# CHAPTER 8

# POLLUTION of GROUNDWATER

# Mass Transport of Pollutants

- **The law of conservation (advective – dispersive equation) for solute transport**
- **Saturated media**
- **Followed Ogata, Bear and Freeze and Cherry**

# Mass Transport of Pollutants

- The solutes in porous media considers the flux of solute into and out of a fixed chemicale:

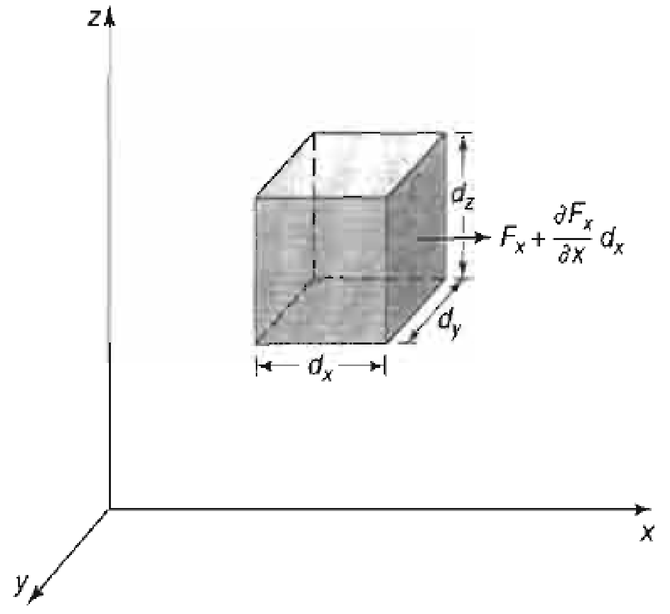


**Figure 8.8.1.** Elemental control volume for derivation of the conservation of mass showing the flux (Freeze and Cherry[33]).

$$\begin{bmatrix}\text{net rate of}\\ \text{change of mass}\\ \text{of solute within}\\ \text{the element}\end{bmatrix} = \begin{bmatrix}\text{flux of}\\ \text{solute out}\\ \text{of the}\\ \text{element}\end{bmatrix} - \begin{bmatrix}\text{flux of}\\ \text{solute into}\\ \text{the}\\ \text{element}\end{bmatrix} \pm \begin{bmatrix}\text{loss or gain}\\ \text{of solute mass}\\ \text{due to}\\ \text{reactions}\end{bmatrix} \qquad (8.8.1)$$

# Mass Transport of Pollutants

- **Solutes could be considered in two classes:**
  - **Conservative solutes: are non reactive with soil, native groundwater (such as Chloride)**
  - **Reactive solutes**
- **Advection: is the transport of solute by the flowing groundwater (Darcy's law)**
- **Hydrodynamic: is dispersion results from mechanical mixing and molecular diffusion**

