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Investigation of Pore Scale Processes That Affect Soil Vapor Extraction

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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. We completed our work using MRI experimentation and the results are summarized in Chu et al, 2004). During the past year a Ph.D. student worked on the project, focusing on a computational investigation of the impact of spatially distributed nonaqueous phase liquid (NAPL) saturation and water content on soil vapor extraction (SVE) in heterogeneous porous media. Our preliminary results were presented at the International Conference on Computational Methods in Water Resources (Yoon et al., 2004). We modified the exiting Subsurface Transport Over Multiple Phases (STOMP) simulator. The modifications were based upon knowledge gained in the MRI experiments and our earlier detailed one-dimensional modeling reported in Yoon et al. (2003). The modified STOMP code now includes slow desorption and mass transfer from trapped NAPL, which were dominant rate-limited mass transfer processes during SVE (Yoon et al., 2003).

This final phase of the research is investigating the core hypothesis that the spatial distribution of NAPL saturation, water content, and soil permeability determines the pore-scale processes that control SVE and the time scales for cleanup. It is now understood that there are three forms of NAPL phase in the vadose zone: free NAPL that is mobile and in contact with gas, residual NAPL that is immobile and in contact with gas, and trapped NAPL that is immobile and surrounded by water (Lenhard et al., J. Contam. Hydrol., 71, 261-282, 2004). We used a new permeability-saturation-pressure (k-S-P) constitutive model that considers all three NAPL forms. Diffusion of trapped NAPL through surrounding pore water to the gas phase is likely to be slow. Hence, we believe that the spatial distribution of total, trapped, and residual NAPL saturation must be accounted for, as well as the corresponding permeability fields, to determine rate-limiting mass transfer processes during SVE.

Numerical simulations for a two-dimensional stratified system based on the Hanford site were performed. STOMP was first used to distribute NAPL in heterogeneous porous media, and then to simulate NAPL removal during SVE. The numerical domain and boundary conditions are presented in Figure 1. Each layer is treated independently and the grid is refined in low permeability layers where most of NAPL is expected to be located. For three low permeability layers, a sequential indicator simulation (SISIM) model was used to generate a two dimensional random field consisting of three discrete soil types and corresponding soil properties, while for top and bottom layers, homogeneous field was used. The water table was placed 6 m from the bottom boundary and was inclined at 0.005 from left to right.

Simulations were performed for 2 cases. Case I represents a realistic recharge scenario where actual CCl_4 and water recharge rates (Figure 2) through the trench on the top boundary are used, along with seasonal natural water recharge rate (Nov-Feb: 7.5 cm/yr, Mar-Oct: 0.5cm/yr) for 38 years. Case II is a hypothetical scenario that uses a constant natural water recharge rate of 7.5 cm/yr over the top boundary for 38 years with the actual CCl_4 recharge rate between 1955-1962. Soil vapor extraction wells are placed in different depths at the same location based on Hanford SVE extraction systems. Simulation of SVE was performed for 7 years by specifying gas flow rates through extraction wells.

