

## Chapter 8. Contaminant Release and Transport from the Source

- Contaminants distributions are commonly quantified using sampling and analysis schemes because monitoring data are more reliable and thus preferred.
- However, in some cases, values obtained from prediction models are useful.

### 1. The Controlling Processes in Contaminant Release and Transport: Sorption, Volatilization, Transformation (p. 405)

- atmospheric and subsurface transport (Fig. 8.1)
  - major contaminants' transport through the subsurface and atmosphere
  - once released from the source, contaminants experience sorption, volatilization, and transformation
- conceptual pathway analysis (Example 8.1)

### 2. Mass Transfer of Contaminants in the Atmospheric and the Subsurface (p. 408)

#### 1) Mass balance

##### a) expressions

- ▶ change in storage of mass  
= mass transported IN - mass transported OUT  
+ mass PRODUCED by sources - mass ELIMINATED by sinks
- ▶ rate of change in storage of mass  
= mass transport rate in - mass transport rate out  
+ mass production rate by sources - mass elimination rate by sinks
- ▶ rate of mass accumulation within the system boundary  
= rate of mass flow into the system - rate of mass flow out of the system -/+ rate of reaction within the system

(\* rate = mass per time [M/T])

*↳ If storage does not change with time the left-hand sides are zero  
--> steady state*

##### b) described by a general mass flux vector

$$\frac{\partial m}{\partial t} = \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}$$

$J$ ; the mass flux vector in the x, y, or z direction  
m; contaminant mass per unit volume  
t; time

##### c) differences between atmospheric and subsurface definitions of mass

- volume of air; total volume of the sample
- in the subsurface; "porosity" and "retardation" concepts included

$$m = C \quad (\text{atmosphere})$$

$$m = n \cdot R \cdot C \quad (\text{subsurface})$$

#### 2) Two important phenomena of movement

##### a) advection (i.e., wind; pore-water velocity)

##### b) dispersion

##### c) flux(es) $J = J_{adv} + J_{disp}$

3) Advective flux

a) mainly resulting from bulk, large scale movement of a medium

(e.g.) wind blows, water flows,....

b) so, transported at the same velocity as the fluid

- macroscale view; center of mass of chemical moves by advection

- microscale view; Fickian transport occurs at the same time

c) convection; often vertical advection (but, considered almost a similar term)

d) flux density ( $J$ )

- mass of chemical transported across an imaginary surface of unit area per unit of time

$$J = C \cdot V$$

$J$ ; advective flux ( $\text{mg}/\text{m}^2\text{-sec}$ ) [ $\text{M}/\text{L}^2\text{T}$ ]

$C$ ; contaminant conc. ( $\text{mg}/\text{m}^3$ ) [ $\text{M}/\text{L}^3$ ]

$V$ ; fluid velocity ( $\text{m}/\text{sec}$ ) [ $\text{L}/\text{T}$ ]

- in groundwater,  $V$  is pore-water velocity

$$J = C \cdot (n v_p)$$

$n$ ; porosity (i.e.,  $n_e$ )

$v_p$ ; seepage (pore-water) velocity ( $\text{m}/\text{sec}$ )

4) Dispersive flux

a) "all of the mass transfer exclusive of advection"

b) Turbulent diffusion ("eddy diffusion")

- resulting from random mixing of air or water by eddies

- carries mass in the direction of decreasing chemical concentration

(e.g.) dye blob injected into a river

- important in surface water and air (**not considered in the subsurface**)

- use Fick's first law to describe

$$J = -nD \cdot \left( \frac{\partial C}{\partial x} \right)$$

$J$  [ $\text{M}/\text{L}^2\text{T}$ ]; dispersive flux in the  $x$  direction

$n$ ; porosity

$D$ ; turbulent diffusion coefficient

$C$  [ $\text{M}/\text{L}^3$ ]; chemical concentration

$x$  [ $\text{L}$ ]; distance over which a concentration change is considered

c) (mechanical) dispersion (hydraulic dispersion)

