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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 research activities and findings during the last year. During this time an M.S. student, a Ph.D. student, and a post-doc worked on the project. The M.S. student was supported as a teaching assistant, while the Ph.D. student and post-doc were fully supported by the project.

Over the past year the post-doc optimized a pulse sequence to image decane in unsaturated flow-through columns, and imaged decane volatilization from six different columns (denoted column 1 through 6) packed with two different silica gel grain sizes (32-63 ìm and 250-550 ìm). Decane was chosen because it is amenable to imaging, its spreading coefficient is less than 1, and it volatilizes in a reasonable time period. Silica gel was used because it contains no ferromagnetic components that interfere with MRI. The pulse sequence used is an inversion recovery sequence that can selectively excite decane in the presence of water. To successfully employ this sequence, water was doped with 2.5 g/L $CuSO_4$ to decrease its relaxation time relative to decane.

Of the six column experiments performed, five were packed with a core-and-shell structure (i.e., a 1 cm core of one grain size surrounded by a 1 cm thick shell of another grain size) and one was packed with only the coarse-grain silica gel. Different methods were evaluated to contaminate the heterogeneous columns. After testing we settled on two approaches that allowed us to control the amount of decane in the different sections of the columns. After the desired decane saturation was achieved in each column, they were purged with water saturated nitrogen gas at 16.4 ml min^{-1}. Stainless steel and Teflon tubing were used throughout the system. Effluent samples and images were taken periodically. Outflow concentrations were measured using a gas chromatograph (GC).

The mass of decane remaining in each column was calculated based on effluent concentrations (via GC) and plotted vs. the MRI signal intensity in Figure 1. Results show a linear relationship, indicating that the MRI signal intensity is linearly correlated to the amount of decane trapped in the columns.

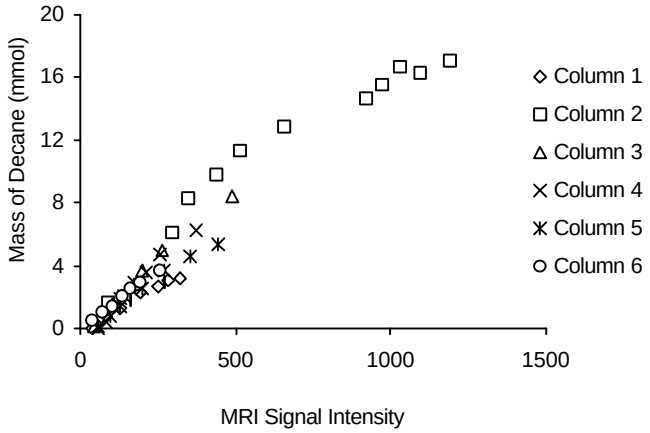

Figure 1. Mass of decane remaining in a column versus MRI signal intensity.

The change in total signal intensity and the column effluent concentration with time are shown in Figure 2 for columns 2 and 6. An example of images obtained are shown in Figure 3.

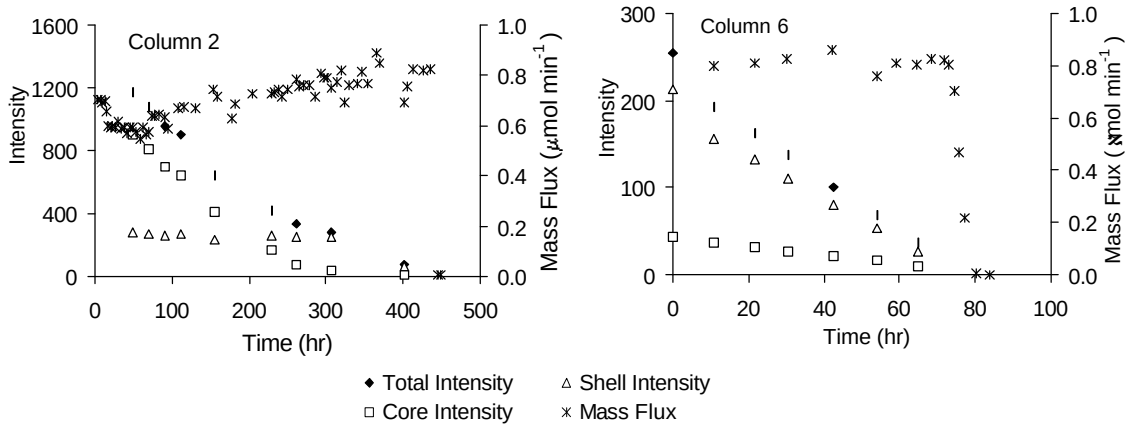

Figure 2. MRI intensity and mass flux from columns 2 and 6 during column puring.

