Effectiveness of Source-Zone Remediation of DNAPL-Contaminated Subsurface Systems: Role of Interphase Mass Transfer

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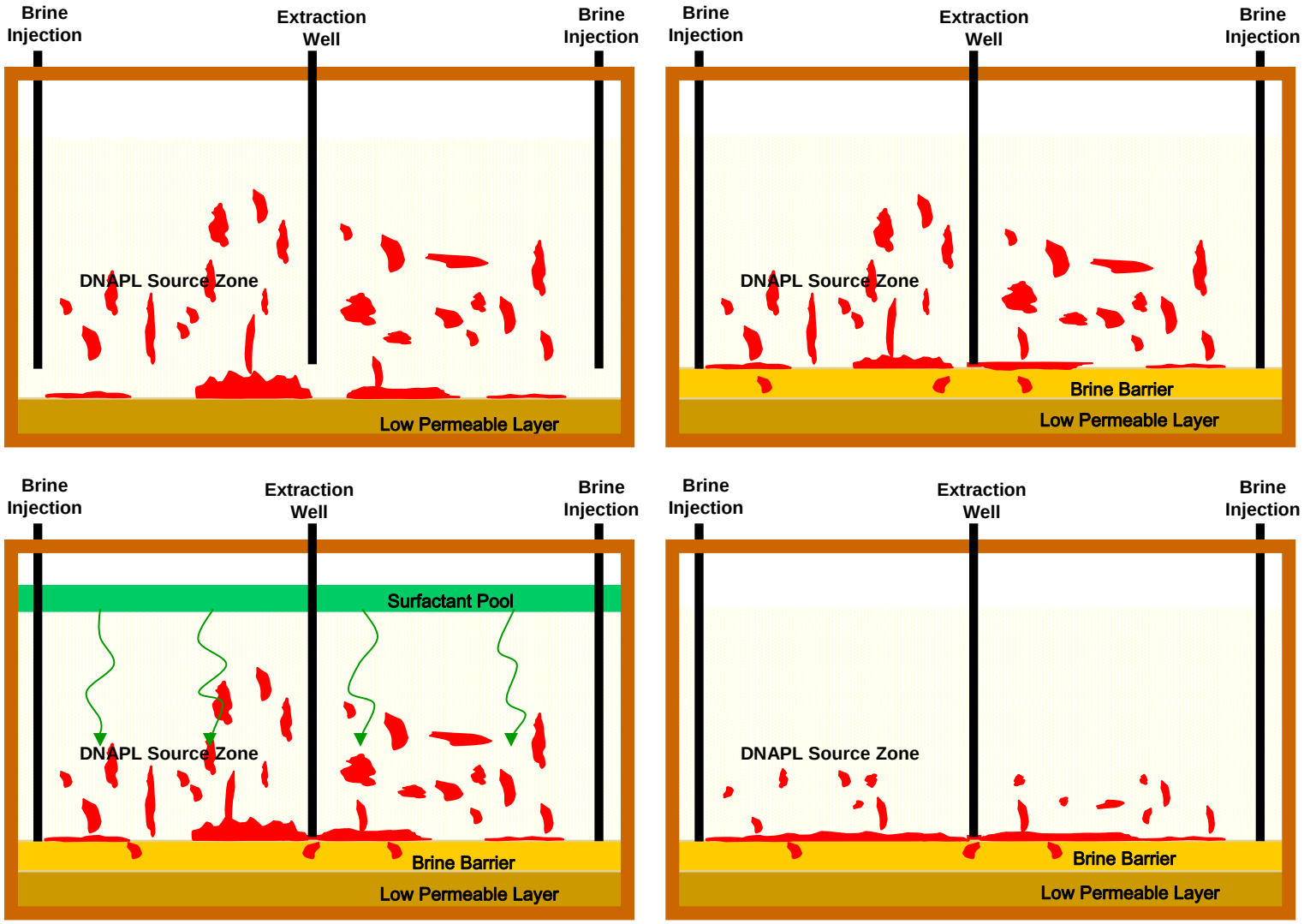
Overview

- Source-Zone Remediation
- Mass Transfer Fundamentals
- Implications for Remediation
- Other Mass Transfer Considerations
- Conclusions
- More Information

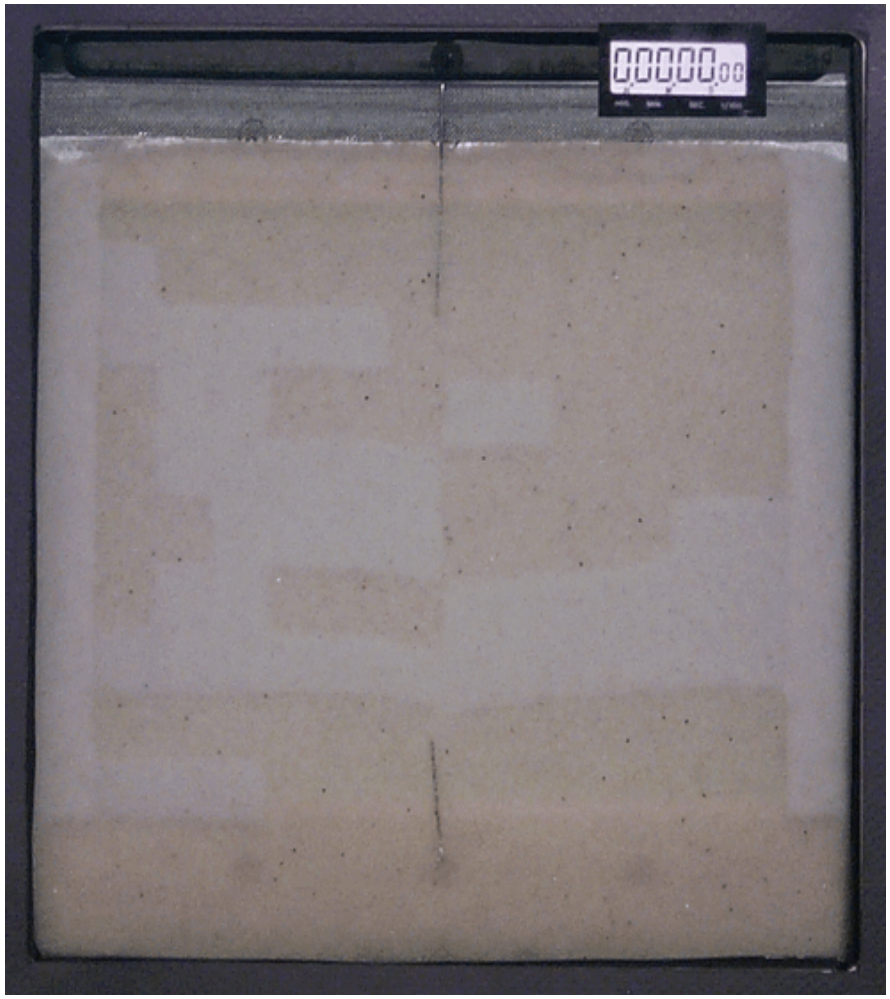
Source-Zone Remediation

- Approaches: mobilization, mass transfer, reactions, or some combination
- Properties of the system will affect the optimal choice
- Common approach of evaluating remediation in terms of fractional mass removal is not a very useful concept
- Basing success of single-stage source-zone remediation on aqueous-phase concentrations by comparing to drinking water standards is destined for failure in most cases

