Transport of Organic Solutes in Clay Formations

Junqi Huang, USEPA

Mark Goltz, Air Force Institute of Technology

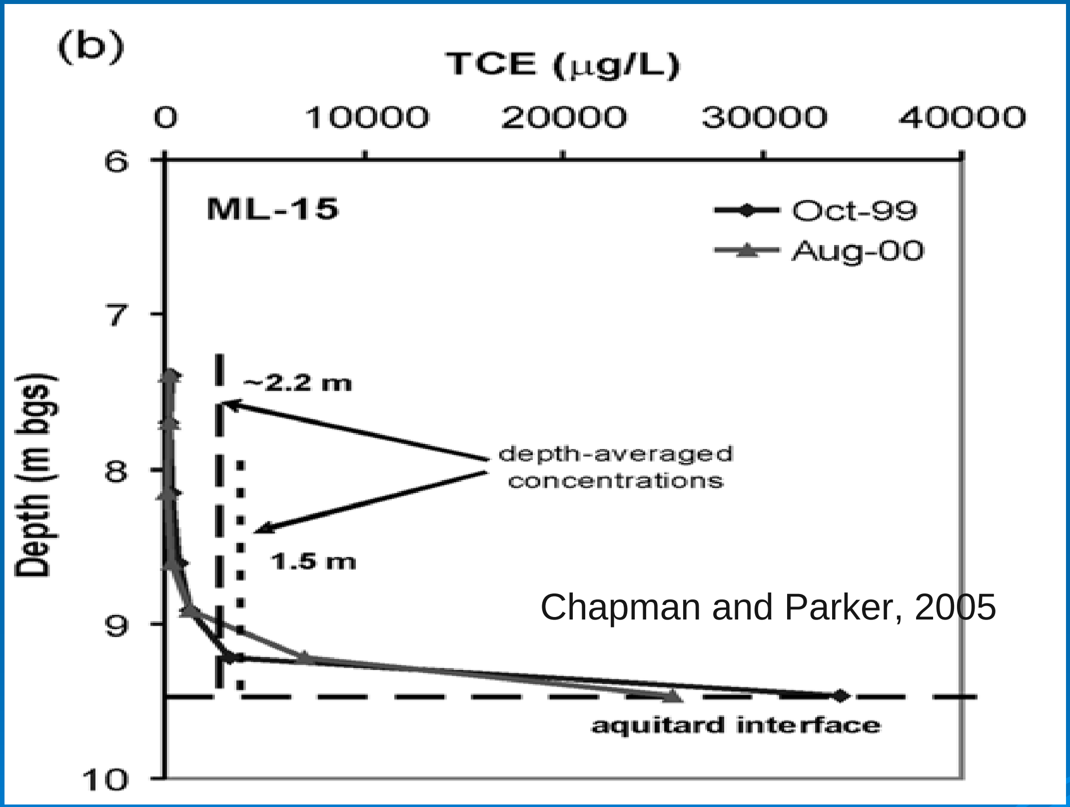
Avery Demond, University of Michigan

Derya Ayral, University of Michigan

EPA United States Environmental Protection Agency

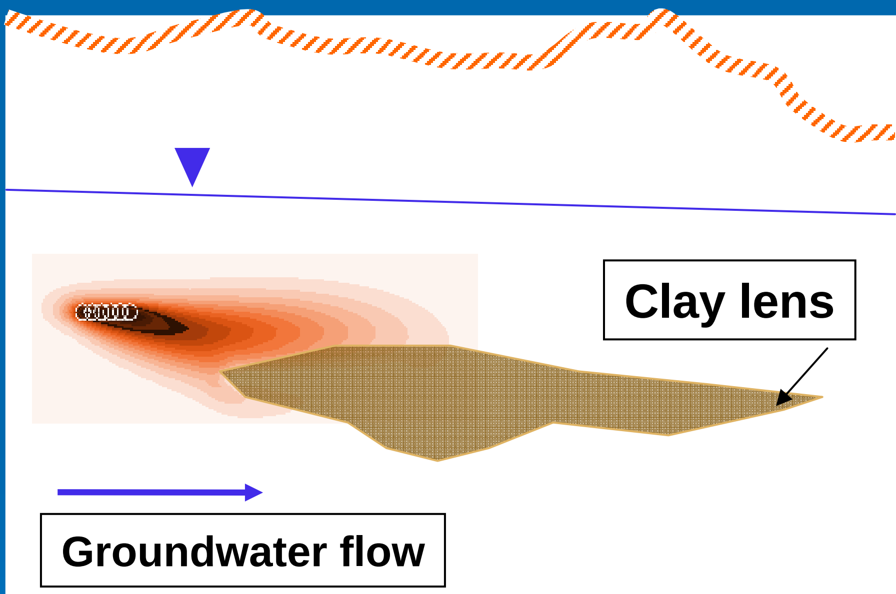
MichiganEngineering

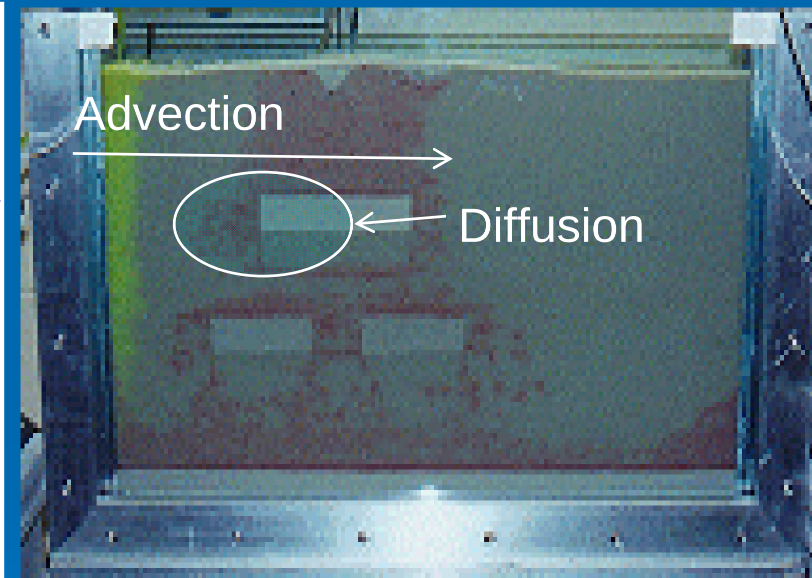
Contamination in Low Permeability Layers



Storage in low permeability layers serves as a long term source of contamination

Contamination of Low Permeability Layers





Process of transport into these layers was believed to be diffusion

Field Observations

- Observed effective diffusion rates through an unweathered clay landfill liner in southwestern Ontario were 1.6 – 5 times higher for benzene, TCE, toluene, ethylbenzene (Johnson et al., 1989) than those based on chloride after correcting for differences in retardation and bulk diffusivity (Ball et al., 1997)
- May be effect of preferential differential pathways for ***diffusion*** through cracks (Mott and Weber, 1991)

Cracking of Clay

- Organic liquids impact basal spacing (Å) of clay

Dried at 175°C	Saturated with water vapor (ε = 80.2 at 20°C)	Saturated with nitrobenzene vapor (ε = 34.8 at 25°C)	Saturated with heptane vapor (ε = 1.9 at 20°C)
9.4	18.7	15.4	9.5

(ε = dielectric constant) (Li et al., 1996)

- "Distinct, large vertical cracks" can form (Abdul et al. 1990)

Objective

- Can enhanced diffusion through cracks or macropores in clay explain the observations of 1.6 to 5 times greater diffusivities?
- Can advective and dispersion transport explain these observations?
- Two mathematical models are proposed to explain the phenomena.