In column 2, decane was present at higher than residual saturation in the fine-grain core, and at or close to residual saturation in the coarse-grain shell. As shown, decane was primarily lost from the fine-grain core before 307 hr, and this loss was uniform along the core length. After this time decane was lost from the coarse-grain shell. We believe that air flows through the coarse-grain shell during column purging; air is restricted from flowing through the fine-grain core at high decane saturation. Hence, it appears counter intuitive that decane is lost from the fine-grain core first. This suggests that when decane is present at higher than residual saturation in the core, but not in the shell, decane flows (i.e., spreads) to the coarse shell during volatilization. It is important to note that decane in the fine-grain core is not lost over a period of several days if the column is not purged. Hence, purging the column increases the difference in matrix potential between the core and the shell and flow occurs.

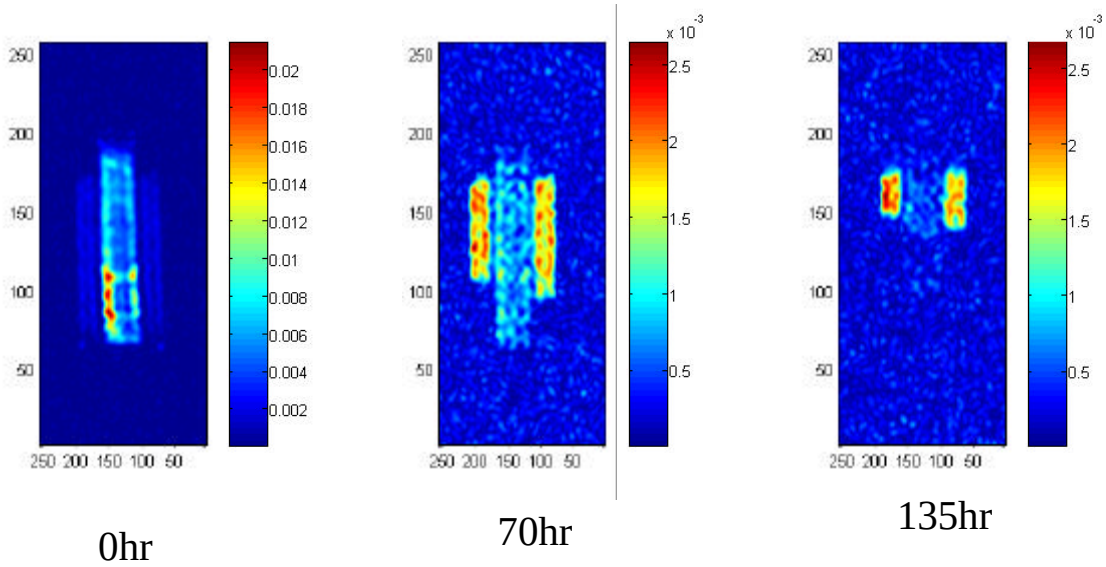

Figure 3. MRI intensity from column 3 at different times during decane volatilization. Color bars represent signal intensity which directly correlate to decane mass.

In column 6 decane was present at residual saturation in both the fine-grain core and the coarse-grain shell. In contrast to column 2, (~100% in the fine core) decane was simultaneously lost from both the core and the shell during column purging. Also, imaging results showed that the mass transfer zone for

decane volatilization was much smaller than the column length, resulting in a sharp transition zone from the clean part of the column to the part of the column at residual saturation. Over time this transition zone moved down the column until the entire column contained no more pure phase decane. This result also appears counter-intuitive because we believe that flow through the coarse-grain shell is much faster than flow through the fine-grain core. However, Peclet numbers in the columns are on the order of 1. This suggests that when advective flow causes decane to volatilize from the shell decane from adjacent region in the core diffuses into the shell causing volatilization in the core.

Results from other columns showed similar trends and are not presented in the interest of space. Results from columns 2 and 6 are important because they indicate that mass transfer from unswept zones can be significant either because of spreading from low to high permeability regions, or because of diffusion.

Over the last year the M.S. student measured sorption isotherms and desorption kinetic profiles for the materials (i.e., silica gel and Ottawa sand) that we are using in the imaging experiments. For the desorption kinetic profiles she used two different equilibration periods (1 and 30 days), and she used materials at 0, 7, 30, and 100% relative humidity. These profiles indicate that increasing relative humidity decreases both the amount of fast and slow desorbing mass. However, between different materials the effects of relative humidity on the amount of slow desorbing mass are not uniform, indicating that competition between water and trichloroethene for sorption sites depends on the surface and pore properties of each material.

The Ph.D. student is responsible for mathematical modeling. A one-dimensional model has been developed that incorporates the following processes: (a) advection and dispersion of vapor-phase contaminants; (b) equilibrium or mass-transfer controlled desorption from the aquifer solids; (c) equilibrium partitioning into the water phase; (d) mass-transfer limited volatilization and dissolution of the separate NAPL phase. These processes are shown schematically below in Figure 4, where f_{weq} is the fraction of sorption from the aqueous phase, f_{veq} is the fraction of equilibrium-controlled sorption from the vapor phase, and f_{mt} is the fraction of mass-transfer controlled desorption from the solid phase. As discussed in our last report, a unique aspect of our model is that we use a power function model for the lumped mass transfer rate to account for the impact of water saturation upon transient NAPL volatilization.