Brine Barrier Remediation Methods



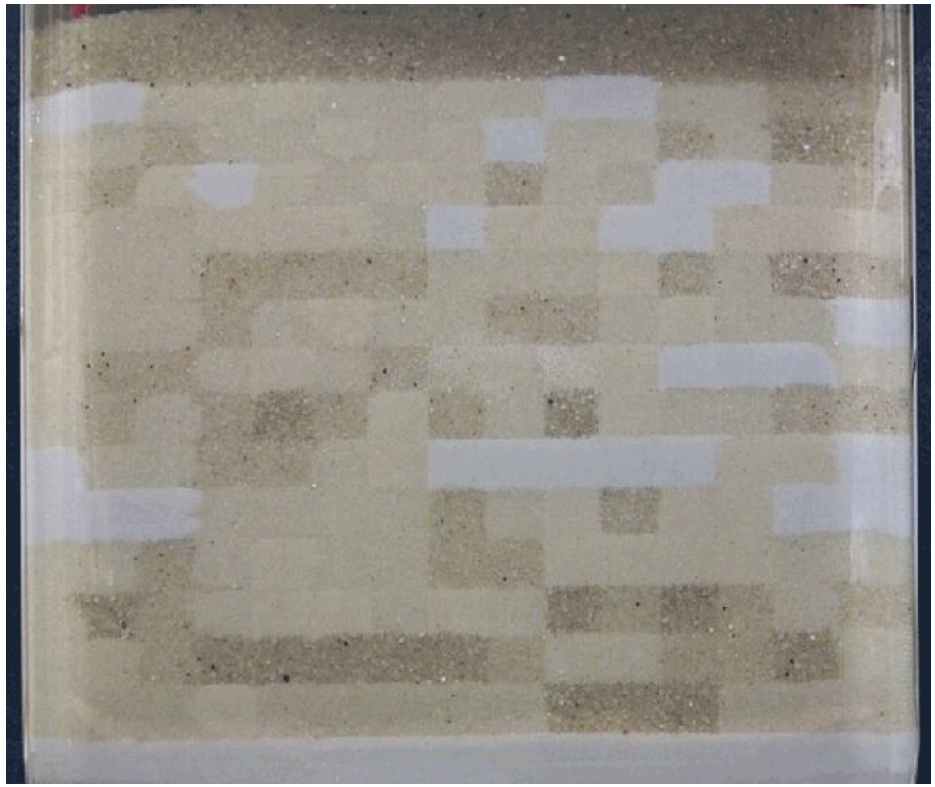
DNAPL Mobilization and Removal



- 21-cm x 21-cm two-dimensional cell
- Pooled TCE established
- TCE dyed with Oil Red O for visualization
- Established bottom brine layer
- Drained to unsaturated conditions
- 0.3 pore-volume downward flush with mixture of sulfosuccinate surfantants
- Measured 80.0% TCE removal, no visible pools
- Reference: Hill et. al. [ES&T, 35(14), 2001]

Two-Stage DNAPL Removal Set-Up

DNAPL Mobilization and Removal



- 22-cm x 24-cm x 16-cm three-dimensional cell
- Pooled TCE established in heterogeneous media
- TCE dyed with Oil Red O for visualization
- Established bottom brine layer
- Drained to unsaturated conditions
- 3.2 pore-volume downward flush with mixture of sulfosuccinate surfantants followed by vapor extraction
- Measured 99% TCE removal of recovered TCE
- Reference: Johnson et. al. [ES&T, 38(19), 2004]

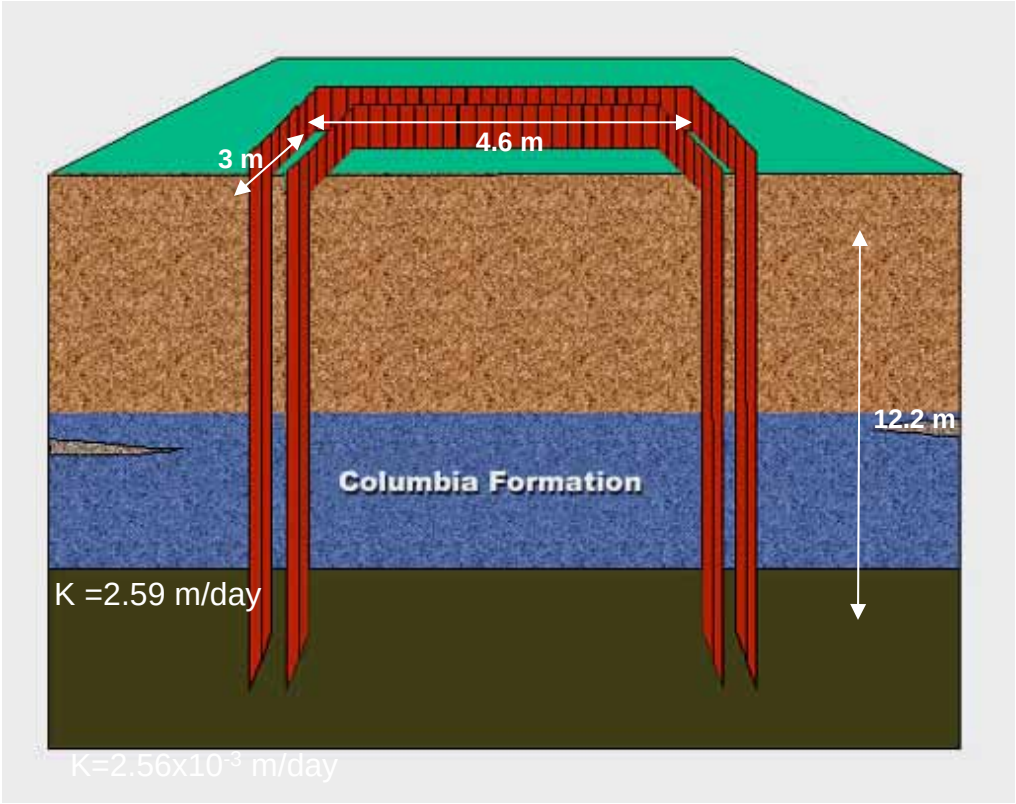
Dover Experimental Design

- Step 1: Establish initial conditions
- Step 2: Drop water table to 39 ft bgs and characterize gas phase flow system
- Step 3: Return water level to 34 ft bgs and characterize concentration distribution
- Step 4: Release PCE according to protocol
- Step 5: Establish water level at 34 ft bgs as starting position after contamination
- Step 6: Establish brine layer

Dover Experimental Design

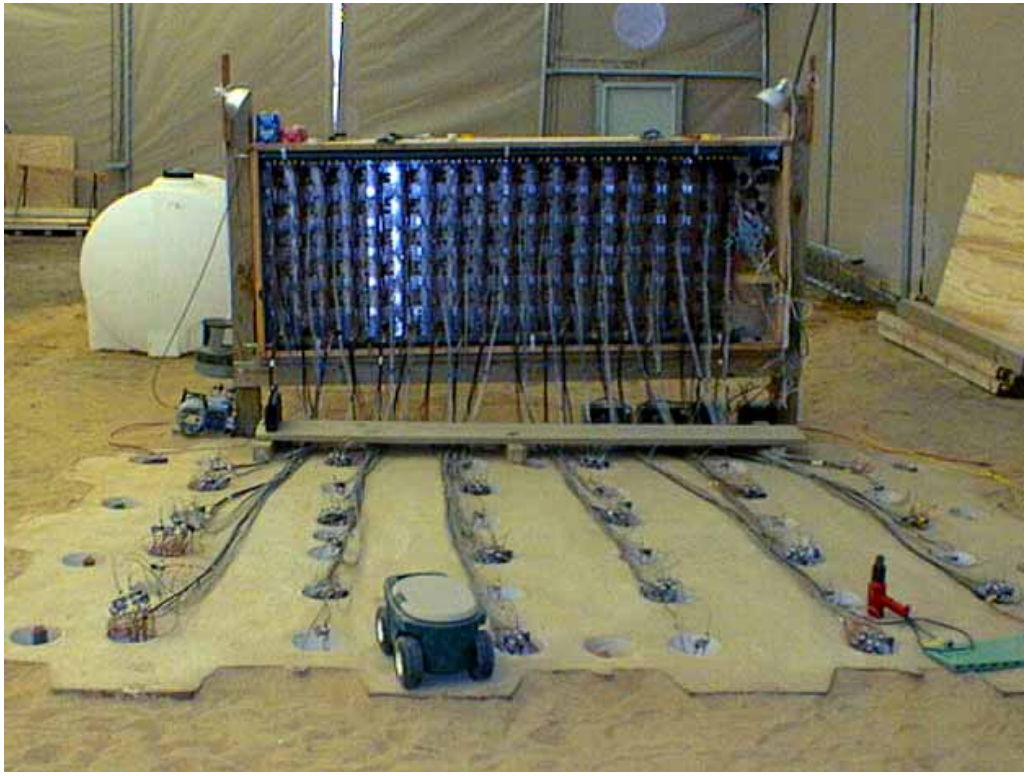
- Step 7: Add surfactant
- Step 8: Dewater to top of brine layer and collect PCE
- Step 9: Apply vapor extraction
- Step 10: Flush brine and vapor extract
- Step 11: Reduce TDS and vapor extract
- Step 12: Return to neutral position and characterize