Diffusion Only, No Macropores

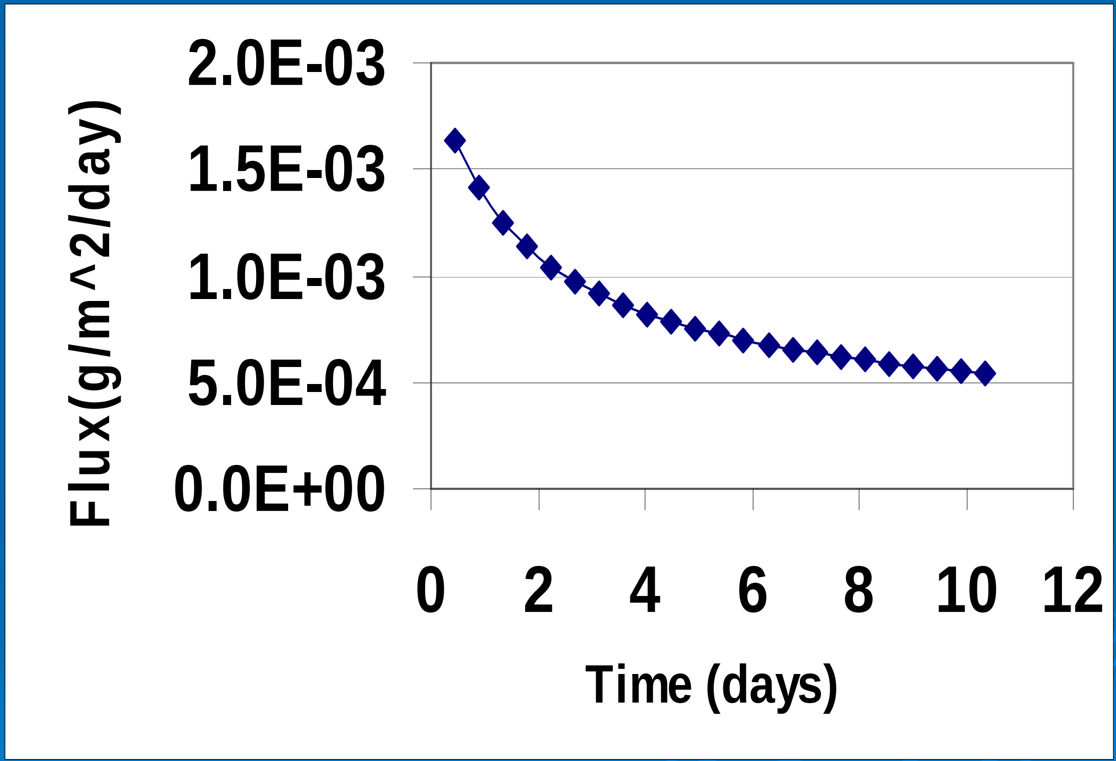
$$J_d = -D_e \frac{\partial C}{\partial x}\bigg|_{z=0}$$

