In-Situ Characterizations of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers

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Contaminated Vadose Zone Characterization Using Partitioning Gas Tracers

ABSTRACT

This paper describes laboratory research conducted to investigate the use of partitioning tracers for the detection, volume estimation, and remediation performance assessment of vadose zones contaminated by nonaqueous phase liquids (NAPLs). These laboratory studies used Ottawa sand and field soil packed columns. The columns were saturated, then reduced to residual saturations of water and NAPL, creating a three phase system of air, water, and NAPL. Conservative and partitioning gas tracers were injected into the column and their elutions were analyzed. The method of moments was used to estimate partition coefficients between the air and NAPL phases for each of the tracers. The partition coefficients and retardation factors are used to select appropriate tracers for NAPL detection and volume estimation in the field. This research identified several perfluorocarbon tracers suitable for use in the field and demonstrated the feasibility of using partitioning tracers as a tool for NAPL detection and volume estimation in the vadose zone.

INTRODUCTION

A widespread and recurring public health problem identified in recent years is the contamination of the subsurface by nonaqueous-phase liquids (NAPLs) (NRC 1994). Contamination at numerous private, government, and industrial facilities is well-documented and is clearly a problem for communities and populations located near these sites.

Nonaqueous-phase liquid contamination of the subsurface occurs as NAPLs migrate from the surface, where in the past they were typically disposed in unlined pits, through the vadose zone to the water table. The migration of the NAPL through the vadose zone leaves a trail or streak of NAPL held in the pore space by capillary forces and is defined as residual or immobile NAPL. As water percolates through a contaminated vadose zone, NAPLs and other contaminants dissolve in the mobile water and may be carried to the saturated zone as dissolved constituents. Previously clean aquifers may receive harmful doses of pollutants without the bulk of the contaminants ever reaching the saturated zone.

In many cases, because of the potential adverse impact of vadose-zone contamination on water supplies, remediation of the vadose zone may be essential. However, to design an effective remediation of an area, a detailed description of the site is necessary. Thus, the first step in site remediation is characterization. Two current methods using core sampling or cone penetrometer testing, which depend upon laboratory analysis, are time-consuming and expensive. To improve the site characterization process, better methods of detecting NAPLs are necessary (EPA 1992).

A potentially better characterization method utilizes a technology developed in the petroleum industry. This technology is the partitioning inter-well tracer test (PITT). Partitioning, both single-well and interwell, tracer tests have been used for years to characterize liquid residuals in oil- and gas-saturated reservoirs (Cooke 1971, Deans 1971, Allison et al. 1991, Tang and Harker 1991a, b). In a PITT, partitioning tracers experience a delay in production with respect to nonpartitioning tracers because of their interaction with fluids present at residual saturations. If the tracer partition coefficient between the carrier fluid and the residual fluid is known, the difference between the breakthrough curves of the partitioning and nonpartitioning tracers can be used to estimate the volume of residual fluid present. PITTs have been used to estimate oil saturations in gas-saturated reservoirs (laboratory and field tests) using partitioning and nonpartitioning gas tracers (Tang and Harker 1991a, b). Their work was similar to estimating NAPL saturations in vadose zones.

Recently, PITT technology has been adapted to detect and characterize NAPL contamination in subsurface saturated zones. This procedure has been successfully applied in column experiments and two- and three-dimensional computational analyses (Pope et al. 1994, Jin et al. 1995) and field experiments (Brown et al. 1996, Brown et al. 1997, Dwarakanath 1997) with DNAPLs.

Once the technology was successfully demonstrated, researchers sought to use the PITT in the vadose zone. Recognizing that the only mobile phase in this region, once the NAPL has migrated through the zone, is the gas phase, researchers began investigating partitioning and nonpartitioning gas tracers that would be suitable for NAPL detection and volume estimation in the vadose zone (Whitley et al. 1995, Whitley 1997). By applying the PITT to the vadose zone, much larger sample volumes may be examined than with core testing. The larger volumes also provide more reliable estimates of average NAPL saturations. Thus, partitioning tracer tests, whether in the saturated or unsaturated zone, can be used to (1) detect and locate NAPL contamination, (2) estimate the NAPL volume present and (3) assess remediation performance.

A successful PITT field test design relies on two primary components: laboratory analysis and computer simulations. Using results from site characterization studies, laboratory analysis is conducted to (1) identify tracers that will be most effective for the specific conditions of the site, (2) estimate the tracers' partition coefficients, (3) evaluate equilibrium flow rates, and (4) assess other necessary parameters such as residence times. Once these variables have been determined, they are used as simulator inputs. The simulator, UTCHEM for the PITT conducted in this case (Delshad et al. 1996), is a multi-phase, multi-dimensional model that uses field and laboratory results to determine the PITT design. The PITT design parameters determined by the use of simulation include injection and production rates, evaluation of site heterogeneity, the injected tracer mass, elution concentrations, effect of open/closed boundary conditions, and multi-dimensional effects. The result of this two-step process, laboratory analysis and simulation, results in a PITT design that may be applied subsequently in the field.

The tracers chosen for NAPL detection in this study are members of the perfluorocarbon family; a family of fully fluorinated alkyl substituted alkanes. Perfluorocarbon tracers (PFTs) have been studied previously for petroleum reservoir characterization (Senum et al. 1992). Potential applications for perfluorocarbons have been described extensively by Dietz (1991). The perfluorocarbon compounds considered in this study are listed in Table 1 along with their molecular weights. The nonpartitioning tracer used in this study was argon.

The laboratory research described in this paper was conducted in support of closure activities at the Chemical Waste Landfill, a field site currently undergoing characterization and remediation testing at Sandia National Laboratories in Albuquerque, NM (Studer et al. 1996, INTERA 1997). This research was motivated by the need to characterize NAPL contamination in the vadose zone beneath the site which has a depth of approximately 500 feet (Studer et al. 1996). Early field studies indicated a high concentration of trichloroethylene (TCE) in addition to other hydrocarbons and inorganic contaminants. The average field NAPL saturation was estimated to be approximately 1-2% (Jin 1995). Using these field results as a guide, the experiments reported here concentrated on evaluating the partitioning of the perfluorocarbon tracers into TCE in two types of porous media: Ottawa sand and soil extracted from the field site.

THEORY

This section presents a review of the fundamental theories applicable to this research: the partition coefficient and the method of moments. For a porous medium containing water and NAPL at residual saturations and air as the carrier phase, the partition coefficient is a ratio of the tracer concentrations in the NAPL and carrier phases. Determining the partition coefficients was the primary goal of this research. This section also describes the method of moments, a method that utilizes the mean residence times of the tracer-response curves to estimate the partition coefficients of the tracers.

Partition Coefficient

The partition coefficient of tracer i between NAPL and air, $K_{N,a}^i$, is defined as the ratio of the concentration (mol/L^3) of tracer i in the NAPL phase (C_{iN}), to the concentration of tracer i in the air phase (C_{ia}), or

$$K_{N,a}^i = \frac{C_{iN}}{C_{ia}}. \quad (1)$$

The partition coefficients of the tracers may be estimated using thermodynamic phase equilibrium theory. The estimation equation is given by

$$K_{N,a}^i = \frac{C_{iN}}{C_{ia}} = \frac{P\bar{V}_a}{\gamma_{iN}P_i^{\text{vap}}\bar{V}_N} \quad (2)$$

where $\bar{V}_a$ and $\bar{V}_N$ are the molar volumes (L^3/mol) of the air and NAPL phases, respectively, γ_{ij} is the activity coefficient between the tracer and the liquid NAPL phase, P_i^{vap} is the vapor pressure of tracer i , and P is the total pressure.

Method of Moments

The Method of Moments is a procedure that can be used to estimate residual saturations based on the breakthrough curves of a nonpartitioning and a partitioning tracer (Jin et al. 1995). The experimental partition coefficient may be expressed as

$$K_{N,a}^2 = \frac{Q}{V_N}(\bar{t}_2 - \bar{t}_1) \quad (3)$$

where $K_{N,a}^2$ is the partition coefficient of tracer 2 between the NAPL and air phases, Q is the volumetric flow rate (L^3/T), V_N is the volume of NAPL (L^3), and $\bar{t}_1$ and $\bar{t}_2$ are the mean residence times of partitioning tracers 1 and 2 (T), respectively. Equation 3 may be used to estimate the partition coefficient given that the volume of NAPL, the flow rate, and the mean residence times are known in a column experiment. In addition, this expression may be

rearranged to estimate the NAPL volume in the tracer swept pore volume, if the partition coefficient is known. The mean residence time estimation may be improved using an extrapolation technique discussed in Jin (1995).

The retardation factor equation provides a multiple by which the partitioning tracer-response curve will lag the nonpartitioning tracer-response curve. The retardation factor may be expressed as

$$R_f = \frac{\bar{t}_2}{\bar{t}_1} = 1 + \frac{K_{N,a}^2 S_N}{S_a} \quad (4)$$

where R_f is the retardation factor, S_N is the NAPL saturation, and S_a is the air (or gas) saturation.

The retardation factor is used to determine whether the experimental tracer-response curves have sufficient separation to accurately estimate the NAPL volume or the partition coefficient. An analysis of the error estimation in PITTs can be found in Jin (1995), and the results indicate that the retardation factor should not be less than 1.2. When retardation factors are less than 1.2, the tracer peaks cannot be resolved to accurately estimate a partition coefficient. An upper limit of 4 is suggested in order to have a reasonable test duration. However, in laboratory experiments the retardation factors for tracers with large partition coefficients often exceeded 4. Because of the scale of the laboratory experiments, this upper limit can be exceeded without unduly delaying the completion of a laboratory experiment

Materials and Methods

This section describes the materials and methods used to conduct the experiments during this research. A review of the porous media, tracer mixtures, analytical methods, and column preparation procedures is presented below.

Porous Media

Two types of porous media were used in the experiments: Ottawa sand and soil extracted from the field site at Sandia National Laboratories in Albuquerque, NM. The Ottawa sand was a

fine grade sand designated F-95. This sand was purchased from U.S. Silica Company in Berkeley Springs, WV. The average grain size is approximately 0.016 cm (90 U.S.A. std. sieve).

The second type of medium was soil extracted from the Chemical Waste Landfill (CWL) at Sandia National Laboratories. Since the laboratory work was supporting a field test which would be conducted at the CWL (INTERA 1997), it was important to examine partitioning in soil taken from the actual site. The sediments in the area consisted of clay, sand, silt and gravel layers cemented by caliche (Jin 1995). The soil sample received from the field was dry and contained a wide range of grain sizes including pebbles measuring 1 to 2 cm in diameter. Grains of this size are unsuitable because their large size is inappropriate for the scale of the column test. Very small particles, or fines, were also observed in the soil sample. Once packed in a column, these fines may be mobilized during waterflooding, resulting in fractures in the porous medium as the sandpack shifts. Both the large grains and fines were removed from the soil before the soil was packed in the column. The final average grain size was approximately 0.147 mm (100 U.S.A. std. sieve).

Tracer Mixtures

To circumvent the problems associated with serial-tracer injections, e.g. long test duration and increased cost, a single-phase multicomponent tracer mixture was determined that could be injected during a column experiment or field test. A single, mixed-tracer injection assumes that the tracers are well-mixed and single-phase. In the case of using tracers for a PITT in the vadose zone, the tracers should exist in the same phase as the mobile phase, i.e., the gas phase.

To determine the phase of a multicomponent mixture requires calculating the vapor-liquid equilibrium state. This determination of phase compositions is commonly referred to as a flash calculation (Reid 1987).

For the particular case of the per-fluorocarbon tracers, flash calculations were conducted at volumes of 1 liter for the laboratory mixture and approximately 6 m³ for the field mixture. Elevated and standard room temperatures were evaluated as were different pressures. Low pressures were preferred because pressures in the vadose zone are also low. The calculations

produced information regarding the number of phases and their compositions at various temperatures and pressures. The goal was to produce a single gas phase composed of the per-fluorocarbon tracers. An implicit assumption was that each tracer mole fraction had to provide sufficient mass in order to conduct a successful column experiment, i.e., result in a satisfactory partitioning tracer-response curve at concentrations suitably above the tracer detection limits.

The flash calculations were conducted using an isothermal, three-dimensional, compositional simulator for miscible gas flooding known as UTCOMP developed by the Center for Petroleum and Geosystems Engineering at The University of Texas at Austin (Chang et al. 1990). The thermodynamic inputs required for each component were molecular weight, critical temperature, critical pressure, and the Pitzer acentric factor. In addition, binary interaction parameters were required for each pair of components.

Flash calculations using the required thermodynamic inputs resulted in the specification of a laboratory tracer mixture. The mixture consisted of eight per-fluorocarbons mixed with nitrogen: **N₂**, **CF₄**, **CHF₃**, **C₂F₆**, **C₃F₈**, **C₄F₈**, **C₆F₁₂**, **C₈F₁₆**, and **C₉F₁₈**. The nitrogen was added to the mixture to assist in the vaporization of the higher molecular weight perfluorocarbons and to meet pressure requirements. At conditions of 1.3×10^5 Pa and 297.22 K, the mixture was a single gas phase. The laboratory mixture of perfluorocarbon tracers was purchased from PCR, Inc. and was assembled in 1-liter cylinders by National Refrigerants, Inc.

Analytical Methods

The analytical method utilized a Buck portable gas chromatograph (GC), a GC capable of being used in the laboratory as well as the field. A Valco automated gas injector was used to inject samples into the GC. The GC was equipped with a Thermal Conductivity Detector (TCD), a Flame Ionization Detector (FID), an Electron Capture Detector (ECD), an air compressor, a liquid injection port, an oven with cooling fans, and a digital display.

The GC used two types of columns to separate compounds. To detect argon, a molecular sieve was used in conjunction with a TCD and a temperature setting of **303°K**. Although oxygen

interferes with argon at this setting, using nitrogen as the carrier gas in the experiment reduces oxygen to negligible levels and argon can be easily detected.

To detect the perfluorocarbons, a 2.44 m carbopack column with a SP-1000 phase was used. This column was very effective in the detection of the perfluorocarbon tracers. Temperature settings of 403 to 473°K were used depending upon which tracers were being detected, peak elution time, and bandwidth preference. At higher temperatures, the perfluorocarbons elute earlier and with narrower peaks. To separate a suite including light and heavy tracers, lower temperatures must be used. Almost all experiments were conducted isothermally because this provided the best output. While temperature programs affect FID response very little, the ECD is very sensitive to temperature changes. Therefore, when using a temperature program and a carbopack column, detecting via ECD is infeasible (Bruner 1993).

Column Experiments

The columns used during these experiments were Kontes **CHROMAFLEX®** chromatography glass columns measuring 4.8 cm inside diameter (i.d.) and 30 cm in length. These columns are equipped with PTFE end caps. In addition, to ensure tight packs, flow adapters were substituted for one of the end caps. The flow adapter is a bed support attached to an adjustable screw. After the sand was funneled into the column, the bed support was adjusted so that it was tight against the top of the pack. The column was always packed with the outlet side down. The flow adapter was attached to the inlet side.

Some additional borosilicate glass chromatography columns used in the experiments measured 2.5 cm i.d. and 60 cm in length. The column end fittings consisted of threaded polypropylene collars. These columns were used as precolumns: to saturate incoming air or nitrogen with water and contaminant during the experiments which minimized stripping of these fluids from the downstream sandpacked column.

The columns were packed with Ottawa sand or Sandia field soil using a vibrating jig. The sand was placed in a separatory funnel and allowed to flow into the column. The vibration assists

in distributing the sand uniformly in the column. The columns were leak checked at 1.72×10^5 Pa and weighed before and after packing to determine porosity and pore volume.

Water was introduced into the primary column using a burette. The water was allowed to gravity drain to a residual, or immobile, saturation. If lower saturations were required, air was forced into the column to mobilize or assist in evaporating some of the water. Gravimetric measurements were used to estimate the water saturation in the column.

Next, NAPL was injected into the column using a 5 cm^3 syringe. The syringe allows close monitoring of the volume of injected NAPL. Final estimates of the residual NAPL were calculated based on the weight of the column before and after injection of the NAPL. Small NAPL volumes were required because average NAPL saturations in the vadose zone at the Sandia site were small (1-2%). Table 2 provides a summary of the experiments including pack dimensions, media type, NAPL, saturations, and tracers injected. The NAPL used in these experiments was trichloroethylene (TCE).

RESULTS AND DISCUSSION

Equilibrium Partitioning

Equilibrium partitioning of the perfluorocarbon tracers into the NAPL is important because all models and thermodynamic theory is based on the assumption that equilibrium conditions are satisfied. Without equilibrium conditions, the tracer test results are unreliable.

During the column experiments, various experimental parameters were adjusted to determine their effect on the tracer-response curves. One of the most important parameters adjusted was the average velocity. Researchers would like to be able to conduct experiments at high velocities to reduce experiment and field test duration. However, as the experiments proceeded, a trend was observed in which the partition coefficient was proportional to the mean residence time. As the mean residence time increased the partition coefficient also increased. This is shown in Fig. 1 for **C4F8**. The partition coefficient at 0.0009 min^{-1} (an average velocity of $3.53 \times 10^{-6} \text{ m/s}$) is approximately 8.5 and at 0.138 min^{-1} (an average velocity of $6.8 \times 10^{-4} \text{ m/s}$),

approximately 2.5. This figure clearly shows a trend of nonequilibrium partitioning at low mean residence times.

An analysis performed on all of the tracers verified this trend. In this analysis, the partition coefficient of each tracer was normalized by the partition coefficient of that tracer at the lowest average velocity. This normalized partition coefficient was plotted against the mean residence time of each tracer and is shown in Fig. 2. In this figure, as the mean residence time of the tracers increases, the partition coefficient also increases reaching a maximum of one where, in most cases, the average velocity is lowest. Several experiments were conducted at various velocities and TCE saturations to construct this figure.

An exponential curve fitted to the data is also plotted in Fig. 2. The equation for the exponential curve is

$$K_N = \frac{K_i}{K_{ilav}} = 1 - \exp(-k_0 \bar{t}_i) \quad (5)$$

where

- K_N = normalized partition coefficient
- K_i = partition coefficient of tracer i
- K_{ilav} = partition coefficient of tracer i at lowest average velocity
- k_0 = lumped mass-transfer coefficient (T^{-1})
- $\bar{t}_i$ = mean residence time of tracer i (T).

This curve was fitted using the mean residence time as the independent variable and the mass-transfer coefficient as the fitting parameter and adjusting it until a best fit was obtained. The lumped mass-transfer coefficient that best fit the data was $k_0 = 1.2 \times 10^{-4} s^{-1}$.

The mass-transfer coefficient estimated from Fig. 2 may be correlated with values reported in the literature by Wilkins et al. (1995). The correlation reported by Wilkins et al. (1995) is

$$k_0 = 10^{-0.42} D_g^{0.38} v_g^{0.62} d_{50}^{0.44} \quad (6)$$

where

D_g = effective gas phase diffusion coefficient (L^2/T)

v_g = average velocity (L/T)

d_{50} = mean grain size (L).

Using Eq. 6 and a representative gas-phase tracer diffusivity of $4.02 \times 10^{-2} \text{ cm}^2/\text{s}$ (Allen 1995) for C_6F_{12} , an average velocity of $3.53 \times 10^{-6} \text{ m/s}$ (1 ft/D), and an average grain size for Ottawa sand of 0.016 cm results in a lumped mass-transfer coefficient of $1.3 \times 10^{-4} \text{ s}^{-1}$. From the fitted curve, the lumped mass-transfer coefficient was estimated to be $1.2 \times 10^{-4} \text{ s}^{-1}$. The results indicate that the mass-transfer coefficient from the perfluorocarbon tracer experiments agrees well with Eq. 6.

These results indicate that it is necessary for experiments to be conducted at mean residence times high enough for equilibrium or near-equilibrium partitioning to occur. Obviously, there is a lower limit to the average velocity and resultant mean residence time that is practical in the laboratory and in the field. Therefore, the experiments should be conducted at an average velocity which allows equilibrium partitioning but is still within the limits of the laboratory or field equipment. For the experiments presented in this paper, the average velocity at which equilibrium or near-equilibrium partitioning occurs is $3.53 \times 10^{-6} \text{ m/s}$ to $1.06 \times 10^{-5} \text{ m/s}$ (1-3 ft/D). Or, in terms of mean residence times, equilibrium partitioning occurs at mean residence times of approximately 0.8 to 0.3 days. The Damkohler numbers which correspond to these mean residence times are 8.3 and 3.1.

The Damkohler number may be used when scaling laboratory tests to field tests. If the length increases from 0.305 m (1 ft) column experiments to 30.5 m (100 ft) well spacing in the field and the average velocity is $3.53 \times 10^{-6} \text{ m/s}$ (1 ft/D), the residence time increases from 1 to

100 days. A duration of 100 days may be too long for most field tests. To estimate the velocity scaling factor, the Damkohler number may be expressed as

$$N_{Da} = \frac{k_0 L}{v} \quad (7)$$

where

$$v = \frac{q}{\phi S_g}, \text{ the average velocity (L/T)}$$

L = length from the injection to production well (L).

The Damkohler number increases as the spacing between the wells increases and the velocity decreases, but to see the precise dependence on velocity requires accounting for the dependence of k_0 on velocity.

Substituting the velocity term from Eq. 6 into Eq. 7 gives

$$N_{Da} = \frac{c v^{0.62} L}{v} \quad (8)$$

or

$$N_{Da} = \frac{c L}{v^{0.38}} \quad (9)$$

where

c = a constant that accounts for the other variables in the equation.

From Eq. 9, the velocity may be increased as the length increases to maintain a Damkohler number representative of equilibrium partitioning in the field. A much more careful and complete analysis of how to scale laboratory results to the field is needed and recommended for future

studies. If NAPL detection, not volume estimation, is the only objective, average velocities in the field may be much higher since detection may be accomplished under nonequilibrium partitioning conditions.

Uncontaminated Column Results

Before investigating a contaminated porous medium, the behavior of the perfluorocarbon tracers in an uncontaminated column containing only two phases, air and water was investigated. This was necessary to evaluate perfluorocarbon adsorption onto the porous media and to ensure negligible water partitioning as well as noting any other effects. The porous media was field soil.

The experiment was prepared as described above except that NAPL was not added to the column. Argon and a perfluorocarbon tracer mixture of **C₄F₈**, **C₆F₁₂**, **C₈F₁₆**, **C₉F₁₈** was injected, and the tracer elution concentrations measured as detailed in the analytical section. The mean residence times for argon, **C₄F₈**, **C₆F₁₂**, and **C₈F₁₆**, **C₉F₁₈** were 1041, 967, 997, 1175, and 1193 minutes, respectively. Using Eq. 4 shows that each of the perfluorocarbon tracers has a retardation factor less than 1.2.

The results indicate that there is negligible partitioning of the perfluorocarbon tracers onto the soil or into the water. The perfluorocarbon tracer-response curve peaks coincide with the peak of the conservative argon tracer, and all of the tracers are eluted at 4 pore volumes.

Contaminated Column Results

Once the potential effect of adsorption was estimated, TCE was injected into the column as described above. The resulting saturations are listed in Table 2. In these experiments, low saturations were used because the field site had a very low average saturation, approximately 1-2%.

Low saturations were also used to evaluate the use of lighter perfluorocarbon tracers as “conservative” tracers due to their negligible partitioning at low saturations. This was done with **C₂F₆** in the Ottawa sand experiments. Argon, which was used in laboratory experiments, was not used in the field because of existing background concentrations and high detection limits. The partition coefficients and retardation factors are given in Table 3 for all of the experiments.

Figures 3 and 4 show the tracer-response curves for several of the per-fluorocarbon tracers in Ottawa sand (AW10) at an average velocity of 3.53×10^{-6} m/s (1 ft/D) and a TCE saturation of 1.6%. Logarithmic plots are preferred because the extrapolation technique requires a logarithmic ordinate and the partitioning effects are better illustrated using a logarithmic ordinate. Figure 3 shows the tracer-response curves for CHF₃, C₂F₆, C₃F₈, and C₄F₈. Because of the low TCE saturation, there was little partitioning of the C₂F₆ and C₃F₈. The retardation factors of C₂F₆ and C₃F₈ were 1.09 and 1.15, respectively. The low retardation factors, less than 1.2, indicate the estimated partition coefficients could have considerable error and are not reliable. The partition coefficients of CHF₃ and C₄F₈ are 6.49 and 8.55, respectively. These estimates are more reliable because their retardation factors are above 1.2. However, these per-fluorocarbon tracers would be marginally useful in the field because they do not sufficiently separate from the conservative tracer-response curve. Field data would be more scattered and estimating the difference between the nonpartitioning and partitioning tracer-response curves would be difficult. Using these tracer-response curves to estimate a NAPL saturation would result in large errors. The results indicate that C₂F₆ may be an acceptable conservative tracer substitute as long as the NAPL saturation is low.

Figure 4 shows C₂F₆, C₆F₁₂, C₈F₁₆, and C₉F₁₈. In this experiment, C₂F₆ was used as the conservative tracer because of the low saturation. The retardation factors for all three of the heavy tracers are much greater than 1.2, thus the partition coefficients are reliable. As partitioning increases, the tail of the perfluorocarbon tracer-response curve increases in slope, approaching horizontal. In Fig. 4, the C₉F₁₈ tails more than the C₆F₁₂ and C₈F₁₆, indicating increased partitioning.

Once a suitable suite of tracers to use in the field test was selected from the Ottawa sand experiments, a final experiment was conducted to simulate the field experiment. The details of the experiment, AW11, are listed in Table 2. The results are shown in Figs. 5 and 6, and Table 3. Only the tracers which were determined to be useful in the field were evaluated. Since the field site

had an average saturation of approximately 1-2%, the light tracers were not evaluated because they would not partition significantly in an environment with a low NAPL saturation.

Figure 5 shows the tracer-response curves of argon, **C4F8**, and **C6F12**. The argon and **C4F8** are not sufficiently resolved to provide a reliable partition coefficient for **C4F8**. The estimated partition coefficient for **C6F12** is 11.6, but its retardation factor is 1.24. This partition coefficient is less than expected and although the retardation factor is above 1.2, it is sufficiently low to suspect the partition coefficient is not reliable. The field partition coefficient for **C6F12** should be approximately 16, the value estimated in the Ottawa sand experiments.

Figure 6 shows argon, **C8F16**, and **C9F18**. The tracer-response curves for **C8F16** and **C9F18** show predictable partitioning behavior and have partition coefficients of 70 and 187, respectively. When field saturations are low, these two per-fluorocarbon tracers will be the most useful for field tests. The argon tracer-response curve falls below its detection level at approximately 2.5 pore volumes produced.

Modeling

Models, even simple ones, serve many useful purposes. A validated model can assist in the interpretation of experimental results and can help the researcher predict experimental outcomes and prepare future experiments. In addition, it is always useful to compare experimental data to an existing model. Finally, experimental results can be used to develop and validate potential models.

One simple model for partitioning tracers in a porous medium was derived by Maroongroge (1994). This model was developed for a water-saturated system, but with a few additional assumptions and calculations, the model can be used to simulate partitioning gas tracers in a column experiment.

The model is valid for (1) gas tracer flow with hydrodynamic dispersion; (2) one-dimensional (1D) porous medium; (3) three phases: an immobile water phase, a constant residual NAPL phase, and a mobile air phase; (4) air injected at a constant rate at $x=0$ and produced at $x=L$; (5) at $t=0$, a finite volume of tracer injected instantaneously, a slug, at $x=0$; and (6) local equilibrium. The model may be expressed as (Whitley 1997)

$$c_D(t_D, x_D = 1) = \frac{1}{2} \left[\left(1 - \operatorname{erf} \frac{1 - \frac{t_D}{R_i}}{2 \sqrt{\frac{S_a t_D}{N_{Pe} R_i}}} \right) + \exp \left(\frac{N_{Pe}}{S_a} \right) \left(1 - \operatorname{erf} \frac{1 + \frac{t_D}{R_i}}{2 \sqrt{\frac{S_a t_D}{N_{Pe} R_i}}} \right) \right]$$

$$- \frac{1}{2} \left[\left(1 - \operatorname{erf} \frac{1 - \frac{(t_D - t_{Ds})}{R_i}}{2 \sqrt{\frac{S_a (t_D - t_{Ds})}{N_{Pe} R_i}}} \right) + \exp \left(\frac{N_{Pe}}{S_a} \right) \left(1 - \operatorname{erf} \frac{1 + \frac{(t_D - t_{Ds})}{R_i}}{2 \sqrt{\frac{S_a (t_D - t_{Ds})}{N_{Pe} R_i}}} \right) \right] \quad (10)$$

where

- c_D = normalized concentration
- R_i = the retardation factor of a partitioning tracer i defined as
 $= S_a + (K_i S_N) = \frac{i_2}{i_1}$
- N_{Pe} = Peclet number
- S_a = air saturation
- t_D = dimensionless time
- t_{Ds} = dimensionless slug size.

The normalizing pore volume in the figure is the swept pore volume, the pore volume occupied by the air and NAPL phases. This equation was used to evaluate the tracer-response curves produced during the experiments.

Figure 7 shows the results of fitting the model to the experimental data for the experiment conducted in Ottawa sand (AW10) at 3.53×10^{-6} m/s. The model was used by fixing the pore volume, NAPL and water saturations, flow rate, and the partition coefficient. Then the Peclet number was adjusted until the peak time of the model matched the peak time of the experimental

data. Because the Peclet number contains several variables, including the average velocity and hydrodynamic dispersion coefficient, which is difficult to estimate, adjusting the Peclet number provides an easy method for fitting the model to the data.

As shown in the Fig. 7, the results of the model compare favorably with the experimental data. Figure 7 shows the computed and experimental results for C_2F_6 , C_8F_{16} , and C_9F_{18} . The tracer-response curves indicate early breakthrough and tailing. These are both characteristics of diffusive transport. C_2F_6 was used to demonstrate this effect because its low partition coefficient shows that the early breakthrough and tailing can only be attributed to the mass-transport processes and cannot be attributed to any interphase-mass-transfer limitations.

Figure 7 also shows that an increased partition coefficient reduces the peak height. Additionally, the tracers with larger partition coefficients tail extensively, whereas the tracers with smaller partition coefficients show reduced tailing.

The model has shown to be an excellent predictor of gas-tracer response behavior in a column experiment. While it cannot substitute for the actual experiment or a field-scale simulator, it may be used to (1) predict and assist in the interpretation of the gas tracer-response curves, (2) assist in the overall design of a 1D column experiment (duration), (3) establish the initial NAPL and water saturations in the column and evaluate their effect on the tracer-response curves, (4) assess equilibrium partitioning, and (5) determine appropriate slug sizes.

Conclusions

Gas tracers that are suitable for characterizing contaminated vadose zones have been identified through laboratory experiments and field tests. These perfluorocarbons tracers appear to be excellent choices as partitioning tracers. Perfluorocarbon gas tracers used in PITTs are expected to be an effective means of NAPL contamination detection, characterization, and remedial action performance assessment within the vadose zone. Some specific conclusions drawn from this study based upon several column experiments in Ottawa sand and field soil are:

1. The perfluorocarbon family of tracers are suitable for detecting TCE contamination in the vadose zone. Additionally, they provide a wide range of K values. These K values range from approximately 3 to 190.
2. Perfluorocarbon tracers with higher molecular weights and lower vapor pressures partition more into TCE than the lighter, more volatile perfluorocarbon tracers.
3. The partitioning trend shows that the lighter tracers may be acceptable conservative tracers at low NAPL saturations.
4. The partition coefficients calculated from column data decreased as the mean residence times decreased, which indicates that equilibrium partitioning is not occurring at lower mean residence times. Thus, column experiments must be conducted at a low enough mean residence time to obtain an equilibrium partition coefficient. In general, the minimum residence time must be determined experimentally for the specific soil and NAPL of interest. In the experiments conducted during this research, tracers that partitioned under equilibrium conditions had a mean residence time of no less than approximately 1000 minutes to ensure equilibrium partitioning. The tracers respond similarly in Ottawa sand and field soil.
5. Adsorption of the perfluorocarbon tracers onto field soil was negligible. Thus, the entire retardation of the tracers can be attributed to partitioning into the residual TCE phase rather than adsorption onto the soil.
6. An experimental protocol has been developed to study tracer-response in the vadose zone. This protocol includes experimental design, tracer mixing, and analytical techniques.
7. Early breakthrough and tailing are associated with low flow rate vadose zone experiments (low Peclet numbers) and do not necessarily indicate channeling or nonequilibrium conditions. These traits are a result of a strong diffusive component in the flowing gas phase.
8. A simple model may be used to predict the behavior of tracers at various saturations and flow rates, and of tracers with different partition coefficients. The model was helpful in attributing the early breakthrough and tailing of tracer-response curves to transport in the gas phase.

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Table 1. Perfluorocarbon Tracer Properties

Tracer	Molecular Weight (g/mol)
Carbon Tetrafluoride, CF ₄	88.005
Trifluoromethane, CHF ₃	70.013
Hexafluoroethane, C ₂ F ₆	138.012
Hexafluoropropene, C ₃ F ₆	150.03
Octafluoropropane, C ₃ F ₈	188.017
Octafluorocyclobutane, C ₄ F ₈	200.028
Decafluorobutane, C ₄ F ₁₀	238.024
Octafluorocyclopentene, C ₅ F ₈	212.05
Dodecafluoropentane, C ₅ F ₁₂	288.031
Dodecafluorodimethylcyclobutane, C ₆ F ₁₂	300.06
Perfluoromethylcyclohexane, C ₇ F ₁₄	350.055
Perfluoro-1,3-dimethylcyclohexane, C ₈ F ₁₆	400.07
Perfluoro-1,3,5-trimethylcyclohexane, C ₉ F ₁₈	450

Table 2. Experimental Summary of Perfluorocarbon Column Experiments

Property/Experiment	AW10	AW11
Pack Dimensions (dia x length - cm):	4.8 x 24.4	4.8 x 23
Porous Media	Ottawa sand	Sandia field soil
NAPL	TCE	TCE
Pore Volume (cm ³)	159.65	161.45
Porosity	0.362	0.388
Water Saturation	0.34	0.382
NAPL Saturation	0.016	0.013
Gas Saturation	0.644	0.605
Average Velocity (m/s)	3.53×10^{-6}	4.6×10^{-6}
Tracers	argon, CHF ₃ , C ₂ F ₆ , C ₃ F ₈ , C ₄ F ₈ , C ₆ F ₁₂ , C ₈ F ₁₆ , C ₉ F ₁₈	argon, C ₄ F ₈ , C ₆ F ₁₂ , C ₈ F ₁₆ , C ₉ F ₁₈

Table 3. Experimental Perfluorocarbon Tracer Partition Coefficients and Retardation Factors

Tracers	AW10, 3.53×10^{-6} m/s, 1.6% TCE saturation*		AW11, 4.6×10^{-6} m/s, 1.3% TCE saturation*	
	K _N	R _f	K _N	R _f
CHF ₃	6.49	1.32	-	-
C ₂ F ₆	3.43	1.09	-	-
C ₃ F ₈	5.37	1.15	-	-
C ₄ F ₈	8.55	1.24	0.95	1.02
C ₆ F ₁₂	16.1	1.44	11.6	1.24
C ₈ F ₁₆	70.9	2.95	70	2.44
C ₉ F ₁₈	162	5.32	187	4.78

* Column headings include experiment title, average velocity, and NAPL saturation.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

figure 6.

Application of a Partitioning Interwell Tracer Test to Characterization of the Unsaturated Zone

1. Introduction

1.1 Statement of Problem

Subsurface contamination by non-aqueous phase liquids (NAPLs) is a ubiquitous problem that threatens the safety of groundwater supplies (Cohen et al., 1993). Much attention has been given to remediation of NAPLs in the saturated zone, where these hazardous substances slowly dissolve into the groundwater, serving as long-term sources of contamination.

A typical scenario for subsurface NAPL contamination would involve waste disposal pits that receive various operational wastes over a number of years. When the NAPLs in the pits build up sufficient hydraulic head, infiltration into the subsurface occurs. During the NAPL infiltration process through the unsaturated zone, some of the bulk liquid is trapped as immobile NAPL by capillary forces in the porous medium. In this way, the volume of liquid in the front is reduced as the migration continues. In geological systems where the water table lies many feet below the ground surface, downward migrating NAPLs may never reach the saturated zone. However, contamination can still occur when percolating water carries dissolved contaminant from the unsaturated zone down to the water table.

The remediation of trapped NAPL in the vadose zone is therefore important for protection of water supplies. Characterization of a contaminated site is imperative for both remediation effectiveness and evaluation of remedial performance (Jackson et al., 1997). In vadose zone characterization, the location and amount of contamination should be determined. In addition, water content in the vadose zone can be an important variable for remedial techniques such as radio-frequency or resistive heating, as well as techniques which rely on biological degradation.

Historically, core sampling has been the method used to quantify the amounts of water and contaminant. However, conventional soil boring analyses may not provide an accurate description of the liquid amounts in an affected area, because of the discrete nature of a core sample (Mayer et al., 1992). A partitioning inter-well tracer test (PITT) can provide a more accurate estimate of average liquid saturations, because the PITT gives averaged information about the entire swept volume.

1.2 The Partitioning Interwell Tracer Test

A partitioning interwell tracer test involves first setting up a hydraulic flow field between injection and extraction wells that bracket the zone of possible contamination. A mix of tracers is then introduced in the injection well and detected at the extraction site. The compounds used in this tracer mix are selected according to a number of tracer performance criteria. Some of these are chemical stability, cost effectiveness, minimal natural occurrence, and low detection limits.

The injected mixture will include a non-partitioning tracer and at least one partitioning tracer. The non-partitioning tracer exists solely in the mobile phase so its travel time is dependent only on the flow rate and swept volume. The partitioning tracer will be distributed between the mobile and resident immobile phases as it moves along the stream paths, and will lag behind relative to the fraction of time spent in the immobile phases. A comparison of the partitioning and non-partitioning tracer response curves can thus provide quantitative information about separate immobile phases present in the subsurface.

The partitioning tracer test has been used since the 1970's for characterizing oil in reservoirs (Allison et al. 1991; Tang, 1992). More recently the PITT has been adapted for detection of NAPLs in the subsurface. This method was first applied to the detection of NAPL contamination in the saturated zone and has been demonstrated effective at both laboratory and field scales (Jin et al., 1995; Brown et al., 1996; Jackson et al., 1997). The PITT technology has also been applied to the detection of NAPLs in the vadose zone (Whitley et al., 1995; INTERA, 1997).

1.3 Objectives

This research was intended to improve and add to existing vadose zone PITT technologies. The first objective of this research was to develop and demonstrate a method of quantifying subsurface water content using a PITT. This involved three tasks: (1) locating a compound suitable for use as a subsurface tracer that partitioned between air and water, (2) completing column studies to determine the partitioning

characteristics of the compound, and (3) demonstrating the technology in a field application.

The second objective of this research was to develop and demonstrate the PITT technology as a method of evaluating remedial efforts in an unsaturated zone contaminated with a complex hydrocarbon mixture. This involved four tasks: (1) selecting tracers suitable for detection of the NAPL mixture, (2) completing column studies to determine the phase behavior of the tracers in the NAPL mixture, (3) designing the field tracer test, and (4) successfully completing the field test.

This report documents the completion of these two objectives.

2. Theoretical Background

2.1 Phase Equilibria Thermodynamics

The foundation of the PITT technology is the partitioning tracer. In a vadose zone PITT, the distribution of a partitioning tracer between the mobile air phase and the immobile NAPL or water phases can be described by equilibrium thermodynamics. The following two sections delineate the phase equilibria theory involved for a vadose zone PUT.

2.1.1 The Partition Coefficient

The partition coefficient, K , of a partitioning tracer quantifies the fraction of tracer in the air and liquid phases at equilibrium. For this case, equilibrium describes the condition whereas there is no net change in the concentration of tracer in the air and liquid phases. The partition coefficient is defined as the ratio of the concentration [M/L³] of tracer i in the liquid phase j to the concentration of tracer i in the air phase, or

$$K_{i,j} = \frac{C_{i,j}}{C_{i,a}} = \frac{x_{i,j} \frac{\rho_j}{MW_j}}{x_{i,a} \frac{\rho_a}{MW_a}} = \frac{x_{i,j} \cdot v_a}{x_{i,a} \cdot v_j} \quad (1)$$

where C_{ij} is the concentration of i in liquid phase j [M/L³]

$C_{i,a}$ is the concentration of i in the air phase [M/L³]

x_{ij} is the mole fraction of i in liquid phase j

$x_{i,a}$ is the mole fraction of i in the air phase

v_j is the molar volume of phase j

v_a is the molar volume of air

MW_j is the molecular weight of phase j

MW_a is the molecular weight of air

For the phase equilibrium of tracer i between phase j and air,

$$\phi_{i,a} \cdot x_{i,a} = \phi_{i,j} \cdot x_{i,j} \Leftrightarrow \frac{x_{i,j}}{x_{i,a}} = \frac{\phi_{i,a}}{\phi_{i,j}} \quad (2)$$

where $\phi_{i,j}$ is the fugacity coefficient of i in phase j [--]

$\phi_{i,a}$ is the fugacity coefficient of i in the air phase

Because the pressure in the air phase is near atmospheric, $\phi_{i,a}$ can be set equal to one. Substituting equation (2) into (1), and inserting $\phi_{i,a} = 1$,

$$K_{i,j} = \frac{v_a}{\phi_{i,j} \cdot v_j} \quad (3)$$

2.1.2 Modeling Tracer Phase Equilibria

It is evident from equation (3) that in order to model equilibrium tracer partitioning, three variables must be measured or estimated: the molar volumes of the air and liquid phases and the fugacity of tracer i in liquid phase j . The molar volumes can generally be measured or found in the literature. The fugacity of tracer i in the liquid phase j can be determined by performing a column experiment to determine $K_{i,j}$, then using equation (3) along with the known partial molar volumes to calculate $\phi_{i,j}$. When the liquid phase consists of a single component such as water, this is the only necessary step. However, when the liquid phase is a complex NAPL mixture, the fugacity is dependent on composition. If the composition varies in the field and the

fugacity is sensitive to this variation, then the compositional dependence must be estimated.

The NAPL studied in this research was predominantly composed of hydrocarbons, so an equation of state (EOS) (Peng and Robinson, 1976) was used to estimate the fugacity of the tracer in the mixture. The equation of state could be “tuned” for each tracer by using laboratory data and a NAPL of known composition. In this way, the “tuned” EOS could be used as a predictive tool to analyze the field tracer data. Hansen (1996) performed the thermodynamic analysis and modeling of the hydrocarbon mixture.

2.2 Method of Moments

It has been shown that method of moments theory in conjunction with a PITT may be used to determine liquid saturations in a porous media, given the difference in mean residence times between two partitioning tracers (Lake, 1989). Lake’s (1989) development was for a steady-state two-phase flow containing a nonadsorbing tracer component which partitions between the two phases. The following development is similar, but allows for three-phase partitioning, since this study deals with NAPL/water/air systems.

The overall flux F_i in a permeable medium flowing N phases is (Lake, 1989)

$$F_i = \sum_{j=1}^N f_j C_{ij} \quad (4)$$

The total fluid phase concentration C_i of tracer i is

$$C_i = \sum_{j=1}^N S_j C_{ij} \quad (5)$$

where C_{ij} = Concentration of tracer i in phase j [M/L³]
 f_j = Fractional flow of phase j
 S_j = Saturation of phase j

Combining equation (1) with equations (4) and (5) and using subscripts N , W and G for NAPL, water and air, respectively, yields

$$F_i = (f_N K_{i,N} + f_G + f_W K_{i,W}) C_{i,G} \quad (6)$$

$$C_i = (S_N K_{i,N} + S_G + S_W K_{i,W}) C_{i,G} \quad (7)$$

The dimensionless residence time for any component i can be expressed as

$$\bar{t}_D = \frac{\partial C_i}{\partial F_i}$$

For steady-state flow,

$$\bar{t}_D = \frac{C_i}{F_i} \quad (8)$$

Combining equation (8) with equations (6) and (7) yields

$$\bar{t}_D = \frac{S_N K_{i,N} + S_G + S_W K_{i,W}}{f_N K_{i,N} + f_G + f_W K_{i,W}} \quad (9)$$

Assuming the NAPL and water phases are immobile, then

$$f_N = 0$$

$$f_W = 0$$

$$f_G = 1$$

and from equation (9),

$$\bar{t}_D = S_N K_{i,N} + S_G + S_W K_{i,W} \quad (10)$$

Since

$$S_N + S_G + S_W = 1$$

then

$$\bar{t}_D = S_W(K_{i,W} - 1) + S_N(K_{i,N} - 1) + 1 \quad (11)$$

For tracers 1 and 2 which have partition coefficients $K_{1,W}$, $K_{1,N}$ and $K_{2,W}$, $K_{2,N}$

$$\bar{t}_{D,1} = S_W(K_{1,W} - 1) + S_N(K_{1,N} - 1) + 1 \quad (12)$$

$$\bar{t}_{D,2} = S_W(K_{2,W} - 1) + S_N(K_{2,N} - 1) + 1 \quad (13)$$

The swept pore volume, V_P , is inherent in $\bar{t}_D$, and allows the dimensionless residence times to be related to the experimentally determined residence times, $\bar{t}$ as follows:

$$V_P = \frac{Q\bar{t}_1}{\bar{t}_{D,1}} = \frac{Q\bar{t}_2}{\bar{t}_{D,2}} \quad (14)$$

where

$$\bar{t}_i = \frac{\int_0^{t_f} t C_i dt}{\int_0^{t_f} C_i dt}$$

and Q is the volumetric flow rate.

Substituting (10) and (11) into (12),

$$\frac{\bar{t}_1}{S_W(K_{1,W} - 1) + S_N(K_{1,N} - 1) + 1} = \frac{\bar{t}_2}{S_W(K_{2,W} - 1) + S_N(K_{2,N} - 1) + 1} \quad (15)$$

Rearranging,

$$S_N = \frac{\bar{i}_2[S_W(K_{I,W} - 1) + 1] - \bar{i}_1[S_W(K_{2,W} - 1) + 1]}{\bar{i}_1(K_{2,N} - 1) - \bar{i}_2(K_{I,N} - 1)} \quad (16)$$

A non-partitioning tracer is generally included as a reference tracer in a PITT. If tracer 1 is a non-partitioning tracer ($K_{N,1} = 0$, $K_{W,1} = 0$), then equation (16) simplifies to

$$S_N = \frac{\bar{i}_2(1 - S_W) - \bar{i}_1[S_W(K_{2,W} - 1) + 1]}{\bar{i}_1(K_{2,N} - 1) + \bar{i}_2} \quad (17)$$

For a NAPL partitioning tracer, where $K_{W,2} = 0$, equation (17) further reduces to

$$S_N = \frac{(\bar{i}_2 - \bar{i}_1)(1 - S_W)}{\bar{i}_1(K_{2,N} - 1) + \bar{i}_2} \quad (18)$$

For a water partitioning tracer, where $K_{N,2} = 0$, equation (17) can be solved for S_W yielding

$$S_W = \frac{(\bar{i}_2 - \bar{i}_1)(1 - S_N)}{\bar{i}_1(K_{2,W} - 1) + \bar{i}_2} \quad (19)$$

Equations 18 and 19 can be solved simultaneously for S_N and S_W .

The volume of NAPL detected can be determined by multiplying the NAPL saturation by the swept pore volume, or

$$V_N = S_N \cdot V_P \quad (20)$$

From equation (18)

$$S_N = \frac{(\bar{i}_2 - \bar{i}_1)S_G}{\bar{i}_1 K_{2,N}} \quad (21)$$

and recognizing that

$$V_P = \frac{Q\bar{t}_1}{S_G} \quad (22)$$

We can substitute equations (21) and (22) in equation (20) to yield

$$V_N = \frac{(\bar{t}_2 - \bar{t}_1)Q}{K_{2,N}} \quad (23)$$

For the case of multiple injection wells and producing wells, the equations apply to each well pair where the flow rate in equations (22) and (23) can be calculated as

$$Q = \frac{m}{M} Q_T \quad (24)$$

where M is the total mass of tracer injected, Q_T is the total rate of all of the extraction wells, and m is the mass recovered from the individual producer.