Test Cell at Dover National Test Site



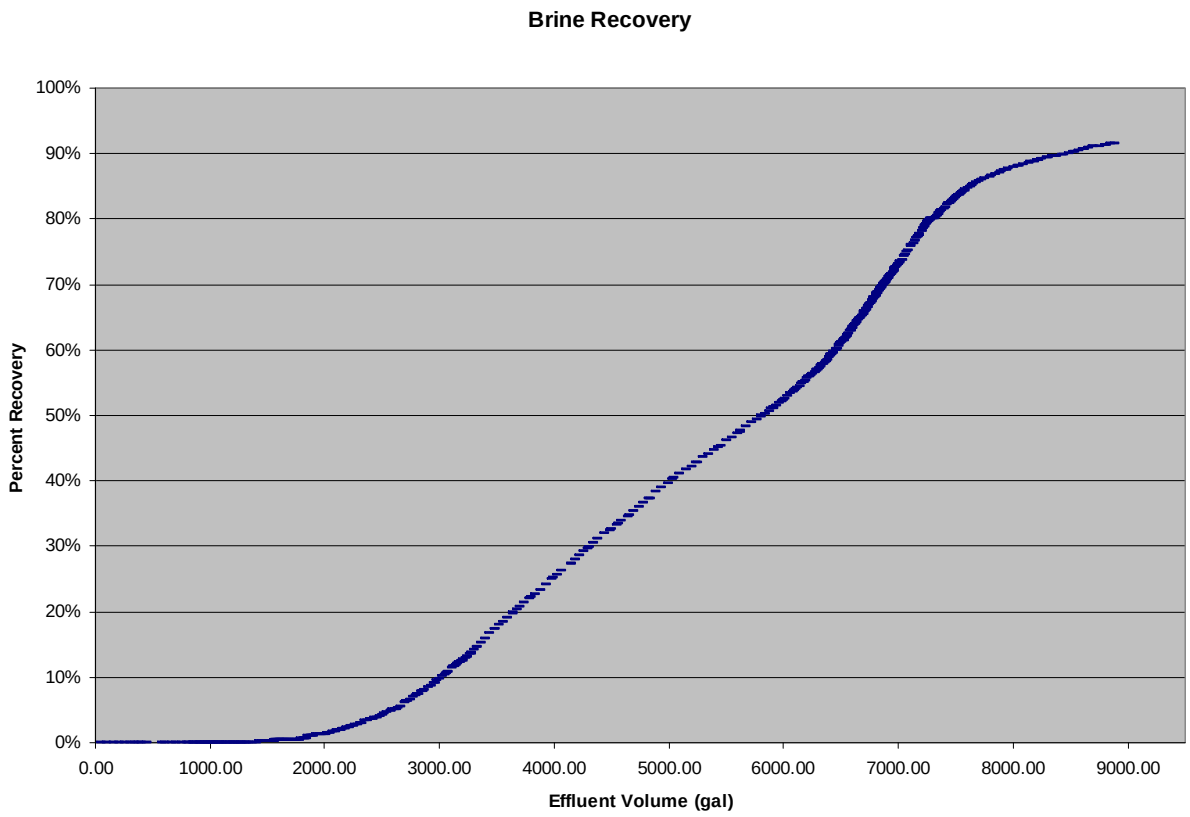
- Depth to the water table is approximately 8.5 m.
- Aquifer depth is approximately 3.7 m.
- Test cells are double-walled sheet piles driven into the clay aquitard.
- Sheet piles are keyed into a confining aquitard approximately 13.7 m below the surface.

DNTS Test Cell 3

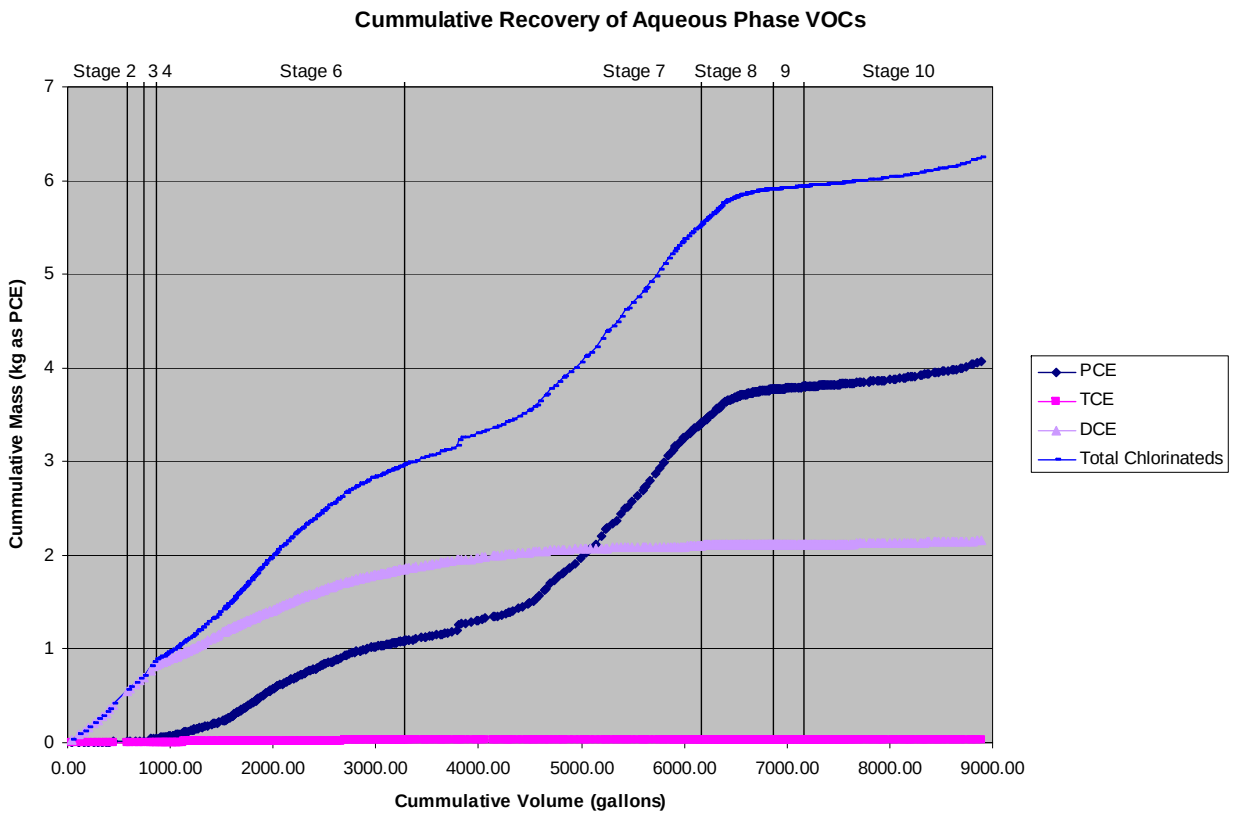


- Multilevel samplers allowed us to monitor:
  - In situ densities
  - Surfactant propagation through the system
  - Changes in aqueous concentrations