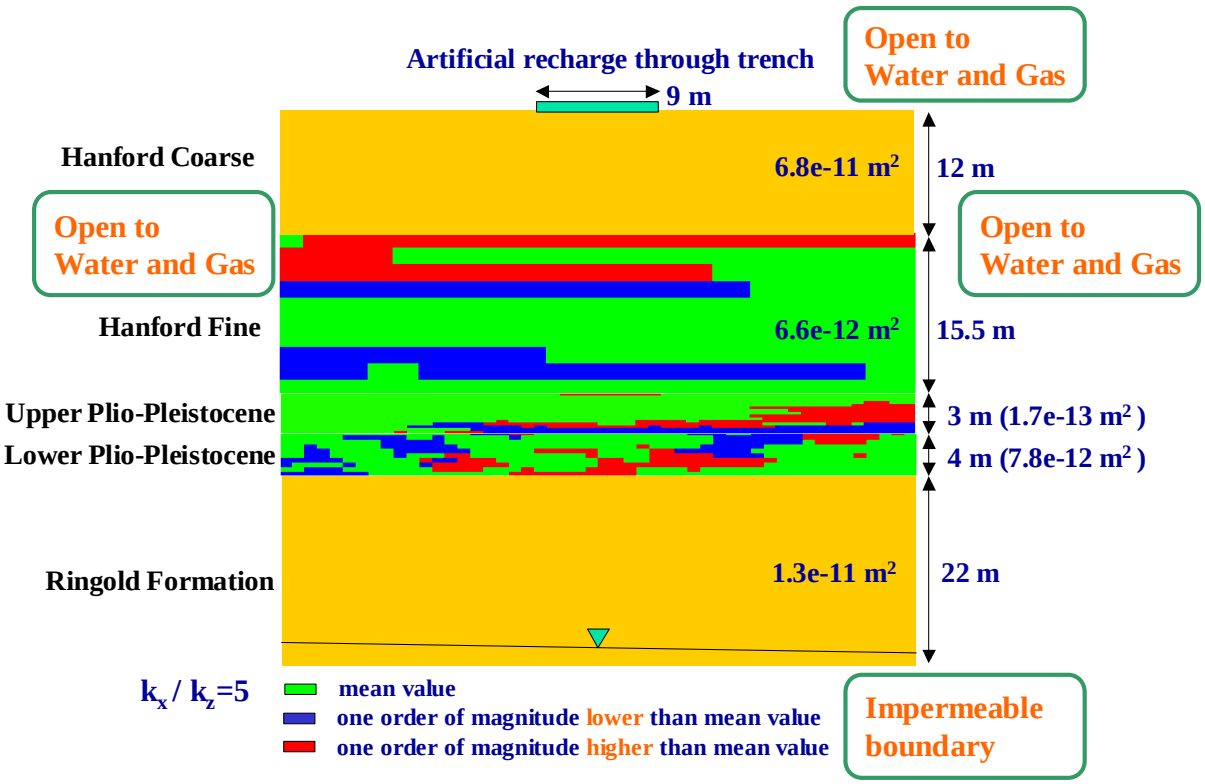

Figure 1. Numerical domain and boundary conditions. Permeability and depth of each layer is shown. On the top boundary there is a source zone, that is a trench for CCl_4 spill.

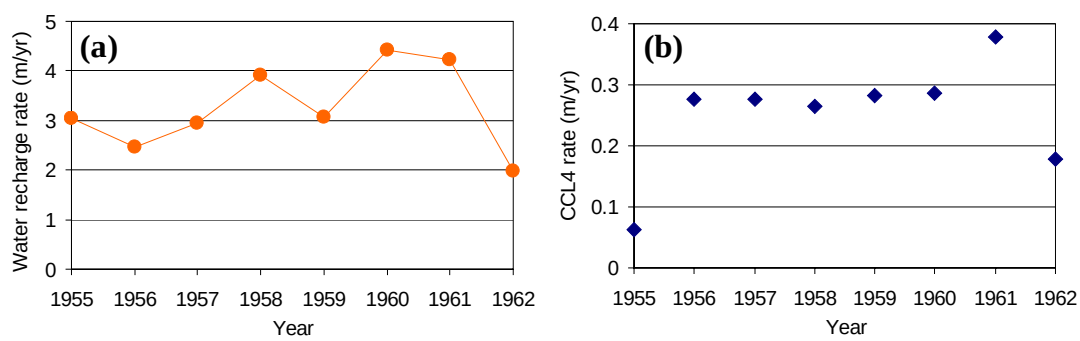

Figure 2. Estimated water (a) and CCl_4 (b) recharge rates through the trench on the top boundary at the Hanford site.

The distributions of total NAPL saturation, trapped NAPL saturation, and residual NAPL saturation at 7 years and 38 years for Case 1, and at 15 years and 38 years for Case 2 are shown in Figure 3 and Figure 4, respectively. The influence of the water saturation and soil permeability on the spatial distribution of total, trapped, and residual NAPL saturation in the vadose zone was investigated. Simulations for two cases revealed the following (see Yoon et al., 2004, for further details):

(1) Use of the new constitutive model (k-S-P model) that allows formation of residual NAPL increased the amount of NAPL retained in the unsaturated zone. It also reduced the NAPL relative permeability be-

cause residual NAPL is immobile. At 7 years (Case I), the advancing front of NAPL was just above the water table, while at 15 years (Case II), the advancing front of NAPL did not reach the water table. In the new k-S-P model, residual NAPL is a function of water saturation and saturation-path history and residual NAPL saturation decreases with increasing water saturation. In Case II, formation of residual NAPL at low water saturation slowed the NAPL movement downward. In addition, the low water infiltration rate causes water to slowly move, resulting in a slow NAPL migration.