If we define a retardation factor $R_F = t_2/t_1$, then equation 19 can be rearranged to

$$R_F = 1 + \frac{K_N S_N}{(1 - S_N - S_W)} \quad (25)$$

Jin (1995) gives criteria for a range of retardation factors that are viable in a field test, where $1.2 < R_F < 3.0$. Values lower than 1.2 are in a noise region, whereas values higher than 3.0 may cause too long a test. Therefore, given a range of K values for a tracer mixture, we can determine a range of likely detectable saturations.

2.3 Extrapolation of Experimental Tracer Response Curves

To ensure the accuracy of the method of moments the tracer data should be complete, since a substantial amount of information is contained in the tail of a

response curve (Jin 1995). Extended tails may be incomplete because of concentrations falling below detection limits, or the necessity for prolonged experimental run times.

An extrapolation technique exists that can improve the accuracy of the response data (Jin, 1995)

For an assumed exponential decline of the tracer data,

$$\bar{t} = \frac{\int_0^{t_b} t C dt + m(m + t_b) C_b}{\int_0^{t_b} C dt + m C_b} - \frac{t_s}{2} \quad (26)$$

where m = inverse slope of the straight line tail when the tracer response curves are plotted on a semi-log scale [T]

C_b = tracer concentration at time t_b

3. Laboratory Studies

In order for the above theory to be put to application, relevant data had to be measured in the laboratory. Column studies were chosen as a means for determining partition coefficients for each tracer/liquid pair.

3.1 Determination of Water Content in Unsaturated Porous Media

3.1.1 Tracer Selection

The initial task was to find a compound suitable for use as an air/water partitioning tracer. Compounds were screened in the literature by the following criteria:

- (1) Good solubility in water
- (2) Mixes easily at high concentrations with air
- (3) Non-toxic
- (4) Low detection limit
- (5) Low NAPL solubility
- (6) Stable

An extensive literature search yielded two likely compounds: trifluoromethane and difluoromethane. The asymmetric structure of these compounds makes them polar enough to yield good water solubility. They are easily detected with GC-FID and are gases at room temperature. They are non-toxic, stable in normal temperature ranges, and bioresistant. Of these two compounds, difluoromethane was selected for testing

because of its higher water solubility compared to trifluoromethane. Table 3.1.1 gives a summary of the physical properties for these substances.

3.1.2 Equipment

Figure 3.1.1 shows a schematic of the equipment setup for these experiments. The injected air was a compressed source throttled to 20 psi before reaching the Porter Model 3VCD-1000 flow controller which was fitted with the low-flow adapter. The tracer injection valve was a ten-port, two position Valco manual switching valve fitted with a 1 mL injection loop. The columns used were glass Supelco chromatography grade, 30cm long and 4.8cm in diameter. Each column was fitted with a flow adapter that could be adjusted according to variations in actual pack length. The auto-sampling system consisted of a ten-port, two-position Valco valve with actuator wired to a Buck Model 610 gas chromatograph. Sampling and analysis were controlled using a Dell Latitude 433cx PC installed with Peaksimple for Windows software. A bubble meter from Fisher Scientific was used to monitor flow rates.

3.1.3 Materials

Ottawa sand was used to pack the columns. This sand was from US Silica with an F-95 designation. The average grain size was measured to be approximately 95 mesh.

The three tracers used in these experiments were methane, argon, and difluoromethane. The argon and methane were chemically pure and acquired from Air

Liquide. The difluoromethane was rated 98% pure and acquired from PCR Research Chemicals. Table 3.1.1 gives a summary of the physical properties for these compounds.

3.1.4 Experimental Procedures

Packed columns for the one-dimensional air/water partitioning tracer experiments were prepared using clean Ottawa sand. While the glass column was vibrated mechanically, the dry Ottawa sand was added vertically through a series of screens which helped to induce a uniform cross-section. Deionized water was then introduced through the inlet port until the pack was saturated. Air was then induced to flow through the pack under 5 psi pressure, forcing some of the water from the outlet, resulting in a residual water saturation. Water saturations for the three experiments ranged from 35% to 54% of porosity. Saturations were determined by mass balance and confirmed by the conservative tracer tests.

The packed column for the one-dimensional air/water/NAPL partitioning tracer experiment was prepared in a similar fashion. After the packed column with 29% water saturation had been prepared, a NAPL mixture of 0.51/.28/.21 mole fraction TCE/benzene/naphthalene was added to create a NAPL residual of 13.1% of porosity. This particular NAPL mixture was used so that results could be compared to those of Whitley et. al., (1995). A precolumn was prepared with the same mixture. This precolumn was necessary to saturate the air stream and eliminate stripping of volatile components from the packed column.

The experiments were carried out at room temperature. A steady flow of nitrogen was established in the system, with the flow rate set by a Porter low-flow controller. Flow rates were set low enough (linear velocities of approximately 4 ft/day) so that local equilibrium partitioning between the air and liquid phases could be assumed (Whitley et al., 1995). Flow rates were checked using a bubble meter. After the carrier flow was established, the conservative tracer, argon, was injected through a 1 mL sample loop. Samples of the effluent were taken using a lo-port two-position Valco autosampling valve which periodically diverted 1 mL fractions of the effluent stream into a Buck Scientific 300 series gas chromatograph. The chromatographic method involved a molecular sieve packed column and a thermal conductivity detector with a helium carrier.

Difluoromethane was injected and sampled in the same manner except that the chromatographic method involved an AT-1000 phase Carbo-Pak column and flame ionization detector with a nitrogen carrier.

3.1.5 Results

Table 3.1.2 summarizes the column characteristics for each experiment and the corresponding results. The determined partition coefficient between air and water for difluoromethane was established to be 1.7. Figure 3.1.2 shows the response curves for the air/water partitioning tracer column experiments. These curves were normalized to show the increased retention with increasing water saturation. Two things should be noted on these curves. First, the exponential decline is evident in the linear tailing on the semi-log plot. Second with increasing water saturation, the increased

partitioning is evidenced not only in the delayed breakthrough but also in the increased slope of the tail of the response curve.

Figure 3.1.3 shows the response curve for the air/water/NAPL partitioning tracer column experiment. In this case, the difluoromethane partitioned both into the water and the NAPL mixture. By solving equations (18) and (19) simultaneously (section 2.2) the air/NAPL partition coefficient was determined to be 2.3.

3.2 Determination of NAPL Residuals in the Vadose Zone

3.2.1 Tracer Selection

Table 3.2.1 summarizes the chemical compounds used as gas tracers in these experiments. The per-fluorocarbon series used in these experiments have been established as a viable set of NAPL partitioning gas tracers (Whitley et al, 1995, INTERA, 1997). These compounds were screened and found to have partition coefficients that spanned a suitable range. A gas tracer mixture containing all of the compounds was made in a 22.4 L vessel and pressurized with nitrogen. The mixture was verified to be single phase through gas chromatographic analysis at elevated temperatures.

3.2.2 Equipment

The equipment setup was identical to the difluoromethane experiments (see section 3.2.1) except for the type of packed column used. A 30cm long by 2.5cm diameter Kontes glass chromatography column was used in the first experiment. The

next two experiments used a 30cm long by 2.2cm diameter stainless steel column with Swagelok end fittings.

3.2.3 Materials

Contaminated soil was obtained from field site push samples (see Section 4.1 for a description of this site). Two composites were made from samples taken at various locations and depths. The soil was mostly sand, with a small percentage of clay and silt. The soil was sieved to a maximum 2mm diameter grain size. A subsample was taken from each composite and solvent extracted (US EPA, 1992) to determine contamination levels. The first soil composite contained 10840mg NAPL/Kg soil and was used for the first column study. The second soil composite contained 13550mg NAPL/Kg soil and was used for the next two column studies. The extracted NAPL in each case had a density of 0.88 g/cc.

3.2.4 Experimental Procedures

The columns were packed by attaching the sleeve to a vibrating jig and adding soil in incremental 1cm lifts. Each lift was lightly tamped and the column rotated to help prevent preferential pathways in the longitudinal direction. Table 3.2.2 includes a summary of column characteristics for each experiment.

After a column was put on-line, the system was allowed to equilibrate overnight to help ensure a constant flow rate over the course of the experiment. The 1 mL sample loop was then filled with the tracer mixture at atmospheric pressure, and the valve was switched to inject the mixture on column.

Effluent sampling occurred every 15 minutes over the course of the experiment. Methane and difluoromethane were detected by flame ionization(FID), while the perfluorocarbons were analyzed using an electron capture detector(ECD). Detection limits were <10ppm-w for the FID detector and <1ppm-w for the ECD detector.

3.2.5 Results

Figure 3.2.1 shows the tracer response curves for experiment Kirt 12, which are typical of all three experiments. Table 3.2.2 gives a summary of the experimental results for the three experiments. The partition coefficient values for each tracer were consistent among the laboratory experiments, varying 9.8% at most. This indicates that the NAPL composition was relatively consistent amongst the different contaminated soil samples tested. Note that in some cases, there was slightly more than 100% tracer recovery. This is due to small errors in the GC calibration.

Table 3.1.1: Physical Properties of Tracers Used
(PCR, 1994)

Name	Formula	MW	Boiling Point (C)	Water Solubility (mg/L)
Argon	Ar	39.9	-186	58
Methane	CH ₄	16.0	-181	24
Difluoromethane	CF ₂ H ₂	52.0	-52	4355
Trifluoromethane	CF ₃ H	70.0	-84	769

Table 3.1.2: Summary of Column Characteristics and Results

Column	Flow Velocity (m/d)	V _P (cm ³)	S _w	S _N	K _w	K _N
1ND2	1.40	155.2	0.541	--	1.67	--
2ND2	1.37	141.6	0.455	--	1.68	--
3ND2	1.01	141.6	0.335	--	1.74	--
NAW9	0.88	148.7	0.286	0.131	1.70*	2.06

* averaged from experiments 1ND2, 2ND2, 3ND2

Table 3.2.1: Summary of Tracers Used

Tracer Name	Formula	M.W. (amu)	B.P. (C)
Methane	CH ₄	16.04	-161.0
Difluoromethane	CF ₂ H ₂	52.02	-51.7
Perfluoromethylcyclohexane	C ₇ F ₁₄	350.05	76.0
Perfluoro-1,3-dimethylcyclohexane	C ₈ F ₁₆	400.06	101.5
Perfluoro-1,3,5-dimethylcyclohexane	C ₉ F ₁₈	450.07	125.0
Perfluorodecalin	C ₁₀ F ₁₈	462.08	141.5

Table 3.2.2: Results for Experiments in Kirtland Field Soil

Test	Tracer	Q (mL/min)	V _P (mL)	S _w	V _N (mL)	S _N	t _i (min)	K _N	Mass Inj. (μg)	Mass Rec. (μg)	% Recovery
Kirt11	CH ₄	0.156	58.3	0.28	3.76	0.065	246	—	39.5	39.7	100.4
	CF ₂ H ₂						422	—	128.4	130.0	101.3
	C ₇ F ₁₄						445	8.3	1.38	1.38	100.3
	C ₈ F ₁₆						622	15.6	1.52	1.56	102.5
	C ₉ F ₁₈						850	25.0	1.24	1.24	99.5
	C ₁₀ F ₁₈							—	—	—	—
Kirt12	CH ₄	.104	44.1	0.32	3.30	0.075	369	—	85.5	79.3	92.8
	CF ₂ H ₂						619	—	68.1	69.0	101.2
	C ₇ F ₁₄						650	8.8	16.8	15.7	93.6
	C ₈ F ₁₆						836	14.7	16.8	16.8	100.3
	C ₉ F ₁₈						1078	22.4	16.8	16.9	100.9
	C ₁₀ F ₁₈						2543	68.6	16.8	18.8	112.3
Kirt14	CH ₄	.100	46.7	0.29	3.18	0.068	430	—	73.9	76.4	103.5
	CF ₂ H ₂						670	—	58.8	61.7	104.8
	C ₇ F ₁₄						729	9.4	14.5	13.9	96.4
	C ₈ F ₁₆						951	16.4	14.5	15.2	104.8
	C ₉ F ₁₈						1222	24.9	14.5	14.0	96.9
	C ₁₀ F ₁₈						2750	73.2	14.5	13.8	95.4

Figure 3.1.1: Experimental Setup for Column Studies

Figure 3.1.2: Tracer Response Curves for CF₂H₂ Column Studies

Figure 3.1.3: Tracer Response Curves for Experiment NAW9

Figure 3.2.1: Tracer Response Curves for ND12

4. Field Test

4.1 Site Background

The field site is located on Kirtland Air Force Base in Albuquerque, NM. On the grounds is a former fire training pit. Various undocumented LNAPLs, including diesel fuel and some heavier hydrocarbon compounds were spread on the ground surface and ignited, so that extinguishing techniques could be demonstrated. Unburned NAPL penetrated the ground surface and infiltrated the vadose zone to a depth of at least 20 ft below ground surface (bgs). Very little information was available regarding the location and amount of contaminant loading that had occurred during the operation of this pit. Push tubes yielded soil samples containing total petroleum hydrocarbon (TPH) levels ranging from less than 5000mg NAPL/kg soil to nearly 20000mg NAPL/kg soil.

This site was chosen for demonstration of a radio frequency heating soil vapor extraction remediation technique (Daniel et al. 1996). The supervisors of the remediation effort chose a treatment volume that consisted of a cube, 10.0 ft per side, at a depth of 10.0 A bgs. A partitioning interwell tracer test (PITT) was to provide site characterization in support of this remediation effort.

4.2 Field Tracer Test Design

The PITT. well layout called for three well pair groupings at three depths per grouping as shown in Figure 4.2.1, plan view. Figure 4.2.2 shows the various depths of each well grouping. Computer simulations with this layout were then run to help

determine the test operational parameters (Nicot, 1996). The purpose of these simulations was to design a test likely to be effective whatever the field parameters, still little known, happen to be. UTCHEM, the three-dimensional UT multicomponent multiphase flow and transport simulator (Delshad et al., 1995) was used for the simulations and the concentration breakthrough curves were analyzed with the method of moments. A base case scenario was set with the following parameters: a total NAPL volume of 5.7 m^3 , a stochastic permeability field assumed to be lognormal with an average $K=10D$, a variance $\ln K$ of 2.2 and a correlation length of 6 ft (1.8 m) in the horizontal plane.

There were two main characteristics that needed to be determined with the simulations: flow rate and mass of tracers injected. The flow rate was adjusted according the minimum mean residence time that should be achieved for nominal accuracy, in this case one day. After the flow rate was set, the mass of tracer injected was adjusted according to the concentration envelope. After the flow rate was set, the mass of tracer injected was adjusted according to the concentration envelope. This envelop is defined as the two curves limiting the concentrations of the 9 wells at any given timestep.

To define this envelope, the simulated response data (tracer concentration at each timestep) is compiled from all nine wells for a single tracer. Here, time is defined by volume of air produced at the extraction wells. At each timestep, the tracer concentrations from all nine wells are compared and the minimum and maximum concentrations are extracted. The curves defined by these minimum and maximum

concentrations are the two curves seen in Figure 4.2.3 which define the concentration envelope for C_0F_{18} . This process is completed for each tracer in the simulation.

The peak tracer concentration needs to fall below the maximum detection limit and approximately two orders of magnitude above the minimum detection limit, to ensure that the breakthrough curve data are complete.

Over 50 simulations were done and suggested the following test characteristics: a total flow rate of 180 m³/day approximately evenly distributed over the nine screens and a total mass of 900 g of conservative tracer and of 200 g of each of the non-partitioning tracers. The test should last a minimum of 5 days but 7 days would increase the accuracy of the results. The slug duration (total tracer injection time) has a minor effect on the results. The expected pressure drops are between 0.1 and 0.2 PSI (700 to 1500 Pa).

4.3 Field Test Materials

The tracer compounds used in the field test were the same as those studied in the lab (Table 3.2.1). The total injected mass of each compound can be found in Table 4.3.1. The tracer mixture was contained in 454 L (120 gal) tank pressurized to 1.72 Mpa (250 psi) with nitrogen.

4.4 Field Test Equipment

Figure 4.4.1 shows a schematic of the field test setup. The gas flow for both injection and extraction was provided by two 1.5 kW Rotron blowers. Main flow lines

consisted of 2.54 cm (1 in) ID flexible PVC tubing. Gas flow rates were measured with an in-line turbine type flowmeter wired to a flow totalizing readout. On the injection side, the main flow was connected to the nine well points with a manifold. Cole-Parmer block-type acrylic rotameters with built in throttling valves were connected to each single well line. The wells were 1.27 cm (.5 in) ID PVC tubes with perforated one foot intervals at the terminal ends. On the extraction side, a similar manifold system was used with 1 L (.26 gal) knockout bottles connected before the rotameters, to prevent water condensation in the meters.

Sampling occurred at each of the extraction well heads. Flexible PVC 0.635 cm (.25 in) ID lines connected the nine well head extraction points to the 10 position Valco dead-end switching valve. The tenth valve position was connected to a gas chromatograph (GC) calibration gas. The sample was drawn from the well head to the GC sample loop under vacuum from a Cole-Parmer 93.2 W high-capacity vacuum pump. The GC sample loop was plumbed to a ten-port Valco valve with a two-position electric actuator. A Buck Model 610 gas chromatograph provided the chemical analysis. A Dell Latitude 433cx PC installed with Peaksimple for Windows software controlled the GC and switching valves. The analytical system was completely automated.

4.5 Field Test Results

Figures 4.5.1 through 4.5.18 show the complete set of response curves for the Kirtland PITT. These figures include the extrapolation lines used in analyzing the results. Table 4.5.1 gives a summary of the averaged (using the results from each of

the four partitioning tracers) field tracer test results for each wellpoint. The complete results for each wellpoint can be found in Table 4.5.2.

There is little indication of spatial trends in NAPL distribution from these results, which is not unexpected considering the sporadic nature of the NAPL infiltration events. Well 4 shows a decrease in average NAPL saturation, S_N , with depth. However, note that the swept volume increased with depth, so less contaminated soil beneath the target zone may have contributed to the decreasing average saturation. This is not seen in the deep zone of well 5, because this well had a low flow rate in comparison to the others. The detected saturations ranged from a low of .007 in the deep zone of well 4 to a high of .027 in the shallow zone of well 5.

Table 4.3.1: Mass Recovery for Field Test

Tracer	Injected (g)	Recovered (g)	Recovery (%)
CH ₄	500	285.1	57.0
CF ₂ H ₂	400	883.6	51.4
C ₇ F ₁₄	100	58.0	58.0
C ₈ F ₁₆	100	57.4	57.4
C ₉ F ₁₈	59	33.2	56.3
C ₁₀ F ₁₈	42	22.9	54.5

Table 4.5.1: Summary of Field Test Results

Well	V_P (ft³)	S_w	V_N (ft³)	S_N
TT4A	513	0.14	11.19	0.022
TT4B	1053	0.06	14.85	0.014
TT4C	1414	0.10	9.88	0.007
TT5A	573	0.26	15.34	0.027
TT5B	343	0.09	5.82	0.017
TT5C	26	0.16	0.60	0.023
TT6A	248	0.16	1.97	0.008
TT6B	386	0.18	7.56	0.020
TT6C	1318	0.15	13.31	0.010
Totals	5875		80.52	0.014

Table 4.5.2: Results from Field Tracer Experiment

Well	Tracer	Residence Time (ft ³)	Average Flow (ft ³ /h)	Mass Recovered (g)	Rf	Swept Volume (ft ³)	K _w	S _w	K _N	V _N	S _N
							(L _c /L _t)		(L _c /L _t)	(ft ³)	
TT4A	CH ₄	917	30	32.2	1.00				0		
	CF ₂ H ₂	1177	30	25.4	1.28		1.7	.140	0		.018
	C ₇ F ₁₄	1037	30	6.4	1.13	530		.140	8.83	6.68	.013
	C ₈ F ₁₆	1188	30	6.3	1.30	523		.140	15.56	8.39	.016
	C ₉ F ₁₈	1636	30	3.5	1.78	508		.140	24.1	13.77	.027
	C ₁₀ F ₁₈	2662	30	2.5	2.90	508		.140	70.9	11.41	.022
	average					513				11.19	.022
TT4B	CH ₄	1368	30	44.6	1.00				0		
	CF ₂ H ₂	1520	30	36.0	1.11		1.7	.060	0		.013
	C ₇ F ₁₄	1592	30	9.3	1.16	1067		.060	8.83	18.25	.017
	C ₈ F ₁₆	1672	30	9.4	1.22	1074		.060	15.56	14.19	.013
	C ₉ F ₁₈	1876	30	5.3	1.37	1028		.060	24.1	14.64	.014
	C ₁₀ F ₁₈	2602	30	3.9	1.90	1043		.060	70.9	12.32	.012
	average					1053				14.85	.014
TT4C	CH ₄	1562	30	49.1	1.00				0		
	CF ₂ H ₂	1866	30	41.3	1.19		1.7	.102	0		.004
	C ₇ F ₁₄	1562	30	10.5	1.00	1409		.102	8.83	0.02	.000
	C ₈ F ₁₆	1563	30	10.5	1.00	1409		.102	15.56	0.04	.000
	C ₉ F ₁₈	1750	30	6.0	1.12	1376		.102	24.1	6.14	.004
	C ₁₀ F ₁₈	2431	30	4.4	1.56	1414		.102	70.9	9.88	.007
	average					1414				9.88	.007
TT5A	CH ₄	808	30	36.9	1.00				0		
	CF ₂ H ₂	1294	30	28.4	1.60		1.7	.255	0		.025
	C ₇ F ₁₄	1013	30	6.9	1.25	591		.255	8.83	12.30	.021
	C ₈ F ₁₆	1327	30	6.7	1.64	581		.255	15.56	17.18	.030
	C ₉ F ₁₈	1732	30	4.0	2.14	592		.255	24.1	19.99	.034
	C ₁₀ F ₁₈	2584	30	2.6	3.20	530		.255	70.9	11.89	.022
	average					573				15.34	.027
TT5B	CH ₄	766	20	22.1	1.00				0		
	CF ₂ H ₂	893	20	16.3	1.17		1.7	.088	0		.009
	C ₇ F ₁₄	787	20	3.9	1.03	382		.088	8.83	1.09	.003
	C ₈ F ₁₆	837	20	3.7	1.09	362		.088	15.56	1.95	.005
	C ₉ F ₁₈	1165	20	2.2	1.52	376		.088	24.1	7.26	.019
	C ₁₀ F ₁₈	1620	20	1.3	2.11	311		.088	70.9	4.39	.014
	average					343				5.82	.017
TT5C	CH ₄	54	1	1.0	1.00				0		
	CF ₂ H ₂	73	1	0.8	1.34		1.7	.163	0		.021
	C ₇ F ₁₄	65	1	0.2	1.21	29		.163	8.83	0.56	.019
	C ₈ F ₁₆	78	1	0.2	1.44	28		.163	15.56	0.63	.023
	C ₉ F ₁₈	99	1	0.1	1.83	29		.163	24.1	0.81	.028
	C ₁₀ F ₁₈	151	1	0.1	2.79	20		.163	70.9	0.40	.021
	average					26				0.60	.023

TT6A	CH ₄	654	30	21.5	1.00			0	
	CF ₂ H ₂	859	30	17.3	1.31		1.7 .155	0	.005
	C ₇ F ₁₄	673	30	4.3	1.03	255	.155	8.83	0.73 .003
	C ₈ F ₁₆	654	30	4.2	1.00	253	.155	15.56	0.01 .000
	C ₉ F ₁₈	782	30	2.5	1.20	251	.155	24.1	1.71 .007
	C ₁₀ F ₁₈	1159	30	1.7	1.77	245	.155	70.9	2.24 .009
	average					248			1.97 .008
TT6B	CH ₄	975	30	22.7	1.00			0	
	CF ₂ H ₂	1360	30	18.2	1.39		1.7 .183	0	.027
	C ₇ F ₁₄	1153	30	4.2	1.18	393	.183	8.83	6.52 .017
	C ₈ F ₁₆	1310	30	4.1	1.34	384	.183	15.56	6.78 .018
	C ₉ F ₁₈	1615	30	2.5	1.66	396	.183	24.1	8.58 .022
	C ₁₀ F ₁₈	2942	30	1.6	3.02	370	.183	70.9	8.35 .023
	average					386			7.56 .020
TT6C	CH ₄	1228	30	55.1	1.00			0	
	CF ₂ H ₂	1611	30	45.9	1.31		1.7 .154	0	.005
	C ₇ F ₁₄	1272	30	12.3	1.04	1379	.154	8.83	4.71 .003
	C ₈ F ₁₆	1307	30	12.3	1.06	1376	.154	15.56	4.76 .003
	C ₉ F ₁₈	1603	30	7.0	1.31	1351	.154	24.1	14.28 .011
	C ₁₀ F ₁₈	2228	30	4.8	1.81	1285	.154	70.9	12.34 .010
	average					1318			13.31 .010

Figure 4.2.1: Plan view of well layout (TT-1 through TT-3, Injection TT-4 through TT-6, Extraction)

Figure 4.2.2: Profile view of well layout

Figure 4.2.3: Example of Simulation Tracer Response Curves(Nicot, 1996)

Figure 4.4.1: Schematic of Field Equipment Setup

Figure 4.5.1: Tracer Response Curves for TT4A

Figure 4.5.2: Tracer Response Curves for TT4A

Figure 4.5.3: Tracer Response Curves for TT4B

Figure 4.5.4: Tracer Response Curves for TT4B

Figure 4.5.5: Tracer Response Curves for TT4C

Figure 4.5.6: Tracer Response Curves for TT4C

Figure 4.5.7: Tracer Response Curves for TT5A

Figure 4.5.8: Tracer Response Curves for TT5A

Figure 4.5.9: Tracer Response Curves for TT5B

Figure 4.5.10: Tracer Response Curves for TT5B

Figure 4.5.11: Tracer Response Curves for TT5C

Figure 4.5.12: Tracer Response Curves for TT5C

Figure 4.5.13: Tracer Response Curves for TT6A

Figure 4.5.14: Tracer Response Curves for TT6A

Figure 4.5.15: Tracer Response Curves for TT6B

Figure 4.5.16: Tracer Response Curves for TT6B

Figure 4.5.17: Tracer Response Curves for TT6C

Figure 4.5.18: Tracer Response Curves for TT6C

5. Conclusions

5.1 Laboratory Determination of Water Saturations

The method of moments development leads to several interesting points of discussion. First, it should be noted that an air/NAPL partitioning tracer test cannot directly determine the NAPL saturation in the vadose zone. An air/NAPL partitioning tracer test will provide a measure of the volume of NAPL that was swept during the test, but requires knowledge of the water saturation to then calculate the NAPL saturation. Second, note that the water saturation cannot be determined using an air/water/NAPL partitioning tracer test without knowledge of the NAPL saturation. However, as indicated before, equations (18) and (19) can be solved simultaneously to provide both the water and NAPL saturations. Therefore, if an air/water/NAPL partitioning tracer such as difluoromethane is included in a vadose zone partitioning tracer test, more information about the swept zone can be determined.

Results from the three air/water partitioning tracer column experiments correlated well, with less than 3% or better deviation from the mean for the determined air/water partition coefficient. The retardation factor for each of these tests falls in the suggested range for a PITT (Jin, 1995).

Results from the column experiment which included the NAPL mixture indicate that difluoromethane does partition into strongly polar organic liquids, such as TCE. For a field test, the air/NAPL partition coefficient would have to be measured experimentally for other organic liquids or mixtures of liquids which would be encountered at that particular site.

As mentioned in the introduction, difluoromethane has the physical characteristics that make it suitable as a gas tracer. The column studies have shown that it has air/liquid partitioning values which make it a suitable candidate for use in a PITT for the estimation of water saturations in the vadose zone.

5.2 Laboratory Determination of NAPL Residuals

The laboratory work done for this study showed that partition coefficients can be reliably determined for NAPLs derived from field samples. The 1-D column test is adequate for both screening candidate tracer compounds, and quantifying their interaction with the resident contaminant.

The perfluorocarbon family of compounds are suitable for use as gas/NAPL partitioning tracers, demonstrating a spectrum of partition coefficient values adequate for detection of a wide range of NAPL saturations. These compounds should be considered for any future gas/NAPL PITT application.

The results for difluoromethane indicated that it did not partition significantly into the NAPL, so it is a very useful tracer for detecting water saturations in this case.

5.3 Field Testing of Liquid Residual Determination

The PITT results indicate that fire training pit at Kirtland APB was shown to have a significant amount of NAPL present in the subsurface (Section 4.5). There was little spatial uniformity of the NAPL distribution evident in the PITT results.

The PITT swept a much larger volume (Table 4.5.1) than was defined as the target remediation volume (Section 4.1). Therefore, the PITT results indicate a larger

total amount of NAPL than would be estimated through soil borings within the target remediation volume only. This is an example of how the large swept volume of a PITT can be a disadvantage in some cases, where a direct comparison to separate measurements is desirable.

For the tracers that had retardation factors (Table 4.5.2) within the acceptable range (Section 2.2), the results for each well were relatively consistent among the different tracers. This indicates that the average composition of the NAPL in the field was similar to that NAPL studied in the lab (Section 3.2.5).

The simulations used in designing the field PITT (Section 4.2) were essential to the success of the project. Although the mean residence time for the conservative tracer in the actual field test averaged 38 hours (Table 4.5.2) which was longer than the 24 hour design., this difference was within acceptable bounds. Also, the concentration response curves fell within the design envelope (Section 4.2) in most cases. Good forward modeling is essential to the PITT design process.

Overall, the PITT was successful at characterizing NAPL contamination in the vadose zone. This technology, and this particular set of per-fluorocarbon compounds should be considered for similar future application.

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The Application of Partitioning Interwell Tracer Tests to the Characterization of Chlorinated Solvent Contamination of Alluvial Aquifers

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Abstract

Zones of dense, non-aqueous phase liquids (DNAPLs) are difficult to characterize as to their volume, composition and spatial distribution using conventional ground-water extraction and soil-sampling methods. Such incompletely characterized sites have negative consequences for those responsible for their remedial design, e.g., the uncertainties in the optimal placement of ground-water extraction wells and in the duration of remediation. However, the recent use of the partitioning interwell tracer test (PITT) to characterize DNAPL zones at sites in New Mexico (unsaturated alluvium) and Texas and Utah (saturated alluvium) demonstrates that the volume and spatial distribution of residual DNAPL can be determined with accuracy. The PITT involves injection of a suite of tracers which reversibly partition to different degrees between the DNAPL and the ground water or soil air, resulting in the chromatographic separation of the tracer signals observed at the extraction well(s). Additionally, a three-dimensional, numerical model of a heterogeneous alluvial aquifer containing DNAPL has been developed for use with the UTCHEM simulator to demonstrate partitioning tracer testing and to address questions that are frequently raised in its application.

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Acronyms and Abbreviations

This list is supplied as an easy-reference guide to the acronyms and abbreviations used throughout this report.

AATDF	Advanced Applied Technology Demonstration Facility
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
bgs	below ground surface
cm	centimeter
c m ³	cubic centimeter
DNAPL	Dense Non-Aqueous Phase Liquid
DOE	Department of Energy
EDC	ethylene dichloride (1,2-dichloroethane
EPA	U.S. Environmental Protection Agency
ft	foot
g	gram
gpm	gallons per minute
GC	gas chromatograph
IPA	isopropyl alcohol
kg	kilogram
K_i	partition coefficient
L	liter
m	meter
mg	milligram
mL	milliliter
NaCl	sodium chloride
NAPL	Non-Aqueous Phase Liquid
PITT	partitioning interwell tracer test
ppm	parts per million
R_f	retardation factor
TCE	trichloroethene
USAF	U. S. Air Force

Terminology

In January 1992, The Environmental Protection Agency published a paper (Estimating Potential for Occurrence of DNAPL at Superfund Sites - Publication 9355.4-07FS) that included a glossary of DNAPL-related terms (adapted from Cherry, 1991). Duke Engineering & Services adheres closely to the definitions included in this glossary in an attempt to minimize the confusion and misuse of many of these terms. The glossary is reproduced below:

DNAPL: A Dense Nonaqueous Phase Liquid. A DNAPL can be either a single-component DNAPL (comprised of only one chemical) or a mixed DNAPL (comprised of several chemicals). DNAPL exists in the subsurface as free-phase DNAPL or as residual DNAPL (see following definitions). DNAPL does not refer to chemicals that are dissolved in ground water.

DNAPL Entry Location: The area where DNAPL has entered the subsurface, such as a spill location or waste pond.

DNAPL Site: A site where DNAPL has been released and is now present in the subsurface as an immiscible phase.

DNAPL Zone: The portion of a site affected by free-phase or residual DNAPL in the subsurface (either the unsaturated zone or saturated zone). The DNAPL zone has organics in the vapor phase (unsaturated zone), dissolved phase (both unsaturated and saturated zone), and DNAPL phase (both unsaturated and saturated zone).

Dissolution: The process by which soluble organic components from DNAPL dissolve in ground water or dissolve in infiltration water and form a ground-water contaminant plume. The duration of remediation measures (either clean-up or long-term containment) is determined by 1) the rate of dissolution that can be achieved in the field, and 2) the mass of soluble components in the residual DNAPL trapped in the aquifer.

Effective Solubility: The theoretical aqueous solubility of an organic constituent in ground water that is in chemical equilibrium with a mixed DNAPL (a DNAPL containing several organic chemicals). The effective solubility of a particular organic chemical can be estimated by multiplying its mole fraction in the DNAPL mixture by its pure phase solubility.

Free-Phase DNAPL: Immiscible liquid existing in the subsurface with a positive pressure such that it can flow into a well. If not trapped in a pool, free-phase DNAPL will flow vertically through an aquifer or laterally down sloping fine-grained stratigraphic units. Also called mobile DNAPL or continuous-phase DNAPL.

Plume: The zone of contamination containing organics in the dissolved phase. The plume usually will originate from the DNAPL zone and extend downgradient for some distance depending on site hydrogeologic and chemical conditions. To avoid confusion, the term “DNAPL plume” should not be used to describe a DNAPL pool; “plume” should be used only to refer to dissolved-phase organics.

Pool and Lens: A pool is a zone of free-phase DNAPL at the bottom of an aquifer. A lens is a pool that rests on a fine-grained stratigraphic unit of limited areal extent. DNAPL can be recovered from a pool or lens if a well is placed in the right location.

Residual DNAPL: DNAPL held in soil pore spaces or fractures by capillary forces (negative pressure on DNAPL). Residual will remain trapped within the pores of the porous media unless the viscous forces (caused by the dynamic force of water against the DNAPL) are greater than the capillary forces holding the DNAPL in the pore. At most sites the hydraulic gradient required to mobilize all of the residual trapped in an aquifer is usually many times greater than the gradient that can be produced by wells or trenches.

Residual Saturation: The saturation (the fraction of total pore space containing DNAPL) at which DNAPL becomes discontinuous and is immobilized by capillary forces. In unsaturated soils, residual saturation typically ranges from 5% to 20% of total pore volume, while in the saturated zone the residual saturation is higher, with typical values ranging from 15% to 50% of total pore volume. At many sites, however, DNAPL migrates preferentially through small-scale fractures and heterogeneities in the soil, permitting the DNAPL to penetrate much deeper than would be predicted from application of typical residual saturation values.

1.0 INTRODUCTION

In August 1996, the Center for Petroleum and Geosystems Engineering at the University of Texas at Austin received approval from the Department of Energy's Office of Energy Research for their research application entitled "In-Situ Characterization of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers". Funding was provided to facilitate a three-year project, and INTERA Inc. was employed as a subcontractor under contract number DE-FG07-96ER14720. Thus far, funding has been used for further in-depth assessment of partitioning interwell tracer tests (PITTs) conducted for the U.S. Air Force and DOE and one commercial solvent manufacturer in Louisiana. This report constitutes a summary of INTERA Inc.'s work during the first year of the project. INTERA Inc. has changed names since October 1997 and is now known as Duke Engineering & Services (DE&S). Therefore, all work performed by INTERA Inc. and described within this report is hereby referred to as the work of DE&S.

The contamination of alluvial aquifers by dense, non-aqueous phase liquids (DNAPLs), such as trichloroethene (TCE) and other toxic chlorinated hydrocarbons, has caused well closure throughout the USA. In the western USA whole alluvial basins have become contaminated with TCE and other chlorinated solvents, while in the east numerous hazardous waste sites have contaminated nearby municipal well fields with TCE and other solvents. Alluvial (i.e., stream-deposited) materials underlie many DOE facilities and have frequently become contaminated with DNAPLs used for metal-surface cleaning by vapor degreasing. Because of concerns with the potentially harmful effects of drinking dissolved chlorinated hydrocarbons or with inhaling their vapors, these compounds are the principal contaminants of concern at most hazardous waste sites (see Table 1.0.1 below which lists certain properties of hydrocarbons mentioned in this report). Unfortunately, as was stated by MacKay and Cherry (1989) of the University of Waterloo, "...very little success has been achieved in even locating the subsurface (DNAPL) sources, let alone removing them."

**Table 1.0.1 Physical and Chemical Properties of Selected Chlorinated .
Hydrocarbons (Values of constants are for a temperature of 20°C
and come from Schwille (1988) unless otherwise noted)**

Chemical Name	Common Name	Molecular Weight (g/mol)	Density (g/cm³)	Aqueous Solubility (mg/L)	K_{oc} (mL/g)	Henry's Constant
1,2-dichloroethane	EDC or 1,2-DCA	99.0	1.26	8,690	14	0.038
1,1,1-trichloroethane	1,1,1-TCA	133.4	1.35	1,252 ⁽¹⁾ 720 ⁽²⁾	152	0.54
trichloroethene	TCE	131.5	1.46	1,421 ⁽¹⁾ 1,385 ⁽³⁾	126	0.30
tetrachloroethene	PCE	165.8	1.63	242 ⁽¹⁾ 239 ⁽³⁾	364	0.54

⁽¹⁾ Solubility at 22-23°C (Broholm, K., and S. Feenstra, 1995. Laboratory Measurements of the Aqueous Solubility of Mixtures of Chlorinated Solvents. Environ. Sci. Technol. 14(1): 9-15.

⁽²⁾ Solubility at 25°C (Schwille, F., 1988. *Dense Chlorinated Solvents in Porous and Fractured Media. Model Experiments*. Lewis Publishers English Language Edition, translated by J.F. Pankow, Chelsea, Michigan).

⁽³⁾ Solubility at 17°C (West, C.C., 1992. Surfactant-enhanced solubilization of tetrachloroethylene and degradation products in pump and treat remediation. *In: Transport and Remediation of Subsurface Contaminants*, edited by D.A. Sabatini and RC. Knox, ACS Symposium Series 491, American Chemical Society, Washington D.C., pp. 149-158).

2.0 METHODS AND NUMERICAL ANALYSIS

2.1 The Partitioning Interwell Tracer Test (PITT)

The partitioning interwell tracer test (PITT) was developed at the University of Texas by GA. Pope of the Department of Petroleum and Geosystems Engineering during the early 1990s. The PITT was developed from a predecessor that had been first used by the oil industry to measure the residual oil saturation that is homogeneously distributed in waterflooded well fields. Dr. Pope and colleagues modified the method so that not only the residual oil saturation but also the swept pore volume and therefore the total volume of heterogeneously-distributed DNAPL could be determined. A particularly important application of the PITT is remediation performance assessment, i.e., the testing of the volume of DNAPL before and after a remediation experiment or operation.

The PITT involves the injection of a suite of conservative and partitioning tracers into one or more wells and the subsequent extraction of the tracer solution from one or more nearby extraction wells. Conservative (nonpartitioning) tracers have a partition coefficient of zero relative to the DNAPL, and therefore pass unretarded through the DNAPL zone. The partitioning tracers have non-zero partition coefficients relative to the DNAPL, and are retarded due to their partitioning into and from the DNAPL. This partitioning is a simple physical process of dissolution and exsolution whereby “like dissolves in like”; no chemical reaction between the tracer and DNAPL occurs. From this partitioning, the chromatographic separation of the tracers is used to measure the volume of DNAPL in the interwell zone between the extraction and injection wells [Jin, et al., 1995, Water Resources Research, 31(5): 1201- 1211]. Therefore, the partitioning tracer test allows the detection and volume estimation of DNAPL.

Gas tracers (i.e. perfluorocarbons) are commonly used in the unsaturated zone of an aquifer, whereas liquid tracers (i.e. alcohols) are used in the saturated zone. Suitable tracers are selected based on specific criteria, which include environmental acceptability, chemical and biological stability, cost, availability in sufficient quantity, low detection limits in produced fluids, suitable partition coefficients, low adsorption on the soil or in the natural organic matter and good solubility and compatibility in the carrier fluid (water or air).

The partition coefficient (K_i) is defined as:

$$K_i = \frac{C_{i,N}}{C_{i,M}} \quad (1)$$

where:

$C_{i,N}$ = the concentration of the “i”th tracer in the DNAPL

$C_{i,M}$ = the concentration of the “i”th tracer in the mobile phase, i.e., the air or ground water transporting the tracer.

The retardation coefficient for the partitioning tracer is a function not only of its own partition coefficient, but also of the volume of the DNAPL present in the interwell space being swept by the tracer solution. Thus, the higher the DNAPL saturation (i.e., percentage volume of pore space occupied by the DNAPL), the greater the retardation of a particular tracer due to partitioning. The retardation of a tracer in a DNAPL-contaminated, water-saturated system is given by:

$$R_f = 1 + \frac{K_i S_N}{1 - S_N} \quad (2)$$

where:

S_N = the average DNAPL saturation.

Because soil moisture can sorb gaseous tracers, the equivalent expression for the retardation factor in the vadose zone, i.e., partially-saturated porous media, is:

$$R_f = 1 + \frac{K_i S_N}{1 - S_N - S_w} \quad (3)$$

where:

S_w = the water saturation of the aquifer.

Thus $S_N + S_w + S_A = \theta$, the porosity, and S_A is the air saturation.

The partitioning process is caused by the dissolution of the partitioning tracers into the DNAPL until equilibrium partitioning has been achieved, then the exsolution of the same tracers back into the ground water as dictated by the partition coefficient (see equation 1). Following the cessation of tracer injection, the partitioning tracer concentration in the ground water adjacent to the residual DNAPL will decline because of continuing injection of tracer-free ground water, and the net flux of partitioning tracers will be from the DNAPL back into the ground water in order to preserve the equilibrium partitioning dictated by the particular partition coefficient for the tracer. During this period of tracer interaction with the DNAPL, it is critical that flow rates of the mobile phase be slow enough to allow tracer equilibrium with the DNAPL, yet fast enough to ensure capture of the majority of the tracers injected. Thus, the recovery of partitioning tracers at the extraction well is delayed (i.e. retarded) relative to the recovery of the conservative tracer which has a zero partition coefficient. Since the retardation factor for each partitioning tracer R_f (as

defined in equation 2) is a function of both the partition coefficient (K_i) for the tracer and the average DNAPL saturation, S_n , of the DNAPL-contaminated aquifer, we can solve for S_n by measuring R_f for tracer pairs with known coefficients, K_i .

Thus, before the tracer test, the average DNAPL saturation and the total DNAPL volume in the swept pore volume, and the tracer-swept pore volume are unknown. Therefore, a suite of partitioning tracers with known partition coefficients for the water/DNAPL system are employed to ensure that at least one tracer response curve will be generated with sufficient separation from the conservative tracer ($K_i = 0$) response curve to calculate the volume of DNAPL in the test zone which is defined by the tracer-swept pore volume (“swept pore volume”). If additional tracer response curves are produced with sufficient separation during the test timespan, then additional DNAPL volume calculations can be made to increase confidence levels for the PITT results. For reasons of economy and tracer-signal detection, it is desirable to employ tracers which yield retardation factors in the range 1.2-40.

The analysis of the tracer response curves has traditionally involved a method of moments analysis which remains the initial data analysis tool. Recently, methods of inverse analysis were introduced to use the tracer data to solve for both permeability and saturation distribution.

2.2 Method of First Moment Analysis

The theoretical foundation of the method of first temporal moment for the NAPL partition interwell tracer test can be found in Jin *et al.* (1995) and Jin (1995). Only some pertinent equations which relate to the estimation of average NAPL saturation and tracer swept volume are given here. For a partitioning tracer test with multiple extraction wells, the following equations apply to each individual extraction well.

The average NAPL saturation in the tracer swept pore volume (S_n) is calculated using the following form of equation 3:

$$S_n = \frac{(R_f - 1)}{R_f + K - 1} \quad (4)$$

where:

K = the partition coefficient of the partitioning tracer

R_f = the retardation factor, defined as:

$$R_f = \frac{\bar{t}_p}{\bar{t}_n} \quad (5)$$

where:

- $\bar{t}_p$ = the first temporal moments of the partitioning tracer
- $\bar{t}_n$ = the first temporal moments of the nonpartitioning tracer

The terms $\bar{t}_p$ and $\bar{t}_n$ can be thought of more simply as the mean residence times (i.e. average travel times) for the partitioning tracer and nonpartitioning tracer to travel from the injection well to the extraction well during a partitioning tracer test, and are calculated as follows:

$$\bar{t}_p = \frac{\int_0^{t_f} t C_p(t) dt}{\int_0^{t_f} C_p(t) dt} - \frac{t_s}{2}, \quad (6)$$

and

$$\bar{t}_n = \frac{\int_0^{t_f} t C_n(t) dt}{\int_0^{t_f} C_n(t) dt} - \frac{t_s}{2}, \quad (7)$$

where:

- t_s = the slug size (i.e. the time period in which the tracer mass was injected during the tracer test)
- t_f = the termination time of the tracer test
- $C_p(t)$ = the partitioning tracer concentration at the extraction well as a function of time
- $C_n(t)$ = the nonpartitioning tracer concentration at the extraction well as a function of time

The average NAPL saturation was estimated by first calculating the first moments of the partitioning and nonpartitioning tracers using equations (6) and (7) and numerical integration of the corresponding tracer response curves. Next, equation (5) was used to calculate the retardation factor. Equation (4) was then used to estimate the average NAPL saturation in the swept pore volume.

With S_n and $\bar{t}_n$ known, the tracer swept pore volume of a particular extraction well (V_p) can be calculated as

$$V_p = \frac{m}{M} \frac{Q \bar{t}_n}{1 - S_n} \quad (8)$$

where:

M = the total mass of tracer injected

m = the total mass of tracer produced from the particular extraction well

Q = the total injection rate

The NAPL volume, V_N , in the tracer swept volume of this extraction well is then calculated by:

$$V_N = V_p * S_n \quad (9)$$

The total volume of NAPL, V_T , is obtained from the summation of the volumes calculated from each extraction well:

$$V_T = \sum_{N_p} V_N \quad (10)$$

where:

N_p = the number of extraction wells.

2.3 Inverse Methods of Analysis

Inverse modeling involves minimizing the difference between the model predictions and observed values by adjusting some unknown model parameters (such as NAPL saturation and formation hydraulic conductivity). The most common technique used in inverse modeling is nonlinear least-squares regression.

Numerical simulators are needed for inverse modeling. There are three simulators we have relied on mostly for the purpose of determining aquifer permeability and NAPL residual saturation distribution from PITT data analysis. The CONJUGATE code, developed at the University of Texas at Austin (Datta-Gupta, 1992; Kurihara, 1995), and later modified at Texas A&M University by Datta-Gupta (1995), for hydraulic conductivity estimation, the UTSTREAM code, developed at the University of Texas at Austin (Kurihara, 1995, Harneshaug, 1997) for the purpose of estimating the NAPL saturation distribution from the partitioning tracer data, and the UTCHEM code, a general purpose, finite-difference model which is also developed at the University of Texas (Delshad *et al.*, 1996).