$$C\big|_{z=0} = 1 \text{ mg/L}$$

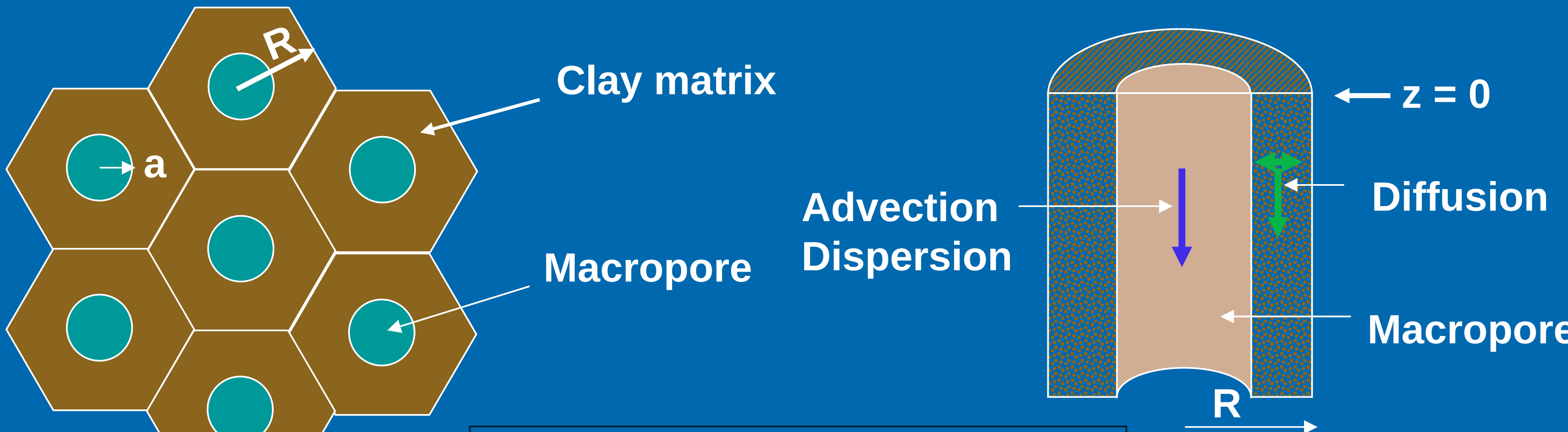
$$D_e = \xi D_{bulk}$$

$$\xi = n^{4/3}$$

$$D_e = 4.5 \times 10^{-6} \text{ cm}^2/\text{sec}$$



Conceptual Model



Averaged flux at z = 0

Advective/Dispersive flux

Diffusive flux

$$\frac{a^2\left[vC_{z=0} - D\frac{\partial C}{\partial z}\Big|_{z=0}\right] + \left(R^2 - a^2\right)\left[-D_m\frac{\partial C}{\partial z}\Big|_{z=0}\right]}{R^2}$$

