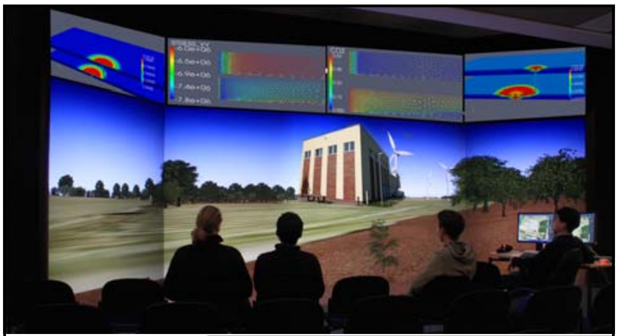

# Mass Transport Processes in Porous Media
## Part I - General Theory

Haibing Shao

24June 2011, TU Dresden, Lecture for Hydro-system Analysis
Hoersaalzentrum 403H, 11:30 – 12:40

HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

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## Outline

- Advection – Diff. / Disp. – Equation (ADE)
- Dispersion and Diffusion
- Sorption Isotherms and Decay



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## Advection – Dispersion/Diffusion – Equation (ADE)



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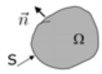
## Governing Equations

If you can only remember one equation, then the **Reynolds Transport Theorem**.

$$\frac{\partial}{\partial t}\int_{\Omega}\psi\, d\Omega = -\oint_{\partial\Omega}\mathbf{\Phi}^{\psi}\cdot d\mathbf{S} + \int_{\Omega} q^{\psi}\, d\Omega \qquad \textbf{(Eq. 0)}$$




Or, you can remember a story.

{Rate of accumulation for unknown Ψ within the volume Ω} = {Net influx of Ψ into the volume Ω through its surface S} + {Net rate of Ψ production within the volume Ω}



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## Governing Equations

Because of the **Gauss Divergence Theorem**.

$$\oint_{\partial\Omega}\Phi^{\psi}\cdot dS = \oint_{\Omega}\nabla\cdot\Phi^{\psi} d\Omega$$

So, our Eq. 0 becomes.

$$\frac{\partial}{\partial t}\int_{\Omega}\psi d\Omega = -\int_{\Omega}\nabla\cdot\Phi^{\psi}d\Omega + \int_{\Omega} q^{\psi}d\Omega \qquad \textbf{(Eq. 1)}$$



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## Advection Diff./Disp. Equation

If write Eq. 1 in derivative form,

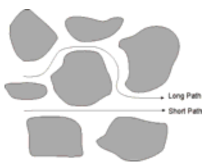
$$\frac{\partial\psi}{\partial t} = \nabla(\Phi) + Q$$

Source / Sink

Our primary unknown is Mass
$\psi = n_e C dA$

Our flux is composed of:
1) Advective flux
2) Diff./ Disp. flux

Advection ( Mass takes a free ride)




Flux of advection $F_{adv} = v_i n_e C dA$

Average Linear Velocity $v_x = -\frac{K}{n_e}\frac{dh}{dl}$

AKA, Pore Velocity $v_x = \frac{q}{n_e}$

Flux

Effective porosity

Velocity of a conservative tracer.

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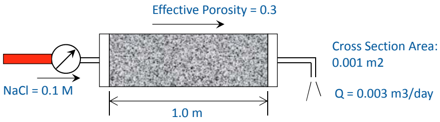
## Advection Diff./Disp. Equation

### Exercise 0.1:




If only considers advection, how far does the Cl- go? Please draw it.

Conc. over Space


Fixed at t = 1 day

Conc. over Time


Fixed location at outlet.



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## Dispersion and Diffusion



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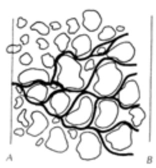
## Dispersion and Diffusion




Dispersion

Diff./ Disp. Flux ( Fick's 1st Law)

$$F_{dis/diff} = -D\frac{dC}{dx} \quad \text{1D}$$

$$F_{dis/diff} = -D\bigtriangledown(C) \quad \text{3D}$$

Think about:

Why negative sign?

Hydrodynamic Dispersion (Mechanical spreading)

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

$$D_T = \alpha_T v_i + D^*$$

Diffusion coefficient

Longitudinal / transverse dispersivity

Note: Dispersivity values are often scale dependent!

$$\alpha_L = 0.83(logL)^{2.414}$$

Xu and Eckstein (1995)

Xu and Eckstein (1995) Use of weighted least-squares method in evaluation of the relationship between dispersivity and field scale. Ground Water 33, no. 6: 905-08



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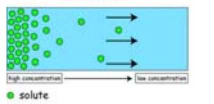
## Dispersion and Diffusion

Diffusion




Solute transport is from the left to the right: movement of the solutes is due to the concentration gradient (dC/dx).

