Investigation of Pore-Scale Processes that Affect Soil Vapor Extraction

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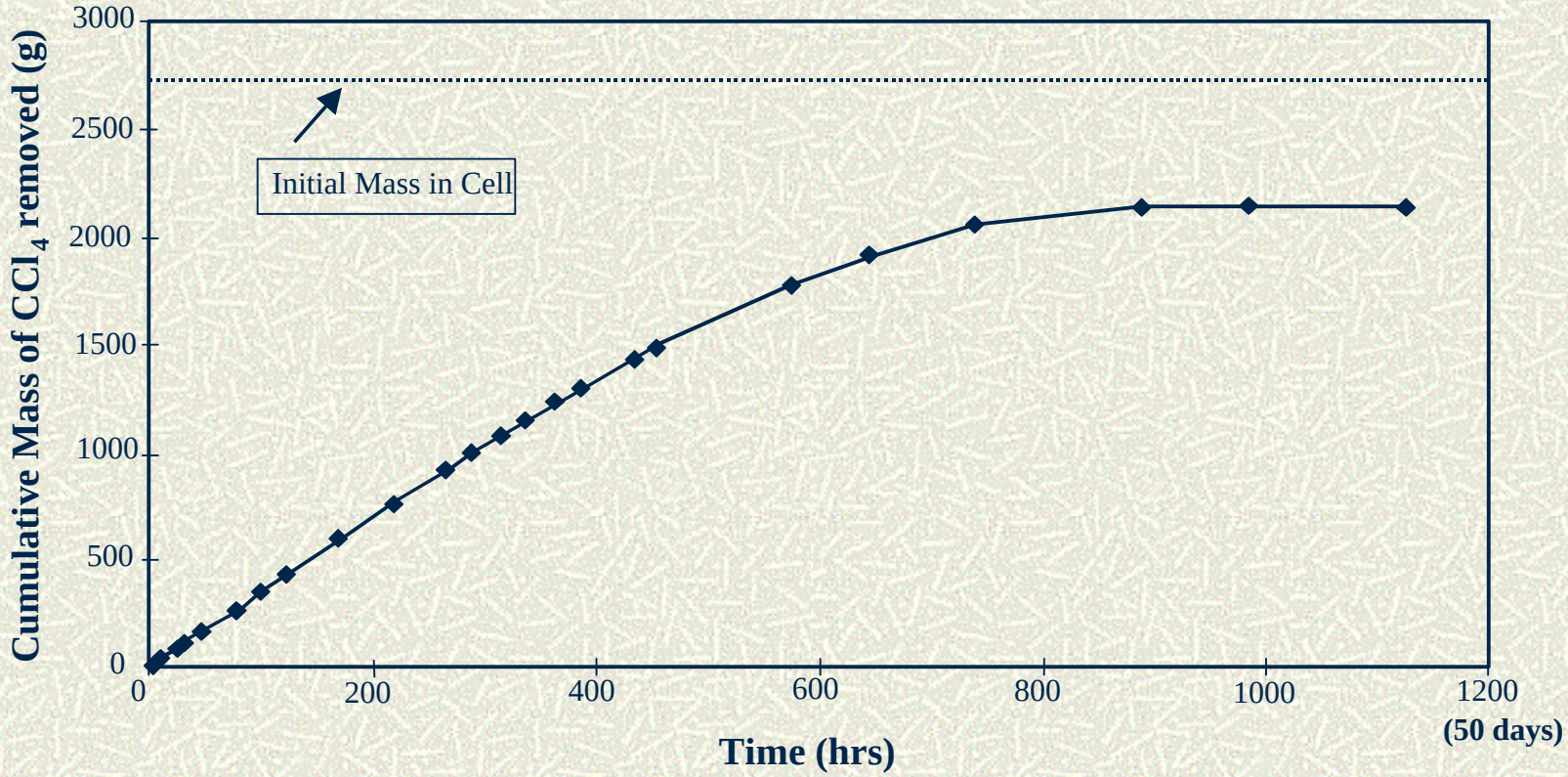
EM Needs and Problem Addressed

- Dense nonaqueous phase liquid (DNAPL) contamination in the vadose zone is a significant problem at Department of Energy sites
  - Chlorinated hydrocarbons identified at over 60% of DOE Facilities (Riley & Zachara, DOE Report, 1992)
  - Approximately 360,000 to 580,000 liters (1.3 to 2 x 10^6 lbs.) of carbon tetrachloride discharged to the vadose zone in the 200-West area at Hanford (Yonge et al.,1996)
  - Approximately 2 x 10^6 lbs. of chlorinated solvents (PCE & TCE) released in M area at the Savannah River Site (Hodges & Falta, 1996)