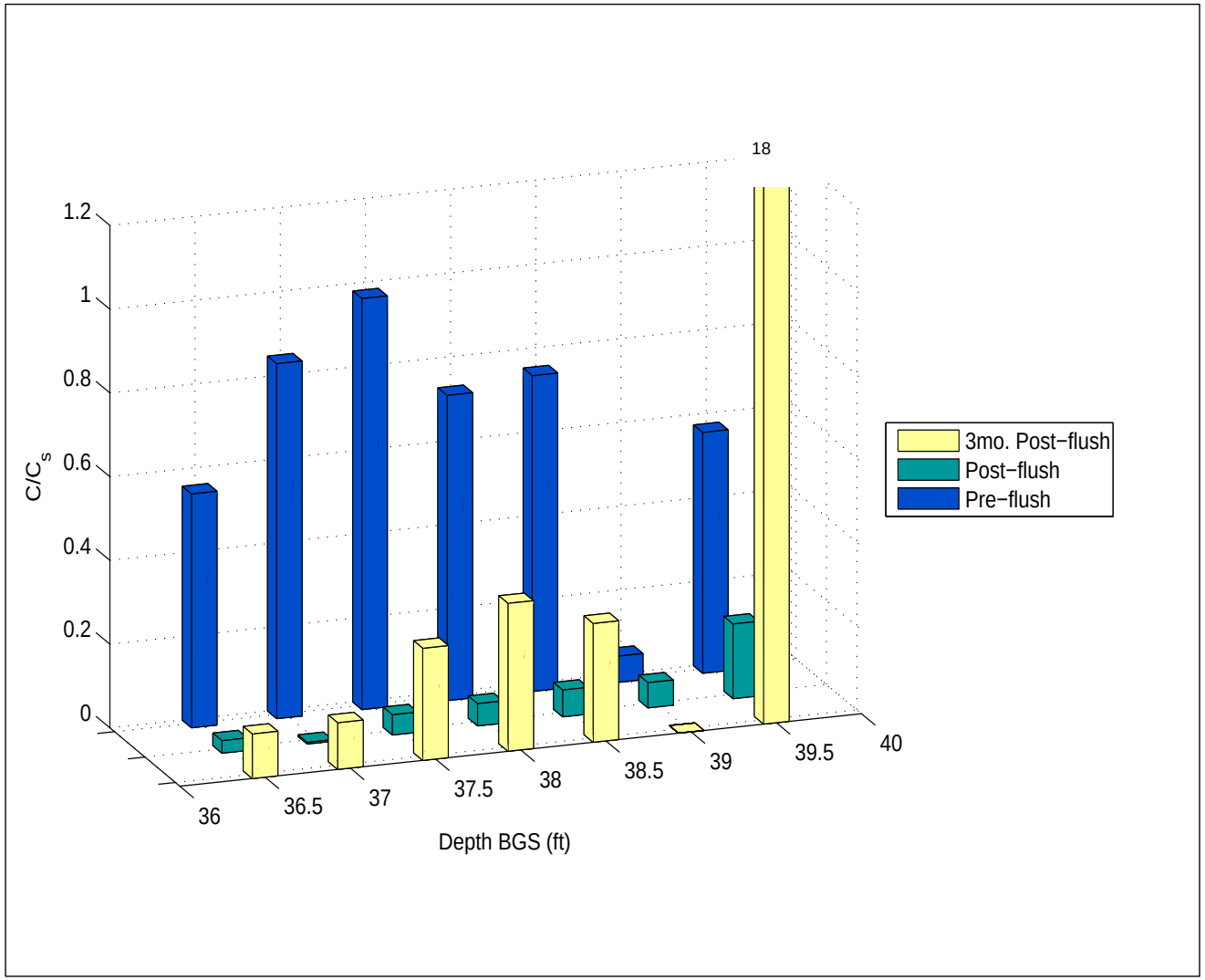
Dover Study – Brine Recovery



Dover Study – Aqueous NAPL Recovery



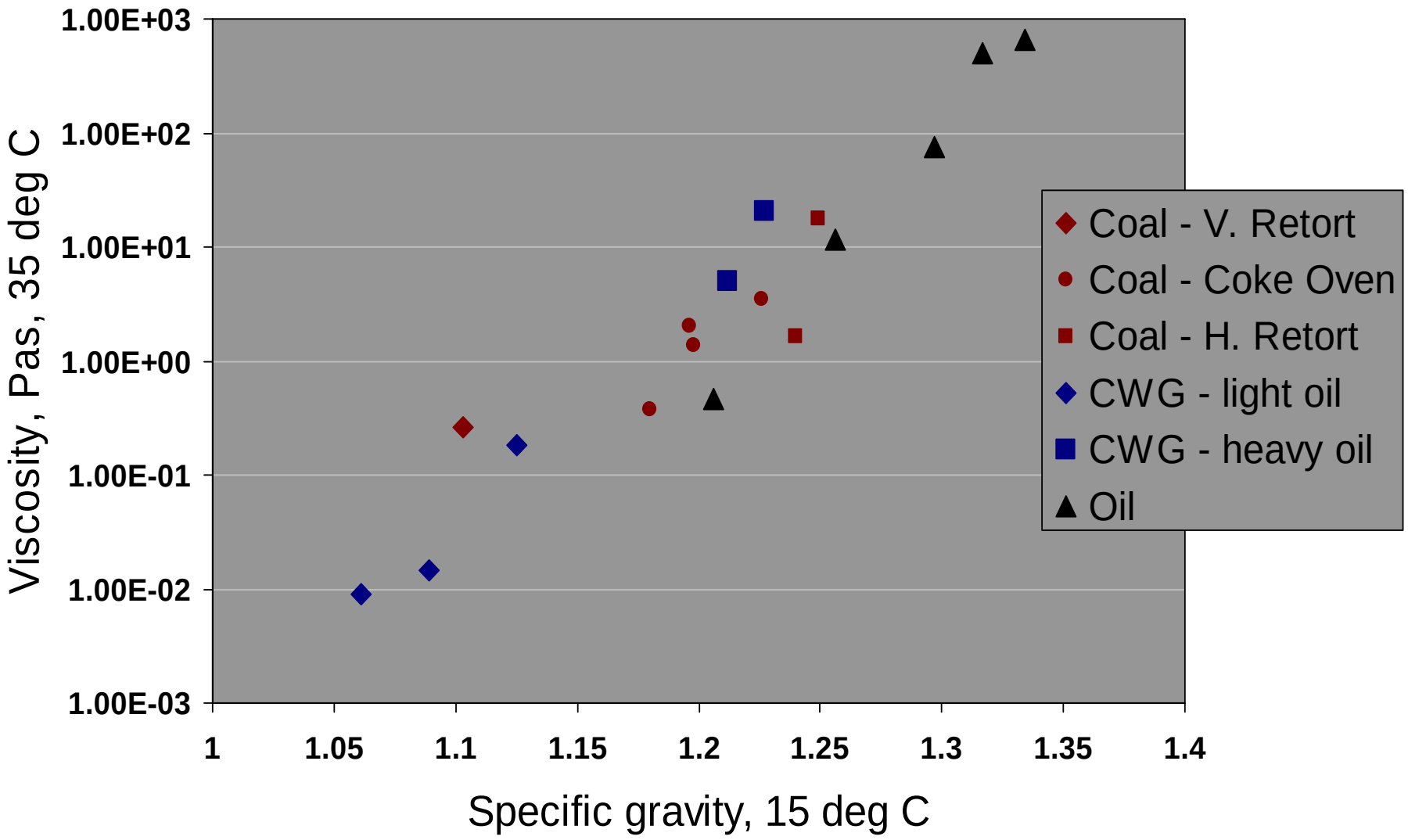
Dover Study---Aqueous Phase Concentrations