There are two main steps in analyzing the test cell tracer data using the method of inverse modeling. The hydraulic conductivity distribution in the test cell is first obtained from the conservative tracer data. This is done by minimizing the differences between field measured tracer concentrations and the model predicted tracer concentrations as

$$\min f(x) = \frac{1}{2} \sum_{i=1}^n (C_{i,model} - C_{i,field})^2$$

where:

$f(x)$ = the objective function

$C_{i,model}$ = the model-predicted concentration at location I

$C_{i,field}$ = the field measured tracer concentration at the same location

Generally, the simulator iteratively changes the hydraulic conductivity in each gridblock to obtain the hydraulic conductivity field for which the objective function reaches a minimum. A minimum objective function implies a good match of the field data.

When a good match of the field data is obtained, the corresponding hydraulic conductivity field is considered to be representative of the actual hydraulic conductivity field. The partitioning tracer data is then used to obtain the NAPL saturation distribution. Again, this is done by minimizing the differences between actual measured tracer concentrations of the partitioning tracers.

The main advantage of the inverse modeling over the method of temporal analysis is that it not only yields the total NAPL volume but also the residual NAPL saturation distribution. However, the NAPL saturation distributions obtained sometimes are not unique, and results obtained contain some uncertainties, even for the case which most of the tracer response data match the model predictions. There are many factors which may affect the final results of inverse modeling. The results are model sensitivity for example. The number of gridblocks and geometry of the simulation grid contributes to the uncertainty of the accuracy of the results. Another disadvantage of the inverse model is that it tends to be computational intensive.

Although the results from inverse modeling contain some uncertainties, the combination of the results from the method of first temporal moment analysis and inverse modeling, however, can provide a reliable assessment of the hydraulic conductivity and NAPL saturation distributions. In common practice, it is always recommended that both the method of first temporal moment analysis and the method of inverse modeling be used for data analysis.

2.4 The University of Texas Chemical Flooding Simulator (UTCHEM)

UTCHEM is a three-dimensional, multicomponent, multiphase (water, NAPL, microemulsion, and air) compositional finite-difference simulator. It can be used to model partitioning interwell tracer tests for the detection and measurement of NAPL and for remediation performance assessment in both saturated and vadose zones. UTCHEM can simulate both enhanced dissolution and separate phase removal of NAPLs from the saturated and vadose zones. The simulator has been verified with several analytical solutions and validated by comparisons with both laboratory and field experiments.

UTCHEM was originally developed at the University of Texas to simulate the enhanced oil recovery process using surfactant and polymer (Pope and Nelson, 1978; Datta-Gupta *et al.*, 1986; Saad *et al.*, 1990). Generalizations have extended the model to include other chemical processes and a variety of geochemical reactions between the aqueous and solid phase (Bhuyan *et al.*, 1990). In past five years, enhancements have been made to adapt UTCHEM to simulate the surfactant/polymer enhanced aquifer remediation process (Delshad *et al.*, 1996). UTCHEM represents the current state of the art, and is the only model available to the environmental community capable of simulating the surfactant-enhanced aquifer remediation (SEAR). This model has been successfully used by DE&S in the past two years to design several surfactant and surfactant/foam flood field tests (INTERA, 1997, INTERA/RICE, 1997).

3.0 BEFORE THE PITT: A PROTOCOL OF OPERATIONS

It is critically important the PITT be conducted in such a manner that unambiguous information may be derived from it. Therefore, based on DE&S's experience in conducting partitioning interwell tracer tests, a protocol of operations has been established that should be completed before the actual PITT is performed. The recommended sequence of operations is listed below:

1. Continuous coring. Continuous cores are collected to [a] determine the structure of the alluvium, [b] provide material for laboratory column testing, [c] determine sedimentary organic carbon content, grain-size distribution and the vertical distribution of DNAPL through the analysis of total soil contaminant concentrations.
2. Core Analysis. Core samples are analyzed using an algorithm which is built into a code called NAPLANAL (see Appendix B). This allows estimation of the saturation and composition of a single or multicomponent DNAPL within a core sample.
3. Wellfield preparation. Injection, extraction and/or monitoring wells are installed, existing wells are redeveloped to remove fine particles, and any free-phase DNAPL is removed to minimize the errors of estimation of the remaining, in-situ volume of DNAPL.
4. Hydraulic testing. Pumping tests are performed to determine the hydraulic properties of the alluvium and any critical overlying or underlying aquitards, the hydraulic boundaries of the system, and, through the injection of clean, chemically-compatible water, the sustainable injection and extraction rates.
5. Chemical Analysis. Using the aquifer materials and liquids recovered during the previous steps, chemical analyses of DNAPL, sedimentary organic carbon, and ground water are performed.
6. Development of the "geosystem" model of the aquifer. A detailed conceptual model of the alluvium-DNAPL-ground water geosystem is developed and used to define the properties of numerical models used in the design step.
7. Design. Finally, the PITT is designed using the UTCHEM simulator following an extensive sensitivity analysis of the geosystem model, including the demonstration of the hydraulic control of the tracers injected, such that this model of the DNAPL distribution is confirmed or denied by the PITT to the extent possible.

Thus, the intent of this protocol is to ensure that the hypotheses posed in the development of the geosystem model are tested, that the results of the PITT provide the maximum amount of useful information, and, therefore, that the probability of failure of the PITT is minimized.

4.0 SENSITIVITY ANALYSIS

The feasibility of using PITTs to characterize DNAPL-contaminated alluvium was demonstrated through three-dimensional numerical simulation, using the UTCHEM simulator. The simulations enabled us to answer frequently-asked questions about four specific areas, namely [1] the estimation of DNAPL volume for the simple case where only residual DNAPL is present in heterogeneous alluvium, [2] the effect of increasingly low residual DNAPL saturation on the tracer signal, [3] the effect of free-phase DNAPL on the estimation of the volume of DNAPL, present, and [4] the potential interference of sedimentary organic carbon as a DNAPL surrogate on the tracer signal. Appendix A outlines the sensitivity models and design protocol for the use of PITTs in alluvial aquifers.

4.1 Three -Dimensional Model Development

The alluvial aquifer used for the simulation studies was based upon several sites being investigated by DE&S and the University of Texas. Figure 4.1.1 shows the aquifer section modeled and well locations. The upper map is in plan view and the lower is a vertical cross section. The section of the aquifer was 16.6 m long, 9.1 m wide and 5.4 m thick. The uniform finite difference grid used was 20 gridblocks in the x-direction, 11 gridblocks in the y-direction, and 9 gridblocks in the vertical z-direction. A typical hydraulic gradient of 0.007 parallel to the x-axis was used for these simulations.

A stochastic hydraulic conductivity field was generated by assuming a log-normal distribution, an exponential variogram, and using the matrix decomposition method. The top 3 m of the aquifer had a mean hydraulic conductivity of 1×10^{-4} cm/s, with a standard deviation ($\sigma_{\ln k}$) of 0.92 and horizontal and vertical correlation lengths of 1.5 m and 0.6 m, respectively. The bottom 2.4 m of the aquifer had a mean hydraulic conductivity of 1×10^{-2} cm/s, with a standard deviation ($\sigma_{\ln k}$) of 0.92 and horizontal and vertical correlation lengths of 1.5 m and 0.6 m, respectively. The porosity of the aquifer was 0.3. The longitudinal and transverse dispersivities were 0.15 m and 0.05 m, respectively. The injection and extraction wells were completed in the bottom 1.2 m of the aquifer and were 7.5 m apart. Injection and extraction rates were both 9.5 liter per minute (L/min). Table 4.1.1 compares the properties of the simulated aquifer with those of two alluvial aquifers in Ontario (Borden and Chalk River) which have been well characterized.

a) XY Plan view (K=9)

b) XZ cross-sectional view (J=6)

Figure 4.1.1 Schematic of simulation grid and well locations.

**Table 4.1.1 Comparison of Aquifer Properties Between
Simulated Aquifer and Borden and Chalk River Aquifers**

Site	Reference	Porosity	Aquifer Thickness (m)	Longitudinal Dispersivity (m)	Transverse Dispersivity (m)	Dispersion Scale (m)	Hydraulic Conductivity	Aquifer Composition
Simulated Aquifer		30%	5.4	0.49	0.05	16.6	1.0E-06 m/sec	Simulated alluvial
Borden	(Sudicky et al., 1983)	38%	7 27	0.26 0.03	0.03 0.0007	11 0.6	1.0E-07 m/sec	Glacio-fluvial sand Moderate heterogeneity
Chalk River	Pickens and Grisak, 1981	38%	8.5	0.5	0.05	8	2.0E-04m/sec	Sand with small cross-bedding

4.2 Partitioning Tracer Testing of a Residual DNAPL Zone

The first scenario simulated a tracer test with only residual TCE DNAPL present. The residual saturation for TCE was 0.1 in the bottom 1.2 m and in the vicinity of the injection and extraction wells. The tracers used in this simulation and other simulations presented in this section are summarized in Table 4.2.1. Tracers were injected for 0.5 days with a total of 5 kg of each tracer being injected.

Table 4.2.1 Tracers And Their Partition Coefficients Between TCE And Water

Tracer Name	Abbreviation	Partition Coefficient
Bromide	-	0.0
3-methyl-3-pentanol	3M3P	4.5
4-methyl-2-pentanol	4M2P	10.2
n-hexanol	-	18.6
2-methyl-2-hexanol	2M2H	28.1
2,2-dimethyl-3-pentanol	22DM3P	70.8

The tracer response curves (concentrations measured in the extraction well) for this case are shown in Figure 4.2.1. The tracer recovery estimated by integrating the tracer response curves over the volume of extraction is shown in Figure 4.2.2 and indicates that the recovery exceeds 60% after 30 days of tracer testing. The TCE volume and tracer retardation factors are calculated

Figure 4.2.1 Tracer response curves for residual DNAPL saturation of 0.1.

Figure 4.2.2 Tracer recovery for residual DNAPL saturation of 0.1.

using the method of first temporal moment analysis and the results are presented in Figures 4.2.3 and 4.2.4. The TCE volume continues to increase with time because the estimated tracer swept volume continues to increase with time as shown in Figure 4.2.5. The swept volume increases with time as tracers are captured due to the arrival of stream tubes that traveled farther away from the direct line between the injection and extraction wells.

Figure 4.2.4 indicates that the DNAPL volume estimation errors are in the range of 4 to 12%, depending on the tracer used, after 40 days of the tracer test corresponding to approximately 60% tracer recovery (Figure 4.2.2). This indicates that virtually all of the contaminated aquifer is swept, even though hydraulic conductivity varies by two and a half orders of magnitude within the sandy gravel unit contaminated by TCE. This observation is very positive in terms of the suitability of the test method in evaluating typical heterogeneous alluvial aquifers. Another important observation is that the loss of substantial amounts of tracer will not affect the accuracy of volume estimation. This is also important as in practice some of the injected tracers will escape capture by the extraction well because of the unconfined aquifer boundary conditions and finite duration of an actual test.

The time of 40 days shown in the above example is specific to conditions assumed in the simulations. There are several parameters controlling the tracer test time required for accurate NAPL volume estimation. These parameters, such as the magnitude and heterogeneity of the hydraulic conductivity, injection and extraction rates, NAPL volume and distribution, tracer partition coefficients, etc., all affect the duration of the test. It is, therefore, very important to model the partitioning interwell tracer test with a numerical simulator before the actual test is conducted. Simulation modeling before the field test can be used to determine the approximate duration of the tracer test. In the actual test, however, the duration of the tracer test could be either slightly shorter or longer. A useful guidance on the test time required can be determined from the tracer recovery curves such as the one shown in Figure 4.2.4. The general guideline is that the tracer test can be terminated when the tracer recovery curves of the nonpartitioning tracer and at least one partitioning tracer with a retardation factor in the range of 1.2 to 4 have reached plateaus, i.e. become asymptotic. For the example shown above, the bromide and 4-methyl-2-pentanol (retardation factor of about 1.3) reached a plateau after 35 days by which time the NAPL volume estimation error had decreased to less than 10%.

The resulting retardation factors shown in Figure 4.2.3 indicate that the retardation factor for 3-methyl-3-pentanol is smaller than 1.2. Such a small retardation factor results in poor separation of the tracer response curves between bromide and 3-methyl-3-pentanol as shown in Figure 4.2.1. It has been shown by Jin (1995) that the retardation factor should be in the range of 1.2 to 4 in order to obtain the response curves of the partitioning tracers in a reasonably short time and yet ensure good separation of the nonpartitioning and partitioning tracer. For this case, the partition coefficient of 3-methyl-3-pentanol is too small when the amount and the distribution of the NAPL in the test area is as presented in the model, i.e. a residual saturation of 0.1.

Figure 4.2.3 DNAPL volume estimation for residual DNAPL saturation of 0.1.

Figure 4.2.4 Retardation factor for residual DNAPL saturation of 0.1.

Figure 4.2.5 Tracer swept volume for residual DNAPL saturation of 0.1.

4.3 Estimating DNAPL Volumes When Residual DNAPL Saturation is Progressively Decreased

Concern has often been expressed to the authors of the effects of very low residual DNAPL saturation on the accuracy of a PITT. Theoretically, there is no requirement on the minimum residual saturation for accurate estimate of DNAPL volume from a PITT because in a sense, the estimation accuracy is independent of DNAPL saturation as long as the separation of tracer response curves between partitioning and nonpartitioning tracers can be distinguished by gas chromatography or the other tracer detection equipment. In reality, however, there is a limit on the capability of detection equipment to distinguish the tracer separation, which in turn contributes to the estimation error.

The separation of the tracer response is, however, not only a function of the DNAPL residual but also the tracer partition coefficient (see equation 2, section 2.1). Therefore, the estimation error can be minimized by using tracers with different partition coefficients. This can be best illustrated by the following sensitivity studies which are based on the 3-D model presented in section 4.1.

The three cases studied differ only in term of the residual TCE saturation considered to be present in the basal sand and gravel shown in Figure 4.1.1. Case #1 has a residual TCE saturation of 0.1. Case #2 has a residual saturation of 0.05 and Case #3 has a residual saturation of 0.02. In all three cases, TCE is present only in the bottom 1.2 m of the basal sand and gravel, as are the injection and extraction well screens. The tracer response curves for these three cases are shown in Figure 4.3.1. Clearly, the degrees of separation of the tracer response curves are different for the different cases. The retardation factors, which measure the separation of tracer response for these three cases, are shown in Figure 4.3.2. As stated in section 4.1, the retardation factor should be in the range of 1.2 to 4 in order to obtain the response curve of the partitioning tracer in a reasonably short time and yet ensure good separation of the nonpartitioning and partitioning tracer. The retardation factors of the two partitioning tracers used in Case #1 meet this criterion. The retardation factors of 4-methyl-2-pentanol in Case #2 and n-hexanol in Case #3 are less than 1.2, and therefore should not be used to estimate the TCE volume. However, 2-methyl-2-hexanol in Case #2 and 2,2-dimethyl-3-pentanol in Case #3 can still give accurate estimation of TCE volume.

These examples illustrate that it is very important that more than one partitioning tracer be used for the actual field test, especially when there is a large range of uncertainty in the quantity and distribution of DNAPL. If the volume of the DNAPL is relatively high, tracers with smaller partition coefficients are sufficient, and it is not mandatory to continue the test to obtain the response curves for the tracers with larger partition coefficients such as 2-methyl-2-hexanol in Case #1. If the volume of the DNAPL is lower than expected, the tracers with larger partition coefficients can ensure good separation of the tracer response curves such as 2,2-dimethyl-3-pentanol in Case #3. The tracers used for TCE volume estimation and the estimation accuracy for these three cases is shown in Figure 4.3.3.

Case #1 Residual DNAPL Saturation of 0.1

Case #2 Residual DNAPL Saturation of 0.05

Case #3 Residual DNAPL Saturation of 0.02

Figure 4.3.1 Tracer response curves for cases with three different DNAPL saturation

Case #1 Residual DNAPL Saturation of 0.1

Case #2 Residual DNAPL Saturation of 0.05

Case #3 Residual DNAPL Saturation of 0.02

Figure 4.3.2 Retardation factors for cases with three different DNAPL saturation.

Case #1 Residual DNAPL Saturation of 0.1

Case #2 Residual DNAPL Saturation of 0.05

Case #3 Residual DNAPL Saturation of 0.02

Figure 4.3.3 DNAPL volume estimation for cases with three different DNAPL saturation.

Therefore, a properly designed and executed partitioning tracer test can accurately estimate the interwell DNAPL volume for even very low residual DNAPL saturation by employing a suite of tracers with high partition coefficients. It may also be necessary to measure the volume of DNAPL solubilized during the PITT, which is a waterflood in itself. This is especially true for DNAPL composed of more soluble compounds such as 1,2-dichloroethane. At low residual saturation, a significant fraction of such residual DNAPL may be dissolved by the tracer test itself (see section 5.5 - Gulf Coast Chemical Plant).

4.4 Partitioning Tracer Testing of Alluvium With Both Residual and Free-Phase DNAPL

An additional scenario was simulated to determine whether a DNAPL pool could be successfully quantified by a PITT. A topographical depression was created in layers 8 and 9, as shown in Figure 4.4.1. In this case, layers 8 and 9 contain the DNAPL pool consisting of TCE at a saturation of 0.25 and 0.60, respectively, and ground water at a saturation of 0.75 and 0.40, respectively. Layer 7 contains residual TCE saturation of 0.1 in the vicinity of the TCE pool. A partitioning interwell tracer test was simulated with an injection and extraction rate of 9.5 L/min at the injection and extraction wells completed in layer 7 as shown in Figure 4.4.1.

Figure 4.4.2 shows the tracer response curves for this case. Figure 4.4.3 indicates that the TCE estimation errors are in the range of 50 to 60%, even though almost all the recoverable mass of the injected tracers is recovered from the extraction wells. Therefore, the ability of a PITT to successfully quantify a DNAPL pool within an aquifer would be dependent on the thickness of the pool and on the DNAPL and residual water saturations within the pool. It is, therefore, always desirable that free-phase DNAPL be recovered from the aquifer by pumping prior to the PITT, or that the PITT be repeated after the pool has been pumped to residual DNAPL saturation.

In the worst case situation, the error of estimation in the DNAPL volume can be approximated by assuming that only the residual DNAPL volume, V_R , is detectable by a PITT while the free-phase DNAPL volume in the pool, V_F , is not. Therefore, the relative error of estimation, E_r , is given by

$$E_r = 1 - \frac{V_R}{V_R + V_F} = 1 - \frac{1}{1 + \frac{V_F}{V_R}} \quad (3)$$

The solid line in Figure 4.4.4 is a graphic illustration of equation (3) and the points were several additional UTCHEM simulation results which were obtained by increasing the depth of the pool (more layers in the z direction) while keeping the residual TCE saturation constant.

a) XZ cross-sectional view (J=6)

b) YZ cross-sectional view (I=10)

Figure 4.4.1 Schematic of simulation grid for the case with DNAPL pool.

Figure 4.4.2 Tracer response curves for the case with DNAPL pool.

Figure 4.4.3 DNAPL volume estimation for the case with DNAPL pool.

Figure 4.4.4 DNAPL volume estimation accuracy as a function of the volume ratio of the DNAPL in pool and the DNAPL in residual.

It should be clearly understood, however, that the above calculations are based on the worst-case scenario, i.e., the aqueous phase flux in the DNAPL pool was negligible compared to that in the residual DNAPL zone mainly due to the model configuration. In reality, the water saturation in a DNAPL pool is not always at its residual value. The free-water phase in the DNAPL pool will allow the transport and partitioning of tracer within the DNAPL pool, provided that the water saturation is above the residual saturation, although its relative permeability will be much reduced. **Moreover, were its location known, the DNAPL pool would be pumped to residual DNAPL saturation prior to the PITT.** In the worst case, even when there are equal amounts of residual- and free-phase DNAPL present, the error of estimation of the DNAPL volume is no more than 50%. This error is small compared to the usual guesses made concerning the volume of DNAPL present at most sites.

4.5 Interference by Sedimentary Organic Carbon

At low residual NAPL saturation, there is a potential for interference due to sorption of tracers to immobile sedimentary organic carbon (SOC) and/or mineral surfaces. The fractional organic carbon content (f_{oc}) of sandy, alluvial aquifer materials typically varies from 0.001 to 0.0001 kg/kg (Schwarzenbach and Westall, 1981; Curtis et al., 1986; Jackson and Inch, 1989; Lesage et al., 1990; Mackay, 1990). Sorption of the partitioning tracers to aquifer materials could potentially increase the retardation of the partitioning tracers. Sorption to SOC typically dominates when f_{oc} is greater than 0.001 kg/kg (Schwarzenbach and Westall, 1981) and greater than about 3-7% of the solid mass fraction of clay (Karickhoff, 1984). The mass of tracer sorbed per unit mass dry sediment is given by $K_{oc,i} f_{oc} C_{i,w}$, where $K_{oc,i}$ is the organic carbon partition coefficient for tracer i in units of volume per mass, and $C_{i,w}$ is the mass of tracer i dissolved in water- per unit volume water. The $K_{oc,i}$ values for a series of normal-alcohols are given in Table 4.5.1, where the NAPL partition coefficient values are divided by NAPL density to obtain units that can be compared to the $K_{oc,i}$ values.

**Table 4.51 Comparison of Partition Coefficients (mL/g)
for Normal-Alcohol Tracers**

<i>Tracer</i>	K_{oc}	K_{LNAPL} / ρ_{LNAPL}	K_{TCE} / ρ_{TCE}
n-ethanol	1.6	0.1	--
n-propanol	3.0	--	--
n-butanol	3.2	--	--
n-pentanol	5.0	1.7	2.6
n-hexanol	10.2	5.5	12.7
n-heptanol	13.8	24.0	110.0
n-octanol	36.3	117.0	--
NAPL Density (g/mL)	na	0.83	1.46

The two NAPLs being compared with SOC are a complex, mixed-waste LNAPL from Operable Unit 1, Hill Air Force Base, Utah (OU1 LNAPL) and TCE.

The condition under which the chromatographic separation of partitioning tracers during a PITT is equally due to sorption onto SOC, and partitioning within NAPL occurs when the tracer mass sorbed equals the tracer mass partitioned. The mass of tracer sorbed onto SOC is given by $K_{oc,i} f_{oc} \rho_b C_{i,w}$ where ρ_b is the dry bulk density of the soil. The mass of tracer partitioned into the NAPL is given by $K_{n,i} S_n \phi C_{i,w}$, where ϕ is the porosity. Solving for the residual NAPL saturation when the mass sorbed equals the mass partitioned within the NAPL gives

$$S_n = \frac{K_{oc,i} f_{oc} \rho_b}{K_i \phi} \quad (4)$$

Thus, for example, assuming f_{oc} is 0.001, ϕ is 0.4, and ρ_b is 1.59g/cm³, the residual OU1 LNAPL or TCE saturation when the amount of n-hexanol sorbed to SOC equals the amount of n-hexanol partitioned into the NAPL would be 0.9% and 0.2% for OU1 LNAPL and TCE, respectively. If the sediments contained no residual NAPL, equation (2) implies that the n-hexanol retardation factors due to organic carbon for OU1 LNAPL and TCE would be about 1.04. If residual NAPL is present, the retardation of n-hexanol will be due to both tracer sorption to the SOC and partitioning to the NAPL phase. Therefore, knowing the value of f_{oc} in such cases allows the potential interference to be corrected for. In this example, the tracer interference from sedimentary organic carbon can be accounted for by subtracting 0.04 from the measured retardation factors.

Laboratory column tests of uncontaminated alluvial aquifer materials can be performed before conducting a PITT to determine potential interference effects and correction factors. So far, such column tests on aquifer materials from Hill AFB, UT, Sandia National Labs, NM; the Portsmouth Gaseous Diffusion Plant in Ohio; and USAF Plant 4, Fort Worth, Texas have shown no evidence of tracer sorption.

5.0 CASE STUDIES

5.1 Sandia National Laboratories, New Mexico

A PITT was conducted for the first time at the field scale to characterize NAPL in the vadose zone. Figure 5.1.1 presents the basic concept of a PITT, as applied to a vadose zone setting. The PITT was applied beneath two side-by-side organic disposal pits at Sandia National Laboratories near Albuquerque, New Mexico (SNL) RCRA Interim Status Chemical Waste Landfill (CWL). NAPL, consisting of a mixture of spent chlorinated solvents and PCB oils, is known to exist in at least one of the two buried pits. According to waste disposal inventory records, trichloroethene (TCE) was disposed of in the greatest quantities. Appendix C outlines the effectiveness of the PITT in site characterization techniques, and presents the results of the field scale pilot test.

The CWL is a 1.9 acre landfill located in Technical Area III of SNL, and was used for the disposal or storage of hazardous wastes generated between 1962 and 1985. The underlying sediments are a heterogeneous sequence of unconsolidated to semi-consolidated cobbles, gravels, very-fine to fine sands, silts, and clays of alluvial origin, which are locally cemented by caliche. Sand and gravel are composed of a mixture of limestone, quartz, and metamorphic clasts. In general, the lithologic sequence, at least to a depth of 700 ft-bgs, shows a fining-downward pattern, with an increasing percentage of clay, clayey sand, and silt layers with depth (SNL, 1995a). The water table at the CWL is approximately 490 ft bgs.

The injection-extraction well array established at the CWL is shown in Figure 5.1.1. A series of three conservative gas tracer tests were run before the PITT to determine the required flow rates through the three zones which were to be tested independently. The PITT was conducted over a period of 18 days in December 1995 by injecting a slug of nonpartitioning and partitioning tracers into and through the zone of interest under a controlled, forced gradient. The forced gradient was created by a balanced extraction of soil gas at a location 55 feet from the injector over a depth of 10 to 80 ft bgs. The extracted gas stream was sampled over time to define tracer breakthrough curves. Soil gas sampling ports from multi-level monitoring installations were sampled to define breakthrough curves at specific locations and depths. Analytical instrumentation such as gas chromatographs and a photoacoustical analyzer, operated autonomously, were used for tracer detection. The tracers included helium, several perfluorocarbons, and sulfur hexafluoride. Figure 5.1.2 shows the tracer breakthrough curves at two (shallow and deep) depths beneath the CWL.

Preparation for the PITT required both laboratory work and computer modeling. Laboratory batch and column studies were performed to select the optimal suite of tracers. UTCHEM was used to determine target injection and extraction flow rates and necessary tracer masses.

Figure 5.1.1 Schematic diagram of vadose zone partitioning interwell tracer test.

Figure 5.1.2 Tracer response curves of SF_6 and C_9F_{18} at the shallow (above) and deep (below) extraction wells.

First moment analysis of the PITT data indicates that TCE has penetrated non-uniformly to a depth of approximately 20 to 30 ft bgs. Breakthrough curves at the multi-level monitor wells indicate that most of the TCE NAPL is located around 10 ft bgs, with a majority in the southern section of the test zone. The average TCE saturation detected within the shallow swept test zone between 10 and 35 A bgs is approximately 0.11%. As a group, the stream tubes that were more rapidly swept appear to have a higher average TCE saturation while the less rapidly swept streamtubes, which were likely farther to the north and south of the direct line between the wells, have lower than average TCE saturations. No TCE NAPL was detected in the intermediate (40-60 ft bgs) and deep (65-80 ft bgs) test zones. Figure 5.1.3 shows an example tracer response of monitor well SM2 at depths of 10 ft bgs and 60 ft bgs.

There is some uncertainty in the actual volumes of vadose zone swept by the tracers in the shallow, intermediate and deep zones. This uncertainty does not affect the calculated average TCE saturation measurements. However, it does result in uncertainty in the estimate of TCE volume in the shallow swept zone because the total volume of TCE detected is proportional to the total volume swept. Tracer recovery calculations indicate that only 22% of the targeted test zone was swept during the test, leading to a conservative estimate of 40 gallons of TCE NAPL detected in 22% of the targeted swept volume. However, the observed high concentrations and early breakthrough of the tracers at the multi-level monitor wells suggest that the entire targeted zone, and thus the entire soil column beneath the pits between 10 and 35 ft bgs, was swept. Thus, if the entire targeted test zone was indeed swept, then 180 gallons of TCE NAPL is present in the entire shallow targeted zone. Similar discrepancies in swept volumes occurred in the intermediate and deep zones. Results of the PITT data analysis are summarized below:

Table 5.1.1 Results of PITT Data Analysis - Sandia

Zone	Tracer Pairs	Estimated Tracer Swept Pore Volume	Retardation Factor	Tracer Recovery (%)	Average Residual Water Saturation	Estimated NAPL Saturation	Estimated NAPL Volume (gal)
Shallow	SF ₆ , C ₉ F ₁₈ (NAPL) SF ₆ , CF ₂ H ₂ (water)	4,000- 18,750 gal	1.2 1.5	6.5 - 7	23%	.14%	42-190
Intermediate	SF ₆ , C ₉ F ₁₈ (NAPL) SF ₆ , CF ₂ H ₂ (water)	18,700- 124,916 gal	1.0 1.25	3.4	13%	0	0
Deep	SF ₆ , C ₉ F ₁₈ (NAPL) SF ₆ , CF ₂ H ₂ (water)	20,196- 100,980 gal	1.0 1.2	7.8; 12.2	10%	0	0

In addition to the NAPL-partitioning tracers, a water-partitioning tracer was included in the PITT to measure water saturations in the test zones. Average water saturations of 23%, 13%, and 10%

Figure 5.1.3. Monitor well SM2 tracer concentration data at 10 ft bgs (above) and 60 ft bgs (below).

were measured for the entire tracer-swept volumes in the shallow, intermediate, and deep zones, respectively. The streamtubes that were more rapidly swept, especially in the shallow zone, appear to have lower average saturations than the more slowly swept streamtubes. This may have been caused by the rapid and prolonged flow of air through the highly swept streamtubes before the PITT.

5.2 Hill Air Force Base, Utah - AFCEE

In the past, Operable Unit 2 (OU2) at Hill Air Force Base, Utah received large volumes of chlorinated solvents from degreasing operations conducted at the base. OU2 is underlain by a shallow alluvial sand aquifer confined on its sides and below by thick clay deposits that form a capillary barrier to DNAPL migration. Despite two pump-and-treat systems which treat free-phase DNAPL and contaminated ground water, the aquifer still contains anywhere from 100,000 to perhaps a million gallons of DNAPL (personal communication with Maj. Ed Heyse, Air Force Institute of Technology), seventy percent of which is TCE.

A subsurface demonstration zone was developed in Spring, 1996 by installing a set of three injection wells and three extraction wells in a 3 X 3 line-drive geometry (See Figure 5.2.1). The well field also contained one hydraulic control (injection) well and one interwell monitor well. The water-table depth was approximately 25 ft below ground surface (bgs) and there was a 4-ft thick zone of free-phase and residual DNAPL approximately 45 ft bgs. The hydraulic conductivity of this alluvium is in the range of 10^{-5} to 10^{-7} m/s.

The demonstration consisted of two phases. The first (pre-flood) PITT, lasting 6 days, was conducted as part of Phase I. The main objective of this PITT was to determine the volume of DNAPL in the demonstration zone before the initiation of surfactant-enhanced remediation efforts. A second objective was to use the conservative tracers (bromide and isopropanol) to determine the volume of the aquifer swept by the tracers. The PITT indicated that there was a total of 346 gallons of DNAPL in the swept volume, corresponding to an average saturation of 2.7% over the entire saturated thickness of the aquifer (~19 feet). However, if the majority of DNAPL volume was distributed over the bottom 5 feet of the aquifer, as was indicated by soil sample analysis, then the average residual saturation of DNAPL would have been closer to 22%. The resulting estimates of the residual DNAPL volume for each well pair are summarized in Table 5.2.1 below:

Table 5.2.1 Initial PITT Residual DNAPL Saturation Estimates

Well Pair	Swept Volume (gal)	DNAPL Volume (gal)	Residual Saturation (%)
SB-1, SB-2	3,890	210	5.4
SB-5, SB-4	5,220	70	1.3
U2-1, SB-3	3,830	66	1.7
Total	12,940	346	2.7

The tracer concentration history for wells SB-5, SB- 1, and U2- 1 are presented in Figures 5.2.2, 5.2.3, and 5.2.4. These figures show that the 1-pentanol, 2-ethyl-1-butanol and 1-heptanol curves clearly have been retarded with respect to the conservative tracer, indicating the presence of substantial quantities of DNAPL in the aquifer volume between the wells. 1-heptanol has the highest partition coefficient ($K=140.5$) of the tracers used, and therefore displays the most retardation.

The results of the Phase I field operations were used to finalize the design of the Phase II surfactant flood. The Phase II flood was preceded by an intermediate PITT and followed by the final PITT so that the performance of the flood could be assessed. The main objective of the intermediate PITT was to determine the remaining volume of DNAPL in the swept volume after the Phase I surfactant flood. To do so, a suite of partitioning tracers with a wide range of partition coefficients was used. High recovery of the injected tracers indicated that hydraulic control of the injected chemicals had been achieved in the swept volume. The resulting estimates of the residual DNAPL volume for each well pair are summarized in Table 5.2.2 below:

**Table 5.2.2 Residual DNAPL Saturation Estimates
Based on the Intermediate PITT**

Well Pair	Swept Volume (gal)	DNAPL Volume (gal)	Residual Saturation (%)
SB-1, SB-2	4,440	57	1.3
SB-5, SB-4	6,040	60	1.0
U2-1, SB-3	3,670	31	0.8
Total	14,150	148	1.0

The total aquifer pore volume swept by the tracers was slightly higher than that of the initial PITT, because of slightly higher injection-extraction rates used during Phase II. The tracer concentration history for wells SB-5, SB-1, and U2- 1 are presented in Figures 5.2.5, 5.2.6, and 5.2.7.

The intermediate PITT was followed by a surfactant flood to solubilize the remaining DNAPL from the swept volume. The total VOC concentration (8 mg/L) at the end of the flood indicated that most DNAPL had been recovered from the swept volume between the injection and extraction wells.

The main objective of the final PITT was to assess the performance of the surfactant flood and to determine the DNAPL volume remaining in the swept volume after the flood. As in the previous PITTs, tracer recovery was very high. Again, the resulting estimates of the residual DNAPL volume for each well pair are summarized in Table 5.2.3 below:

Figure 5.2.2. Initial PITT extraction well SB5 tracer concentration data.

Figure 5.2.3. Initial PITT extraction well SB1 tracer concentration data.

Figure 5.2.4. Initial PITT extraction well U2-1 tracer concentration data.

Figure 5.2.5. intermediate PITT extraction well SB5 tracer concentration data.

Figure 5.2.6. intermediate PITT extraction well SB1 tracer concentration data.

Figure 5.2.7. intermediate PITT extraction well U2-1 tracer concentration data.

**Table 5.2.3 Residual DNAPL Saturation Estimates
after Surfactant Flooding Based on the Final PITT**

Well Pair	Swept Volume (gal)	DNAPL Volume (gal)	Residual Saturation (%)
SB-1, SB-2	4,880	5	0.10
SB-5, SB-4	6,030	0	0.00
U2-1, SB-3	4,450	0	0.00
Total	15,360	5	0.03

The tracer concentration history for wells SB-5, SB-1, and U2-1 are presented in Figures 5.2.8, 5.2.9, and 5.2.10, and illustrate virtually no partitioning between the tracers, indicating a near-absence of DNAPL in the interwell zone.

Analysis of the final PITT indicated that the average residual DNAPL saturation over the 20-ft thick swept zone of the aquifer had been reduced from 0.036 in early May 1996 to 0.0004 in late August 1996 in a swept volume of approximately 15,000 gallons. Therefore, the PITT's had shown that the two surfactant floods had recovered 341 of the 346 gallons of DNAPL within the test zone of the OU2 alluvial aquifer. This represents a total recovery of 98.5% of the DNAPL determined by the Phase I PITT to be present in the test zone. Appendix C presents both a description of the effectiveness of the PITTs performed at Hill AFB, and the results of the field scale pilot test discussed above.

Furthermore, the recovery of some 500 gallons of free-phase DNAPL before the surfactant flood, and therefore prior to its dissolution and subsequent downgradient extraction and treatment, resulted in a cost savings of approximately \$15 million to the USAF. This cost savings underlines the importance of source-zone removal prior to the natural attenuation of aqueous plumes.

5.3 Portsmouth Gaseous Diffusion Plant (PORTS), Ohio

Area X-701B (see Figure 5.3.1) at the Portsmouth Gaseous Diffusion Plant in southern Ohio comprises an unlined waste disposal pond which was used from the mid-1950s to the late 1970s. This pond received solvent waste from vapor degreasing and other industrial operations conducted nearby and had been identified by DOE as the source of contamination of the Gallia alluvium, which is hydraulically connected to Little Beaver Creek, approximately 500 m to the east. The X-701B area is underlain by lacustrine silts and clays and the deeper Gallia alluvium which is contaminated by a multi-component DNAPL (i.e., mainly TCE, and some PCBs and other chlorinated solvents). Despite continuous efforts to remove dissolved-phase contamination, there still remained a significant volume (possibly more than 10,000 gallons) of DNAPL.

Figure 5.2.8. Final PITT extraction well SB5 tracer concentration data.

Figure 5.2.9. Final PITT extraction well SB1 tracer concentration data.

Figure 5.2.10. Final PITT extraction well U2-1 tracer concentration data.

The initial, pre-flood PITT was conducted in July 1996 and lasted approximately 10 days. Figure 5.3.2 shows a comparison of the conservative (IPA) tracer response in different zones (upper gravely silt; $K = 3.5E-4$ cm/s), INT-5 (middle sand; $K = 2.1E-3$ cm/s) and INT-1 (basal sand and gravel; $K = 2.1E-2$ cm/s). The low hydraulic conductivity in the upper gravely silt indicated that fluid flow through the upper unit during the PITT was not significant. Also, the tracer response data for the middle sand illustrated simultaneous arrival of both the conservative and partitioning tracers, indicating that little or no residual TCE was present in the middle sand unit of the Gallia formation (see Figure 5.3.3). The average residual saturation of DNAPL in the test zone was determined to be between 0.09 to 0.2%, which equated to a volume of approximately 4-10 gallons of DNAPL in the basal gravel layer of the Gallia alluvium. This indicates that the DNAPL migrated into the Gallia laterally from the direction of the X701B pond and not through the overlying silt.

The second PITT, conducted immediately after a solubilization test in late September, measured only 2 gallons of DNAPL remaining in the alluvium between the injection and extraction wells, indicating that 50% of DNAPL had been removed by solubilization (see Figure 5.3.4, which shows the tracer response curves measured at BW2G). However, not all of the solubilized DNAPL was recovered at BW2G, the extraction well, because of hydraulic interference recorded by pressure transducers placed throughout the site. The remaining DNAPL was most likely captured by the influence of other pumping sources and moved downgradient into the paleochannel of the Gallia. Results of the PITT data analysis are summarized below:

Table 5.3.1 Results of PITT Data Analysis - Portsmouth

PITT	Duration of PITT	Swept Pore Volume (gallons)	Average NAPL Saturation	Tracer Recovery	NAPL Volume (gallons)
Initial PITT	10 days	1,500	0.09-0.2%		4-10
Final PITT	7 days	1,300		80%	2

The difference between the DNAPL recovery at Hill AFB in August (98.5%) and at PORTS one month later (~50%), by the same team, reflects the significant differences in the detail of site characterization and in hydraulic control. At Hill AFB, the hydraulic and capillary properties of the site were well established before surfactant flooding. This was not the case at PORTS. In fact, at the end of the first PITT it became apparent that an extremely permeable paleochannel zone of the Gallia ran through the BW2G site and was hydraulically connected with two horizontal wells sighted 150 m to the east. Speculation about such a paleochannel had existed at PORTS for some time and was confirmed by DE&S's field work. There can be no question that the paleochannel is critically important in controlling the spatial distribution and migration of

Figure 5.3.2. IPA tracer concentration data of the monitoring wells in different zones.

Figure 5.3.3. Pre-flood PITT extraction well BW2G tracer data and corresponding fitting curves

Figure 5.3.4. Tracer response curves measured at BW2G for propanol/heptanol (above) and propanol/octanol for the second PITT.

DNAPL beneath the X701B site. However even with the horizontal wells inactive, there was considerable hydraulic interference with the injection-extraction operations during the solubilization test so that only about 20% of the DNAPL in the interwell swept zone was recovered at BW2G while the other 30% solubilized was not recovered.

5.4 Air Force Plant 4, Fort Worth, Texas

Since aircraft manufacturing began in 1942, it is suspected that tens of thousands of gallons of TCE have leaked into the subsurface beneath USAF Plant 4 from a vapor degreasing operation at the south end of the main plant building. TCE is suspected of migrating vertically through the fill and alluvium beneath Plant 4 and migrating downdip along the surface of the bedrock contact between the alluvium and the limestone aquitard. The alluvium is composed of a basal sandy gravel, grading upward into poorly-sorted terrace materials composed of interbedded clay, silt, sand and gravel. In the area around monitor well HM-88, which is situated in the middle of the East Parking Lot (see Figure 5.4.1), the water table is approximately 27 feet below ground surface. The horizontal hydraulic conductivity of the surficial terrace material is 10^{-4} cm/s, that of a silty sand. The basal sandy gravel has a (horizontal) hydraulic conductivity of approximately 10^{-2} cm/s. The limestone forms an aquitard because of its very low mean vertical hydraulic conductivity, $K_v = 7.0 \times 10^{-10}$ cm/s, such that the underlying Paluxy sandstone is only partially saturated immediately beneath the aquitard. This sandstone aquifer is the water supply for the nearby community of White Settlement.

In December 1996, a PITT was conducted in the terrace alluvial aquifer beneath the East Parking Lot (EPL) to measure the average saturation and volume of DNAPL in this area of the site. Data analysis indicated that no DNAPL was present in the interwell aquifer volume swept by the tracers; The calculations were performed using the method of first moment analysis, which is described in section 2.2. Details of the PITT setup and data analysis are presented below.

The PITT location was adjacent to well HM-88 in the East Parking Lot. The test utilized an inverted 5-spot well configuration, with tracer injection at well 027, and extraction from wells 031, 032, 034, as shown in Figure 5.4.2. The PITT began at 0900 on December 6, 1996, and ended 10 days later on December 16. Design flow rates for the PITT were determined by combining the results of UTCHEM design simulations with the results of three pre-PITT NaCl conservative tracer tests.

Tracer breakthrough was observed at wells 031, 034, and 036, but not at well 032. The results of the PITT data analysis is shown in Figures 5.4.3 through 5.4.8 for wells 031, 032, and 036. Results of the PITT data analysis are summarized below:

Analysis of the PITT data indicated that no residual DNAPL was present in the pore volume of aquifer swept by the tracers.

Figure 5.4.1 Aqueous TCE plume (in $\mu\text{g/L}$) and suspected DNAPL zone in the alluvial aquifer, East Parking Lot, USAF Plant 4, Fort Worth, Texas (after RUST, 1993).

LEGEND

- Tracer Test Injection Well ●
- Tracer Test Extraction Well ⊕
- Existing Monitor Well ⊙
- Soil Boring ○

File: pit1-loc.dwg

Date: 10/28/96

Ref. Number: 1133-002

TRACER TEST WELL CONFIGURATION

USAF Plant 4
Fort Worth, Texas

Figure 5.4.2

Figure 5.4.3. Extraction well #34 propanol and heptanol response data and corresponding fitting curves.

Figure 5.4.4. Extraction well #34 propanol and heptanol recovery.

Figure 5.4.5. Extraction well #36 propanol and heptanol response data and corresponding fitting curves.

Figure 5.4.6. Extraction well #36 propanol and heptanol recovery.

Figure 5.4.7. Extraction well #31 propanol and heptanol response data and corresponding fitting curves.

Figure 5.4.8. Extraction well #31 propanol and heptanol recovery.

Table 5.4.1 Results of PITT. Data Analysis - Plant 4

Well	Tracer Recovery (%)	Tracer Pair Used for Calculation	Tracer Swept Pore Volume (gallons)	Retardation Factor	Average NAPL Saturation (%)
#31	4	Propanol with Heptanol	337	~1.0	~0.0
#32	0				
#34	55	Propanol with Heptanol	2244	~1.0	~0.0
#36	13	Propanol with Heptanol	1683	~1.0	~0.0
Total	72		4264		

The PITT data analysis used propanol as a conservative tracer, and heptanol as the partitioning tracer. Hexanol was not used in the PITT data analysis because its low partition coefficient is effective only when relatively high residual DNAPL saturations are encountered. Tracer response curves for propanol and heptanol are shown for wells 034, 036, and 031, in Figures 5.4.3, 5.4.5, and 5.4.7, respectively. All curves show no discernible tracer separation (i.e. tracer separation between the conservative and partitioning tracers is less than the analytical error of the gas chromatography (GC) method of sample analysis). The tracer response for octanol was virtually the same as the heptanol tracer response, i.e. no separation between propanol and octanol tracer response curves. Octanol has a significantly lower aqueous solubility than the other tracers, and the late time samples collected during the PITT contained octanol concentrations that approached, or were below, the GC detection limit.

Tracer recovery curves for wells 034, 036, and 031 (see Figures 5.4.4, 5.4.6, and 5.4.8) show a total tracer recovery of approximately 72 % from all wells combined. Approximately 55 % of the total tracer mass injected at well 027 was recovered at well 034, which is located directly downgradient of the injection well. Tracer recovery was approximately 13 % and 4% at wells 036 and 031, respectively. Approximately 28% of the total tracer mass was not recovered during the PITT.

As mentioned above, no tracer breakthrough was observed at well 032. It is likely that most of the unrecovered tracer escaped capture through the terrace alluvial aquifer in the area between wells 032 and 034. The screened interval in well 032 may not be hydraulically well-connected to the fossiliferous limestone interval that is screened in injection well 027. Geologic cross sections A-A' and B-B' (see Figures 5.4.9 and 5.4.10) show that wells 027, 031, and 036 are located in the fossiliferous limestone, whereas wells 032 and 034 are located in a transition zone from fossiliferous limestone to sand and gravel.

5.5 Gulf Coast Chemical Plant

The method of inverse modeling (see section 2.3) was used to estimate the spatial distribution of the hydraulic conductivity and DNAPL saturation in a test cell at a Gulf Coast chlorinated-solvents manufacturing plant. The test cell was constructed to limit the ground-water flow and to later contain injected surfactant solution. It was located in a sequence of clay and silty clays with thin interbedded water-bearing sand units. The PITT was designed, supervised, and analyzed by DE&S and conducted by IT, the on-site contractor, during January 1997. A surfactant flood was performed following the PITT, during late February and March, 1997.

The PITT began on January 11, 1997 and finished on February 10, 1997. The 10-ft water-bearing unit was the focus of both the PITT and surfactant flood. The test was configured as a three-row line drive. The central row consisted of three injection wells and the western and eastern rows both consisted of three extraction wells (see Figure 5.5.1). For the tracer test, bromide and 2-propanol (IPA) were used as the conservative tracers while 1-hexanol and 1-heptanol were used as the partitioning tracers. The tracer test was performed by injecting 5 kg of each tracer dissolved in water at a concentration of about 700 mg/L as a tracer slug for 3.4 days followed by approximately 27 days of water flood. The effluent tracer concentrations in each of the six extraction wells were recorded as a function of time. Figures 5.5.2, 5.5.4, 5.5.6, 5.5.8, and 5.5.10 show conservative (IPA) vs. partitioning tracer results (heptanol) as compared to model predicted tracer concentrations. Figures 5.5.3, 5.5.5, 5.5.7, 5.5.9, and 5.5.11 show the comparison of actual and model predicted EDC concentrations.

Analysis of PITT results is normally done using the method of first temporal moment analysis, because it is assumed that the volume of NAPL does not significantly decrease due to either mobilization of free phase NAPL or dissolution of NAPL into the water phase during the duration of the tracer test. However, due to the relatively high aqueous solubility (8,520 mg/L) of 1,2-dichloroethane or ethylene dichloride (EDC) DNAPL in the 10-ft water bearing unit, substantial dissolution of the EDC occurred during the PITT. Consequently, the method of first moment analysis could not be used and the method of inverse modeling was used instead to estimate the amount and distribution of EDC in the subsurface based on both the EDC and tracer concentrations measured during the tracer recovery.