EM Need and Problem Addressed

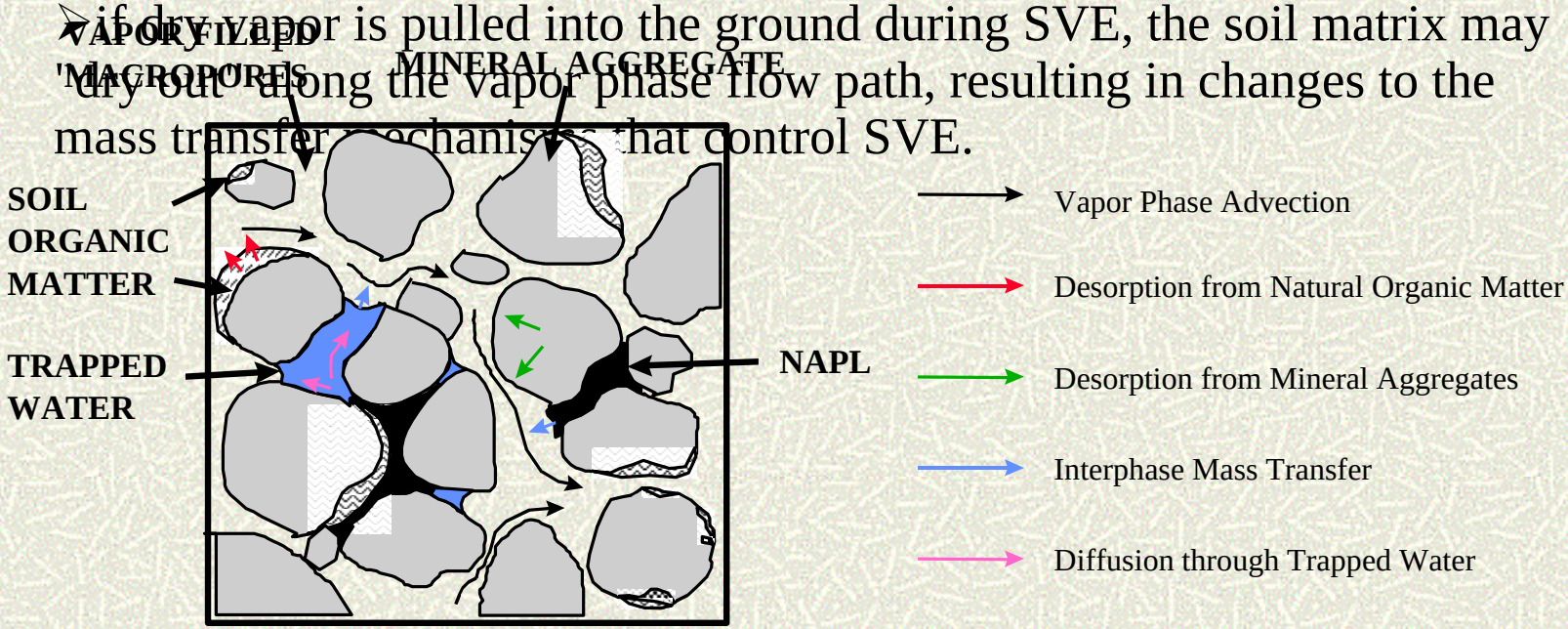
- Soil vapor extraction (SVE) is commonly used to remediate DNAPLs from the vadose zone
  - In most cases, a period of high recovery has been followed by a sustained period of low recovery.
    - This behavior has been attributed to multiple processes including slow interphase mass transfer, retarded vapor phase transport, and diffusion from unswept zones of low permeability.

Sand Box Experiments using Hanford Soils (Yonge, et al. 1996)



Complex Problem

- Processes that control SVE vary at the pore scale and with time
  - if dry vapor is pulled into the ground during SVE, the soil matrix may dry out along the vapor phase flow path, resulting in changes to the mass transfer mechanisms that control SVE.



Research Objective

- Determine the pore-scale processes that limit the removal of DNAPL components in heterogeneous porous media during SVE. More specifically:

  – determine the effect of unswept zones on DNAPL removal during SVE

  (2) determine the effect of retarded vapor phase transport on DNAPL removal during SVE

  (3) determine the effect of interphase mass transfer on DNAPL removal during SVE

  -- all as a function of changing moisture and DNAPL content.

Approach

- Batch and Column Studies of Vapor-Phase Sorption

  -Investigate the impact of relative humidity upon vapor phase retardation and slow desorption

- Magnetic Resonance Imaging (MRI)

  -Observe and quantify the location and size of individual pores containing DNAPL, water, and vapor in flow through columns filled with model and natural sediments

Approach

- Numerical Modeling

  -Develop spatially and temporally dependent constitutive relations that describe the transient distribution of phases inside a column experiment, and the effects of these phase distributions on mass transfer

  -Incorporate constitutive relations into a site-scale transport model to evaluate how the different processes affect SVE performance in practical applications.