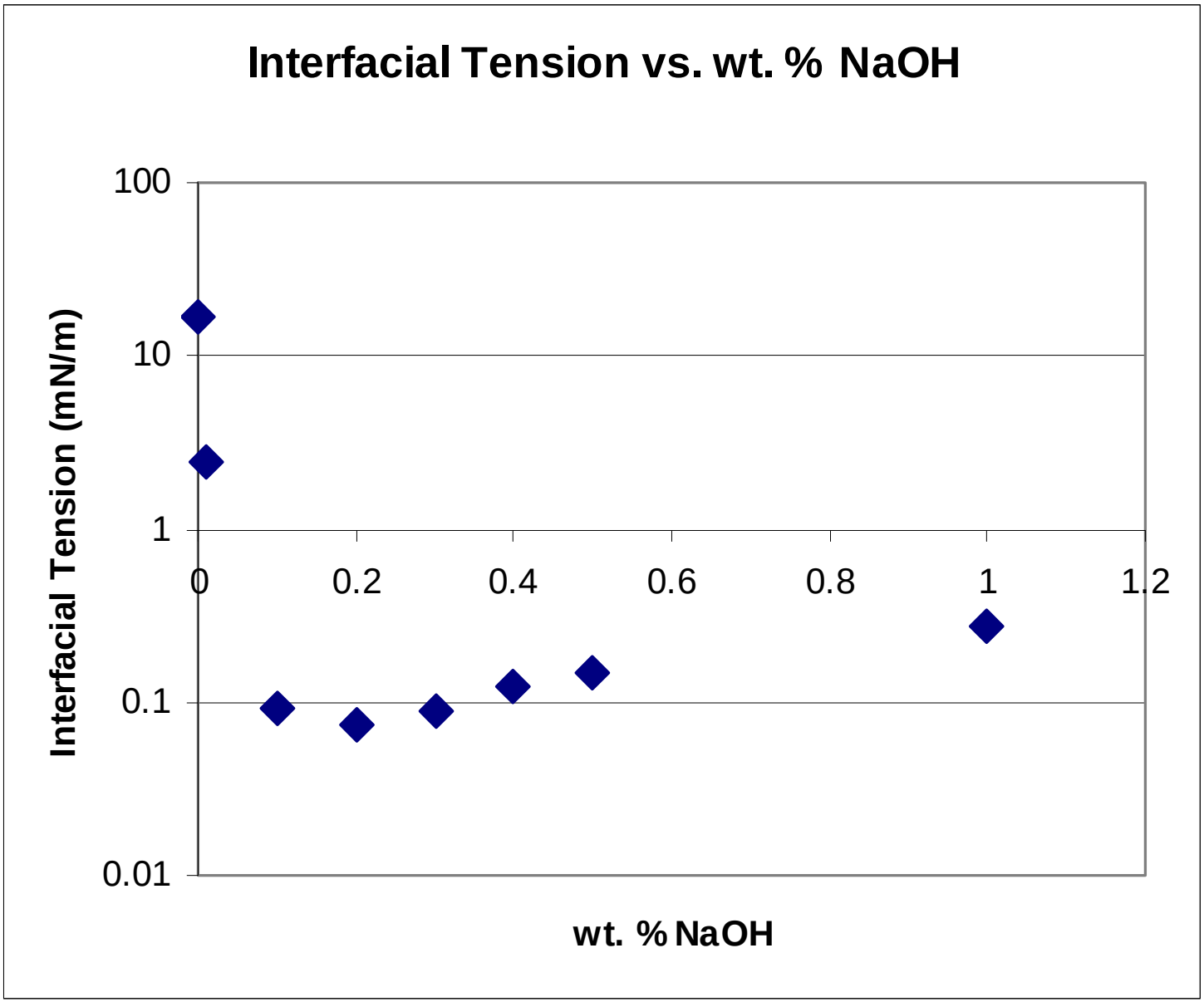
Composition and Properties of Tars

- Highly variable, complex mixture
  - Contains MAHs, PAHs, heterocyclic compounds, asphaltenes, trace metals, other inorganic compounds
  - No one compound is typically more than 5-10%
  - Molecular weights varying from 70-10,000
- Extremely difficult to remediate
  - Recalcitrant - extremely low solubility
  - Denser than water
    - Sink in the subsurface
    - Dense non-aqueous phase liquids (DNAPLS)
  - Highly viscous
    - Slow moving plumes
    - Oil wet systems - coat sand grains
  - Heterogeneity

Viscosity and Density for Various Tars



Alkaline-Based Tar Mobilization



Alkaline Mobilization of Tars

10-cm glass column packed with field sand
Initially ~80% tar saturated
Flushed with water to create residual tar saturation
Flushed with 0.5% NaOH solution to mobilize tar
Second water flush
Final alcohol flush removes additional tar

Mass Transfer Fundamentals

- Essentially all systems will become mass transfer limited at some point
- Local equilibrium is a convenient assumption, but never realized at the field scale
- Non-dimensional description
- Experimental basis
- Issues of scale

Mass Transfer Modeling

Conservation of mass

$$\frac{\partial(\epsilon^{\alpha}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\partial t} = -\nabla\cdot\left(\epsilon^{\alpha}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}\right) - \nabla\cdot\left(\epsilon^{\alpha}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right) + r^{i\alpha} + \sum_{\kappa\in\mathfrak{I}_{c\alpha}} \overset{i\kappa\rightarrow i\alpha}{M} \quad (1)$$

Linear equilibrium between phases

$$\left(\rho^{w}\omega^{i\overline{w}}\right)_{eq} = K_{na}\rho^{n}\omega^{i\overline{n}} \quad (2)$$

For single solute NAPL phase in dilute system

$$\left(\rho^{w}\omega^{i\overline{w}}\right)_{eq} = C_{s} \quad (3)$$

Linear local equililibrium model

$$C = C_{s}, \qquad \text{if } \epsilon^{n} > 0 \quad (4)$$

First-order model

$$\overset{in\rightarrow iw}{M} = \epsilon^{w}\rho^{w}\hat{k}_{na}\left(\omega_{eq}^{iw} - \omega^{i\overline{w}}\right) = \epsilon^{w}\rho^{w}\epsilon^{na}k_{na}\left(\omega_{eq}^{iw} - \omega^{i\overline{w}}\right) \quad (5)$$

Non-Dimensional Analysis

Variables of potential importance

$$\mathcal{V} = \left\{ k_{na}, \rho^w, \rho^n, \hat{\mu}^w, \hat{\mu}^n, \hat{D}^{nw}, \mathbf{v}^{\overline{w}}, \mathbf{g}, \gamma^{na}, \mathcal{M} \right\} \tag{6}$$

Common morphology and topology measures include

$$\mathcal{M} = \{\epsilon, \epsilon^n, \cos\varphi, d, \epsilon^{na}, \mathbf{G}^n, \ldots\} \tag{7}$$

This leads to a minimum of 12 non-dimensional parameters to define k_{na}. Typical forms based upon laboratory experiments are of the form

$$Sh = \beta_0 Re^{\beta_1} \left(\epsilon^n\right)^{\beta_2} Sc^{\beta_3} \tag{8}$$

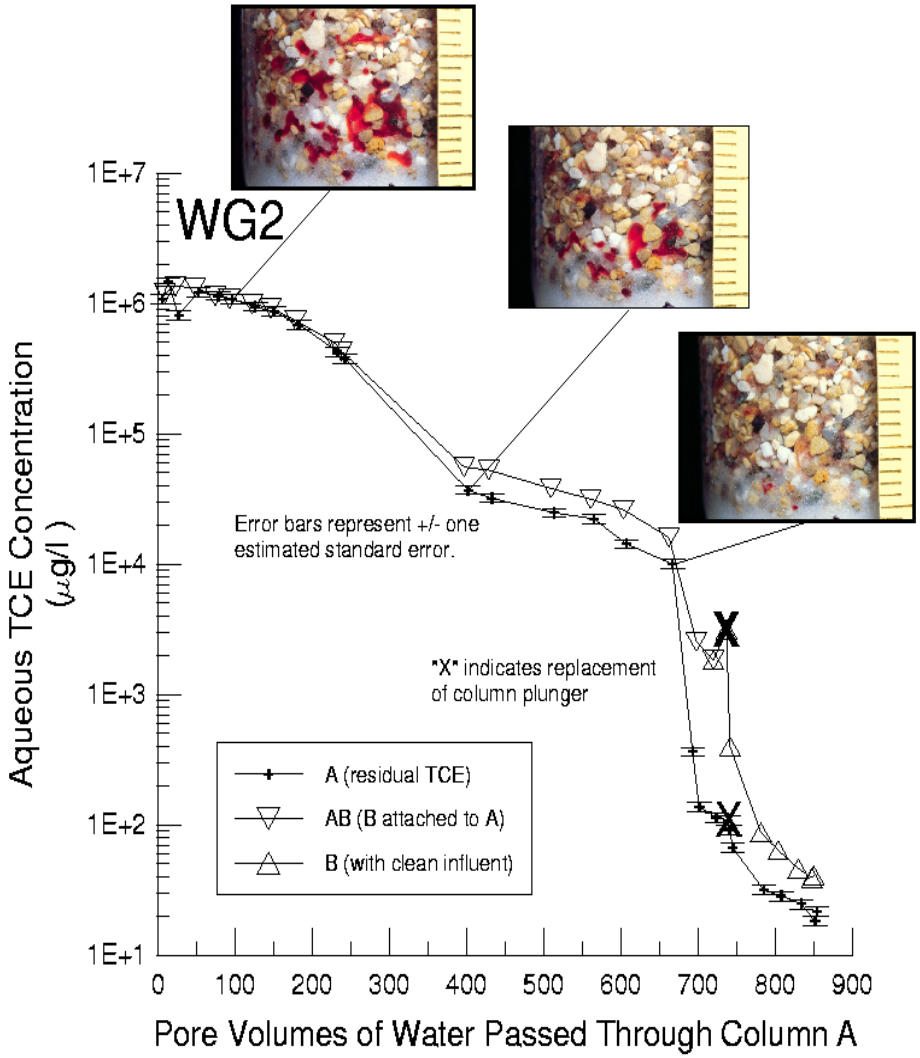
Non-dimensional parameters are defined as

$$Sh = \frac{k_{na} d}{\hat{D}^{nw}} \tag{9}$$

$$Re = \frac{|\mathbf{v}^{\overline{w}}| \rho^w d}{\hat{\mu}^w} \tag{10}$$

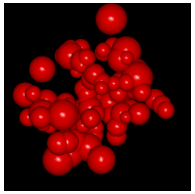
$$Sc = \frac{\hat{\mu}^w}{\rho^w D^{nw}} \tag{11}$$