- fluctuations in the velocity field at scales smaller than advection

- groundwater flow;

. no eddies present due to its low velocity

. but still random detours exist, causing mixing chemicals

- transport of a chemical from regions of higher to lower concentration

- use Fick's first law to describe

$$J = -nD_{\text{mech}} \cdot \left( \frac{\partial C}{\partial x} \right)$$

$J$  [ $\text{M}/\text{L}^2\text{T}$ ]; dispersive flux in the  $x$  direction

$n$ ; porosity

$D_{\text{mech}}$ ; mechanical dispersion coefficient

$C$  [ $\text{M}/\text{L}^3$ ]; chemical concentration

$x$  [ $\text{L}$ ]; distance over which a concentration change is considered

- related to the tortuous path of water through the subsurface solids
- tortuosity of flow paths and contaminant concentration result in the longitudinal mixing of contaminants

**d) molecular diffusion**

- random movement of chemicals due to local concentration gradient
- lower flux density compared to other Fickian transport processes
- use Fick's first law to describe

$$J = -nD_{\text{mole}} \cdot \left( \frac{\partial C}{\partial x} \right)$$

J [M/L<sup>2</sup>T]; dispersive flux in the x direction

n; porosity

D; molecular diffusion coefficient

C [M/L<sup>3</sup>]; chemical concentration

x [L]; distance over which a concentration change is considered

- not related to advective, dispersive, or turbulent motion but dependent on contaminants' molecular properties (primarily, size) and temperature

**e) hydrodynamic dispersion**

- the spreading of a tracer beyond the region expected to the average flow alone
- the macroscopic outcome of the actual movements of individual tracer particles through the pores and the various physico-chemical phenomena that take place within the pores
- $J_{\text{disp}} = J_{\text{mech}} + J_{\text{mole}}$
- $D = D_{\text{mech}} + D_{\text{mole}}$

※ Transport in total

$$J = J_{\text{adv}} + J_{\text{dis}}$$

※ One-dimensional situation is considered, flow is **anisotropic**

- flow direction vs. perpendicular to flow,
- homogeneous medium vs. heterogeneous medium,
- time

5) The advection-dispersion equation

- for the subsurface transport; characteristics of the medium

$$R \left( \frac{\partial C}{\partial t} \right) = -v_i \left( \frac{\partial C}{\partial t} \right) + D_i \left( \frac{\partial^2 C}{\partial i^2} \right)$$

- analytical methods
- numerical methods

**3. Atmospheric Transport Following Volatilization Releases (p. 413)**

**4. Subsurface Transport of Contaminants (p. 421)**

1) Subsurface transport and exposure

- a) migration through the unsaturated zone to groundwater
- b) exposure routes

- subsurface contamination; volatilization, leaching to groundwater
  - groundwater; drinking water wells, other uses
- 2) Nature of the subsurface environment (Fig. 8.12)
- a) vadose zone
    - subsurface region where the pore-water pressure is less than atmospheric pressure
    - pore-water pressure increases linearly with depth
    - water present as a thin film on solid surfaces
    - consists of solid particles, water (i.e., volumetric water content) and air (i.e., empty pore space)
    - unsaturated zone;
  - b) saturated zone
    - boundary of water table; pore-water pressure = atmospheric pressure
    - below the water table where the pore spaces are filled with water
    - pore-water pressure is greater than atmospheric, and increases linearly with depth
  - c) more terms
    - capillary fringe; an area where the upward movement of water from the saturated zone due to surface tension and capillary forces
    - aquifer; a saturated permeable geologic unit that can transmit sufficient water under ordinary hydraulic gradients
    - aquitard; the strata that are less permeable than an aquifer
    - unconfined aquifer;
    - confined aquifer;
  - d) porous and heterogeneous; most important subsurface properties!!!**
  - e) Darcy's Law
    - basis for advection in groundwater
    - an empirical mathematical description between the flow rate of a fluid through a porous medium and the head gradient
  - f) hydraulic conductivity
    - a parameter that describes the ease with which a fluid passes through porous media
    - a function of a fluid and a medium
    - hydraulic conductivities of soils (Table 8.2)
  - g) pore-water velocity (seepage velocity)
    - the velocity that accounts for the cross-sectional area
    - related to porosity of a medium