Research Activities

ACTIVITY	DATE
Awarded EMSP project	September 1999
Developed algorithm to analyze MRI data	January 2000 through May 2000
Began measuring sorption isotherm and desorption kinetic profiles for a silica gel and a sand	July 2000
Began MRI experiments using a silica gel	August 2000
Began developing SVE code to analyze SVE experiments	September 2000

Vapor Phase Sorption Method

- Isotherm method

  -Measure sorption isotherms on a silica gel and a sand at 0% and 100% relative saturation (RS)

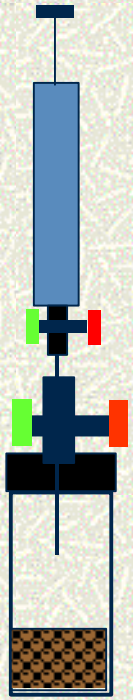
  -Determine sorption at intermediate RSs using the method of Unger et al. (ES&T, 1996)

  $$-q_{SORB} = f_V * q_{SV} + (1-f_V) * q_{SL}$$

  f_V = fraction of soil surface exposed to vapor phase

  q_{SV} = sorbed concentration at 0% RS

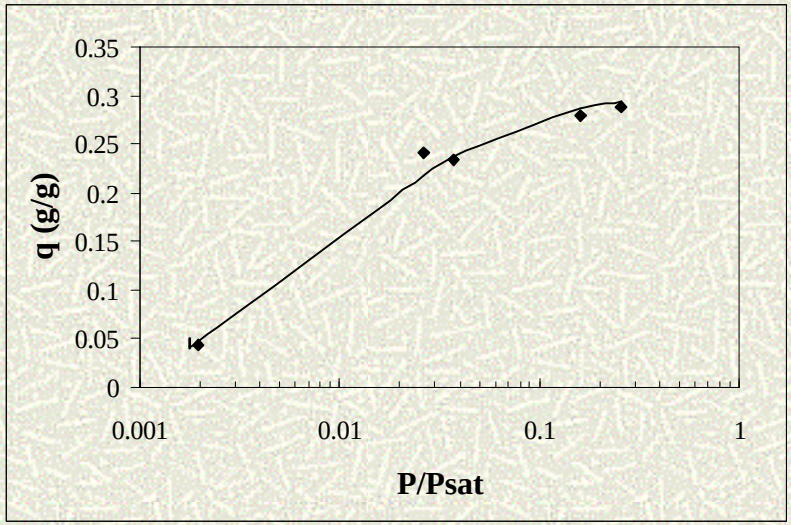
  q_{SL} = sorbed concentration at 100% RS



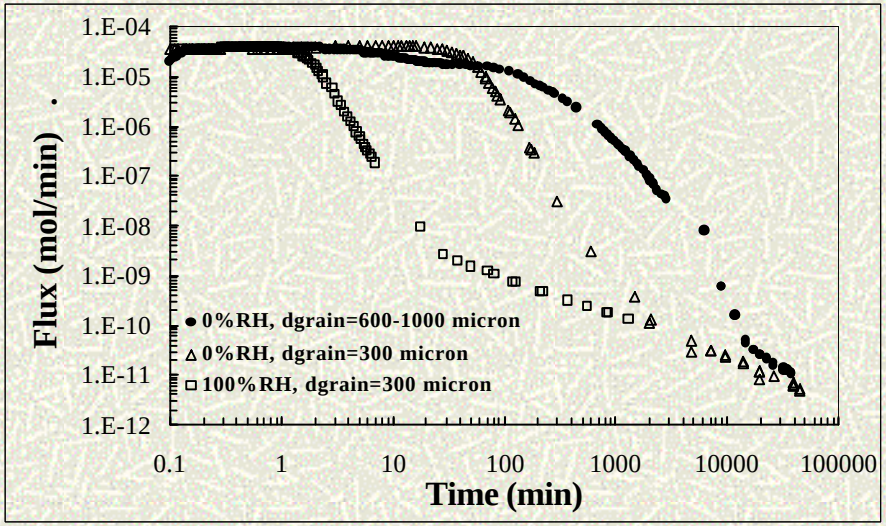
Vapor Phase Sorption Method

- Kinetic method
  - -Measure kinetic desorption profiles for a silica gel and a sand at relative saturations between 0 and 100%
  - -Fit the data with a two-site model
  - -Determine if fast desorption:
    - -can be treated as an equilibrium process
    - -can be predicted using the measured isotherms
  - -Determine if slow desorption:
    - -can be approximated using a first order rate process
    - -comprises a larger fraction of the desorbing mass with decreasing RH
    - -becomes slower as the relative humidity decreases

