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The First Vadose Zone Partitioning Interwell Tracer Test for Nonaqueous Phase Liquid and Water Residual

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In 1995, a partitioning interwell tracer test was conducted in the vadose zone beneath two buried organic liquid disposal trenches at Sandia National Laboratories in New Mexico. The purpose was to estimate the amount and distribution of trichloroethylene (TCE) trapped by capillary forces as residual dense nonaqueous phase liquid (DNAPL). Screened injection and extraction wells, placed 16.8 m apart, and two monitor wells with multilevel sampling capability allowed vertical testing from 3.0 to 24.4 m below ground surface. Seven tracers were injected, but the most useful tracers in the final analysis were sulfur hexafluoride (nonpartitioning), perfluoro-1,3,5-trimethylcyclohexane (TCE-partitioning), and difluoromethane (water-partitioning). Both a TCE-partitioning tracer and a water-partitioning tracer were needed to determine average TCE DNAPL saturation. Average saturations of DNAPL and water were measured to be 0.11 ± 0.02% and 23 ± 2.0%, respectively, in the shallow zone between 3.0 and 10.7 m. Monitor well data showed no evidence of DNAPL below a depth of 9 m. These results had important implications for remedial actions at the site.

Introduction

In the spring of 1994, laboratory results were first presented illustrating the concept of an environmental partitioning interwell tracer test (PITT) for quantifying residual nonaqueous phase liquid (NAPL) contamination in the subsurface (*1*). The only previously performed PITTs for quantifying residual NAPL had been applied to oil reservoirs to measure residual oil saturation prior to enhanced oil recovery operations (*1*). By 1998, more than 30 environmental PITT field tests across the United States had been performed. While a majority of these PITTs were conducted below the water table, several were conducted in the vadose zone (*2*−*4*). This article presents results of the first PITT ever conducted in the vadose zone for NAPL and water residual.

A PITT is a new environmental application of chromatography. Chromatography is the separation of compounds by injecting a mixture of the compounds into a gas or liquid carrier stream that flows past a stationary phase. The compounds partition into the stationary phase to different degrees, resulting in slower migration of those compounds that have higher affinities for the stationary phase. In a vadose zone PITT, the mobile carrier is air and the stationary phase is typically water and/or NAPL residual.

A compound's affinity for a stationary phase is represented by the equilibrium partition coefficient, K_i. K_i is the equilibrium ratio of compound *i*'s concentration in the stationary phase divided by its concentration in the mobile phase. A high value for K_i implies a high affinity for the stationary phase.

A vadose zone PITT begins with the injection and extraction of air at opposite ends of a subsurface test zone. Once steady flow is established between the wells, a mixture of partitioning and nonpartitioning tracers is added to the injection stream for a short period of time, followed by continued air injection and extraction. During the PITT, tracer concentrations are monitored at the extraction wells and monitor locations. Plots of the tracer concentrations at these locations versus time (or versus cumulative injection volume) produce tracer concentration breakthrough curves that are used to quantify average NAPL and water saturations within the swept regions.

The retardation factor (R_i) for each tracer *i* provides a measure of the relative chromatographic separation of the tracers. R_i is computed directly from the set of tracer breakthrough curves at each sample location and is equal to the mean residence time of tracer *i* divided by the mean residence time of a nonpartitioning, conservative tracer (*5*). R_i can also be defined as (*6*)

$$R_i = 1 + \frac{\rho}{\theta}k_i \tag{1}$$

where ρ is the dry bulk density of the porous medium (kg L^{-1}), θ is the porosity, and k_i is the distribution coefficient for *i* (L kg^{-1}). The second term in eq 1 can be shown by dimensional analysis to be the ratio of the mass of *i* in the immobile phase to the mass of *i* in the mobile phase. For a vadose PITT, this ratio can be represented by the mass of tracer *i* in the immobile water and NAPL phases divided by the mass of tracer *i* in the soil air

$$R_i = 1 + \frac{c_{w,i}V_w + c_{n,i}V_n}{c_{a,i}V_a} \tag{2}$$

where $c_{a,i}$, $c_{w,i}$, and $c_{n,i}$ are the phase-specific concentrations (mg L^{-1}) of tracer *i* in the air, water, and NAPL and V_a, V_w, and V_n are the volumes (L) of air, water, and NAPL. Rearranging this equation and dividing the numerators and denominators by the volume of pore space V_t (i.e., the sum of V_a, V_w, and V_n) gives

$$R_i = 1 + \frac{\dfrac{c_{w,i}V_w}{c_{a,i}V_t} + \dfrac{c_{n,i}V_n}{c_{a,i}V_t}}{\dfrac{V_a}{V_t}} \tag{3}$$