Diffusion (Molecular spreading)

- It is orders magnitudes lower than dispersion effect.
- Need to be considered in no-flow conditions.
- Note: Temperature dependent.
- Use it with caution (e.g. charges in mineral structure)

Diffusion

Diffusion of ions in sea water and in deep-sea sediments 705

Table 1. Tracer and self-diffusion coefficients of ions at infinite dilution

| Cation | $D_i^0$ ($10^{-6}$ cm²/sec) 0°C | 18°C | 25°C | Anion | $D_i^0$ ($10^{-6}$ cm²/sec) 0°C | 18°C | 25°C |
|---|---|---|---|---|---|---|---|
| $H^+$ | 56·1 | 81·7 | 93·1 | $OH^-$ | 25·6 | 44·9 | 52·7 |
| $Li^+$ | 4·72 | 8·69 | 10·3 | $F^-$ | — | 12·1 | 14·6 |
| $Na^+$ | 6·27 | 11·3 | 13·3 | $Cl^-$ | 10·1 | 17·1 | 20·3 |
| $K^+$ | 9·86 | 16·7 | 19·6 | $Br^-$ | 10·5 | 17·6 | 20·1 |
| $Rb^+$ | 10·6 | 17·6 | 20·6 | $I^-$ | 10·3 | 17·2 | 20·0 |
| $Cs^+$ | 10·6 | 17·7 | 20·7 | $IO_3^-$ | 5·05 | 8·79 | 10·6 |
| $NH_4^+$ | 9·80 | 16·8 | 19·8 | $HS^-$ | 9·75 | 14·8 | 17·3 |
| $Ag^+$ | 8·50 | 14·0 | 16·6 | $S^{2-}$ | — | 6·95 | — |
| $Tl^+$ | 10·6 | 17·0 | 20·1 | $HSO_4^-$ | — | — | 13·3 |
| $Cu(OH)^+$ | — | — | 8·30 | $SO_4^{2-}$ | 5·00 | 8·90 | 10·7 |
| $Zn(OH)^+$ | — | — | 8·54 | $SeO_4^{2-}$ | 4·14 | 8·45 | 9·46 |
| $Be^{2+}$ | — | 3·64 | 5·85 | $NO_2^-$ | — | 15·3 | 19·1 |
| $Mg^{2+}$ | 3·56 | 5·94 | 7·05 | $NO_3^-$ | 9·78 | 16·1 | 19·0 |
| $Ca^{2+}$ | 3·73 | 6·73 | 7·93 | $HCO_3^-$ | — | — | 11·8 |
| $Sr^{2+}$ | 3·72 | 6·70 | 7·94 | $CO_3^{2-}$ | 4·39 | 7·80 | 9·55 |
| $Ba^{2+}$ | 4·04 | 7·13 | 8·48 | $H_2PO_4^-$ | — | 7·15 | 8·46 |
| $Ra^{2+}$ | 4·02 | 7·45 | 8·89 | $HPO_4^{2-}$ | — | — | 7·34 |

Li Yuan-Hui, Sandra Gregory (1974) Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta, Volume 38, Issue 5, 703-714*

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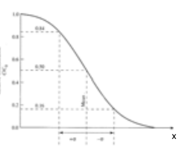
## Dispersion and Diffusion



Complementary Error function

Governing Equation with only dispersion / diffusion,

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

Analytical solution (Crank 1956)

$$C(x,t) = C_0\ erfc(\frac{x}{2\sqrt{Dt}})$$

$$erfc(B) = 1 - erf(B)$$

$$erf(B) = \frac{2}{\sqrt{\pi}}\int_0^B e^{-t^2}dt$$

Use a checking table,
Or in Excel and other soft., it is provided.

The Advection - Dispersion / Diffusion equation,

$$\frac{\partial C}{\partial t} + v_x\frac{\partial C}{\partial x} - D\frac{\partial^2 C}{\partial x^2} = Q$$

Analytical solution (Ogata 1970)

$$C(x,t) = \frac{C_0}{2}[\ erfc(\frac{L - v_x t}{2\sqrt{D_L t}}) + exp(\frac{v_x L}{D_L})erfc(\frac{L + v_x t}{2\sqrt{D_L t}})]$$

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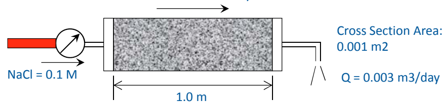
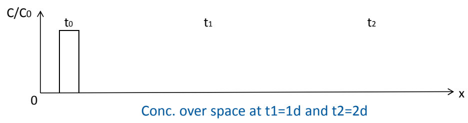
## Dispersion and Diffusion

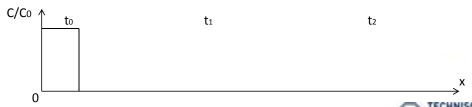
### Exercise 0.2:




A point source

Conc. over space at t1=1d and t2=2d




A continuous source

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## Sorption Isotherms and Decay



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| | |
|---|---|
| Henry | $C^* = K_D C$ |
| Freundlich | $C^* = K_1 C^{K_2}$ |
| Langmuir | $C^* = \frac{K_1 C}{1 + K_2 C}$ |
| 1st-order decay | $\frac{\partial C}{\partial t} = -\lambda C$ |



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Quick Question 1: What could be the unit of Henry sorption coefficient?

A) mL/L;
B) mg/L;
C) mL/kg;
D) g/g (-);
E) m3/kg;



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From KD to retardation factor.

What is the unit of retardation factor?



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Quick Question 2: How can you quickly get λ values by the half life?
Try I-131, half life = **8.0197 days**
and Cs-137, half life = **30.17 years**



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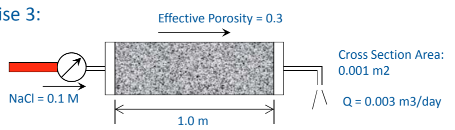
Exercise 3:




(1) Soil grain density is 2000 kg/m3, Kd = 2.0 mL/g, how much is the retardation factor R?

(2) What if there is a 1st order decay on the transported contaminant with ( λ = 0.7 1/day )