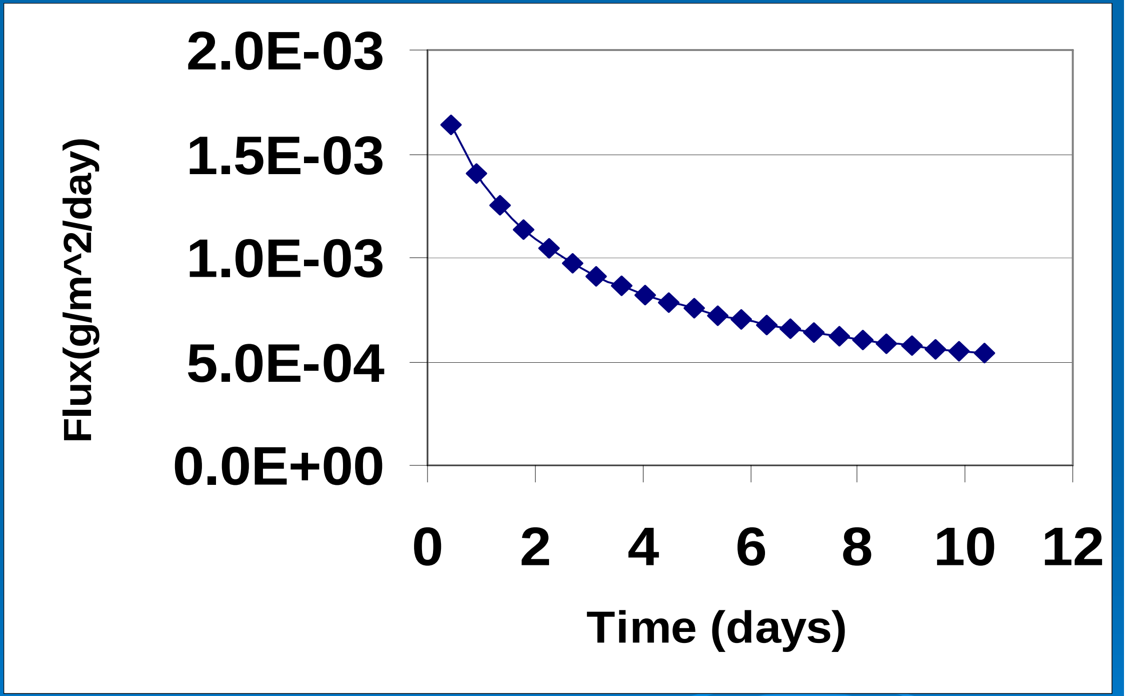
Characteristics of Cracks or Macropores

Property of Field Cores	Perret et al. (1999)	Armstrong et al. (2000)
Clay content	10-20%	50-60%
Macroporosity (%)	2.2-3.8	2-5
Tortuosity (L_e/L)	1.2-1.3	2
Hydraulic radius (mm) (vol/wall area)	0.12-0.14	NA
K_{sat} in cracks (mm/hr)	NA	40
Crack spacing (cm)	NA	5-20

Parameter	Model Parameter Values
Macropore radius, a (m)	3×10^{-4}
Velocity, v (m/day)	1
Distance between macropore centers, 2R (m)	0.06

Diffusion in Matrix, Enhanced Diffusion in Macropores

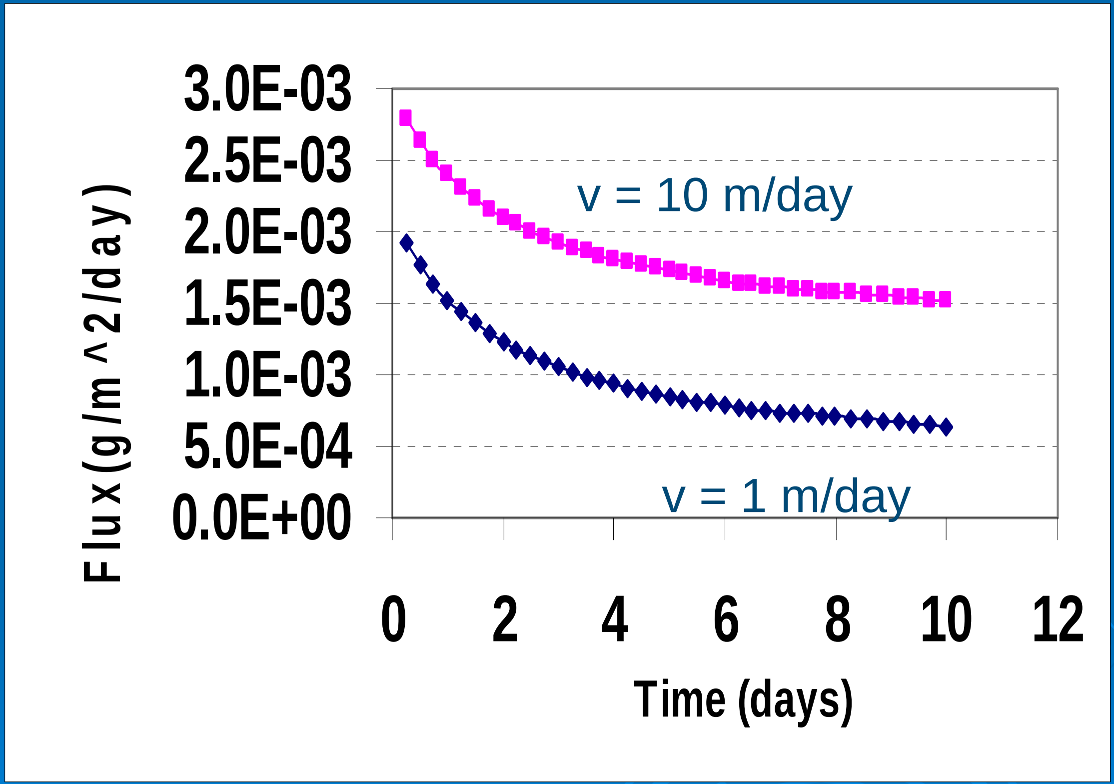
Parameter	Model parameter values
Diffusion coefficient in clay matrix (cm^2/sec)	4.5×10^{-6}
Diffusion coefficient in macropores (cm^2/sec)	1×10^{-5}



With the diffusion coefficient = maximum in macropores (same value as in bulk water), increase in flux = 1×10^{-4} g/($m^2 \cdot$day)!

