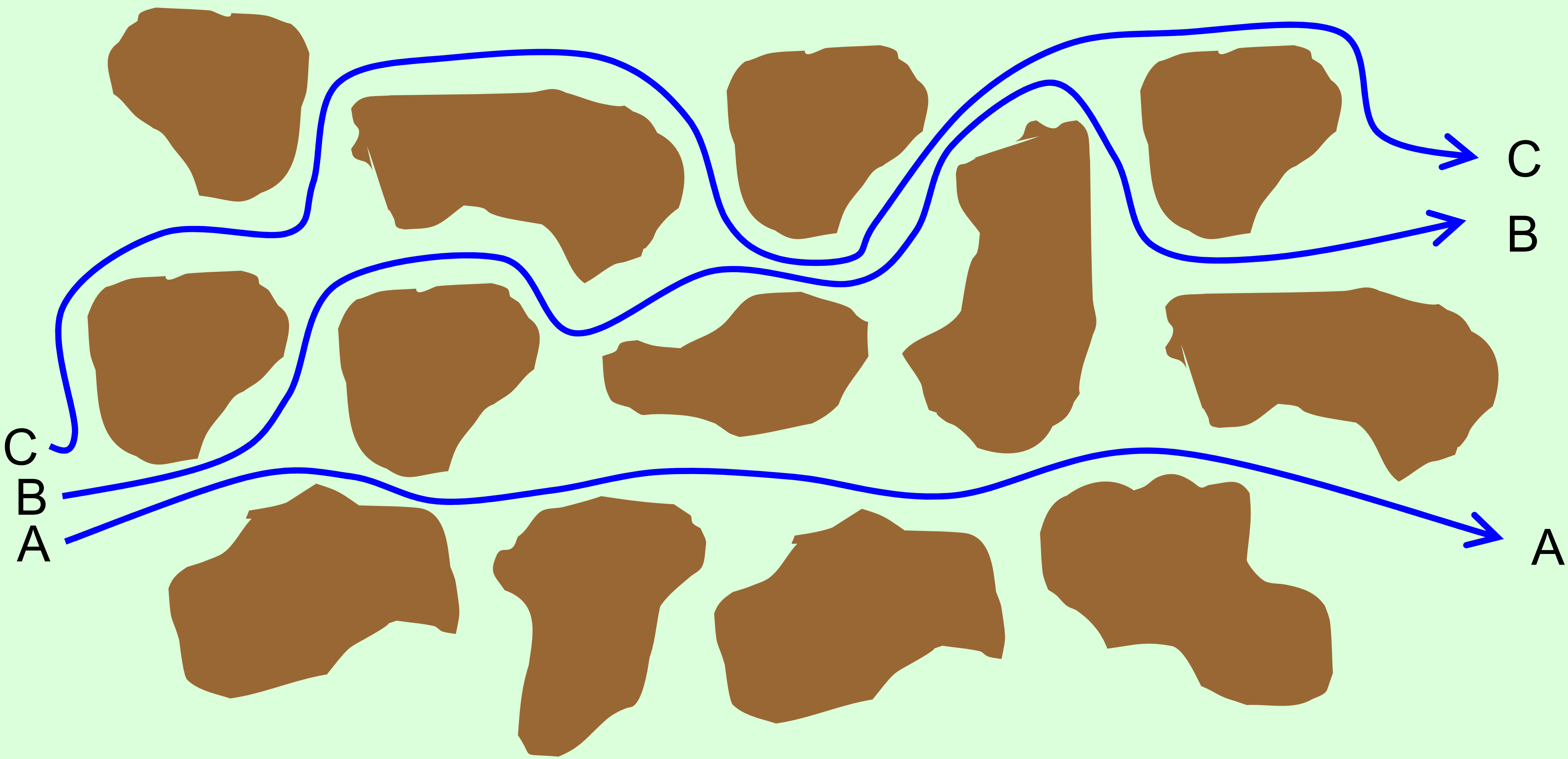
$\tau \approx 0.7$ for sand

NOTES ON DIFFUSION

Diffusion is not a big factor in saturated ground-water flow – dispersion dominates diffusion

Diffusion can be important (even dominant) in vapor transport in unsaturated zone

MECHANICAL DISPERSION



A arrives first, then B, then C → mechanical dispersion

MECHANICAL DISPERSION

Viewed at micro-scale (i.e., pore scale) arrival times A, B, and C can be predicted

Averaging travel paths A, B, and C leads to apparent spreading of contaminant about the mean

Spatial averaging → dispersion

MECHANICAL DISPERSION

Dispersion can be effectively approximated by the same relationship as diffusion—i.e., that flux is proportional to concentration gradient:

$$\mathbf{J_M} = -\mathbf{D_M}\,\mathbf{n}\frac{\partial \mathbf{C}}{\partial \mathbf{x}}$$

Dispersion coefficient, $D_M = \alpha_L u$

α_L = longitudinal dispersivity (units of length)

TRADITIONAL VIEW OF HYDRODYNAMIC DISPERSION

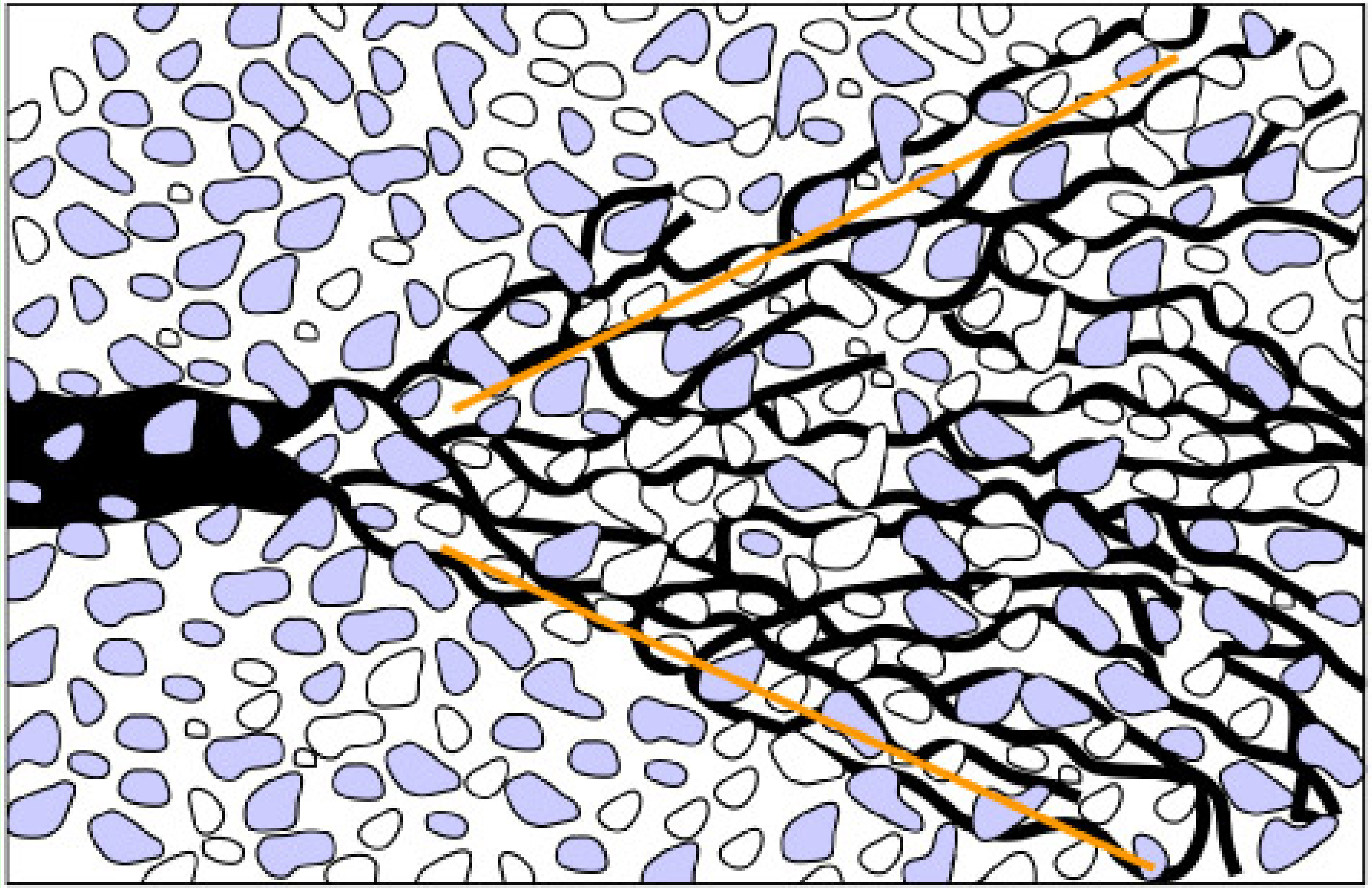


Image adapted from: Freeze, R.A., and J.A. Cherry, 1979. Groundwater. Prentice Hall, Englewood Cliffs, New Jersey. Pg. 384.