Although the main purpose of the inverse modeling simulation was to determine the hydraulic conductivity and NAPL saturation distribution, several forward simulation runs were conducted to estimate the effective porosity, dispersivity, and the effective aqueous solubility of the EDC. The results indicate that a dispersivity of 0.5 ft and an effective EDC solubility of 4,500 mg/L seemed suitable. The effective EDC solubility was used instead of the literature-reported EDC solubility of 8,520 mg/L (Mercer et al, 1990), for two reasons. First the literature value was for pure EDC, while the DNAPL present in the test cell is a mixture of different NAPL components with EDC as the dominant component. Secondly, the observed effluent EDC concentration in the

DATE: 4/15/97

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Figure 5.5.1 Plan and cross sectional view of the test cell installed at the Gulf Coast chemical plant

Figure 5.5.2. Comparison of actual and model predicted tracer concentrations for extraction well 94WOO5-10 (EW-1).

Figure 5.5.3. Comparison of actual and model predicted EDC concentration for extraction well 94WOO5-10 (EW-1).

Figure 5.5.4. Comparison of actual and model predicted tracer concentrations for extraction well 96SWO02-10 (EW-2).

Figure 5.5.5. Comparison of actual and model predicted EDC concentration for extraction well 96SWO02-10 (EW-2).

Figure 5.5.6. Comparison of actual and model predicted tracer concentrations for extraction well 96SWOO1-10 (EW-3).

Figure 5.5.7. Comparison of actual and model predicted EDC concentration for extraction well 96SWOO1-10 (EW-3).

Figure 5.5.8. Comparison of actual and model predicted tracer concentrations for extraction well 96SWOO8-10 (EW-5).

Figure 5.5.9. Comparison of actual and model predicted EDC concentration for extraction well 96SWOO8-10 (EW-5).

Figure 5.5.10. Comparison of actual and model predicted tracer concentrations for extraction well 96SW007-10 (EW-6).

Figure 5.5.11. Comparison of actual and model predicted EDC concentration for extraction well 96SW007-10 (EW-6).

monitor and extraction wells indicated the equilibrium mass transfer between EDC and the water phase was not achieved during the tracer test. It should be noted, however, that the value of EDC solubility used in the model has no effect on the estimated total volume of EDC as long as the observed effluent EDC concentration is in good agreement with the concentration data predicted by the model. The porosity of the test cell was estimated to be 0.25, which was consistent with a previously reported value of 0.25 (INTERA, 1995).

Three different numerical simulators were used for the data analysis, including UTCHEM, which was used to estimate the NAPL saturation distribution from the actual measured tracer (heptanol) and EDC concentration data. The results from the inverse modeling indicate that there were approximately 24 gallons of residual EDC initially present in the pore space swept by tracers. Approximately 75% of the residual EDC, however, was dissolved by the end of the tracer test, leaving only about 6 gallons as residual. The residual EDC was non-uniformly distributed in the test cell, ranging from 0 to 20% saturation. The average NAPL saturation in the tracer swept pore space at the beginning of the PITT was calculated to be about 1.4%

5.6 Hill Air Force Base, Utah - AATDF

A second project at Hill APB, OU2 was conducted about twenty feet from the 1996 AFCEE demonstration - this time to demonstrate a surfactant/foam aquifer remediation process in the field. The objective of the demonstration was to evaluate the effectiveness of using the foam process as a mobility controlling agent for the surfactant remediation process. The use of foam in a surfactant flood effectively “blocks off” higher permeability zones in the aquifer after they have been swept clean by the surfactant flood, thereby forcing the surfactant into the lower permeability layers so that the DNAPL entrained in these areas is solubilized more quickly and efficiently. The DNAPL at OU2 consists of a mixture of several chlorinated hydrocarbons, including about 70% TCE.

As in the AFCEE project, the shallow aquifer in the area of interest is defined by an elongated deep and narrow depression in a thick aquiclude of low permeability clay. This feature, interpreted to be a buried channel, is oriented roughly north-northwest and has localized subsurface depressions conducive to the pooling of DNAPL.

The surfactant/foam demonstration project was divided into Phase I and Phase IIa and b. Phase I consisted of the remediation process development and design using experimental laboratory and numerical modeling (UTCHEM) studies. Phase II was the field demonstration of the surfactant/foam remediation. Phase IIa included the wellfield development, hydraulic testing and the initial testing of in-situ foam generation. The PITTs were conducted as part of Phase IIb. The results for both the pre-flood PITT and the post-flood PITT are summarized in Tables 5.6.1 and 5.6.2, found below.

Analysis of the pre-flood PITT determined that there was a total of approximately 22 gallons of DNAPL in the test zone (see Figures 5.6.1 - 5.6.3 for the tracer response curves). During the surfactant/foam flood, over 35 gallons of DNAPL were recovered, indicating that DNAPL was produced from outside the pattern due to foam migration during the flood. The post-surfactant PITT detected a small amount of DNAPL (-1.7 gallons) left in the center of the pattern. Soil samples acquired after the flood confirm that all of the DNAPL was removed from the swept volume except for a small amount left in the deepest portion of the test area. There is evidence that DNAPL was re-invading the test area during the surfactant flood from an adjacent pool and accumulating in a shallow depression in the center of the well pattern.

Table 5.6.1 Pm-Flood PITT Results

Well Name	Swept Volume (gallons)	NAPL Volume (gallons)	Average NAPL Saturation
Ex-1	3,760	0.9 ± 0.7	$0.02\% \pm 0.02\%$
Ex-2	2,760	18.4 ± 0.6	$0.56\% \pm 0.02\%$
Ex-3	2,280	2.3 ± 0.5	$0.08\% \pm 0.02\%$
Total	8,800	21.6 ± 1.8	0.16%

**Table 5.6.2 Post-Flood PITT based on Propanol and Heptanol tracer data
(the results are not QA/QC and subject to change)**

Well Name	Swept Volume (gallons)	NAPL Volume (gallons)	Average NAPL Saturation
Ex-1	2,740	0.7 ± 0.2	$0.03\% \pm 0.007\%$
Ex-2	2,420	1.8 ± 0.2	$0.07\% \pm 0.007\%$
Ex-3	3,688	1.1 ± 0.3	$0.03\% \pm 0.007\%$
Total	8,848	3.6 ± 0.7	0.04%

The post-remediation saturation of DNAPL, as determined by the final PITT and confirmed by soil sampling is very low (0.04%), proving that surfactant enhanced aquifer remediation is extremely effective in removing residual DNAPL from contaminated aquifers (see figures 5.6.4 through 5.6.6 which show the tracer response curves for the post-flood PITT). Finally, this project provided additional confirmation that PITTs provide the most accurate characterization and performance assessments currently available for dealing with DNAPL contamination and remediation.

Figure 5.6.1. Initial PITT extraction well EX1 tracer data and their corresponding fitting curves.

Figure 5.6.2. initial PITT extraction well E21 tracer data and their corresponding fitting curves.

Figure 5.6.3. Initial PITT extraction well EX3 tracer data and their corresponding fitting curves.

Figure 5.6.4. Final PITT extraction well EX1 tracer data and their corresponding fitting curves

Figure 5.6.5. Final PITT extraction well E21 tracer data and their corresponding fitting curves.

Figure 5.6.6. Final PITT extraction well EX3 tracer data and their corresponding fitting curves.

6.0 SUMMARY AND CONCLUSIONS

This report has described the successful application of the PITT to the determination of the spatial distribution and volume of DNAPL in both water-saturated and unsaturated alluvium. Table 6.0.1 summarizes these results. PITTs have been used for the following specific purposes:

- determination of the presence or absence of DNAPL (USAF Plant 4);
- determination of the spatial distribution of DNAPL (Sandia, Gulf Coast plant, Portsmouth, Hill APB);
- determination of the total volume of DNAPL present (Sandia, Gulf Coast plant, Portsmouth, Hill APB); and
- assessment of the performance of surfactant-enhanced aquifer remediation by before-and-after PITTs.

The results of these ten PITTs clearly indicate the necessity of the careful planning and exertion of each PITT, without which successful analysis will be impossible. This is the most important lesson learned. Budget-induced short cuts can only reduce the reliability of and total information contained in the results.

Table 6.0.1 Summary of PITT Results for all PITT Sites

Site		Duration of PITT	Swept Pore Volume (gallons)	Average NAPL Saturation	Tracer Recovery	NAPL Volume (gallons)
Sandia		18 days	30,000-100,000	0.11%	6.5-7%	40-180 (shallow)
			20,000-80,000	0	3.4%	0 (intermediate)
			20,000-80,000	0	7.8; 12.2%	0 (deep)
Hill AFB-AFCEE	PITT 1	6 days	12,940	2.7%	89%	346
	PITT 2	5 days	14,150	1.0%	92%	148
	PITT 3	6 days	15,360	0.03%	83%	5
Portsmouth	Initial PITT	10 days	4,500	0.09-0.2%	75%	4-10
	Final PITT	7 days	4,500	0.04%	70%	2
AF Plant 4		10 days	4264	0	72%	0
Gulf Coast Plant		30 days	1,730	1.4%	90%	24
Hill AFB-AATDF	PITT 1	5 days	8,800	0.16%	90%	21.6
	PITT 2	7 days	8,400	0.04%	84%	3.6

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APPENDIX A

Sensitivity Models and Design Protocol for Partitioning Tracer Tests in Alluvial Aquifers

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Sensitivity Models and Design Protocol for Partitioning Tracer Tests in Alluvial Aquifers

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Abstract

Zones of dense, nonaqueous phase liquids (DNAPLs) are difficult to characterize as to their volume, composition, and spatial distribution using conventional ground-water extraction and soil-sampling methods. Such incompletely characterized sites have negative consequences for those responsible for their remedial design, e.g., the uncertainties in the optimal placement of ground-water extraction wells and in the duration of remediation. However, the recent use of the partitioning interwell tracer test (PITT) to characterize DNAPL zones at sites in New Mexico [unsaturated alluvium] and in Ohio, Texas, and Utah [saturated alluvium] demonstrates that the volume and spatial distribution of residual DNAPL can be determined with accuracy. The PITT involves injection of a suite of tracers which reversibly partition to different degrees between the DNAPL and the ground water or soil air resulting in the chromatographic separation of the tracer signals observed at the extraction well(s). The design of a PITT requires careful consideration of the hydrostratigraphic, hydraulic, and certain geochemical properties of the alluvium being tested. A three-dimensional, numerical model of a heterogeneous alluvial aquifer containing DNAPL has been developed for use with the UTCHEM simulator to demonstrate partitioning tracer testing and to address questions that are frequently raised in its application. The simulations include (1) the estimation of DNAPL volume for the simple case where only residual DNAPL is present in heterogeneous alluvium, (2) sensitivity studies to demonstrate the effect of increasingly low residual DNAPL saturation on the tracer signal, and (3) the effect of free-phase DNAPL on the estimation of the volume of DNAPL present. Furthermore, the potential interference of sedimentary organic carbon as a DNAPL surrogate on the tracer signal is considered and shown to be readily resolved by the careful choice of tracers. Finally, a protocol for the use of PITTs in alluvial aquifers is presented.

Introduction

In their review of pump-and-treat remediation, Mackay and Cherry (1989) reported that "very little success has been achieved in even locating the subsurface sources (i.e., zones of nonaqueous phase liquids or NAPLs), let alone removing them." More recently, Bedient et al. (1994) and the National Research Council (1994) Committee on Ground-Water Cleanup Alternatives have restated this finding. It is our contention that this situation has arisen because NAPL site characterization methods generally involve a particular reliance on the analysis of recovered core from small zones of the contaminated aquifers or on monitor well data.

We recommend instead the testing of large zones of aquifers for the presence of NAPL by transmitting fluids between separate injection and extraction wells through which are circulated gaseous or liquid partitioning tracers (Jin et al., 1995; Wilson and Mackay, 1995). This technique allows (1) the detection of

NAPLs in the interwell zone, (2) the quantification of the volume of NAPL present, and (3) the determination of the spatial distribution of the NAPL in situ. A complementary interwell method, the NAPL solubilization test, uses micellar surfactant solutions to determine the compositional analysis of any multicomponent NAPL. However, this has been discussed in detail elsewhere (Butler et al., 1995) and will not be considered in this article.

The failure of core-recovery methods to provide meaningful subsurface characterization of NAPL zones is perhaps due to the very large representative elementary volumes for residual NAPL which might be expected in nonuniform porous media. Mayer and Miller (1992) have shown that the scale of measurement for residual NAPL in aquifers probably is much larger than the aquifer sample provided by a core. They reported that as the porous medium became more nonuniform, the necessary volume of aquifer to be sampled to yield a representative value of residual NAPL saturation (percentage of pore volume occupied by residual NAPL) increased rapidly.

Interwell tracer tests which sample large volumes of aquifer appear to be particularly attractive for successful characterization of the subsurface distribution of NAPLs. For similar reasons, hydrogeologists have long used pumping tests to measure the hydraulic conductivity field around an extraction well rather than relying on permeameter measurements of cores taken during well installation. We believe that interwell tracer tests, coupled with core recovery and analysis (Feenstra et al., 1991; Cohen et al., 1992; Mariner et al., 1997) and the careful interpretation of ground-water quality data (Jackson and

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Mariner, 1995), provide the only practical approach to meeting EPA's guidance that "if NAPL contamination is likely, characterization of the potential nature and extent of such contamination is recommended to determine appropriate remedial actions" (EPA, 1992).

The purpose of this paper is to demonstrate, by three-dimensional numerical simulation using the UTCHEM simulator, the feasibility of using partitioning interwell tracer tests or PITT's to characterize the DNAPL zone of an alluvial aquifer. By doing so, we wish to answer frequent questions posed to us regarding the use of PITTs to characterize DNAPL-contaminated alluvium. The heterogeneity of the alluvium is modeled by generating a stochastic permeability field. Sensitivity analyses of the effects of small residual DNAPL saturation and of a DNAPL pool on the measurement of the DNAPL volume by a PITT are presented. The potential interference of sedimentary organic carbon present within alluvial aquifers on tracer retardation is also quantified. Finally we present a protocol for conducting a PITT.

The Partitioning Inter-well Tracer Test

The PITT involves the injection of a mixture of conservative and partitioning tracers in one or more wells and the subsequent extraction of the tracer solution from one or more nearby extraction wells. The partition coefficient of tracer "i" is given by

$$K_i = \frac{C_{i,n}}{C_{i,w}} \quad (1)$$

where $C_{i,n}$ is the tracer concentration in the NAPL, and $C_{i,w}$ is the tracer concentration in the ground water at local chemical equilibrium. Conservative tracers have a partition coefficient of zero with respect to the NAPL, whereas the partitioning tracers have nonzero partition coefficients. The retardation factor of the tracers in a NAPL-contaminated, water-saturated aquifer is given by (Pope et al., 1994):

$$R_i = 1 + \frac{K_i S_n}{1 - S_n} \quad (2)$$

where S_n is the average NAPL saturation in the tracer swept volume. While the conservative tracers will be unaffected by the presence of NAPL in the subsurface pore spaces, the partitioning tracers undergo retardation by their partitioning into and from the NAPL. The chromatographic separation of the tracers due to this partitioning is used to measure the volume of NAPL in the interwell zone between the two wells. The detailed procedure for estimating average NAPL saturation (S_n) and total volume of NAPL in the tracer swept volume using the method of first temporal moment analysis can be found in Jin et al. (1994,1995) and Jim (1995).

It should be noted that the value of S_n obtained using the method of first temporal moment analysis represents the average over the tracer-swept pore volume and is not necessarily equal to the local residual NAPL saturation. NAPL is often present as residual saturation in the subsurface and more than likely only exists along the migration pathway of the original mobile NAPL. Because of the heterogeneity of typical alluvium, the residual NAPL saturation is also more than likely nonuniformly distributed. For a partitioning interwell tracer test, the tracer-swept volume of an extraction well can be very large and may contain pore space in which residual NAPL is not present.

Therefore, S_n obtained using the method of first temporal moment analysis is typically less than the local residual NAPL saturation. Of course, this does not affect the estimation of the total volume of NAPL in the swept pore volume.

Annable et al. (1994) present an example of PITT in a field-scale test in an LNAPL site at Operable Unit 1, Hill Air Force Base, Utah. Whitley et al. (1995) present a complementary method for measuring the average NAPL saturation in the vadose zone using partitioning gas tracers. During 1995 and 1996, the authors designed and conducted PITT's in unsaturated alluvium at the chemical waste landfill at the Sandia National Laboratories in New Mexico and in saturated alluvium at Operable Unit 2, Hill AFB, Utah, USAF Plant 4, Fort Worth, Texas, and the Portsmouth Gaseous Diffusion Plant in Ohio. These sites were contaminated with a mixed-component DNAPL mainly composed of trichloroethene (TCE) and other chlorinated solvents. These PITTs are presently undergoing final analysis and will soon be submitted for publication as illustrations of the principles set forth in this paper.

Simulations presented in this article were performed using UTCHEM (the University of Texas Chemical Flood Simulator, see Delshad et al., 1996; Brown et al., 1994). UTCHEM is a three-dimensional, multiphase, finite-difference, numerical simulator originally developed to model enhanced oil recovery. The following sections discuss the results of the three-dimensional simulations.

PITT Simulation Studies

Three-Dimensional Model Development

The alluvial aquifer used for the simulation studies is based upon several sites being investigated by INTERA Inc. and the University of Texas. Figure 1 shows the aquifer section modeled and well locations. The upper map is in plan view and the lower is a vertical cross section. The section of the aquifer was 16.6 m long, 9.1 m wide, and 5.4 m thick. The uniform finite-difference grid used was 20 grid blocks in the x direction, 11 gridblocks in the y direction, and 9 gridblocks in the vertical z direction. The aquifer was assumed to be horizontal and water-saturated. A typical hydraulic gradient of 0.007 parallel to the x-axis was used for these simulations.

A stochastic hydraulic conductivity field was generated by assuming a lognormal distribution, an exponential variogram, and using the matrix decomposition method (Yang, 1990). The top 3 m of the aquifer has a mean hydraulic conductivity of 1×10^{-4} cm/s, with a standard deviation (σ_{hk}) of 0.92 and horizontal and vertical correlation lengths of 1.5 m and 0.6 m, respectively. The bottom 2.4 m of the aquifer has a mean hydraulic conductivity of 1×10^{-2} cm/s, with a standard deviation (σ_{hk}) of 0.92 and horizontal and vertical correlation lengths of 1.5 m and 0.6 m, respectively. The porosity of the aquifer is 0.3. The longitudinal and transverse dispersivities are 0.15 m and 0.05 m, respectively. The injection and extraction wells are completed in the bottom 1.2 m of the aquifer and are 7.5 m apart. Injection and extraction rates were both 9.5 liters per minute (1/min).

Partitioning Tracer Testing of a Residual DNAPL Zone

The first scenario simulated a tracer test with only residual TCE DNAPL present. The residual saturation for TCE was 0.1 in the bottom 1.2 m and in the vicinity of the injection and extraction wells. The tracers used in this simulation and other simulations presented in the paper are summarized in Table 1.

Fig. 1. Schematic of simulation grid and well locations.

Tracers were injected for 0.5 days with a total of 5 kg of each tracer being injected.

The tracer response curves (concentrations measured in the extraction well) for this case are shown in Figure 2. The tracer recovery estimated by integrating the tracer response curves over the volume of extraction is shown in Figure 3 and indicates that the recovery exceeds 60% after 30 days of tracer testing. The TCE volume and tracer retardation factors are calculated using the method of first temporal moment analysis (Jim et al., 1995; Jim, 1995) and the results are presented in Figures 4 and 5. The TCE volume continues to increase with time because the estimated tracer swept volume continues to increase with time as shown in

Table 1. Tracers and Their Partition Coefficients Between TCE and Water

Tracer name	Abbreviation	Partition coefficient (mg/l)/(mg/l)
Bromide	—	0.0
3-methyl-3-pentanol	3M3P	4.5
4-methyl-2-pentanol	4M2P	10.2
n-hexanol	—	18.6
2-methyl-2-hexanol	2M2H	28.1
2,2-dimethyl-3-pentanol	22DM3P	70.8

Fig. 2. Tracer response curves for residual DNAPL saturation of 0.1.

Fig. 3. Tracer recovery for residual DNAPL saturation of 0.1.

Fig. 4. DNAPL volume estimation for residual DNAPL saturation of 0.1.

Fig. 5. Retardation factor for residual DNAPL saturation of 0.1.

Figure 6. The swept volume increases with time as tracers are captured due to the arrival of stream tubes that traveled farther away from the direct line between the injection and extraction wells.

Figure 5 indicates that the NAPL estimation errors are in the range of 4 to 12% depending on the tracer used for NAPL volume calculations after 40 days of tracer test which corresponds to approximately 60% recovery (Figure 3). This indicates that virtually all of the contaminated aquifer is swept, even though hydraulic conductivity varies by two and a half orders of magnitude within the sandy gravel unit contaminated by TCE. This observation is very positive in terms of the suitability of the test method in evaluating typical heterogeneous alluvial aquifers. Another important observation is that the loss of tracer will not affect the accuracy of volume estimation. This is also important as in practice some of the injected tracers will escape capture by the extraction well because of the unconfined aquifer boundary conditions and finite duration of an actual test.

The time of 40 days shown in the above example is specific to conditions assumed in the simulations. There are several parameters controlling the tracer test time required for accurate NAPL volume estimation. These parameters, such as the magnitude and heterogeneity of the hydraulic conductivity, injection

Fig. 6. Tracer swept volume for residual DNAPL saturation of 0.1.

and extraction rates, NAPL volume and distribution, tracer partition coefficients, etc., all affect the duration of the test. It is, therefore, very important to model the partitioning interwell tracer test with a numerical simulator before the actual test is conducted. Simulation modeling prior to the realization of the field test can be used to determine the approximate duration of the tracer test. In the actual test, however, the duration of the tracer test could be either slightly shorter or longer. A useful guidance on the test time required can be determined from the tracer recovery curves such as the one shown in Figure 5. The general guideline is that the tracer test can be terminated when the tracer recovery curves of the nonpartitioning tracer and at least one partitioning tracer with a retardation factor in the range of 1.2 to 4 have reached plateaus, i.e., become asymptotic. For the example shown above, the bromide and 4-methyl-2-pentanol (retardation factor of about 1.3) reached a plateau after 35 days by which time the NAPL volume estimation error has decreased to less than 10%.

The resulting retardation factors shown in Figure 5 indicate that the retardation factor for 3-methyl-3-pentanol is smaller than 1.2. Such a small retardation factor results in poor separation of the tracer response curves between bromide and 3-methyl-3-pentanol as shown in Figure 2. It has been shown by Jin (1995) that the retardation factor should be in the range of 1.2 to 4 in order to obtain the response curves of the partitioning tracers in a reasonably short time and yet ensure good separation of the nonpartitioning and partitioning tracer. For this case, the partition coefficients of 3-methyl-3-pentanol are too small when the amount and the distribution of the NAPL in the test area is as presented in the model, i.e. residual saturation of 0.1.

Estimating DNAPL Volumes When Residual DNAPL Saturation Is Progressively Decreased

Concern has often been expressed to the authors of the effects of very low residual DNAPL saturation on the accuracy of a PITT. Theoretically, there is no requirement on the minimum residual saturation for accurate estimate of DNAPL volume from a PITT because in a sense, the estimation accuracy is independent of DNAPL saturation as long as the separation of tracer response curves between partitioning and nonpartitioning tracers can be distinguished by gas chromatography or the other tracer detection equipment. In reality, however, there is a limit on the capability of detection equipment in distinguishing the tracer separation, which in turn contributes to the estimation error.

The separation of the tracer response is, however, not only a function of the DNAPL residual but also the tracer partition coefficient [see equation (2)]. Therefore, the estimation error can be minimized by using tracers with different partition coefficients. This can be best illustrated by the following sensitivity studies which are based on the 3-D model presented in the previous section.

The three cases studied differ only in terms of the residual TCE saturation. Case #1 has a residual TCE saturation of 0.1. Case #2 has a residual saturation of 0.05 and Case #3 has a residual saturation of 0.02. In all three cases, TCE is present only in the bottom 1.2 m. The tracer response curves for these three cases are shown in Figure 7. Clearly, the degrees of separation of the tracer response curves are different for the different cases. The retardation factors, which measure the separation of tracer response for these three cases, are shown in Figure 8. As we have

Case #1 Residual DNAPL Saturation of 0.1

Case #2 Residual DNAPL Saturation of 0.05

Case #3 Residual DNAPL Saturation of 0.02

Fig. 7. Tracer response curves for cases with three different DNAPL saturation.

pointed out in the previous section, the retardation factor needs to be in the range of 1.2 to 4 in order to obtain the response curve of the partitioning tracer in a reasonably short time and yet ensure good separation of the nonpartitioning and partitioning tracer. The retardation factors of the two partitioning tracers used in Case #1 meet this criterion. The retardation factors of 4-methyl-2-pentanol in Case #2 and n-hexanol in Case #3 are less than 1.2, and therefore, cannot be used to estimate the TCE volume accurately. However, 2-methyl-2-hexanol in Case #2 and 2,2-dimethyl-3-pentanol in Case #3 can still give accurate estimation of TCE volume.

These examples illustrate that it is very important that more than one partitioning tracer be used for the actual field test, especially when there is a large range of uncertainty in the quantity and distribution of DNAPL. If the volume of the DNAPL is relatively high, tracers with smaller partition coefficients are sufficient, and it is not mandatory to continue the test to obtain the response curves for the tracers with larger partition coefficients such as 2-methyl-2-hexanol in Case #1. If the volume of the DNAPL is lower than expected, the tracers with larger partition coefficients can ensure good separation of the tracer response curves such as 2,2-dimethyl-3-pentanol in Case #3. The tracers used for TCE volume estimation and their estimation accuracy for these three cases are shown in Figure 9.

Therefore, a properly designed and executed partitioning tracer test can accurately estimate the interwell DNAPL volume for even very low residual DNAPL saturation by employing a suite of tracers with high partition coefficients. It may also be necessary to measure the volume of DNAPL solubilized during

Case #1 Residual DNAPL Saturation of 0.1

Case #2 Residual DNAPL Saturation of 0.05

Case #3 Residual DNAPL Saturation of 0.02

Fig. 8. Retardation factors for cases with three different DNAPL saturation.

Case #1 Residual DNAPL Saturation of 0.1

Case #2 Residual DNAPL Saturation of 0.05

Case #3 Residual DNAPL Saturation of 0.02

Fig. 9. DNAPL volume estimation for cases with three different DNAPL saturation.

the PITT, which is a water flood in itself. This is especially true for DNAPL composed of more soluble compounds such as 1,2-dichloroethane. At low residual saturation, a significant fraction of such residual DNAPL may be dissolved by the tracer itself.

Partitioning Tracer Testing of Alluvium with Both Residual and Free-Phase DNAPL

An additional scenario was simulated to determine whether a DNAPL pool could be successfully quantified by a PITT. A topographical depression was created in layers 8 and 9, as shown in Figure 10. In this case, layers 8 and 9 contain the DNAPL pool consisting of TCE at a saturation of 0.25 and 0.60, respectively, and ground water at a saturation of 0.75 and 0.4, respectively. Layer 7 contains residual TCE saturation of 0.1 in the vicinity of the TCE pool. A partitioning interwell tracer test was simulated with an injection and extraction rate of 9.5 l/min at the injection and extraction wells completed in layer 7 as shown in Figure 10.

Figure 11 shows the tracer response curves for this case. Figure 12 indicates that the TCE estimation errors are in the range of 50 to 60%, even though almost all the recoverable mass of the injected tracers is recovered from the extraction wells. Therefore, the ability of a PITT to successfully quantify a DNAPL pool within an aquifer would be dependent on the

a) XZ cross-sectional view (J=6)

b) YZ cross-sectional view (I=10)

Fig. 10. Schematic of simulation grid for the case with DNAPL pool.

Fig. 11. Tracer response curves for the case with DNAPL pool.

Fig. 12. DNAPL volume estimation for the case with DNAPL pool.

thickness of the pool and on the DNAPL and residual water saturation within the pool. It is, therefore, always desirable that free-phase DNAPL be recovered from the aquifer by pumping prior to the PITT, or that the PITT be repeated after the pool has been pumped to residual DNAPL saturation.

In the worst-case situation, the error of estimation in the DNAPL volume can be approximated by assuming that only the residual DNAPL volume, V_R , is detectable by a PITT while the free-phase DNAPL volume in the pool, V_F , is not. Therefore, the relative error of estimation, E_r , is given by

$$E_r = 1 - \frac{V_R}{V_R + V_F} = 1 - \frac{1}{1 + \frac{V_F}{V_R}} \quad (3)$$

The solid line in Figure 13 is a graphic illustration of equation (3), and the points were several additional UTCHEM simulation results which were obtained by increasing the depth of the pool (more layers in the z direction) while keeping the residual TCE saturation constant.

It should be clearly understood, however, that the above calculations are based on the worst-case scenario, i.e., the aqueous phase flux in the DNAPL pool was negligible compared to that in the residual DNAPL zone mainly due to the model configuration. In reality, the water saturation in a DNAPL pool

Fig. 13. DNAPL volume estimation accuracy as a function of the volume ratio of the DNAPL in pool and the DNAPL in residual.

is not always at its residual value. The free-water phase in the DNAPL pool will allow the transport and partitioning of tracer within the DNAPL pool, provided that the water saturation is above the residual saturation, although its relative permeability will be much reduced. Moreover, provided its location is known, the DNAPL pool would be pumped to residual DNAPL saturation prior to the PITT. In the worst case, even when there are equal amounts of residual and free DNAPL present, the error of estimation of the DNAPL volume is no more than 50%. This error is small compared to the usual guesses made concerning the volume of DNAPL present at most sites.

Interference by Sedimentary Organic Carbon

At low residual NAPL saturation, there is a potential for interference due to sorption of tracers to immobile sedimentary organic carbon (SOC) and/or mineral surfaces. The fractional organic carbon content (f_{oc}) of sandy, alluvial aquifer materials typically varies from 0.001 to 0.0001 kg/kg (Schwarzenbach and Westall, 1981; Curtis et al., 1986; Jackson and Inch, 1989; Lesage et al., 1990; Mackay, 1990). Sorption of the partitioning tracers to aquifer materials could potentially increase the retardation of the partitioning tracers.

Sorption to SOC typically dominates when f_{oc} is greater than 0.001 kg/kg (Schwarzenbach and Westall, 1981) and greater than about 3-7% of the solid mass fraction of clay (Karickhoff, 1984). The mass of tracer sorbed per unit mass dry sediment is given by $K_{oc,i} f_{oc} C_{i,w}$, where $K_{oc,i}$ is the organic carbon partition coefficient for tracer i in units of volume per mass, and $C_{i,w}$ is the mass of tracer i dissolved in water per unit volume water. The $K_{oc,i}$ values for a series of normal alcohols are given in Table 2, where the NAPL partition coefficient values are divided by NAPL density to obtain units that can be compared to the $K_{oc,i}$ values. The two NAPLs being compared with SOC are a complex, mixed-waste LNAPL from Operable Unit 1, Hill Air Force Base, Utah (OU1 LNAPL) and TCE.

The condition under which the chromatographic separation of partitioning tracers during a PITT is equally due to sorption onto SOC and partitioning within NAPL occurs when the tracer mass sorbed equals the tracer mass partitioned. The mass of tracer sorbed onto SOC is given by $K_{oc,i} f_{oc} \rho_b C_{i,w}$ where ρ_b is the dry bulk density of the soil. The mass of tracer parti-

tioned into the NAPL is given by $K_{a,i} S_a \phi C_{i,w}$, where ϕ is the porosity. Solving for the residual NAPL saturation when the mass sorbed equals the mass partitioned within the NAPL gives

$$S_a = \frac{K_{oc,i} f_{oc} \rho_b}{K_{a,i} \phi} \quad (4)$$

Thus, for example, assuming f_{oc} is 0.001, ϕ is 0.4, and ρ_b is 1.59 g/ml, the residual OU1 LNAPL or TCE saturation when the amount of n-hexanol sorbed to SOC equals the amount of n-hexanol partitioned into the NAPL would be 0.9% and 0.2% for OU1 LNAPL and TCE, respectively. If the sediments contained no residual NAPL, equation (2) implies that the n-hexanol retardation factors due to organic carbon for OU1 LNAPL and TCE would be about 1.04. If residual NAPL is present, the retardation of n-hexanol will be due to both tracer sorption to the SOC and partitioning to the NAPL phase. Therefore, knowing the value of f_{oc} in such cases allows the potential interference to be corrected for. In this example, the tracer interference from sedimentary organic carbon can be accounted for by subtracting 0.04 from the measured retardation factors.

Laboratory column tests of uncontaminated alluvial aquifer materials can be performed prior to conducting a PITT to determine potential interference effects and correction factors. So far, such column tests on aquifer materials from Hill AFB, UT, Sandia National Labs, NM; the Portsmouth Gaseous Diffusion Plant in Ohio; and USAF Plant 4, Fort Worth, TX have shown no evidence of tracer sorption.

A Protocol for Undertaking a PITT

From our experience in conducting partitioning interwell tracer tests in a variety of alluvial aquifers, we believe it to be appropriate to identify a protocol of operations that should be undertaken prior to the PITT itself. The sequence of operations we recommend is as follows:

1. *Continuous coring.* Continuous cores should be collected to (a) determine the structure of the alluvium, (b) provide material for laboratory column testing, (c) determine sedimentary organic carbon content, grain-size distribution, and the vertical distribution of DNAPL through the analysis of total soil contaminant concentrations (see Mariner et al., 1997).

2. *Wellfield preparation.* Injection, extraction and/or monitoring wells are then installed, existing wells are redeveloped to remove fine particles, and any free-phase DNAPL is removed in order to minimize the errors of estimation of the remaining in situ volume of DNAPL.

Table 2. Comparison of Partition Coefficients (ml/g) for Normal Alcohol Tracers

Tracer	K_{oc}	K_{LNAPL}/ρ_{LNAPL}	K_{TCE}/ρ_{TCE}
n-ethanol	1.6	0.1	—
n-propanol	3.0	—	—
n-butanol	3.2	—	—
n-pentanol	5.0	1.7	2.6
n-hexanol	10.2	5.5	12.7
n-heptanol	13.8	24.0	110.0
n-octanol	36.3	117.0	—
NAPL density (g/ml)	na	0.83	1.46

Sources of data: K_{oc} : Meylan et al., 1992. K_{LNAPL} : Annable et al., 1994. K_{TCE} : Wang et al., in press.

3. *Hydraulic testing.* Pumping tests are then performed to determine the hydraulic properties of the alluvium and any critical overlying or underlying aquitards, the hydraulic boundaries of the system, and, through the injection of clean, chemically compatible water, the sustainable injection and extraction rates.

4. *Chemical analysis.* Using the aquifer materials and liquids recovered during the previous steps, chemical analyses of DNAPL, sedimentary organic carbon, and ground water are performed.

5. *Development of the "geosystem" model of aquifer.* A detailed conceptual model of the alluvium-DNAPL-ground-water geosystem is then developed and used to define the properties of numerical models used in the design step (Jackson and Jin, 1997).

6. *Design.* The PITT is then designed using the UTCHEM simulator (Delshad et al., 1996) following an extensive sensitivity analysis of the geosystem model, including the demonstration of the hydraulic control of the tracers injected, such that this model of the DNAPL distribution is confirmed or denied by the PITT to the extent possible.

Thus, the intent of this protocol is to ensure that the hypotheses posed in the development of the geosystem model are tested, that the results of the PITT provide the maximum amount of useful information, and, therefore, that the probability of failure of the PITT is minimized.

Discussion and Conclusions

There are several benefits obtained in using partitioning tracer tests during the characterization and remediation of DNAPL-contaminated alluvium or, for that matter, other aquifers of varying stratigraphy, lithification, water saturation, and NAPL density. First, the PITT provides a definitive method of detecting DNAPL should there be doubt of its presence. Second, the PITT provides a means by which the volume of DNAPL can be accurately measured. Third, the volume of DNAPL in the test area can be determined before, during, and after remediation, thus providing a reliable measure of the performance of the remedial operations. For the examples simulated, it is shown that a PITT conducted in a heterogeneous alluvial aquifer can measure the volume of residual DNAPL present to within a few percent of the actual DNAPL volume, while the presence of a DNAPL pool in a depression at the base of the aquifer would cause the error to increase to 30-50%. The minimization of this error is the subject of present research. However, notwithstanding such an error, the estimate provided by a PITT in such circumstances is a significant improvement in the estimation of DNAPL volumes at most hazardous waste sites. At such sites, DNAPL volume estimation is usually a matter of inspired guesswork based upon anecdotal information concerning past industrial practices leading to the spillage of DNAPL and other unreliable information.

If soil column tests show detectable interference of sedimentary organic carbon on the PITT, then knowledge of the fractional organic carbon content of the alluvium should be useful to improve the accuracy of PITT. Furthermore, such interference can be minimized by the careful choice of tracers. In fact, partitioning tracers can be chosen to measure the fractional organic carbon content of the alluvium and, for unsaturated alluvial aquifers, the fractional water content of the aquifer, as was done in the Sandia PITT.

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APPENDIX B

An Algorithm for the Estimation of NAPL Saturation and Composition from Typical Soil Chemical Analyses

An Algorithm for the Estimation of NAPL Saturation and Composition from Typical Soil Chemical Analyses

by Paul E. Mariner, Minquan Jin, and Richard E. Jackson

Abstract

An algorithm is presented that allows estimation of the saturation and composition of a single or multi-component NAPL within a core sample. These estimates are possible because, in addition to distributing the organic chemicals between aqueous, sorbed, air, and NAPL phases according to traditional partitioning equations, the algorithm incorporates equations for the conservation of mass and volume. A unique solution is obtained by solving the set of nonlinear equations implicitly. The algorithm is built into a code called NAPLANAL, which is tested and applied to actual core samples collected in the field.

Introduction

It is an extraordinary feature of modern hydrogeological practice that estimating the mass or volume of nonaqueous phase liquid (NAPL) in a soil or rock is not deemed essential to the design of remediation systems. A brief inspection of past issues of this journal will show that NAPL volumes are seldom estimated from field data. Such a volume estimate permits the calculation of an approximate remediation period for the NAPL-contaminated soil or rock. An essential parameter for estimating NAPL volumes in a NAPL-contaminated soil or rock is the NAPL saturation of the porous medium. Mercer and Cohen (1990) have tabulated NAPL saturation data from the literature.

Paraphrasing Bear (1972), when the pore space of an aquifer sediment or fractured rock is contaminated with NAPL, the saturation (or degree of saturation) of NAPL at a particular point is defined as the fraction of pore space occupied by NAPL within a representative elementary volume (REV) around the considered point:

$$S_N = \frac{\text{volume of NAPL within REV}}{\text{total pore volume within REV}} \quad (1)$$

As pointed out by Corey (1994), "saturation can be conceptualized (but not measured) as a point property varying in space in a manner entirely analogous to porosity." The constraint of being unable to measure the saturation at a point arises from the size of the REV, which

Mayer and Miller (1992) found to vary directly with the nonuniformity of the porous medium such that "the upper range of these REV estimates (i.e., $\sim 10^{-10} \text{ cm}^3$) exceeds the scale of . . . field samples typically taken to estimate NAPL residual saturation levels." It is for this reason of scale that Jin et al. (1995) have proposed using a partitioning interwell tracer test for measuring NAPL volume over a large interwell pore volume.

While soil cores cannot provide reliable NAPL saturations over large zones of the subsurface, they can provide information on the approximate volumes of NAPL present in the core samples. Furthermore, continuous coring can indicate the relative NAPL saturations with depth, which may allow an experienced observer to deduce whether pooling of NAPL may be occurring upon some capillary barrier, such as a clay lens. In addition, the analysis and interpretation of soil chemical data from cores indicate the nature of the chemical composition of the NAPL in the source zone. Finally, the chemical analysis of soil cores provides an approximate initial value of NAPL saturation which can be used in multiphase, multicomponent simulators such as UTCHEM for modeling surfactant-enhanced aquifer remediation (e.g., Brown et al. 1994) and the application of partitioning interwell tracer tests (e.g., Jin et al. 1995).

We are not aware of any published method for calculating NAPL saturation from a soil sample chemical analysis when more than one organic compound is identified in the analysis. Feenstra et al. (1991) showed how a measured organic concentration can be used to assess whether a single- or multicomponent NAPL is present in a soil sample, but not how NAPL saturation could be calculated. In addition, the method requires an a priori assumption of the NAPL chemical composition. **Mott (1995) improved on the Feenstra et al. (1991) method by presenting a method that can be used to estimate multicomponent NAPL composition from a complete organic chemical soil sample analysis and to determine whether NAPL is present in the sample. The method, which is incorporated in a code called SOIL-CALC, distributes mass among all phases including the NAPL phase. However, because the method assumes that NAPL occupies no pore space, SOILCALC cannot be used to calculate NAPL saturation. Consequently, its calculations of NAPL composition and the concentrations of organic compounds in each phase are not accurate unless NAPL saturation is approximately two orders of magnitude lower than typical residual NAPL saturations. Typical residual NAPL saturations range from 10 percent to 20 percent in the vadose zone and from 15 percent to 50 percent in the saturated zone (Mercer and Cohen 1990).**

In this paper, a model is presented for the implicit calculation of NAPL saturation, NAPL composition, and phase distribution of organic compounds in a core sample of soil or rock. This model was developed in 1993 as an extension of the model presented in Feenstra et al. (1991). In addition to the phase partitioning relationships, the model incorporates equations for the con-

servation of mass and volume. The algorithm **distributes the organic chemicals among aqueous, air, sorbed, and NAPL phases** so that both the NAPL saturation and the correct NAPL composition are determined regardless of the amount of NAPL in the sample.

Partitioning Theory

If NAPL exists in a core sample from the unsaturated zone, the NAPL components will be distributed among four physical phases: air, soil, water, and NAPL. Each NAPL component (i.e., each compound in the NAPL) is distributed among the phases according to thermodynamic equilibrium principles and mass transfer kinetic factors. The system reaches equilibrium when the chemical potential of any constituent is equal in all phases. Figure 1 shows a schematic representation of the equilibrium relationship.

Figure 1. Schematic representation of phase equilibrium and partitioning.

To estimate the distribution of the total mass of a chemical among the phases at equilibrium, the chemical's phase partitioning behavior must be known. All nonaqueous concentrations are defined using traditional equilibrium equations that are functions of aqueous concentrations. These relationships are presented later. In each relationship, at least one chemical property of each organic compound (e.g., aqueous solubility, vapor pressure, and partition coefficient) must be known. In each case, the value of the chemical property is temperature dependent. Consequently, the values used in the model must be representative of the original soil or rock temperature. Values for these properties at specific temperatures can be found in the literature (e.g., Mercer et al. 1990) or estimated (e.g., Lyman et al. 1990, Drefahl and Reinhard 1995).

NAPL-Water Partitioning

NAPL-water partitioning depends on the aqueous solubilities of the NAPL components and the concentrations of the NAPL components in the NAPL. The relationship is analogous to Raoult's law for ideal gas mixtures. For an ideal NAPL in contact with water the

aqueous phase concentration of a NAPL component is equal to the pure phase aqueous solubility of the component multiplied by the mole fraction of the component in the NAPL mixture. Mathematically, this relationship is written as:

$$C_w^i = x_i S_i \quad (2)$$

where C_w^i is the aqueous phase concentration of component i (mass i in water per volume water); x_i is the mole fraction of the component in the NAPL mixture (mole i in NAPL per mole NAPL); and S_i is the aqueous solubility of pure component i (mass i in water per volume water). Feenstra et al. (1991) refers to C_w^i as the effective aqueous solubility of component i when the aqueous phase is at equilibrium with a NAPL. This general NAPL-water partitioning relationship has been confirmed by Banerjee (1984), Mackay et al. (1991), Cline et al. (1991), Lee et al. (1992a,b), and Broholm and Feenstra (1995) for NAPL mixtures of structurally similar compounds. This relationship is not highly dependent on temperature.

Air-Water Partitioning

The equilibrium concentration of component i in air is related to the aqueous concentration by Henry's law. Henry's law states that equilibrium water-air partitioning is described by a linear relationship. The relationship can be written as:

$$C_a^i = K_H^i C_w^i \quad (3)$$

where C_a^i is the concentration of i in air (mass i in air per volume air), and K_H^i is the dimensionless Henry's constant. The Henry's constant is often reported in the literature in its dimensional form, $K_H^{i'}$ (e.g., atm-L/mol). The dimensional Henry's constant is calculated from the equation:

$$K_H^{i'} = \frac{P_{\text{vap}}^i}{S_i} MW_i \quad (4)$$

where P_{vap}^i is the component's vapor pressure (e.g., atm), and MW_i is the component's molecular weight (mass i per mole i), which is needed to convert the previously defined mass-based aqueous solubility S_i to molar units. The two Henry's constants are related through the equation:

$$K_H^i = \frac{K_H^{i'}}{RT} \quad (5)$$

where R is the universal gas constant (0.08206 atm-L/mol-K) and T is temperature in Kelvin. As the equation reveals, air-water partitioning is highly dependent on temperature.

Soil-Water Partitioning

Sorption to soil organic matter can also be described by a linear function of the aqueous organic compound concentration. The relationship can be written as:

$$C_s^i = K_{oc}^i f_{oc} C_w^i \quad (6)$$

where C_s^i is the sorbed concentration of component i (mass i sorbed per mass soil); K_{oc}^i is the organic carbon to water partition coefficient of component i (mass i sorbed per mass organic carbon divided by mass i in water per volume water); and f_{oc} is the mass fraction of natural organic carbon within the soil matrix (mass natural organic carbon per mass soil).

The mass fraction of natural organic carbon has to be measured for the particular soil to be evaluated. Although the effect of temperature is small, the K_{oc}^i value can be highly sensitive to pH if the organic compound is ionizable (Drefahl and Reinhard 1995).

The linear isotherm model of Equation 6 has been experimentally verified for various organic compounds by Karickhoff et al. (1979), Chiou et al. (1979), Schwarzenbach and Westall (1981), and Chiou et al. (1983). It has been noted, however, that linear sorption is valid only for f_{oc} greater than about 0.001 (Schwarzenbach and Westall 1981) and greater than about 3 to 7 percent of the solid mass fraction of clay (Karickhoff 1984); otherwise, sorption of organic compounds on clays and mineral surfaces can be significant.

Conservation Equations and Relationships

Soil, water, air, and NAPL account for the total volume of a soil sample containing NAPL. The volume conservation equation is:

$$\phi_s + \phi_w + \phi_a + \phi_n = 1 \quad (7)$$

where ϕ_s is the volumetric soil content (volume soil per total volume); ϕ_w is the volumetric water content (volume water per total volume); ϕ_a is the volumetric air content (volume air per total volume); and ϕ_n is the volumetric NAPL content (volume NAPL per total volume). The soil porosity ϕ (volume void per total volume) is equal to the sum of the volumetric air, water, and NAPL contents:

$$\phi = \phi_a + \phi_w + \phi_n \quad (8)$$

Thus, the volumetric soil content ϕ_s equals $1 - \phi$.

Each NAPL component in a soil sample is distributed among the phases present. As a result, the total mass of component i in the sample equals the sum of the masses of component i in all phases. The mass conservation equation is:

$$\rho_t C_t^i = \phi_w C_w^i + \phi_a C_a^i + \phi_n C_n^i + \phi_s \rho_s C_s^i \quad (9)$$

where ρ_t is the total density of the soil sample (mass of sample per volume of sample); C_t^i is the measured total concentration of i in the sample (mass i in sample per mass of sample); C_n^i is the concentration of i in the NAPL (mass i in NAPL per volume NAPL); and ρ_s is the density of the solid (approximately 2.65 kg/L for sand). The total density, ρ_t , is approximately equal to

the weighted average of the densities of the four phases:

$$\rho_t = \phi_w \rho_w + \phi_a \rho_a + \phi_n \rho_n + \phi_s \rho_s \quad (10)$$

where ρ_w is the density of water (approximately 1.0 kg/L); ρ_a is the density of air (approximately 0.0013 kg/L at 20°C); and ρ_n is the density of the NAPL mixture (mass NAPL per volume NAPL). ρ_n can be expressed as:

$$\rho_n = \frac{\sum x_i MW_i}{\sum \frac{x_i MW_i}{\rho_i}} \quad (11)$$

where ρ_i is the density of pure component i in liquid form (mass i per volume i). Some components, such as vinyl chloride or anthracene, may not occur as liquid in their pure form under environmental conditions. For these components, hypothetical pure phase liquid densities are computed by extrapolation.

