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Investigation of Pore Scale Processes That Affect Soil Vapor Extraction

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Number of Graduate Students: 1 ½
Number of Post-Docs: 1

Research Objective: Dense nonaqueous phase liquid (DNAPL) contamination in the vadose zone is a significant problem at Department of Energy sites. 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.

Prior attempts to uncouple and quantify these processes have relied on column experiments, where the effluent concentration was monitored under different conditions in an effort to quantify the contributions from a single process. In real porous media these processes occur simultaneously and are inter-related. Further, the contribution from each of these processes varies at the pore scale and with time.

This research aims to determine the pore-scale processes that limit the removal of DNAPL components in heterogeneous porous media during SVE. The specific objectives are to: 1) 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, and 3) determine the effect of interphase mass transfer on DNAPL removal during SVE, all as a function of changing moisture and DNAPL content. To fulfill these objectives we propose to use magnetic resonance imaging (MRI) to 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. Imaging results will be used in conjunction with modeling techniques to develop spatially and temporally dependent constitutive relations that describe the transient distribution of phases inside a column experiment. These constitutive relations will be incorporated into a site-scale transport model to evaluate how the different processes affect SVE performance in practical applications. This will allow decision makers to better assess the risk associated with vadose zone contamination and the effectiveness of SVE at hazardous waste sites.

Research Progress and Implications: This report summarizes progress after approximately one year of work. An M.S. student began work on the project in June of 2000. In August of 2000 a post-doc and a Ph.D. student began work on the project. The post-doc and Ph.D. student are fully supported by the project; the M.S. student is partially supported by the project. Over the past year the post-doc has focused on developing the flow-through column and magnetic resonance imaging techniques to image the soil vapor extraction of nonaqueous phase liquids at different water contents. In the Fall of 2000 the post-doc designed and built a flow-through column that fits into our MRI spectrometer. With the flow-through column he investigated how flow rate, grain size, and relative humidity affect the water content in the column over time. In most cases silica gel was used as a model sand because this solid facilitates magnetic resonance imaging. In the Fall of 2000 the post-doc also began testing different NAPL compounds. The choice of NAPL is critical, as it must volatilize over a time period that is long enough to capture multiple MRI images (>1 day) and short enough to avoid unreasonably long experiments (<3 days), it must have wetting properties similar to common NAPLs found at Department of Defense sites, and it must be distinguishable from water using MRI. Table 1 details some of the chemicals evaluated, and the conditions under which they were tested.

Table 1: NAPL volatilization in columns.

Exp.	Chemical	Porous Media	Particle Size (mm)	N_2 Purging for Driving Free NAPL Out: Rate(cm min^{-1}), Time	Fraction of Pores Occupied by NAPL	N_2 Purging Rate (cm min^{-1})	Time Required to Vaporize
1	Trichloroethylene (TCE)	Silica Gel	0.6-1.0	7.8, 13.00 hr	3%	7.8	26 min
2	TCE	Silica Gel	0.6-1.0	7.7, 2.08 hr	12%	7.7	2.3 hr
3	Trifluorobenzene	Silica Gel	0.6-1.0	7.8 , 0.72 hr	1%	7.8	15 min
4	Trifluorobenzene	Silica Gel	0.5-0.6	1.1, 0.25 hr	3%	1.1	9.13 hr
5	Trifluorobenzene	Silica Gel	0.354-0.425	1.1, 0.25 hr	4%	1.1	11.68 hr
6	3-(trifluoromethyl)benzyl bromide*	Silica Gel	0.25-0.55	1.1, 0.33 hr	N/A	7.6	309 days
7	Decane	Glass Bead	0.25	3.7, 0.51 hr	16%	7.6	3.65 days
8	Tetradecane*	Silica Gel	0.25-0.55	1.0, 0.52 hr	N/A	7.6	303 days
9	Tetradecane*	Silica Gel	0.25-0.55	1.0, 0.52 hr	N/A	86.1	34.6 days

* Estimated based on vapor phase effluent concentrations from columns.