Results - Vapor Phase Sorption



Measured and best fit Langmuir Isotherm for TCE and silica gel at 0% RS



Desorption flux profiles for TCE from silica gel at 0% and 100% RS

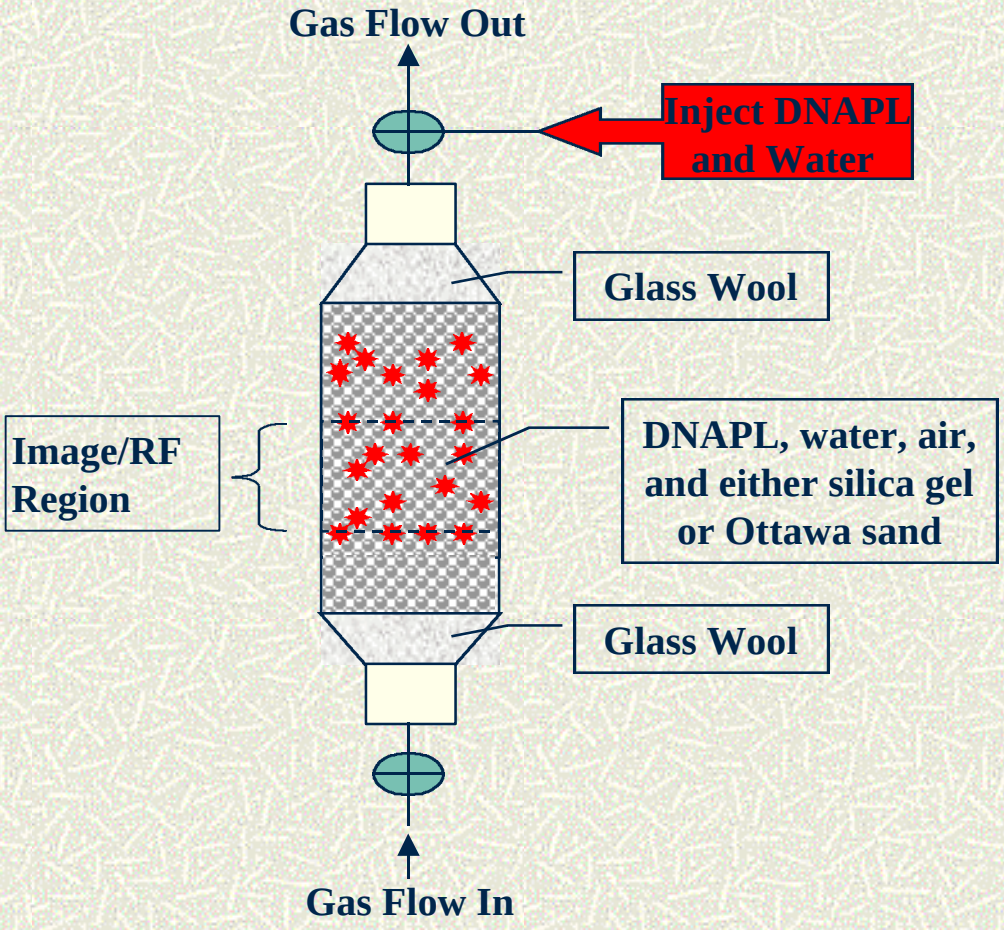
MRI Method

- Noninvasive method that allows us to take snapshots of in situ processes
  - 3D Images at pore scale resolution (voxels~60 μm^3)
    - 16×10^6 voxels in a 3-D image
  - Excite nuclear spins in RF region
  - 3D saturation-recovery spin-echo imaging sequence
    - Water is doped with $CuSO_4$ and DNAPL is doped with $Cr(acac)_3$ to reduce the T1 relaxation time
  - Signal intensity based on density of nuclei - more nuclei, stronger signal
    - ^1H imaging for water, ^{19}Fl imaging for DNAPL

MRI Method - ^{19}Fl DNAPL Evaluation

Property	Carbon Tetrachloride	Trichloroethene	1,3,5-Tri-fluorobenzene	1-Fluoropentane
Melting point (ºC)	-23	-85	-5.5	< 15
Boiling point (ºC)	77	87	76	63
Aqueous solubility (g/L)	1.8	1.4	0.37	0.28
Henry's constant (-)	1.2	0.42	0.010	2.3
Octanol-water solubility (-)	676	245	186	209