The mole fraction of component i in the NAPL mixture is related to mass concentration by the equation:

$$x_i = \frac{C_n^i MW_n}{\rho_n MW_i} \quad (12)$$

where MW_i is the equivalent molecular weight of the NAPL mixture (mass NAPL per mole NAPL). MW_i is approximately equal to the weighted average of the molecular weights of the NAPL components:

$$MW_n = \sum x_i MW_i \quad (13)$$

Finally, the sum of the NAPL mole fractions is equal to 1:

$$\sum x_i = 1 \quad (14)$$

Estimation of NAPL Saturation and Composition

A complete chemical analysis of a core sample provides the total mass of each component per unit mass of sample (i.e., the value of C_i for each component). To determine the saturation and composition of NAPL in the sample, the total mass of each component in each phase and the total volume of each phase must be determined. The partitioning theory and conservation relationships presented in the previous section can be used for this purpose. The solution allows calculation of the NAPL saturation from the equation:

$$S_N = \frac{\phi_n}{\phi} \quad (15)$$

The method presented here is a numerical solution of the partitioning and conservation equations. PC software called NAPLANAL was developed to perform the numerical simulation. NAPLANAL can be used to estimate the following: (1) the NAPL saturation and composition in a soil sample containing NAPL; (2) the concentrations of organic compounds in each phase; and

(3) the NAPL composition and NAPL volume in samples of NAPL-water emulsions ($\phi_s = 0$). A copy of NAPLANAL is available from the INTERA web site (<http://www.intera.com>) for a small fee.

The algorithm is first demonstrated by considering a hypothetical soil sample from an unsaturated formation containing NAPL with N chemical components. Calculation of NAPL saturation and composition requires the following measurements or estimates as input: total concentrations of NAPL components in the soil sample (C_i), volumetric water content (ϕ_w), soil porosity (ϕ), volumetric soil content ($\phi_s = 1 - \phi$), soil organic carbon content (f_{oc}), partition coefficients (K_{oc}^i , K_H^i),

$$(MW_i), (\rho_w, \rho_a, \rho_s, \text{ and } \rho_i).$$

Equations 2, 3, 6, and 8 through 14 provide a total of $5N+5$ independent equations that describe partitioning and conservation of organic compounds in a soil sample. Given the measurements and estimates listed in the previous paragraph, there are $5N+5$ unknowns. These unknowns are as follows: NAPL component concentrations in water, air, soil, and NAPL (C_w^i, C_a^i, C_s^i , and C_n^i); component mole fractions in the NAPL mixture (x_i); volumetric contents of air and NAPL (ϕ_a and ϕ_n); density of sample (ρ_t); and the equivalent density and molecular weight of the NAPL (ρ_n and MW_n).

An equal number of unknowns and independent equations guarantees a unique solution. NAPLANAL solves the system of equations and unknowns using an algorithm that combines the rapid local convergence of the Newton-Raphson method for a system of nonlinear equations with a globally convergent strategy. For the sample problems tested so far, the computation time for reaching a solution is less than one minute using a 486 DX66 PC.

For core samples from the saturated zone, the air volumetric content (ϕ_a) and air phase concentrations (C_a^i) are equal to zero. Thus, the terms and equations involving the air phase are dropped from the system of equations. As a result, the number of equations reduces to $4N+5$, while the number of unknowns reduces to $4N+4$. Because there are fewer unknowns than equations, a measurement for either soil porosity (ϕ) or soil volumetric water content (ϕ_w) is sufficient for estimation purposes. Users of NAPLANAL have the choice of treating either ϕ or ϕ_w as an unknown parameter. A gas chromatography method is currently being developed to allow simultaneous measurement of ϕ_w and the concentrations of organic compounds in a soil sample.

The NAPLANAL code begins with the assumption that there is no NAPL present in the sample (i.e., $\phi_n = 0$). The density of the sample can then be calculated from Equation 10 as:

$$\rho_t = \phi_w \rho_w + (\phi - \phi_w) \rho_a + (1 - \phi) \rho_s \quad (16)$$

The first approximation of the aqueous concentration can be calculated from Equation 9 by:

$$C_w^i = \frac{C_i \rho_i}{\phi_w + K_H^i (\phi - \phi_w) + f_{oc} K_{oc}^i \rho_s (1 - \phi)} \quad (17)$$

as shown by Feenstra et al. (1991). If NAPL exists in the sample, then this first approximation of C_w^i should exceed the effective aqueous solubility of component i . Equations 2 and 14 imply that C_w^i equals the effective aqueous solubility when:

$$\sum \frac{C_w^i}{S_i} = 1 \quad (18)$$

Thus, a summation exceeding 1 when Equation 17 is used to estimate C_w^i implies that NAPL is present in the sample and that the NAPL saturation algorithm must be used instead to estimate C_w^i . A summation in Equation 18 equal to or less than one indicates there is no NAPL in the sample (i.e., S_N and ϕ_n equal zero). In this case, Equation 17 provides valid explicit estimates of aqueous concentrations. Air and sorbed concentrations are then calculated directly from Equations 3 and 6. When the summation in Equation 18 is less than 1, C_w^i is less than the effective aqueous solubility and calculation of x_i from Equation 2 is invalid.

Petroleum Hydrocarbon Example

In this example, the petroleum hydrocarbon data from Mott (1995) are used to compare the results of NAPLANAL and SOILCALC. The example problems consider hypothetical soil samples contaminated with C6 through C9 n-aliphatic hydrocarbons. For direct comparison of NAPLANAL and SOILCALC results, the input data are identical. The physical and chemical properties of the soil samples and the petroleum hydrocarbons used in the calculations are summarized in Table 1.

Table 1 Chemical Property Data Used in the Examples by Mott (1995)					
Component i	K_{oc}^i (mL/g)	K_H^i	S_i (mg/L)	ρ_i (kg/L)	MW_i (g/mol)
Hexane	6025.60	46.49	12.31	0.66	86.07
Heptane	22908.68	63.59	3.06	0.68	100.20
Octane	77624.71	95.74	0.68	0.70	114.22
Nonane	263026.8	45.80	0.47	0.72	128.26
Soil Sample Data		f_{oc}	ϕ_w	ϕ	
		0.01	0.08	0.4	

The three soil samples differ only in the total hydrocarbon component concentration. These data are shown in Table 2. The first data set represents a soil sample containing 250 mg/kg of each component. The second data set, which is a borderline case (NAPL may or may not be present based on SOILCALC results), represents a soil sample containing 192 mg/kg each component.

The third data set, which is a no NAPL case, represents a soil sample containing 100 mg/kg each component. Results from SOILCALC and NAPLANAL are summarized in Table 2. SOILCALC results are in parentheses.

SOILCALC assumes that NAPL occupies zero void space (i.e., the NAPL saturation is assumed insignificant relative to water and air content). Because of this assumption, SOILCALC does not have NAPL saturation estimation capability. In contrast, NAPLANAL implicitly calculates NAPL saturation. For the first two sets of data, the results indicate NAPL saturations of 0.15 percent and 0.02 percent, respectively. At such low NAPL saturations (i.e., approximately 1 percent or less of typical residual NAPL saturations [Mercer and Cohen 1990]), the pore space occupied by NAPL is indeed insignificant relative to pore space occupied by water and air. As a result, the two models give similar results, as shown in Table 2. However, there are still differences in the component mass distributions, especially for the mass of components in the NAPL phase. Because NAPLANAL calculates NAPL saturation, it should provide more accurate results than SOILCALC, especially at higher NAPL saturations.

Field DNAPL Examples

NAPLANAL was used to calculate the saturations and compositions of DNAPL and the phase distributions of DNAPL components in several core samples collected from a chemical plant on the Gulf Coast. DNAPL is NAPL that is denser than water. The plant has manufactured a variety of chlorinated ethanes and ethenes, such as 1,2-dichloroethane (EDC), trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA),

Figure 2. Cross-sectional view of soil sample location and total soil concentration.

<p align="center">Table 2 Comparison of NAPLANAL and SOILCALC Results SOILCALC Results Are in Parentheses (Mott 1995). Concentrations Are Normalized by Total Sample Mass. For Comparison Purposes, Calculations Are Not Rounded to Reflect Significant Figures.</p>						
Component i	Measured Sample Conc. C_i (mg/kg)	Sample Conc. in Aq. Phase $C_w^i \phi_w \rho_i^{-1}$ (mg/kg)	Sample Conc. in Air Phase $C_a^i \phi_a \rho_i^{-1}$ (mg/kg)	Sample Conc. Sorbed $C_s^i \phi_s \rho_s \rho_i^{-1}$ (mg/kg)	Sample Conc. in NAPL $C_n^i \phi_n \rho_i^{-1}$ (mg/kg)	Mole Fraction in NAPL x_i
Data Set #1						
Hexane	250	1.467E-01 (1.493E-01)	2.680E+01 (2.795E+01)	1.735E+02 (1.800E+02)	4.953E+01 (4.193E+01)	0.2460 (0.2429)
Heptane	250	3.949E-02 (4.062E-02)	9.871E+00 (1.040E+01)	1.776E+02 (1.861E+02)	6.251E+01 (5.347E+01)	0.2667 (0.2663)
Octane	250	1.055E-02 (1.104E-02)	3.970E+00 (4.258E+00)	1.607E+02 (1.715E+02)	8.530E+01 (7.427E+01)	0.3193 (0.3245)
Nonane	250	3.852E-03 (3.926E-03)	6.936E-01 (6.710E-01)	1.989E+02 (2.065E+02)	5.040E+01 (4.272E+01)	0.1680 (0.1663)
NAPL saturation = 0.15%						$\sum x_i = 1.0000$ (1.0000)
Data Set #2						
Hexane	192	1.366E-01 (1.378E-01)	2.499E+01 (2.580E+01)	1.615E+02 (1.661E+02)	5.322E+00 (1.060E-02)	0.2290 (0.2241)
Heptane	192	3.894E-02 (3.968E-02)	9.749E+00 (1.016E+01)	1.751E+02 (1.818E+02)	7.114E+00 (1.445E-02)	0.2629 (0.2602)
Octane	192	1.160E-02 (1.207E-02)	4.374E+00 (4.653E+00)	1.768E+02 (1.873E+02)	1.083E+01 (2.224E-02)	0.3511 (0.3546)
Nonane	192	3.601E-03 (3.637E-03)	6.493E-01 (6.710E-01)	1.859E+02 (1.913E+02)	5.438E+00 (1.087E-02)	0.1570 (0.1540)
NAPL saturation = 0.02%						$\sum x_i = 1.0000$ (0.9929)
Data Set #3						
Hexane	100	7.316E-02 (7.177E-02)	1.339E+01 (1.344E+01)	8.654E+01 (8.648E+01)	(6.720E-15)	(0.1167)
Heptane	100	2.106E-02 (2.067E-02)	5.274E+00 (5.293E+00)	9.471E+01 (9.469E+01)	(8.132E-15)	(0.1355)
Octane	100	6.404E-03 (6.285E-03)	2.415E+00 (2.423E+00)	9.758E+01 (9.757E+01)	(1.364E-15)	(0.1847)
Nonane	100	1.930E-03 (1.894E-03)	3.481E-01 (3.495E-01)	9.965E+01 (9.965E+01)	(7.434E-15)	(0.0802)
No NAPL						$\sum x_i = (0.5171)$

1,1-dichloroethane (1,1-DCA), and 1,1-dichloroethene (1,1-DCE). Spillage, waste-disposal operations, and pipeline leakage of these solvents have resulted in ground water contamination at the site. Previous investigations at the site have revealed silty water-bearing sand units separated by fractured clay units. In some areas, the clays are discontinuous and have allowed DNAPL to migrate to a sand unit 80 feet beneath the ground surface. Pumping tests have confirmed hydraulic communication between the sand units.

Total soil chemical concentrations in four core samples from a single borehole were measured to evaluate the suitability of the site for a pilot-scale test of surfactant-enhanced aquifer remediation. The saturation and composition of the DNAPL mixture are important parameters in the decision-making process. The locations of the core samples and the analyzed soil chemical concentrations are shown in Figure 2. The samples are as follows: B-1, located in a sand unit at about 10 feet below ground

<p align="center">Table 3 Chemical Property Data Used in the Analysis of the Soil Samples</p>					
Component i	K_{oc}^i (mL/g)	K_H^i	S_i (mg/L)	ρ_i (kg/L)	MW_i (g/mol)
1,1-dichloroethene	65	0.87	400	1.22	97
1,2-dichloroethane	14	0.038	8690	1.26	99
1,1,1-trichloroethane	152	0.54	720	1.35	133.4
1,1,2-trichloroethane	56	0.031	4500	1.44	133.4
trichloroethene	126	0.3	1100	1.47	131.5
tetrachloroethene	364	0.54	200	1.63	165.8

surface (bgs); B-2, located in a sand unit at about 20 feet bgs; B-3, located in a unit of clayey sand with silt pockets at about 43 feet bgs; and B-4, located in a sand unit at about 80 feet bgs. The volumetric water contents of the core samples were not measured. The porosity and fraction organic carbon content of the sands were assumed

Table 4

NAPLANAL Calculations from Soil Sample Analyses

Concentrations Are Normalized by Total Sample Mass. Results Are Rounded to Two Significant Figures.

Component i	Measured Sample Conc. C_i (mg/kg)	Sample Conc. in Aq. Phase $C_w \phi_w \rho_i^{-1}$ (mg/kg)	Sample Conc. Sorbed $C_s \phi_s \rho_s \rho_i^{-1}$ (mg/kg)	Sample Conc. in NAPL $C_n \phi_n \rho_i^{-1}$ (mg/kg)	Mole Fraction in NAPL x_i
Sample B-1					
1,2-dichloroethane	83	50	0.74	32	0.032
trichloroethene	356	46	6.4	300	0.23
tetrachloroethene	1290	27	11	1300	0.74
NAPL saturation = 0.54%					
Sample B-2					
1,2-dichloroethane	90	89	1.7		
1,1,2-trichloroethane	23	22	1.4		
No NAPL					
Sample B-3					
1,2-dichloroethane	1170	300	4.8	860	0.19
1,1,1-trichloroethane	383	8.2	1.4	370	0.063
1,1,2-trichloroethane	200	24	1.5	170	0.029
trichloroethene	1230	40	5.7	1200	0.20
tetrachloroethene	3820	18	7.6	3800	0.51
NAPL saturation = 2.3%					
Sample B-4					
1,2-dichloroethane	9620	370	6.8	9200	0.28
1,1,1-trichloroethane	4760	12	2.3	4700	0.11
1,1,2-trichloroethane	1260	19	1.4	1200	0.028
1,1-dichloroethene	842	1.6	0.14	840	0.026
trichloroethene	10700	40	6.8	11000	0.24
tetrachloroethene	17600	9.6	4.6	18000	0.32
NAPL saturation = 17%					

to be 0.375 and 0.0015, respectively. These values are equivalent to average values measured by Liljestrand and Charbeneau (1987) in similar shallow sands in the area. Table 3 lists the physical properties attributed to the chlorinated solvents in the core samples.

According to the results of the NAPLANAL calculations, presented in Table 4, only a small amount of DNAPL is present in sample B-1. The ground water in B-2 appears to contain no DNAPL. Samples B-3 and B-4 have calculated NAPL saturations of about 2.3 percent and 17 percent, respectively. The computed NAPL composition in each of these core samples is different. Although PCE appears to be the predominant NAPL component in all samples containing NAPL, the mole fraction of PCE decreases with depth while the TCE and EDC mole fractions increase. This trend suggests historical variations in the composition of infiltrating DNAPL and/or different locations of DNAPL releases having different DNAPL compositions.

In the aforementioned calculations, soil porosity was estimated. Neither porosities nor water contents had been measured for these samples. A graph relating the porosity to the calculated NAPL saturation and composition for samples B-3 and B-4 is shown in Figure 3. Samples B-3 and B-4 represent soil samples having relatively low and high NAPL saturations, respectively. The graph shows that the uncertainty of the porosity value

Figure 3. Effect of porosity on NAPL saturation and composition estimation results.

on the calculations of NAPL saturation and composition is small considering the relatively small possible range of soil porosity in sandy sediments.

Conclusions

The NAPL saturation algorithm presented in this paper provides a useful tool to investigators involved in site characterization studies at NAPL-contaminated sites. This algorithm allows the quantification of NAPL saturation and NAPL composition in a soil sample from

a typical soil chemical analysis. This information is useful' in modeling and designing site-specific surfactant-enhanced aquifer remediation strategies (e.g., Brown et al. 1994) and partitioning interwell tracer tests (e.g., Jin et al. 1995). The calculations require only the soil information typically gathered in ground water contamination studies, specifically total chemical concentrations, water moisture content, porosity, natural organic content, and specific physical and chemical properties of the contaminants. A PC software program, NAPLANAL, was developed to perform these calculations.

The accuracy of the calculations depends on the accuracy of the input data. A sample's chemical analysis can be compromised by improper sampling and preservation, failure to identify and quantify all organic contaminants, and incomplete extraction of contaminants. In addition, the values of the physical properties of the soil sample and the chemical properties of the NAPL components affect the results. Thus, sensitivity analyses, such as the example shown for porosity, are strongly encouraged. Such sensitivity analyses can be performed easily using NAPLANAL.

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APPENDIX C

Development of Partitioning Tracer Tests for Characterization of Nonaqueous-Phase Liquid-Contaminated Aquifers

Development of Partitioning Tracer Tests for Characterization of Nonaqueous-Phase Liquid-Contaminated Aquifers

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Abstract

The partitioning interwell tracer test (PITT) was used by the petroleum industry to measure the residual oil saturation in water flooded oil fields. Extensive laboratory studies and field-scale tests have been conducted over the past years to transfer this technique to the environmental community for the purpose of nonaqueous phase liquid (NAPL) site characterization and remediation performance assessment. This technique was specifically enhanced and modified to address the new challenges related to NAPL site characterization problems. This paper describes the differences of PITTs between the oil field tracer applications and NAPL site characterization application, and the design and data interpretation strategy that is crucial for the successful field implementation. Both the method of first temporal moment analysis and the method of inverse modeling for the tracer data analysis are presented. To demonstrate the effectiveness of the PITT technique in NAPL site characterization application, the results from two field scale pilot tests are also presented.

Introduction

Groundwater is an important natural resource. In the United States, more than half of the population relies upon groundwater as the source of drinking water¹. Unfortunately, the contamination of groundwater reserves by nonaqueous phase liquids (NAPLs) has become a major and widespread problem² and are found in a wide variety of hydrogeological

environments throughout the US. NAPLs can be either denser than water or lighter than water. Chlorinated hydrocarbons (CHCs) such as trichloroethene (TCE), tetrachloroethene (PCE), and carbon tetrachloride (CTET) are denser than water and frequently present in the subsurface as dense, nonaqueous phase liquids (DNAPLs). Petroleum hydrocarbons such as benzene are lighter than water and frequently present as light, nonaqueous phase liquids (LNAPLs). Fig. 1 shows a possible scenario of NAPL contamination³. When NAPL is released at the surface, free-phase NAPLs move downward through soil under the force of gravity or laterally along the surface of sloping fine-grained stratigraphic units. As DNAPL travels downward through the soil, it leaves a trail of small globules of NAPL trapped within the pore space of the soil. These trapped globules can be located in either the vadose or saturated zones of the aquifer. Along with the trapped globules, there may be pools of NAPL which have collected within stratigraphic traps as shown in Fig. 1. Quantifying the amount and spatial distribution of NAPLs trapped in the soil like this is a very difficult task. However, in order for any NAPL remediation method to be effective, it is essential that the NAPL zones be properly characterized.

The traditional methods in the last 15 years of hydrogeological practice for characterizing the zone containing DNAPL involve (1) analysis of soil samples, (2) observations during drilling and other field activities, and (3) NAPL detection in wells⁴. The first of these methods is inadequate in that soil cores do not allow sufficiently large volumes of typical aquifers to be sampled in order to permit a meaningful estimate of the residual NAPL saturation and chemical composition⁵. The other methods are based on random observations and luck in the choice of drilling site. For example, Savannah River, SC, is a site which has been known to be contaminated with NAPLs. Over three hundred boreholes were drilled within a five-acre plume before any free-phase DNAPL was actually located. This lack of NAPL site characterization techniques has prompted EPA to call for improved field methods for rapid and inexpensive detection of NAPL zones⁴.

Tracers have been extensively used in petroleum reservoir

characterization. Partitioning tracer tests, both single-well and interwell, have been used to estimate residual oil saturation prior to the beginning of enhanced oil recovery operations⁶⁻¹⁸. The single-well test has been applied to over 300 oil field reservoirs throughout the world in an extremely wide variety of settings. The strengths and weaknesses of the tests have been determined and the latter remedied by improved tracers and test designs. Therefore, it would be very important and beneficial to transfer the partitioning tracer technique for the purpose of NAPL site characterization and remediation performance assessment. However, the conventional application of single-well tracer test technology to aquifers suffers from the principal drawback of geophysical logging and coring, namely, that a borehole must penetrate very near NAPL contamination for it to be effective. Consequently, the emphasis of our technology transfer research is on the partitioning interwell tracer test (PITT).

During the past five years, extensive laboratory studies and field-scale tests have been conducted over the past years to transfer this technique to the environment by the authors and their colleagues of this **paper**¹⁹⁻²⁶. This technique was specifically enhanced and modified to address the new challenges related to NAPL site characterization problems.

In this paper, we first give a brief description of the PITT and its advantage over the other methods followed by a discussion of the differences of PITTs between the oil field tracer applications and NAPL site characterization application. The PITT design and data interpretation strategy that is crucial for the successful field implementation is then presented. Both the method of first temporal moment analysis and the method of inverse modeling for the tracer data analysis are described. To demonstrate the effectiveness of the PITT technique in NAPL site characterization application, the results from two field scale pilot tests are also presented in this paper.

General Description of PITT

Tracers are chemicals that can be added to fluids in small concentrations and used to follow their movement without affecting their physical properties. The partitioning interwell tracer test consists of the simultaneous injection of several tracers with different partition coefficients at one or more injection wells and the subsequent measurement of tracer concentrations at one or more production or monitoring wells. During the transport of the tracers by soil air or ground water through the interwell zone, the partitioning tracers are retarded in their transport by interaction with any NAPL present while the conservative tracers are not retarded. The chromatographic separation of the tracers indicates the presence of NAPL in the interwell zone and is used to determine the volume of NAPL present.

The particular advantage of partitioning interwell tracer test (PITT) method over the other methods is that the sample volume for assessing NAPL saturation is much larger than that available from either core samples or geophysical logs

and yields more reliable estimates of NAPL saturation. Since the test is based on the flow-field in contact with the NAPL, the tracer test results can be used for the design of physical, chemical or biological remediation methods that target the NAPL source region using adjuvants delivered by fluids. Thus, the PITT has the potential of saving enormous amounts of time and money by focusing the expensive remedial fluids on the NAPL source zone.

Differences between Oil Reservoir and NAPL Site Characterization Applications

There are many significant differences in conditions between an oil field and an aquifer and many fundamental scientific questions remain to be addressed before this technology can be used in the widest possible range of contaminated-aquifer conditions. First of all the environmental acceptability of the tracers can be used in aquifers is much more restricted. This rules out a considerable number of tracers which have commonly been used in the oil field. For examples, radioactive tracers such as tritium, commonly used in the oil field are not acceptable in the aquifers even at very low concentration. Chlorofluoro-carbons (freons) which has been used in the oil field affect the ozone layer and pose a major threat to the environment can not be used in aquifers even these compounds have very low detection limits. Thus, new non-hazardous and non-toxic tracers need to be developed. Alcohols such as isopropyl, 1-pentanol, 1-heptanol, and 1-octanol, have been tested in our lab column experiment and been used in field pilot tests. Tracers of this type, however, have been limited by their water solubility and detection limits. The detection limits of near one part per million are the best we have achieved so far in the lab. This would potentially limit the field application to a well spacing of less than 100 ft.

Secondly, the oil-reservoir applications of the interwell tracer tests are normally undertaken in water-flooded oil fields. By the time these tests were taking place, most of the oil reservoirs have been well characterized and the composition of the oil were well known. On the other hand most waste sites are typically poorly characterized and contain complex organic liquid mixtures. The composition of the mixtures are unknown in most cases. The physical thermodynamic models, therefore, need to be developed for assessing the variations of tracer partition coefficients with the composition of the NAPL for aquifer applications.

Thirdly, NAPL distribution is much more uneven and complex in typical subsurface waste sites than residual oil saturation in typical oil reservoirs.

There are many other differences between oil field and aquifer tracer applications. For example, oil reservoirs are very deep, confined and have higher temperatures and pressures than typical aquifers. Most waste sites are unconfined. These and some other differences need to be taken into account when applying partitioning interwell tracer

tests to subsurface waste site characterization. More detailed discussions on this subject can be found in Ref. 27.

Tracer Data Interpretation Methods

Method of First Temporal Moment Analysis. The simplest and most robust way to interpret PITT data is to use temporal moments of the tracer response data. The volume of NAPL and/or the average saturation of NAPL can be determined using this method for the swept volume between the injection well and the location where the tracer is sampled. The details of the method of first moment theory can be found in Refs 22 and 28. Only pertinent equations which relate to the estimation of NAPL volume and average saturation are presented here.

For a partitioning interwell tracer test with balanced injection and production rates (q), the equation for the volume of NAPL in the tracer swept pore volume (V_n) is calculated as,

$$V_n = \frac{q(\bar{t}_p - \bar{t}_n)}{K} \quad (1)$$

where K is the partition coefficient of the partitioning tracer defined as the ratio of the tracer concentration in NAPL phase to that in water phase (or air phase if air is the carrier fluid), $\bar{t}_n$ and $\bar{t}_p$ are the first moments of the nonpartitioning (conservative) and partitioning tracers, respectively, and obtained by integrating corresponding tracer response curve overtime as

$$\bar{t} = \frac{\int_0^{t_f} tC(t)dt}{\int_0^{t_f} C(t)dt} - \frac{t_s}{2} \quad (2)$$

where t_f is tracer test cutoff time. For accurate NAPL estimation it should be the time when the tracer concentration falls below the detection limit. t_s is the tracer slug time and $C(t)$ is the tracer concentration in extraction well as a function of time.

Another important parameter which represents the separation of the tracer response curve is the retardation factor defined as the ratio of the first moment of the partitioning tracer to that of the conservative tracer and is related to the partition coefficient by

$$R_f = 1 + \frac{KS_n}{1 - S_n} = \frac{\bar{t}_p}{\bar{t}_n} \quad (3)$$

where (S_n) is the average NAPL saturation in the tracer swept pore volume.

In order to estimate the NAPL volume accurately, the tracer response curves should be complete, because much of the information is contained in the tails of the response curves. Unfortunately, the tracer response curves are often incomplete either due to dilution of the tracer concentration below the detectable limit limitations in the duration of the tracer test, or some other reasons. However, the tracer response curves can be extrapolated with an exponential function provided the duration of the test is sufficient to establish this decline⁶. The first moments of the tracer response curves can be obtained by dividing the data into two parts. The first part represents the data from zero to the time t_b where time becomes exponential, and the second covers the exponential part in which it goes from t_b to infinity.

After time t_b , the tracer response is assumed to follow an exponential decline given by,

$$C = C_b e^{-\frac{t-t_b}{a}} \quad (4)$$

where $1/a$ is the slope of the straight line when the tracer response curves are plotted on a semi-log scale, and C_b is the tracer concentration at time t_b , when the curve becomes exponential.

Hence the first moment ($\bar{t}$) of the tracer response curve can now be calculated as

$$\bar{t} = \frac{\int_0^{t_b} tCdt + a(a+t_b)C_b}{\int_0^{t_b} Cdt + aC_b} - \frac{t_s}{2} \quad (5)$$

A more complete description of the theory and its applications to both saturated and unsaturated zones and with multiple injection and extraction wells can be found in the dissertation of Jin²⁸. It should be noted, however, the method of moments to the interpretation of the tracer data yields only a limited amount of information about the distribution of NAPL in the soil. Although it is possible to perform multiple tracer tests using different combinations of well pairs and thus estimate different swept volumes, this takes more time, costs more than a single test, and still only yields average values over a limited number of swept volumes. Alternatively, one can inject and extract tracers at multiple depths and infer saturation averages over multiple swept volumes. Thus, although the method of moments is remarkably simple, robust, and only weakly depends on aquifer heterogeneity and other complexities, more general distribution methods as described below under inverse modeling are also needed as a complement.

Method of Inverse Modeling. The idea of using the method

of inverse modeling for NAPL characterization based on the data obtained from a partitioning interwell tracer test was proposed in Ref. 22. Recently, Harneshaug²⁹ has successfully used this method to analyze the data from a partitioning tracer test at the Operable Unit 1 (OU1) site at Hill Air Force Base, Utah. INTERA has also successfully used the same technique to analyze a similar partitioning tracer test in a different test cell at the same site³⁰ and a tracer test conducted at PPG Chemical Plant at Lake Charles, Louisiana³¹. Inverse modeling is a significant improvement over trial-and-error parameter adjustment, reducing the time required for estimation and resulting in more accurate, robust, and consistent parameter estimates. It involves minimizing the difference between the model predictions and observed values by adjusting some unknown model parameters (such as NAPL saturation and formation hydraulic conductivity). The most common technique used in inverse modeling is nonlinear least-squares regression.

Numerical simulators are needed for inverse modeling. There are three simulators we have relied mostly for the purpose of determining aquifer permeability and NAPL residual saturation distribution from PITT data analysis; The CONJUGATE code, developed at the University of Texas at Austin^{32,33} and later modified at Texas A&M University by Datta-Gupta³⁴, for hydraulic conductivity estimation; The UTSTREAM code, developed at the University of Texas at Austin³³ for the purpose of estimating the NAPL saturation distribution from the partitioning tracer data, and the UTCHEM code, a general purpose, finite-difference model which is also developed at the University of Texas³⁵.

There are two main steps in analyzing the tracer data using the method of inverse modeling. The permeability distribution is obtained from the conservative tracer data. This is done by minimizing the differences between field measured tracer concentrations and the model predicted tracer concentrations as

$$\min f(x) = \frac{1}{2} \sum_{i=1}^n (C_{i,model} - C_{i,field})^2 \quad (6)$$

where $f(x)$ is the objective function, $C_{i,model}$ the model-predicted concentration at location i , and $C_{i,field}$ the field measured tracer concentration at the same location. Generally, the simulator iteratively changes the permeability in each grid-block to obtain the permeability field for which the objective function reaches a minimum. A minimum objective function implies a good match of the field data.

When a good match of the field data was obtained, the corresponding permeability field was considered to be representative of the actual permeability field. The partitioning tracer data were then used to obtain the NAPL saturation distribution. Again, this was done by minimizing the differences between actual measured tracer concentrations of the partitioning tracers.

The main advantage of the inverse modeling over the

method of temporal analysis is that it not only yields the total NAPL volume but also the residual NAPL saturation distribution. However, the permeability and NAPL saturation distributions obtained may not be unique, and results obtained contain some uncertainties, even for the case which most of the tracer response data match the model predictions. There are many factors which may affect the final results of inverse modeling. The results are model sensitivity for example. The number of gridblock and geometry of the simulation grid contributes to the uncertainty of the accuracy of the results. Another disadvantage of the inverse model is that it tends to be computational intensive.

Although the results from inverse modeling contain some uncertainties, the combination of the results from the method of first temporal moment analysis and inverse modeling, however, can provide a reliable assessment of the permeability and NAPL saturation distributions. In common practice, it is always recommended that both the method of first temporal moment analysis and the method of inverse modeling are used for data analysis whenever possible.

Development of Optimal Design Strategy

The successful implementation of the field test requires the development of an engineering design strategy. A good design strategy should minimize the risk of failure, optimize the information collected, and save time and money. The engineering design of a partitioning tracer field test consists of the following major components:

- selection of tracers with suitable characteristics
- determining the amount of each tracer to inject
- determining the optimum number of tracers to inject
- estimating the optimum properties of each tracer
- determining the injection and extraction locations and rates
- determining the sampling locations and frequencies
- estimating the uncertainty and robustness of the design
- demonstrating the suitability of the interpretation method under test conditions

The design must also be consistent with all known constraints of cost, time, safety, regulations, available facilities and many other factors. Both laboratory experiments and modeling play a significant role in this design process.

The selection of the best tracers to use is of course the crucial first step in any successful design. The criteria for suitable tracers include the following: (1) non-hazardous, (2) non-toxic, (3) non-degrading, (4) low volatility, (5) reasonable cost and availability, (6) good detection in the presence of the contaminants and a known dependence on the composition of the NAPL, (7) low sorption on the soil, and (8) partition coefficients in the desired range for the conditions of interest. These are very demanding criteria, yet several classes of promising tracers have been identified to date. First, one selects suitable conservative tracers to serve as a reference for

the partitioning tracers as well as potentially other purposes such as for use in characterizing the hydraulic properties of the soil, especially variations in hydraulic conductivity and heterogeneities in general.

Partition coefficients can be measured in equilibrium batch tests with the NAPL and the carrier fluid, presumed here to be either water or air. The details of these and other measurements will differ for the two cases of saturated or unsaturated zones. An activity coefficient model can be used to minimize the number of measurements. We have found that a modified UNIFAC model works well for the water tracers³⁶ whereas the simpler regular solution model is adequate for the gas tracers. These models should be particularly useful for assessing the variations of tracer partition coefficients with the composition of the NAPL.

The next step in the laboratory phase of tracer selection is to conduct column experiments. Ottawa sand is normally used in the column experiments for screening purposes since it is convenient and easy to work with. Many other sands or soils, of course, could be used for this same purpose. Tracers that appear to be suitable in the Ottawa sand are then tested in a core of soil from the field site. An example can be found in Ref. 19. Once it has been determined that the first six selection criteria have been satisfied, the issue of the desired range of partition coefficient is the most important design variable. This cannot be decided based entirely on laboratory performance since the core or soil may not contain the same NAPL saturation as the average for the swept pore volume the tracer will see in the field site. The retardation factor should not be too small since this results in a very large estimation error and it should not be too large since this results in an unacceptably long test duration. Reasonable retardation factors are likely to be in the range of 1.2 to 4.0, although this will vary and should be optimized using a site specific model. As seen from Eq. 3, this implies that the product of the partition coefficient and the NAPL saturation should be in the approximate range of 0.2 to 3.0. Thus, if the average residual NAPL saturation is say 0.1, then the partition coefficient should be in the range of 2 to 30. Most likely, tracers that have partition coefficients both toward the low end and the high end of this range are normally used to decrease the risk of failure since the NAPL saturation will often be poorly known. There are other reasons for doing this as well.

Another tracer test needs to be done in the column after remediation assuming that this is planned for the field test. One reason for this is because the amount and composition of the NAPL will have changed. Another reason is because complications can occur in some cases as a result of the remedial fluid. For example, some surfactants under some conditions can form gels, emulsions, precipitates and other complex phases and this can cause a false signal. Actually, the tracers are valuable diagnostic tools for detecting and eliminating such problems when they have not become apparent from other laboratory measurements, but we do not

want these remediation problems to occur in the field.

Considerable skill is required to perform these tests accurately and to avoid major mistakes. For example, many experimentalists conduct these column tests at flow rates that are too high. This results in non-equilibrium partitioning and the apparent partition coefficients are then too low. This seems to be more likely to happen when gas tracers are used than when water tracers are used and will in general depend on the number and distribution of the phases in the soil. The most likely explanation for this difference is that under some conditions the tracers must diffuse through a water film before they can diffuse into and then out of the NAPL phase. This will depend on the wetting state of the system and additional data and analysis is needed to provide reliable guidelines on these tests.

Once basic laboratory measurements have been made, a model of the fluid flow can and should be constructed. This model is useful in addressing all of the design components listed above. We have relied mostly on the UTCHEM to date for this purpose^{22,26}. This is because it has all of the features needed to model (1) the spill event to establish the initial distribution of the NAPL, (2) the re-distribution of the NAPL under natural gradients conditions, bioremediation, surfactant enhanced remediation, and co-solvent enhanced remediation, and (3) the partitioning tracer test before and after remediation. Both water and air tracers can be modeled.

Some of the uses of the model, such as determining the amount of tracer needed, are relatively simple. The amount of tracer needed will depend on the size of the domain and the dilution factor, which in turn is a function of the heterogeneity of the flow domain and the mixing and partitioning characteristics of the tracer. A few forward simulations will often be sufficient to estimate the required amount of tracer within a sufficient accuracy. Other design components are much more complex and have not been adequately addressed to date. The number and location of sampling points and the frequency of sampling are particularly important and need additional research. When a partitioning tracer test is to be applied to sites with NAPL mixtures of unknown composition (no liquid samples available) or poorly known or highly variable composition, then a large number of partitioning tracers could be injected so that the composition of the NAPL can be inferred from the tracer data. Even under more favorable conditions where NAPL samples are available and have been tested in the laboratory and the scale is small enough to assume only small variations in NAPL composition, it is desirable to use several partitioning tracers even though some will be redundant.

It is intuitively obvious that the more sample locations and the more often the tracer is sampled the more useful and accurate the tracer data will be. However, in practice we are limited in this effort by cost. It is also intuitively obvious that for a given number of sample points, some arrangements are better than others. For example, it is clearly advantageous to

have multi-level samplers at a relatively few locations rather than the same number of sample points all at the same depth or with no depth differentiation (as in a conventional extraction well). The multi-level data form the basis for estimating NAPL saturation as a function of depth and this is likely to be important under almost all natural conditions of interest.

Field Demonstrations of PITT

In the past two years INTERA and the University of Texas at Austin have successfully conducted several PITTs at different test sites. To demonstrate the effectiveness of this technique for detection, estimation, and remediation performance assessment of the NAPL contaminated subsurface, the results from one of the saturated zone PITTs and one of the unsaturated (vadose) zone PITTs are presented in this section.

Hill Air Force Base, Utah, Operable Unit 2 (OU2). From 1967 to 1975, spent degreasers and other chemicals were disposed of in shallow trench at the Hill AFB OU2 site. The disposal trenches allowed DNAPL to drain into the aquifer underneath. Site investigation indicates that 93% of the DNAPL consist of trichloroethene (TCE), 1,1-trichloroethane (1,1,1-TCA) and tetrachloroethene (PCE). This site has been chosen to test the applicability of surfactant enhanced DNAPL removal and the use of partitioning tracers for both estimation of DNAPL in place and the performance assessment. This project was funded through a technology demonstration contract with the Air Force Center for Environmental Excellence.

The project combined extensive field testing and data acquisition, laboratory batch and column experiments, and use of UTCHEM simulator and was implemented based on the design strategies presented in the previous section. The detailed information can be found in Refs. 37 and 38. Only a brief description of the test and PITT results are presented here.

The test area was located in the unconsolidated and heterogeneous silt, sand, and gravel deposits of the Provo formation. The Provo formation, approximately, 45 ft thick in the test area, rests on the Pleistocene-age Alpine formation, with a depth to groundwater of approximately 29 ft. The Alpine formation is over 100 ft thick at the site and consists of layered clays with occasional stringers of silt. It provides an effective capillary barrier beneath the Provo formation, inhibiting the further vertical migration of DNAPL.

Fig. 2 presents a schematic illustration of the general configuration of the test area and the location of the test wells. The well array used for the demonstration was a 3X3 (three extraction and three injection wells) line drive configuration in a 20 ft X 20 ft square pattern. Wells SB-2, SB-3, and SB-4 were used as the line of injection wells, while U2-1, SB-1, and SB-5 served as the injection wells. Well SB-6 was used as a monitor well.

The demonstration was conducted in two phases. The first of these phases was comprised of a PITT followed by a short DNAPL solubilization test. The PITT was for the purpose of determining the spatial distribution and volume of DNAPL in the test zone. The solubilization test was for the purpose of verifying the efficiency of the selected surfactant and addressing the issue of the effect of the surfactant-rich effluent on the efficiency of the stream stripping system at the site.

The PITT was conducted by injecting a solution of two conservation tracers (isopropyl and bromide) and three partitioning tracers (1-pentanol, 2-ethyl-1-butanol, and 1-heptanol) for half a day. The tracer injection was followed by 5.5 days of water flooding and extraction operations to recover the majority of the injected tracer mass.

Fig. 3 shows the tracer concentration for this initial PITT measured in the effluent of extraction well SB-1. The concentrations shown for isopropyl, the conservative tracer, reached the highest level in the shortest amount of time, since this tracer was not retarded by the DNAPL in the contaminated zone. The bromide data was not shown in the figure because it is identical to the isopropyl. The other three conservative tracers, 1-pentanol, 2-ethyl-1-butanol, and 1-heptanol, each had lower concentrations and longer recovery periods, indicating that they had partitioned to varying degrees into the DNAPL. Applying the method of moments analysis to the tracer data from the three extraction wells respectively yielded an estimate of 360 gallons of DNAPL in the approximately 13,000 gallons of tracer swept pore volume with an average saturation of about 2.8%.

Phase II of the test was comprised of a surfactant flood followed by a PITT. The surfactant flood was for the purpose of cleaning up the residual DNAPL in the 13,000 gallons of interwell pore space, while the PITT was for performance assessment purpose. After the surfactant flood was completed, the PITT was conducted by injecting a solution of two conservation tracers (1-propanol and bromide) and two partitioning tracers (1-hexanol and 1-heptanol) for 1 day and followed by 5 days of water flooding.

Fig. 4 shows the tracer concentration response of the same well (SB-1) as shown in Fig. 3. This figure indicates both the conservative and partitioning tracers have essentially the same peak arrival times which means that essentially all of the DNAPL in the test area had been removed. Analysis of the tracer data from this PITT indicated an average saturation of 0.04%, or approximately 5 gallons of DNAPL remaining in the test area.

The results from this demonstration field project confirms that PITT can be used as an effective technique to estimate the amount of NAPL in subsurface environments before remediation and also as a performance assessment technique to evaluate the effectiveness of subsurface remediation in the saturated zone. The results presented in the next section will demonstrate that the PITT technique can be effectively use in an unsaturated environment.

Sandia National Laboratories, New Mexico. Chemical Waste Landfill: A PITT was conducted with gas tracers in the Sandia Chemical Waste Landfill (CWL) vadose-zone in fall 1995 to measure the volumes of DNAPL present in the vadose zone at three depths beneath the Landfill.

The CWL is a 1.9 acre landfill located in Technical Area III of Sandia National Laboratories (SNL) and was used for the disposal or storage of hazardous wastes generated at SNL between 1962 and 1985. During this period, different types of waste, including spent solvents, acids and bases, metals, and debris were segregated and placed into separate trenches or pits. According to waste disposal inventory records, TCE was disposed in the greatest quantities. At the CWL, the water table is approximately 490 ft below ground surface (bgs). The purpose of the PITT was to measure the volume and distribution of NAPL in the vadose zone beneath two organics disposal pits. The results are to be used as critical information in the design of corrective actions aimed at eliminating or controlling the NAPL-contaminated sediment. This project was funded by SNL.

PITT design involved laboratory batch and column studies for the tracer selection and numerical modeling using UTCHEM simulator and was implemented based on the design strategies presented in the previous section. The detailed information can be found in Refs. 24, 25 and 28. Only a brief description of the test and PITT results are presented here.

The PITT was applied beneath two side-by-side organic disposal pits. A two-well configuration (one injection well and one extraction well) was chosen. The well couplet was designed for a 55 ft horizontal spacing and development of a forced-gradient flow field over an approximately 70 ft vertical section of the vadose zone, from 10 to 80 ft bgs (see Fig. 5). Well screen intervals were selected so that three zones within the overall 70 ft test zone, each with a separate injection screen and extraction screen, could be isolated with down-hole packers and separately controlled if the need arose. The three zones are referred to as the shallow zone (10 to 35 ft bgs), intermediate zone (40 to 60 ft bgs), and deep zone (65 to 80 ft bgs). This configuration would allow estimation of not only the total volume of the NAPL within the 70-ft zone but also the NAPL volume within each of the three zones. In addition of these two extraction wells, two monitor wells (MW1 and MW2) were also installed as shown in Fig. 5. Multi-level soil gas sampling instrument was installed in the monitor wells to monitor the tracer response at different depth to infer information on the distribution of DNAPL.

Sulfur hexafluoride was used as the conservative and a group of perfluorocarbons tracers (CH_4 , C_4F_{10} , C_6F_{12} , C_8F_{16} , and C_9F_{18}) as the partitioning tracers in this field test. The PITT was conducted by injecting this mixture of tracers for two hours. The tracer injection was followed by 15 days of air injection and extraction operations. The injection and

extraction rates are varied during the duration to ensure sufficient tracer residence time.

Figs. 6 and 7 show the tracer response at the shallow and deep zones of the extraction wells. Only data of one partitioning tracer (C_9F_{18}) are shown in these graphs because the partition coefficients for the other partitioning tracers are too small to show sufficient separations with the conservative tracer SF_6 . The separation of the tracer response curves in Fig. 5 indicates the existence of the DNAPL in the shallow zone, however, the lack of tracer separation in the deep means the lack of DNAPL in the deep zone. Tracer response at multi-level sampling points also confirms the finding of the extraction wells. Figs. 8 and 9 are the example tracer response of MW2 at depths of 10 ft bgs and 60 bgs.

First moment analysis of the PITT data from these test indicates that DNAPL has penetrated non-uniformly to a depth of approximately 20 to 30 ft bgs. The tracer response data at the multi-level monitor wells indicate that most of the DNAPL is located around 10 ft bgs. The average DNAPL saturation detected in the shallow zone between 10 and 35 ft bgs is approximately 0.11%. No DNAPL was detected in the intermediate (40–60 ft bgs) and deep (65–80 ft bgs) test zone.

The results of this tracer test demonstrate that PITT works equally well in the unsaturated zone as in the saturated zone.

Conclusions

There are significant differences between oil-field tracer applications and NAPL characterization applications. The partitioning interwell tracer test has been enhanced and modified over the years to address the new challenges related to NAPL-site characterization problems. We have shown in this paper through PITT demonstrations that this technology has successfully been used as an effective tool to detect and estimate the amount of NAPL in subsurface environments before remediation and as a performance assessment technique to evaluate the effectiveness of the remediation method used. This technique can be used in both saturated and unsaturated soils which have been contaminated by either light or dense nonaqueous phase liquids.

The successful application of the PITT in the field, however, requires the development of an engineering design strategy. Both laboratory experiments and modeling play a significant role in this design process. A good design strategy should minimize the risk of failure, optimize the information collected, and save time and money.

In common practice, it is always recommended that both the method of first temporal moment analysis and the method of inverse modeling are used for data analysis whenever possible. The method of first moment analysis technique, however, should always be used first because it is much simpler and faster to make and independent of the assumptions required by a fluid flow model. The first moment method also uses all the information from the whole

tracer response and it is not limited by the shape of the response curves of the conservative and partitioning tracers.

Nomenclature

C = tracer concentration, m/L^3 , mg/L

K = tracer partition coefficient, volume ratio

q = well flow rate, L^3/t , gallons/day

S_N = average NAPL saturation, dimensionless

$\bar{t}$ = first moment of tracer response curve, t , day

t_f = tracer test cutoff time, t , day

$\bar{t}_n$ = first moment of the nonpartitioning tracer, t , day

$\bar{t}_p$ = first moment of the partitioning tracer, t , day

t_s = tracer slug time, t , day

V_n = NAPL volume, L^3 , gallons

Subscripts

n = nonpartition tracer

p = partitioning tracer

N = NAPL

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SI metric Conversion Factors

ft x 3.048 E-01 = m

acre x 4.046873 E+03 = m²

gallon x 3.785434 E-03 = m³

Fig. 1 A possible scenario of DNAPL migration through soil matrix (from Ref. 3).