# Mass Transport of Pollutants

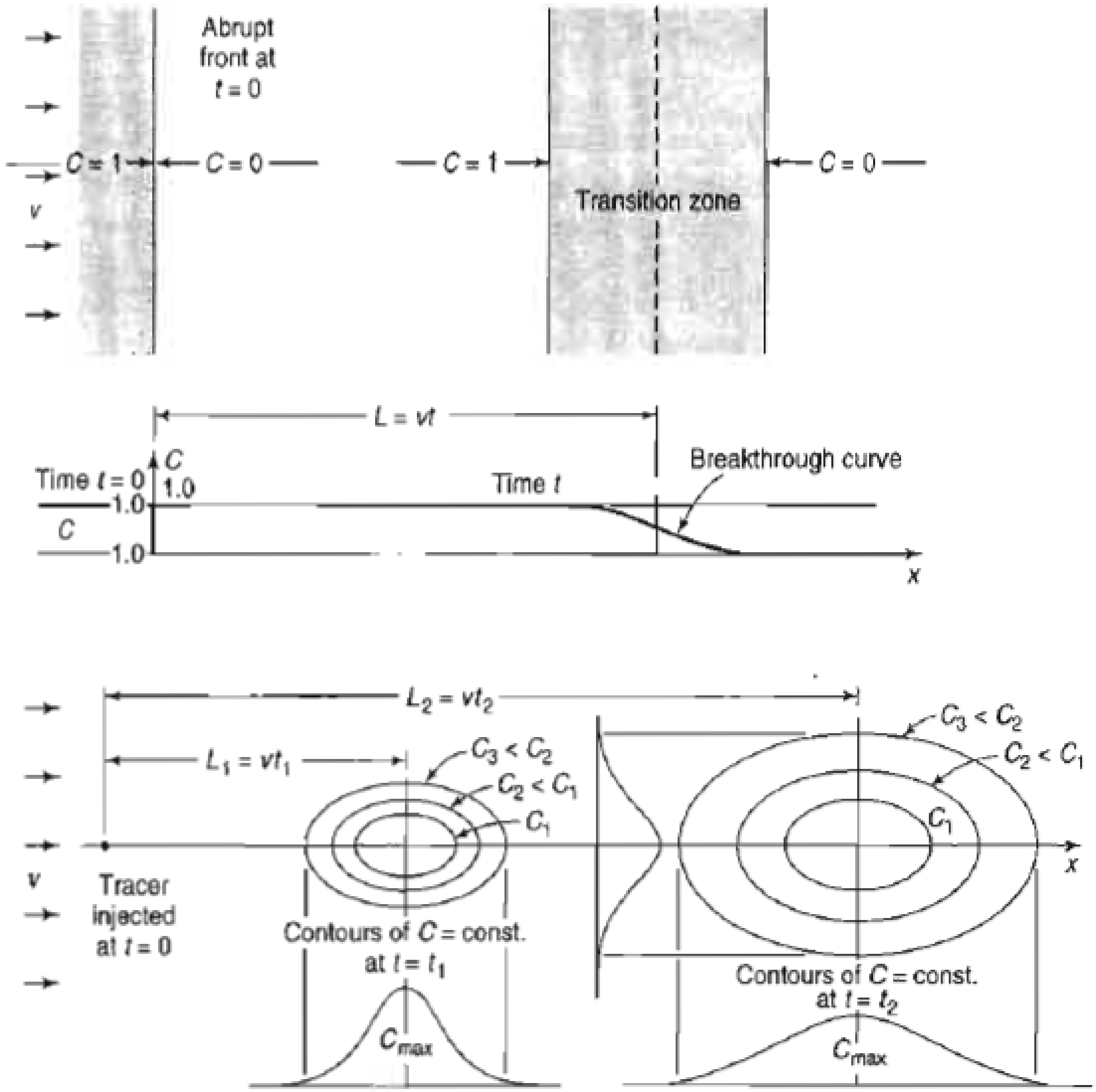


**Figure 8.8.2.** Longitudinal and transverse spreading due to mechanical dispersion (from Bear and Verruijt[9] with permission).

# Mass Transport of Pollutants

- **Diffusion: is the mass flux of solute from a zone of higher concertation to zone of lower concertation**
- **The diffusion by Fick's law for steady state condition:**

$$F = -D\frac{dC}{dx} \qquad (8.8.2)$$

where $F$ is the mass flux of solute per unit area per unit time ($M/L^2/T$); $D$ is the diffusion coefficient ($L^2/T$); $C$ is the solute concentration ($M/L^3$); and $dC/dx$ is the concentration gradient ($M/L^3/L$). The negative sign indicates the movement from greater to lesser concentration. Dif-

# Mass Transport of Pollutants

- The negative sign indicates the movement from greater to lesser concentration
- The diffusion coefficients for major ions (Na, Mg, Ca, Cl, HCO, SO4) is $1*10^{-9}$ to $2*10^{-9}$ $m^2/s$