MRI Method – Column Set-up



Results - ^{1}H Imaging of Water

2-D slices from 3-D images of a flow-through column

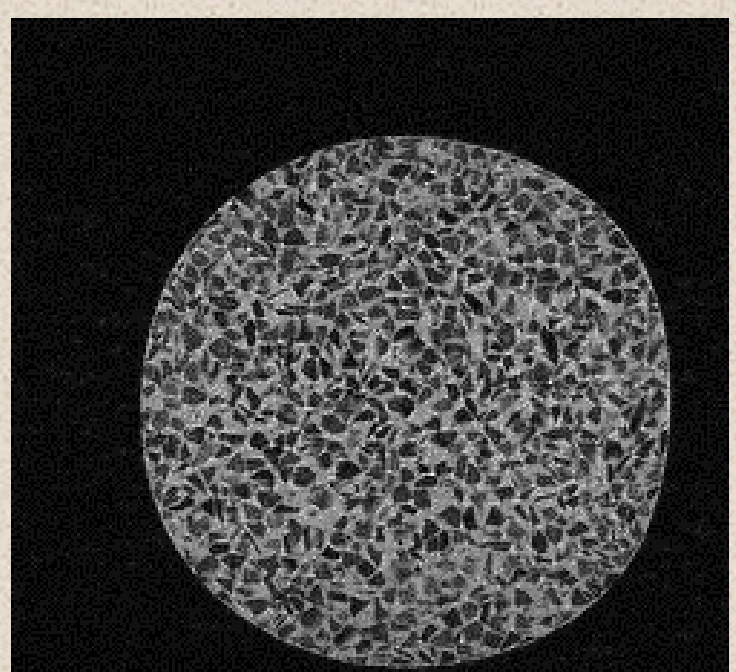


Image of Water Between Silica Gel Grains

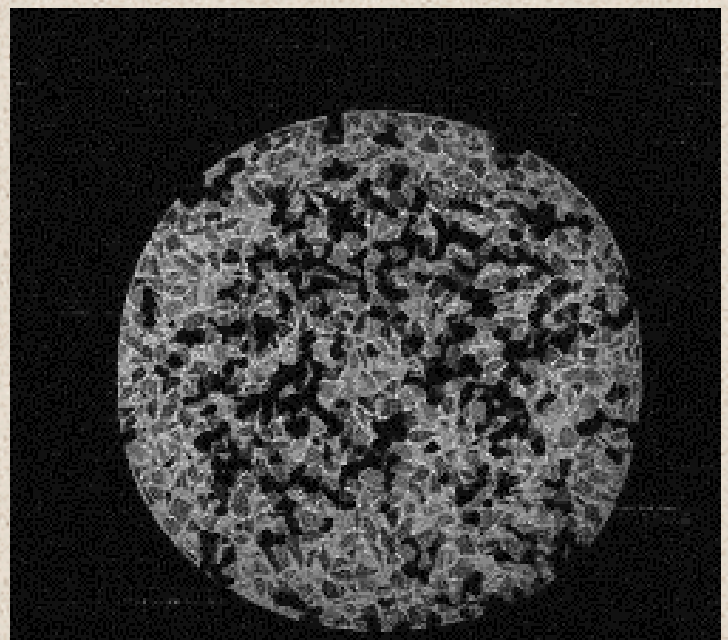
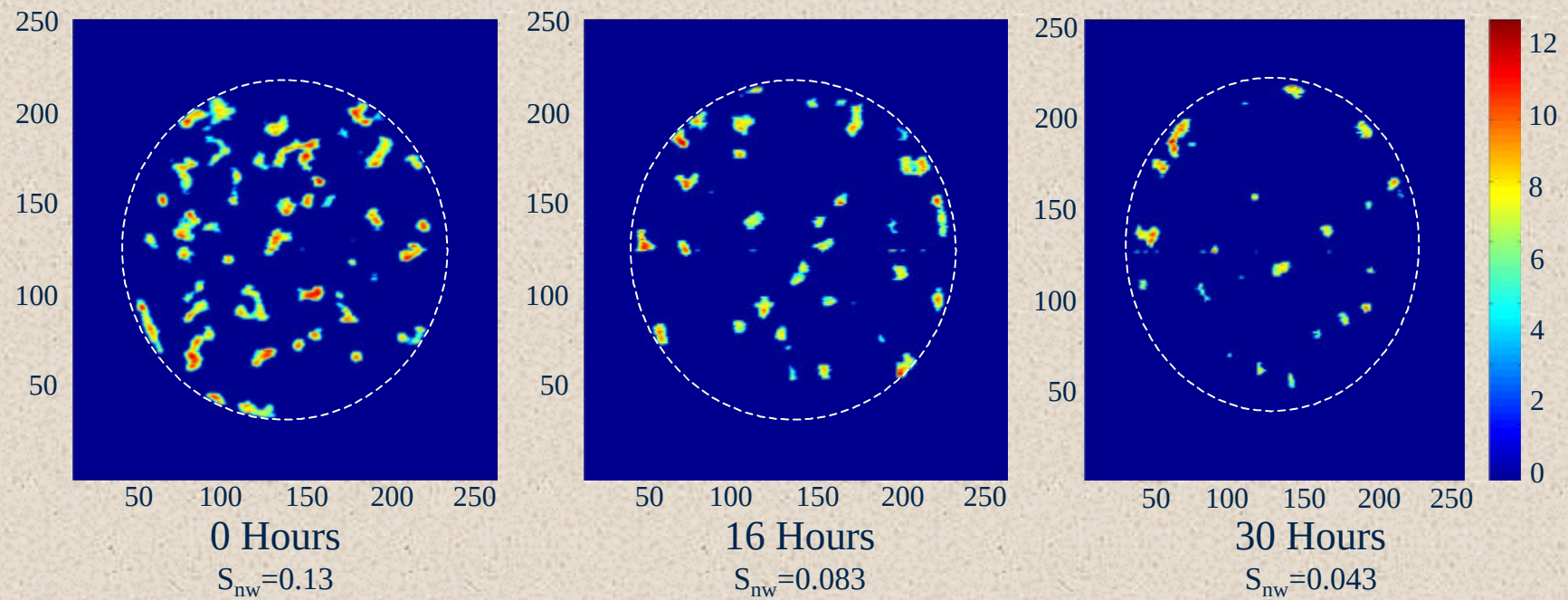