#### 4.1. Development and use of groundwater transport equations

- a) factors influencing subsurface transport (rates) of contaminants
  - media; characteristics of subsurface
  - fluid; flow (rate) of groundwater
  - interactions; sorption, transformation, volatilization,...
- b) assumptions
  - the media are characterized by constant density and viscosity
  - the media are isotropic

- the flow is incompressible
- the system is saturated
- c) many models are available
  - one-, two-, three-dimensional flow
  - pulse contaminant input and continuous contaminant input
  - presence or absence of transformation reactions
  - BUT, limited by estimation of parameters such as dispersion coefficient, transformation rate,...
- d) one-dimensional advection-dispersion equations
  - simple models relatively accurate for simple systems  
e.g.) soil columns, landfill leachate migration,...
  - a pulse input with or without transformation
  - a continuous input with or without transformation

1) Pulse model

- a) describes a pulse input of contamination such as hazardous materials spill
- b) derived with zero background concentration at the beginning ( $x = 0$ )
- c) a pulse input model without transformation;  
at a distance  $x$  downgradient and time  $t$

$$C(x,t) = \frac{M}{\sqrt{4\pi D_x t}} \cdot \exp\left[-\frac{(x - v'_x t)^2}{4D_x t}\right]$$

$M$ ; the mass spilled per cross-sectional area ( $\text{g}/\text{m}^2$ )

$D'_x$ ;  $D/R$  ( $\text{m}^2/\text{day}$ )

$D_x$ ; dispersion coefficient in the  $x$  direction

$x$ ; distance from the source (from the point of spill)

$v'_x$ ;  $v/R$  ( $\text{m}/\text{day}$ )

$v_x$ ; pore-water velocity in the  $x$  direction

$R$ ; retardation factor

- d) a pulse input equation with transformation

$$C(x,t) = \frac{M}{\sqrt{4\pi D_x t}} \cdot \exp\left[-\frac{(x - v'_x t)^2}{4D_x t}\right] \cdot e^{-k't}$$

$k'$ ;  $k/R$  ( $\text{day}^{-1}$ )

$k$ ; first-order transformation rate constant ( $\text{day}^{-1}$ )

- e) estimation of downgradient concentration from a source with transformation  
(Example 8.4)

2) Plume model

- a) describes a continuous input from a source (e.g., landfill)
- b) a plume input equation without transformation

$$C(x,t) = \frac{C_0}{2} \left[ \operatorname{erfc}\left(\frac{x - v'_x t}{2\sqrt{D_x t}}\right) - \exp\left(\frac{v'_x x}{D_x}\right) \cdot \operatorname{erfc}\left(\frac{x + v'_x t}{2\sqrt{D_x t}}\right) \right]$$

$C(x,t)$ ; contaminant conc. at point  $x$  and time  $t$  ( $\text{mg}/\text{L}$ )

$\operatorname{erfc}$ ; the complementary error function

under most conditions, the right-hand term becomes negligible,

$$C(x,t) = \frac{C_0}{2} \left[ \operatorname{erfc} \left( \frac{x - v_x t}{2\sqrt{D_x t}} \right) \right]$$

- c) estimation of downgradient concentration from a surface impoundment without transformation (Example 8.5)

### 3) Advection-Dispersion-Reaction Equation (ADRE)

- a) from the advection-dispersion equation  $R \left( \frac{\partial C}{\partial t} \right) = -v_x \left( \frac{\partial C}{\partial x} \right) + D_x \left( \frac{\partial^2 C}{\partial x^2} \right)$ ,