ACTUAL OBSERVATIONS OF PLUMES

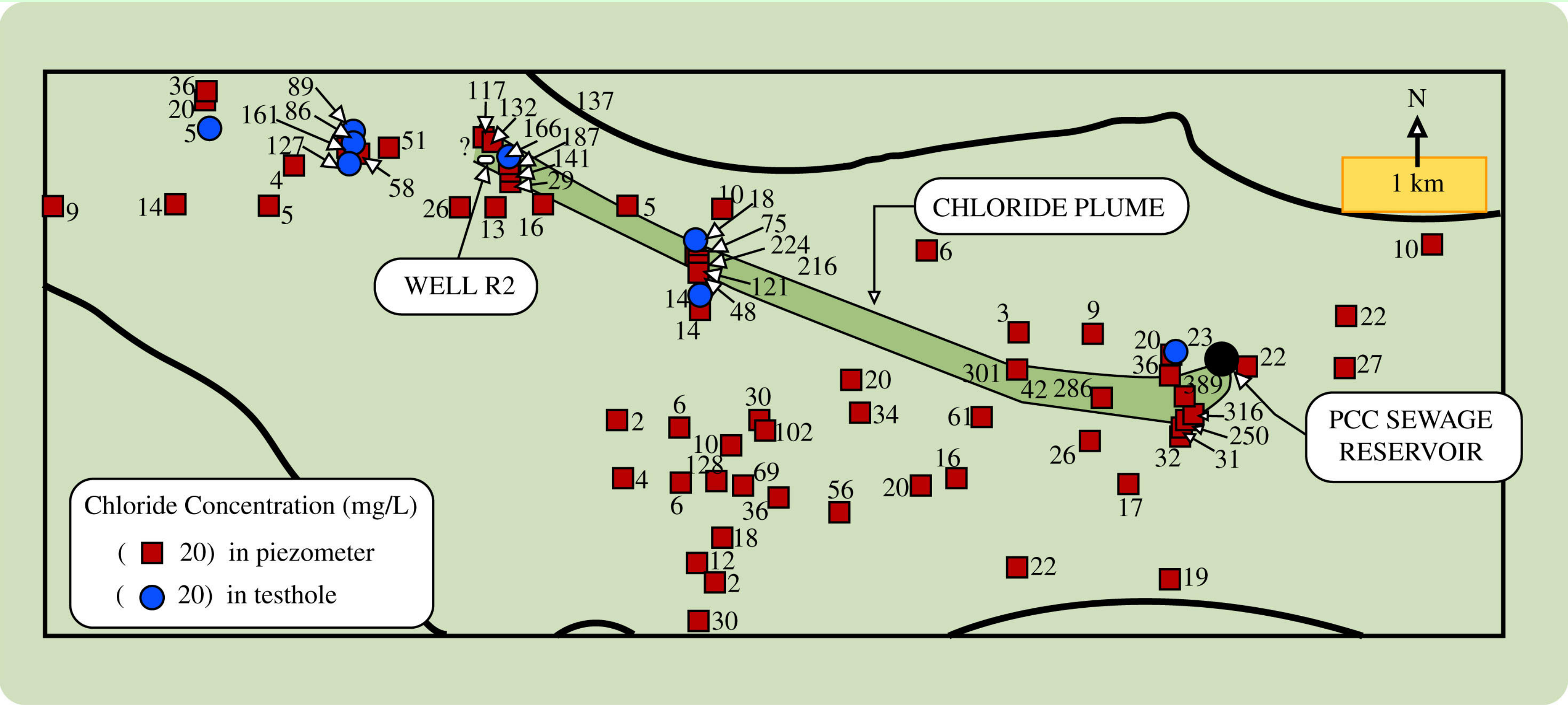
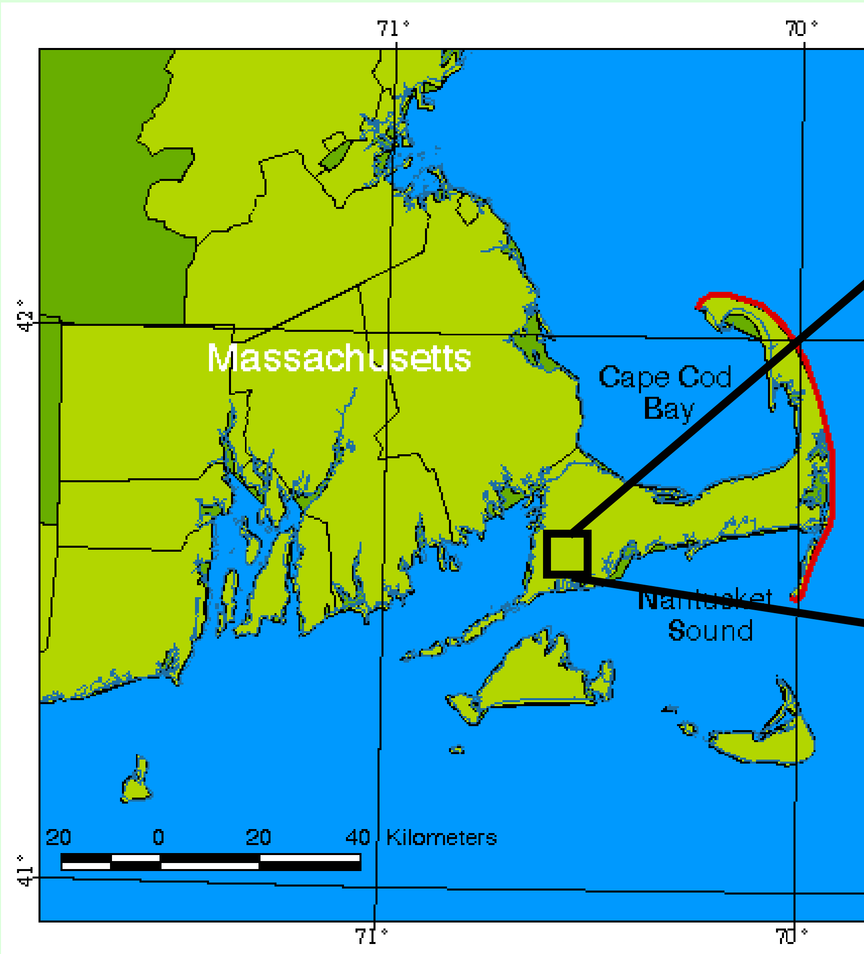
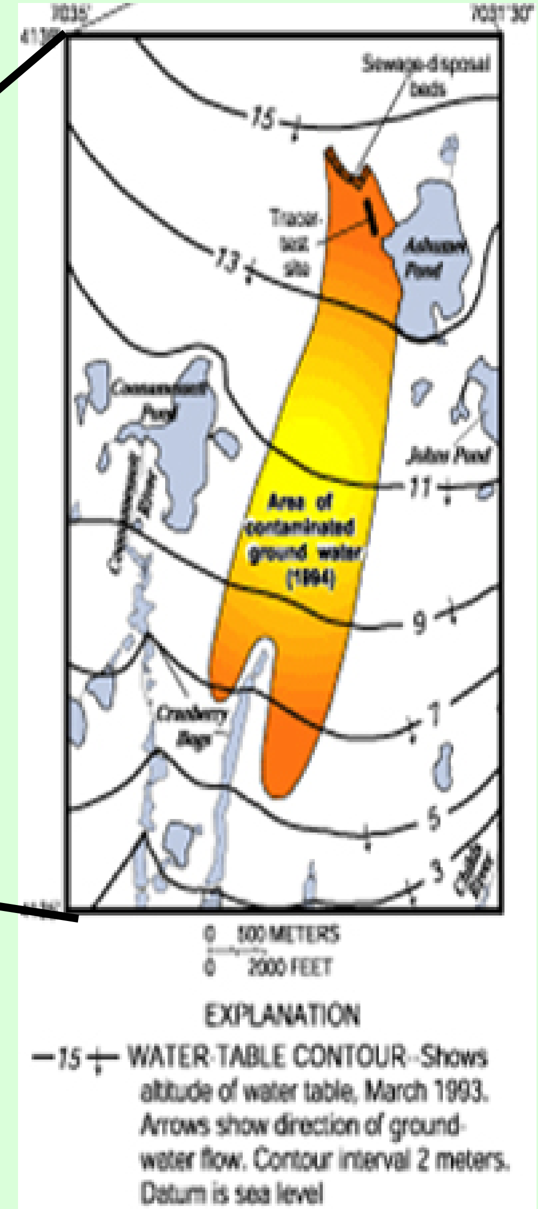