Image of Water Between Silica Gel Grains in the Presence of DNAPL

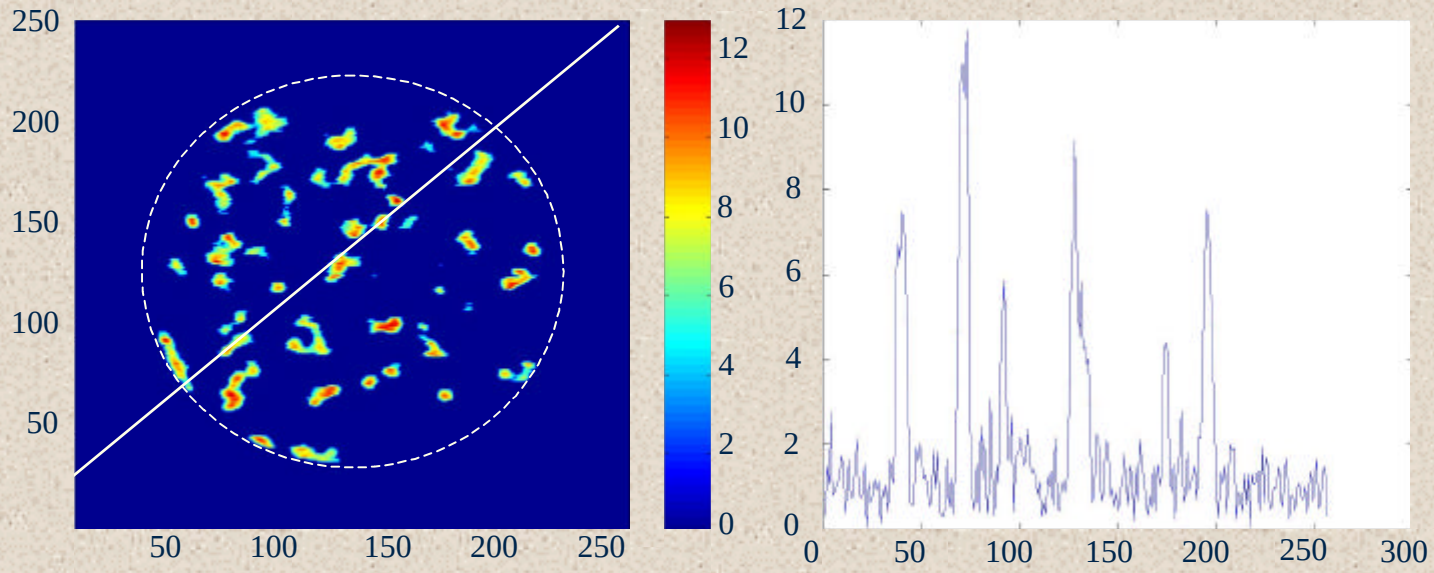
Results – ^{19}Fl Imaging of DNAPL

- 2-D Slices from 3-D Images Taken at Selected Time Intervals During DNAPL Dissolution



Results – MRI Analysis

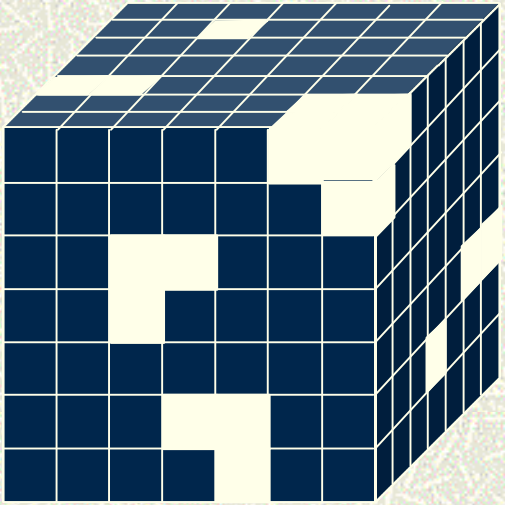
- MRI images contain 16 million voxels that span 256 gray scales
- DNAPL blobs are associated with voxels that are above some threshold value



