Groundwater hydraulics

9

Contaminants

Types of Contaminants

- The list of potential contaminants number in **the tens of thousands** and organization of this list is a major problem.
- **Six major categories**: (1) **radionuclides** (2) **trace metals** (3) **nutrients** (4) **other inorganics** (5) **organics** and (6) **biological**.
- *All the contaminants have the potential to produce health problems*. Too much of anything is a potential health hazard but tolerable **thresholds are finite**.
- For some contaminants, particularly radionuclides, the threshold level is such that **anything above natural background is of concern.**

Contamination Attributes

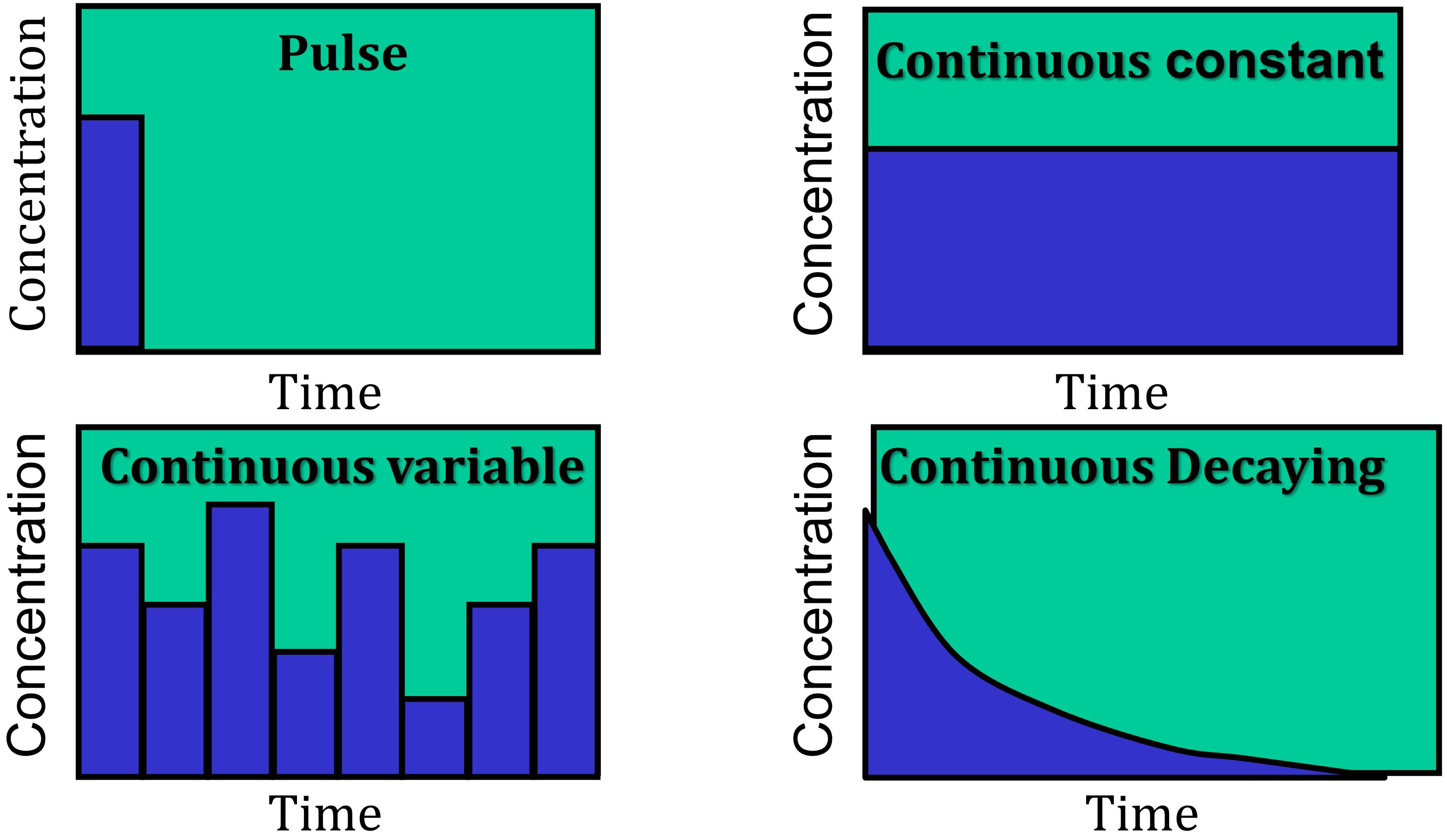
- **Three important attributes distinguish sources of groundwater contamination:**
  - **degree of localization**
    - point or local
    - non-point or diffuse
  - **loading history**
    - pulse
    - continuous
  - **contaminant type**
    - radionuclides
    - trace metals
    - nutrients
    - other inorganics
    - organics
    - biological

Degree of Localization of Source

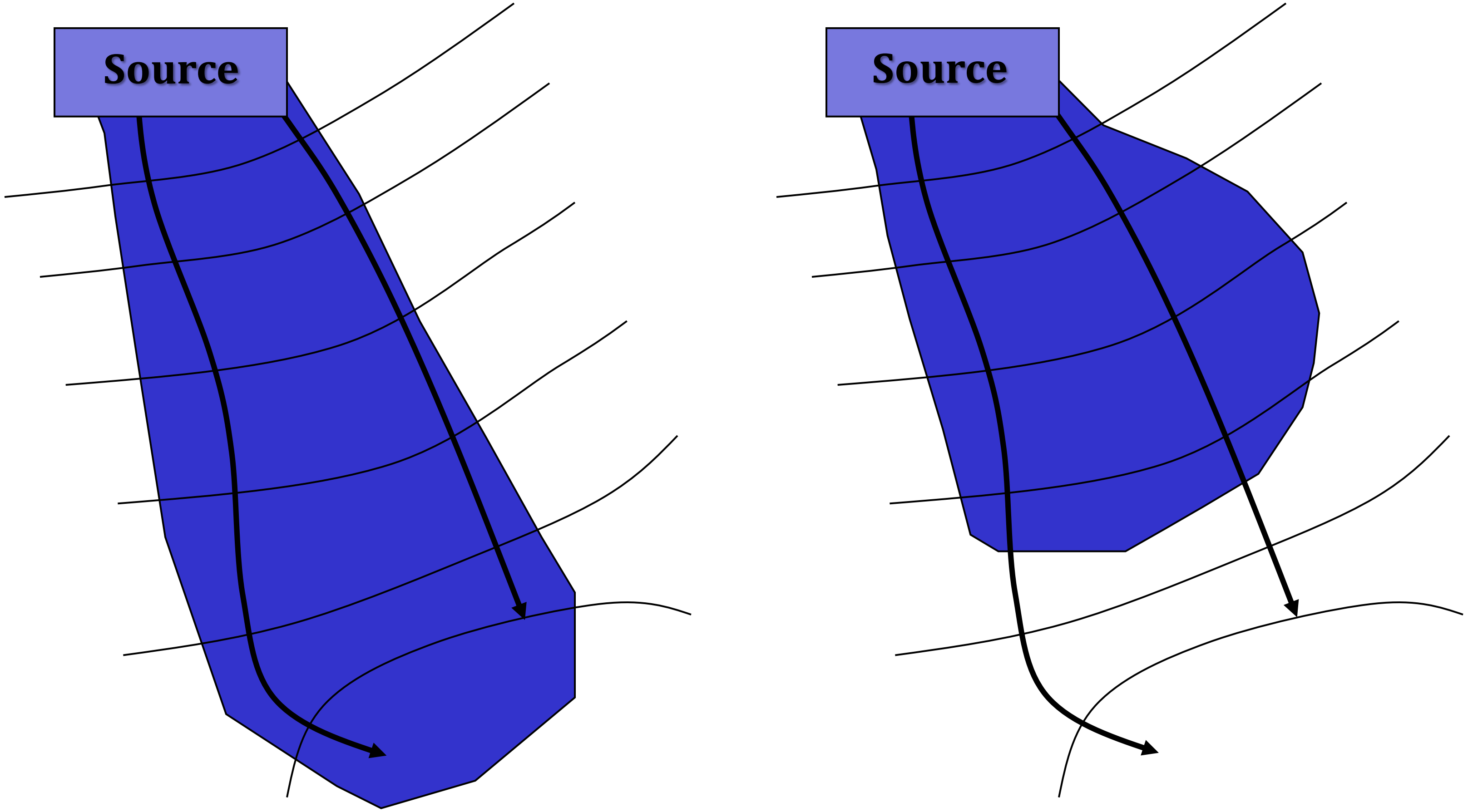
- **Point source** is characterized by the presence of an identifiable small-scale source such as **leaking tank**, **spill**, a **small pond** or **landfill**.
- **Diffuse source (non-points)** refers to a source emanating from many poorly defined locations. **Pesticides, fertilizers, acid rain** and **highway salt** are typical non-point diffuse sources.

