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Investigation of Pore Scale Processes That Affect Soil Vapor Extraction

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Number of Graduate Students: 1
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. This work will lead to improved models that 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 a Ph.D. student and a post-doc worked on the project. Over the past year the post-doc: i) analyzed data from SVE experiments performed using flow-through columns packed with regions of different grain size, ii) wrote and submitted a manuscript with this data (Chu et al., 2003), and iii) performed new SVE experiments where the wetting properties of fine-grain material in a heterogeneously packed column were varied.

Analysis of the MRI data focused on four column experiments. These columns were packed with silica gel grains in three ways: coarse grains (250-550 ?m) only, fine grains (32-63 ?m) only, and a core of fine grains surrounded by a shell of coarse grains. All columns were initially saturated with water and then drained under a constant suction head. After drainage, the columns were contaminated with decane, and then drained to different decane saturations. The column with only coarse grains and one of the core-and-shell columns was drained to residual decane saturation. The column with only fine grains and the remaining core-and-shell column were drained such that the fine grains were initially above residual. After decane drainage, each column was then continuously purged with water saturated nitrogen gas and magnetic resonance imaging (MRI) was used to observe and quantify the amount and location of NAPL in the columns over time. MRI is unique because it is non-destructive, allowing three-dimensional images to be taken of the phases as a function of space and time.

Analysis of the MRI data for all four columns yielded three main results. First, at residual saturation, a sharp volatilization front moved through the columns filled with either coarse or fine-grain silica gel only. A numerical model developed by Yoon et al. (2003) was applied to these columns, and mass transfer coefficients for decane volatilization were obtained by fitting NAPL saturation profiles. Mass transfer rate constants for both columns were greater than literature values. In previous work, mass transfer coefficients were obtained by fitting models similar to ours to vapor phase concentrations of NAPL in the column effluent. Small variations in column temperature and pressure give rise to significant errors in measured effluent concentrations. Hence, we hypothesized that previously determined mass transfer coefficients are in error, and use of the NAPL saturation profile will provide more accurate mass transfer coefficient for NAPL volatilization.

Second, in the heterogeneous column at residual saturation, the volatilization front in the core lagged just behind that in the shell. This is illustrated below in Figure 1. Pressure drops across all columns were measured; these were used to calculate flow rates in the core and shell of the heterogeneous columns. With these, advection and diffusion rates of decane vapor from the fine grain core were compared to advection rates of decane vapor from the coarse grain shell. This analysis indicated that advection dominated mass removal from the coarse-grain shell. But in the fine-grain core, mass removal was controlled diffusion radially outward from the core to the clean part of the shell.

Third and last, when decane in the core of the heterogeneous column was above residual saturation, decane volatilization occurred near the inlet, the relative decane saturation throughout the core dropped uniformly, and decane in the core flowed in the liquid phase to the shell to replenish volatilized decane. This is illustrated below in Figure 2. Hofstee et al. (*J. Contam. Hydrol.*, 25, 235-247, 1997) measured capillary-pressure saturation curves for a nonspreading NAPL (tetrachloroethene) in a three-phase (air-water-NAPL) system. Above residual saturation, applied suction was required to displace the NAPL with air, indicating that capillary forces held the NAPL in place above residual saturation, and that gradients in capillary pressure could potentially cause flow. Also Hayden and Voice (*J. Contam. Hydrol.*, 12, 217-226, 1993) observed by cryo-scanning electron microscopy with X-ray analysis that in a three-phase (air-water-NAPL) porous media system, a non-spreading NAPL forms continuous films and lenses at intermediate saturations. This indicates that when decane was above residual saturation in our system, it was continuous and capillary pressure gradients during purging caused it to flow.