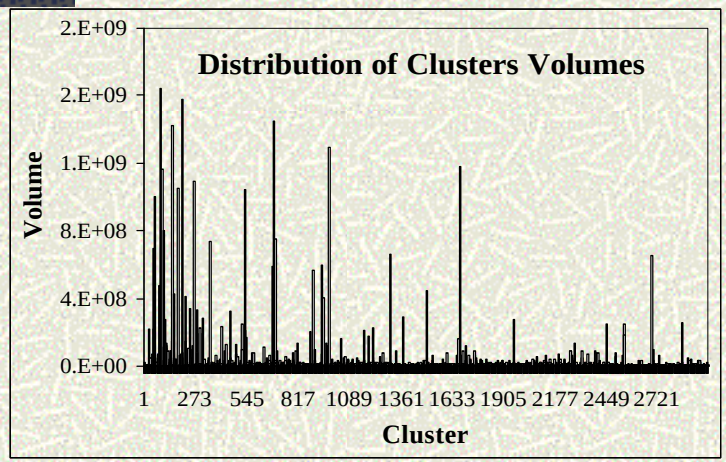
2D slice of residual DNAPL **Signal intensity along a line**

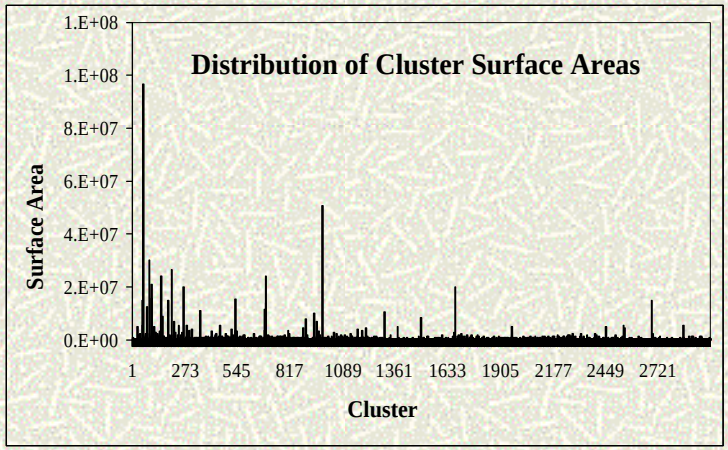
Results – MRI Analysis

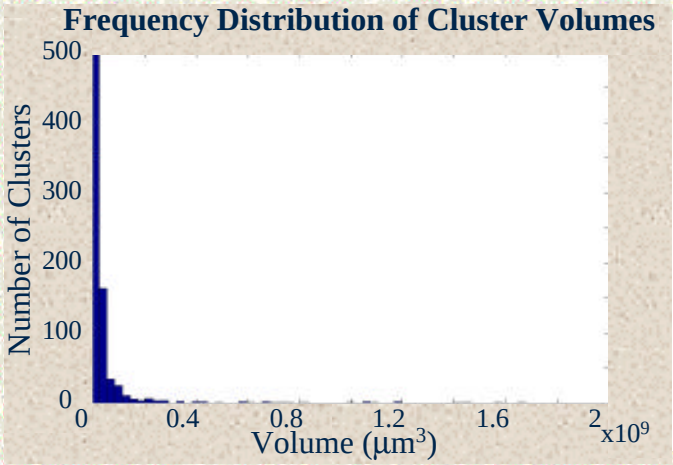
- A computer algorithm was developed that:
  - Identifies all voxels above some minimum signal intensity
  - Uses nearest neighbor arguments to identify clusters of voxels above the minimum signal intensity
  - Calculates the surface area and volume of all clusters (i.e. of all DNAPL blobs)