NAPL Dissolution Tailing for TCE



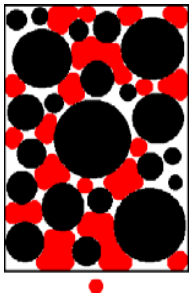
- Column brought to residual saturation with TCE
- Water flushing in an attempt to obtain drinking water standard concentrations of TCE
- Large TCE residual feature determines clean-up time
- Eventually complex TCE region breaks up and drinking water standards reached
- Reference: Imhoff et al. [ES&T, 32(16), 1998]

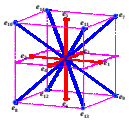
Modeling DNAPL Dissolution

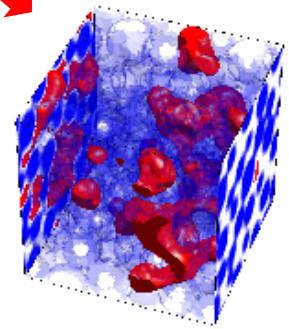


1 **Pore morphology and topology**

Morphological analysis of pore space

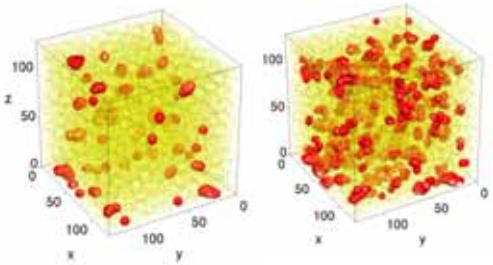




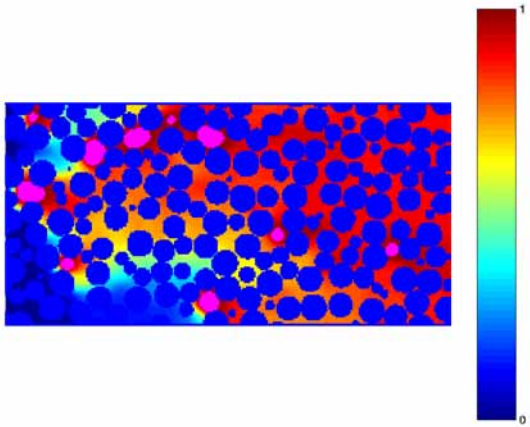


Residual NAPL distribution **2**

LB two-fuid phase simulation

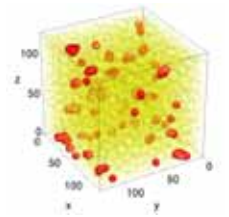


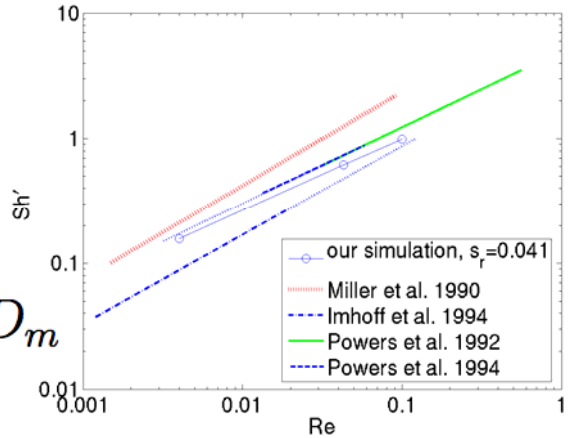
3 **NAPL dissolution**

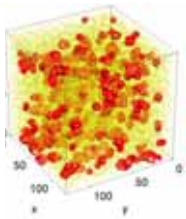


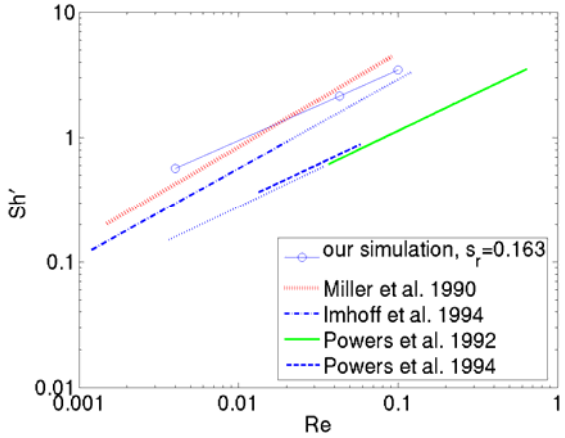
Pore-scale ADE solver with adaptive-stencil finite-volume scheme