Loading History

- Loading history describes how the source concentration varies as a function of time.



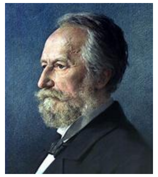
Predicting contaminant movement



Same "average" flow field, but different contaminant distribution.
What are the likely causes?
Understand principles of solute transport / average flow field not sufficient

LINEAR TRANSPORT LAWS

- **Fick's law** – **mass** is transferred from a region of higher concentration to a region of lower concentration



Adolf Eugen Fick
1829-1901

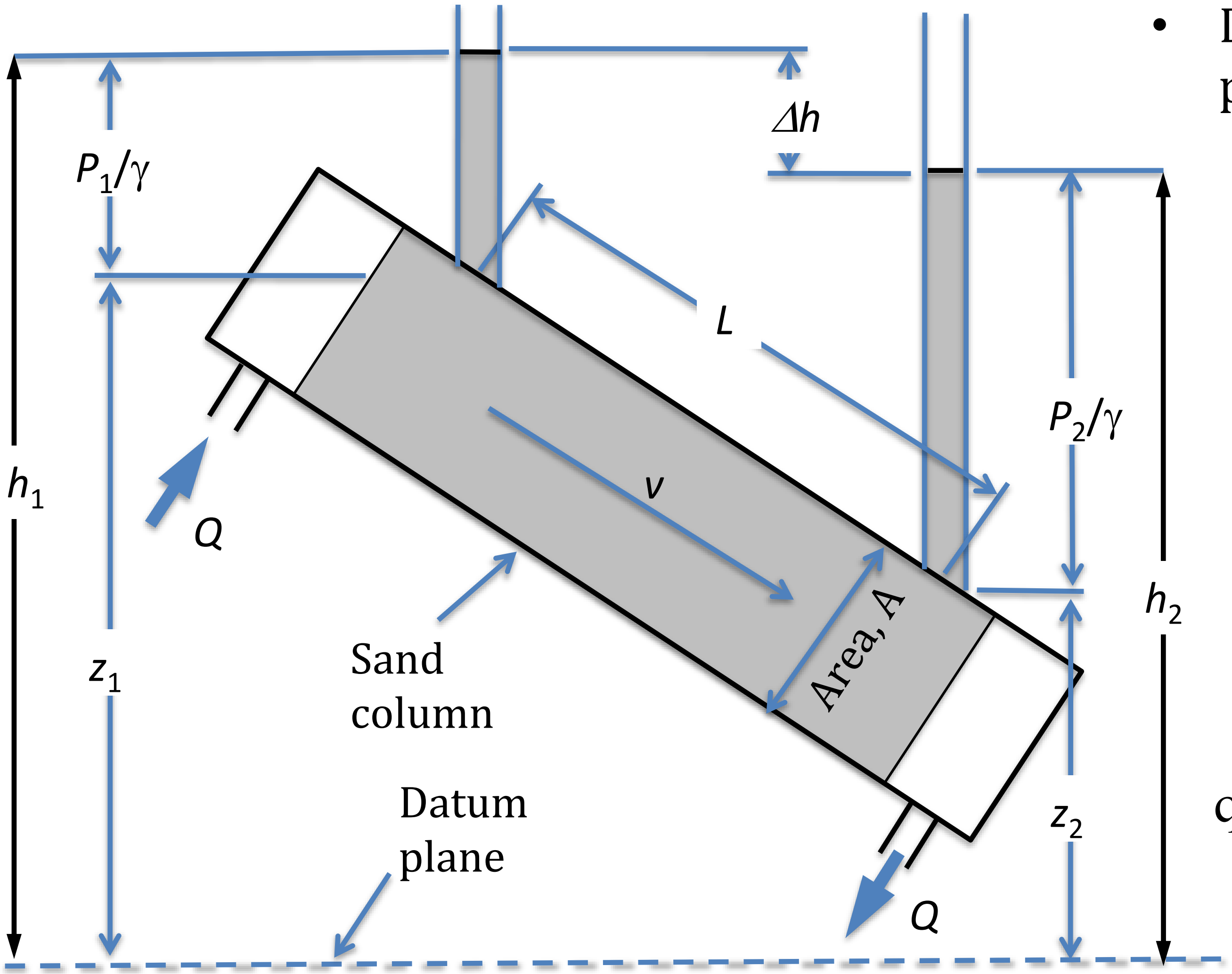
$$J = -DA\frac{dC}{dx}$$

- **Darcy´s law** – „transport of water“ through porous medium

Henry Darcy
1803 - 1858

$$J = -K.A\ C\ \frac{dh}{dx}$$

DARCY'S EXPERIMENT



- Flow through sand filters
- Discharge (Q) proportional to
  - Area, A
  - Head drop, h_1-h_2
  - Inverse of length, L

$$Q = K.A\frac{h_1 - h_2}{L}$$

$$\Delta h = h_2 - h_1$$

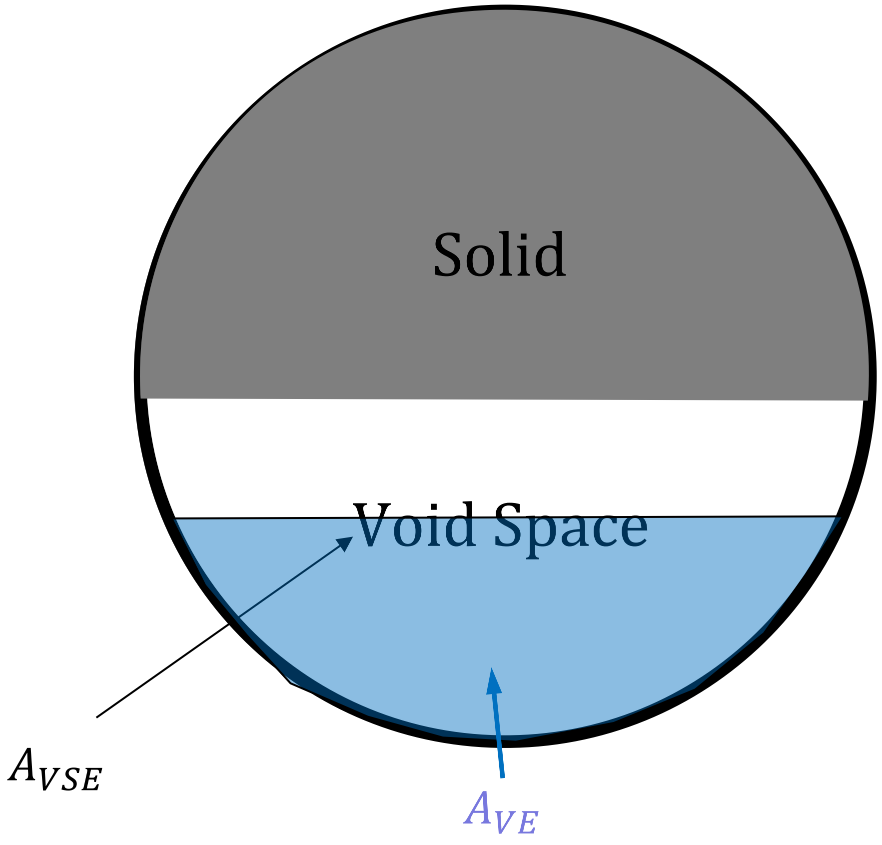
$$q = v = \frac{Q}{A} = -K\frac{\Delta h}{L}$$