Image adapted from: Kamp, G.v.d., L..D. Luba, J.A. Cherry, and H. Maathuis, 1994. Field Study of a Long and Very Narrow Contaminant Plume. *Ground Water.* Vol. 32, No. 6, Pg. 1008. November/December 1994.

USGS Cape Cod Research Site

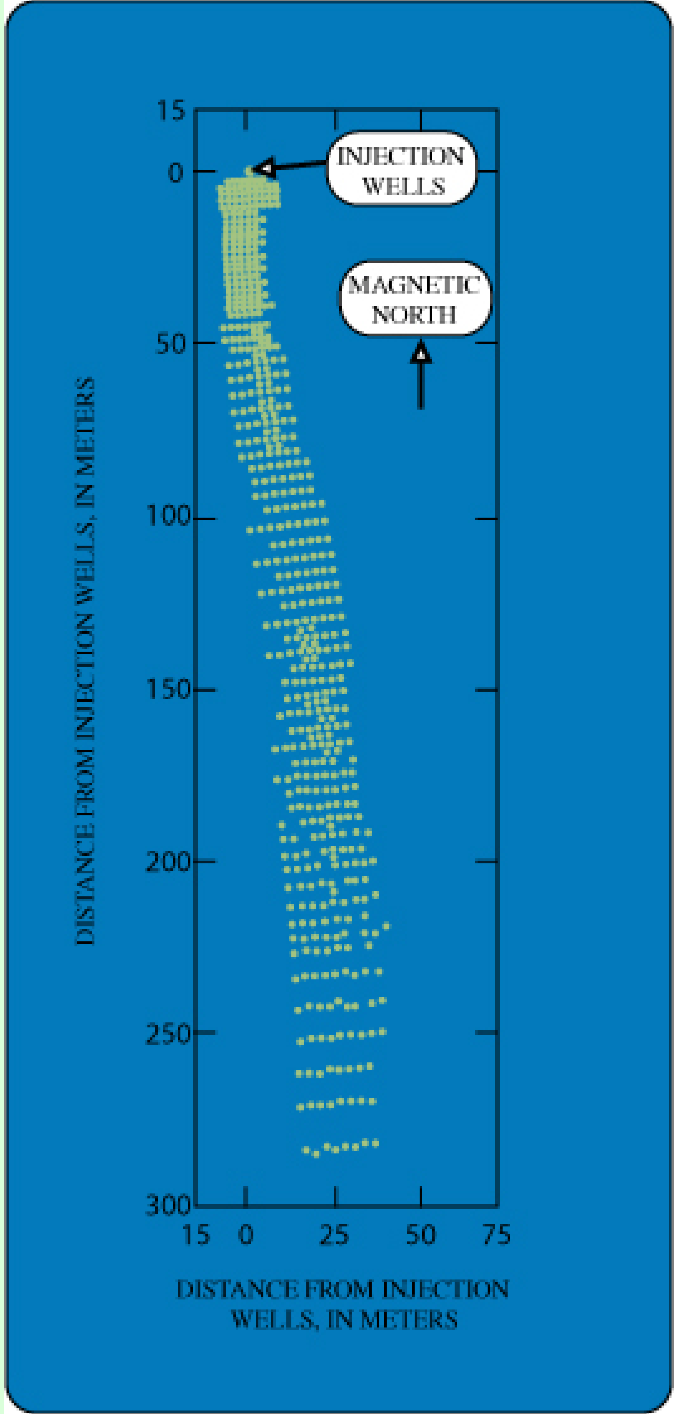


Source: NOAA Coastal Services Center,
http://www.csc.noaa.gov/crs/tcm/98fall_status.html
Accessed May 14, 2004.



Source: U.S. Geological Survey, Cape Cod Toxic Substances Hydrology Research Site,
http://ma.water.usgs.gov/CapeCodToxics/location.html.
Accessed May 14, 2004.