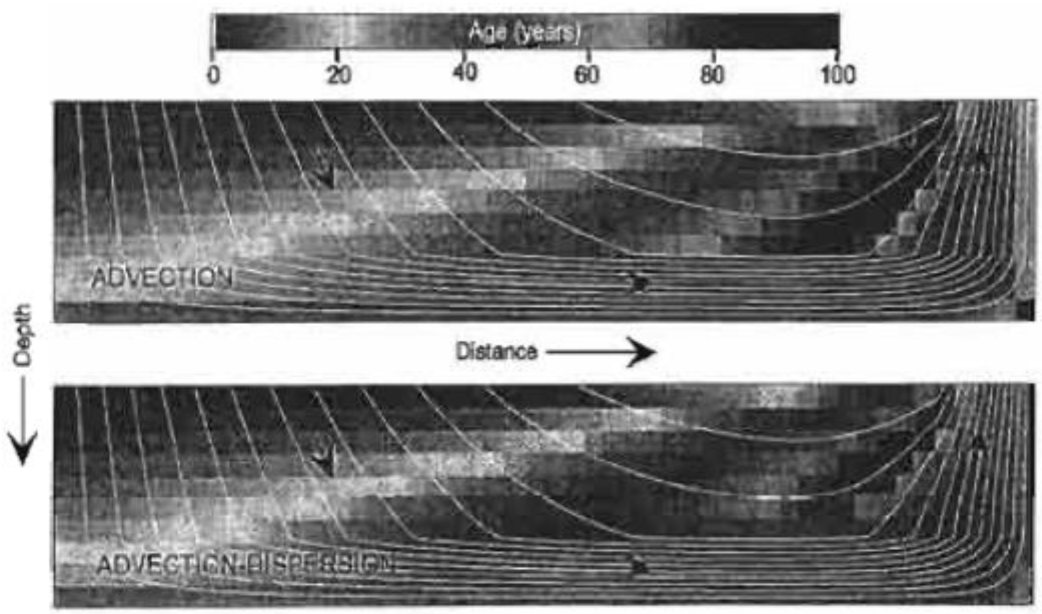


**Figure 8.8.3.** Streamlines and groundwater age distributions with and without dispersion in a regional layered aquifer system (Goode[40]).

# Mass Transport of Pollutants

- Fick's second law described the change of concentration over time:

$$\frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} \qquad (8.8.3)$$

where $\partial C/\partial t$ is the change in concentration with time. The above expressions of Fick's first and

- Diffusion coefficient for nonabsorded species in porous media flow:

$$D^* = \omega D \qquad (8.8.4)$$

where $\omega$ is an empirical coefficient (<1) that takes into account the effect of the solid phase of the porous media on the diffusion. Freeze and Cherry[33] suggest using the above effective diffusion coefficient with $\omega$ ranging from 0.5 to 0.01, to account for the tortuosity of the flow path.

# Mass Transport of Pollutants

- **The longitudinal coefficient of hydrodynamic dispersion (DL) is expressed as:**

$$D_L = \alpha_L \bar{v} + D^* \quad (8.8.5)$$

where $\alpha_L$ is the dynamic longitudinal dispersivity, a characteristic property of the porous medium; $\bar{v}$ is the average linear groundwater velocity; and $D^*$ is the molecular diffusion

# Mass Transport of Pollutants

A rough approximation of $\alpha_L$ based on averaging published date (Gelhar et al.[38]) is

$$\alpha_L = 0.1L \tag{8.8.6}$$

where $L$ is the length of the flow path (m). For lengths less than 3,500 m, Neuman[72] gave

$$\alpha_L = 0.0175L^{1.46} \tag{8.8.7}$$

For transverse (lateral) dispersivity, $\alpha_T$ is typically 1/10 to 1/100 of the longitudinal dispersivity $\alpha_L$. Xu and Eckstein[109] used a statistical study to develop the following relationship

$$\alpha_L = 0.83(\log L)^{2.414} \tag{8.8.8}$$

where $L$ is in ft or m and $\alpha_L$ is in ft or m.

# Mass Transport of Pollutants

- ***Advection-Dispersion Equation:***
  - **Solute transport in saturated porous media**
  - **Consider the following elemental volume:**

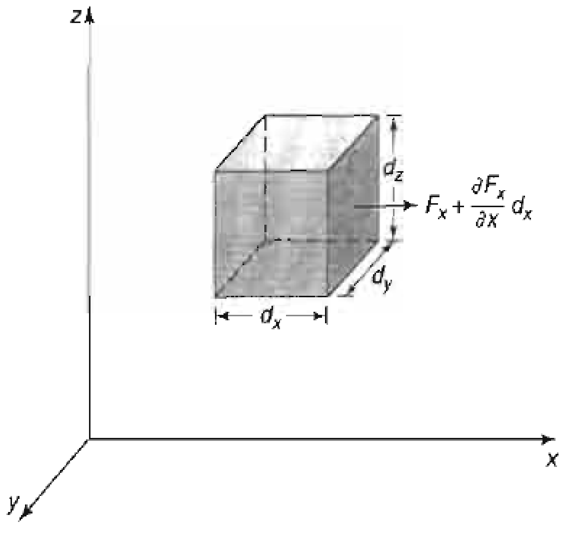


**Figure 8.8.1.** Elemental control volume for derivation of the conservation of mass showing the flux (Freeze and Cherry[33]).