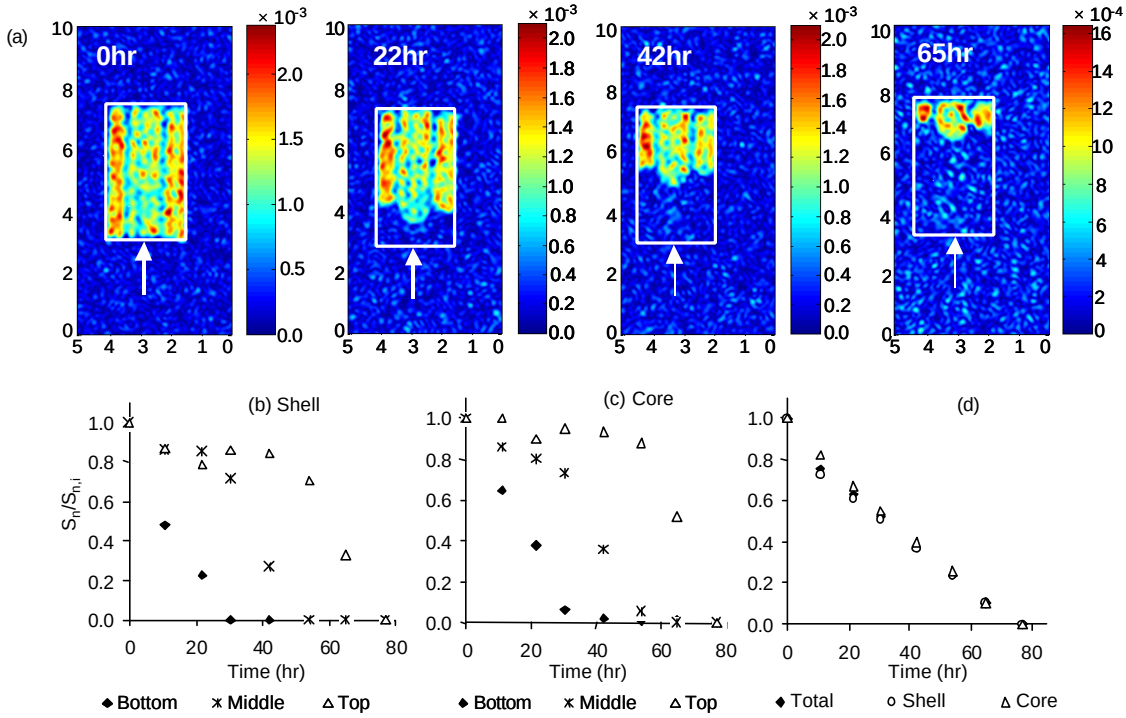

Figure 1. Column 3: Core (fine) and shell (coarse) column initially at residual decane saturation: (a) Image slices were obtained at different times. Only the center image of 22 slices is shown at each time point. Horizontal and vertical scales are in centimeters. The menu bar intensity is proportional to the decane saturation. (b) Change of the relative decane saturation (S_n/S_{ni}) with time in bottom, middle and top sections of the shell. (c) Change of the relative decane saturation (S_n/S_{ni}) with time in bottom, middle and top sections of the core. (d) Change of the relative decane saturation (S_n/S_{ni}) with time in the whole column.

A more detailed discussion of the imaging results presented here is in the manuscript we recently submitted to Journal of Contaminant Hydrology (Chu et al., 2003). It is important to note that our results are directly applicable to the Hanford site, where SVE is actively being used to remediate carbon tetrachloride. Like decane, carbon tetrachloride is a nonspreading chemical. Hence, we suspect that in fine grain sediments, carbon tetrachloride removal is limited by diffusion when it is at or below residual saturation, and possibly by capillary-driven flow to higher permeability regions where volatilization is occurring when it is above residual saturation.

For the last several months, the post-doc has been using MRI to investigate SVE in heterogeneously-packed columns, where the fine-grain core contains a mixture of hydrophobic and hydrophilic silica gel grains. The grains are made hydrophobic through silanization, where C10 functional groups are attached to the silica gel surface. In one column, all of the fine grains in the core are hydrophobic. In another, only 25% by weight of the fine grains in the core are hydrophobic. In both cases, decane in the core was initially above residual saturation.