As noted, decane volatilized in a time frame that was convenient for our experiments. Like tetrachloroethene and, in part, trichloroethene, decane also became trapped as discrete ganglia in silica gel and glass beads. This is in contrast to fluorinated DNAPLs tested, that formed thin films (that were too thin to be detected with MRI) around silica gel grains.

In the Spring of 2001 the post-doc began developing the MRI pulse sequences necessary to distinguish decane from water. He is currently optimizing an inversion-recovery, spin-echo pulse sequence that allows us to detect either decane or water depending on the inversion time selected. For example, if $Ti=0.65*T1_{water}$, only decane is detected, and if $Ti=0.65*T1_{decane}$, only water is detected. Our initial images show that we can distinguish water from decane. However, our current images take too long to acquire so we are exploring ways to decrease our acquisition time.

Over the past year the post-doc has also worked with another Ph.D. student to develop Matlab algorithms to analyze 3D MRI results. In the Spring of 2000 we developed an algorithm that allows us to take a 3D data set (that consists of 16 million voxels) and determine the number, volume, surface area, and location of every NAPL blob in a column. This past year we developed algorithms that allow us to categorize blob sizes in a column, and in different sections of the column, and to display these blob categories for multiple data sets collected over time. Output from these algorithms is shown in Figure 1.

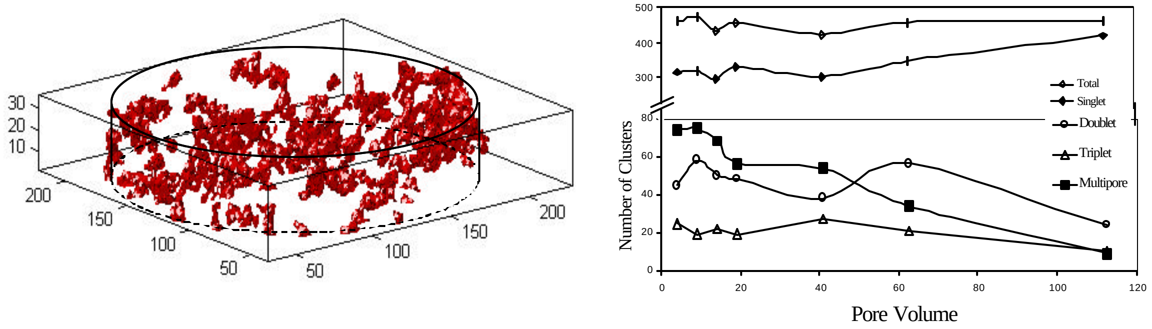

Figure 1. a) 3D MRI image of a DNAPL trapped in water saturated silica gel. b) Categorization of blob sizes (i.e., clusters) in a column as a function of the number of pore volumes of water flushed through the column.

Over the last year the M.S. student has focused on measuring the sorption isotherms and desorption kinetic profiles for the materials that we are using in the imaging experiments. Thus far she has contaminated and desorbed duplicate columns of silica gel and Ottawa sand under dry and moist (i.e., 100% relative humidity) conditions for both 30 and 1 day equilibration times. As shown in Figure 2a, TCE desorbs faster from the moist columns than from the dry columns. Also much more TCE sorbs to the silica gel than to the Ottawa sand. In Figure 2b, the equilibrium time has no effect on initial desorption of TCE from moist silica gel. However, it does marginally affect the tailing portion of the TCE desorption profile. The M.S. student has also measured isotherms for TCE on dry silica gel this past semester. Over the next year she will measure isotherm and desorption kinetic profiles for silica and Ottawa sand under different moisture conditions.

