

# Determining the entrapment architecture in the DNAPL source zone using down-gradient mass flux measurements: A combined numerical and stochastic study

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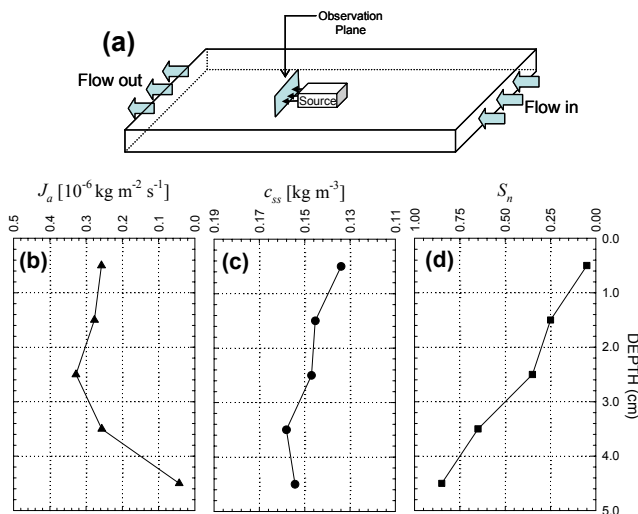
## ABSTRACT

The presence of dense non-aqueous phase liquids (DNAPL) in source zones in the subsurface generates continuous mass flux long after the initial spill. Observed dissolved concentration in a screened monitoring well downstream of a DNAPL source zone will provide very little information on the entrapment architecture that is needed to design effective remediation schemes. Non-intrusive techniques based on traditional partitioning tracer methods will only provide volume estimates that are in error under complex entrapment architecture that may include pools. This paper presents an alternate non-intrusive technique where measured spatial distribution of mass flux emanating from the source zone could be used to get knowledge of entrapment architecture that contributes to the generation of the plume. Determination of locations where mass flux is generated within the source zone will assist in targeting the hotspots for DNAPL mass removal through remediation. It is our hypothesis that mass flux emanating from the entrapment zone is controlled largely by the vertical distribution of the DNAPL. The proposed method analyses measured vertical distribution of mass flux using a modified mass transfer model based on MODFLOW and RT3D and inverse modeling using UCODE to determine DNAPL entrapment morphology as well as the hydrodynamically accessible mass in the source zone. This theoretical study uses subsurface stochastic methods to address issues related to heterogeneity within the source zone.

## INTRODUCTION

Non-aqueous phase liquids (NAPLs) such as gasoline and chlorinated solvents are common organic compounds found in contaminated soils and aquifers [Mercer and Cohen, 1990]. These organic liquids in the entrapment zone slowly dissolve into the flowing ground water generating a downstream contaminant plume in which concentrations are usually found to exceed regulatory standards. Mass transfer limitations due to rate-limited dissolution result in a long-term persistence of the source even in cases of small entrapped DNAPL mass. The identification of DNAPL sources located beneath the water table is critical to achieve goals of site remediation and aquifer restoration. Traditional soil coring is not widely used in DNAPL contaminated sites since it is considered to be intrusive and results in cross contamination and remobilization of entrapped DNAPLs. In addition, the estimation of entrapped mass using point data obtained from cores is strongly sensitive to the choice of interpolation techniques and the estimates tends to associated with high uncertainty [Pankow and Cherry, 1996].

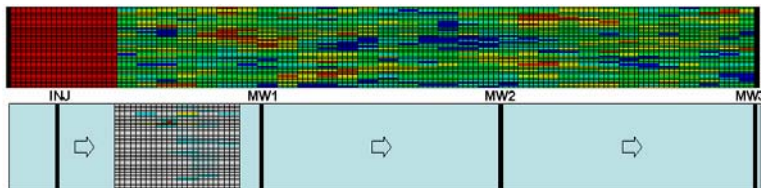
The emergence of partitioning interwell tracer tests offers an in situ, non-intrusive site characterization method that minimizes the risk of remobilization of DNAPL [Jin *et al.*, 1995]. This technique utilizes conservative and suite of partitioning tracers to detect the presence and to estimate the *hydrodynamically accessible* DNAPL mass in the entrapment zone [Rao *et al.*, 2000]. Results obtained from this technique provide only the average saturation and total DNAPL volume in the tracer-swept zone. In addition, analyses of the tracer data are limited to the use of method of temporal moment where equilibrium partitioning is assumed. This may not be the case when higher saturation zones of DNAPLs are encountered because the limited contact time between flowing aqueous phase containing tracers and DNAPL is not sufficient for equilibrium partitioning to take place. As a result, DNAPL volume is always underestimated [Dai *et al.*, 2001]. Current research by Moreno-Barbero and Illangasekare [2003] is attempting to improve the accuracy of this technique in detecting and distinguishing DNAPL in pools and intermediate saturation zones as well as estimating the volume. The methods they have developed treat a pool to have two zones: a zone of high saturation at the bottom bounded at the top by a transition zone where NAPL saturation decreases gradually to residual. Preliminary results indicate that multiple tracers test detect portions of DNAPL which is mostly in the transition zone whereas DNAPL in the high saturation zone is by-