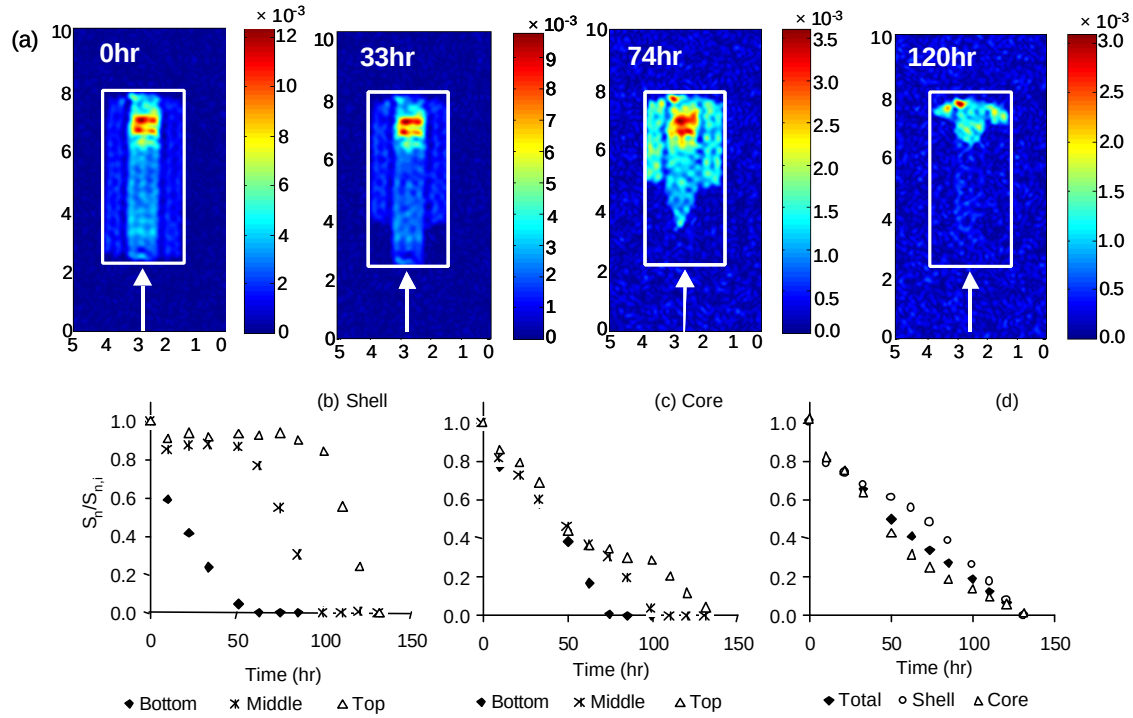

Figure 2. Column 4: Core (fine) and shell (coarse) column with core initially above residual decane saturation: (a) Image slices obtained at different times. (a) Image slices were obtained at different times. Only the center image of 22 slices is shown at each time point. Horizontal and vertical scales are in centimeters. The menu bar intensity is proportional to the decane saturation. (b) Change of the relative decane saturation (S_n/S_{ni}) with time in bottom, middle and top sections of the shell. (c) Change of the relative decane saturation (S_n/S_{ni}) with time in bottom, middle and top sections of the core. (d) Change of the relative decane saturation (S_n/S_{ni}) with time in the whole column.

Initial results from the experiments with a 25/75% mix of hydrophobic/hydrophilic silica gel grains in the core, and all hydrophobic silica gel grains in the core, are presented in Figure 3. Like previous column experiments (e.g., Figure 2), a volatilization front moved through the shell of both columns with hydrophobic silica gel. This front is more pronounced in the 25/75% column than in the 100% column. Also, a volatilization front moved through the core of the 25/75% column. However, in contrast to previous column experiments, mass removal occurs relatively uniformly over the length of the core in the 100% column. This indicates that in hydrophobic silica gel grains, NAPL can spread to the clean part of the core where volatilization is occurring until almost no NAPL remains in the core. In contrast, NAPL in the core of the columns filled with hydrophilic silica gel grains only moved to the clean part of the shell when the NAPL was above residual saturation. After it reached residual saturation, a volatilization front moved through the core.