The concentration ratios in this equation are equivalent to the water−air and NAPL−air partition coefficients for tracer *i* ($K_{w,i}$ and $K_{n,i}$), and the volume ratios are equivalent to the

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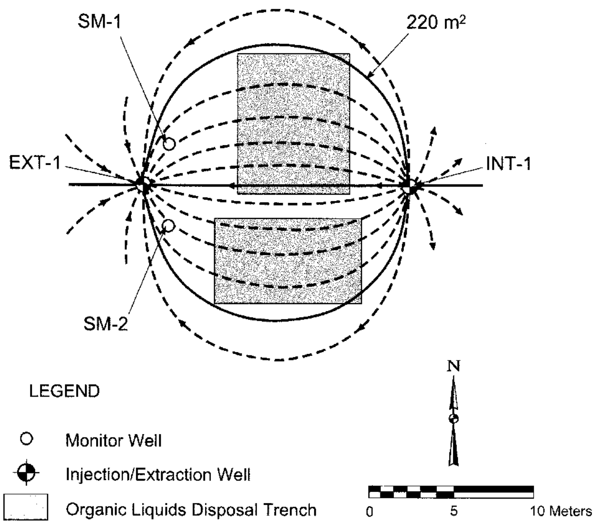

FIGURE 1. Aerial view of disposal trenches, wells, and flow field design.

average water, NAPL, and air saturations (S_w, S_n, and S_a). Thus, eq 3 reduces to

$$R_i = 1 + \left(\frac{K_{w,i}S_w + K_{n,i}S_n}{1 - S_w - S_n}\right) \qquad (4)$$

The denominator in eq 4 is equivalent to S_a.

The retardation factor for each breakthrough curve is determined from a first temporal moment analysis. Comparison of the integrated mean residence times of the partitioning and nonpartitioning tracers determines retardation factors for the partitioning tracers. These retardation factors, combined with the known partition coefficients, allow calculation of the average water and NAPL saturations within the swept volume. The swept volume is determined directly from the injection and extraction rates and the recoveries and first moments of the breakthrough curves of a nonpartitioning tracer. Detailed discussions of the analysis of PITT breakthrough curves, measurement and estimation of partition coefficients, and protocol for conducting a PITT can be found elsewhere (*1, 5, 7*−*11*).

Methods

Early in December of 1995, INTERA Inc. (now part of Duke Engineering & Services) and the University of Texas at Austin conducted a vadose zone PITT beneath two side-by-side organic liquid disposal trenches at the Chemical Waste Landfill, Sandia National Laboratories, Albuquerque, New Mexico. The purpose was to quantify residual dense nonaqueous phase liquid (DNAPL) in the alluvium beneath the disposal trenches and to estimate the depth of DNAPL penetration. Trichloroethene (TCE) had been recently discovered in five groundwater wells at the site at concentrations ranging from 0.005 to 0.023 mg kg^{-1}. These observations raised concerns that TCE DNAPL had possibly traveled to the water table 150 m below ground surface. A shallow and deep soil vapor survey revealed a vapor plume that encompassed an area of approximately 60 000 m^2 (at maximum extent) and vertically extended to the water table. On the basis of a sample of DNAPL recovered in a core, the DNAPL consisted of a mixture of TCE, other chlorinated hydrocarbons, PCB oils, and high molecular weight hydrocarbons. TCE, according to disposal records, was the DNAPL disposed in the greatest quantities at the landfill.

Figure 1 is a schematic aerial view of the buried disposal trenches at the site with the superimposed PITT flow field design. One injection well and one extraction well were installed 16.8 m apart on opposite sides of the trenches. Each well was screened and packed off at depths of 3.0 to 10.7, 12.2 to 18.3, and 19.8 to 24.4 m to allow injection and extraction for each of these intervals. In addition, two monitor wells were installed 3 m northeast and southeast of the extraction well to allow separate monitoring of zones to the north and south. Each monitor well contained eight sample points evenly spaced at depths of 3.05 to 24.4 m to allow high vertical resolution of measured DNAPL and water residual saturations.