MONITORING WELL ARRAY

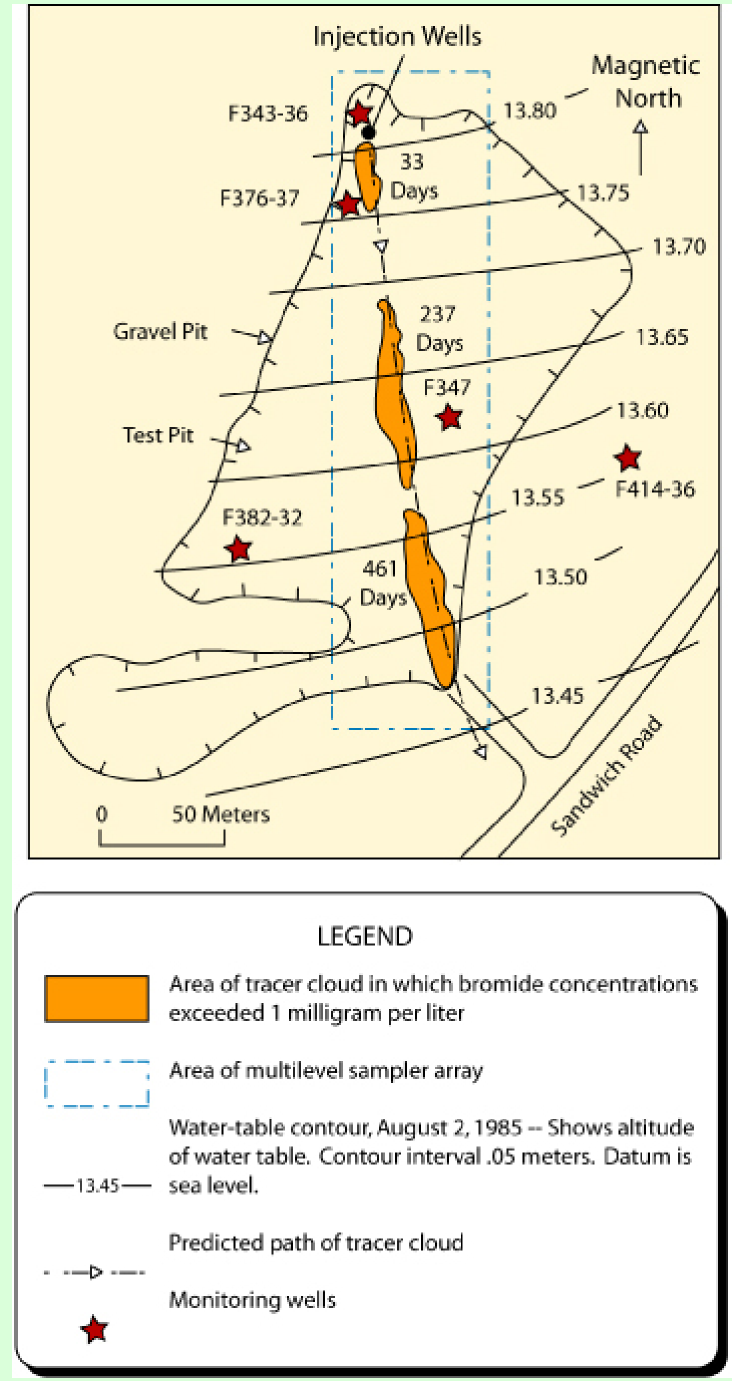


USGS MONITORING NETWORK

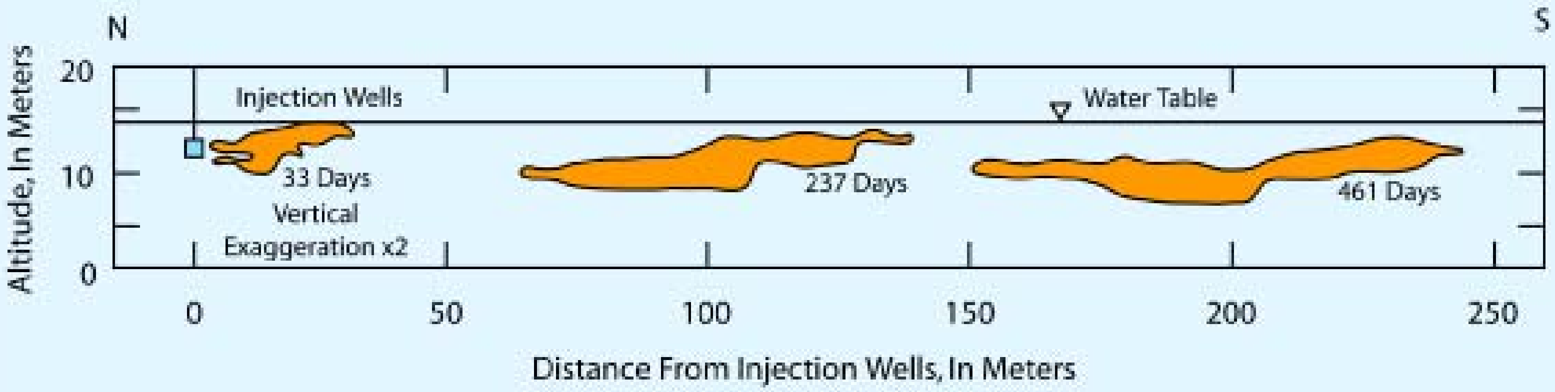
Source: http://ma.water.usgs.gov/CapeCodToxics/photo-gallery.html Photo by D.R. LeBlanc.

OBSERVED BROMIDE PLUME – HORIZONTAL VIEW

Significant longitudinal dispersion, but limited lateral dispersion



OBSERVED BROMIDE PLUME – VERTICAL VIEW



Vertical location of bromide tracer cloud at 33, 237, and 461 days after injection. Cloud locations defined by zones in which bromide concentration exceeded 1 mg/L.

Limited vertical dispersion

LONGITUDINAL DISPERSION VS. LENGTH SCALE

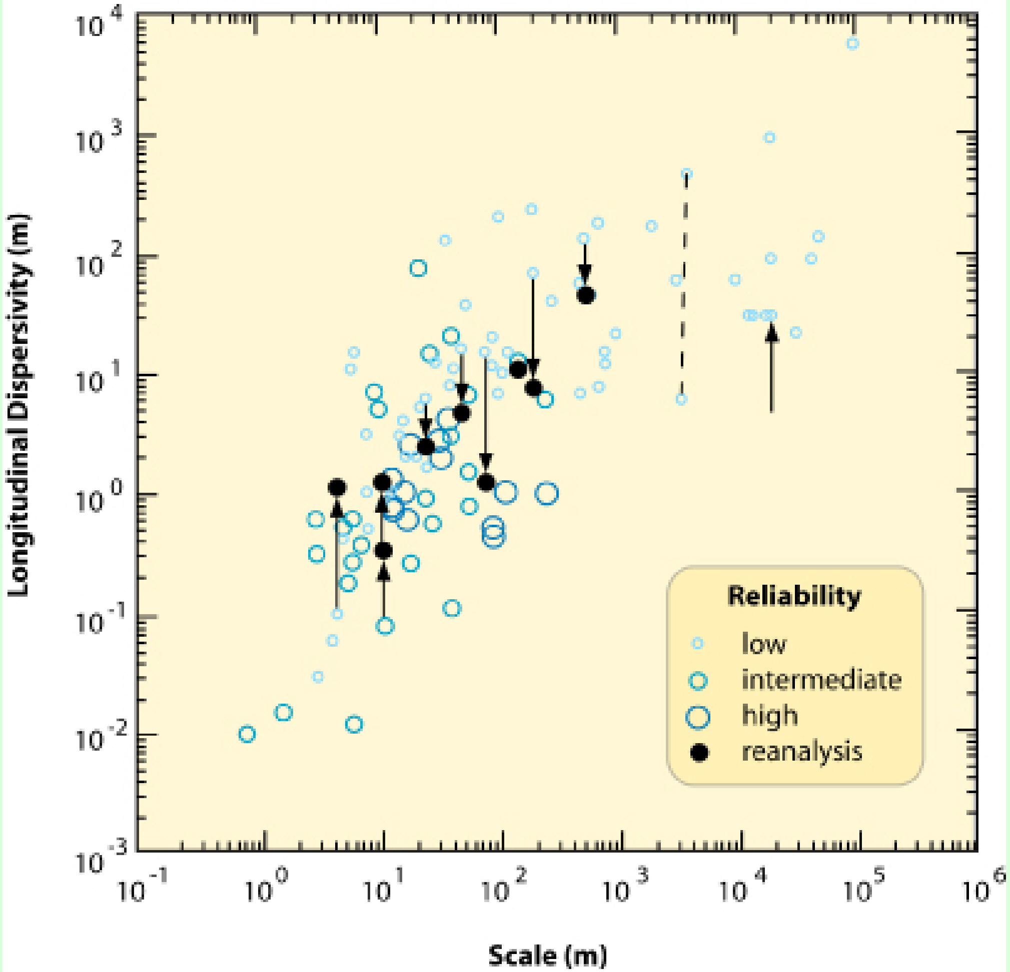


Image adapted from: Gelhar, L.W., C. Welty, and K.R. Rehfeldt, 1992. A critical review of data on field-scale dispersion in aquifiers. *Water Resources Research*. Vol. 28, No. 7, Pg. 1955. July 1992.