The Ph.D. student is responsible for mathematical modeling. During the past year we have completed development and analysis of a one-dimensional model. Our results will be published soon (Yoon at al., 2003). The model 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. The contaminant transfer and transport model was coupled with moisture flow and heat transport to investigate the effect of water saturation and temperature changes on NAPL mass transfer, vapor phase retardation, and slow desorption during SVE. A relationship developed in the literature was used to express the fraction of soil surface area exposed to the vapor phase as a function of water satura-

tion. Also, a new constitutive relationship between the NAPL-gas mass transfer rate and the water saturation was developed based on data in the literature.

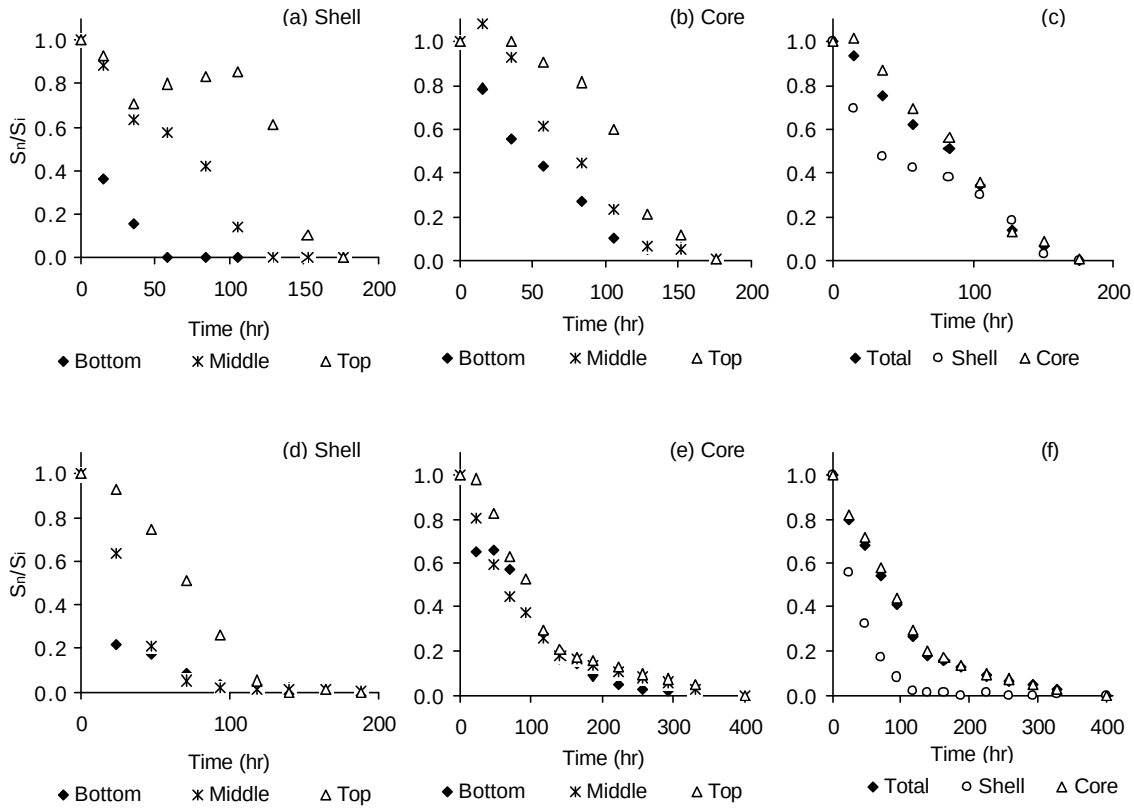

Figure 3. Core (fine) and shell (coarse) columns with a,b,c,) 25% / 75% mix of hydrophobic / hydrophilic silica gel in the core, and d,e,f) 100% hydrophobic silica gel in the core. (a,d) Change of the relative decane saturation (S_n/S_{ni}) with time in bottom, middle and top sections of the shell. (b,e) Change of the relative decane saturation (S_n/S_{ni}) with time in bottom, middle and top sections of the core. (c,f) Change of the relative decane saturation (S_n/S_{ni}) with time in the whole column.