(2) Water saturation had a great influence on the trapped NAPL saturation when initial water saturation was low and the water infiltration front advanced the distributed NAPL in the low permeability layer. At 38 years for Cases I and II, distributions of total NAPL saturation are very similar, although more NAPLs are retained in the vadose zone for Case II. Comparison of trapped and residual NAPL saturations (Figures 3 and 4), however, reveals that at 38 years the distributions of trapped and residual NAPL are totally different. Compared to residual NAPL saturation (Case I), trapped NAPL saturation was negligible because at later time, water infiltration rate is very low and resulting water saturation is also low. Meanwhile, compared to the trapped NAPL saturation (Case II), residual NAPL saturation was very small, because a constant water infiltration of 7.5 cm/yr causes the water infiltration front to pass through the distributed NAPL in the low permeability layer, resulting in formation of trapped NAPL at later time.

These results indicate that the amount of each form of NAPL depends on the water saturation, infiltration events, and the soil permeability. The amount of trapped NAPL saturation also depends on the formation of residual NAPL saturation. In addition, these results imply that in many heterogeneous field situations, the cleanup time will be significantly influenced by diffusion through the water phase from the trapped NAPL at high water saturation in low permeability zones during SVE.

The NAPL distributions at 38 years in Cases 1 and 2 served as initial conditions for SVE. Since SVE is applied to remove contaminants in the unsaturated zone, contaminants located below the water table surface were not considered during SVE. Equilibrium partitioning among NAPL, gas, and aqueous phases was assumed for Case I where trapped NAPL was negligible. Simulations of equilibrium partitioning among phases and slow mass transfer rate (10^{-7} s^{-1}) from trapped NAPL for Case 2 were performed. Slow desorption was not considered. The water infiltration rate during SVE is 0.5 cm/yr. The results of SVE simulations indicate the following:

(1) As expected, most of NAPL was removed from high permeability layers and diffusion from a low permeability layer is a dominant process for low removal rate at later time during SVE as shown in Figures 5 and 6. For all simulated cases total NAPL saturations after 7 years of SVE (Figures 5 and 6) are very similar. It is important to note that trapped NAPL in the Hanford fine sand layer for the non-equilibrium case became free or residual NAPL due to a decrease of water saturation and then was removed by fast volatilization. The change of various NAPL forms and water saturation during SVE should be considered.

(2) Trapped NAPL may persist even after long term SVE operation due to slow dissolution rate.
For the equilibrium partitioning case, trapped NAPL that exists at the NAPL plume boundary dissolves very fast and volatilizes. Then, volatilized NAPL in the low permeability layer diffuses toward the advective gas flow in the high permeability zone, as shown in Figure 7(a). Hence, the NAPL plume shrinks as trapped NAPL at the boundary is removed. For the non-equilibrium case, trapped NAPL is dissolved slowly and mass removal occurs by volatilization of free NAPL inside the NAPL plume which then diffuses toward the advective gas flow, as shown in Figure 7(b). Hence, the NAPL plume does not shrink, but rather trapped NAPL is left along the boundary. In the presence of trapped NAPL, the rate-limited mass transfer from trapped NAPL in low permeability zones should be considered during SVE.