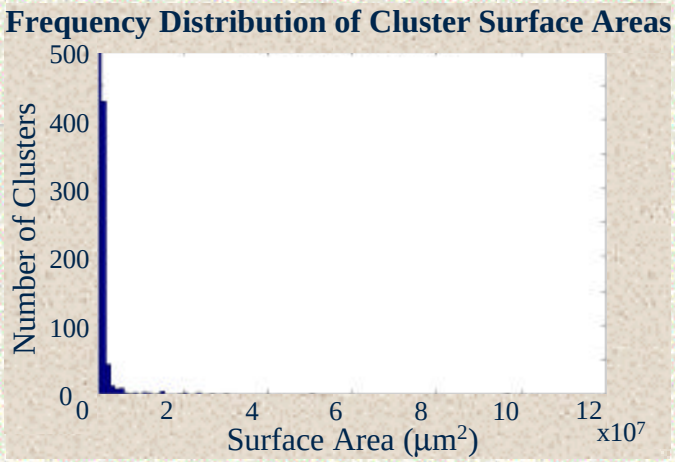


Results –Surface Area and Volume Distributions of DNAPL Blobs





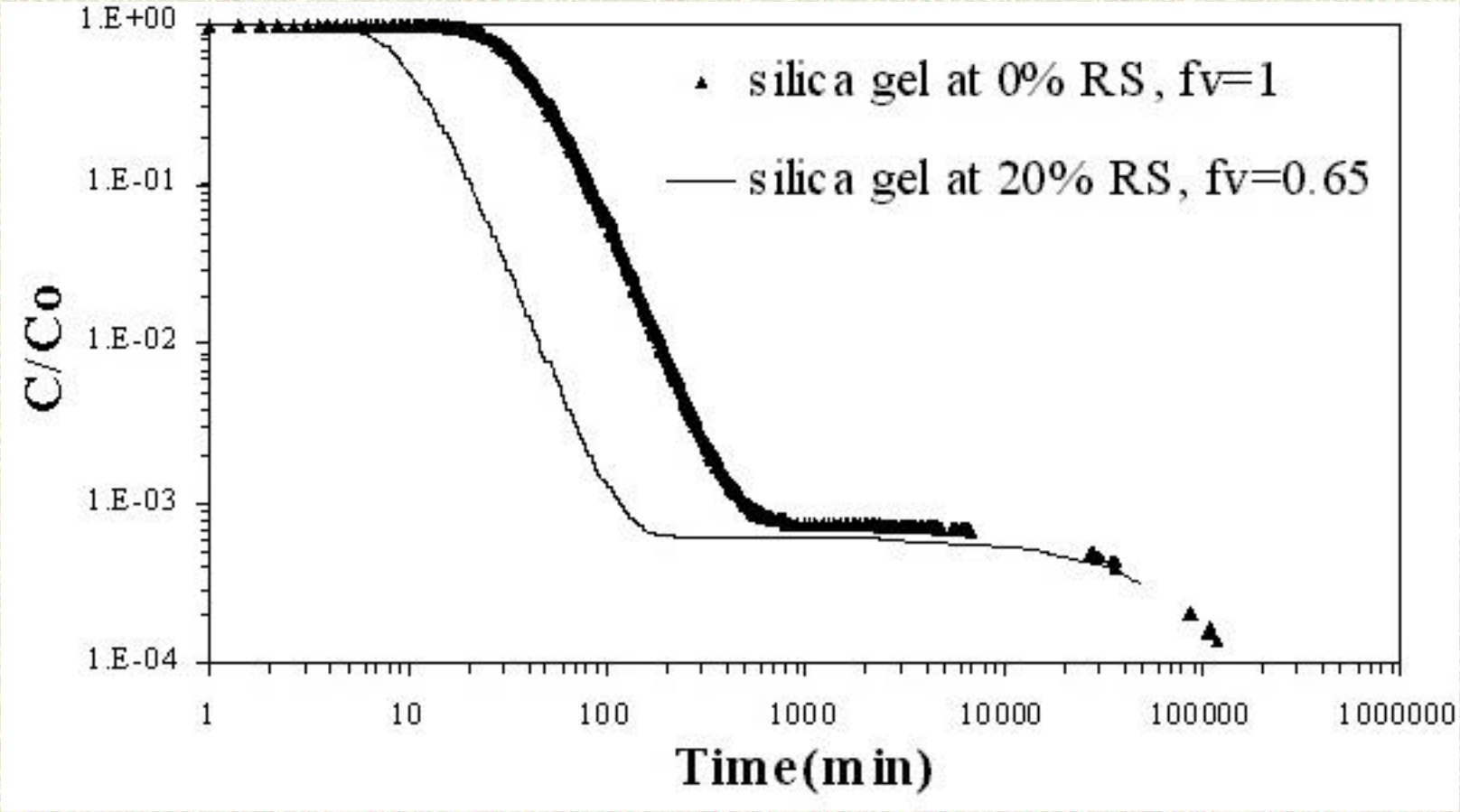




Modeling Method

- Develop 1-D transport model to analyze SVE experiments under uniform water saturated conditions
  - Account for advection, dispersion, sorption, interphase mass transfer
    - Evaluate the effects of relative saturation on sorption
    - Evaluate the effects of water saturation and DNAPL surface area on interphase mass transfer
- Develop 3-D transport model to analyze SVE experiments when the relative saturation changes in space and time.
  - Account for advection, dispersion, sorption, interphase mass transfer
  - Evaluate the effects of spatially and temporally varying water saturation on sorption and interphase mass transfer

Results - Modeling



TCE desorption profiles for silica gel under dry and partially wet conditions

Benefits to DOE

- Improved understanding of pore-scale processes
- Improved engineering models of long-term performance of SVE systems
- Improved assessment of uncertainty of long-term DNAPL removal
- Establishment of realistic treatment goals and better assessment of long-term risk

Future Plans

- Continue to measure isotherm and desorption kinetic profiles at different relative saturations
- Begin to measure SVE efficiency at different water & DNAPL saturations using MRI
- Develop double tuned radio frequency coil for simultaneously imaging water (^{1}H) and DNAPL (^{19}Fl)
- Continue to refine 3D image analysis algorithm to evaluate spatial and temporal variability
- Continue with mathematical model development

- *Would like to get core samples of unsaturated Hanford sediments*