The coupled model was used to investigate the effect of water saturation and temperature changes on SVE cleanup time. Simulations over a 5m distance were performed for two scenarios: low water saturation in a high permeability soil (Case I) where the gas flow rate is high, soil drying is expected and vapor sorption to soil may be important, and high water saturation in a low permeability soil (Case II) where the gas flow rate is low and NAPL mass transfer to the gas phase is rate-limited. Input parameters for Case I were based on the Hanford sandy soil and input parameters for Case II were based on the Hanford silty sand and Plio-Pleistocene (Caliche) soil. Gas flow rates were chosen in the range from 10 to 100 m/d at low water saturation and 0.5 m/d at high water saturation. These gas flow rates are similar to those encountered at the Hanford SVE site and many other sites beyond the vicinity of an extraction well. Simulation parameters varied in Case I and II are shown in Table 1.

Run 1 is defined by intermediate values of all input parameters obtained from the literature. For CASE I the time to remove NAPL, 95% of the sorbed mass, and 99% of the sorbed mass was calculated in Figure 4, while for CASE II only the time to remove NAPL was calculated as shown in Figure 5 since the time scale required for the mass removal was similar for the NAPL and sorbed phases. Two sets of simulations for cases of low and high water saturation revealed the following: (see Yoon et al., 2003, for further details)

(1) At low water saturation (CASE I) in high permeability soils, the time to removal the sorbed mass was markedly prolonged by slow desorption (Runs 1 and 9). NAPL mass was removed very fast relative to other processes due to high NAPL-gas mass transfer rates and high gas flow rates. Even at low RH (25 %) and high gas flow rate, soil drying was slow relative to NAPL removal (Runs 1 and 4) and the effects of water evaporation on NAPL removal were marginal. Also, water evaporation (Runs 1and 2), the fraction of slow desorbing mass (Runs 1 and 11), and Freundlich parameters (Runs 1 and 13-15) affected the cleanup time, however, the effect was marginal.

(2) At high water saturation (CASE II) in low permeability soils, the efficiency of mass removal was primarily controlled by NAPL removal. The prolonged cleanup time was most significant in runs having a low dissolution rate (Runs 1 and 3) and ? (Runs 1 and 4-5) in which a higher ? value represents a high water saturation. For these cases, NAPL mass transfer was limited by diffusion through the water phase. Simulation results indicated that the limiting NAPL removal mechanism changed from volatilzation to dissolution (i.e., diffusion through surrounding water) as soil moisture increased. This was accounted for in the parameter ?. The effect of the total simulation length scale was examined in Runs 6 and 7. For Runs 2 and 7 with a high k_{dis} ($1.5x10^{-6}$ s^{-1}) the cleanup time was nearly proportional to the length, while for Runs 1 and 6 with a lower k_{dis} ($1.5x10^{-7}$ s^{-1}) the cleanup time differed by only 25 %. These results imply that in many heterogeneous field situations, the cleanup time will be significantly influenced by diffusion through the water phase even over a short length of contaminant zones at high water saturation.

(3) For all cases simulated, temperature and water content changes due to water evaporation were only marginally important in our one-dimensional system. Results in this study indicate that simplified models that neglect temperature change and water evaporation are valid under most field conditions.

Table 1. Parameters varied in simulations

CASE I: Parameters varied in low water saturation simulations

RUN	Evapo-ration	q (m/d)	Relative Humidity (%)	k_{ws} (s^{-1})	$k_{gn,i}$ (s^{-1})	f_{vmt}	f_{veq}‡	K_{F2}(mg/kg)/ (mg/l)^{n}F2
RUN 1	ON	50	50	8.E-07	0.01 §	0.4	0.0218(20%)	100
RUN 2	OFF							
RUN 3				8.E-07 †				
RUN 4			25					
RUN 5		10			0.003 §			
RUN 6		100			0.015 §			
RUN 7				4.E-06				
RUN 8				4.E-07				
RUN 9				1.E-07				
RUN 10					1.E-05			
RUN 11						0.6		
RUN 12								500
RUN 13							0.11 (4.56%)	500
RUN 14							0.05 (10.0%)	725
RUN 15			25				0.25 (1.76%)	500