Lateral and vertical dispersivity

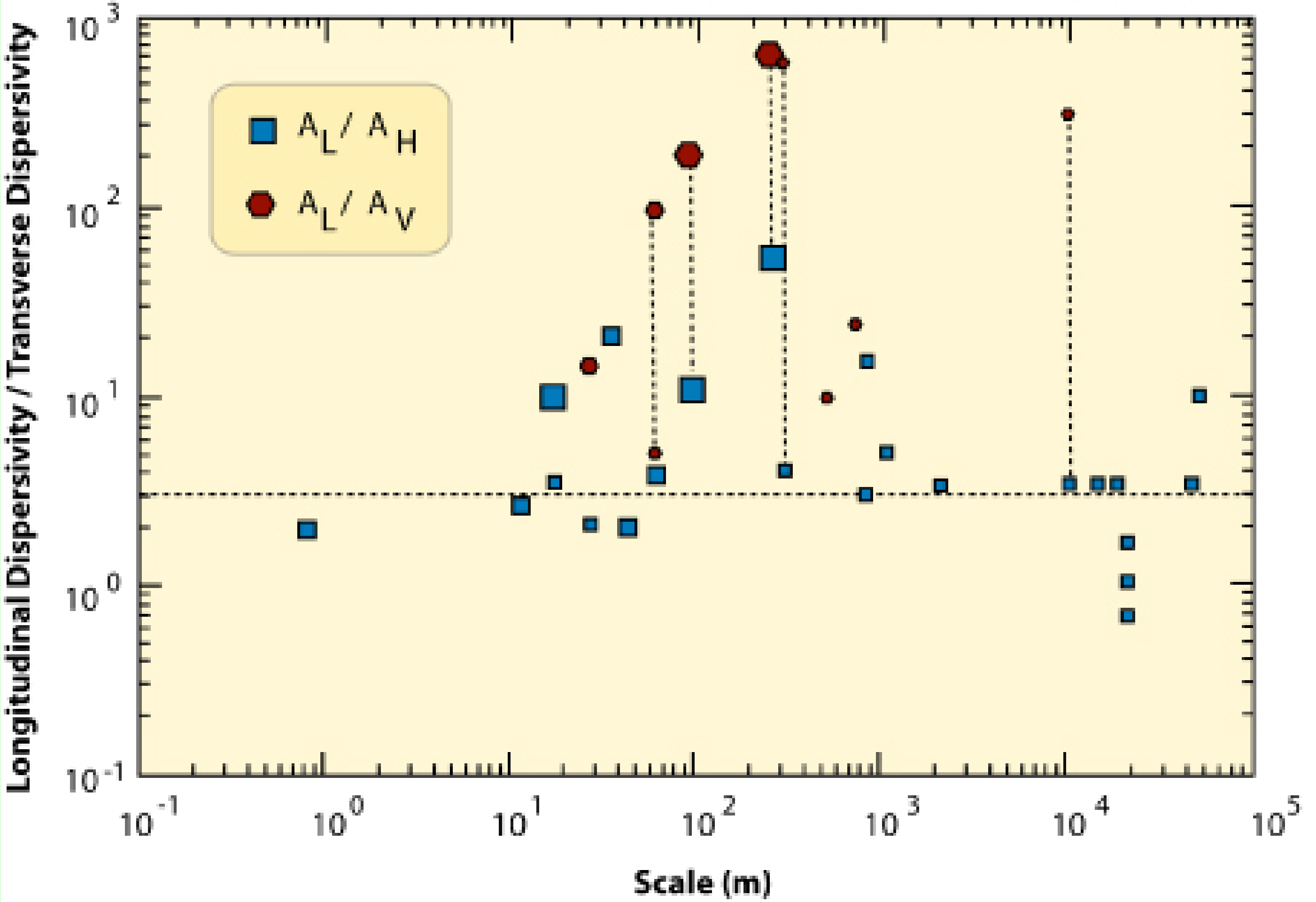


Image adapted from: Gelhar, L.W., C. Welty, and K.R. Rehfeldt, 1992. A critical review of data on field-scale dispersion in aquifers. *Water Resources Research*. Vol. 28, No. 7, Pg. 1955. July 1992.

TRANSPORT EQUATION

Combined transport from advection, diffusion, and dispersion (in one dimension):

$$J = J_A + J_D + J_M$$

$$J = nuC - D^* n \frac{\partial C}{\partial x} - D_M n \frac{\partial C}{\partial x}$$

$$J = nuC - D_H \frac{\partial C}{\partial x}$$

$D_H = D^* + D_M = \tau D_O + \alpha_L u$

= hydrodynamic dispersion

TRANSPORT EQUATION

Consider conservation of mass over control volume (REV) of aquifer.

REV = Representative Elementary Volume

REV must contain enough pores to get a meaningful representation (statistical average or model)

TRANSPORT EQUATION

Change in contaminant mass with time

Flux in less flux out of REV

Sources and sinks due to reactions

$$\frac{\partial \mathbf{C_T}}{\partial \mathbf{t}} = -\nabla \bullet \mathbf{J} \pm \mathbf{S/S} \qquad (1)$$

$$\frac{\partial \mathbf{C_T}}{\partial \mathbf{t}} = -\frac{\partial \mathbf{J}}{\partial \mathbf{x}} \pm \mathbf{S/S} \qquad (2)$$

TRANSPORT EQUATION

C_T = total mass (dissolved mass plus mass adsorbed to solid) per unit volume

$$= \rho_b C_S + n C_W = \rho_b C_S + n C \qquad (3)$$

Note: W subscript dropped for convenience and for Consistency with conventional notation

Substitute Equation 3 into Equation 2:

$$\frac{\partial(\rho_b C_s)}{\partial t} + \frac{\partial(nC)}{\partial t} = -\frac{\partial}{\partial x}\left(nuC - D_H n \frac{\partial C}{\partial x}\right) \pm S/S \qquad (4)$$

↑ no solid phase in flux term

TRANSPORT EQUATION

$C_S = K_d C$ by definition of K_d

Assume spatially uniform n, ρ_b, K_d, u, and D_H and no S/S

$$\left(\rho_b K_d + n\right)\frac{\partial C}{\partial t} = -nu\frac{\partial C}{\partial x} + nD_H\frac{\partial^2 C}{\partial x^2} \qquad (5)$$

$$\frac{\partial C}{\partial t} = -\frac{u}{\left(\dfrac{\rho_b K_d + n}{n}\right)}\frac{\partial C}{\partial x} + \frac{D_H}{\left(\dfrac{\rho_b K_d + n}{n}\right)}\frac{\partial^2 C}{\partial x^2} \qquad (6)$$

TRANSPORT EQUATION

"Retardation factor", R_d

$$\frac{\rho_b K_d + n}{n} = 1 + \frac{\rho_b K_d}{n} = R_d \qquad (7)$$

Substituting Equation 7 into Equation 6:

$$\frac{\partial C}{\partial t} = -\frac{u}{R_d}\frac{\partial C}{\partial x} + \frac{D_H}{R_d}\frac{\partial^2 C}{\partial x^2} \qquad (8)$$