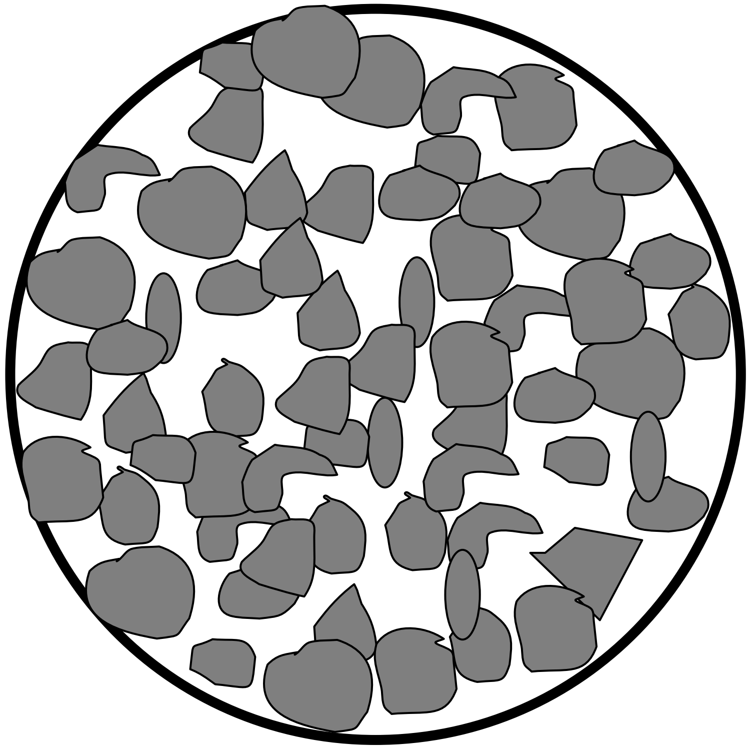
VELOCITY THROUGH POROUS MEDIUM

Darcy velocity:
v =Q/A

Porous Medium

$$n_e = \frac{V_t}{V_{EFF}}$$





$$v_R = \frac{Q}{A_{VE}}$$ (real velocity)

$A_{VSE} - area\ of\ all\ pores$

$A_{VE} - area\ of\ effective\ pores$

DARCY & „REAL“ VELOCITY

- From the Continuity eq. (steady flow):

$$Q = A\,v_D = A_{VE}\,v_R$$

– where:

Q = flow rate

A = total cross-sectional area of material

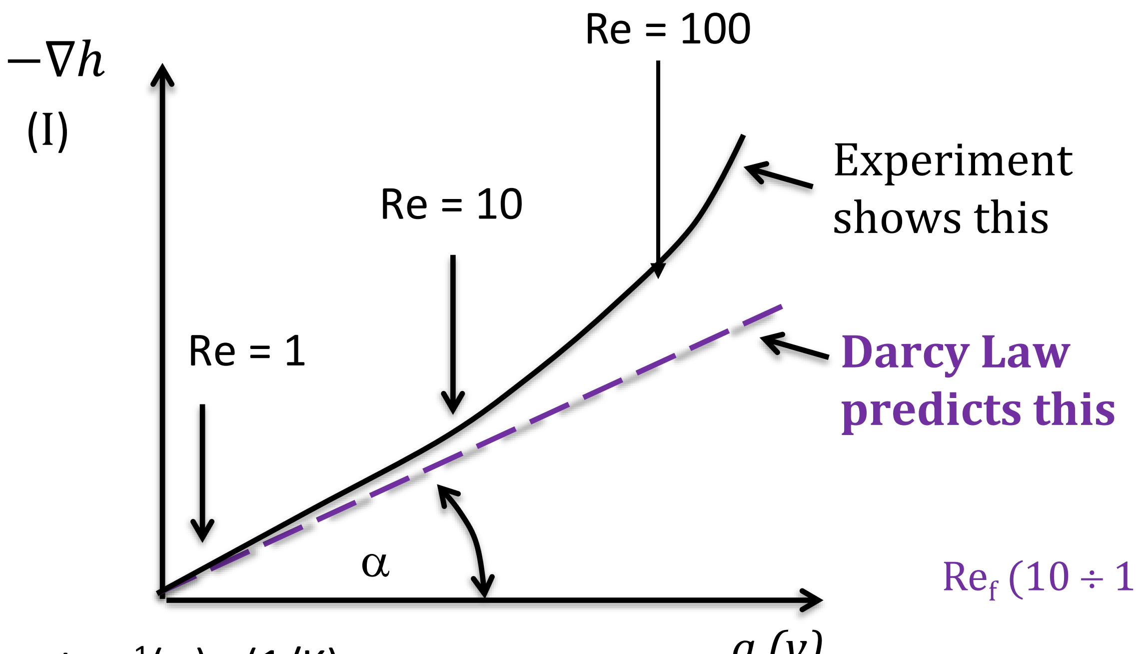
A_{VE} = area of effective voids

v_R = real velocity

v_D = Darcy´s velocity

$$v_R = v_D \frac{A}{A_{VE}} \quad \ldots\ldots\ldots. \quad \rightarrow \quad v_D = n_{ef}\,v_R$$

VALIDITY OF DARCY'S LAW



$\tan^{-1}(\alpha) = (1/K)$

$Re_f\,(0 \div 1)$ – Darcy eq. is valid

$$v = -K\,I \quad \Rightarrow \quad I = av$$

kde $a = 1/K$

$Re_f\,(1 \div 10)$ Darcy eq. is also valid

$Re_f\,(10 \div 100)$ -Nondarcian flow (Darcy eq. is not valid)

$$I = av + b.\,v^m$$

where **m** $= 1{,}6 \div 2{,}0$

$Re_f > 100$ turbulent flow (Darcy eq. is not valid)

$$I = b\,v^2$$

Contaminant transport in groundwater

- In order to assess risk to
  - current groundwater environment
  - groundwater user (health and economic)
  - ecosystem at discharge (environment)
  - future groundwater resources
- We need to
  - understand how solutes move in groundwater
  - identify solute transport pathways
  - predict travel times and when contaminants arrive

Why do some contaminant plumes behave differently from others?

- Some contaminants move at the same rate as groundwater, some move more slowly than groundwater

TRANSPORT PROCESSES

What controls the transport of contaminants?

There are three basic physical mechanism, by which contaminants are transported in porous media:

1) **Advection**
2) Diffusion
3) Mechanical dispersion

2) + 3) → **Hydrodynamic dispersion**

We'll start with those that move at the same rate: **advection**

- **ADVECTION**
  - Contaminants moves at **average linear velocity** (v_{avg}) of groundwater
  - all solute arrives at the same point at the same time
  - we can calculate the **advective front** from: $\mathbf{v_{avg} = -K\nabla h/n_e}$

Darcy velocity

- **Advection** is mass transport due simply to the flow of the water in which the mass is carried.
- The direction and rate of transport coincide with that of the groundwater flow.

The one-dimensional flux of solute through a porous medium can be expressed:

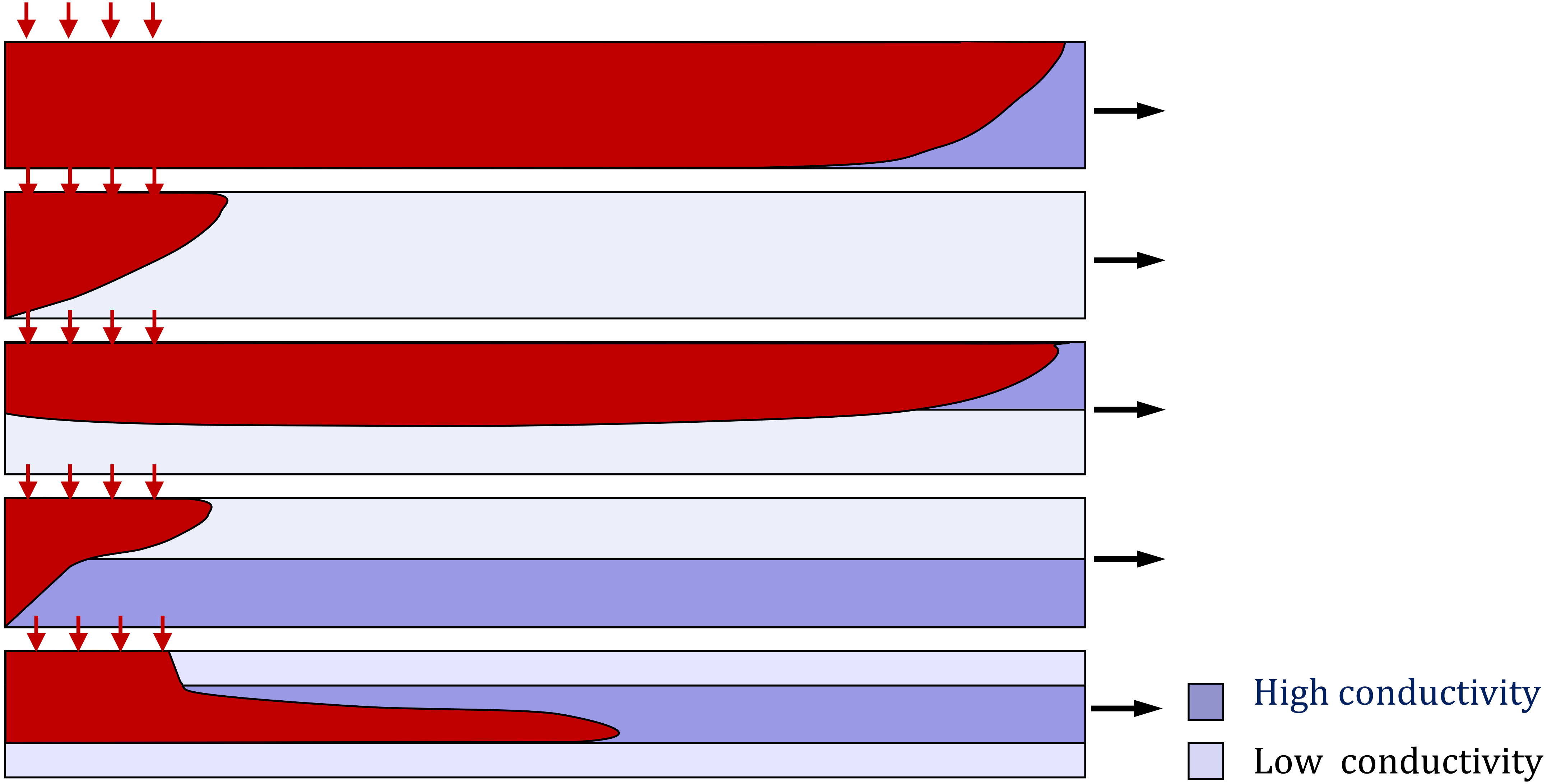
$$J = v_x . c . n_e$$

Where: J= mass flux per unit area per unit time; v_x– average linear groundwater velocity in the direction of flow; C- concentration in mass per unit volume of solution; n_e- effective porosity of the porous medium

CONTROLS ON ADVECTION

- **Magnitude and direction of advective transport is controlled by**:
  - **hydraulic conductivity** field
  - **potentiometric head distribution**
  - distribution of sources and sinks
  - **shape of the flow domain**
- All these factors influence groundwater flow velocity, which drives advective transport.

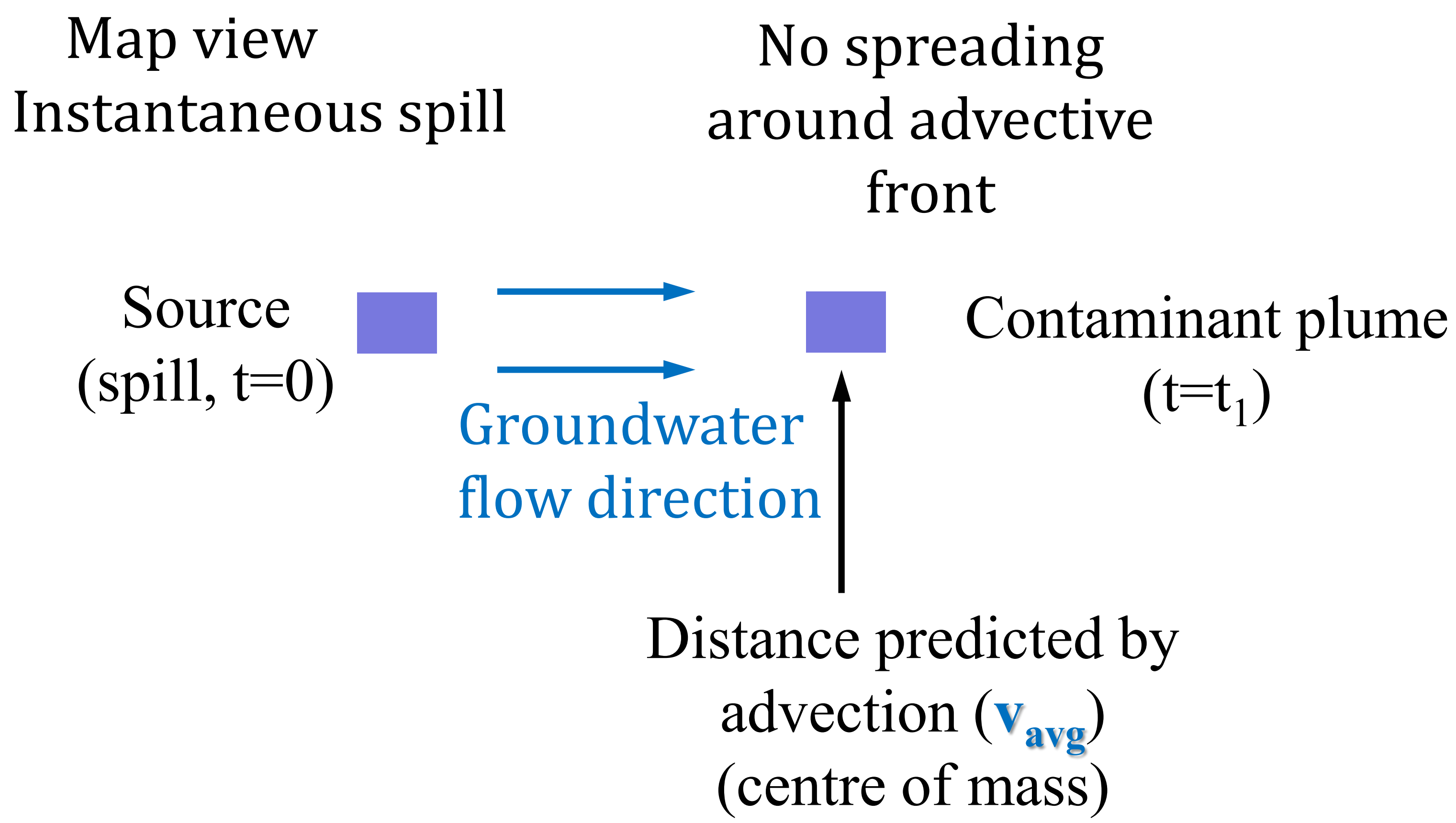
Hydraulic Conductivity Field



Hydraulic Conductivity

- **Plume advects faster** with **increasing K**.
- Plume migrates in highest K horizon
- **Low K near** Development
- Plumes tend **not to invade low K units**.

Advective front contaminant plume transport



v_{avg} is the <u>average velocity</u> over the time that the plume took to develop
If the flow field is at steady state, then v_{avg} is easy to calculate

Hydrodynamic dispersion (D_x, D_h)

- Hydrodynamic dispersion causes all solutes in groundwater to spread as they move through an aquifer
- Spreading is due to 2 processes
  - Mechanical dispersion ($D_m = \alpha v_l$)
  - Molecular diffusion (D^*)

$$D_h = \alpha v_l + D^*$$

where α is a property of the porous medium, called *dispersivity (m)*

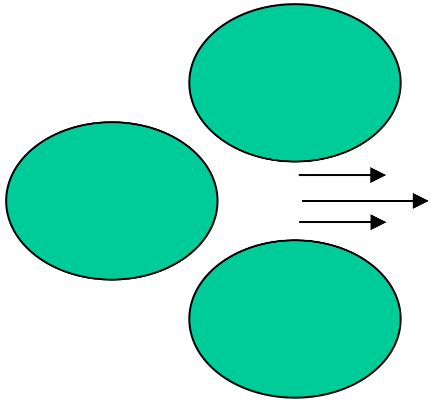
Dispersion

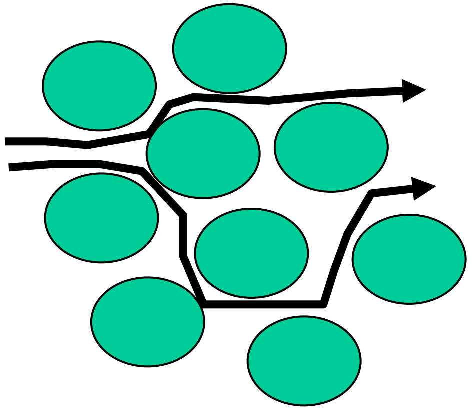
- Increased dispersion gives broader plume.
- Concentration pattern is spread and high concentration zone is reduced with increasing dispersivity.
- Increasing α_T results in increased vertical spreading.
- High α_L and high α_T gives most mixing.