CASE II: Parameters varied in high water saturation simulations

RUN	k_{dis} (s^{-1})	?	Length (m)
RUN 1	1.5E-07	4.4	5
RUN 2	1.5E-06		
RUN 3	1.5E-05		
RUN 4		3.0	
RUN 5		0‡	
RUN 6			2
RUN 7	1.5E-06		2

Run 1 is a reference case for CASE I and CASE II. Other Runs use the parameters in Run 1 except where values are given

CASE I:

† k_{ws} is not a function of temperature for this run.

‡ The value in parentheses is the initial water saturation corresponding to f_{veq}.

§ $k_{gn,i}$ is from the empirical correlation presented by Wilkins et al. (1995).

CASE II:

$k_{gn,i}$ (0.00004) is from the empirical correlation presented by Yoon et al. (2002).

‡ k_{gn} is constant (=$k_{gn,i}$)

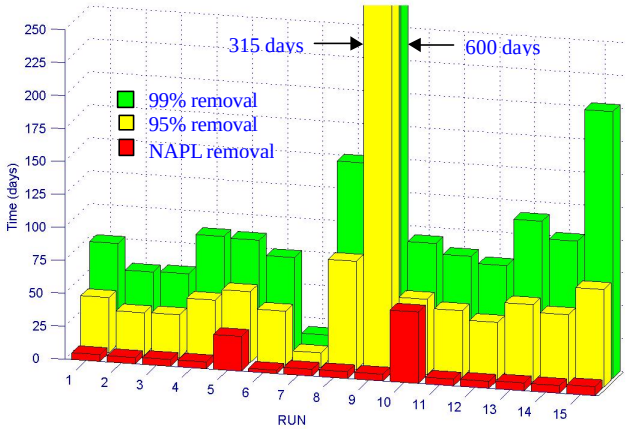

Figure 4. Cleanup time for CASE I in Table X.

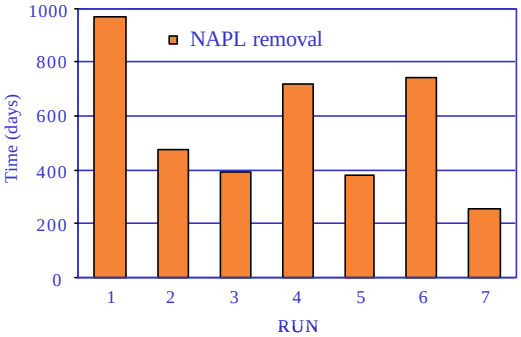

Figure 5. Cleanup time for CASE II in Table X.

Planned Activities: In the coming months we will further analyze the results from the new MRI experiments, determine if additional experiments are necessary to explain the results, and prepare a manuscript for publication. The post-doc has just completed his studies and has begun a new position as a research associate at the University of California. The project is in its final year, and we have submitted a renewal proposal to extend our results to investigate the impact of multidimensional spatial heterogeneity of permeability and moisture content upon field-scale SVE performance. The renewal project will fund the Ph.D. student to extend his modeling analysis to include multiphase flow in 3D heterogeneous systems. We will modify the exiting Subsurface Transport Over Multiple Phases (STOMP) simulator, which we have recently obtained. In June 2003 the student will attend a short course on the STOMP model. Over the next few months, we will begin initial modification of the model to include mass-transfer limited volatilization processes.

Information Access: The following publications have resulted from the project.

1. Yoon, H., Valocchi, A.J., and Werth, C.W. (2003). Modeling the influence of water content on soil vapor extraction, *Vadose Zone Journal*, to appear August 2003.
2. Chu, Y., Werth, C.W., and Valocchi, A.J. (2003). Magnetic resonance imaging of nonaqueous phase liquid during soil vapor extraction in heterogeneous porous media. *J. Contam.,Hydrol.*, submitted.