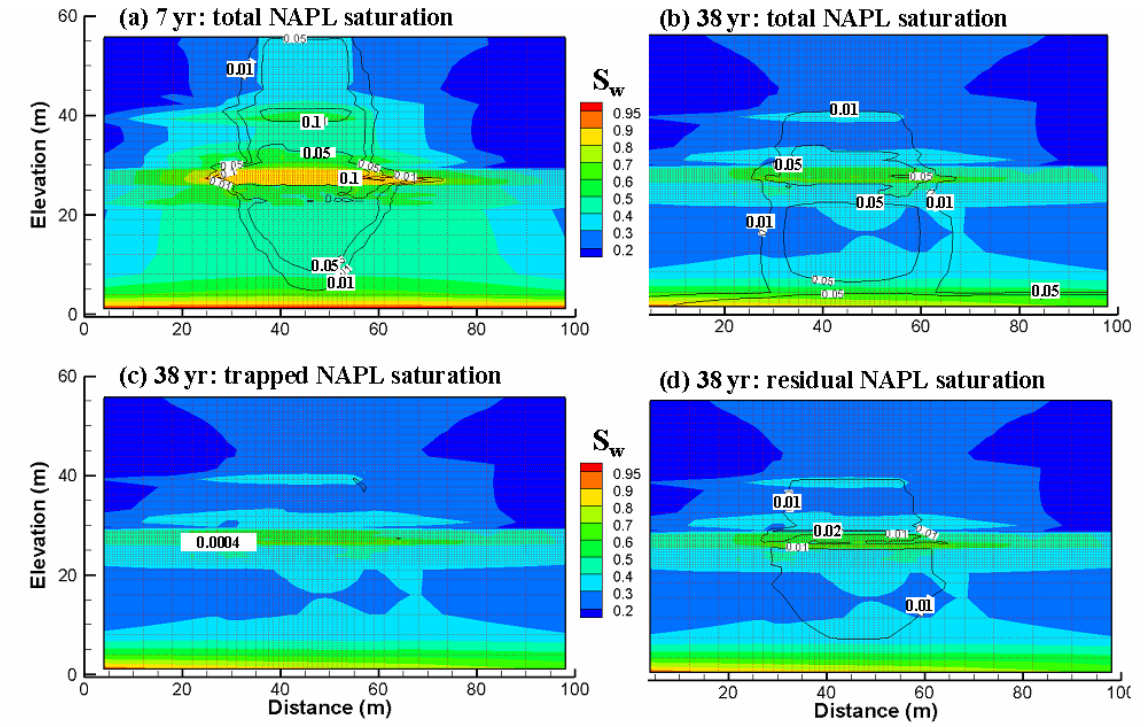

Figure 3. Total NAPL saturation at (a) 7 years and (b) 38 years, (c) trapped NAPL saturation at 38 years, and (d) residual NAPL saturation at 38 years for Case I. Color bar stands for water saturation and contour label stands for NAPL saturation.