Nonaqueous Phase Dissolution



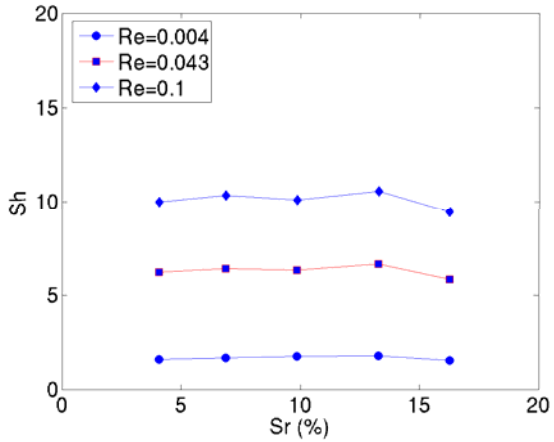


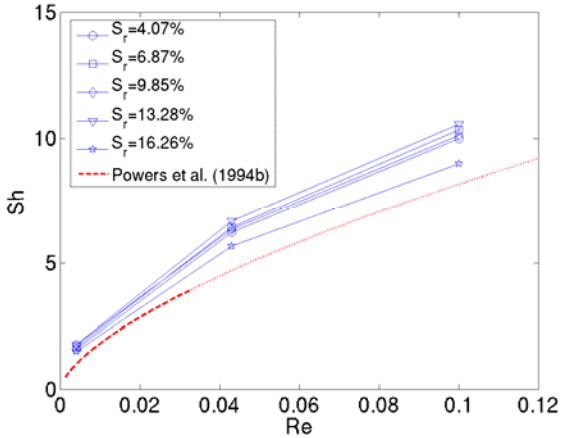




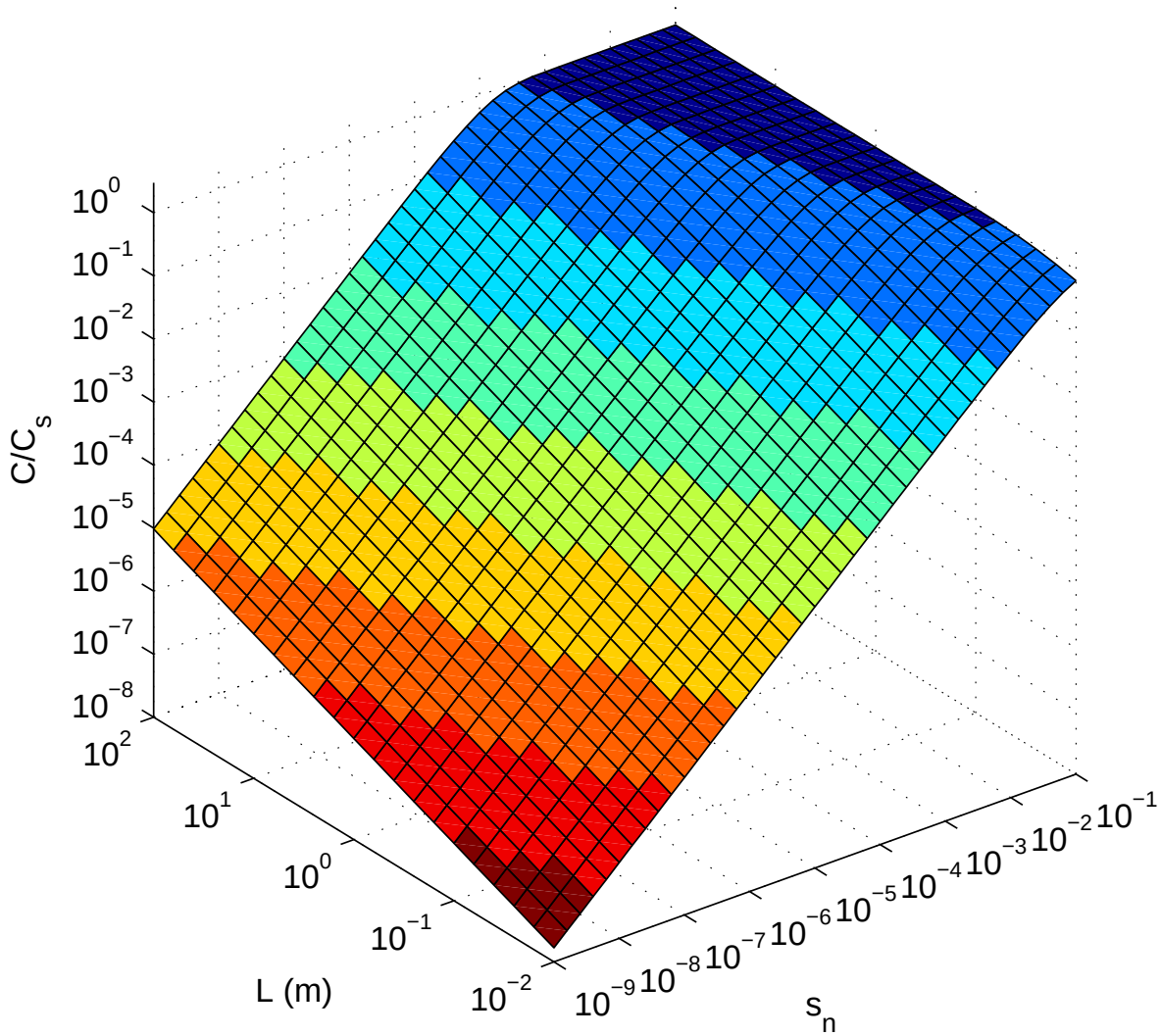
$$Sh' = K_l d_g^2 / D_m$$

$$Sh = k_l d_g / D_m$$





Mass Transfer Limitations



Implications for Remediation

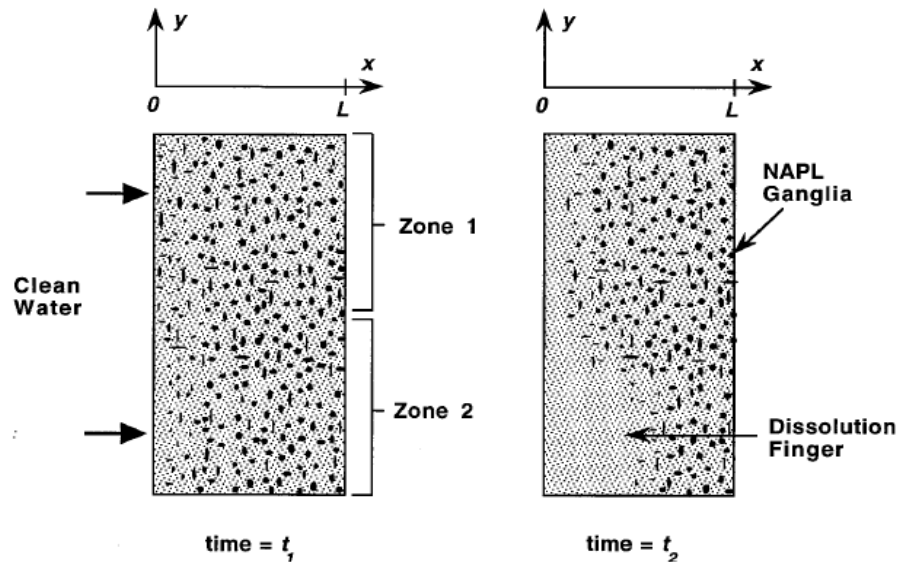
- If drinking water standards are of concern, mass transfer limitations must be dealt with at some point
- Laboratory mass transfer relationships are not of much use at the field scale
- A non-dimensional analysis of the problem is of some use at the field scale in considering factors that are important
- Rate of mass transfer will decrease as heterogeneity of a site increases

Other Mass Transfer Considerations

- Dissolution fingering will occur in virtually all field-scale systems
- Heterogeneity will play an important role in the rate of mass transfer as well
- Significant hope for improved models going forward

Dissolution Fingering

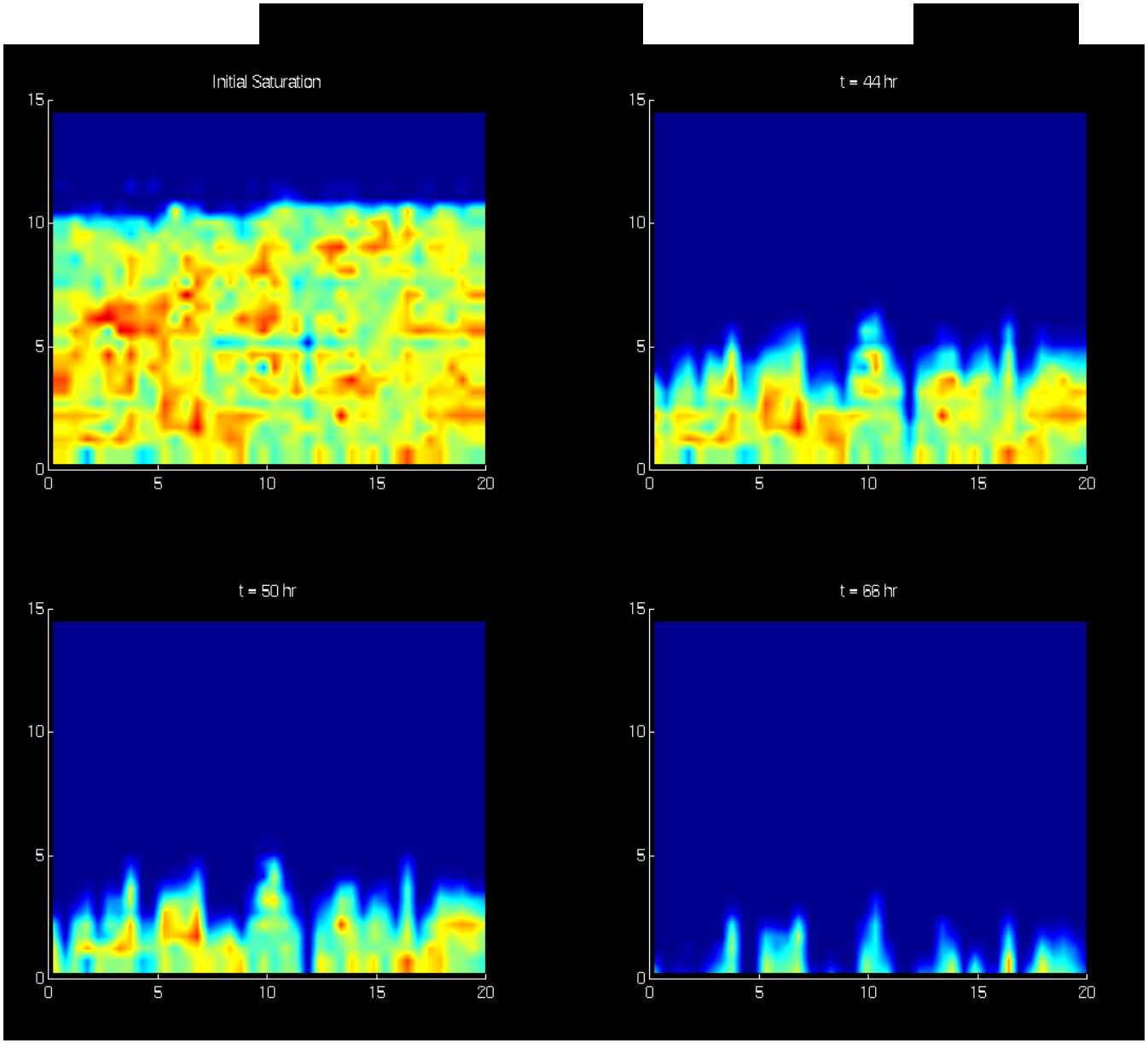
- Fingers develop in homogeneous porous media due to heterogeneously distributed NAPL residual saturation
  - Observed in physical experiments (Imhoff et al. 1996) and simulated in numerical studies (Imhoff et al. 2002)
  - Linear stability (Imhoff and Miller 1996)
  - Dissolution finger growth due to positive feedback into relative permeability function.