**Fig. 1: Experimental setup and results in mass transfer study of entrapped DNAPL in a simple heterogeneous system [Saenton, 2003a].**

from the transition zone although the concentration at downstream of the pool is significant (see Figs. 1b and 1c). The experiments were repeated at different seepage velocities and, based on these observations, it can be concluded that the transition zone produces the most dissolved DNAPL mass flux. Saenton [2003a] also commented that, although a large fraction of DNAPL mass resides in the pool, a much small fraction of mass present in the transition zone contributes to a majority of flux producing the plume. In addition, when tracers are used to detect entrapped DNAPL mass, most of the partitioning occurs within this transition zone. Knowing the hotspots of the entrapment zone where the most DNAPL mass flux is produced is critical for remediation design and source zone management. In site remediation, most of the removable DNAPL mass resides in the transition zone since this region can be easily accessed by the injected treating reagents (e.g. surfactants, oxidants, and augmented microbes) compared to the high saturation zone in the pool. This paper investigates the use of measured steady-state concentration and dissolved DNAPL mass flux distributions in 2-D plane downstream of the source in combination to characterize the entrapment architecture. A transport model in combination with inverse modeling algorithm are used.

It should be pointed out that pore water concentration distribution has been used to infer the presence of DNAPL. If pore water concentration of contaminant is near solubility limit (or effective solubility in case of multicomponent DNAPL), DNAPL is presumed to be located within the vicinity of the sample collection location [Feenstra, 1991]. Anderson et al. [1992] analyzed downgradient concentration patterns resulting from well-defined residual NAPL source using 3-D analytical model and equilibrium dissolution assumption. They used concentration-matching method to determine the entrapment architecture (i.e. differentiation between residual ganglia and pools). Although, this was an initial attempt to determine source zone architecture, Saenton [2003a] illustrated that, based on the experimental and numerical simulation studies, concentration distribution alone is not sufficient to use in inverse modeling to infer entrapment architecture in complex heterogeneous systems.



**Fig. 2: Heterogeneous distribution of five different sands in the test tank used in this study (top). The bottom diagram shows the locations of the injection wells, the source zone.**

passed due to permeability reduction. This tracer-detectable DNAPL in transition zone plays a very important role in interphase mass transfer or, in this case, a dissolution process. Saenton [2003a] conducted a dissolution experiment of a single-source tetrachloroethene (or PCE) entrapped in a simple heterogeneous test aquifer. PCE saturation in the source zone varies gradually from residual in the transition zone to high saturation at the bottom. Mass transfer rate and dissolved PCE concentration were monitored at different depths. Fig. 1a illustrates the schematic experimental setup of the dissolution cell. The source zone is 10.5-cm long, 5-cm wide, and 5-cm thick. Results of Fig. 1b shows measured steady-state mass flux  $J_a$  [ $\text{ML}^2\text{T}^{-1}$ ] of dissolved PCE is higher in the transition zone than in the pool at the bottom. Mass flux is maximum at mid-depth where intermediate DNAPL saturation is present. However, in case of pool, the dissolved mass flux is always smaller than the flux emanating from the

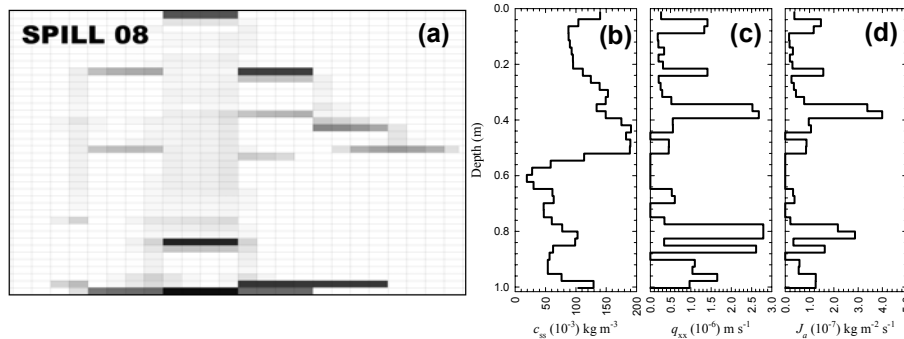
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up-scalable, and validated three dimensional numerical code for dissolution is required. The dissolution model developed by Saenton [2003a] was used. This model has been validated experimentally to be up-scalable from small 1-D column to intermediate-scale 2-D tank, and shown to be valid over a wide range of NAPL saturations.