Mechanical Dispersion

- Spreading occurs in all porous media due to processes that occur at different scales

1) Pore throat velocity variations





2) Path length variations

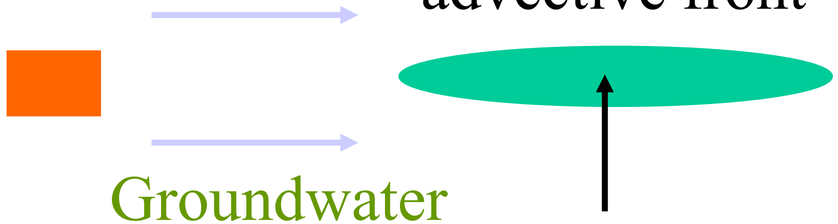
Dispersion

- In the real world even plumes of conservative solutes are dispersed
  - the plumes don’t have sharp boundaries

- Instead the solutes are spread ahead and behind the advective front
  - grade gradually into the background concentration in the aquifer
    - along sides
    - at leading edge/front of plume
    - at rear of plume (if a discrete spill)
  - this is referred to hydrodynamic dispersion

Dispersed Plume – lower concentrations

Map view
Instantaneous spill



v_{avg} is the average velocity over the time that the plume took to develop
If the flow field is at steady state, then v_{avg} will indicate centre of plume for a conservative solute

Mechanical Dispersion (D_m)

- Mechanical Dispersion -D_m
  - produces spreading in ALL porous material
    - even in homogeneous glass beads

- some solute migrates faster than v_{avg}
  - spread ahead of centre of mass
- some migrates slower than v_{avg}
  - spread behind centre of mass

- Why??

Dispersion Coefficient

- The hydrodynamic dispersion coefficient (D) is a combination of mechanical dispersion (D') and bulk diffusion (D'_d):

$$D = D' + D'_d$$

- The advective flow velocity (v) and mean grain diameter (d_m) have been shown to be the main controls on longitudinal dispersion (D_L) parallel to the flow direction.
- Transverse dispersion (D_T) also takes place normal to the flow direction.

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Peclet Number

- D/D_d is a convenient ratio that normalizes dispersion coefficients by dividing by the diffusion coefficient.
- $V.d_m /D_d$ is called the **Peclet Number** (N_{PE}) a dimensionless number that expresses the advective to diffusive transport ratio.

Transport Regimes

- For $N_{PE} < 0.02$

  diffusion dominates
- For $0.02 > N_{PE} < 8$

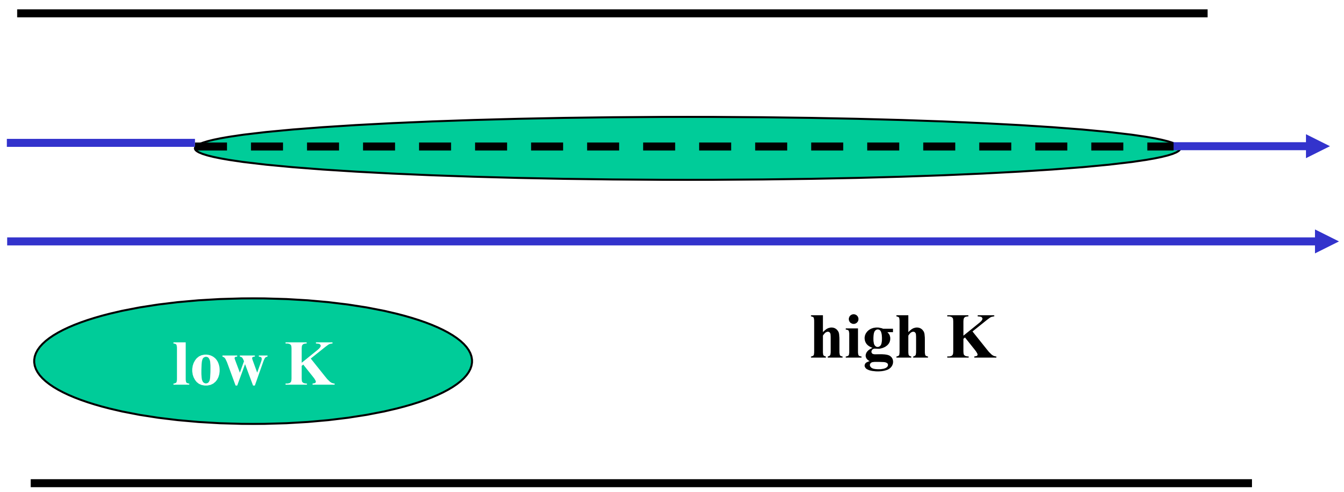
  diffusion and mechanical dispersion
- For $N_{PE} > 8$

  mechanical dispersion dominates

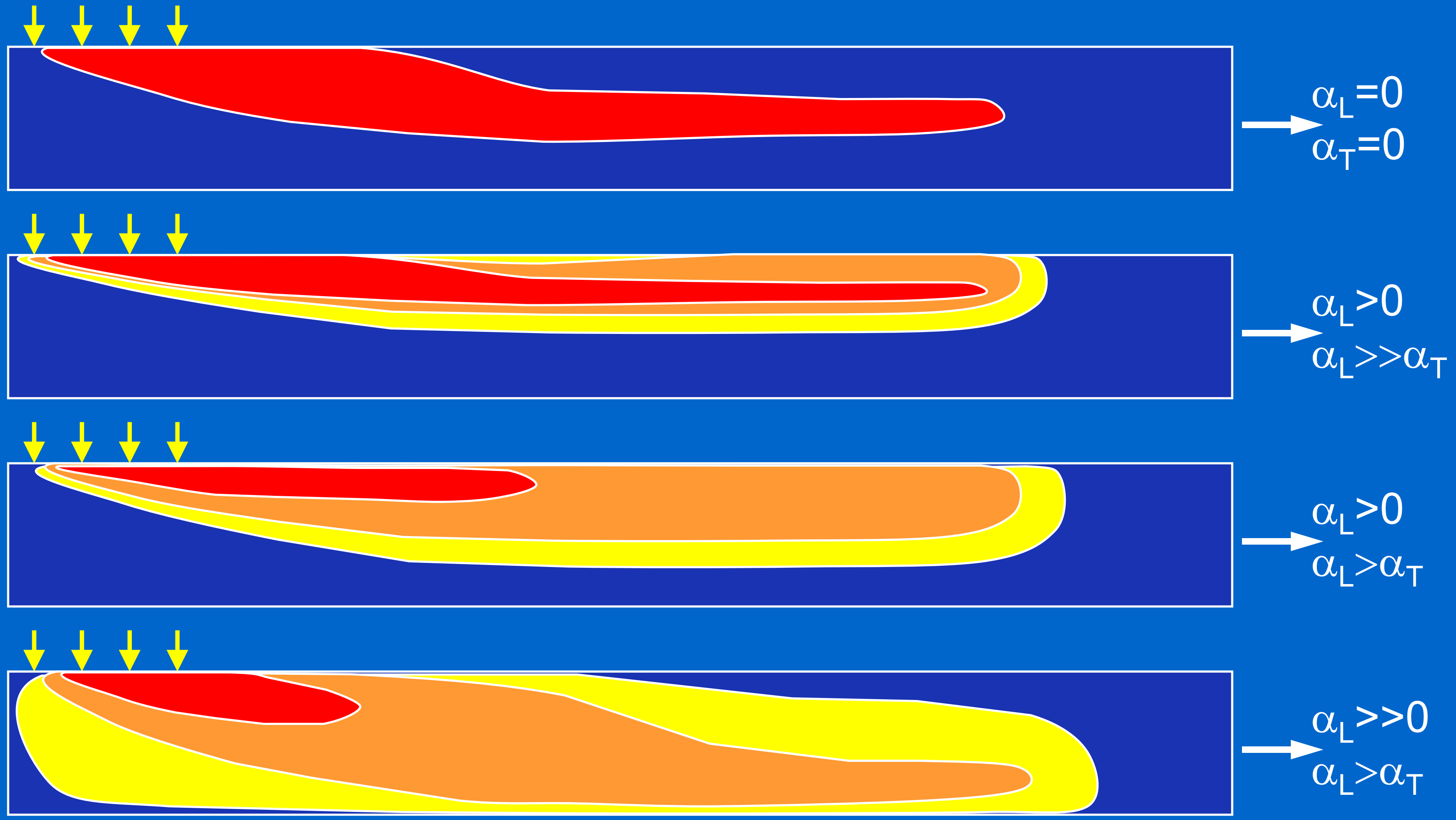
Some authors place the boundaries at 0.01 and 4 rather than 0.02 and 8