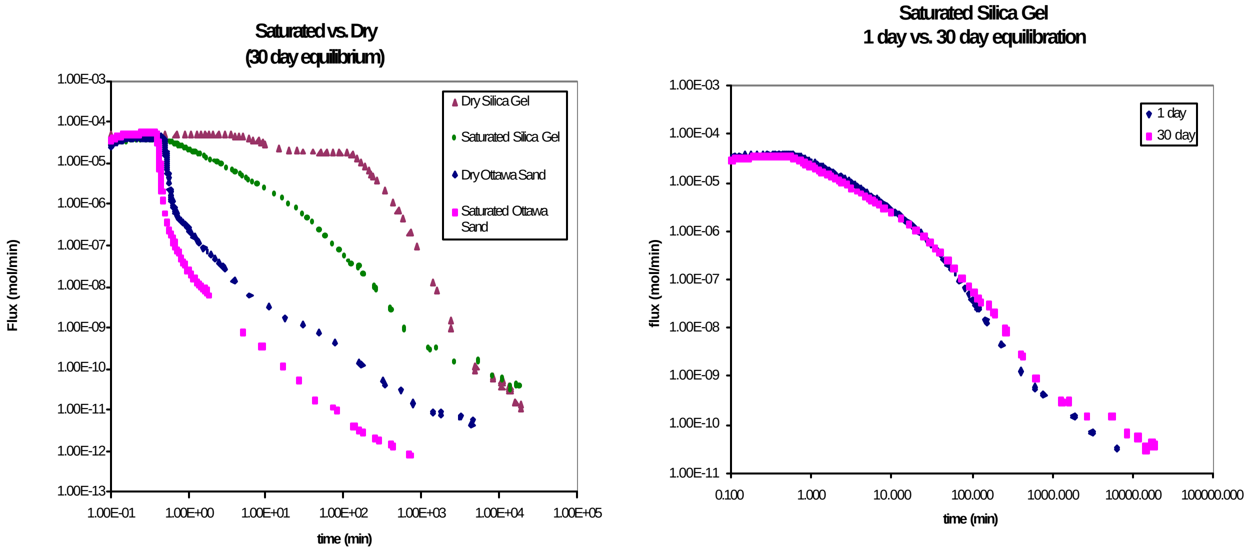

Figure 2. TCE desorption profiles for silica gel and Ottawa sand a) equilibrated for 30 days under dry and moist (i.e., saturated) conditions and b) equilibrated for 1 or 30 days under moist conditions.

The Ph.D. student who started in September 2000 is responsible for mathematical modeling. The student has developed a one-dimensional model that incorporates the following processes: (a) advection and dispersion of vapor-phase contaminants; (b) equilibrium or mass-transfer controlled sorption and desorption onto the aquifer solids; (c) equilibrium partitioning into the water phase; (d) mass-transfer limited volatilization of the separate NAPL phase. These processes are shown schematically in Figure 3, where f_w is the fraction of sorption from the aqueous phase, f_{sveq} is the fraction of equilibrium-controlled sorption from the vapor phase, and f_{svmt} is the fraction of mass-transfer controlled sorption from the vapor phase. A finite element method is used to obtain a numerical solution to the model. The numerical solution algorithm has been verified against known analytical solutions.

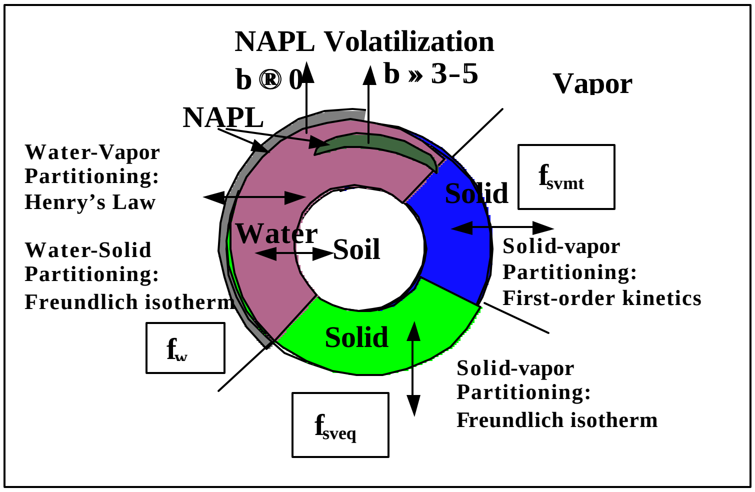

Figure 3. Conceptual model of mass transfer processes during SVE.