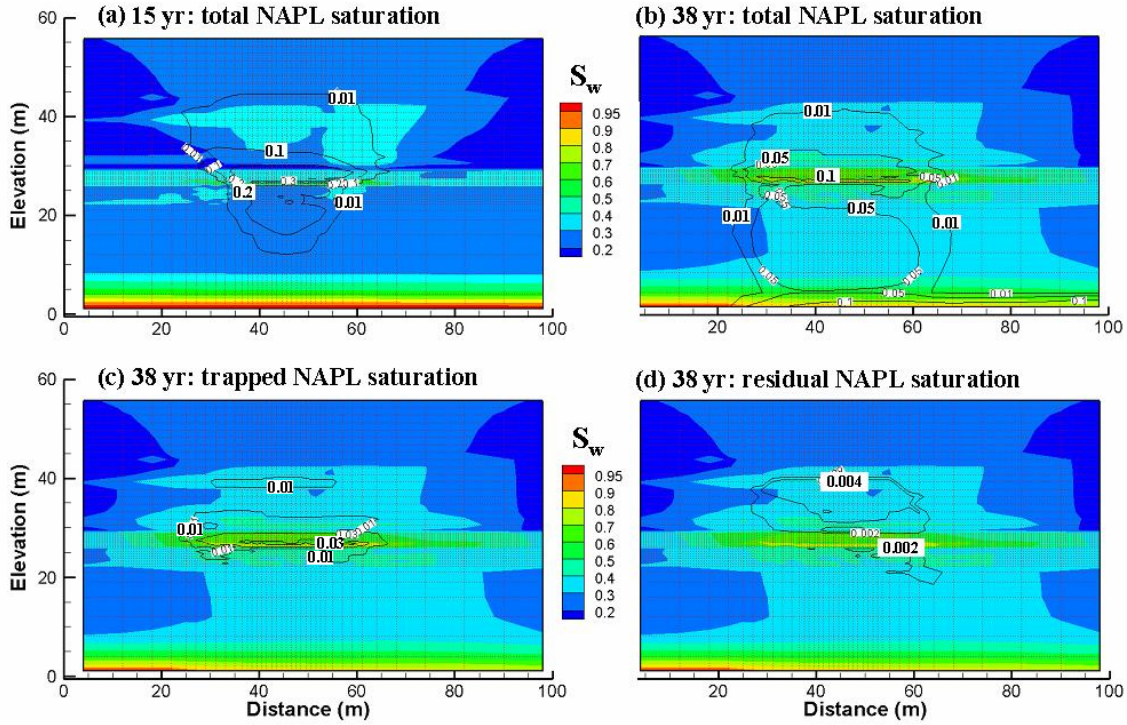

Figure 4. Total NAPL saturation at (a) 15 years and (b) 38 years, (c) trapped NAPL saturation at 38 years, and (d) residual NAPL saturation at 38 years for Case II. Color bar stands for water saturation and contour label stands for NAPL saturation.

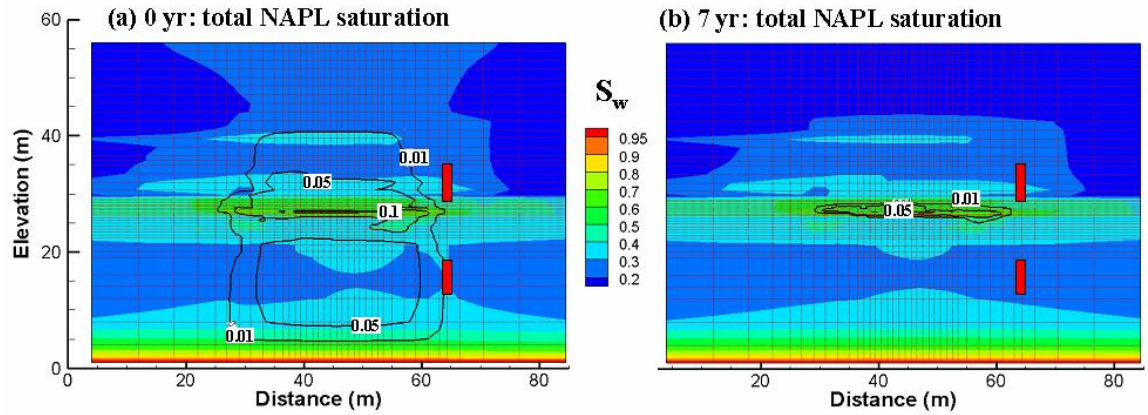

Figure 5. Total NAPL saturation at (a) 0 years and (b) 7 years for Case I. Color bar stands for water saturation and contour label stands for NAPL saturation. Vertical columns are extraction wells at same locations.

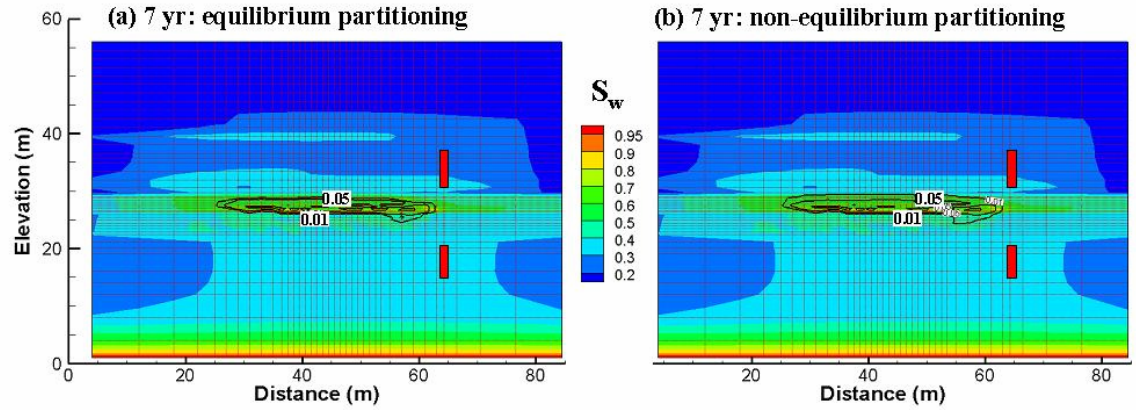

Figure 6. Total NAPL saturation at 7 years for (a) equilibrium partitioning and (b) non-equilibrium partitioning for Case II. Color bar stands for water saturation and contour label stands for total NAPL saturation. Vertical columns are extraction wells at same locations.