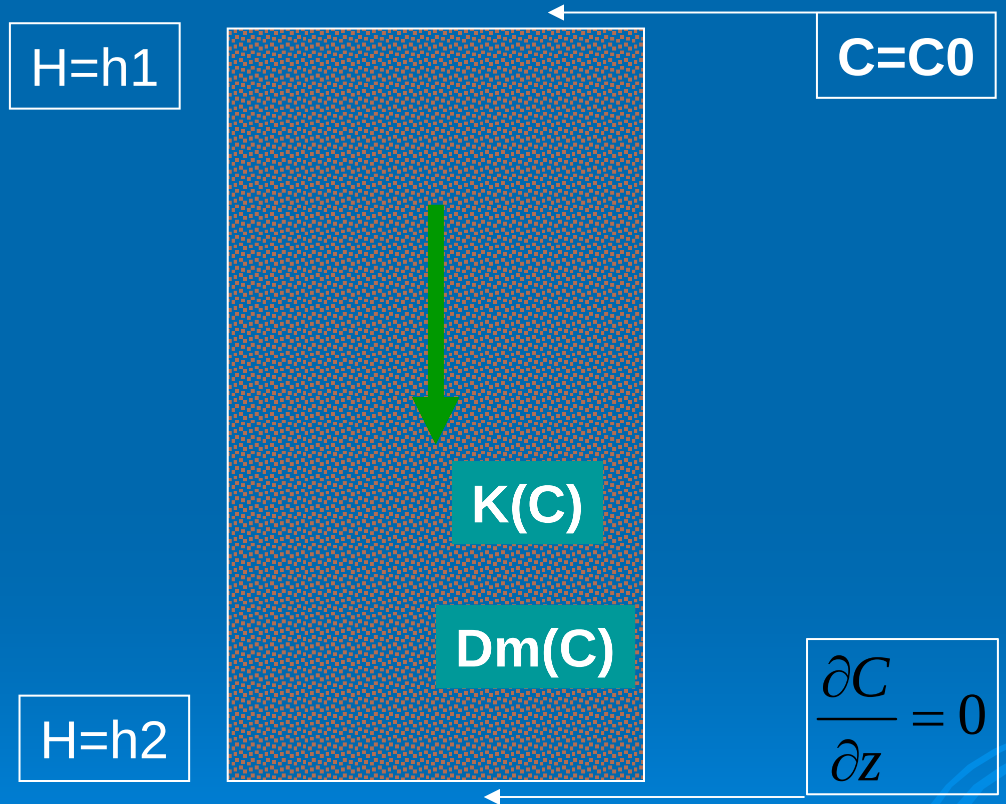
Diffusion in Matrix, Advection and Dispersion in Macropores

Parameter	Model paramete r values
Macropore radius, a (m)	3×10^{-4}
Distance between macropore centers, 2R (m)	0.06
Dispersion coeff. (m^2/day)	0.02



Flux can be raised if advection and dispersion considered in macropore

General non-linear transport model



Mathematical Model

Transport in porous media (convection and dispersion):

$$\theta \frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left([D(C) + D_m] \frac{\partial C}{\partial z} \right) - \frac{\partial}{\partial z}\left(v(C)C \right)$$