$$\begin{bmatrix}\text{net rate of}\\ \text{change of mass}\\ \text{of solute within}\\ \text{the element}\end{bmatrix} = \begin{bmatrix}\text{flux of}\\ \text{solute out}\\ \text{of the}\\ \text{element}\end{bmatrix} - \begin{bmatrix}\text{flux of}\\ \text{solute into}\\ \text{the}\\ \text{element}\end{bmatrix} \pm \begin{bmatrix}\text{loss or gain}\\ \text{of solute mass}\\ \text{due to}\\ \text{reactions}\end{bmatrix} \qquad (8.8.1)$$

# Mass Transport of Pollutants

- The mass of solute is transported in the x – direction by advection and by dispersion expressed as:

$$\text{Mass transported by advection} = \bar{v}_x nC\, dA \qquad (8.8.9)$$

$$\text{Mass transported by dispersion} = nD_x 2C/2x\, dA \qquad (8.8.10)$$

where $dA$ is the elemental cross-sectional area of the cubic element and $D_x$ is the dispersion coefficient in the $x$-direction defined by

$$D_x = \alpha_x \bar{v}_x + D^* \qquad (8.8.11)$$

where $\alpha_x$ is the dynamic dispersivity and $\alpha_x v_x$ is the *mechanical dispersion.*

# Mass Transport of Pollutants

$F_x$ is now represented as

$$F_x = \bar{v}_x nC - nD_x \frac{\partial C}{\partial x} \qquad (8.8.12)$$

with the negative sign for the dispersive term indicating that the contaminant (solute) moves toward the zone of lower concentration. In a similar manner, $F_y$ and $F_z$ are respectively

$$F_y = \bar{v}_y nC - nD_y \frac{\partial C}{\partial y} \qquad (8.8.13)$$

$$F_z = \bar{v}_z nC - nD_z \frac{\partial C}{\partial z} \qquad (8.8.14)$$

The total solute entering (flux entering) the cubic element is

$$F_{\text{entering}} = F_x\,dz\,dy + F_y\,dz\,dx + F_z\,dx\,dy \qquad (8.8.15)$$

and the total solute leaving (flux leaving) the cubic element is

$$F_{\text{leaving}} = \left(F_x + \frac{\partial F_x}{\partial x}dx\right)dy\,dz + \left(F_y + \frac{\partial F_y}{\partial y}dy\right)dz\,dx + \left(F_z + \frac{\partial F_z}{\partial z}dz\right)dx\,dy \qquad (8.8.16)$$

# Mass Transport of Pollutants

- Partial terms indicated the spatial change of solute mass in the respective direction
- For nonreactive dissolved substance, the flux into element the flux out of the element is equal to the net rate of change of mass of solute:

$$\Delta F = -n\frac{\partial C}{\partial t}\,dx\,dy\,dz \qquad (8.8.17)$$

Combining the above three expressions (Equations 8.8.15–8.8.17) and simplifying gives

$$\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} = -n\frac{\partial C}{\partial t} \qquad (8.8.18)$$

Substituting Equations 8.8.12–8.8.14 into Equation 8.8.18 gives

$$\left[\frac{\partial}{\partial x}\left(D_x\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z\frac{\partial C}{\partial z}\right)\right] - \left[\frac{\partial}{\partial x}(\bar{v}_x C) + \frac{\partial}{\partial y}(\bar{v}_y C) + \frac{\partial}{\partial z}(\bar{v}_z C)\right] = \frac{\partial C}{\partial t} \qquad (8.8.19)$$