ADRE can be derived to account for transformation through the addition of a new term for first-order degradation (at a distance  $x$  and time  $t$ )

$$\frac{\partial C}{\partial t} = \frac{D}{R} \left( \frac{\partial^2 C}{\partial x^2} \right) - \frac{v}{R} \left( \frac{\partial C}{\partial x} \right) - \frac{k}{R} C$$

$C$ : contaminant conc. in the aqueous phase (mg/L)

$R$ : retardation factor  $\left( 1 + \frac{\rho_B}{n} \cdot K_d \right)$

$D$ : groundwater dispersion coefficient (m<sup>2</sup>/day)

$v$ : pore-water velocity (m/day)

$k$ : first-order degradation rate constant (day<sup>-1</sup>)

- b) effect of retardation on contaminant profile (Fig. 8.13)  
 c) effect of transformation on contaminant profile (Fig. 8.14)  
 d) an analytical solution to the ADRE equation (Eq. 8.35, p. 431)  
 - one-dimensional contaminant transport with transformation (Example 8.6)  
 --> used to estimate the time required for a relative contaminant concentration to reach a distance downgradient  
 - development of a contaminant profile in groundwater (Example 8.7)  
 --> used to estimate a contaminant conc. profile as a function of time at a set distance (or as a function of distance at a set time)

## 4.2. Contaminant Transport in the Vadose Zone

- a) vadose zone  
 - may be less than a meter to hundreds of meters deep  
 - higher organic matter, more metal oxides, more microbial activity  
 b) contaminants can move in the vadose zone  
 - as a solute in the water phase  
 - as a separate, immiscible NAPL phase  
 - as a gas resulting from volatilization  
 c) percolation rate  
 - increases as a function of porosity  
 - ranges from cm/h to cm/yr (*recall infiltration rate!!!*)

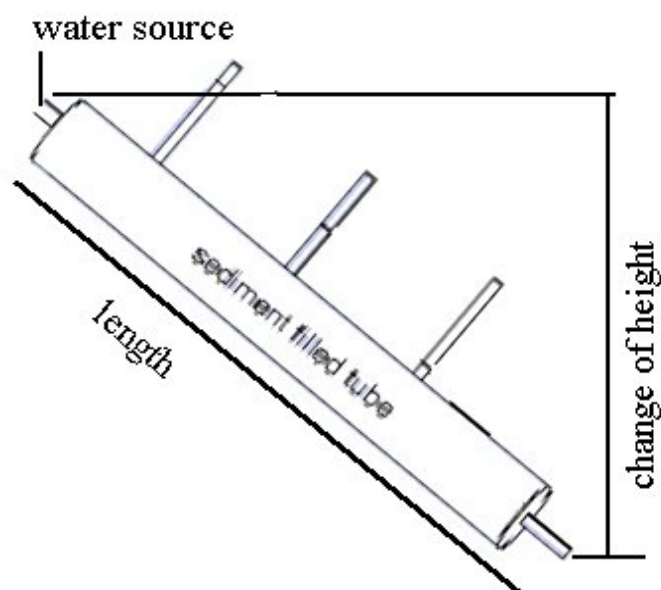
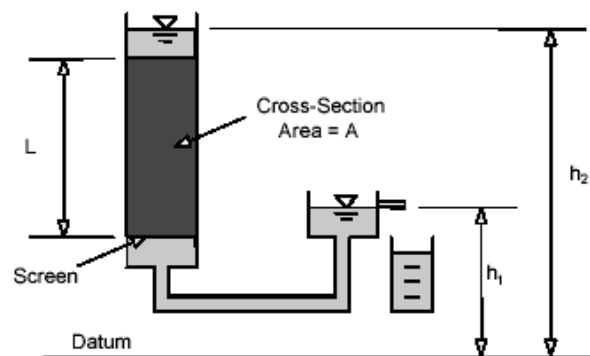
## ▣ Darcy's Law – Darcy experiment

### 1. Darcy Experiment

Darcy, 17th century Paris:

Darcy measured the discharge of a tube by measuring the volume of water that flows out the outlet during a fixed period of time (e.g., 1 minute) (discharge in terms of the milliliters per minute (a liter is  $10^{-3}$  m<sup>3</sup> and a ml is  $10^{-6}$  m<sup>3</sup>)). The discharge is usually expressed in units of m<sup>3</sup>/sec.