Fig. 4 Tracer concentration response of the extraction well SB-1 in post-surfactant flood PITT.

Fig. 2 Schematic of Hill AFB test area.

Fig. 3 Tracer concentration response of the extraction well SB-1 in pre-surfactant flood PITT.

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In-Situ Characterizations of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers

1st Progress Report
September 15, 1996 - September 14, 1997

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In-Situ Characterizations of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers

SUMMARY

This is a progress report on the first year of our DOE EMSP research project on In-Situ Characterization of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers. The report consists of five sections.

The first section reports on the status of one of several approaches that we are investigating to solve the inverse problem of how to estimate the three-dimensional distribution of DNAPL from the tracer response data at extraction and monitoring wells. Partitioning interwell tracer test (PITT) data from the Hill APB OU1 field test was used as a test case to evaluate inverse modeling using simulated annealing with regularization. This approach has been extensively investigated and improved as part of this research at Texas A&M University. Another approach that has shown significant promise utilizes an analogy between 'ray tracing' in seismology and streamlines for tracer transport in order to compute sensitivity of tracer response to heterogeneity and residual NAPL. The approach utilizes gradient-based inversion techniques and can be orders of magnitude faster than simulated annealing. Recently, it has been applied to determine permeability variations at the OU1 based on a set of conservative tracer response (Vasco and Datta-Gupta, 1997). Other research on the inverse problem using a gradient method can be found in the thesis of Harneshaug (1996) and still another approach based upon the genetic algorithm is being investigated by J.P. Nicot. Nicot has also used the gradient approach to estimate the distribution of NAPL from the vadose PITT at Kirkland APB. All of these results indicate that it is indeed feasible to estimate the spatial distribution of DNAPL when sufficient data are available such as for the Hill APB OU1 field test. Research on the best tracer inverse

modeling approach and the accuracy of the results and related issues in this fast developing area are ongoing.

The second section reports our most complete and accurate compilation of alcohol partition coefficients to date and compares these data with our new correlation for estimating partition coefficients based upon the equivalent alkane carbon number (EACN) concept. This new approach is the best alternative evaluated by us to date and has already been of great benefit in our research on tracers. It is simple, easy to use and more accurate than the solubility-modified UNIFAC method that we published recently (Wang et al., 1998).

The third section reports on the laboratory behavior of partitioning tracers with an emphasis on the sorption of alcohol tracers on various soils and how this effects the accuracy of the PITT under various conditions. Complete details of our experimental procedures and results can be found in Dwarakanath (1997) and Edgar (1997). Several new tracers have been evaluated including the use for the first time of fluorocarbons in water (the use of fluorocarbons in air for vadose tests is reported below).

The fourth section reports on the laboratory evaluation of gas tracers for vadose applications and the field data from one of these applications. Complete details on the laboratory investigation of per-fluorocarbon tracers for the detection and volume estimate of DNAPL can be found in Whitley (1997). Additional laboratory data and field results at Kirkland AFB have been obtained by Deeds (1997). The Kirkland field data are of exceptionally high quality and showed that vadose PITTs can be very useful as a complement to soil analysis. A second PITT was done at this site following the AATDF RF Heating remediation test and these results show that the PITT can be used to assess the performance of remediation by heating in the vadose zone. Furthermore, we were able to show for the first time that we could estimate the change in composition of the NAPL due

to the selective volatilization of the heavy hydrocarbons in this NAPL, which is another type of inverse problem. The Peng-Robinson equation-of-state was used to quantify the thermodynamic behavior of this NAPL as a function of temperature in a way that is similar to what petroleum engineers do in thermal enhanced oil recovery, but which is completely novel in this application.

The fifth section reports on several of the most important design and analysis issues of the PITT, quantifies these effects, and then shows six field test examples performed by INTERA, Inc. (now Duke Engineering and Services). Both saturated and vadose tests are included. Several examples of performance assessment following surfactant remediation are presented. These results taken together are the most complete and convincing evidence of the efficacy of the PITT in alluvial aquifers contaminated by DNAPL than anything previously presented. At the same time, the limitations and errors associated with PITTs must be recognized and dealt with the optimization of the design and the interpretation of the data are crucial for accurate and reliable results and research on these errors continues.

Research is underway to extend the use of PITT technology to more difficult environments and conditions such as fractured aquifers. Deeds (1998) has recently completed a series of laboratory experiments in a fractured rock which show the potential for the use of PITTs in fractured aquifers, but much more research needs to be done to analyze these results and scale them to the field so that we can make good engineering designs and accurate interpretations of such tests.

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**Analysis of Partitioning Tracer Test at the Hill Air Force Base to Determine
Residual NAPL Saturation : Simulated Annealing with Regularization**

Summary

The focus of our efforts during the first year has been on the development and testing of combinatorial optimization based inversion techniques for analysis of partitioning tracer response. Specifically, we have applied the simulated annealing approach to analyze the partitioning tracer tests conducted at the Hill Air Force Base (HAB). We have adopted a two-stage approach for analyzing the data. First, the conservative tracer response (Bromide) was used to derive a stochastic distribution of permeability and porosity in the test cell. Next, the spatial distribution of NAPL saturation was obtained through inversion of the partitioning tracer response (Dimethyl Pentanol). The results were compared with the traditional analysis based on the first moment of the breakthrough response and a qualitative correspondence is shown with results from the inverse analysis. Future work will involve further validation of the approach using synthetic examples, improvement in computational efficiency and model assessment to quantify resolution and uncertainty.

Results and Discussion

The details of the partitioning tracer test conducted at the Hill Air Force base can be found in Annable et al (1994). Multiple tracers were injected in an isolation test cell 11.4 x 14.2 x 20 ft in dimensions using four injection wells. Tracer breakthrough responses were measured at three extraction wells and several multilevel samplers between the injection and extraction wells. For our analysis, we have used Bromide as the non-partitioning tracer and 2,2-Dimethyl-3-Pentanol (DMP) as the partitioning tracer from the suites of field tracer response. The choice of Bromide was obvious because it was the only non-partitioning tracer that was injected. We chose DMP as the partitioning tracer because of its higher partitioning coefficients compared to other tracers as shown in Table I.

Tracer transport in the test cell was modeled using a three-dimensional semianalytic streamline simulator which is very fast computationally and is also free from numerical artifacts such as artificial dispersion (Dattat-Gupta and King, 1995). We divided the test cell into 14x11x10 grid blocks. Each grid block in the x and y direction was 1 ft in dimension. The thickness of each grid block was 0.5 ft in the vertical direction. We assumed that the NAPL is immobile and the tracer is being transported in the water phase only. Small but finite amount of tracer productions were assumed at each of the multilevel samplers for simulation purposes.

For inversion of the conservative tracer response, we started with a stochastic permeability field generated using the sequential Gaussian approach with a mean permeability of 20000 md and a log permeability variance of 2.8. The bottom layer of the model was conditioned to represent the clay layer in the test cell and was assigned a low permeability value of 1 md. The concentration response of Bromide from 46 multilevel samplers (MLS) and the three extraction wells were used to derive the permeability and porosity distribution in the test cell. Simulated annealing with regularization was used to invert the tracer response. Starting with the initial permeability and porosity field, we first simulate the tracer response at each of the MLS and extraction wells. An objective (also called ‘energy’) function is defined to quantify the misfit between the model predictions and the experimental data. The permeability and porosity are then perturbed at randomly selected locations. . The permeability values were drawn from a log-normal distribution with mean permeability of 20,000 md and a log standard deviation of 1.65. The porosity values were sampled from a uniform distribution ranging between 15% and 25 %. In the simulated annealing approach, the misfit function is recomputed after each perturbation. If it decreases, then the change is accepted; otherwise, the change is accepted with a probability given by the Gibb’s distribution (Kirkpatrick et al., 1983). By allowing for the acceptance of unfavorable changes, the approach provides a ‘stochastic hill climbing’ mechanism to escape from local minima. For making the inverse problem well-posed, we incorporated regularization criteria which impose smoothness conditions specified by the discrete model Laplacian, a finite difference approximation to

the second spatial derivative of the model parameters (Tikhonov and Arsenin, 1977). We also imposed a norm constraint to honor the estimated mean permeability of 20000 md.

Figs. 1 and 2 show a realization of permeability and porosity fields obtained after 50,000 iterations. The computations were performed on a 200 MHz 24 processor SGI Power Challenge 10000 XL with an average run time of about 10 hours. A comparison of simulated tracer response of bromide versus the actual response for a sample of tracer response curves is shown in Fig.3 . A permeability cut-off was imposed to identify the high permeability regions indicating preferential transport of tracer and the results are shown in Fig. 4 for permeabilities greater than 55 Darcy.

Once we derive a realization of permeability and porosity distribution, the next step is to match the partitioning tracer response in order to determine the NAPL saturation distribution. We started the inversion procedure with a uniform saturation field of 6.5% NAPL saturation at all the grid blocks. The saturation at randomly selected blocks were changed using the simulated annealing procedure until the predicted tracer response of DMP matched with the observed DMP tracer response in a least-squares sense. The resulting saturation distribution is shown in Fig. 5 after 60,000 iterations.

sample of observation points are shown in Fig. 6. Fig. 7 indicates regions of higher NAPL saturation values by imposing a cut-off ($>12\%$ NAPL). The results tend to show higher NAPL saturation in the west side of the test cell compared to the east side.

For comparison purposes, we also carried out an analysis using the method of moments (Jin et al., 1995). First moments of the breakthrough traces for the partitioning and non-partitioning tracers were computed over the elapsed time period. Spatial distribution of tracer retardation factors were then derived as shown in Fig. 8. Retardation factor is the ratio of the first moments of the partitioning tracer to that of the non-partitioning tracer and a higher retardation factor implies higher NAPL saturation. In Fig. 8 we have also shown the saturation distribution obtained from inversion of the tracer response. There is an obvious correspondence between high retardation and higher NAPL saturation and these results tend to validate the inversion approach, at least in a qualitative sense.

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**Table I Tracer partitioning coefficients (K_{nw})
Hill AFB test cell and tracer concentration used
1996).**

Tracers	K_{nw}
Bromide	0.0
Ethanol	0.1
n-Pentanol	1.4
n-Hexanol	4.6
2,2,-Dimethyl-3-Pentanol	12.9
n-Heptanol	20.0
n-Octanol	97.0

Fig. 1 Realization of permeability field obtained using the Bromide data.

Fig. 2 Realization of porosity field obtained using the Bromide data.

Fig. 3 Tracer response of bromide from the test cell and from the simulation using inverted permeability and porosity distribution.

Fig.4 High permeability region shown using a cut-off.

Fig.5 Realization of NAPL saturation.

Fig. 6 Tracer response of DMP from the test cell and from the simulation using inverted permeability and porosity and saturation distribution.

Fig. 7 High NAPL saturation values shown by imposing a cut-off.

Fig. 8 Comparison with tracer retardation factors using moment analysis.

A New Approach for Estimating Alcohol Partition Coefficients between Nonaqueous Phase Liquids and Water

Abstract

The partitioning interwell tracer test (PITT) has emerged during the past few years as a useful tool for characterizing aquifers contaminated by nonaqueous phase liquids (NAPLs) and in particular the location and volume of NAPLs. Accurate partition coefficients are needed for a wide variety of tracers and NAPLs to use this technology to its maximum benefit. A new approach to estimate the partition coefficients of alcohol tracers partitioning between NAPL and water is presented. This approach is based upon defining an equivalent alkane carbon number (EACN) for each contaminant and for each alcohol tracer and is very useful for both minimizing the number of experiments required and for extracting the maximum information from such experiments.

Introduction

The contamination of aquifers with nonaqueous phase liquids (NAPLs) is a wide spread and serious environmental problem. The location and quantitative characterization of dense nonaqueous phase liquids (DNAPLs) is an especially difficult problem (*1*). The partitioning interwell tracer test (PITT) has been developed and demonstrated in the field during the past few years to address this difficult characterization problem. About 30 field demonstrations were completed by the end of 1997. The PITT involves the simultaneous injection of partitioning and nonpartitioning tracers into the subsurface at sufficiently dilute concentrations that the tracers by definition have negligible effect on

the properties of the pore fluids. The partitioning tracer molecules partition into and out of the NAPL and are retarded relative to the nonpartitioning tracer. The chromatographic separation of the tracers is directly proportional to the volume of NAPL contacted. The simplest and most robust method for calculating the NAPL volume is based upon the fast temporal moment of the tracer response data. The difference between the first temporal moments of the partitioning and nonpartitioning tracers is used to estimate either the volume of the NAPL or the residual NAPL saturation in the swept volume of the subsurface (2-5). Alternately, the three-dimensional spatial distribution of the NAPL saturation can be estimated using inverse methods if sufficient tracer data are collected for this purpose and with the compositional correlation presented in this paper it may also be possible to compute the composition of the in-situ NAPL in some cases.

Partitioning tracers are very useful tools for quantifying NAPL volume and assessing performance of remediation projects. Partitioning tracers can be used to estimate the volume of NAPL before a remedial action and they can also be used for estimating the volume of NAPL remaining after remedial actions and hence as a performance assessment method (2-11). A design protocol for PITTs can be found in (10).

The most common partitioning tracers that have been used to date in saturated zones are aliphatic alcohols such as n-hexanol and n-heptanol since these have been found to have sufficiently high partition coefficients for many NAPLs at the low average saturations typical of most sites. The partition coefficient (K_{ij}) is defined as the concentration of the alcohol in mg/l in the NAPL divided by the concentration of the alcohol in mg/l in the water. At sufficiently low concentrations, alcohol tracers show a linear partitioning into the NAPL as the aqueous concentration of the alcohol increases, and thus the partition coefficient is constant over the dilute range of interest in field tests. This behavior is a good approximation for the data presented here, but should always be checked for the conditions of interest. In addition to the desirable range of partition

coefficients, aliphatic alcohols are environmentally acceptable as groundwater tracers, have sufficient water solubility up to n-octanol to use as partitioning tracers, have very low adsorption on typical alluvium soils, are easy to detect and have low analytical detection limits and are relatively inexpensive, thus making them suitable for many saturated zone field applications. However, other suitable tracer candidates have also been identified and merit further research.

The accuracy of a PITT is contingent on selection of suitable tracers and the accurate measurement of their partition coefficients between NAPL and water (or air in the case of vadose PITTs). The error in NAPL volume estimates based on PITTs is directly proportional to the error in the partition coefficients. Accurate experimental measurements of partition coefficients are essential for final tracer selection and use, but are time consuming and costly. In some cases, NAPL samples may not be available, may not be representative of the in-situ NAPL, or may have been altered by the remediation process. Therefore, it is advantageous to use estimation techniques for preliminary estimates, for identifying errors in the measurements, for use in inverse models and for estimating the values for mixtures from pure component values.

Several predictive techniques to estimate partition coefficients are discussed in the literature. For example, the partition coefficients for many organic components between octanol and water have been estimated using empirically derived group fragment constants (12, 13, 14) or linear free energy relationships (14). Octanol-water partition coefficients have also been estimated using UNIFAC (15). This approach was recently applied to estimating the partition coefficients of aliphatic alcohols between water and various NAPLs (16). Although the UNIFAC estimates of the partition coefficients were sufficiently accurate to be useful, the partition coefficients for alcohols between pure NAPL and water were not in general within the experimental error of the measurements. Furthermore, the binary interaction parameters of all groups of typical NAPL mixtures are often not known and this was another limitation of the UNIFAC-solubility approach.

More recently, we have discovered that an approach based upon the concept of equivalent alkane carbon number (EACN) is both simpler and more accurate, and this is the approach presented in this paper.

Equivalent Alkane Carbon Number Correlation from Surfactant data

The Equivalent Alkane Carbon Number (EACN) concept was introduced by Wade and Schechter and co-workers in the 1970's for understanding and correlating the behavior of surfactants for enhanced oil recovery (17, 18) and more recently was found to be of great value in understanding and evaluating surfactant enhanced remediation of chlorocarbons (19). The EACN of a pure alkane is just its carbon number. For example, alkane carbon numbers (ACN) of 6, 7 and 8 were assigned for linear alkanes such as n-octane and n-decane. Phase behavior experiments were carried out with various anionic surfactants and the linear alkanes and the optimum salinity for each of these surfactants and hydrocarbons measured. Optimal salinity is defined as the electrolyte concentration (sodium chloride in this context) at which equal volumes of water and oil (or NAPL) are solubilized by the microemulsion (18). The logarithm of the optimal salinity was observed to be a linear function of the alkane carbon number. The optimum salinity of the same surfactant was then measured for various other hydrocarbons and mixtures of hydrocarbons including even very complex mixtures of unknown composition such as crude oils. The EACN of each of these other hydrocarbons and mixtures was then estimated by interpolation on the straight line established by the normal alkane data. More recently, the same approach was found to work for a wide variety of chlorocarbons and mixtures of chlorocarbons and hydrocarbons (19, 20). A very useful and significant aspect of the EACN approach is that the EACN of a multicomponent oil or NAPL is the mole fraction average of the pure component values:

$$N_{\text{mixture}} = \sum_{i=1}^n x_i N_i \quad (1)$$

Equivalent Alkane Carbon Number Correlation from Alcohol Partitioning Data

When the logarithm of the partition coefficient of various alcohols was plotted versus the EACN of the NAPL (NAPL EACNs from 19, 20), a linear relationship was observed that was analogous to that of optimum salinity for surfactants. An example is shown in Figure 1. It can also be seen that the slope of these curves is the same for all the alcohol tracers plotted. By analogy with the EACN of normal alkanes, the EACN of the linear aliphatic alcohols such as 1-pentanol is defined as the number of carbon atoms in the alcohol. The logarithm of the partition coefficient for several alcohols and two representative NAPLs were plotted against the alcohol ACNs as shown in Figure 2 and a linear relationship was again observed. Based on these results, we propose the following bilinear equation for correlating partition coefficients as a function of the alcohol EACN (A_j) and the NAPL EACN (N_i).

$$\ln K_{i,j} = g + MA_j + mN_i \quad (2)$$

where g , M and m are correlation constants obtained by regression on experimentally measured data.

A total of 198 measurements of partition coefficient was made using 22 alcohols and 9 NAPLs (9). A 10 ml aliquot of a 1,000 mg/l alcohol in water was placed in a separatory funnel with 10 ml of the NAPL. These samples were prepared in triplicate. The samples were thoroughly shaken for one hour, allowed to separate for 1 hour and re-shaken. These samples were allowed to separate for at least 12 hours and then centrifuged for 1 hour to allow a complete separation of the phases to occur. Six aqueous samples were then analyzed for alcohol using a gas chromatograph with a Flame Ionization Detector (FID). Six more samples were measured after another 36 hours of equilibration time. If the results were the same as those at 12 hours within experimental error, they were considered equilibrium results. This was always the case for the data reported here. For tracers with partition coefficients greater than 15, 3 ml of NAPL was mixed with 18

ml of aqueous solution in a 24 ml vial. Otherwise, the aqueous alcohol concentration of the equilibrated samples is too low for accurate GC measurements. The partition coefficient was then calculated using a mass balance on the alcohol. The estimated error of the partition coefficient measured this way is 12% (9). Additional measurements such as column tests have been used to reduce this error to about 7% (9), but this has been done for only a few selected cases of special interest to date.

The initial estimates of alcohol and NAPL EACNs were made graphically by plotting all of the data using the defined values of EACN for the linear alcohols and normal alkanes plus the literature values of EACN for chlorocarbons and jet fuel (19, 20). The three constants g , M and m in Equation (2) were then estimated by linear regression. Then some of the values of A_j were adjusted for the branched alcohols and the values of N_i were adjusted for the chlorocarbons to give a better linear fit of the data. A comparison of the EACNs for the NAPLs estimated this way with those from the Literature (19, 20) is given in Table 1. The EACN values are in generally good agreement considering the completely different types of data from which they were derived and the difficulty of making some of the surfactant measurements accurately. The estimated EACNs of the alcohols are given in Table 2. The final regression equation is as follows:

$$\log_{10} K_{i,j} = -2.9562 + 0.6548A_j - 0.0505N_i \quad (3)$$

A comparison between the experimental and computed partition coefficients is given in Table 3. Based on the regression of the data, the standard deviation in $\log_{10} K_{i,j}$ is 8.3%. The correlation coefficient r^2 of the regression is 0.984. The standard deviation of the partition coefficients ($K_{i,j}$) for this correlation is 18%.

For a multicomponent NAPL, Equation (2) can be generalized to

$$\log K_{\text{mixture},j} = g + MA_j + mN_{\text{mixture}} \quad (4)$$

and using Equation (1)

$$\log K_{\text{mixture},j} = g + M A_j + m \sum_{i=1}^n x_i N_i \quad (5)$$

It follows that:

$$\ln K_{\text{mixture},j} = \sum_{i=1}^n x_i \ln K_{i,j} \quad (6)$$

If the composition of a multicomponent NAPL is known and the partition coefficient for each pure component in the NAPL is known or can be estimated, then Equation (6) can be used to estimate the partition coefficient of each alcohol j for the NAPL mixture. Conversely, if a sufficiently large number of tracers are used in a PITT, both the volume and composition of a field NAPL could in principle be estimated using Equation (6) and the first temporal moments of the tracers (4) and/or inverse modeling.

A comparison of predicted and measured partition coefficients for several alcohols with TCE and PCE are shown in Figure 3. Similar results for 1,1,1-trichloroethane and jet fuel (JP4) are shown in Figure 4 and for octane and decane NAPLs in Figure 5. Excellent agreement between the measured and estimated partition coefficients is observed in all these cases.

As a further test of the mixture correlation, the partition coefficients of a mixture of 1,2-dichloroethane (DCA) and PCE were estimated and compared with our mixture data. From Figure 6 it is evident that the predicted and measured partition coefficients are in good agreement and in fact are within the experimental error of our measurements. In order to further extend the applicability of the EACN approach, the EACN of a DNAPL from Hill AFB OU2 was estimated based on the composition of its principal components of TCE (approximately 73% by weight), TCA (approximately 14% by weight) and PCE (approximately 8% by weight). Small amounts of other volatile organic carbon components and grease were neglected since they made up less than 5% of the mass of the DNAPL. The measured and estimated partition coefficients are in good agreement as shown in Figure 7. Some of the variations between the measured and estimated partition coefficients is likely due to the uncertainty in the DNAPL composition.

Based on the results presented in this paper, we conclude that a modified EACN approach is very effective and useful in estimating the partition coefficients of alcohol tracers between water and typical NAPLs found in contaminated aquifers. Excellent agreement was obtained between measured and estimated partition coefficients for various NAPLs.

Nomenclature

A_j	= EACN of alcohol 'j'
CTET	= Carbon Tetrachloride
DCB	= o-Dichlorobenzene
Dec	= Decane
Est	= Estimated Value
Exp	= Experimentally Measured Value
JP4	= Jet Fuel
$K_{i,j}$	= partition coefficient of alcohol 'j' with NAPL 'i'
$K_{\text{mixture},j}$	= partition coefficient of alcohol 'j' with multicomponent NAPL
n	= number of components in the NAPL mixture
NAPL	= Nonaqueous Phase Liquid
N_i	= EACN of NAPL 'i'
N_{mixture}	= EACN of multicomponent NAPL
PCE	= Tetrachloroethylene
TCA	= 1,1,1-Trichloroethane
TCE	= Trichloroethylene
TCM	= Chloroform
x_i	= mole fraction of NAPL component 'i' in the mixture

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Table 1: Comparison of Estimated and Literature values of EACNs for Several NAPLs

NAPL	EACN Estimated	EACN from Literature (19, 20)
Trichloroethylene	-5.41	-3.81
Tetrachloroethylene	2.27	2.9
1,1,1-Trichloroethane	-3.05	-2.5
1,2-Dichloroethane	-8.1	-12.10
Carbon Tetrachloride	-0.40	-0.06
Trichloromethane (Chloroform)	-15.13	-13.67
Jet Fuel (JP4)	6.31	6.9

Table 2 : Estimated EACNs of Alcohol Tracers

Alcohol	EACN
1-Pentanol	5.00
1-Hexanol	6.00
1-Heptanol	7.00
1-Octanol	8.00
2-Methyl-2-Butanol	4.29
2-Methyl-1-Pentanol	5.85
3-Methyl-1-Pentanol	5.75
2-Methyl-2-Pentanol	5.33
3-Methyl-2-Pentanol	5.70
4-Methyl-1-Pentanol	5.93
2-Methyl-3-Pentanol	5.25
4-Methyl-2-Pentanol	5.63
3-Methyl-3-Pentanol	5.28
2,3-Dimethyl-2-Butanol	5.30
3,3-Dimethyl-2-Butanol	5.70
3,3-Dimethyl-1-Butanol	5.49
3-Methyl-3-Hexanol	6.31
2-Methyl-3-Hexanol	6.52
3-Methyl-2-Hexanol	6.76
2-Methyl-2-Hexanol	6.33
5-Methyl-2-Hexanol	6.77
3-Ethyl-3-Pentanol	6.39
4,4-Dimethyl-2-Pentanol	6.67
2,3-Dimethyl-3-Pentanol	6.38
2,2-Dimethyl-3-Pentanol	6.95

Table 3. Comparison of Measured and Estimated Partition Coefficients

Alcohol	PCE	PCE	TCE	TCE	TCA	TCA	JP4	JP4	Dec	Dec	Oct	Oct	DCB	DCB	CTET	CTET	TCM	TCM
	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est	Exp	Est
1-Pentanol	1.40	1.60	3.80	3.90	3.10	2.96	0.90	1.00	0.50	0.65	0.60	0.82	2.20	2.11	1.90	2.18	10.8	12.1
1-Hexanol	6.80	7.21	18.6	17.6	15.2	13.4	4.00	4.50	2.70	2.93	3.00	3.70	13.2	9.54	11.0	9.83	57.5	54.6
1-Heptanol	35.4	32.5	94.4	79.5														
1-Octanol			389	359														
2-Methyl-2-Butanol	0.40	0.54	1.30	1.33	0.70	1.01	0.50	0.34	0.40	0.22	0.40	0.28	0.50	0.72	0.90	0.74	3.10	4.11
2-Methyl-1-Pentanol	5.40	5.73	14.5	14.0	11.6	10.6	3.90	3.58	2.30	2.33	2.60	2.94	9.00	7.58	7.80	7.82	36.7	43.4
3-Methyl-1-Pentanol	4.70	4.92	12.8	12.0	9.70	9.14	2.80	3.07	1.90	2.00	2.00	2.53	8.40	6.51	6.50	6.71	41.2	37.2
2-Methyl-2-Pentanol	2.60	2.62	6.30	6.40	5.10	4.87	1.70	1.64	1.20	1.07	1.30	1.35	3.40	3.47	3.40	3.57	19.7	19.8
3-Methyl-2-Pentanol	6.20	4.58	11.3	11.2	8.20	8.51	2.80	2.86	1.90	1.86	2.10	2.35	6.00	6.06	5.90	6.25	32.5	34.7
4-Methyl-1-Pentanol	5.70	6.47	16.0	15.8	12.8	12.0	3.70	4.04	2.70	2.63	3.00	3.32	9.20	8.56	8.50	8.83	58.9	49.0
2-Methyl-3-Pentanol	2.20	2.31	4.50	5.65	4.40	4.30	1.50	1.45	1.10	0.94	1.20	1.19	3.20	3.06	3.30	3.16	18.3	17.5
4-Methyl-2-Pentanol	6.30	5.83	13.0	14.3	10.8	10.8	3.40	3.64	2.40	2.38	2.70	3.00	7.70	7.72	7.50	7.96	37.3	44.1
2,3-Dimethyl-2-Butanol	2.80	2.50	6.30	6.11	4.40	4.65	1.70	1.56	1.20	1.02	1.30	1.29	3.00	3.31	3.30	3.41	16.4	18.9
3-Methyl-2-Pentanol	4.50	4.60	9.60	11.2	8.90	8.55	3.20	2.88	2.20	1.87	2.40	2.36	5.80	6.09	6.50	6.28	31.5	34.8
3,3-Dimethyl-1-Butanol	3.80	3.33	9.50	8.13	6.70	6.18	2.10	2.08	1.20	1.36	1.50	1.71	4.40	4.40	4.10	4.54	25.9	25.2
3-Methyl-3-Hexanol	11.8	11.5	27.9	28.1	20.6	21.3	7.90	7.18	5.40	4.68	6.00	5.90	14.4	15.2	15.9	15.7	68.3	87.0
2-Methyl-3-Hexanol	20.0	15.8	43.2	38.7	35.4	29.4	9.90	9.89	5.80	6.45	4.70	8.14	23.8	21.0	29.8	21.6	81.2	119.9
3-Methyl-2-Hexanol	19.2	22.6	56.9	55.1	42.2	41.9	12.4	14.1	9.80	9.19	10.5	11.6	29.3	29.8	30.0	30.8	216	171
2-Methyl-2-Hexanol	10.9	11.8	28.1	28.7	21.8	21.9	7.80	7.35	5.80	4.79	6.60	6.05	14.9	15.6	16.1	16.1	70.1	89.1
5-Methyl-2-Hexanol	17.1	23.1	55.3	56.4	39.8	42.9	10.3	14.4	7.20	9.39	8.60	11.85	33.7	30.5	30.4	31.5	554	175
3-Ethyl-3-Pentanol	13.9	13.0	31.9	31.8	23.9	24.2	8.30	8.12	5.40	5.30	6.20	6.68	16.4	17.2	17.1	17.7	99.2	98.4
4,4-Dimethyl-2-Pentanol	22.6	19.8	51.3	48.3	37.6	36.7	12.0	12.3	8.30	8.05	9.50	10.15	22.1	26.1	24.7	27.0	152	150
2,3-Dimethyl-3-Pentanol	12.3	12.7	29.0	31.1	23.8	23.6	8.20	7.95	6.20	5.18	6.90	6.54	15.8	16.8	17.6	17.4	81.6	96.3
2,2-Dimethyl-3-Pentanol	26.4	30.2	80.2	73.9	45.1	56.1	19.2	18.9	13.9	12.3	16.1	15.5	32.4	40.0	39.1	41.2	293	229

Figure 1: Partition Coefficient as a Function of NAPL EACN

Figure 2: Partition Coefficient as a Function of Alcohol EACN

Figure 3: Comparison of Predicted and Measured Partition Coefficients of Various Alcohol Tracers with PCE and TCE NAPLs

Figure 4: Comparison of Predicted and Measured Partition Coefficients of Various Alcohol Tracers with TCA and JP4 NAPLs

Figure 5: Comparison of Predicted and Measured Partition Coefficients of Various Alcohol Tracers with Decane and Octane NAPLs

Figure 6: Comparison of Predicted and Measured Partition Coefficients of 1-Hexanol with a mixture of PCE and DCA

Figure 7: Comparison of Predicted and Measured Partition Coefficients of Various Alcohol Tracers with Hill DNAPL

Laboratory Evaluation of Partitioning Tracers

Abstract

The main objectives of this work were to experimentally investigate suitable partitioning tracers for estimating the volume and/or saturation of dense nonaqueous phase liquid (DNAPL) in saturated aquifers before and after surfactant remediation, and to quantify the adsorption of partitioning tracers on soil from the aquifers. The contaminants studied were trichloroethylene (TCE) and a DNAPL from Hill Air Force Base, site Operable Unit 2. The Hill DNAPL is a mixture of TCE and lesser amounts of other chlorinated solvents and grease. Adsorption of several hydrophobic organic chemicals (various alcohols used at low concentration as partitioning tracers) by three field soils ranging in fractional organic carbon (f_{oc}) from 0.07% to 0.20% was measured using column experiments.

Partitioning tracer experiments were performed to identify suitable tracers with high partition coefficients that could be used to estimate low residual TCE saturations. Good agreement between the residual TCE saturation estimated based on mass balance and partitioning tracers was obtained in column experiments. The first step in screening suitable candidates for partitioning tracers involved performing a batch experiment to determine the static partition coefficient between the DNAPL and water. This tracer was then tested in a column experiment to further evaluate its suitability.

At low residual NAPL saturation, there is a potential for interference due to adsorption of the alcohol tracers to sedimentary organic carbon (SOC) and/or mineral

surfaces. Adsorption of the partitioning tracers to aquifers increases the retardation of the partitioning tracers. Many of the tracers with high partition coefficients have low aqueous solubilities, which makes them more likely to adsorb to SOC. Column experiments to measure alcohol tracer adsorption of 1-octanol and 1-heptanol were conducted with three types of field soils with a range of SOC content to determine when and to what extent adsorption represents a significant contribution to the measurement error of partitioning inter-well tracer tests.

Chapter 1: Introduction

The research presented in this work is part of the ongoing subsurface remediation and characterization research at the University of Texas at Austin. The main focus of this work was the application of partitioning tracers for estimation of dense nonaqueous phase liquid (DNAPL) saturation in contaminated aquifers. In the following sections, the motivation and objectives for this research and an overview of the remaining chapters is provided.

1.1 MOTIVATION AND OBJECTIVES

Groundwater is the source for drinking water for many people around the world, especially in rural areas. In the United States groundwater supplies 42.4% of the population served by public water utilities. Virtually all homes that supply their own water have wells and use groundwater. In all, more than half of the population (52.5%) of the United States relies upon a groundwater source for drinking water (Solley *et al.*, 1988).

Unfortunately, the contamination of groundwater reserves by DNAPLs has become a major and widespread problem (Cohen *et al.*, 1993). Chlorinated organic solvents like trichloroethylene (TCE) are common groundwater contaminants. If spilled into the subsurface in sufficient quantities, a DNAPL has the capacity to penetrate below the water table where it can provide a long term source of contamination.

Pankow and Cherry (1996) have described other reasons why chlorinated solvents are common groundwater contaminants. They exhibit: 1) low liquid

viscosities (are able to move easily into the subsurface); 2) low interfacial tensions with water (are able to enter into water-wet fractures relatively easily); 3) high volatilities (are able as gases to diffuse rapidly downwards into the unsaturated zone); 4) low absolute solubilities (are difficult to remove from the groundwater zone); 5) high solubilities relative to drinking water limits (are able to cause significant contamination even when small amounts dissolve); 6) low partitioning to soils (are not retarded by aquifer materials); and 7) low degradabilities.

Due to all these properties, DNAPLs can easily penetrate the soil and contaminate groundwater. Once these DNAPLs penetrate the soil, they are held in place in the form of DNAPL blobs or ganglia by capillary forces (Hunt et al., 1988a,b). This process of entrapment of DNAPL in the subsurface is similar to trapping and release of oil in natural petroleum reservoirs. The factors which affect trapping and mobilization of oil in porous media are described by Lake (1989) among many others. The trapped blobs or ganglia remain as sources of contaminant for indefinite time periods in subsurface soils and present a long term threat to groundwater quality as they slowly dissolve into groundwater (Mackay and Cherry, 1989). In some instances the DNAPL may accumulate in depressions and on top of low permeability formations in the form of mobile pools. In order to eliminate continual contamination of groundwater by slow dissolution of NAPL blobs and pools by flowing water, the source of contamination must be removed.

One of the oldest technologies to remediate these DNAPL blobs is the pump and treat method. This involves the pumping of contaminated water from

the contaminated zones followed by treatment of the contaminated water at the surface by air stripping, steam stripping, and various other methods. The recovery of contaminant by pump and treat is very slow (several years to several decades) due to the limited aqueous solubilities and various other properties of DNAPLs discussed earlier.

Surfactant remediation is one of the emergent technologies being developed to remediate contaminated soil. Surfactants can be used to vastly increase the solubility of the contaminants in water, hence the potential for increasing the rate of DNAPL dissolution (Fountain *et al.*, 1996). Surfactants also lower the interfacial tension (IFT) at the water-DNAPL interface which if sufficiently low will result in mobilizing the DNAPL (Fountain *et al.*, 1991). The goal of surfactant enhanced oil recovery is to achieve ultra-low IFT so that the oil can be economically recovered with a small amount of surfactant that mobilizes the residual oil efficiently. However, mobilization of DNAPL in aquifers is not always desirable because of concerns of downward migration (Pankow and Cherry, 1996).

Before DNAPLs can be removed, they must be located and properly characterized. The characterization of DNAPLs involves the location of DNAPL zones, the compositional characterization of the DNAPL, and the estimation of the volume and spatial distribution of DNAPL within the zones. In the last 15 years of hydrogeological practice, several methods have been developed for characterizing dissolved-phase plumes of contaminants. Conventional coring methods provide point measurements of contaminant concentrations and require interpolation of often sparsely distributed data to estimate total DNAPL volumes

in the flow domain. The number of sampling locations is usually limited by cost, including the high cost of obtaining the cores and subsequent laboratory analysis for contaminant concentrations (Mayer and Miller, 1992). This lack of DNAPL site characterization techniques has prompted the Environmental Protection **Agency** (EPA) to call for improved field methods for rapid and inexpensive detection of DNAPL zones (EPA, 1992).

Tracers have been extensively used in petroleum reservoir characterization. Partitioning tracer tests, both single-well and interwell, have been used by oil companies to estimate residual oil saturation (Zemel, 1995). Tracers are chemicals that can be added to fluids in small concentrations and used to follow their movement without affecting their physical properties. Partitioning tracers are tracers which have the ability to partition between two distinct phases. The Partitioning Interwell Tracer Test (PITT) consists of the simultaneous injection of several tracers (conservative and partitioning) with different partition coefficients and one or more injection wells and measurement of tracer concentrations in one or more extraction or monitoring wells. A conservative tracer follows only the water path and moves with the velocity of the water (Jin *et al.*, 1995; Wilson and Mackay, 1995). The presence of low saturations of DNAPL in the aquifer has little effect upon the tracer path or its velocity. If we wish to detect the DNAPL phase we need a tracer that can interact with it in some manner. One way to do this is to introduce a nonideal water tracer that can partition between the DNAPL and water phases. The difference in residence times between tracers of different partition coefficients is used to estimate the

residual DNAPL saturation in the pore volume swept by the tracers (Jin *et al.*, 1997a).

The advantage of the PITT method over other methods is that the sample volume for assessing DNAPL saturation is much larger than that available from either core samples or geophysical well logs and yields more reliable estimates of DNAPL saturation. The tracers average over a volume which is large enough to exceed a representative elementary volume whereas the other methods may not (Mayer and Miller, 1992). There are of course differences between oil field tracer applications and DNAPL subsurface characterization. The distribution of DNAPL is more uneven and complex in typical subsurface waste sites than residual oil saturations in typical oil reservoirs. Most DNAPL sites are unconfined on top and are found at shallower depths. DNAPL sites also contain complex organic mixtures and lower average residual oil saturations and some of the contaminant may be adsorbed on natural organic carbon or the soil itself and some will be in the water phase. Well distances, completions and injection/production methods are different. Shallow soils are often aerobic whereas oil reservoirs are anaerobic (Pope and Wade, 1995). Therefore, these and other considerations should be taken into account in applying tracers to subsurface characterization.

Recently, partitioning tracers have been used successfully to measure NAPL saturations in aquifers. The design of a partitioning tracer test for field application has been described by Pope *et al.* (1994) in which several laboratory experiments and computer simulations were carried out to design a PITT at Hill Air Force , site Operable Unit 1 (Annable *et al.*, 1994; Rae *et al.*, 1997). In this

study, 1-hexanol and 2,2-dimethyl-3-pentanol were used as partitioning tracers and ethanol and bromide were used as conservative tracers. This first field test was of very high quality and helped establish partitioning tracers as a valid and useful method for characterizing NAPLs in aquifers. A field partitioning tracer test using sulfur hexafluoride as a partitioning tracer was conducted by Nelson and Brusseau (1996). Very poor tracer recoveries were reported suggesting poor hydraulic control and the possibility of nonequilibrium mass transfer between the tracer and the NAPL.

Three field tests were completed at Hill Air Force base Operable Unit 2 to demonstrate the PITT in an alluvial aquifer contaminated by DNAPL (Brown et al., 1996; Brown et al., 1997). Simulations were conducted to determine test design variables such as rates, injected chemical quantities, and test duration and to predict contaminant and injected chemical recovery, degree of hydraulic confinement, and pore volume of the aquifer swept by the test area wells. The PITTs were used to estimate the volume of DNAPL in the swept pore volume of an unconfined well pattern both before the surfactant flood and after the surfactant flood.

The selection of the best tracers to use for a PITT is of course the crucial first step in any successful design. The criteria for suitable tracers includes the following: (1) non-hazardous, (2) non-toxic, (3) non-degrading, (4) low volatility, (5) reasonable cost and availability, (6) good detection in the presence of contaminants and a known dependence on the composition of the DNAPL, (7) low sorption on the soil, and (8) partition coefficients in the desired range for the conditions of interest (Pope *et al.*, 1994). Average

saturations in the field are often low (less than 3% of the swept pore volume), so there is a need to identify suitable tracers with high partition coefficients. To date, most of the research in this area has been done with two types of tracers, alcohols with carbon numbers between two and eight (Jin, 1995; Jin *et al.*, 1995; Shotts, 1996; Dwarakanath, 1997; Dwarakanath *et al.*, 1997) as partitioning tracers for the saturated zone and fluorocarbons with carbon numbers between one and ten for the vadose zone (Whitley *et al.*, 1995; Whitley, 1997, Whitley *et al.*, 1997). However, some fluorocarbons can also be used as water tracers with high partition coefficients.

One concern when using alcohols that partition into NAPLs is the potential for sorption onto sedimentary organic carbon (SOC). Sorption can be defined as the interaction of an organic chemical with a solid (Karickhoff, 1984). Sorption to natural solids is an underlying process affecting the transport, degradation, and biological activity of organic compounds in the environment (Pignatello and Xing, 1995). At low DNAPL saturation, there is a potential for interference due to sorption of partitioning tracers to SOC and/or mineral surfaces.

Soil, in its natural state, is primarily composed of sand, silt, clay, water, and a highly variable amount of natural organic carbon (Piwoni and Keeley, 1990). The fractional organic carbon content (f_{oc}) of sandy, alluvial aquifer materials typically varies from 0.001 to 0.0001 kg/kg (Schwarzenbach *et al.*, 1993). These natural organic constituents offer a relatively nonpolar environment into which a hydrophobic compound (such as 1-heptanol and 1-octanol) may escape without undue competition with water. Sorption of the partitioning tracers to aquifer materials increases the retardation of the partitioning tracers and if

significant compared to the retardation due to the partitioning into the NAPL must be accounted for to avoid contributing to the error in the NAPL volume estimate. Thus, a measurement of tracer adsorption was a major part of this investigation.

1.2 REVIEW OF CHAPTERS

A brief description of all the equipment and materials used is given in Chapter 2. A description of all the experimental procedures is detailed in Chapter 3. In Chapter 4, data analysis techniques are discussed. Various calculations needed for experiments are also discussed. A description of all the column experiments with contaminated soil are detailed in Chapter 5. This chapter includes both a surfactant column experiment and several partitioning tracers experiments. Chapter 6 addresses the problem of tracer adsorption on uncontaminated field soil. Finally, summary and conclusions are presented in Chapter 7.

Chapter 2: Experimental Equipment and Materials

The equipment and materials used to conduct the soil column experiments are presented in this chapter.

2.1 EXPERIMENTAL EQUIPMENT

2.1.1 Pumps

Injection of fluids into the soil column was done with an Instrument Specialties Company, ISCO LC-5000 Precision Pump. The ISCO LC-5000 is a syringe pump with a 500 ml capacity, flow rate range of 0.1 ml/hr to 400 ml/hr, and a 3,700 psi pressure rating. The pump operates in a constant flow mode and has a digital display of pressure in psi. The syringe barrel and piston are made of 304 stainless steel. The pump seals are graphite-filled Teflon. The pump is designed for applications requiring precise, pulse-free delivery of liquids.

2.1.2 Fraction Collectors

ISCO fraction collectors were used for collection of effluent samples during tracer and surfactant tests. The Model 1850 Fraction Collector is a general purpose sample collection apparatus. It may be used for the automatic collection of sequential samples of effluent from the soil columns. Sample size may be based upon time, drop counting, or volumetric measurement. It holds 140 18 mm tubes in removable test tube racks. The racks are mounted on shuttles, which are recirculated through a rectangular pattern in a removable stainless steel tray. Sample volumes and sampling times varied depending on the pore volume of the soil column and the rate of injection.

2.1.3 Stainless Steel Columns

The steel columns were custom made using a 1 inch outside diameter stainless steel pipe as a column and using 1 inch Swagelok fittings as end pieces. The 1 inch piece was connected to 1/2 inch fitting which was finally connected to a Swagelok connector capable of supporting 1/8 inch nylon tubing. A brass piece was machined into all the Swagelok end pieces to reduce the end volume. The steel columns were 1 foot in length. Stainless steel screens (304 ss) screens were used to contain the soil in column. The screens used were #60 mesh (250 μ m opening) and # 150 mesh (99 μ m opening).

2.1.4 Tubing

Nylon tubing was used for most of the experimental work because of its flexibility and ability to handle relatively high pressures. The tubing was rated to a burst pressure of 1,500 psi. The tubing had an outer diameter of 1/8 inch and an inner diameter of 1/16 inch. The commercial name for the tubing is Nyloflow. In some experiments, stainless steel tubing with the same dimensions was used to prevent any adsorption of chemicals on the tubing.

2.1.5 Pressure Transducers

Validyne differential pressure transducers were used to measure the pressure drop across the soil column. Pressure drop data were recorded during surfactant floods and to measure the permeability of the different soils used. In all experiments, Validyne DPI5 variable reluctance differential pressure transducers were used. Diaphragms with different pressure ranges were used depending on the nature of the experiment and the soil. Deflection of the diaphragm caused by

an applied differential pressure is converted to an output voltage which is measured by the carrier demodulator. The transducers have a bypass valve to allow them to be rezeroed for calibration purposes.

2.1.6 Liquid Scintillation Counter

A Beckman Liquid Scintillation Counter model LS 9800 was used to measure radioactive ^3H and ^{14}C concentrations. The counter has a capacity of 300 samples and is equipped with a control keyboard, printer, three count channels, two-phase warning monitor, 10 user programs, and a CRT display. The LSC counter has the capability to measure three different isotopes during one program.

Liquid scintillation samples were prepared by adding 0.25 ml of the effluent sample to 5 ml of liquid scintillation cocktail. The scintillation cocktail used was Ready-Solv HP, produced by Beckman.

2.1.7 Gas Chromatographs

Concentrations of the alcohols and contaminants were measured on three different gas chromatographs (GCs) depending on the nature of the experiment. The GCs used were the Varian 3400, Varian STAR 3400cx, and Buck Scientific models. The samples were passed through a 60 m long, 0.53 mm diameter, 5.0 mm thick bonded poly (5% diphenyl, 95% dimethyl siloxane) megabore capillary column (made by Supelco).

2.1.8 Viscometer

A Contraves Low Shear (LS 30) viscometer was used to measure bulk viscosity. The LS 30 is a couette type viscometer, which analyzes the shear stress

between a cup and a bob. The stress is converted into units of viscosity. The range of shear rates for which the instrument will measure viscosity is 0.0174 to 128.5 sec⁻¹. The sample size for each measurement is 1 ml.

2.1.9 Filter Press

Filtration was done using a FANN model 12BL filter press. This press is of stainless steel construction with several openings. The fluid was stored in a stainless steel cup with a Viton O-ring, which was clamped to the filter press. Polymer solutions were filtered using a 1.2 µm Millipore filter paper at 20 psid. Water was filtered using a 0.45 µm filter paper at 20 psid.

Filters are manufactured by Millipore. The filters are made of cellulose acetate, cellulose nitrate mixture. The diameter of the filters is 47 mm. The diameters of the filters is 47 mm. A 1.2 µm opening and a 0.45 µm opening were the two sizes used.