# Mass Transport of Pollutants

- For a homogenous medium *v* steady and uniform in space and time, then the previous equation is simplified as:

$$\left[D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}\right] - \left[\bar{v}_x \frac{\partial C}{\partial x} + \bar{v}_y \frac{\partial C}{\partial y} + \bar{v}_z \frac{\partial C}{\partial z}\right] = \frac{\partial C}{\partial t} \qquad (8.8.20)$$

For one dimension, the conservation of mass (advection–dispersion equation) is

$$D_x \frac{\partial^2 C}{\partial x^2} - \bar{v}_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad (8.8.21)$$

which can also be expressed along a flowline by using $L$ for $x$ where $L$ is the coordinate direction along the flowline. $D_L$ is the longitudinal coefficient of hydrodynamic dispersion and $\bar{v}_L$ is the average linear velocity along the flowline.

# Mass Transport of Pollutants

- The analytical solution of Equation (8.8.21) is:

| | | |
|---|---|---|
| Initial condition | $C(x, 0) = 0$ | $x \geq 0$ |
| Boundary condition | $C(0, t) = C_0$ | $t \geq 0$ |
| Boundary condition | $C(\infty, t) = 0$ | $t \geq 0$ |

$$C(x,t) = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{x - vt}{2\sqrt{D_L t}}\right) + \exp\left(\frac{vx}{D_L}\right)\operatorname{erfc}\left(\frac{x + vt}{2\sqrt{D_L t}}\right)\right] \tag{8.8.22}$$

where $x$ is the distance from the injection point.

The argument of the exponential ($\bar{v}_L x/D_L$) is the Peclet number, $P_e = \bar{v}_L x/D_L$, which is a measure of the ratio of the rate of transport by advection to the rate of transport by diffusion.

# Mass Transport of Pollutants

**EXAMPLE 8.8.1**

The objective of this example is to illustrate the use of Equation 8.8.22 to compute the concentration of a pollutant as a function of time and distance from a point or line source in an aquifer with known properties. The aquifer properties are: hydraulic conductivity = $2.5 \times 10^{-5}$ m/s; hydraulic gradient = 0.001; effective porosity = 0.25; and an effective diffusion coefficient = $0.75 \times 10^{-9}$ m²/s. A chloride solution with a concentration of 600 mg/l penetrates (enters) the aquifer along a line source. Determine the chloride concentration at a distance of 25 m from the source after one year, two years, and four years.

Step 1: Compute the pore velocity (average linear velocity) using Darcy's law:

$$\bar{v}_L = \frac{Ki}{n_e} = \frac{(2.5\times10^{-5})0.001}{0.25} = 1\times10^{-7}\ \text{m/s}$$

Step 2: Compute the longitudinal dispersivity using the approximation of Neuman,[72] Equation 8.8.7:

$$\begin{aligned}\alpha_L &= 0.0175L^{1.46}\\ &= 0.0175(25)^{1.46}\\ &= 1.92\ \text{m}\end{aligned}$$

Using the approximation by Xu and Eckstein,[109] Equation 8.8.8, we have

$$\begin{aligned}\alpha_L &= 0.83(\log L)^{2.414}\\ &= 0.83(\log 25)^{2.414}\\ &= 1.86\ \text{m}\end{aligned}$$

# Mass Transport of Pollutants

Step 3: Compute the coefficient of longitudinal mechanical dispersion–diffusion (coefficient of longitudinal hydrodynamic dispersion) using Equation 8.8.11 where $\alpha_L = 1.86$ m:

$$D_L = \alpha_L v_L + D^*$$

$$= 1.86 \times (1 \times 10^{-7}) + 0.75 \times 10^{-9}$$

$$= 1.9 \times 10^{-7}\ \text{m}^2/\text{s}$$

Step 4: Use Equation 8.8.22 to compute the concentration for times of $t = 1$ year $= 60$ s/min $\times$ 1,440 min/day $\times$ 365 days/yr $= 3.15 \times 10^7$ s; $t = 2$ years $= 6.31 \times 10^7$ s; and $t = 4$ years $= 12.6 \times 10^7$ s; $\bar{v}_L = 1 \times 10^{-7}$ m/s; $C_0 = 600$ mg/l; $x = L = 25$ m; $D_L = 1.9 \times 10^{-7}$ m$^2$/s.