## METHODOLOGY/RESULTS

**Intermediate-Scale Test Tank:** A set of numerical simulations (80 realizations) was conducted to represent conditions in a two-dimensional, intermediate-scale, heterogeneous-packed test tank with the dimension of 9.53-m long 1.02-m high and 0.05-m thick. The tank consists of homogeneous and heterogeneous zones (see Fig. 2). Two constant-head supplies are used to maintain a steady hydraulic gradient along the length of the tank. The homogeneous part of the tank consists of #8 sand within which a fully-penetrated injection well is placed to deliver a treating agent for NAPL mass removal by enhanced dissolution. The heterogeneous zone is packed using five sands of different sieve sizes (#16, #30, #50, #70, and #110). The heterogeneity was designed as a spatially correlated random field with statistical parameters similar to heterogeneous field sites. This heterogeneous packing assumes a log-normal distribution of hydraulic conductivity with a mean value  $\mu_{\ln K}$  of 4.18 (K in cm/hr) and a variance  $\sigma_{\ln K}^2$  of 1.22. The correlation lengths in lateral ( $\lambda_h$ ) and vertical ( $\lambda_v$ ) directions are 0.508 and 0.0508 m, respectively. The heterogeneous zone consists of 1280 cells of 0.254 m in length and 0.0254 m in depth which corresponds to 32 columns and 40 layers resulting in 16 lateral and 20 vertical correlation lengths.

**PCE Spill Simulation:** The NAPL source zone (1.54-m $\times$ 1.02-m) is created from a spill simulation using version 9.3 of UTCHEM [Delshad et al., 1996]. The location of the source zone is shown in Fig. 2. The source zone is discretized into 1 row, 40 layers and 24 columns. The capillary pressure-saturation relationship assumes Brooks-Corey drainage model. Total PCE spill mass is 1.62 kg or 1.0 L (the average saturation is  $\bar{S}_n = 3.59 \times 10^{-2}$ ) and the spill rate is  $1.93 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$ . The spill location is at the center of the



**Fig. 3: Simulation results from natural dissolution of entrapped PCE in heterogeneous aquifer (realization #8).**

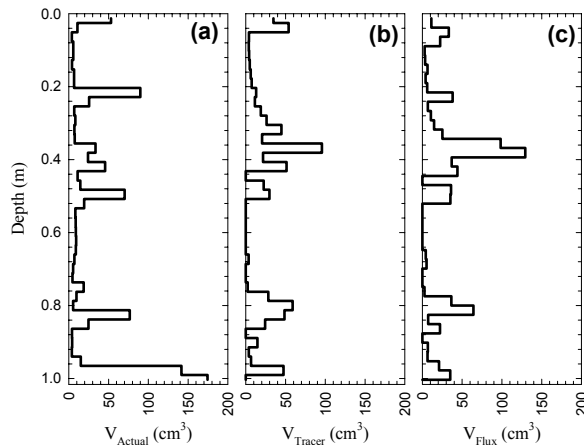
top layer. A total of 80 simulations were conducted in heterogeneous formations generated as a realization of the random field with the assumed statistics. Each simulation was conducted for a long time for the spill (migration of PCE) to reach a static state. An example of resulting simulated PCE distributions are shown in Fig. 3a (realizations #8). As can be seen from the distribution patterns, most of the PCE is entrapped in high permeability zones. Some PCE is pooled on top of the low permeability lenses while PCE residuals (i.e. transition zone) are found in several locations throughout the source zone. These saturation distributions will be used in the subsequent natural dissolution and multiple tracers simulation.

**Natural Dissolution Simulation:** A hydraulic gradient of  $10^{-3}$  is applied to the test tank to generate a steady ground water flow field. Ground water samples are collected at multi-level sampling well MW1 that is capable of collecting samples for each layer (total = 40 layers). In this way, the vertical profile of steady-state PCE concentrations  $c_{ss}$  and mass flux  $J_a$  can be obtained (simulation were conducted until steady-state is attained). Fig. 3 shows PCE distribution (3a), vertical profile of steady-state concentration (3b), flux of ground water in x-direction (3c), and dissolved mass flux (3d) of an example simulation (realization #8). As expected, results, large mass flux is, as expected, observed in the intermediate saturation zone. This numerical simulation agrees with observations in experiments (see Fig. 1). PCE in pool produces a

Entrapment Morphology	Mass Flux, $J_a$	Concentration, $c_{ss}$
Pool – High $S_n$	Low	Low to Intermediate
Transition Zone	Intermediate $S_n$	High
	Residual $S_n$	Intermediate to High