$$D = a_L * v$$

$$v = \frac{\Delta h}{\sum_{i=1}^{m} \frac{1}{k(C_i)}}$$

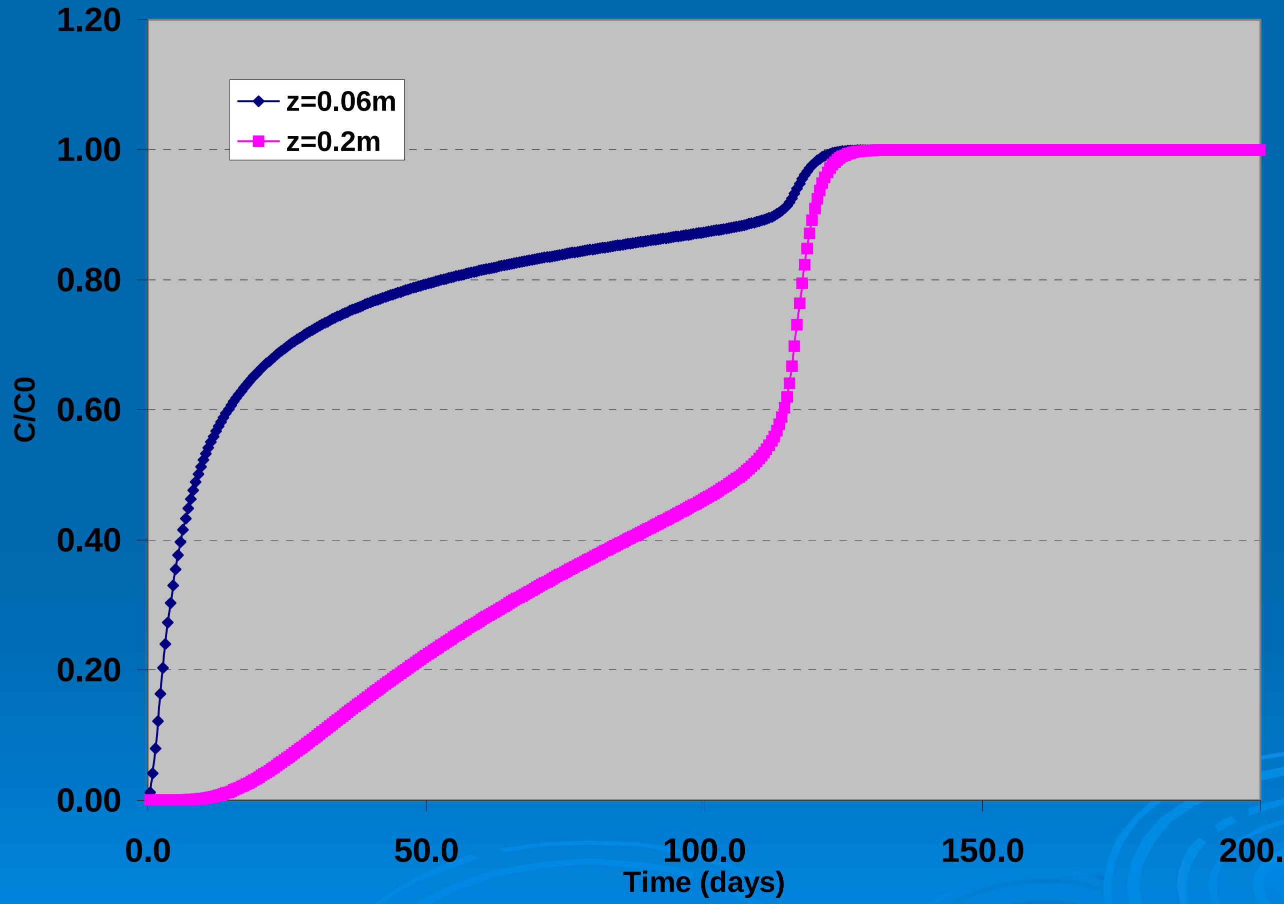
Conductivity change

Langmuir adsorption isotherm

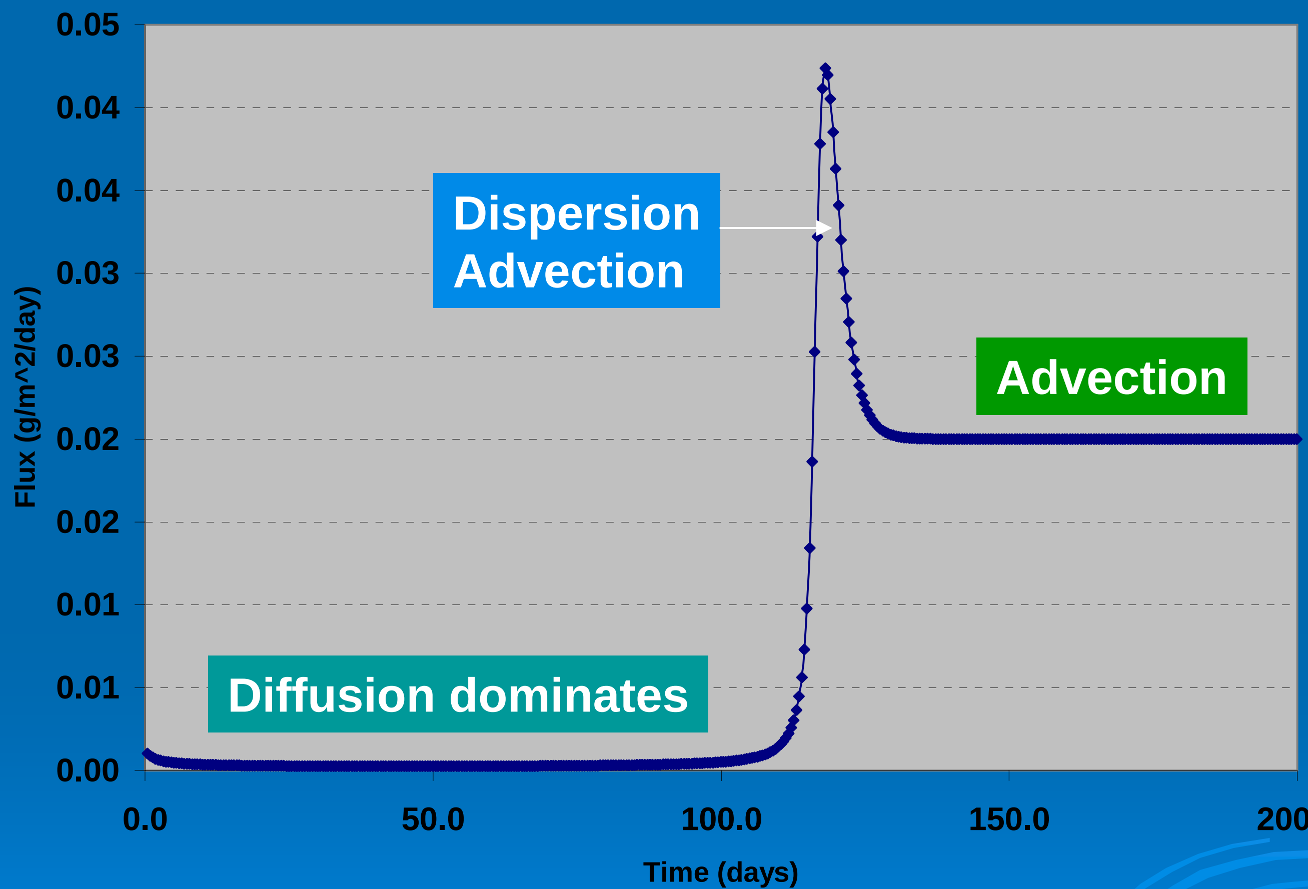
Linear relationship assumption between K and absorbed NAPL

$$k(C) = k_{\min} + \left(k_{\max} - k_{\min}\right)\frac{2C}{C + C_{\max}}$$

Concentration breakthrough at selected location



Flux at inlet vs time



With the selected parameters, the averaged flux gets ten times higher than when involving diffusion only transport

Conclusions

- Previous research has shown that contact with organic liquids can cause clay to crack, forming macropores or increasing conductivity.
- Diffusion through "preferential pathways" through these macropores is not significant

Conclusions (continue)

- Advective fluxes through these macropores or altered porous media, calculated using field-measured parameters, can significantly increase the transport through clay
- The formation of cracks or macropores (hence conductivity increasing) is a likely explanation of field observations of enhanced diffusivities

Model plan

- Proposed 1-D transport models will be used to fit experiment data, determining relationship between properties of porous media and organic contaminant.
- The enhanced diffusion mechanism will be integrated into an applied simulator to guide site remediation where clay formations exist.