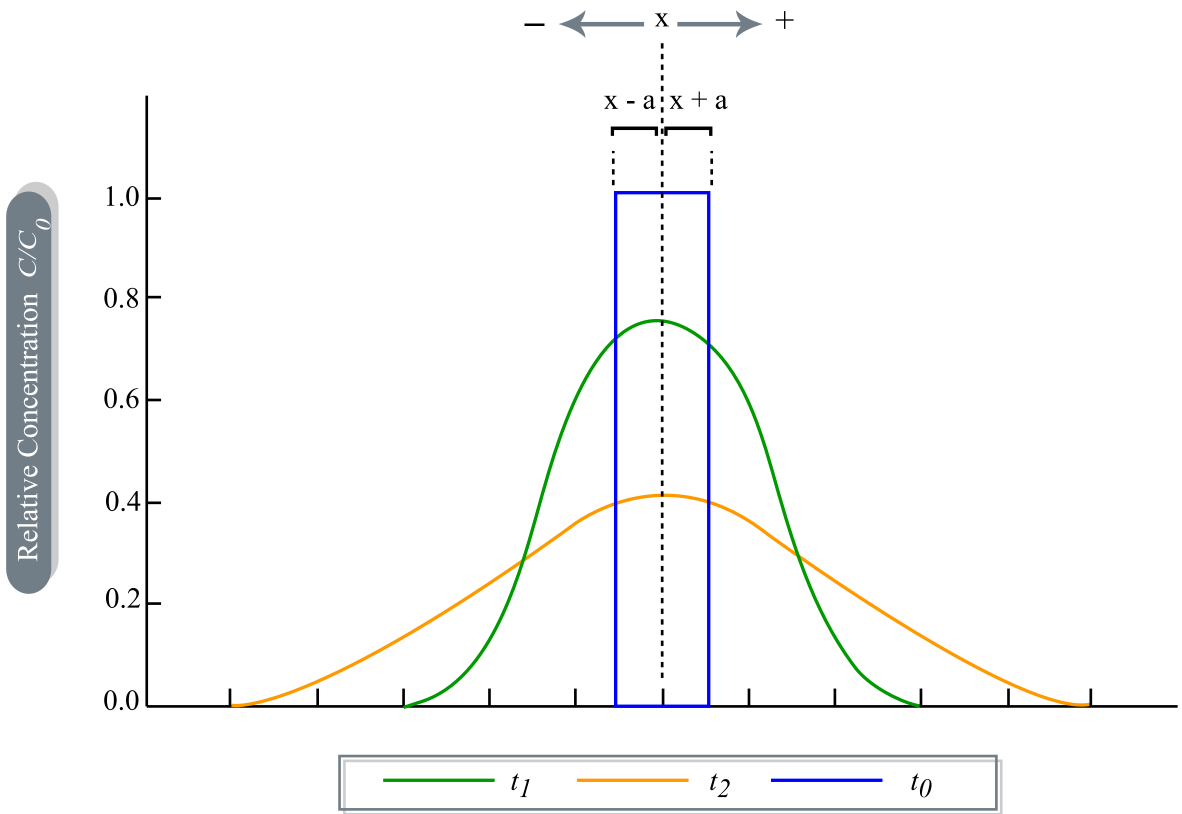
Effect of adsorption to solids is an apparent slowing of transport of dissolved contaminants

Both u and D_H are slowed

SOLUTION OF TRANSPORT EQUATION

Equation 8 can be solved with a variety of boundary conditions

In general, equation predicts a spreading Gaussian cloud



Spreading of a solute slug with time due to diffusion. A slug of solute was injected into the aquifer at time t_0 with a resulting initial concentration of C_0.

Adapted from: Fetter, C. W. *Contaminant Hydrogeology.* New York: Macmillan Publishing Company, 1992.

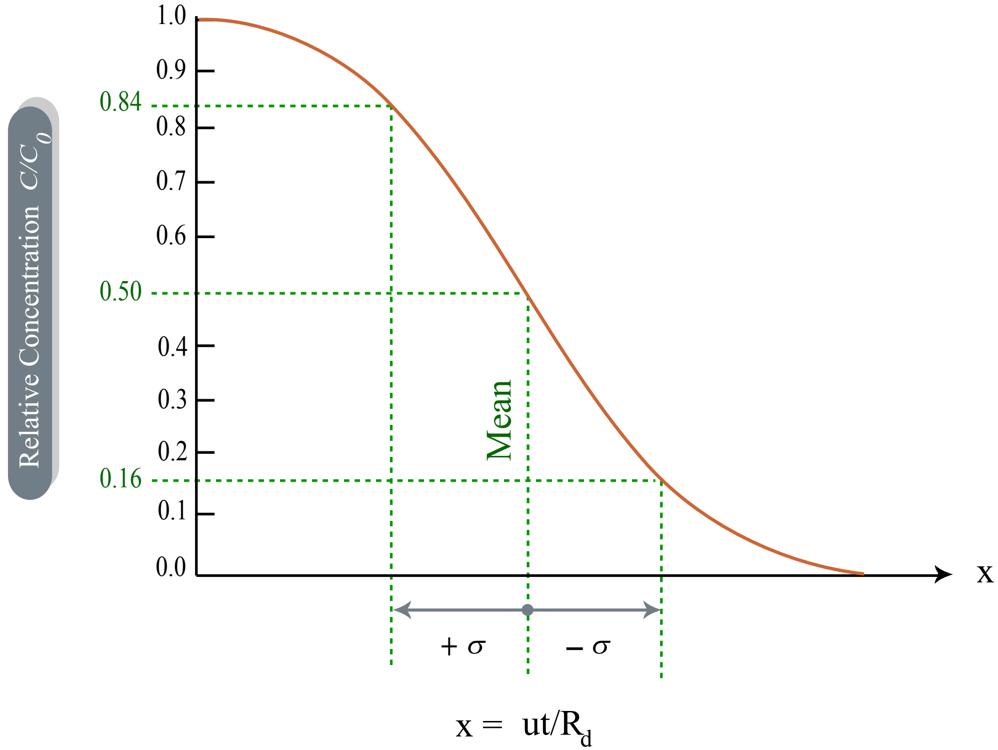
1-D SOLUTION OF TRANSPORT EQUATION

For instantaneous placement of a long-lasting source (for example, a spill that leaves a residual in the soil), solution is:

$$C(x,t) = \frac{C_o}{2}\,\mathrm{erfc}\left(\frac{R_d x - ut}{\sqrt{4 R_d D_H t}}\right)$$

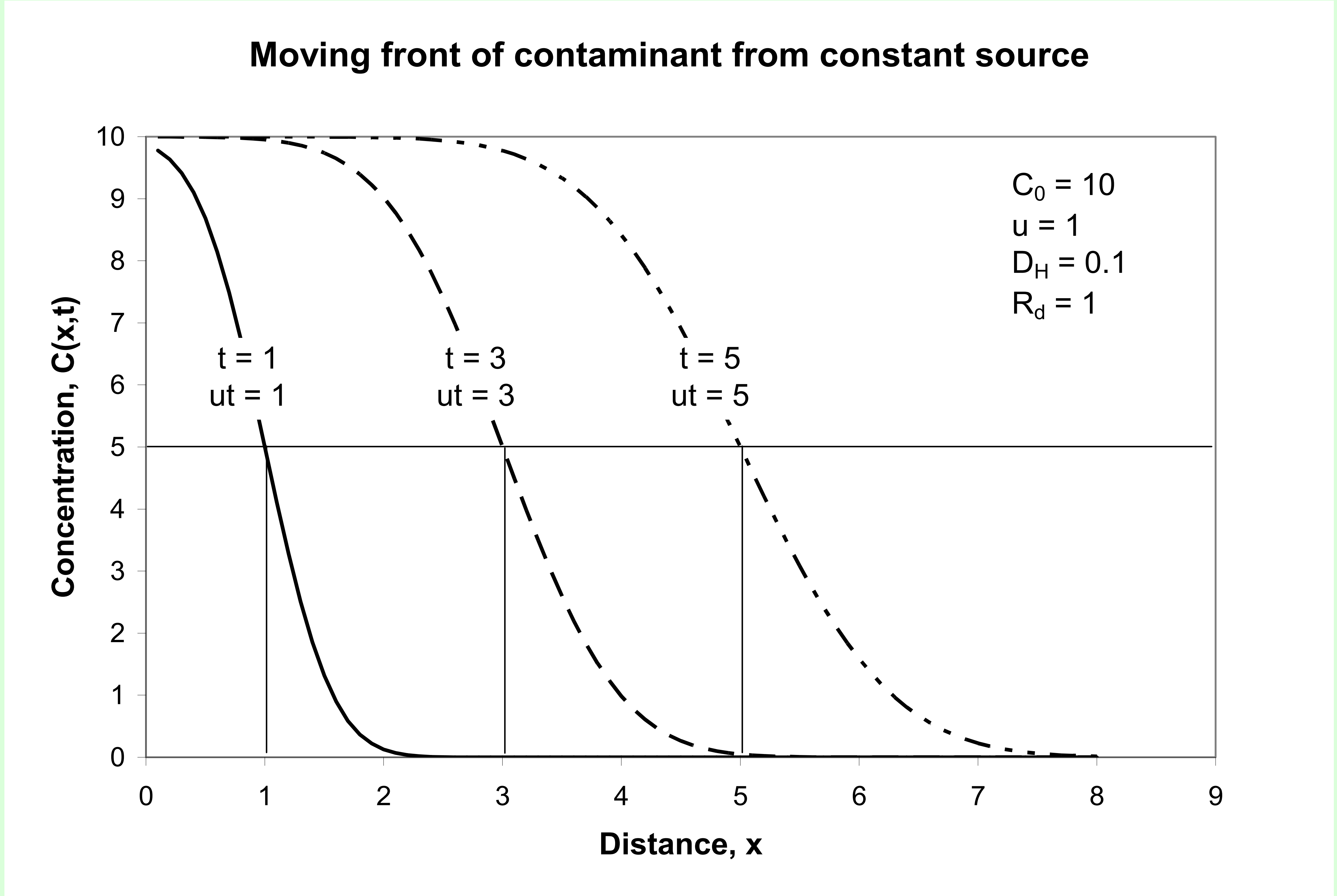
Where C_o = C(x=0, t) = constant concentration at source location x = 0