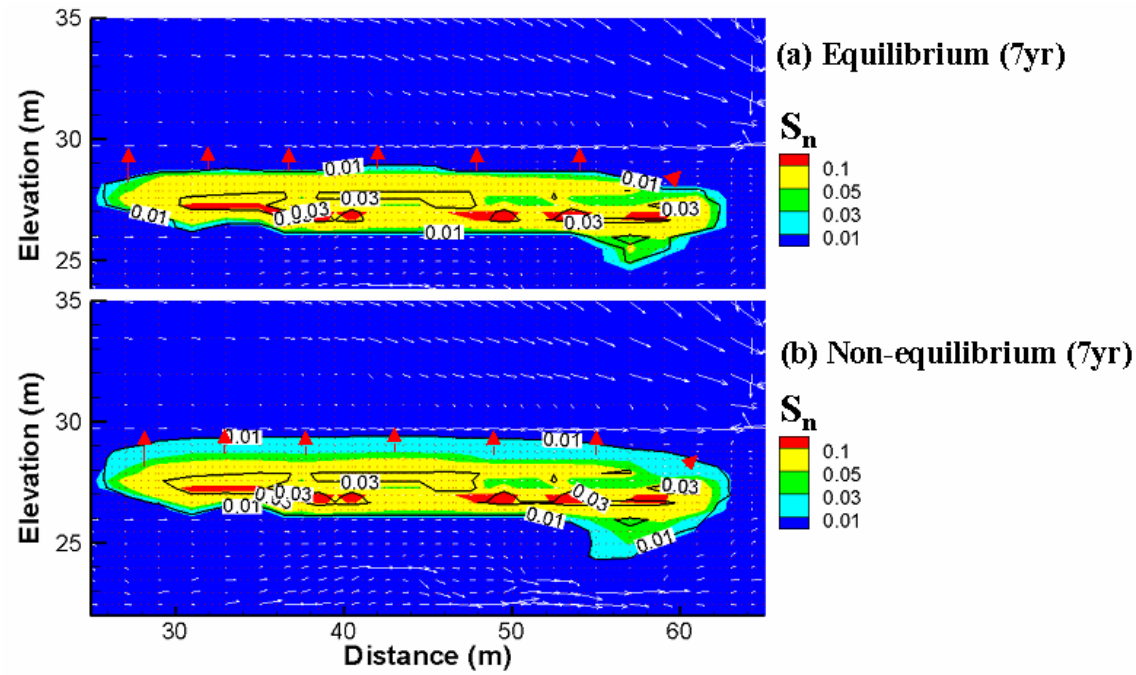

Figure 7. NAPL saturation at 7 years for (a) equilibrium partitioning and (b) non-equilibrium partitioning for Case II. Color bar stands for total NAPL saturation and contour label stands for trapped NAPL saturation. Arrows on the NAPL plume indicate a diffusion process. Gas flow rate field is shown. The magnitude of arrow is proportional to gas flow rate.

Planned Activities: The project is in its final year as a no-cost extension and all work will be completed by September 30, 2004. In the remaining time we plan to complete our simulations of carbon tetrachloride spills and SVE cleanup for the Hanford scenario. In these simulations we will focus upon the influence of nonequilibrium processes upon SVE performance. All our results will be summarized in our final report.

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

1. Chu, Y., Werth, C.W., Valocchi, A.J., Yoon, H. and Webb, A. (2004). Magnetic resonance imaging of nonaqueous phase liquid during soil vapor extraction in heterogeneous porous media. *J. Contam.,Hydrol.*, article in press.

2. 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.

3. Yoon, H., Valocchi, A.J., and Werth, C.W. (2004). Impact of spatially distributed nonaqueous phase liquid saturation and water content on soil vapor extraction in heterogeneous porous media, pp. 757-786, in Computational Methods in Water Resources XV, edited by C.T. Miller, M.W. Farthing, W.G. Gray, and G.F. Pinder, Elsevier.