3) Field scale heterogeneity

eg. sand aquifer with clay lenses



Dispersion



α_L=0
α_T=0
α_L>0
α_L>>α_T
α_L>0
α_L>α_T
α_L>>0
α_L>α_T

Molecular Diffusion

Solutes can also be spread as a result of chemical gradients (molecular diffusion)

- effects of diffusion are most often seen in low K material (aquitards)
  - clays, shales etc
- effects are negligible in high K aquifers
  - overwhelmed by mechanical dispersion
- driven by concentration gradient (dC/dx)
  - so spreading occurs even when hydraulic gradient (dh/dl) is 0
- porosity dependent
  - higher porosity increase the mass diffused for the same concentration gradient

Diffusion Law

- Darcy’s law for relates fluid flux to hydraulic gradient:

  q = -K.grad(h)

- For mass transport, there is a similar law (**Fick’s law**) relating solute flux to concentration gradient in a pure liquid:

  $J = -D_d.\mathrm{grad}(C)$

  where J is the chemical mass flux [moles. $L^{-2}T^{-1}$]

  C is concentration [moles.L^{-3}]

  D_d is the diffusion coefficient [L^2T^{-1}]

Diffusion

- **Diffusion** is the process of mixing that occurs as a result of concentration gradients in porous media.
- Diffusion can occur when there is no hydraulic gradient driving flow and the pore water is static.
- Diffusion in groundwater systems is a very slow process.

Summary of controls

- Advection
  - all solute arrives at the same time
  - v_{avg} controls rate of transport and arrival time
- Dispersion
  - this is what we see in the real world
  - spreads solute around advective front
    - mainly parallel to flow direction
  - mechanical dispersion + molecular diffusion
    - diffusion primarily only in aquitards
  - affects all solutes – even conservative solutes

Advection-dispersion (A-D) equation

- this is the equation used to describe/model transport of solutes in groundwater
- Simplest case
  - 1-dimensional, non-reactive solute

$$D_x \frac{\partial^2 C}{\partial x^2} - v_{x_{avg}} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

dispersive transport

advective transport

change in concentration with time

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Fate and transport of solute affected by

- Sorption
  - solute is delayed compared to v_{avg}
  - long or short term delay
- Dissolution/Precipitation
  - solute enters or leaves groundwater
- Biodegradation
  - compound degrades producing daughter products (new components in plume)
- Radioactive decay
  - radioactive decay produces daughter elements (new components in plume)
- volatilisation, chemical degradation etc.
  - remove or change solute in solution

Plume characteristics

Different from conservative solute plume

- Different transport rates
  - plumes for different solutes will separate
  - eg when one component is delayed and one is not
- Mass lost from original contaminant plume
  - total mass in plume declines due to biodegradation, decay, precipitation etc.
- New plumes form made of new contaminants
  - these are daughter products of the degradation or decay process

Leads to a sequence of different, but related plumes

Diffusion

- **Diffusion** is the process of mixing that occurs as a result of concentration gradients in porous media.
- Diffusion can occur when there is no hydraulic gradient driving flow and the pore water is static.
- Diffusion in groundwater systems is a very slow process.

Dispersion

- **Dispersion** is the process of mechanical mixing that takes place in porous media as a result of the movement of fluids through the pore space.
- **Hydrodynamic dispersion** is a term used to include both diffusion and dispersion.

Peclet Number

- D/D_d is a convenient ratio that normalizes dispersion coefficients by dividing by the diffusion coefficient.
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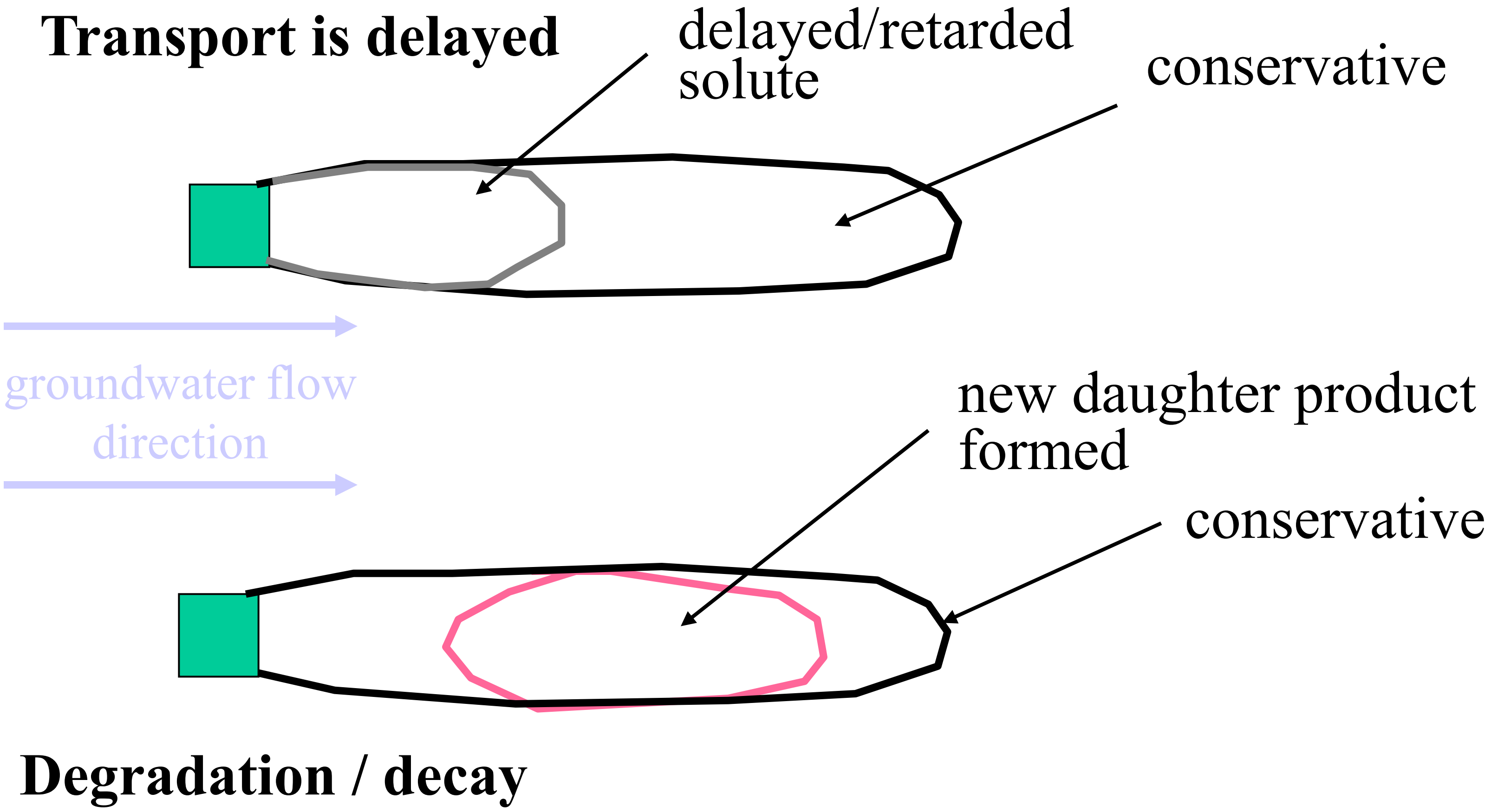
Reactive plumes