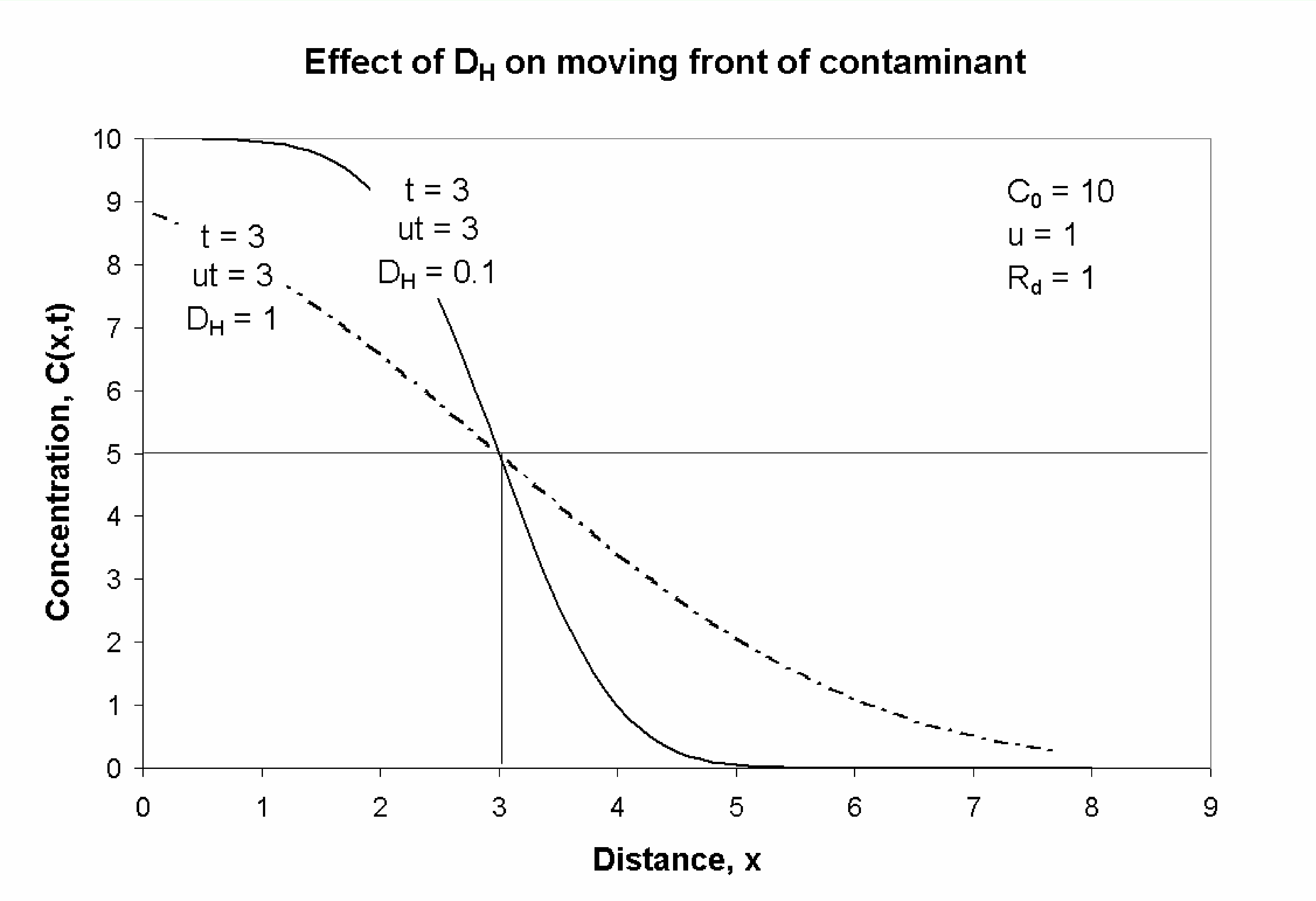
Solution is a front moving with velocity u/R_d



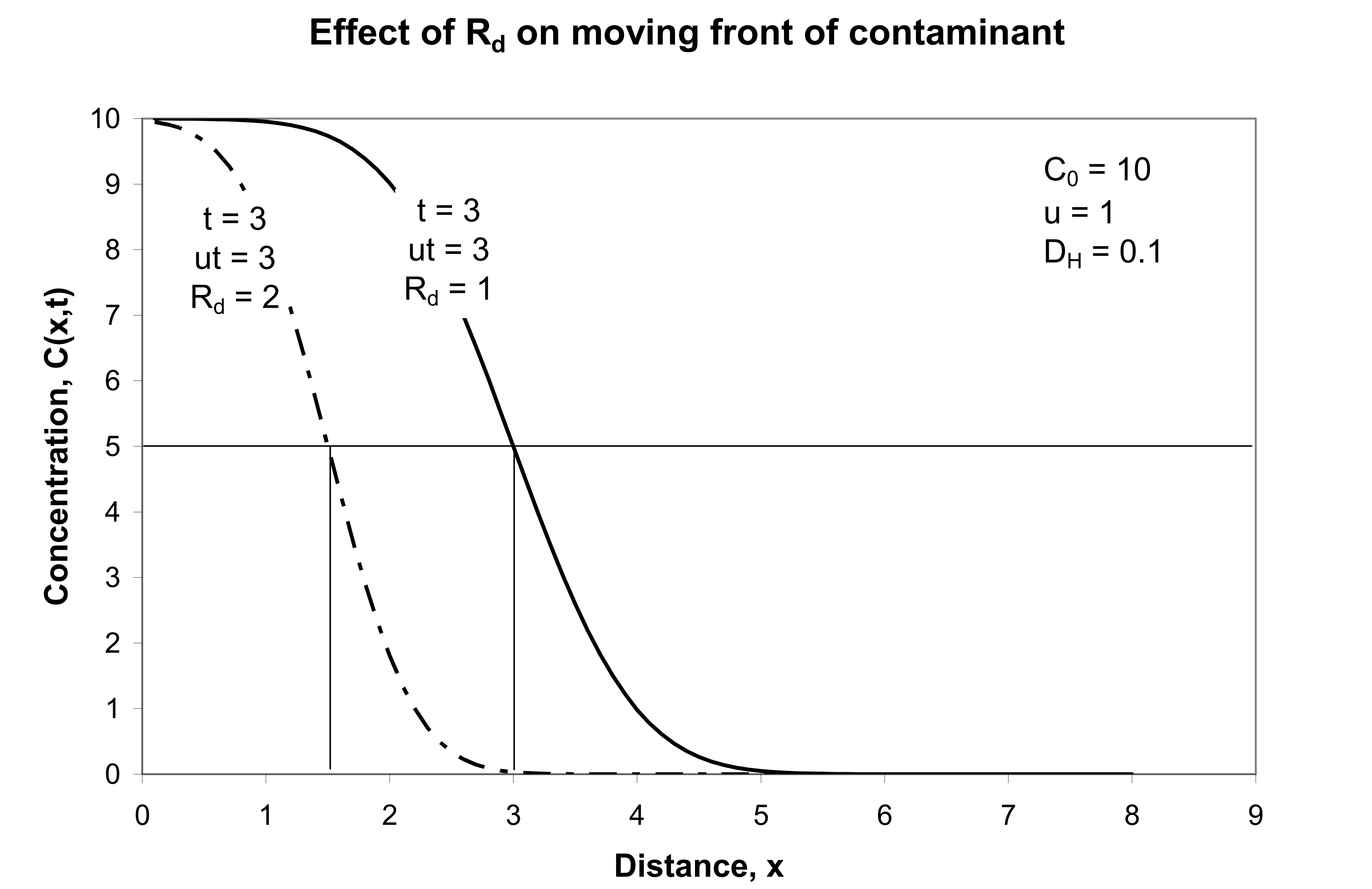
The profile of a diffusing front as predicted by the complementary error function.