For $t = 1$ year: $C(25\text{m}, 1\text{ yr}) = 0.0$ mg/l

For $t = 2$ years: $C(25\text{m}, 2\text{ yr}) = 0.037$ mg/l

For $t = 4$ years: $C(25\text{m}, 4\text{ yr}) = 21.6$ mg/l ■

# Mass Transport of Pollutants

- ***Transport of Reactive Pollutants:***

  - ***Sorption*: is the exchange of molecules and ions between the solid phase and liquid phase**
  - ***Adsorption*: is the attachment of molecules and ions from solute to the rock material**
  - ***Desorption*: is the release of molecules and ions from the solid phase to the solute**

# Mass Transport of Pollutants

- ***Transport of Reactive Pollutants:***
- **The one-dimensional transport for advection-dispersion:**

$$D_x \frac{\partial^2 C}{\partial x^2} - \bar{v}_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad (8.8.21)$$

- **Can be extended to include the effects of retardation of solute transportation**

# Mass Transport of Pollutants

- ***Transport of Reactive Pollutants:***
- **The form of the one-dimensional equation that included retardation, in a homogenous saturated media due to adsorption is expressed as:**

$$D_L \frac{\partial^2 C}{\partial l^2} - \bar{v}_L \frac{\partial C}{\partial l} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} = \frac{\partial C}{\partial t} \qquad (8.8.23)$$

(dispersion term) (advection term) (reaction term)

where $\rho_b$ is the bulk mass density of the porous medium, $n$ is the porosity, and $S$ is the mass of chemical constituent adsorbed on a unit mass of the solid part of the porous medium. $\partial S/\partial t$ is the rate at which the constituent is adsorbed [M/MT] and $(\rho_b/n)(\partial S/\partial t)$ is the change in concentration in the groundwater caused by adsorption or desorption $[M/(L^3T)]$.

# Mass Transport of Pollutants

- ***Transport of Reactive Pollutants:***
- **Adsorption relationships could be plotted as straight line on log-log paper:**

$$\log S = b \log C + \log K_d \qquad (8.8.24)$$
$$S = K_d C^b$$

where $S$ is the mass of solute species adsorbed or precipitated on the solids per unit bulk dry mass of the porous medium, $C$ is the solute concentration, and $K_d$ and $b$ are coefficients. These

- **These coefficients depend on the solute species, nature of the porous medium, and other conditions**
- ***b*** **is the slope**
- ***Kd = dS/dC***

# Mass Transport of Pollutants

- ***Transport of Reactive Pollutants:***
- **The retardation equation *Ra* is expressed as:**

$$R_a = 1 + \frac{(1-n)\rho_b}{n} K_d \qquad (8.8.25)$$

where $n$ is the porosity and $\rho_b$ is the bulk mass density of the soil, gm/cm$^3$; and $K_d$ is the distribution coefficient for the solute with the soil. Also $1/\theta = (n-1)/n$ where $\theta$ is the volumetric content of the soil, which is dimensionless. The retardation factor ranges from 1 to 10,000. A

- **The velocity of solute front *Vc*:**

$$v_c = \overline{v}/R_a \qquad (8.8.26)$$

# Mass Transport of Pollutants

- ***Transport of Reactive Pollutants:***
- **The amount of contaminant adsorbed by solids is a function of the concentration in solution:**

$$-\frac{\partial S}{\partial t} = \frac{\partial S}{\partial C} \cdot \frac{\partial C}{\partial t} \qquad (8.8.27)$$

and

$$-\frac{\rho_b}{n} \cdot \frac{\partial S}{\partial t} = \frac{\rho_b}{n} \cdot \frac{\partial S}{\partial C} \cdot \frac{\partial C}{\partial t} \qquad (8.8.28)$$

# Mass Transport of Pollutants

- ***Transport of Reactive Pollutants:***
- **Using *Kd = dS/dC, and governing* the previous equations in equation (8.8.21), the one-dimensional advection-dispersion equation in retardation terms is expressed as:**

$$\frac{\partial C}{\partial t} = -\frac{v}{R_a}\frac{\partial C}{\partial x} + \frac{D_L}{R_a}\frac{\partial^2 C}{\partial x^2} \qquad (8.8.29)$$

- **The first term is the retarded advective inflow – outflow**
- **The second term is retarded diffusion and dispersion**