Retardation

- Describes processes that delay arrival of a contaminant (eg sorption)
  - delays arrival time compared to conservative contaminant
    - solute is NOT removed from system (eg sits on aquifer matrix)
  - eventually all contaminant arrives
    - time frame for delay can vary from days to 100,000 years

- Retardation Factor (R)

$$R = 1 + \rho_b/n\ K_d \quad \text{(Freeze \& Cherry 1979)}$$

K_d = distribution coefficient

ρ_b = bulk density = ρ_s (1-n)

Distribution Coefficient (K_d)

- describes the distribution of a contaminant between the water and the soil or sediment
  - provides an idea of the extent of retardation
- Depends on
  - soil mineralogy
  - contaminant concentration
  - solution composition, pH
- Determine values extent of retardation from
  - laboratory tests (measure K_d)
  - plume matching (estimate R to fit field data)

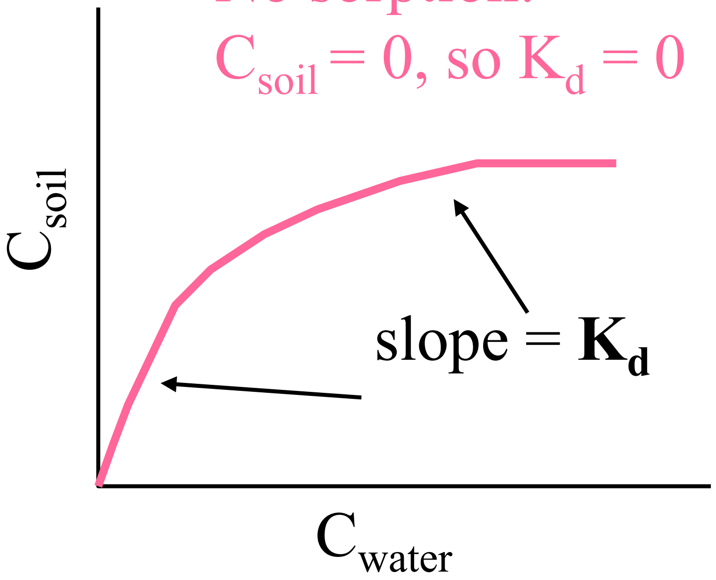
Sorption isotherms (K_d)

- Equilibrate solution with soil
  - over concentration range

$K_d = C_{soil} / C_{water}$

- Sorption isotherm
  - slope = K_d
  - condition specific
  - K_d may be constant or may vary
    - eg diagram

No sorption:
$C_{soil} = 0$, so $K_d = 0$



Retardation Factor vs K_d

$$R = 1 + \rho_b/n\ K_d$$

- $R = 1$, $K_d = 0$, no retardation
- $R > 1$, $K_d > 0$, solute slower than v_{avg}
  - assumes K_d linear
- range
  - $R = 1$ (conservative solute)
  - $R \sim 10^6$ (essentially immobile - soil contaminant)

Retardation effects

- Delays advective front of retarded solute (B)

source

groundwater flow direction

B
advection only
with retardation
$x_B = (v_x/R_B)t$

A
advection only
no retardation
$x_A = v_x t$

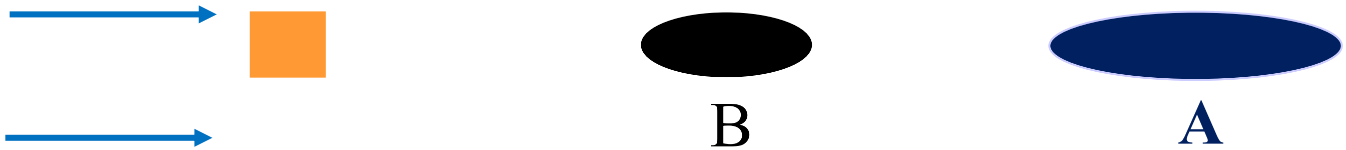
A is conservative solute

B is retarded, $R_B \sim 2$

Dispersion

- If t equal, dispersion of B (retarded) less than for A (unretarded)
  - less porous medium travelled through

source



groundwater flow direction

B

$x_B = (v_x/R_B)t$

D_x/R_B

A

$\mathbf{x_A = v_x t}$

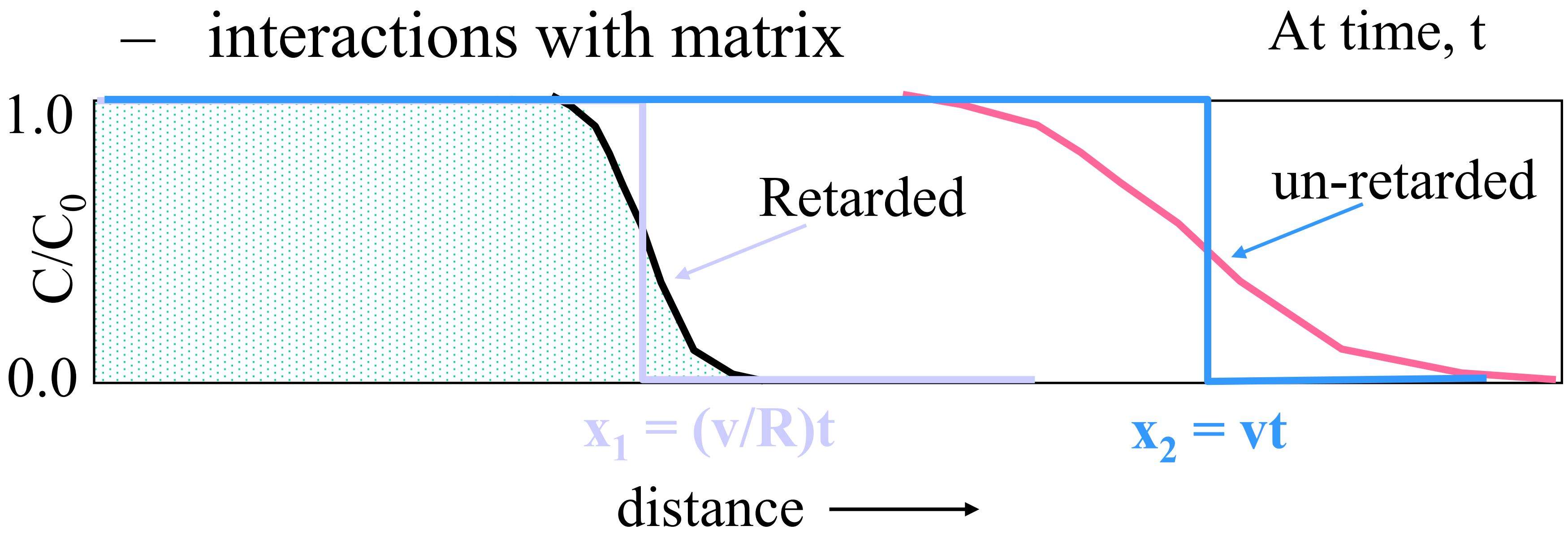
$\mathbf{D_x}$

A is conservative

B is retarded, $R_B \sim 2$

Breakthrough curves - retarded solutes

- Retarded solute
  - migrate less far ($v_{retarded} = v_{conserv}/R$)
  - be dispersed less ($D_{x\ (retarded)} = D_{x\ (conserv)}/R$)
  - interactions with matrix



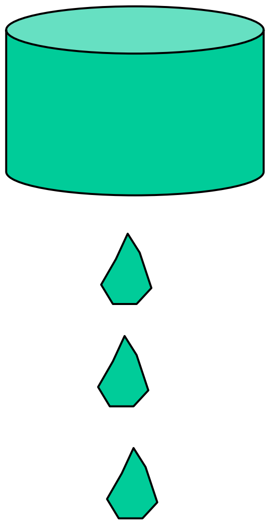
Assessing solute transport

- Breakthrough curves are a a useful tool in evaluating contaminant transport. They:
  - show solute concentration vs distance or time
  - indicate amount of spreading, delay or mass loss of the plume
  - can compare the migration of different solutes
    - one curve per solute
- To construct a breakthrough curve you need:
  - concentration (C_0) and duration of solute source
  - groundwater flow rate, flow field, and initial concentration in aquifer
    - most breakthrough curves assume a steady state flow field
  - an estimate of hydrodynamic dispersion (amount of spreading)
    - later on we will look at delay and mass loss