Adapted from Fetter, C. W. *Contaminant Hydrogeology*.
New York: Macmillan Publishing Company, 1992.


Moving front of contaminant from constant source
Concentration, C(x,t)
Distance, x
C0 = 10
u = 1
DH = 0.1
Rd = 1
t = 1
ut = 1
t = 3
ut = 3
t = 5
ut = 5
0
1
2
3
4
5
6
7
8
9
10



Effect of D_H on moving front of contaminant
t = 3
ut = 3
D_H = 0.1
t = 3
ut = 3
D_H = 1
C_0 = 10
u = 1
R_d = 1
Concentration, C(x,t)
Distance, x
0
1
2
3
4
5
6
7
8
9
10



Effect of R_d on moving front of contaminant
10
9
8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
6
7
8
9
Concentration, C(x,t)
Distance, x
t = 3
ut = 3
R_d = 2
t = 3
ut = 3
R_d = 1
C_0 = 10
u = 1
D_H = 0.1

1-D SOLUTIONS

Transport of a Conservative Substance from Pulse and Continuous Sources

Dimensions

1-D

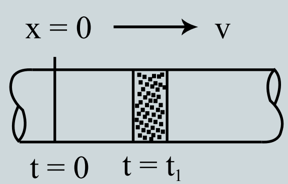
M, $\dot{M}$ are instantaneous or continuous plane sources

$$M \left[\frac{M}{L^2}\right]$$

$$\dot{M} \left[\frac{M}{L^2 T}\right]$$

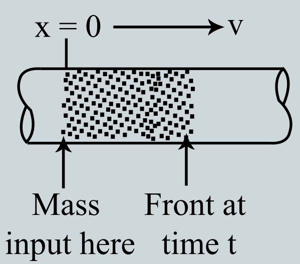
Pulse Input of Mass M

$$C = \frac{M}{2n\pi^{1/2}\, t^{1/2}\sqrt{D_x}} \exp - \left[\frac{(x-vt)^2}{4D_x t}\right]$$



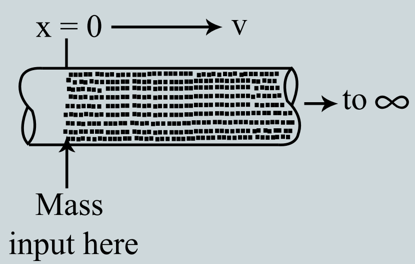
Continuous Input of Mass Per Unit Time $\dot{M}$ Starting at Time t = 0

$$C = \frac{\dot{M}}{2nv} \operatorname{erfc}\left(\frac{x-vt}{2\sqrt{D_x t}}\right)$$



Continuous Input of Mass Per Unit Time $\dot{M}$ in Steady State

$$C = \frac{\dot{M}}{nv} \quad (\text{for } x > 0)$$

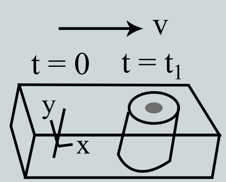


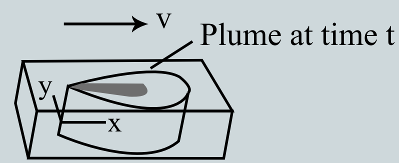
Adapted from: Hemond, H. F. and E. J. Fechner-Levy. *Chemical Fate and Transport in the Environment.* 2nd ed. San Diego: Academic Press, 2000.

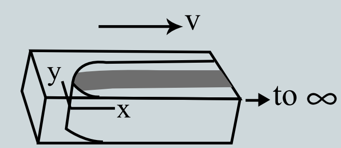
2-D SOLUTIONS

Transport of a Conservative Substance from Pulse and Continuous Sources

Dimensions	Pulse Input of Mass M	Continuous Input of Mass Per Unit Time $\dot{M}$ Starting at Time t = 0	Continuous Input of Mass Per Unit Time $\dot{M}$ in Steady State
2-D M, $\dot{M}$ are instantaneous or continuous line sources $M\left[\frac{M}{L}\right]$ $\dot{M}\left[\frac{M}{L\text{-}T}\right]$	$C=\frac{M}{4n\pi t\sqrt{D_x D_y}}\exp-\left[\frac{(x-vt)^2}{4D_x t}+\frac{y^2}{4D_y t}\right]$	$C=\frac{\dot{M}}{4n\pi^{1/2}(vr)^{1/2}\sqrt{D_y}}\exp\left[\frac{(x-r)v}{2D_x}\right]\mathrm{erfc}\left(\frac{r-vt}{2\sqrt{D_x t}}\right)$	$C=\frac{\dot{M}}{2n\pi^{1/2}(vr)^{1/2}\sqrt{D_y}}\exp\left[\frac{(x-r)v}{2D_x}\right]$







Adapted from: Hemond, H. F. and E. J. Fechner-Levy. *Chemical Fate and Transport in the Environment.* 2nd ed. San Diego: Academic Press, 2000.

3-D SOLUTIONS

Transport of a Conservative Substance from Pulse and Continuous Sources

Dimensions

3-D

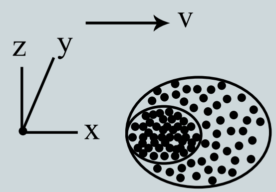
M, $\dot{M}$ are instantaneous or continuous point sources

$$M\left[\frac{\mathrm{M}}{\mathrm{L}}\right]$$

$$\dot{M}\left[\frac{\mathrm{M}}{\mathrm{T}}\right]$$

Pulse Input of Mass M

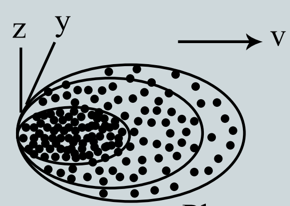
$$C = \frac{M}{8n\pi^{3/2}\,t^{3/2}\sqrt{D_x D_y D_z}}\exp-\left[\frac{(x-vt)^2}{4D_x t}+\frac{y^2}{4D_y t}+\frac{z^2}{4D_z t}\right]$$



t = 0 t = t_1

Continuous Input of Mass Per Unit Time $\dot{M}$ Starting at Time t = 0

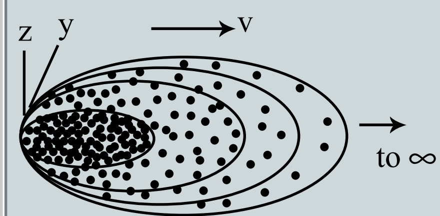
$$C=\frac{\dot{M}}{8n\pi r\sqrt{D_y D_z}}\exp\left[\frac{(x-r)v}{2D_x}\right]\mathrm{erfc}\left(\frac{r-vt}{2\sqrt{D_x t}}\right)$$



Plume at time t

Continuous Input of Mass Per Unit Time $\dot{M}$ in Steady State

$$C=\frac{\dot{M}}{4n\pi r\sqrt{D_y D_z}}\exp\left[\frac{(x-r)v}{2D_x}\right]$$



Adapted from: Hemond, H. F. and E. J. Fechner-Levy. *Chemical Fate and Transport in the Environment.* 2nd ed. San Diego: Academic Press, 2000.