2.1.10 Water Deionizer

A NANOPURE system with a recirculation pump, remote dispenser, resistivity monitor, and on/off standby membrane switches was used to supply deionized water for all experiments. The system is composed of three pre-filters and one post filter. The pre-filters are made of cellulose acetate fibers with a pore size of 5 µm. The post filter has a pore opening of 0.45 µm to remove particulates and microorganisms.

2.2 EXPERIMENTAL EQUIPMENT

2.2.1 Soils

Field soils were the porous medium for all experiments. These soils were shipped to the University of Texas at Austin in various forms depending on the site conditions. Soils used in experiments were sent from Portsmouth, Ohio; Ft. Worth, Texas; and Galveston County, Texas. If the soil was thought to contain any DNAPL, the soil samples were sealed and shipped inside a cooler in order to reduce volatilization of any DNAPL.

2.2.2 Surfactant and Polymer

The surfactant used in this study was sodium dihexyl sulfosuccinate. The surfactant was purchased from CYTEC Chemicals. The sodium dihexyl sulfosuccinate is commercially available as Aerosol MA-801 and is 80% active.

The form of polymer used was a 12.3% xanthan gum broth (FLOCON 4800C) and was purchased from Oil Field Products Group Inc.

2.2.3 Alcohols and Solvents

Several alcohols were used in this study. Isopropanol (2-propanol) was used in large quantities and was purchased from EM Science. 2,4-dimethyl-3-pentanol was purchased from ACROS Chemicals. 1-octanol, 1-heptanol, 1-hexanol, and 1-pentanol were purchased from Aldrich Chemicals. All radioactive tracers were purchased from American Radiolabeled Chemicals Inc. Trichloroethylene (TCE) was the only pure solvent used in this study and was purchased from Aldrich Chemicals.

2.2.4 Source Water

Ground water was collected from Portsmouth, Ohio and used for all experiments with Portsmouth field soil. However, once the supply was gone, a synthetic ground water mixture was used based on a water composition analysis obtained from Lockheed Martin Energy Systems. This composition is given in Table 2.1.

For all other field soils a mixture of 1000 ppm CaCl_2 in deionized water was used for the synthetic ground water.

Table 2.1: Synthetic groundwater composition for Portsmouth field soil

Cation/Anion	Concentration (mg/L)
Magnesium	24
Sodium	43
Calcium	41.1
Sulfate	178
Chloride	73.6
Total	359.7

Chapter 3: Experimental Procedures

The experimental and analytical procedures used during the completion of this work are described in this section.

3.1 GAS CHROMATOGRAPHY CALIBRATION

To measure absolute concentrations of the alcohols in the GC, standards were prepared for each alcohol. A stock solution was made for each alcohol by adding a measured weight to a known volume. Serial dilutions were made of each stock to provide several concentrations for analysis. Duplicate samples were then prepared for each alcohol and were analyzed in the gas chromatograph. A regression analysis of the data was then made to produce a calibration curve.

3.2 STATIC PARTITION COEFFICIENT TEST

A batch experiment was performed to determine the static partition coefficient of 1-octanol with trichloroethylene (TCE) and water. The samples were shaken vigorously for one hour and then allowed to separate for 36 hours. Once equilibrium was reached they were drained into centrifuge tubes and centrifuged at approximately 1,000 g for 1 hour to allow a complete separation of the phases to occur. For this experiment, 3 ml of TCE was mixed with 18 ml of a 1-octanol standard in a 24 ml vial and sealed with aluminum lined caps. Three aqueous aliquots on duplicate aqueous samples were then analyzed with a gas chromatograph for a total of six measurements of the alcohol concentrations in the aqueous phase.

3.3 SOIL COLUMN PREPARATION

Preparation of field soil for column experiments involved many procedures. All field soil for adsorption experiments was placed in a fume hood to remove any traces of contaminants still present in the soil. Once the soil was dried it was ground up with a pestle and hammer and sieved with screen openings of 4.699 mm, 3.327 mm, 2.2362 mm, and 1.651 mm to ensure a uniform grain size. The end pieces of the steel column were fitted with end pieces and weighed dry. The end pieces were then filled with water and weighed again. The end volume was calculated based on the difference in weight of the dry and saturated end pieces.

The empty column and fittings were weighed before the addition of field soil. The soil was slowly packed into a steel column using a vibrating jig. The soil was kept in place by the stainless steel screens at each end of the column. The steel column was then weighed with dry soil to later determine the porosity and pore volume.

3.4 INITIAL SATURATION OF FIELD SOIL

The packed column was oriented in a vertical position and flooded with carbon dioxide (CO_2) from the bottom as shown in Figure 3.1. It is very important to ensure that all air is removed from the column to ensure 100% water saturation. CO_2 is very soluble with water and aids in achieving 100% water saturation. After CO_2 flooding for 1 hour, the column was sealed and hooked up to the saturation apparatus as shown in Figure 3.1. The fresh water used for saturation was de-aired by pulling a vacuum on the water reservoir for 30

minutes. The de-aired fresh water was injected into the bottom of the column at 0.25 ml/min until the soil column was fully saturated. The column was weighed after saturation to calculate the pore volume and porosity.

3.5 DNAPL SATURATION PROCEDURES

The column experiments described in Chapter 5 required the presence of a DNAPL for a partitioning tracer test or surfactant flood. The column was oriented in a vertical position as shown in Figure 3.2. DNAPL was stored in a 5 cm diameter, 60 cm long chromatographic column. Water was injected into the chromatography column storing the DNAPL to force the DNAPL into the soil column. The DNAPL was injected into the bottom of the soil column. This was done to ensure gravity stable displacement of the water. An injection rate of 0.25 ml/min was used for the steel column.

For the Hill and Portsmouth experiments described in Chapter 5, DNAPL was injected continuously into the column until no water production was observed. The column was then flooded with fresh water at the same flow rate from the top of the column until no NAPL production was observed in the effluent. This procedure was used to achieve a uniform residual DNAPL saturation.

In all other experiments in Chapter 5, it was desired to achieve a very low residual DNAPL saturation (1% to 5%). Therefore, DNAPL was injected into the bottom of the column until about 5 ml of water was produced in the effluent. The column was then flooded at high rates with water from the bottom for 3.0 pore

volumes to displace any free phase DNAPL that did not remain trapped by capillary forces in the soil column.

For all experiments in Chapter 5, the soil column was weighed and the difference in weights between the uncontaminated and contaminated soil column and the density of the DNAPL was used to calculate the residual DNAPL saturation.

3.6 MIXING OF ALCOHOL TRACERS

Alcohol tracers were mixed using weight measurements. For example, for a 250 mg/L solution of 1-octanol, 0.025 g of 1-octanol was weighed into a 100 ml volumetric flask. Fresh water was then added to make the total volume 100 ml. The solution was then mixed with a magnetic stir bar on the stir plate overnight to fully dissolve the alcohol.

3.7 MIXING OF RADIOLABELED TRACERS

Radiolabeled tracers were added to alcohol solutions already mixed to the desired concentration. Depending on the half life and activity of the isotope, a small volume was added to the alcohol tracer mixture. For example, the activity of tritium (^3H) is 1 mCurie/cc. For this activity, 2.2×10^9 disintegrations Per minute (DPM) equals 1 mCurie. To obtain 100 ml of 200,000 DPM/ml tritium, 0.009 ml of 1 mCurie/ml tritium stock was added to 100 cc of alcohol tracer solution. The small quantity of radioactive tracer added to the tracer suite produced $\pm 10,000$ DPM/cc variations in injected concentrations of the radiolabeled tracer in all experiments.

3.8 MIXING OF SURFACTANT ALCOHOL POLYMER SOLUTIONS

The procedures for preparing xanthan gum polymer are described in detail in Garver (1988), Wreath (1989) and Shotts (1996). The xanthan gum was obtained as 12.3% active broth from Gil Field Products Group, Inc. This broth was used for preparing a stock solution of 1% by weight xanthan gum and 2% by weight sodium chloride. The water used for preparing polymer was filtered using a 0.45 μm filter paper to remove undissolved solids and bacteria. The stock was further diluted to prepare the surfactant solutions. For 250 g of polymer stock, 20.33 g of broth, 5.0 g of sodium chloride, and 224.67 g of source water were mixed in a blender for 2 minutes. Polymer broth was added taking care not to allow any broth to accumulate on the sides of the blender. This produced a stock solution of 1% xanthan gum and 2% sodium chloride.

The polymer solution was then diluted to obtain the desired polymer concentration. For example, a 1000 ml solution of 4% by weight sodium dihexyl sulfosuccinate, 4% by weight isopropanol, 11,250 mg/L NaCl, and 500 mg/L xanthan gum needed the following: 50 g polymer stock, 50 g sodium dihexyl sulfosuccinate, 40 g isopropanol, 10.25 g sodium chloride, and 849.75 g of source water. The surfactant/alcohol/polymer mixture was stirred for 2 hours until the contents were completely dissolved. The dissolved mixture was then filtered through 1.2 μm filter paper at 20 psid.

3.9 PHASE BEHAVIOR

Phase behavior procedures were similar to the procedures used by Baran et al. (1994a,b,c and 1996a,b,c), Jin (1995), Shotts (1996), and Dwarakanath

(1997a,b). Phase behavior tests were performed with a specific surfactant solution and a particular contaminant. All phase behavior experiments are carried out at surfactant concentrations greater than the critical micelle concentration of the surfactant to study micellar solubilization.

The procedure involved mixing 2.0 cc of NAPL with 2.0 cc of aqueous surfactant solution at different sodium chloride concentrations in a 5.0 cc pipette. The ends of the pipette were heat sealed to prevent volatilization. The initial levels of the NAPL and surfactant volumes were recorded. The pipette was vigorously shaken and allowed to equilibrate for several hours. Once equilibrium was reached, the phase volumes were noted and solubilization parameters and ratios were calculated.

3.10 DETERMINATION OF FRACTIONAL ORGANIC CARBON OF FIELD SOILS

The procedures used to determine the fractional organic carbon (f_{oc}) were similar to those developed by Nelson and Sommers (1982). The oven was heated to 950° C. A Nesbitt bulb was swept with oxygen until the weight was constant. The soil sample was inserted for 10 minutes. The Nesbitt bulb collected the volatilized carbon. The bulb was removed and the weight gain was recorded. The weight gain divided by the total weight of the soil sample gives the fraction of organic carbon. The f_{oc} laboratory work was done by Dr. C.T. Hallmark at The Soil and Crop Sciences Department at Texas A&M University.

Figure 3.1: Core setup to fully saturate core with water

Figure 3.2: Core setup to fully saturate core with DNAPL

Chapter 4: Equations for the Analysis of Tracer Tests and Soils

Several techniques were used for data analysis. The equations used to calculate porosity, permeability, residual saturations, and static partition coefficients are presented in this chapter.

4.1 POROSITY AND PORE VOLUME CALCULATION

The porosity and pore volume of soil columns used in experiments were determined by gravimetric balance. The weight of the unsaturated soil, steel column and fittings were recorded after pulling a vacuum and removing all air from the column. Then the weight of the column was recorded after complete saturation with water. The same scale was used to minimize error. The porosity and pore volume of the soil pack were calculated using the formulae:

$$\phi = \frac{W_{sat} - W_{dry}}{\pi r^2 L} \quad (4.1)$$

$$V_p = \frac{W_{sat} - W_{dry}}{\rho_w} \quad (4.2)$$

4.2 PERMEABILITY DETERMINATION

Darcy's Law was used to calculate the permeability of the soil columns. Water was flowed into the saturated soil column until steady state was reached. The pressure was measured at a range of flow rates. The permeability of the soil column was calculated from the slope of a plot of ΔP vs. Q , the length of the soil column, cross-sectional area of the soil column and viscosity of water. Using lab

units of ml/min for flow rate, cp for viscosity, cm for length, cm² for cross sectional area and psi for pressure drop, the permeability in Darcies is given by,

$$k(\text{Darcy}) = 0.242 \frac{Q\mu L}{A\Delta P} \quad . \quad (4.3)$$

4.3 ESTIMATION OF RESIDUAL DNAPL SATURATION IN SOIL COLUMNS

Residual DNAPL saturation was determined by gravimetric and volumetric balances. A gravimetric balance was obtained by the difference in weight of the contaminated soil column at residual DNAPL saturation and the uncontaminated soil column at 100% water saturation. The density difference between the DNAPL and water was used to estimate the residual DNAPL volume. All measurements were done at room temperature. The following equations were used to estimate the residual DNAPL saturation by gravimetric balance:

$$S_N = \left(\frac{W_{SN} - W_{sat}}{\rho_N - \rho_w} \right) \frac{1}{V_p} \quad (4.4)$$

$$V_{DNAPL} = \left(\frac{W_{SN} - W_{sat}}{\rho_N - \rho_w} \right) \quad . \quad (4.5)$$

Volume balance was calculated by measuring the difference in volume of water produced during the DNAPL flood and the volume of DNAPL produced during the water-flood. The volume balance is less accurate and was done only as a qualitative check. The following equations were used to estimate the residual DNAPL saturation by volume balance:

$$S_N = \frac{V_{wp} - V_{np}}{V_p} \quad (4.6)$$

$$V_{\text{NAPL}} = V_{\text{wp}} - V_{\text{np}} \quad (4.7)$$

4.4 STATIC PARTITION COEFFICIENT CALCULATION

The equilibrium static partition coefficient, K_i , was measured for 1-octanol with trichloroethylene (TCE) and water. The static partition coefficient can be defined as,

$$K_i = \frac{C_{i,\text{TCE}}}{C_{i,\text{Water}}} \quad (4.8)$$

The concentration of 1-octanol in the aqueous phase was measured in the GC. Because the concentration of the tracers in the nonaqueous phase was not measured, the partition coefficient was calculated from a mass balance developed by Dwarakanath (1997):

$$K_i = \frac{V_{\text{w}}}{V_{\text{N}}} \left(\frac{C_{i,\text{NJ}}}{C_{i,\text{Water}}} - 1 \right) \quad (4.9)$$

4.5 METHOD OF MOMENTS

The theory of the method of moments for the NAPL partitioning interwell tracer test (PITT) is given by Jin *et al.* (1995).

In a PITT, a conservative or nonpartitioning tracer is used as a reference tracer because the tracer's behavior will be independent of the composition of the NAPL. For a PITT with a nonpartitioning and a partitioning tracer, the equation for the NAPL saturation is

$$S_{\text{N}} = \frac{\bar{V}_{\text{P}} - \bar{V}_{\text{N}}}{(K_{\text{N,w}} - 1)\bar{V}_{\text{N}} + \bar{V}_{\text{P}}} \quad (4.10)$$

and the volume of NAPL is

$$V_N = \frac{\bar{V}_P - \bar{V}_N}{K_{N,w}} \quad . \quad (4.11)$$

where $K_{N,w}$ is the partition coefficient of the partitioning tracer, and V_p and V_n are the first moments of the partitioning and nonpartitioning tracers in terms of cumulative volume of fluid produced, respectively.

4.6 EXTRAPOLATION OF TRACER DATA

In order to estimate the NAPL volume accurately, the tracer response curves should be complete, because much of the information is contained in the tails of the response curves. Unfortunately, the tracer response curves are often incomplete either due to dilution of the tracer concentration below the detectable limit or because of limitations in the tracer test. However, the tracer response curves can be extrapolated with an exponential function provided the duration of the test is sufficient to establish this decline (Pope *et al.*, 1994). The first temporal moments of the tracer response curves can be estimated by dividing the data into two parts. The first part represents the data from zero time to the time t_b where the tracer response becomes exponential, and the second covers the exponential part in which the tracer response goes from t_b to infinity. After time t_b the tracer response is assumed to follow an exponential decline given by,

$$C = C_b e^{-\frac{(t-t_b)}{a}} \quad (4.12)$$

where $1/a$ is the slope of the straight line when the tracer response data are plotted on a semi-log graph, and C_b is the tracer concentration at time t_b .

It can be shown by integration that

$$\int_{t_b}^{\infty} C_b e^{-\left(\frac{t-t_b}{a}\right)} dt = aC_b \quad (4.13)$$

and

$$\int_{t_b}^{\infty} C_b e^{-\left(\frac{t-t_b}{a}\right)} dt = a(a + t_b)C_b \quad (4.14)$$

Hence the first temporal moment (i) of the tracer response curve can be calculated as

$$\bar{t} = \frac{\int_0^{t_b} tC dt + a(a + t_b)C_b}{\int_0^{t_b} C dt + aC_b} \quad (4.15)$$

This technique of extrapolation can be used to improve the accuracy of the NAPL volume estimate, which otherwise is biased on the low side, but only if a clear linear trend (on semi-log plots) in the tracer concentration data is well established to enable a reliable extrapolation. It should not be used as a substitute for measuring the tracer tail if the analytical technique and good practice will permit (time and cost in the field allow). If no extrapolation is used, then the first temporal moment (i) is calculated as

$$\bar{t} = \frac{\int_0^{t_b} tC dt}{\int_0^{t_b} C dt} \quad (4.16)$$

On several plots in Chapter 5 and Chapter 6 the starting point of the extrapolation is identified by a straight line over the data on the tracer tail. In all tracer experiments, the extrapolation technique was used.

4.7 TRACER SELECTION GUIDELINES

An important parameter related to the separation of the tracer response curves is the retardation factor R_r , which is related to the partition coefficient K and NAPL saturation S_N by

$$R_r = 1 + \frac{KS_N}{1 - S_N} \quad (4.17)$$

When considering the accuracy and the duration of a tracer test, a good range of retardation factor is

$$1.2 < R_r < 3 \quad (4.18)$$

This implies the desired range of $KS_N/(1 - S_N)$ is

$$0.2 < \frac{KS_N}{1 - S_N} < 2 \quad (4.19)$$

or for the typical low values of S_N in the field, this rule of thumb becomes

$$0.2 < KS_N < 2.0 \quad (4.20)$$

Another important parameter in the design of a partitioning tracer test is the number of tracers to be used. Theoretically, at least two tracers (one nonpartitioning and one partitioning) should be used. However, two or more partitioning and two nonpartitioning tracers will improve the accuracy of NAPL estimation. When there is a large range of uncertainty in the quantity and distribution of NAPL, partitioning tracers with a wide range of partition coefficients will help clarify this uncertainty.

4.8 ADSORPTION CALCULATIONS

At low residual saturation, there is a potential for errors due to sorption of tracers on sedimentary organic carbon (SOC) and/or mineral surfaces. Several calculations are made in Chapter 6 to quantify the tracer adsorption. The percent recovery of each tracer is calculated by mass balance and is

$$\% \text{Tracer Recovery} = \frac{\sum C \Delta V}{C_{\text{inj}} V_{\text{inj}}} \quad (4.21)$$

where $\sum C \Delta V$ is the mass of tracer recovered in mg, V_{inj} is the slug size of the tracer in L, and C_{inj} is the injected concentration of the tracer in mg/L.

The retardation factor (R_f) for each partitioning tracer studied was calculated as the ratio of the first temporal moment for the partitioning tracer to the first temporal moment for the conservative tracer. This value was then used to calculate a soil distribution coefficient (K_d) in L/kg from the equation

$$R_f = 1 + \frac{\rho_b K_d}{\phi} \quad (4.22)$$

where ρ_b is the dry bulk density of the soil in kg/L and ϕ is the porosity.

The adsorption (C_s) of each tracer in mass of tracer adsorbed/mass of soil with units of mg/g is

$$C_s = K_d C_{\text{inj}} \quad (4.23)$$

where K_d has units of L/g and C_{inj} has units of mg/L.

An apparent TCE saturation was calculated using the equation developed by Jin *et al.* (1997b). The condition under which the chromatographic separation of partitioning tracers during a PITT is equally due to sorption onto SOC and partitioning within TCE occurs when the tracer mass sorbed equals the tracer

mass partitioned into the NAPL. The mass of tracer sorbed onto SOC is given by $K_{d,i} \rho_b C_{i,w}$ where $K_{d,i}$ is the soil distribution coefficient for tracer i in units of volume per mass, and $C_{i,w}$ is the mass of tracer i dissolved in water per unit volume water. The mass of tracer partitioned into TCE is given by $K_{TCE,i} S_{TCE} \phi C_{i,w}$. Solving for the residual TCE saturation when the mass sorbed equals the mass partitioned within the TCE gives

$$S_{TCE} = \frac{K_{d,i} \rho_b}{K_{TCE,i} \phi} \quad (4.24)$$

4.9 INTERSTITIAL VELOCITY CONVERSION

In Chapters 5 and 6, a laboratory flow rate is given in cc/min and an interstitial velocity is given in ft/day. This is done to make a correlation between laboratory units and field units. The interstitial velocity is defined as

$$v(\text{ft / day}) = 47.24 \frac{Q}{A \phi} \quad (4.25)$$

Chapter 5: Column Experiments with Contaminated Soil

Soil column experiments were performed to evaluate surfactant and tracer methods. Experiment HILLOU2#6 was done with Ottawa sand contaminated with a field DNAPL. All other experiments in Chapter 5 were done with field soil contaminated with trichloroethylene (TCE).

5.1 HILL AFB, OPERABLE UNIT 2, UTAH

5.1.1 Site History

Operable Unit 2 at Hill AFB has been identified as a disposal area for chlorinated solvents such as trichloroethylene and tetrachloroethylene. At least two DNAPL pools have been identified at OU2. A further assessment of the DNAPL distribution can be found in Oolman *et al.* (1995). The site had been chosen to test the applicability of surfactant enhanced aquifer remediation and a partitioning interwell tracer test.

5.1.2 Experiment HILLOU2#6

Experiment HILLOU2#6 was the first experiment performed in this work. The objectives of this experiment were to gain experience in performing soil column experiments and to compare with the results obtained by Dwarakanath (1997). HILLOU2#6 was a column experiment designed to evaluate a remediation technique for a field DNAPL in Ottawa sand. This technique uses a Type III surfactant/alcohol/polymer mixture with mobilization as the primary mechanism for DNAPL recovery. The contaminant used for this experiment was collected from the Operable Unit #2 at Hill AFB in Utah and is approximately

73% TCE, 14% 1,1,1-trichloroethane, 8% tetrachloroethylene, 3% freon 113. Carbon tetrachloride, toluene, and dichloromethane are present in concentrations less than 1%. The column experiment involved the injection of a surfactant solution composed of 500 ppm xanthan gum polymer, 4% sodium dihexyl sulfosuccinate tagged with ^{14}C , 4% 2-propanol as the cosolvent, and NaCl as the electrolyte (11,250 mg/L).

Phase Behavior

Phase behavior experiments were conducted to determine the effects caused by varying the salinity of the surfactant solution used. The volume fraction diagram for 4% sodium dihexyl sulfosuccinate, 4% 2-propanol and 500 ppm xanthan gum mixed in fresh tap water obtained from Hill AFB is shown in Figure 5.1. It was known from previous work with this field DNAPL that the optimum salinity was around 11,000 mg/L (Dwarakanath, 1997). It was observed that type III behavior occurred in a NaCl concentration range between 10,500 and 11,750 mg/L, and type II+ behavior was observed for NaCl concentrations greater than 11,750 mg/L NaCl. All measurements were made at room temperature of 23° C and after approximately eight hours of equilibration.

The volumes of oil and water solubilized in the microemulsion were approximately equal at a sodium chloride concentration of 11,250 mg/L. This defines the optimum salinity for the surfactant. The oil solubilization ratio is the volume of oil divided by the volume of surfactant in the microemulsion. The water solubilization ratio is the volume of water divided by the volume of

surfactant in the microemulsion. A plot of the water and oil solubilization ratios versus NaCl concentration is presented in Figure 5.2.

Initial Column Data

A 2.21 cm diameter, 75 cm long stainless steel column was used to enclose the sand. Two stainless steel (304 ss) wire mesh screens were used to contain the sand in the column and disperse the flow of fluid as it enters the column from the end piece. The sizes used were Mesh #150 and Mesh #60.

Table 5.1: Initial column data for HILLOU2#6

The length of the column=	75.0 cm
The diameter of the column=	2.21 cm
Initial water permeability=	8.54 darcies
Porosity=	35.5%
Initial saturated weight of column=	2209.45 g

The soil used for this column experiment was clean F-95 grade Ottawa sand.

Initial Tracer Test

The initial tracer used was approximately 200,000 DPM/cc tritium. About 0.10 pore volumes, or 11.1 cc of tracer solution was injected. The sample size collected was approximately 2.7 cc. The effluent tritium response curve was analyzed in order to determine the initial pore volume of the soil column. The tracer response curve is shown in Figure 5.3. The calculated amount of tritium which was recovered in the effluent was 105.8% of the amount injected. The pore volume estimate based on the first moment of the initial tritium tracer response

was 103.6 cc. The pore volume by gravimetric balance was 102.1 cc which agrees well with the tritium estimate.

DNAPL Flood/Water Flood

With the column in a vertical orientation, DNAPL was injected into the column from the bottom at 1.0 cc/min (about 40 ft/day) until no water production was observed. A residual water saturation of 19.42% was reached based on the pore volume derived from the initial tritium response curve. Water was then injected into the column from the top, at a rate of 1.0 cc/min, until no DNAPL production was observed. The weight of the column at the end of the water flood was 2218.35 g. A residual DNAPL saturation of 26.86% was reached (volume material balance). This residual saturation corresponded to a DNAPL volume of 28.0 cc produced from the effluent of the column.

Residual DNAPL Tracer Test

200,000 DPM/cc of tritium was used to estimate the residual DNAPL saturation. Tritium was used as the partitioning tracer to find the pore volume estimate and this value was compared to the tritium response in the initial tracer test to obtain a residual saturation estimate. About 0.20 pore volumes or 19.7 cc of tracer was injected at 0.8 cc/min (30 ft/day). The effluent sample size was approximately 3.6 cc. Three estimates of residual DNAPL saturation are shown in the Table 5.2. There is some error with the residual DNAPL saturation estimated by tritium because it is a conservative tracer. The mass balance estimate is the most accurate. A plot of the tracer concentration versus cumulative volume produced from the column are shown in Figure 5.4.

Table 5.2: Comparison of residual DNAPL saturations. in HILLOU2#6

Residual DNAPL saturation by Weight=	22.29%
Residual DNAPL saturation by Volume=	26.86%
Residual DNAPL saturation (Tritium)=	28.51%
Average=	25.89%

Surfactant Flood

The first surfactant/water floods were completed with the column in a vertical orientation. The surfactant was injected from the top of the column to achieve a gravity stable displacement. To study the effect of a Type III surfactant with mobilization as the primary recovery mechanism, approximately 2 pore volumes of a solution of 4% sodium dihexyl sulfosuccinate, 4% 2-propanol and 500 ppm xanthan gum mixed in Hill AFB source water with an addition of 11,250 mg/L NaCl was injected into the column at a rate of 0.11 cc/min (4.2 ft/day). The surfactant solution was at optimal salinity so that the interfacial tension would be sufficiently low to mobilize a large portion of the residual DNAPL within the 'column. The viscosity of the injected surfactant solution is plotted in Figure 5.5.

Injection of the surfactant solution was routine and caused no flow problems within the column. Figure 5.6 is a plot of the pressure drop versus pore volumes produced. The pressure drop across the column for the first pore volume increased up until the breakthrough of the oil bank at approximately 1.25 pore volumes, then decreased until the end of the surfactant injection. There was a malfunction with the pressure transducer just after 3.2 pore volumes.

Figure 5.7 shows a plot of DNAPL recovery and DNAPL fraction produced in the effluent versus cumulative volume produced. The first DNAPL was observed in the effluent after 18.2 cc of water were produced and continued until 114 cc of total fluid were produced. Therefore, 91% of the DNAPL was produced due to mobilization after approximately 1.1 pore volumes of the surfactant flood. The remaining DNAPL was solubilized in the microemulsion during the surfactant flood or the aqueous phase during the polymer flood following the surfactant flood.

The surfactant concentration was measured in the effluent using 18,930 DPM/cc ^{14}C labeled sodium dihexyl sulfosuccinate. A plot of the surfactant concentration and percent recovery of the surfactant versus cumulative volume produced is presented in Figure 5.8. The surfactant breakthrough time was observed at approximately 0.9 pore volumes. The concentration increased up to the injected concentration for the duration of the surfactant flood. The concentration then decreased down to nondetectable levels very rapidly after -polymer breakthrough. A mass balance of surfactant was performed and it was determined that 105% of the surfactant was recovered in the effluent.

Polymer Flood

To flush out all of the surfactant/DNAPL/NaCl, approximately 2.25 pore volumes of 500 ppm xanthan gum polymer in Hill AFB source water was injected into the column at a rate of 0.11 cc/min (4 ft/day). Figure 5.6 shows that the potential drop across the column for this time period was relatively constant after a slight decline early on. No mobilization of DNAPL was observed during the

polymer flood. Figure 5.9 shows contaminant concentrations in the effluent after a volume of 160 cc was injected. A sharp decrease in contaminant concentration occurred after about 220 cc were produced.

Water Flood

In order to flush out all of the polymer/DNAPL/NaCl, fresh water was injected into the column. Approximately 5 pore volumes of water were flushed through the column. No pressure drop data or contaminant concentrations were measured during the water flood. A permeability of 7.56 darcies was measured at the end of the water flood compared to the initial permeability of 8.54 darcies.

Final Tracer Test

Partitioning tracers were used to determine the effectiveness of the surfactant remediation in the column. The tracers used were 164,536 DPM/cc tritium, 1,000 mg/L 1-heptanol, 2,000 mg/L 1-hexanol, and 2,000 mg/L 2,2-dimethyl-3-pentanol. About 0.10 pore volumes or 12.1 cc of tracer was injected at 0.2 cc/min (7.3 ft/day). The sample size was approximately 4.5 cc. Figure 5.10 is a semi-log plot of the tracer response curves. The percent recovery of each tracer as well as the estimates of residual DNAPL saturation are shown in Table 5.3.

Table 5.3: Comparison of final DNAPL saturation and percent tracer recovery

Tracer and Partition Coefficient	Saturation	Tracer Recovery
2-2-dimethyl-3-pentanol, K= 68.3	0.0009	91.5%
1-hexanol, K= 30.2	0.0000	94.1%
1-heptanol, K= 140.5	0.0005	98.7%
Average of Tracers	0.0005	
Mass Balance	-0.0225	

The tracers indicate that the surfactant successfully remediated the soil column. The negative mass balance suggests possible air in the column.

Results

A column experiment was performed using the surfactant solution described previously. There were no compatibility problems such as gelling or pore plugging observed between the soil, DNAPL, surfactant, and polymer during the course of the experiment.

An estimate of the total DNAPL recovered from the column was found to be 99.9% using the average value for the final partitioning tracer data. It was observed that 91% of the DNAPL was mobilized within the first 1 .l pore volumes of surfactant injected into the column. The remaining DNAPL was either produced in the microemulsion during the surfactant flood or the aqueous phase during the polymer flood following the surfactant flood.

Conclusions

1. The surfactant concentration was reduced to less than 0.1% after 1.4 pore volumes of polymer injection and surfactant flood. In addition, about 105% of the surfactant was recovered indicating negligible adsorption of the surfactant by the Ottawa sand.
2. The low pressure drops during the course of the surfactant/polymer flood allowed for the enhanced viscosities due to the 500 ppm xanthan gum polymer. Low pressure drops and absence of liquid crystals/gels/emulsions were due in part to the presence of 4% 2-propanol cosolvent with the surfactant.
3. The permeability of the soil column after remediation (7.56 darcies) was close to the initial permeability (8.54 darcies). Based on this information it can be inferred that the surfactant solution did not cause pore plugging by crystallization and that the soil was restored to its original condition after surfactant remediation.
4. A close overlap of partitioning and nonpartitioning tracers was observed in the final tracer test. Based on the final partitioning tracer test and the method of moments, an average residual DNAPL saturation of 0.0005 was computed. This low value indicates that this surfactant is extremely effective in removing essentially all the OU2 DNAPL from Ottawa sand.

Suggestions for Future Experiments

1. Use better transducers to measure AP during surfactant and water floods.
2. Measure DNAPL concentration in effluent for the entire experiment.

5.2 PORTSMOUTH OHIO

5.2.1 Site History

The area of study is the Hazardous Waste Management Unit (HWMU) identified as the X-70 1B Holding Pond at Portsmouth Gaseous Diffusion Plant in Ohio. X-701B was an unlined holding pond used to treat wastes from the X-700 Chemical Cleaning Building, X-705 Decontamination Building, and X-710 Laboratory Building. The holding pond was used for solids-settling and pH adjustment. Chlorinated solvents were identified as 'components of DNAPL found in the subsurface at X-701B. The DNAPL consists predominantly of trichloroethylene (TCE), although several other components have been identified in trace amounts. No DNAPL from the site could be obtained so pure TCE was used in all the laboratory experiments.

5.2.2 Experiment Ports#3

Objectives

1. Verify tracer compatibility with the Portsmouth field soil saturated with trichloroethylene as a contaminant at residual saturations.
2. Assess the characterization performance of the chosen tracer suite.
3. Measure soil permeability to assess its representation of field conditions as reported by other investigators based upon pump tests and other core data.

Column Preparation

The soil which was used to pack the column was obtained as a field sample from the Portsmouth site. A soil sample near the contaminated area was

used in order to utilize the most representative material obtained from the field location. The soil was placed into the empty column and incrementally packed with an aluminum rod. The column was packed with the moist soil as received from the field. A vacuum was pulled on the column and water was percolated through from the top to compact the soil.

Initial Column Data

A 2.21 cm diameter, 30.48 cm long stainless steel column was used to enclose the soil. A final value obtained for the permeability of the column used in Ports#3 was 0.5 millidarcies. This value is much lower than the 500 millidarcies field estimate, but was determined to be adequate for a laboratory study of the tracers.

Initial Tracer Test

An initial tracer test was performed to determine the quality of the sand pack. The initial tracers used were 200,000 DPM/cc tritium, approximately 1,500 mg/L 2-propanol, 1,500 mg/L, 3-methyl-3-pentanol, 1,500 mg/L, 1 -hexanol, 1,500 mg/L 2,2-dimethyl-3-pentanol, and 1,500 mg/L 1-heptanol. About 0.11 pore volumes, or 7.25 cc, of tracer solution was injected at 0.033 cc/min (about 1.3 ft/day). The sample size collected was about 2.0 cc. The tracer response curves are shown in Figure 5.1 la. A semi-log plot of the tracer response curves is given in Figure 5.11 b. The pore volume estimate based on an average of the first moments of the initial tracers used in the test was 61.2 cc.

TCE Flood/Water Flood

The column was packed with wet soil so there was no need for an initial water flood. An initial weight of the saturated column was found to be 1401.2 g. With the column in a vertical orientation, TCE was injected into the column at 0.1 cc/min (3.5 ft/day) from the bottom end of the column until no water production was observed (about 38 cc of TCE was injected). 0.21 pore volumes or 13.1 cc of water was displaced by the injected TCE. The weight of the column after the TCE flood was 1408.9 g. Water was then injected into the column from the top, at 0.04 cc/min (1.6 ft/day), until no TCE production was observed. A total of 1.17 pore volumes or 72.5 cc of water was injected into the column. 11.3 cc of TCE was displaced by the water. The weight of the column at this point was 1403.9 g. A summary of the residual saturations and estimated volume of TCE in column at the end of the water flood are presented in Table 5.4.

Table 5.4: Initial TCE saturation estimation summary for experiment Ports#3

Material Balance	Residual Saturation Estimation (%)	Estimated TCE volume in column (cc)
Volume	2.94	1.8
Gravimetric	9.59	5.87
Average	6.27	3.84

It should be noted that there is a significant discrepancy in the mass balance and volumetric balance. At the end of the experiment the column was opened and examined. The soil pack had compacted on both ends because of the

large pressure drops sustained by the column. Therefore, it is inconclusive which material balance is correct.

Residual TCE Tracer Test

Partitioning tracers were used to determine the residual saturation of TCE in the column. The tracers used were 200,000 DPM/cc tritium, approximately 1,500 mg/L 2-propanol, 1,500 mg/L 3-methyl-3-pentanol, and 1,500 mg/L 1-hexanol. About 0.10 pore volumes or 6.6 cc of tracer solution was injected at 0.025 cc/min (1 ft/day). The sample size was about 3.0 cc. The estimates of residual TCE based on the partitioning tracers are shown in the Table 5.5. The first tracer listed in Table 5.5 is the conservative tracer and the second is the partitioning tracer used to calculate the residual TCE saturation with the method of moments. The Portsmouth field soil had a low relative permeability at residual TCE saturation (0.08). Because of the low permeability and higher pressure drops obtained (due to the residual TCE in the soil) the tracer test had to be run at very low flow rates. This increased the duration of the tracer test beyond the typical duration. Samples were taken every six hours for eight days. Figure 5.12 shows a plot of the tracer response curves for the suite of tracers described above.

The weight of the column at the end of the tracer test was determined and found to be 1403.6 g. This corresponds to a TCE saturation of 8.2 %. However, the soil pack had compacted on both ends because of the large pressure drops sustained by the column. This created a large dead volume on either end of the column that would not be swept by the tracers. Table 5.5 shows that there is not

good agreement with the material balances and the tracer estimates. Therefore, the results of the residual TCE tracer test are inconclusive.

Table 5.5: Comparison of residual TCE concentrations for experiment Ports#3

gravimetric balance	8.2%
volumetric balance	2.9%
tritium, 3-methyl-3-pentanol (K=4.5)	1.9%
tritium, 1-hexanol (K=18.6)	3.4%
3-methyl-3-pentanol, 1-hexanol (K18.6)	3.6%
Average Tracers	3.0%

Due to a malfunction with the 2-propanol data on the GC, 2-propanol was not used as a conservative tracer to calculate the residual TCE saturations with the method of moments.

Results/Conclusions

1. The permeability of the soil column was found to be 0.5 millidarcies which is not representative of the field site..
2. The tracer response curves for the selected suite of tracers appeared to be normal when flowed through a field sand pack contaminated with TCE.
3. The final tracer test suggests that the residual saturation of TCE cannot be accurately measured using the chosen tracers with this soil column.

Cqnclusions

1. The measured permeability of the sand pack was much lower than the estimated field site values and thus of some concern. This caused

problems for the laboratory column experiment, and should be considered when considering field test designs.

2. The data from this experiment are inconclusive and the experiment should be repeated.

Suggestions for Future Experiments

1. Repeat experiment with a more permeable soil pack. A different method of packing the field soil should be tried.
2. Obtain a sample of DNAPL from the field to test tracer response on actual site contaminant.

5.2.3 Experiment Ports#5

Objectives

The main objectives of this experiment were to repeat the previous experiment with a more permeable pack and to assess the characterization performance of the chosen tracer suite.

Initial Column Data

A 2.21 cm diameter, 30.48 cm long stainless steel column was used to enclose the soil. A different method of packing the soil was used. The soil was packed according to Section 3.3. A final **value** obtained for the permeability of the column used in Ports#5 was 0.2 darcies. This value is slightly lower than the 0.5 darcy field estimate, but was determined to be adequate for a laboratory study of the tracers.

Initial Tracer Test

An initial tracer test was performed in order to determine the pore volume of the soil column. The initial tracers used were 200,000 DPM/cc tritium, approximately 2,000 mg/L 3-methyl-3-pentanol and 2,000 mg/L 1-hexanol. Tritium was the conservative tracer whereas 3-methyl-3-pentanol ($K=45$) and 1-hexanol ($K=18.6$) were the partitioning tracers used. About 0.11 pore volumes, or 6.4 cc, of tracer solution was injected at 0.25 cc/min (10 ft/day). The sample size collected was about 2.6 cc. The tracer response curves are shown in Figure 5.13a. A semi-log plot of the tracer response curves is shown in Figure 5.13b. The pore volume estimate based on the average first moment of the initial tracers used in the test was 63.5 cc.

TCE Flood/Water Flood

An initial weight of the saturated column was found to be 1387.86 g. With the column in a vertical orientation, TCE was injected into the column at a flow rate of 1.0 cc/min (35 ft/day) from the bottom end of the column until no water production was observed (about 30 cc of TCE was injected). 13.7 cc of water was displaced by the injected TCE. The weight of the column after the TCE flood was 1392.84 g. Water was then injected into the column from the top at a flow rate of .05 cc/min (2 ft/day), until no TCE production was observed. A total of 1.13 pore volumes or 72 cc of water was injected into the column. 6.9 cc of TCE was displaced by the water. The weight of the column at this point was 1390.20 g. A summary of the residual saturations and estimated volume of TCE in column at the end of the water flood are presented in Table 5.6. The mass

balance is more accurate due to uncertainties encountered with the volume of free phase TCE produced.

Table 5.6: Material balance estimates of residual TCE saturation for experiment Ports#5

Material Balance	Residual Saturation Estimation (%)	Estimated TCE volume in column (cc)
Volume	10.8	6.8
Mass	7.21	4.54
Average	9.0	5.67

Residual TCE Tracer Test

Partitioning tracers were used to determine the residual saturation of TCE in the column. The tracers used were 200,000 DPM/cc tritium, approximately 1,500 mg/L 3-methyl-3-pentanol, and 1,500 mg/L 1-hexanol. About 0.15 pore volumes or 10.2 cc of tracer solution was injected at 0.15 cc/min (4 ft/day). The sample size was about 2.4 cc. The estimates of residual TCE based on the partitioning tracers are shown in the Table 5.7. Figure 5.14 shows a plot of the tracer response curves for the suite of tracers described above. The duration of the tracer test was 3 days. There were problems with the gas chromatograph and the samples were not analyzed until 6 days after the tracer test was started. This may account for the unusually large errors apparent in Figure 5.14.

The weight of the column at the end of the tracer test was measured and found to be 1,389.56 g. This corresponds to a TCE saturation of 7.2 %. Table 5.7 shows the residual TCE saturations calculated with the suite of tracers using the method of moments. The first tracer listed in Table 5.7 is the conservative tracer

and the second is the partitioning tracer used to calculate the residual TCE saturation with the method of moments. The average of the tracers is almost identical to the mass balance.

Table 5.7: Comparison of residual TCE saturations for experiment Ports#5

gravimetric balance	7.2%
tritium, 3-methyl-3-pentanol (K=5)	6.8%
tritium, 1-hexanol (K=18.6)	7.1%
3-methyl-3-pentanol, 1-hexanol (K=18.6)	7.4%
Average Tracers	7.1%

Results/Conclusions

1. The permeability of the soil column was 0.2 darcies.
2. No separation of the tritiated water and the alcohol tracers occurred in the initial tracer flood, which indicates no adsorption of the alcohols on the Portsmouth soil.
3. The final tracer test suggests that the residual saturation of TCE can be accurately measured using the chosen tracers. All tracer estimates agree well with the mass balance. However, since the DNAPL saturations in the field may be much lower than in the column, additional tracers with higher partition coefficients (2,4-dimethyl-3-pentanol, K=40.5 and 1-heptanol, K= 163) were evaluated next.

Suggestions for Future Experiments

1. Repeat experiment with a soil column that has a lower residual TCE saturation.
2. Use tracers with higher TCE partition coefficients such as 2,4-dimethyl-3-pentanol and 1-heptanol.

5.2.4 Experiment Ports#7

Objectives

The objectives of this experiment were to test 2,4-dimethyl-3-pentanol ($K=40.5$) and 1-heptanol ($K=163$) in a soil column with a residual TCE saturation similar to the reports of the field value. In addition, 2-propanol was used as the conservative tracer because it was planned for use in the field test.

Initial Column Data

The same soil column was used as in experiment Ports#5. The soil column data can be found in the Section 5.2.3.

Water Flood

The column was waterflooded over a period of three weeks until a residual TCE saturation of 3.67% by mass was reached. Therefore, it was not possible to record a volumetric balance.

Residual TCE Tracer Test

Partitioning tracers were used to determine the residual saturation of TCE in the column. The tracers used were 200,000 DPM/cc tritium, approximately 750 mg/L 2-propanol ($K=0.05$), 750 mg/L 3-methyl-3-pentanol ($K=4.45$), 750

mg/L 1-hexanol ($K=18.6$), 750 mg/L 2,4-dimethyl-3-pentanol ($K=38.2$), and 750 mg/L 1-heptanol ($K=163.1$). About 0.25 pore volumes or 16.3 cc of tracer solution was injected at 0.15 cc/min (4 ft/day). The sample size was about 2.6 cc. The estimates of residual TCE based on the partitioning tracers are shown in the Table 5.8. Figure 5.15 is a semi-log plot of the tracer response curves at residual TCE saturation.

The weight of the column at the end of the tracer test was determined to be 1,388.96 g. This corresponds to a TCE saturation of 3.67 %. The table below shows the residual TCE saturations calculated with the suite of tracers using the method of moments. The average of the tracers is almost identical to the gravimetric balance. The residual TCE saturation for each partitioning tracer was calculated with 2-propanol as the conservative tracer.

Table 5.8: Comparison of residual TCE saturations for experiment Ports #7

gravimetric balance	3.67%
3-methyl-3-pentanol ($K=4.5$)	3.67%
1-hexanol ($K=18.6$)	3.62%
2,4-dimethyl-3-pentanol ($K=40.5$)	3.61%
1-heptanol ($K=163$)	3.47%

Conclusion

1. The final tracer test suggests that a low residual saturation of TCE can be accurately measured using the chosen tracers in Portsmouth field soil. All tracer results agree well with the mass balance.

5.3 OCTANOL TRACER EXPERIMENTS

Contaminant concentrations in the field are typically low (less than 3%) so a primary objective of this work was to identify suitable tracers with high partition coefficients. 1-octanol was identified as a suitable candidate so both a static partition coefficient and a dynamic partition coefficient were determined.

5.3.1 Results of Static 1-Octanol Partition Coefficient

A batch experiment was performed to determine the static partition coefficient of 1-octanol with trichloroethylene (TCE) and water. The samples were shaken vigorously for one hour and then allowed to separate for 36 hours. Once equilibrium was reached they were drained into centrifuge tubes and centrifuged at approximately 1,000 g for 1 hour to allow a complete separation of the phases to occur. For this experiment, 3 ml of TCE was mixed with 18 ml of a 1-octanol standard in a 24 ml vial and sealed with aluminum lined caps. Duplicate samples of the alcohol concentrations in the aqueous phase were made and then analyzed in a gas chromatograph for a total of six measurements. The static partition coefficient for 1-octanol with TCE and water was measured to be 393. The standard deviation of the six measurements was 30.5.

5.3.2 Experiment P4/OCT

P4/OCT is a column experiment designed to evaluate the performance of the chosen tracer suite on field soil obtained from the Plant 4 in Fort Worth, Texas. The field soil was contaminated with trichloroethylene (TCE).

Objectives

1. Determine the dynamic partition coefficient for 1-octanol and TCE.

2. Determine if there is any adsorption of the chosen tracer suite on uncontaminated field soil.

Initial Column Data

The soil which was used to pack the column was obtained as a field sample from the Plant 4. A 2.21 cm diameter, 30.48 cm long stainless steel column was used to enclose the soil. A final value obtained for the permeability of the column used in P4/OCT was 13 darcies. The pore volume determined by gravimetric balance was 59.29 cc.

Initial Tracer Test

An initial tracer test was performed in order to determine the quality of the soil column. The initial tracers used were 32,000 DPM/cc tritium, approximately 1100 mg/L 2-propanol, 200 mg/L 1-octanol, 600 mg/L 1-heptanol, 800 mg/L 1-hexanol and 800 mg/L 1-pentanol. Tritium and 2-propanol were the conservative tracers whereas 1-octanol ($K=393$), 1-heptanol ($K=163$), 1-hexanol ($K=18.6$), and 1-pentanol ($K=3.8$) were the partitioning tracers used. About 1/3 of a pore volume, or 20 cc, of tracer solution was injected at 0.25 cc/min (6 ft/day). The sample size collected was about 2.8 cc. The normalized tracer response curves are shown in Figure 5.16. The pore volume estimate based on an average of the initial tracers used in the test was 62.1 cc.

Tracer Adsorption

An attempt was made to determine if any of the heavier alcohols used in the suite of tracers (1-heptanol and 1-octanol) adsorbed onto the uncontaminated field soil. The tables below show the results calculated using the moment analysis.