His experiments were meant to investigate the fundamental controls on ground water flow. It uses a "Darcy tube", a tube that is packed with sediment through which water can flow.



Water flows from an elevated reservoir into the inlet of the tube, through the sediment and then out the outlet of the Darcy tube. Can vary the drop in hydraulic head that occurs across the tube by changing the elevation of inlet reservoir.

Darcy related the discharge (Q) to the hydraulic gradient (head drop/distance), cross-sectional area (A) of the tube and to a property of the sediment that he referred to as the hydraulic conductivity (K).

## 2. Quantitative Expression

1) Discharge proportional to properties of material and pressure head (gradient),

$$Q \propto \frac{A \cdot P}{l}$$

A = cross sectional area

P = pressure

l = path length

if k (proportionality constant; hydraulic conductivity) is included,

$$Q = k \cdot \left( \frac{A \cdot P}{l} \right)$$

P can be expressed as difference in elevation (i.e., elevation or pressure head) between the start of flow length  $h_1$  and end  $h_2$ , or in the field, as the change in elevation of saturated zone.

$$Q = k \cdot \left( \frac{A \cdot (h_1 - h_2)}{l} \right)$$

$(h_1 - h_2)/l$  = the hydraulic gradient

2) Units

$$\frac{L^3}{T} = k \cdot L^2 \frac{(L - L)}{L} = k \cdot L^2$$

therefore, the unit of k should be L/T ( e.g., cm/sec)

## 3. Permeability

1) ability of water to flow through soil/sediment/rock.

2) controlled by:

a) porosity

b) grain size

c) interconnection of the pores



- sand/gravel: high permeability- high porosity, good interconnection of pores (  $k = 0.1 - 1000$ 's m/day)
- clay: very low permeability- high porosity, moderate interconnection of the pores, very small pore size (  $k = <0.01$  m/day)
- sedimentary rocks: high to very low permeability- high to very low porosity, good to poor int erconnection of the pores
- sandstone (  $k = 0.3-3$  m/day)
- shale (  $k = <0.01$  m/day)
- crystalline rocks: moderate to very low permeability- usually low porosity, often good interconnection of fractures (  $k= 0.0003-3$  m/day)

### 3. Hydraulic conductivity

1) an indication of an aquifer's ability to transmit water

$$2) k = k_{\text{intrinsic}} \cdot \left( \frac{\rho \cdot g}{\mu} \right)$$

$k$ ; hydraulic conductivity (m/day, cm/sec)

$k_{\text{intrinsic}}$ ; intrinsic permeability ( $\text{m}^2$ , darcy; 1 darcy =  $0.987 \text{ m}^2$ )

$\rho$ ; fluid density

$g$ ; gravitational constant

$\mu$ ; dynamic viscosity

$k$  depends on the medium and fluid properties (ground water hydrology).

(e.g.) sand  $10^{-2}$  cm/sec

silt  $10^{-4}$  cm/sec

clay  $10^{-7}$  cm/sec

$k_{\text{intrinsic}}$  is a function of the medium only, independent of fluid property (petroleum industry).