NAPL volatilization is typically described by a linear driving force model with a lumped mass-transfer coefficient. A unique aspect of our model is that we modify the mass-transfer to account for the impact of water saturation upon transient NAPL volatilization. A power function model, $k_o=k_{o,i}(S_{NAPL}/S_{NAPL,i})^{\beta}$ (subscript i represents an initial value and S_{NAPL} is NAPL saturation), for the lumped mass transfer coefficient is used where the exponent term, β, is a function of water saturation. We tested our model with experimental data from the literature and found that β ranged from near zero for low water contents to values approaching 5 for higher water contents. In unsaturated soils water preferentially occupies the smallest pores, filling pore bodies and creating water films along soil particles. At relatively low water saturation, NAPL may form continuously thin films along air-water interfaces, depending upon the spreading properties of the contaminant. The thin film of NAPL provides a large interfacial area for NAPL volatilization and a large mass transfer coefficient ($\beta \approx 0$). At high water saturations, however, a large portion of the entrapped NAPL may become isolated within pore throats or between water wedges, resulting in a significant decrease of the interfacial area between the NAPL and gas phase, thus limiting accessibility of the nonwetting gas phase to the NAPL. As a result, diffusion of NAPL through the interparticle and immobile water into vapor phase must occur before volatilization ($\beta = 3 \sim 5$), as indicated above in Figure 3.

Illustrative results from the one-dimensional model are shown in Figure 4. For the case where NAPL volatilization is not hindered by soil water (â =0) and all the desorption is equilibrium-controlled (f_w=1), the contaminant is rapidly removed from the system (blue curve in Figure 4). When slow mass-transfer controls desorption (f_{svmt}=1), long tailing results following initial rapid volatilization of the NAPL (green curve in Figure 4). When the value of â is high (=4.0), NAPL volatilization is significantly hindered by high water saturation. This results in a dramatic increase in the tailing effect.

Planned Activities: The post-doc is working to optimize the MRI pulse sequence for detecting decane and water. We expect to complete this work in the next several months, at which time the post-doc will start to image soil vapor extraction experiments under different flow, grain size, and moisture conditions. The M.S. student is currently measuring desorption kinetic and isotherm profiles under moisture conditions not yet tested. By next year we plan to complete all the necessary sorption experiments for this project. The Ph.D. student will continue to enhance the model, and he is currently working on adding water evaporation and temperature effects. The model will eventually be extended to multiple dimensions, and be applied to the desorption and MRI experiments.

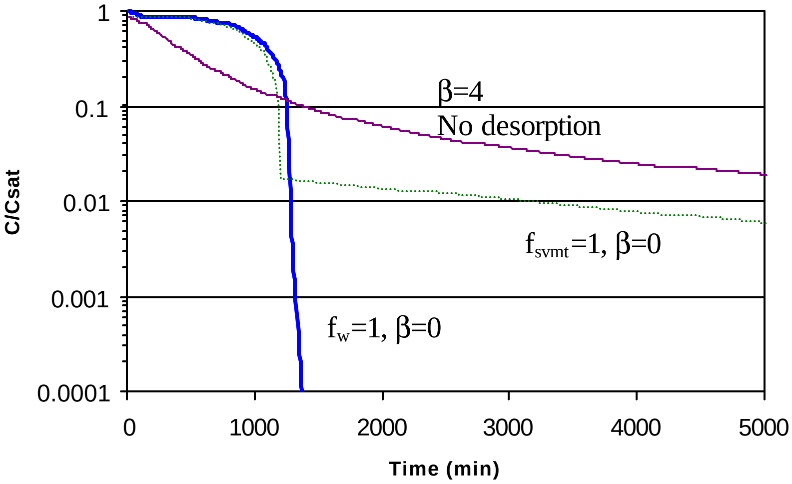

Figure 4. Numerical modeling results showing the effect of mass transfer and water saturation on the vapor-phase effluent concentration in a one-dimensional column.