Table 5.9 gives the results using tritium as the conservative tracer and Table 5.10 gives the results using 2-propanol as the conservative tracer. Figure 5.17 is a normalized semi-log plot of the tracers in uncontaminated Plant 4 soil.

Table 5.9: P4/OCT adsorption data using tritium as the conservative tracer

Tracer	R_f	K_d (L/kg)	adsorption (mg/g)
1-heptanol	0.981	-0.00475	-0.0028
1-octanol	1.025	0.00625	0.0014

Table 5.10: P4/OCT adsorption data using 2-propanol as the conservative tracer

Tracer	R_f	K_d (L/kg)	adsorption (mg/g)
1-heptanol	1.013	0.00325	0.0019
1-octanol	1.058	0.0145	0.0032

The results show that there is negligible adsorption of 1-heptanol in all cases. However, 1-octanol is slightly retarded ($R_f > 1.03$) with respect to 2-propanol.

TCE Flood

An initial weight of the saturated column was found to be 1389.24 g. In this experiment, it was desired to achieve a low residual TCE saturation. With the column in a vertical orientation, TCE was injected into the column at a flow rate of 1.0 cc/min (35 ft/day) from the bottom end of the column until about 1.4 cc of water was displaced. The weight of the column after the TCE flood was 1389.98 g. This corresponded to a TCE saturation of about 2.75 %.

Residual TCE Tracer Test

Partitioning tracers were used to determine the residual saturation of TCE in the column. The tracers used were 32,000 DPM/cc tritium, approximately 200

mg/L 1-octanol ($K=393$), 600 mg/L 1-heptanol ($K=163$), 700 mg/L 1-hexanol ($K=18.6$) and 800 mg/L 1-pentanol ($K=3.8$). About 0.33 pore volumes or 20 cc of tracer was injected at 0.25 cc/min. (6 ft/day). The sample size was about 2.7 cc. Figure 5.18 is a semi-log plot of the tracers at residual TCE saturation.

The weight of the column at the end of the tracer test was 1,389.88 g. This corresponds to a TCE saturation of 2.37%.. Table 5.11 shows the residual TCE saturations calculated with the suite of tracers using the method of moments. The average of the tracers agrees within 10% of the gravimetric balance.

Table 5.11: Comparison of residual TCE saturations for experiment P4/OCT

gravimetric balance	2.37%
1-pentanol ($K=3.8$)	2.84%
1-hexanol ($K=18.6$)	2.42%
1-heptanol ($K=163$)	1.87%
1-octanol ($K=393$)	1.84%
Average of Tracers	2.24%

1-pentanol and 1-hexanol agree well with the mass balance. However, 1-heptanol and 1-octanol slightly under predicted the residual TCE saturation.

Results/Conclusions

1. Slight separation of the tritiated water and the 1-octanol tracer occurred in the initial tracer flood, which indicates some adsorption of 1-octanol on the uncontaminated Plant 4 soil. More experiments should be done to quantify the adsorption with different soils.

2. The final tracer test suggests that the experiment should be repeated so that a definitive tail for the 1-octanol data can be generated. A larger tracer slug and a higher 1-octanol concentration should allow more data to be gathered.
3. The flow rate should be reduced from 6 ft/day to 3 ft/day to increase the residence time of the tracers. Increasing the residence time may improve the accuracy predicted by 1-octanol and 1-heptanol at such a low residual TCE saturation.

5.3.3 Experiment P4/OCT#2

P4/OCT2 Residual TCE Tracer Test

The P4/OCT residual TCE tracer test did not accurately predict the TCE saturation with 1-heptanol and 1-octanol. Therefore this portion of the experiment was repeated with several changes to improve the accuracy of the results. The slug size of tracer was increased as well as the 1-octanol concentration. This was done to obtain more 1-octanol data and generate a definitive tail. In addition, the flow rate was 3 ft/day (0.125 cc/min) instead of 6 ft/d (0.25 cc/min) to allow the tracers more residence time. The aqueous tracer solution consisted of 1,260 mg/L IPA, 290 mg/L 1-octanol ($K=393$), 710 mg/L 1-heptanol ($K=163$), 790 mg/L 1-hexanol ($K=18.6$), 840 mg/L 1-pentanol ($K=3.8$). About 0.67 pore volumes or 40 cc of tracer solution was injected at 0.125 cc/min. (3 ft/day). The sample size was about 3.0 cc. Figure 5.19 is a semi-log plot of the tracers at residual TCE saturation.

The weight of the column at the end of the tracer test was determined and found to be 1,389.12 g. This corresponds to a TCE saturation of 1.98 %. Table 5.12 shows the residual TCE saturations calculated with the suite of tracers using the method of moments. The average of the tracers agrees within 10% of the mass balance. It should be noted that the retardation factor for 1-pentanol was less than 1.2 so it was neglected in the average of the tracers since this low retardation leads to large errors and does not meet the usual design criteria for PITTs.

Table 5.12: Comparison of residual TCE saturations for experiment P4/OCT2

gravimetric balance	1.98%
1-pentanol (K=3.8)	3.89%
1-hexanol (K=18.6)	1.91%
1-heptanol (K=163)	1.88%
1-octanol (K=393)	1.94%
Average of Tracers	1.91%

Results/Conclusions

1. The retardation factor for 1-pentanol was less than 1.2 so it should not have been used as partitioning tracer in this experiment. As expected, it over predicted the low TCE residual saturation.
2. The residual TCE tracer test suggests that 1-octanol can be used to measure very low TCE saturations. A sufficient slug size (2/3 of a pore

volume) and a concentration of at least 250 mg/L are needed for enough 11-octanol mass to accurately predict the TCE saturation.

3. A dynamic partition coefficient of $K = 386$ was calculated from the P4/OCT2 residual TCE tracer test. This agrees well with the static partition coefficient of 393.

5.4 PERFLUOROCARBON TRACER EXPERIMENT

Perfluorocarbons mixed with air have been used as partitioning gas tracers in the vadose zone. Perfluorocarbons dissolved in water can also be used as tracers in the saturated zone. However, the limited aqueous solubility and extremely volatile nature of perfluorocarbons that have high partition coefficients made this a difficult experiment

5.4.1 Experiment Per2

PER2 is a column experiment designed to evaluate the performance of the chosen tracer suite on field soil obtained from the Plant 4 in Fort Worth, Texas saturated with trichloroethylene (TCE). The column was saturated with pure TCE to a low residual saturation. The tracers were injected and their response curves were analyzed for the presence of TCE.

Objective

The objective of this experiment was to determine the dynamic partition coefficient for hexafluoropropene (C_3F_6) and TCE in a partitioning tracer test and evaluate it as a possible candidate for a tracer in the saturated zone. Help for this experiment was received from Neil Deeds who has done extensive research in the area of perfluorocarbons as tracers in the vadose zone.

Preliminary Results

The soil which was used to pack the column was the same Plant 4 soil and steel column used in the octanol tracer experiments. The column data, permeability, and pore volume are given in Section 5.3.

TCE Flood

An initial weight of the saturated column was found to be 1389.24 g. In this experiment, it was desired to achieve a low residual TCE saturation. The weight of the soil column was 1389.98 g. This corresponded to a TCE saturation of 1.5%.

Tracer Preparation

Methanol was used as the conservative tracer in this experiment because of its cosolvency properties. Hexafluoropropene (C_3F_6) was the partitioning tracer. The tracer solution was prepared by bubbling the pure gas from the bottom of a 100 ml closed column containing 1% methanol solution until the headspace was pressurized with approximately 5 psi of the gas. The solution was injected on the GC to ensure that the relative response was adequate.

Per2 Residual TCE Tracer Test

The slug size of tracer solution was 0.75 pore volumes (45 cc). This was done to obtain more C_3F_6 data and generate a definitive tail. The flow rate used was 0.15 cc/min (3.5 ft/day) to allow the tracer sufficient residence time. The partitioning tracer used was hexafluoropropene (C_3F_6). The injected concentration was not known but was estimated to be approximately 300 mg/L. The conservative tracer used was 1260 mg/L methanol. The sample size was

about 3.0 cc. The duration of the tracer test was 3 days. Figure 5.20 shows a normalized plot of the tracer response curves for the suite of tracers described above at residual TCE saturation. A residual TCE saturation of 1.5% by mass balance gave a dynamic partition coefficient of 217 for C_3F_6 .

Results/Conclusions

1. The TCE/water dynamic partition coefficient for hexafluoropropene was calculated to be 217.
2. Detection remained stable throughout the experiment. The linearity of the FID detector should ensure a good estimate of the partition coefficient.
3. This should only be considered as a screening experiment. The initial injection concentrations were not known and the GC was not calibrated to these chemicals. In addition, due to the volatile nature of C_3F_6 , the experiment had to be run in a closed system. This should be considered for potential field test applications.

Figure 5.1: Volume fraction diagram for 4% by weight sodium dihexyl sulfosuccinate, 4% by weight IPA and 500 ppm xanthan gum in Hill source water

Figure 5.2: Solubility ratio versus salinity. Aqueous phase concentrations are: 4% MA, 4% IPA, 500 ppm xg in Hill OU2 source water. Oleic phase is Hill OU2 DNAPL

Figure 5.3: Initial tracer concentration history, experiment HILLOU2#6

Figure 5.4: Tracer concentration history at residual DNAPL saturation, experiment HILLOU2#6

Figure 5.5: Viscosity of aqueous surfactant solution, experiment HILLOU2#6

Figure 5.6: Pressure drop versus cumulative volume produced, experiment HILLOU2#6

Figure 5.7: DNAPL recovery and DNAPL fraction produced, experiment HILLOU2#6

Figure 5.8: Surfactant concentration and recovery, experiment HILLOU2#6

Figure 5.9: Effluent DNAPL concentration, experiment HILLOU2#6

Figure 5.10: Final tracer concentration histories, experiment HILLOU2#6

Figure 5.11a: Initial tracer concentration histories, experiment Ports#3

Figure 5.11b: Semi-log plot of initial tracer concentration histories, experiment Ports#3

Figure 5.12: Tracer concentration histories at residual TCE saturation. experiment Ports#3

Figure 5.13a: Initial tracer concentration histories, experiment Ports#5

Figure 5.13b: Semi-log plot of initial concentration histories, experiment Ports#5

Figure 5.14: Tracer concentration histories at residual TCE saturation, experiment Ports#5

Figure 5.15: Tracer concentration histories at residual TCE saturation, Ports#7

Figure 5.16: Initial tracer concentration histories, experiment P4/OCT

Figure 5.17: Semi-log plot of initial tracer concentration histories, experiment P4/OCT

Figure 5.18: Tracer concentration histories at residual TCE saturation, experiment P4/OCT

Figure 5.19: Tracer concentration histories at residual TCE saturation, experiment P4/OCT2

Figure 5.20: Tracer concentration histories at residual TCE saturation, experiment Per2

Chapter 6: Tracer Adsorption on Uncontaminated Field Soil

At low residual NAPL saturation, there is a potential for error due to adsorption of tracers to immobile sedimentary organic carbon (SOC) and/or mineral surfaces. Adsorption of the partitioning tracers to aquifer materials could potentially increase the retardation of the partitioning tracers during the tracer flood. Experiments to quantify alcohol tracer adsorption in the saturated zone were conducted with three types of field soils with a range of SOC content.

These experiments were dynamic tests as opposed to static tests. Adsorption of an alcohol tracer on soil is typically very small and difficult to measure accurately with static tests. However, a well designed column experiment provides many more data points and improves the accuracy of the value obtained for adsorption. In addition, a dynamic column experiment provides a more representative value for adsorption than a static experiment for applications in field tracer tests. This is because the contact between the aqueous and solid phases is more like the natural field conditions than it is in batch experiments.

In all experiments, partitioning tracers tagged with ^{14}C were used. Alcohols tagged with a beta emitter can be accurately measured in the Liquid Scintillation Counter (LX), which has a lower equivalent detection limit than the Gas Chromatograph (GC) with Flame Ionization Detector (FID). Much of the data that is crucial to quantifying adsorption occurs at low concentrations (on the order of 1 mg/L) and is contained in the tail of the tracer curve. Although the

minimum detection limit for the GC FID for the alcohols used in this study is approximately 1 mg/L, the practical limit for measurement is approximately 10 mg/L. Below this the data show considerable scatter and noise. The LCS detection limit is approximately 100 DPM/cc, which equates to an activity of 4.5×10^{-11} Curies of ^{14}C labelled alcohol per cc. Concentrations of ^{14}C alcohols used in the experiments were several orders of magnitude higher than this, in the range of 10^{-7} Curies/ml of final solution and at relatively low total alcohol concentrations. This allows for accurate measurement of alcohol concentrations into the range of less than 0.1 mg/L. All experiments were performed at room temperature (23°C) and at a flow rate of 0.25 cc/min (6 ft/day) which equates to a residence time of 4 hours/pore volume.

6.1 PORTSMOUTH FIELD SOIL

The first soil tested was from Portsmouth, Ohio and had a fractional organic carbon content (f_{oc}) of 0.07%.

6.1.1 Experiment ^{14}C IPA and ^{14}C 1-Oct#1

Objectives

1. Determine if there is any adsorption of the alcohols on Portsmouth field soil.
2. Measure tracer effluent concentrations down to an equivalent of 0.1 mg/L.

Preliminary Results

The soil which was used to pack the column was obtained as a field sample from the Portsmouth Gaseous Diffusion Plant. A 2.21 cm diameter, 30.48

cm long stainless steel column was used to enclose the soil. The permeability of the soil was 0.012 Darcy (1.2×10^{-5} cm/s). The pore volume determined by gravimetric balance was 56.6 cc. This corresponds to a porosity of 47% and a bulk density of 1.59 g/cc. The water composition used is given in Table 2.1.

¹⁴C IPA Tracer Test

The ¹⁴C IPA tracer test was performed first to measure if any adsorption of a conservative tracer occurs in this soil. The tracers used were 2,446,000 DPM/cc tritium and 766,740 DPM/cc ¹⁴C IPA. The concentration of IPA in the radioactive tracer mixture was 20 mg/L. This concentration was low because there was only IPA present in the ¹⁴C radioactive solution that was added to fresh water. About 0.2 pore volumes, or 11.4 cc, of tracer solution was injected at 0.25 cc/min (6 ft/day). The sample size collected was about 2.0 cc. The normalized tracer response curves are shown in Figure 6.1. The percent recovery of each tracer is shown in Table 6.1 below. The estimated percent recovery error is $\pm 10\%$ (Dwarakanath, 1997). Tritium is within this experimental estimate error but IPA is slightly under.

An estimate of tracer adsorption was made by calculating the first temporal moment of each tracer (Table 6.1) and comparing this value with the aqueous pore volume of the soil measured from a mass balance. The errors for retention volume by first temporal moment calculation should be within $\pm 3.5\%$ of the volume estimation by mass (Dwarakanath, 1997). Equivalently, a retardation factor within 1 ± 0.03 with respect to a mass balance is considered to be within experimental error (Dwarakanath, 1997). The value for IPA is within 1.4% of the

56.6 cc estimate from the mass balance, so it is within the experimental errors of both measurements. Therefore, adsorption of IPA is less than the amount that can be detected under these conditions. However, tritium adsorbs and this will be addressed in detail in Section 6.4.

Table 6.1: Tracer data for ^{14}C IPA using mass balance

Tracer	Volume (cc)	R_f	Percent Recovery
tritium	60.6	1.07	101 %
^{14}C IPA	57.4	1.01	89 %
mass balance	56.6		

^{14}C 1-octanol Tracer Test

The tracers used were 2,512,975 DPM/cc tritium and 598,154 DPM/cc ^{14}C 1-octanol. The concentration of 1-octanol in the radioactive tracer mixture was 8 mg/L. This concentration was low because there was only 1-octanol present in the ^{14}C radioactive solution that was added to fresh water. Tritium was the conservative tracer and 1-octanol the partitioning tracer. About 0.1 pore volumes, or 5.66 cc, of tracer solution was injected at 0.25 cc/min (6 ft/day). The sample size collected was about 2.0 cc. The normalized tracer response curves are shown in Figure 6.2. The straight lines indicate the starting point and slope of the extrapolation used to calculate contribution of the tail to the first moment as per Equation 4.15. It should be noted from this figure that the tracer test was stopped for 15 hours after 2.7 pore volumes were produced. This is because previous initial tracer experiments had a duration of 2 pore volumes. However, once the data was reviewed the following day, the tracer test was resumed.

An estimate of tracer adsorption was made by calculating the first temporal moment of each tracer (Table 6.2) and comparing this value with the aqueous pore volume of the soil measured from a mass balance. The 23% tracer recovery for 1-octanol was low because such a low concentration (8 mg/L) was used. This corresponds to a total mass of 0.045 mg of 1-octanol injected into the soil column. This mass quantity is two orders of magnitude less than what is typically used in field PITTs and accounts for the low recovery and high retardation factor with respect to the mass balance.

Table 6.2: Tracer data for ^{14}C 1-Oct#1 using mass balance

Tracer	Volume (cc)	R_f	Percent Recovery
tritium	60.6	1.07	101%
^{14}C 1-octanol	1178.8	20.8	23 %
mass balance	56.6		

The 1-octanol retardation factor (R_f) was also calculated using IPA as the conservative tracer. This value was then used to calculate a soil distribution coefficient (K_d in L/kg), and the 1-octanol adsorption in mg per g of soil (table 6.3). Table 6.3 gives the adsorption data for 1-octanol using IPA as the conservative tracer.

Table 6.3: Adsorption Data for ^{14}C 1-oct#1 using IPA as conservative tracer

	1-octanol
R_f	16.5
K_d (L/kg)	5.3
Adsorption (mg/g)	0.0424

1-octanol showed significant adsorption in this experiment. However, there is significant error in the estimated adsorption due to the low concentration of 1-octanol used. In addition, when comparing 1-octanol to IPA, the error is compounded because the alcohols were injected in separate displacements rather than at the same time, which is the preferred method.

Conclusions/Recommendations

1. The retardation factors were calculated from the results of two different experiments. This experiment should be repeated with IPA and 1-octanol in the same tracer mixture so that the errors will not be compounded.

6.1.2 Experiment ^{14}C 1-Hept#1, ^{14}Cl -Oct#2 and ^{14}Cl -Oct#4

This section is a summary of experiments designed to evaluate the performance of the chosen tracer suite on field soil obtained from the Portsmouth Gaseous Diffusion Plant. The objectives of this experiment were to measure the adsorption of 1-heptanol and 1-octanol at concentrations representative of field PITT concentrations.

Initial Column Data

The soil which was used to pack the column was obtained as a field sample from the Portsmouth Gaseous Diffusion Plant. A 2.21 cm diameter, 30.48 cm long stainless steel column was used to enclose the soil. The permeability of the soil column was 0.20 Darcy (2.0×10^{-4} cm/s). The pore volume determined by mass balance was 56.14 cc. This corresponds to a porosity of 47% and a soil bulk density of 1.59 g/cc. The water composition is given in Table 2.1.

¹⁴C 1-Heptanol Tracer Test

The ¹⁴C 1-heptanol tracer test was performed in order to determine if any adsorption of 1-heptanol occurs on Portsmouth field soil. The tracers used were 1,942 mg/L IPA and 226,773 DPM/cc ¹⁴C 1-heptanol. Unlabelled 1-heptanol was added to the ¹⁴C 1-heptanol radioactive solution. The concentration of 1-heptanol in the radioactive tracer mixture was 84 mg/L which is still lower than typical field use. About 0.10 pore volumes, or 5.6 cc, of tracer solution was injected at 0.25 cc/min (about 6 ft/day). The sample size collected was about 3.0 cc. The normalized tracer response curves are shown in Figure 6.3. The straight lines in the figure represent the extrapolation of the tracer tail. Figure 6.3 shows that the IPA was retarded relative to the 1-heptanol indicating negligible adsorption of 1-heptanol. The percent recovery of each tracer is shown in Table 6.4.

Table 6.4: Tracer data for ¹⁴C 1-hept#1

Tracer	Volume (cc)	R_t	Percent Recovery
IPA	59.6		93.4 %
1-heptanol #1	58.9	0.988	95.2%

¹⁴C 1-octanol#2 Tracer Test

The ¹⁴C 1-octanol tracer test was performed to measure the adsorption of 1-octanol in the Portsmouth field soil column at a higher 1-octanol concentration and in an aqueous solution with IPA. The tracers used were 491,220 DPM/cc ¹⁴C. 1-octanol and 1,047 mg/L IPA. Unlabelled 1-octanol was added to the ¹⁴C 1-

octanol radioactive solution. The concentration of 1-octanol in the radioactive tracer mixture was 144 mg/L. IPA was the conservative tracer and 1-octanol the partitioning tracer. About 0.10 pore volumes, or 5.4 cc, of tracer solution was injected at 0.25 cc/min (about 6 ft/day). The sample size collected was about 3.0 cc. The normalized tracer response curves are shown in Figure 6.4. The straight lines in the figure represent the extrapolation of the tracer tails. Slight retardation of the 1-octanol from the IPA occurred in this experiment. The last portion of the IPA tail was neglected for the slope of the extrapolation because it was GC noise. The percent recovery of each tracer is given below in Table 6.5. The 1-octanol recovery was excellent compared to experiment ^{14}C 1-octanol. By increasing the mass of 1-octanol from 0.045 mg to 0.778 mg (as it is in ^{14}C 1-oct#2) the recovery improved from 23% to 95%.

An estimate of tracer adsorption was made by calculating the first temporal moment of each tracer (Table 6.5) and comparing the ratio of the partitioning tracer to the conservative tracer. The 1-octanol retardation factor is greater than 1.03. The adsorption for this experiment is summarized in Table 6.7.

Table 6.5: Tracer data for ^{14}C 1-oct#2

Tracer	Volume (cc)	R_t	Percent Recovery
IPA	60.0		87.7 %
^{14}C 1-octanol	66.7	1.117	95.0 %

¹⁴C 1-octanol#4 Tracer Test

The ¹⁴C 1-octanol tracer test was repeated to compare the results with the previous experiment. The tracers used were 115,664 DPM/cc ¹⁴C 1-octanol, 303,476 DPM/cc tritium, and 2,227 mg/L IPA. Unlabelled 1-octanol was added to the ¹⁴C 1-octanol radioactive solution. The concentration of 1-octanol in the radioactive tracer mixture was 108 mg/L. IPA and tritium were the conservative tracers and 1-octanol the partitioning tracer. About 0.10 pore volumes, or 5.9 cc, of tracer mixture was injected at 0.25 cc/min (about 6 ft/day). The sample size collected was about 3.0 cc. The normalized tracer response curves are shown in Figure 6.5. The straight lines in the figure represent the extrapolation of the tracer tails. Slight retardation of 1-octanol and tritium from IPA occurred in this experiment. The percent recovery of each tracer is given below in Table 6.6.

An estimate of tracer adsorption was made by calculating the first temporal moment of each tracer (Table 6.6) and comparing the ratio of the partitioning tracer to the conservative tracer (IPA). The retardation factor for 1-octanol and tritium are greater than 1.03. The adsorption for 1-octanol is summarized in Table 6.7. The adsorption of tritium with respect to IPA is discussed in more detail in Section 6.4.

Table 6.6: Tracer data for ¹⁴C 1-oct#4

Tracer	Volume (cc)	R _t	Percent Recovery
IPA	55.2		90.2 %
tritium	59.7	1.08	115.8 %
¹⁴ C 1-octanol	62.5	1.13	102.3 %

Table 6.7 below shows the adsorption data calculated using the 1st temporal moment for the ^{14}C 1-hept#1, ^{14}C 1-oct#2, and ^{14}C 1-oct#4 experiments with Portsmouth soil.

Table 6.7: Adsorption Data for Portsmouth Soil ($f_{oc} = 0.07\%$)

Experiment	Injected Conc. (mg/L)	Retardation Factor	K_d (L/kg)	Adsorption (mg/g)
^{14}C 1-hept	83.9	0.9880	-0.00357	-0.00003
^{14}C 1-oct#2	144.1	1.1117	0.03713	0.00535
^{14}C 1-oct#4	108.4	1.1306	0.03866	0.00450

The distribution coefficient, K_d for 1-heptanol and 1-octanol are given in Table 6.7. The measured value of K_d for 1-heptanol is negligible but the values of K_d for 1-octanol are between 0.037 and 0.039 L/kg. For comparison, the K_d of ethanol in Na-montmorillonite is on the order of 0.00015 L/kg (for a surface area of 800 m^2/g , Schwarzenbach, *et al.*, 1993).

If the K_d of the soil is known, then Equation 4.24 can be used to calculate the error in the residual TCE saturation estimate. If the sediments contain no residual TCE, the retardation factor will be due only to the presence of SOC. If residual TCE is present, the retardation factor will be due to both tracer adsorption and partitioning into the TCE phase. If adsorption is large compared to partitioning into the NAPL, then it will contribute significant error to the NAPL saturation estimate. Table 6.8 gives this error calculated from the measured K_d values expressed as an apparent NAPL saturation. These values are very low.

Table 6.8: Residual TCE Saturation

Experiment	Error in TCE Saturation Estimate from Adsorption
¹⁴ C 1-hept	-0.007%
¹⁴ C 1-oct #2	0.032%
¹⁴ C 1-oct#4	0.033%

At a residual TCE saturation of 1%, the partitioning of 1-octanol into SOC would not add significant error in the estimate of the saturation. However, at a residual TCE saturation of 0.1%, the partitioning of 1-octanol into SOC would create an additional 35% error in the estimate since the retardation data would yield a value for S_N of 0.133% rather than the true value of 0.100%.

Conclusions

1. Negligible adsorption of 1-heptanol occurred in uncontaminated Portsmouth field soil.
2. Figures 6.4 and 6.5 show a retardation of the 1-octanol data compared to the IPA data in the tracer flood, which indicates adsorption of the alcohol in the uncontaminated Portsmouth field soil. The average retardation factor from two experiments was 1.12. The average estimate for adsorption in the 1-octanol experiments is 0.005 mg/g.

6. 2 GALVESTON FIELD SOIL

The second soil tested was from Galveston County, Texas and had a f_{oc} of 0.11%.

6.2.1 Experiment ^{14}C 1-Hept#1 and ^{14}C 1-Oct#1

This section is a summary of experiments designed to evaluate the performance of the chosen tracer suite on field soil obtained from Galveston County. The fractional organic carbon content of the soil was measured to be $f_{oc} = 0.11\%$. The objectives of this experiment were to quantify adsorption of 1-heptanol and 1-octanol on soil with a higher f_{oc} .

Initial Column Data

The soil which was used to pack the column was obtained as a field sample from Galveston County. This soil has a fractional organic carbon content of 0.11%. A 2.21 cm diameter, 30.48 cm long stainless steel column was used to enclose the soil. The permeability of the soil column was 10 Darcy (1.0×10^{-2} cm/s). The pore volume measured by mass balance was 55.6 cc. This corresponds to a porosity of 46.6% and a soil bulk density of 1.63 g/cc. The water composition used for all experiments with Galveston field soil was 1,000 mg/L CaCl_2 .

^{14}C 1-Heptanol Tracer Test

The ^{14}C 1-heptanol tracer test was performed in order to determine if any adsorption of 1-heptanol occurs in the Galveston field soil column. The tracers used were 1,479 mg/L IPA, 1,308,044 DPM/cc tritium, 268 mg/L 1-pentanol, 331 mg/L 1-hexanol, and 216,620 DPM/cc ^{14}C 1-heptanol. Unlabelled 1-heptanol was added to the ^{14}C 1-heptanol radioactive solution. The concentration of 1-heptanol in the radioactive tracer mixture was 113 mg/L. About 0.20 pore volumes, or 9.4 cc, of tracer solution was injected at 0.25 cc/min (about 6 ft/day).

The sample size collected was about 3.0 cc. The normalized tracer response curves are shown in Figure 6.6. Figure 6.7 is a normalized plot excluding 1-pentanol and 1-hexanol to better illustrate the slight retardation of 1-heptanol from IPA and tritium. The straight lines in the figure are the extrapolation of the tracer tails. The percent recovery of each tracer is shown in Table 6.9.

An estimate of tracer adsorption was made by calculating the first temporal moment of each tracer (Table 6.9) and comparing the ratio of the partitioning tracer to the conservative tracer (IPA). The retardation factor for 1-heptanol is 1.049 which is not within experimental error of 1 ± 0.03 . The adsorption for 1-heptanol is given in Table 6.11.

Table 6.9: Tracer data for ^{14}C 1-heptanol in Galveston soil

Tracer	Volume (cc)	R_f	Percent Recovery
IPA	55.6		98.9 %
tritium	56	1.007	100.1 %
1-pentanol	56	1.007	96.2 %
1-hexanol	56.6	1.017	92.9 %
^{14}C 1-heptanol	58.3	1.049	93.1 %

^{14}C 1-Octanol Tracer Test

The ^{14}C 1-octanol tracer test was performed in order to determine if any adsorption of 1-octanol occurs in the Galveston field soil. The tracers used were 1,951 mg/L IPA, 653,708 DPM/cc tritium, 821 mg/L 1-pentanol, and 80,654 DPM/cc ^{14}C 1-octanol. Unlabelled 1-octanol was added to the ^{14}C 1-octanol aqueous mixture. The concentration of 1-octanol in the tracer solution was 207 mg/L. IPA is the conservative tracer and 1-octanol the partitioning tracer. About

0.20 pore volumes, or 9.9 cc, of the tracer solution was injected at 0.25 cc/min (6 ft/day). The sample size collected was 3.0 cc. The normalized tracer response curves shown in Figure 6.8 show retardation of 1-octanol compared to IPA and tritium. The percent recovery of each tracer is given below in Table 6.10. The straight lines in Figure 6.8 are the extrapolation of the tracer tails.

An estimate of tracer adsorption was made by calculating the first temporal moment of each tracer (Table 6.10) and comparing the ratio of the partitioning tracer to the conservative tracer. The retardation factor for 1-octanol is 1.182 which is not within experimental error of 1 ± 0.03 . However, this was expected because data for 1-octanol had a R_f greater than 1.03 on Portsmouth soil, which had a lower f_{oc} than the Galveston soil tested in this experiment.

Table 6.10: Tracer data for ^{14}C 1-oct#1 in Galveston soil

Tracer	Volume (cc)	R_f	Percent Recovery
IPA	54.8		100.4 %
tritium	55.4	1.011	105.9%
1-pentanol	55.4	1.011	94.9%
^{14}C 1-octanol	64.8	1.182	102.9 %

Table 6.11 shows the adsorption data calculated using the 1st temporal moment for the ^{14}C 1-hept#1 and ^{14}C 1-oct#1 experiments in Galveston soil. The adsorption in mg per gram of soil is an order of magnitude larger for 1-octanol than for 1-heptanol.

Table 6.11: Adsorption Data for Galveston Soil ($f_{oc} = 0.11\%$)

Experiment	Injected Conc. (mg/L)	Retardation Factor	K_d (L/kg)	Adsorption (mg/g)
^{14}C 1-hept	112.8	1.0486	0.01389	0.00157
^{14}C 1-oct	207.3	1.1825	0.05217	0.01082

Table 6.12 gives error calculated from the K_d values expressed as an apparent NAPL saturation. These errors are larger than for Portsmouth soil but still very small in absolute terms.

Table 6.12: Residual TCE Saturation

Experiment	Error in TCE Saturation Estimate from Adsorption
^{14}C 1-hept	0.0295%
^{14}C 1-oct	0.0463%

Based on the data in Table 6.12, 1-heptanol and 1-octanol would have an affect on the residual TCE saturation estimate from the partitioning tracer data. At a residual TCE saturation of 1%, the partitioning of 1-octanol or 1-heptanol into SOC would add only 3% error in the estimate. However, at a residual TCE saturation of 0.1 %, the partitioning of 1-octanol or 1-heptanol into SOC would over predict the saturation by 30% for 1-heptanol and 46% for 1-octanol.

Conclusions/Recommendations

1. Adsorption of 1-heptanol (0.00157 mg/g) and 1-octanol (0.01082 mg/g) occurred in uncontaminated Galveston field soil ($f_{oc} = 0.11\%$).

2. Figures 6.7 and 6.8 show a retardation of the 1-heptanol and 1-octanol data compared to IPA in the tracer flood. The retardation factor of 1-heptanol was 1.05 (Figure 6.7) and 1.18 for 1-octanol (Figure 6.8).

6.3 CAMP LEJEUNE SOIL

The partitioning tracer selection for the Camp Lejeune soil was done by Varadarajan Dwarakanath of Duke Engineering and Services. The purpose of this section is to add data with a higher f_{oc} soil. The fractional organic carbon content of the soil was measured to be $f_{oc} = 0.182\%$ for experiment CL#1 and $f_{oc} = 0.2014\%$ for experiment CL#2. The objectives of these experiments were to quantify adsorption for 1-heptanol on a soil with a higher f_{oc} and compare with previous work. In both experiments, 1-propanol is the conservative tracer and 1-heptanol is the partitioning tracer. The water composition used in the experiments with Camp Lejeune field soil was 1,000 mg/L CaCl_2 .

Experiment CL#1

The following data were reported by Dwarakanath for experiment CL#1 and are summarized below in Table 6.13.

Table 6.13: Experimental Data for CL# 1

Tracer	1-heptanol
Injected Concentration (mg/L)	1034
Soil Bulk Density (g/cc)	1.534
Porosity	41%

A plot of the normalized tracer curves are shown in Figure 6.9. This plot shows considerable separation of the 1-heptanol data in the tail of the experiment relative to the IPA tail. In addition, the peak concentration for 1-heptanol lags behind the peak concentration for IPA. Table 6.14 gives the adsorption data for this experiment. The error in residual TCE saturation predicted by the distribution coefficient would overpredict a NAPL saturation of 0.1% by 58%.

Table 6.14: Adsorption Data for 1-heptanol in Experiment CL#1 ($f_{oc} = 0.182\%$)

Retardation Factor, R_f	1.126
Distribution Coefficient, K_d (L/kg)	0.03368
Adsorption (mg/g)	0.03482
Error in TCE Saturation Estimate from Adsorption	0.0577%

Experiment CM

The following data were reported by Dwarakanath for experiment CL#2 and are summarized below in Table 6.15.

Table 6.15: Experimental Data for CL#2

Tracer	1-heptanol
Injected Concentration (mg/L)	577
Soil Bulk Density (g/cc)	1.5
Porosity	42.3%

A plot of the normalized tracer curves are shown in Figure 6.10. This plot shows considerable retardation of 1-heptanol compared to IPA. In addition, the peak concentration for 1-heptanol lags behind the peak concentration for IPA. Table 6.16 gives the adsorption data for this experiment.

Table 6.16: Adsorption Data for 1-heptanol in Experiment CL#2 ($f_{oc} = 0.2014\%$)

Retardation Factor, R_f	1.169
Distribution Coefficient, K_d (L/kg)	0.04766
Adsorption (mg/g)	0.02750
Error in TCE Saturation Estimate from Adsorption	0.0605 %

This column was contaminated with about 6 saturation percent PCE and then a partitioning tracer test was performed using 1-propanol, 2,4-dimethyl-3-pentanol, 1-hexanol and 1-heptanol as the tracers. The estimated PCE saturation calculated from all of these partitioning tracers including 1-heptanol agreed with the mass balance estimate within the estimated experimental error of about 0.7 saturation percent. The saturation estimates from all of the partitioning tracers were within 0.2 saturation percent or 4 % of the PCE saturation. This difference is less than the apparent saturation of 0.48 % that would be expected from the additional retardation of 1-heptanol due to adsorption on this soil. This apparent saturation was calculated as before using the measured K_d and a partition coefficient for PCE of $K=35$. Thus, it would appear that the adsorption of the 1-heptanol did not contribute any significant error to the estimate of the PCE saturation. The reason for this is not understood but suggests that more research

needs to be done to investigate the effect of tracer adsorption using contaminated soil.

Table 6.17 gives the retardation factors for various alcohols in various clean soils measured experimentally in this study and by Dwarakanath (1997) and the corresponding values computed from substituting $K_{oc}f_{oc}$ for K_d in Equation 4.24. K_{oc} is the organic carbon partition coefficient with the same units as K_d . These values were reported by Jin *et al.* (1997b) for several alcohols. Although there are some differences larger than the expected experimental error, the trends with f_{oc} are the same and the overall agreement between the experimental and computed R_f values is good. Thus, when K_d has not been measured but the f_{oc} and K_{oc} values are known, one can make a first approximation of the retardation due to adsorption and the corresponding error in the estimated NAPL saturation from a PITT from this calculation, but of course direct measurements are always preferred and should be done on both clean and contaminated soil if possible using the actual NAPL and soil of interest.

Table 6.17: Comparison of experimental retardation factors with values computed from K_{oc}

Soil	f_{oc} (%)	3-Methy-3-pentanol	1-Pentanol		1-Hexanol		2,2-Dimethy 1-3-pentanol	1-Heptanol		1-Octanol	
			exp	calc	exp	calc		exp	calc	exp	calc
PPG	0.04				1.00	1.01		0.99	1.02		
Portsmouth	0.07	1.01			1.03	1.02	1.01	0.99	1.03	1.12	1.09
Plant4	0.09	1.02			1.02	1.02	1.01	1.00	1.03	1.04	1.09
Galveston	0.11		1.01	1.02	1.02	1.04		1.05	1.05	1.18	1.14
Hill	0.16	1.00			1.01	1.06	1.02				
Camp Lejeune	0.19				1.06	1.07		1.15	1.09		

Results/Conclusions

1. Adsorption of 1-heptanol occurred in uncontaminated Camp Lejeune field soil ($f_{oc} = 0.182\%$, 0.2014%). Experiment CL#1 had an adsorption of 0.03482 mg/g and experiment CL#2 had an adsorption of 0.0275 mg/g .
2. Figures 6.9 and 6.10 show a lag in peak concentrations and a retardation of the tracer tails of 1-heptanol compared to 1-propanol in the tracer flood.

6.4 TRITIUM ADSORPTION

Tritium was used as a conservative tracer for many of the experiments in this work. The tritiated hydrogen ion, ^3H , is exchangeable just like any other H^+ ion, especially replacing water that is bound to soil (Zemel, 1995). This exchange causes a slight lag in experiments of the tritium peak concentration with respect to IPA. This lag is evident in Figure 6.11, which was an experiment with a calcite field soil (Plant 4). Figures 6.12 and 6.13 are examples of two separate experiments done in Portsmouth field soil and the lag is more pronounced. Table 6.18 gives the retardation factor of tritium with respect to IPA. In each of these experiments, the retardation factor is not within the estimated experimental error.

Table 6.18: Adsorption Data for tritium from Plant4 and Portsmouth Field Soil

Experiment	Field Soil	f_{oc} (%)	Figure Reference	R_f
P4/OCT	Plant4	0.09	6.11	1.032
^{14}C 1-oct#1	Portsmouth	0.07	6.12	1.055
^{14}C 1-oct#4	Portsmouth	0.07	6.13	1.082

From the above data it is evident that ^3H exchanges with connate water and had a delayed arrival time with respect to IPA. Zemel(1995) describes a field test in the North Sea in which the tritium response was delayed with respect to an iodide tracer (I-125) that was used in the same field test. The results were explained on the basis that tritium tagged water was imbibed into the formation, thus delaying the arrival time. Agca (1987) used a reservoir simulator to model the reversible adsorption of tritiated water used as a waterflood tracer in an oil reservoir containing high amounts of montmorillonite and found it to be significant. Thus, tritium is not the best conservative tracer to use under some conditions. Light alcohols such as ethanol and propanol rather than tritiated water have been used as conservative tracers in the saturated aquifer PIITs to date.

6.5 CONCLUSIONS

It can be seen from the experiments presented in this chapter that there is an increase in the retardation factor for 1-heptanol and 1-octanol with increasing f_{oc} of the soil. More specific conclusions are:

1. Solution effects of adsorption typically act through their effects on solubility. In general, mechanisms which decrease solubility also increase adsorption of organic compounds, and vice-versa. However, the presence of high concentrations of alcohols can reduce adsorption and thus enhance mobility.
- 2 . Figure 6.14 illustrates the increase in K_d is proportional to the increase in f_{oc} for 1-heptanol and 1-octanol. Both tracers show an approximate linear correlation. The lines illustrating this correlation on the plot are a straight

line “eyeball” approximation with more weight being given to the data with a higher f_{oc} .

3. Figure 6.15 illustrates the increase in adsorption expressed in mg per g of soil with increasing f_{oc} for 1-heptanol and 1-octanol. The relationship is approximately linear for 1-octanol but not for 1-heptanol. The Galveston data point represents an injected concentration of 113 mg/L whereas the CL#1 and CL#2 data points represent injected concentrations of 1034 mg/L and 577 mg/L, respectively. This also accounts for CL#1 having a higher adsorption but a lower K_d because adsorption is strongly influenced by the injected aqueous concentration.
4. Adsorption is not always a single, simple process (Westall, 1987). Rather, some combination of interactions may be responsible for governing the association of any particular chemical with any particular solid. In many experiments, there is not a linear relationship between the concentrations in the adsorbed state (solid) and the dissolved state (aqueous). Schwarzenbach (1993) describes a situation in which previously sorbed molecules lead to a modification of the solid surface which favors further sorption. This phenomena is illustrated in Figures 6.1, 6.2, 6.3, 6.6, 6.7, and 6.8. There is an increased retardation of the tracers due to the coating of the solid which increasingly exhibits a nonpolar nature. This coating creates an increasingly nonpolar environment into which a hydrophobic compound (such as 1-heptanol and 1-octanol) may easily escape without undue competition from water.

Figure 6.1: Tracer concentration histories, experiment ^{14}C IPA#1 in Portsmouth soil ($f_{oc}=0.07\%$)

Figure 6.2: Tracer concentration histories, experiment ^{14}C 1-oct#1 in Portsmouth soil ($f_{oc}=0.07\%$)

Figure 6.3: Tracer concentration histories, experiment ^{14}C 1-hept#1 in Portsmouth soil ($f_{oc}=0.07\%$)

Figure 6.4: Tracer concentration histories, experiment ^{14}C 1-oct#2 in Portsmouth soil ($f_{oc}=0.07\%$)

Figure 6.5: Tracer concentration histories, experiment ^{14}C 1-oct#4 in Portsmouth soil ($f_{oc}=0.07\%$)

Figure 6.6: Tracer concentration histories, experiment ^{14}C 1-hept#1 in Galveston soil ($f_{oc}=0.11\%$)

Figure 6.7: Tracer concentration histories, experiment ^{14}C 1-hept #1 in Galveston soil (f_{oc} 11%). Figure excludes 1-pentanol and 1-hexanol data

Figure 6.8: Tracer concentration histories, experiment ^{14}C 1-oct#1 in Galveston soil ($f_{oc}=0.11\%$)

Figure 6.9: Tracer concentration histories, experiment CL#1 in Camp Lejeune soil ($f_{oc}=0.182\%$)

Figure 6.10: Tracer concentration histories, experiment CL#2 in Camp Lejeune soil ($f_{oc}=0.2014\%$)

Figure 6.11: Tracer concentration histories, experiment P4/OCT showing tritium lag in Plant 4 soil

Figure 6.12: Tracer concentration histories, experiment ^{14}C IPA#1 showing tritium lag in Portsmouth soil

Figure 6.13: Tracer concentration histories, experiment ^{14}C 1-oct#4 showing tritium lag in Portsmouth soil

Figure 6.14: Observed increase in K_d for 1-heptanol and 1-octanol as a function of the f_{oc} of the solid in a variety of soils

Figure 6.15: Observed increase in adsorption for 1- heptanol and 1- octanol as a function of f_{oc} of the solid in a variety of soils

Chapter 7: Summary and Conclusions

7.1 SUMMARY AND CONCLUSIONS

The main objectives of this work were to experimentally investigate suitable partitioning tracers for estimating the volume and/or saturation of dense nonaqueous phase liquids (DNAPLs) in saturated aquifers before and after surfactant remediation, and to quantify the error in the estimated NAPL saturation due to the adsorption if any of the partitioning tracers on soil from these aquifers. Column experiments were performed using soils of different organic carbon content.

1. A surfactant solution containing xanthan gum polymer to increase its viscosity was successfully used to remediate a soil column contaminated by Hill OU2 DNAPL. Approximately 99.9% of the DNAPL was recovered and no loss of hydraulic conductivity occurred due to the surfactant solution. The estimated residual DNAPL saturation before and after the surfactant flood of the soil column was measured using both a mass balance and partitioning tracers. The agreement between these measurements was good and helped validate the selection and use of partitioning tracers in the Hill OU2 DNAPL field tests done during 1996.
2. Previously, the heaviest alcohol that had been evaluated as a partitioning tracer was 1-heptanol. There is a need for partitioning tracers with even higher partition coefficients when the NAPL saturation is very low such as after a highly effective surfactant flood of an aquifer. Therefore, the static partition coefficient was measured for 1-octanol with TCE and water and

then a column experiment was performed using 1-octanol as one of the partitioning tracers. A very close agreement (2.5 %) between the partition coefficient measured using static experiments and column experiments was observed.

3. Experimental techniques for performing partitioning tracer tests were further developed by performing several column experiments to estimate residual DNAPL saturation in several different field soils. The average difference between the estimated residual DNAPL saturation based on mass balance and partitioning tracers was 0.1 saturation percent, which is only 3.1% of the DNAPL saturation measured by mass balance.
4. Hexafluoropropene was evaluated as a potential partitioning tracer for saturated tests with low NAPL saturation since it was expected to have a high partition coefficient due to its low water solubility and as a possible alternative to the heavy alcohols with high partition coefficients. A dynamic partition coefficient of 217 between TCE and water was estimated for C_3F_6 from a saturated soil column experiment contaminated with a known amount of TCE using the method of moments. C_3F_6 showed excellent tracer recovery and a good linear response in the gas chromatograph. Thus, hexafluoropropene is a promising candidate for a partitioning tracer for saturated tests and should be further investigated.
5. Experiments were done on uncontaminated soils with an f_{oc} of 0.07% and 0.11%. The retardation factor for 1-octanol was greater than 1.03 for both of these soils, which means adsorption was significant.

6. Experiments were done on soils with an $f_{oc} = 0.11\%$, 0.182% and 0.2014% . The retardation factor for 1-heptanol was greater than 1.03 for all three of these soils, which means that adsorption was significant.
7. A linear relationship was observed between K_d and f_{oc} with 1-heptanol and 1-octanol.
8. Tritium showed a retardation with respect to IPA in several soil column experiments indicating that it is not a completely satisfactory conservative tracer under these conditions.
9. When the DNAPL saturation is less than on the order of 0.1% , the adsorption of 1-heptanol and 1-octanol contributes significantly to the relative error of the DNAPL saturation estimate unless accounted for. A comparison with these and several other alcohol partitioning tracers measured in several soil column tests showed that the effect of adsorption could be approximately predicted from the f_{oc} and K_{oc} when known. Both direct measurements and estimates from K_{oc} indicate that in general the effect of alcohol adsorption on the estimated TCE saturation is negligible for soils with f_{oc} less than 0.1% and alcohols such as 1-hexanol that are lighter than 1-heptanol and 1-octanol although careful measurements should always be made for the precise case of interest.

7.2 FUTURE WORK

The following recommendations are made for future work:

1. More adsorption experiments should be done with soils having a f_{oc} in the range 0.15% to 1.0% to further investigate this relationship. Each

experiment should be conducted with the same tracers and injected concentrations so that they can be compared with each other appropriately.

2. Identify and develop suitable tracers with high partition coefficients that can accurately estimate low residual DNAPL saturations. The use of other perfluorocarbon tracers in saturated zone partitioning tracer tests should be investigated. In addition, there are a number of radiosotopes with short half lives that may be acceptable under some aquifer conditions.
3. More experiments should be conducted to identify the adsorption mechanism(s) responsible for the interaction of partitioning tracers and field soils.
4. Study the effect of tracer adsorption in non-isothermal applications. In addition, the accuracy of DNAPL estimation should be studied under non-isothermal conditions.
5. Study the applicability of partitioning tracers in naturally fractured media or dual porosity aquifers.

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