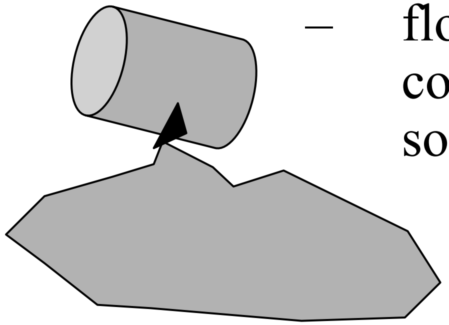
Source Characteristics

Affect configuration of plume

- Duration



continuous source



instantaneous source (eg spill)

- Concentration (C_0)
  - concentration constant if continuous source
  - flow system constant for continuous or instantaneous sources

Breakthrough Curves

Show the effects of advection & dispersion

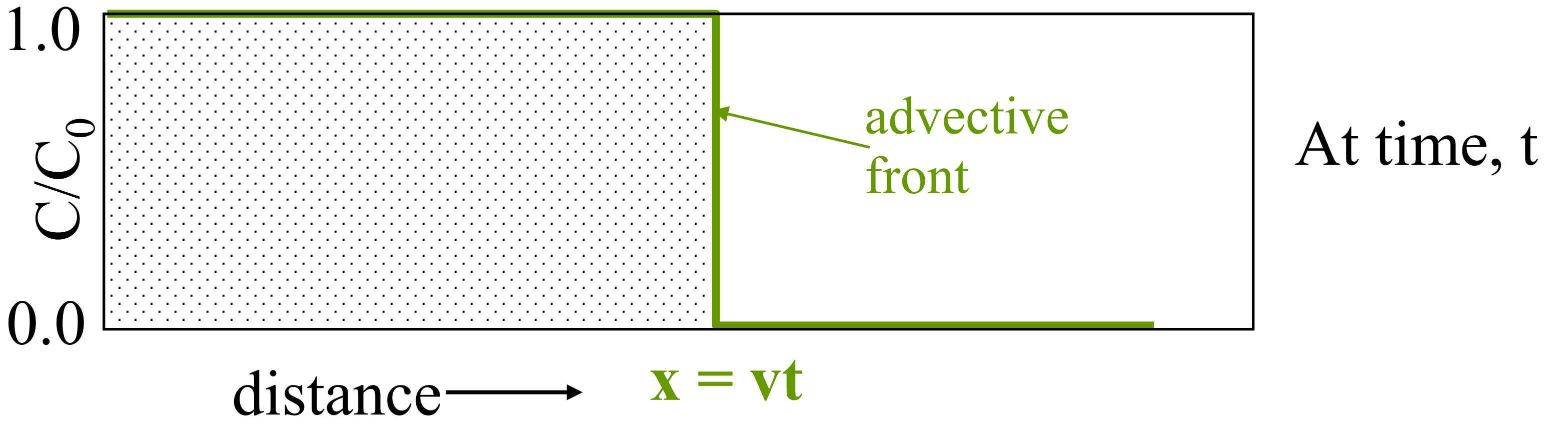
- combine with plume maps or cross sections to assess how contaminants have moved

- Solute concentration vs distance
  - for a given time
- Solute concentration vs time
  - for a given location

- normalised conc (C/C_0)
  - measured concentration is divided by initial concentration introduced at the source
- absolute conc (mg/L)
  - measured concentration

Breakthrough curves (vs distance) - 1

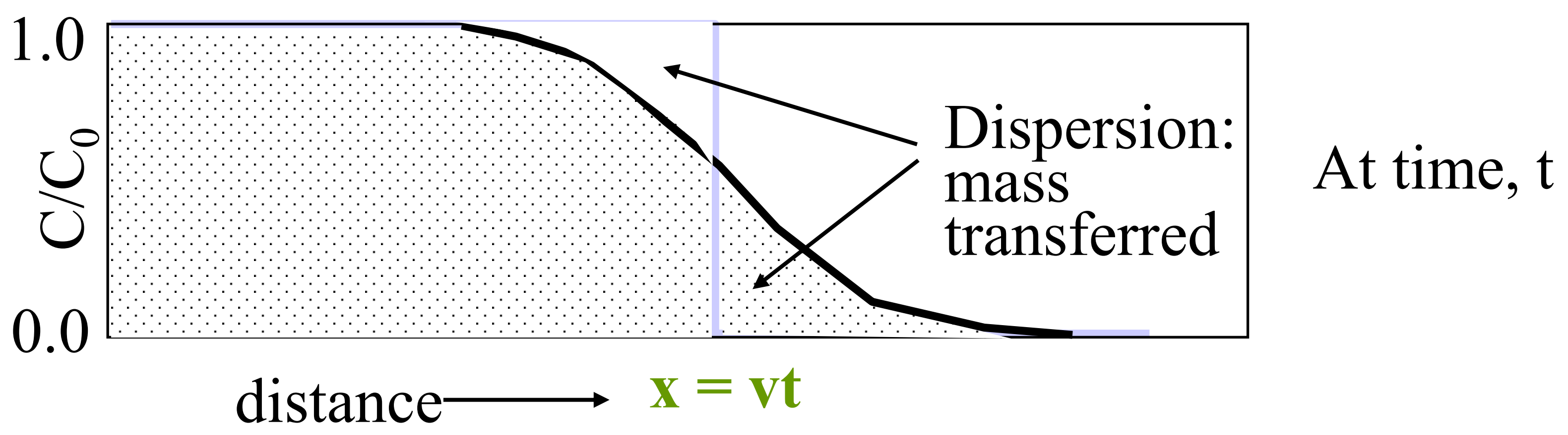
- Advection only, continuous source



- all solute arrives at time predicted by v_{avg}
- no spreading of the plume
  - not what we see in real situations

Breakthrough curves (vs distance) – 2

- Advection + dispersion, continuous source

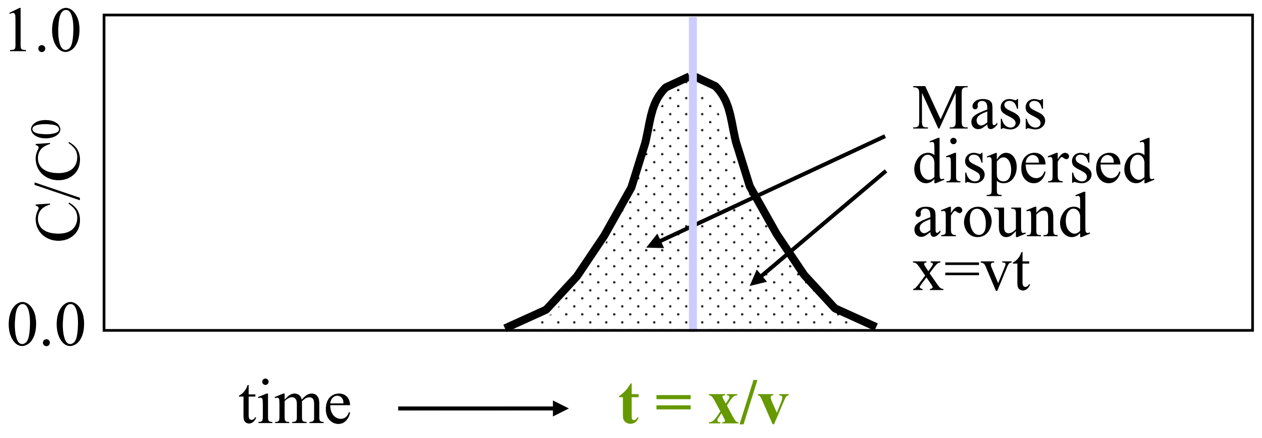


  - non-reactive tracer
  - constant C_0
  - homogeneous, isotropic

- spreading symmetric about $C/C_0 = 0.5$
  - more similar to what we see in real systems
- curve is reversed for C/C_0 vs time

Instantaneous Source (advection + dispersion)

- Breakthrough curve vs distance (or time)



At distance, x

- total mass constant
  - different aquifer volume taken up
- symmetric around advective front
  - homogeneous, isotropic, steady state