**Table 1: Mass flux and steady-state concentration characteristics of the three zones of saturation.**

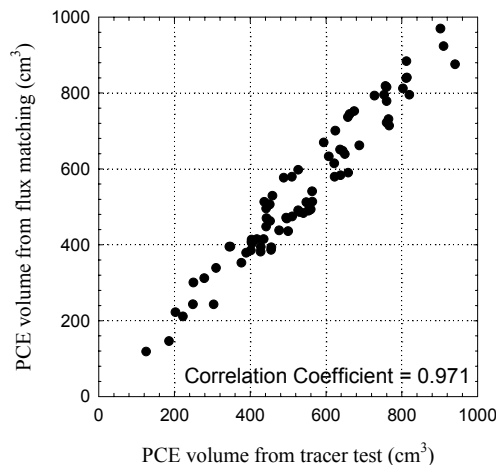
relatively high concentration but the associated mass flux is smaller compared to the intermediate  $S_n$  region in the transition zone. These dissolution characteristics are summarized in Table 1. The results obtained from natural dissolution simulation will be used as observations in subsequent flux-matching for inverse modeling purpose.



**Fig. 4: Actual PCE volume distribution after spill (a), and volumes estimated from tracer test (b), and from flux matching technique (c).**

**Multiple Tracers Simulation:** In multiple tracers simulation, pulse injection of bromide (conservative tracer) and 2,2-dimethyl-3-pentanol or DMP (partitioning tracer with partition coefficient of 27.51) solution is introduced at the fully-screened injection well. Tracers are allowed to flow under natural gradient ( $10^{-3}$ ) and equilibrate with the contacted free phase PCE (in case of DMP). The numerical model used in this simulation is MODTRACER which is developed by Saenton [2003b]. This model assumes equilibrium partitioning of DMP. Thus, each layer will have its own tracers' breakthrough curves. The method of temporal moment analysis is then applied to determine the *hydrodynamically accessible* PCE volume for each sampling location. Fig. 4a shows the vertical distribution of actual PCE volume (total spill volume =  $1000 \text{ cm}^3$ ) while Fig. 4b illustrates the vertical distribution of PCE volume obtained from multiple tracers test. The total volume

calculated from moment analysis using tracer data is  $759.7 \text{ cm}^3$  for realization #8 (24% underestimation error). In other simulations, PCE volume detected by this tracer test technique ranged from  $125.1$  to  $979.3 \text{ cm}^3$  (87%-2% error). Obviously, most of the entrapped PCE is unseen by tracers due to hydrodynamic constraint as a result of complex entrapment involving PCE pools.



**Fig. 5: Relationship between hydrodynamically accessible mass calculated from tracers and flux-matching methods.**

**Concentration and Flux Matching Method:** Inverse modeling tool UCODE [Poeter and Hill, 1998] coupled with the numerical mass transfer model was used to match concentrations and mass flux generated from natural dissolution previously. Each realization was executed to simulate natural dissolution and steady-state concentrations and mass fluxes for each model layer in the MW1 were recorded. These values were used as observations to be matched in inverse modeling. For each realization, a new dissolution model was setup. This time, the actual PCE distribution was not used. Rather, PCE saturation was assumed to be constant within the layer. Therefore, in each case, there will be 40 unknown saturations (i.e. parameters to be determined in UCODE) for each layer. With 80 observations (concentrations and fluxes in 40 layers), determination of 40 parameters is possible. UCODE searched for the best values of saturation distribution to match the downstream concentrations and fluxes. Fig. 4c illustrates PCE volume obtained from flux matching method for realization #8. The vertical distributions of PCE volume obtained from tracers test and flux-matching method are almost identical where hotspots

are identified. From this example simulation, most of the entrapped PCE in the transition zone can be de-

tected whereas PCE in the pool is still partially hidden. Total PCE volume obtained from this procedure is 778.4 cm<sup>3</sup> (22% error) which is a little higher than the volume obtained from tracer technique. For all 80 simulations, the range of PCE volume obtained from flux matching method is 118.5–987.0 cm<sup>3</sup>. Fig. 5 illustrates the relationship between the total PCE volumes obtained from both methods (tracers vs. flux-matching) for all 80 realizations. The correlation coefficient is impressively high (R = 0.971). Although the two methods (tracer and flux-matching) underestimate the total volume of PCE in the source, both seem to have been able to detect the same amount of hydrodynamically accessible PCE volume. This detectable volume represents the remediable free-phase when chemical injection-based clean-up technique is employed.

## CONCLUSIONS

In this theoretical study, we demonstrate that concentration/flux matching method can be used to determine hydrodynamically accessible DNAPL volume as well as its entrapment architecture in the source zone. Although it is a computationally intensive method, it works as equally well as the costly multiple tracers technique and can be considered an alternate choice for site characterization method. Ongoing research is conducted to determine the practical applicability of this technique to analyze data from fields.

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