If incoming air is dry (much less than 100% relative humidity), water evaporation may occur, resulting in a change in soil temperature and a decrease of water saturation. NAPL volatilization also results in a temperature decrease. Therefore, we have coupled our contaminant transport model with a one-dimensional water and thermal energy balance model. As water saturation decreases due to evaporation, the fraction of the retarded vapor transport (f_{veq}) increases in accordance with experimentally-derived data in the literature. As temperature decreases due to water and NAPL evaporation, the rate of slow desorption (k_{ws}) will also decrease since it is expressed as a function of temperature using the Arrhenius relationship. Other contaminant properties such as saturated vapor pressure (P_{sat}), Henry's Law constant (H_{cc}) and Solubility (C_{sol}) are also affected by the change in temperature, as illustrated in Figure 4. The coupled model is solved using numerical solution algorithms that have been verified against known analytical solutions.

The coupled model is used to investigate the effect of temperature and water saturation changes on SVE cleanup time. Illustrative results for a five-meter long system with a relatively low water saturation are shown below in Figure 5. Table 1 indicates the parameter values for each of the cases plotted in Figure 5. Examination of the various cases reveals that the most significant temperature effect is its influence on the slow desorption mass transfer process (e.g. compare cases 1, 2 and 4). For the sake of brevity, we do not discuss other cases in detail here.

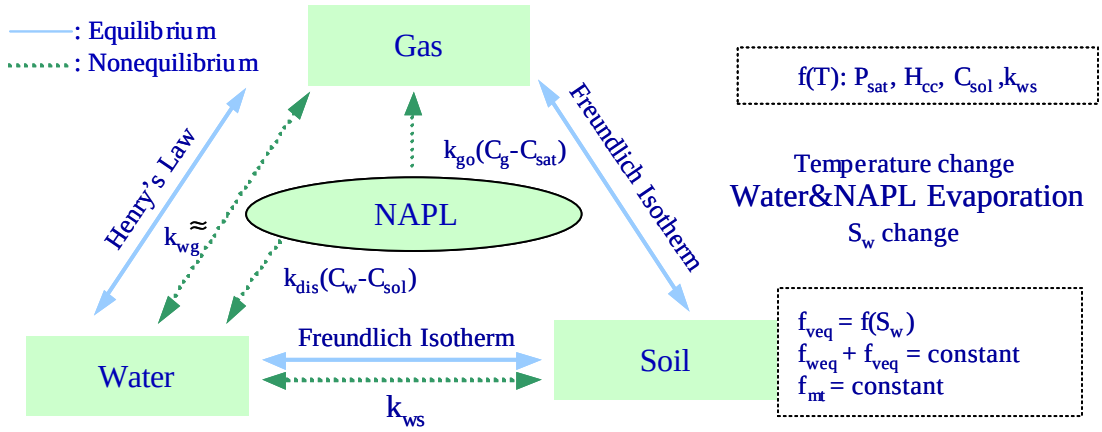

Figure 4. Conceptual Model of Mass Transfer Processes and the Impact of Water and NAPL Evaporation during Soil Vapor Extraction.

Table 1. Simulation cases at low S_w

	q (m/d)	Evaporation	RHin	kws(initial)	kgo (s^{-1})
case 1	50	ON	50%	8.00E-07	0.01
case 2		OFF			
case 3				8.00E-07 (constant)	
case 4			25%		0.01
case 5	10				0.003
case 6	100				0.015
case 7				4.00E-06	
case 8				4.00E-07	
case 9				4.00E-07 (constant)	
case 10				1.00E-07	
case 11					0.00001

Case 1 is a base case. Blank space=base case.

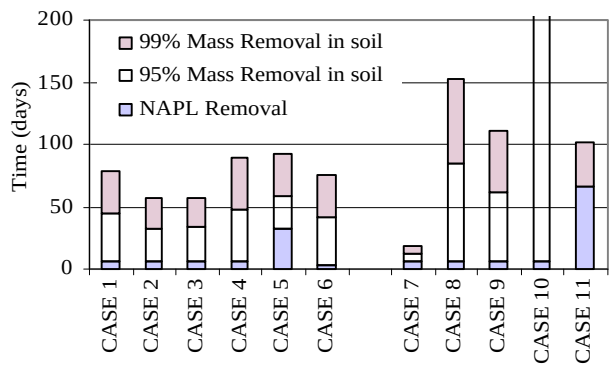

Figure 5. Cleanup time for cases in Table 1

Planned Activities: In the coming months the post-doc will complete experiments to determine the air flow rates in the fine and coarse-grain silica gels. The post-doc will also complete the analysis of his first set of experiments and write up the results. After this the post-doc will start image dissolution under variably water saturated conditions. In the next two months the M.S. student will complete desorption kinetic profiles for trichloroethene from Hanford sand and Hanford caliche. After this the M.S. student will be done with her studies and she will get a job in consulting. Last, in the next few months the Ph.D. student will complete a manuscript detailing the new model results and implications. After this the Ph.D. student will start to develop a multidimensional model that takes into account heterogeneities in water saturation, permeability, and NAPL distribution.