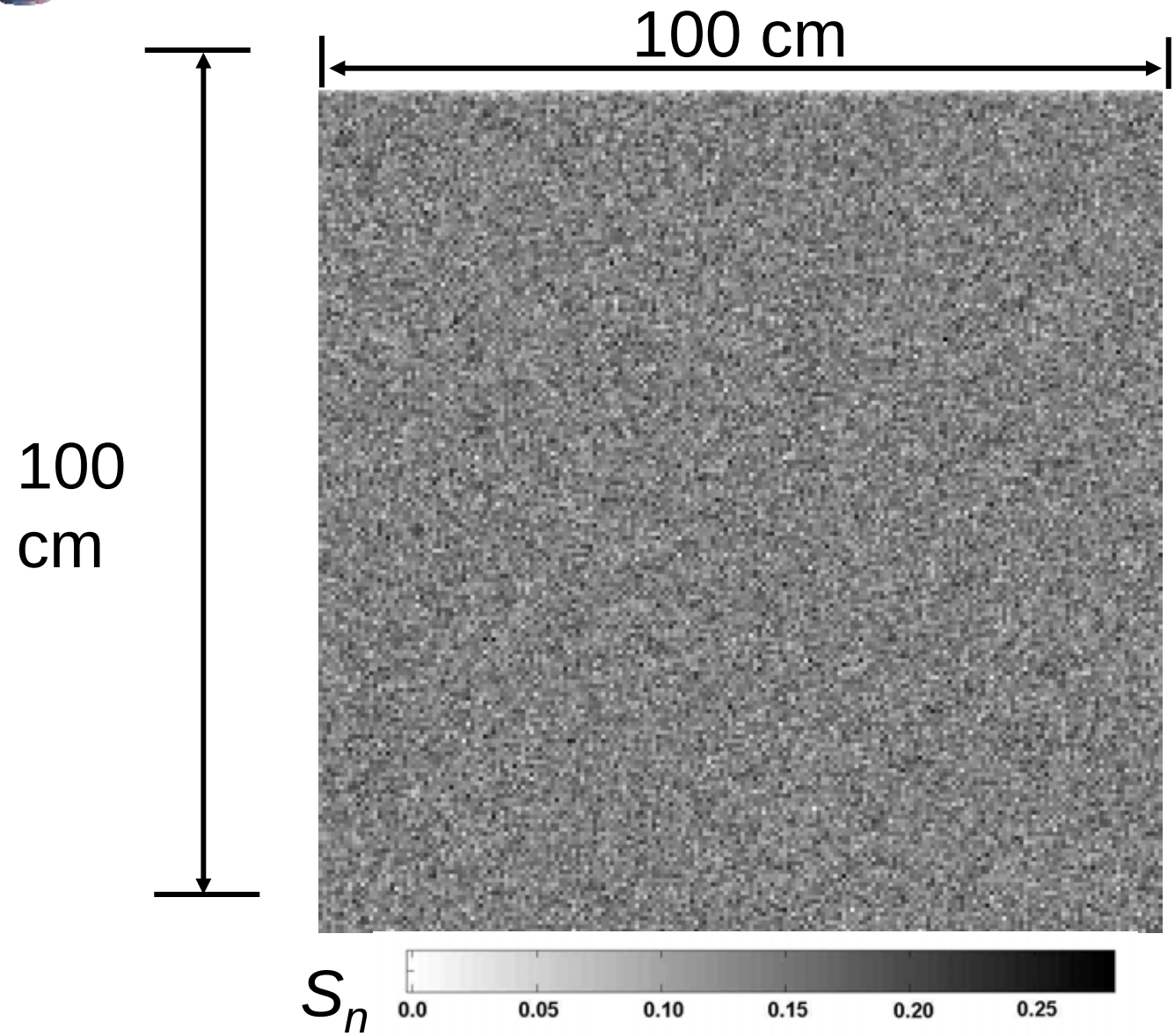
Imhoff and Miller, 1996

- Heterogeneous media can lead to dissolution fingering
  - Homogeneous residual NAPL
  - Preferential flow paths in higher-permeability zones

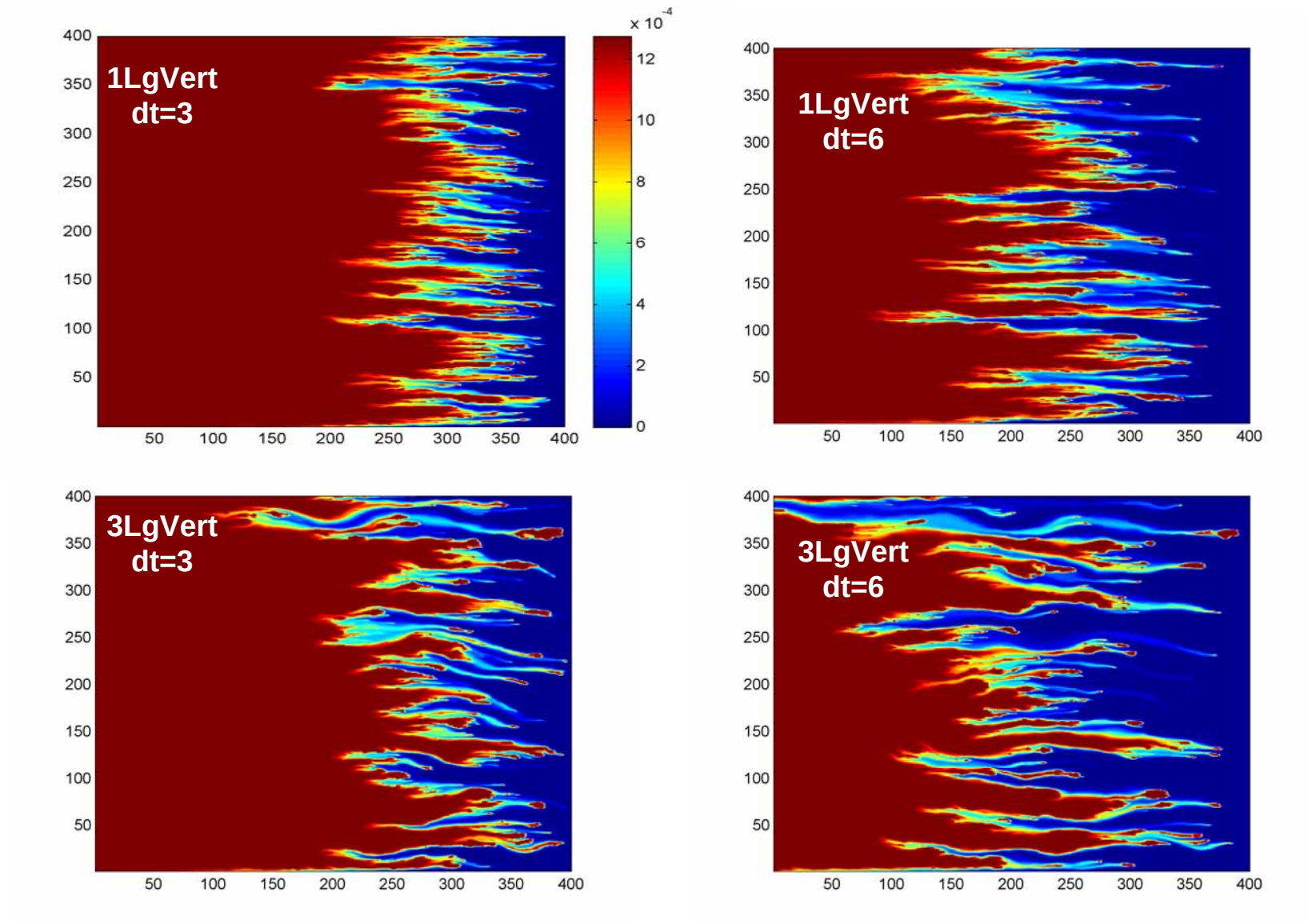
Dissolution Experiment: Simulated Results



Dissolution Fingering Simulation



Fingering in Heterogeneous Systems



Conclusions

- Mobilization can be an effective remediation strategy for residual DNAPL saturations above 2%
- Mass transfer limitations will occur for DNAPL saturations <2%
- Combinations of treatment approaches are an attractive approach

Conclusions

- DNAPL-aqueous phase mass transfer is a complex process that plays an important role in subsurface remediation
- Assuming local equilibrium at the field scale is not a useful approach to modeling the mass transfer process
- Additional guidance is available now, and much better models will be available in the very near future

More Information

- Email: casey_miller@unc.edu
- Johnson Wright et. al. (2010) Journal of Environmental Engineering, 136(5), pp.452-465.
- Johnson Wright et al. (2010) Journal of Contaminant Hydrology, In press.
- Johnson et al. (2004) Environmental Science & Technology, 38(19), pp. 5149-5156.