**\* transmissivity ( $\text{m}^2/\text{day}$ );  $k \cdot$  (saturated thickness of aquifer)**

### 4. Specific velocity (Darcy velocity)

1) average velocity of flow across a cross-section of an aquifer

$$v = Q/A$$

2) Now, we can express Darcy's Law as velocity and in differential form

$$\frac{Q}{A} = v_d = k \cdot \left( \frac{dh}{dl} \right)$$

$v_d$  = Darcy velocity (Darcy flux)

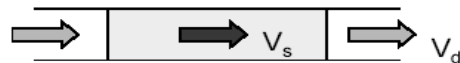
3) This  $v$  is for macroscopic scale – it represents the combination of all the impossible to measure individual velocities through the porous media. It is a **"macroscopically averaged description of microscopic processes"**.

\* specific velocity = specific discharge = Darcy velocity = Darcy flux = discharge velocity

## 5. Seepage velocity

1) Actual average velocity of water particles

$v_d$  = "discharge velocity" or "Darcian velocity"



$v_s$  = "seepage velocity"

Actual velocity is higher because the water flows a longer path through the soil particles.



"Tortuosity" is a measure of the distance traveled vs. linear distance.

$$v_s = \frac{v_d}{n} \text{ (seepage velocity = } \frac{\text{Darcy velocity}}{\text{porosity}} \text{)}$$

and

$$v_s = \frac{k}{n} \cdot \frac{dh}{dl}$$

2) Porosity ranges from 0 to <100% therefore, seepage velocity is always higher than Darcy velocity (by a factor of 3 or 4)

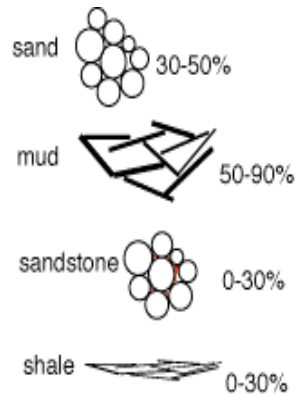
**6. Porosity:** % open space/void in a rock or sediment

a) sand/gravel: voids between grains. 30–50% porosity

b) clay: voids between sheets of clay. Charges on the clay particles produce a house of cards like structure. 50–90% porosity (often very high)

c) sedimentary rocks: sandstone is like sand except that the pores are

partially filled with mineral cement. 0–30% porosity



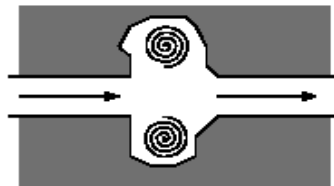
d) shale is like mud except that compaction has closed many of the pores.

0–30% porosity (often very low)

e) crystalline rocks: fracture porosity. 0–30% porosity (often very low)

## 7. Effective porosity ( $n_e$ )

1) Not all pores in porous media conduct flow. Some are clogged (i.e, dead-end pores)



$$n_e = \lambda n$$

$\lambda$  is effective porosity factor (determined experimentally);

$\approx 1$  for sands and gravels

$\approx 0.01$  to  $0.5$  for clays

2) Seepage velocity ( $v_s = \frac{k}{n} \cdot \frac{dh}{dl}$ ) is more appropriate if  $n$  is substituted with  $n_e$

$$v_s = \frac{k}{n_e} \cdot \frac{dh}{dl}$$

## 8. Darcy's law applies to laminar flow in porous media

1) "Reynolds number ( $Re$ )" as the boundary between laminar and turbulent flow

$$Re = \frac{vD\rho}{\mu}$$

$v$ ; Darcy velocity

$D$ ; mean particle size

$\rho$ ; mass density of water ( $1.94 \text{ lb-sec}^2/\text{ft}^4$ )

$\mu$ : dynamic viscosity of water ( $2.35 \times 10^{-5}$  lb-sec/ft<sup>2</sup>)

- 2) In natural conditions (aquifers), it is known that the boundary occurs at  $Re < 1$  to  $10$
- 3) In most cases, ground water travels at slow enough velocity for Darcy's law to be valid (i.e., true laminar flow)
- 4) Groundwater contamination migrates with the water. The rate and direction is controlled by Darcy's law.