Several conservative (nonpartitioning) tracer tests using perfluoromethane (CF_4) preceded the PITT to determine optimum PITT flow rates. They provided information about air permeability, channeling, concentrations to expect at the extraction well, and mean travel times for the test zone. After steady-state air injection and extraction rates were established, slugs of CF_4 were metered into the injection stream. The CF_4 injection rate was held constant at 0.037 L s^{-1}. Depending on the test, the duration of tracer injection ranged from 21 to 54 min and the air injection rate ranged from 3.5 to 9.9 L s^{-1}. Concentrations at the extraction and monitor wells were monitored every 5 min using an online photoacoustic analyzer until the breakthrough curves were obtained.

The PITT tracer slug was composed of a mixture of TCE-partitioning, water-partitioning, and nonpartitioning tracers, each having a total mass of 1 kg (except for methane which was 0.1 kg). The nonpartitioning tracers were methane (CH_4) and sulfur hexafluoride (SF_6). The TCE DNAPL-partitioning tracers were octafluorocyclobutane (C_4F_8), dodecafluorodimethylcyclobutane (C_6F_{12}), perfluoro-1,3-dimethylcyclohexane (C_8F_{16}), and perfluoro-1,3,5-trimethylcyclohexane (C_9F_{18}). The TCE−air partition coefficients for these six tracers were measured in column experiments to be 0, 1, 9, 16, 72, and 162 (nondimensional units by volume), respectively, while the corresponding water−air partition coefficients were all measured to be 0 (*8, 9*). On the basis of the likely range of average saturations of TCE in the test zone, the value of the partition coefficient of the "nonpartitioning" tracer SF_6 was too low for perceptible SF_6 retardation. The water-partitioning tracer, difluoromethane (CF_2H_2), which was included in the PITT tracer mixture, was measured to have a water−air partition coefficient of 1.7 and a TCE−air partition coefficient of 2.0 (*8*). Although these measurements indicate a slightly higher affinity for TCE than for water, eq 4 shows that the overall retardation of CF_2H_2 by TCE in the test zone is negligible when the average TCE saturation is less than 5% of water saturation, as it was in this case.

The tracer partition coefficients were measured in column experiments containing soil from the site under imposed water and DNAPL saturations (*8, 9*). In column experiments containing dry and moist clean soil from the site, the TCE-partitioning tracers behaved conservatively, which indicated that background soil organic matter or other materials in these soils would not retard the transport of these tracers.

The PITT tracers were mixed in an evacuated 6.25 m^3 holding tank. The tank pressure was then brought to 130 kPa with nitrogen. A large holding tank was needed to ensure that the heavier tracers remained in the gas phase. After steady-state air injection and extraction rates were established, air injection was diverted through the tank for 2 h to inject the tracers. Concentrations of the tracers were measured at 19 sample locations using two automated stream selectors connected to two online gas chromatographs. Each gas chromatograph could analyze approximately 30 samples per day.

Injection and extraction rates began at 3.3 L s^{-1} and increased to 5.7, 11, and 25 L s^{-1} after 2.0, 4.0, and 6.7 days,

TABLE 1. Average TCE DNAPL Saturations (%) Measured from the Breakthrough Curves at the Extraction Well (EXT-1) and Monitoring Wells (SM1 and SM2)

depth zone	EXT-1	depth (m)	SM1	SM2
shallow		3.0	0.18 ± 0.02	0.21 ± 0.05
(3.0−10.7 m)	0.11 ± 0.02	6.1	nd[a]	0.10 ± 0.016
		9.1	nd	nd
intermediate		12.2	nd	nd
(12.2−18.3 m)	nd	15.2	nd	nd
		18.3	nd	nd
deep		21.3	nd	nd
(19.8−24.4 m)	nd	24.4	nd	nd

[a] nd = not detected (less than 0.05%).

respectively. A low rate was needed at the start to allow time for tracer interaction with the NAPL and water. Time was also needed for sufficient sampling and analysis at the monitor locations to define the early parts of the breakthrough curves. As the PITT progressed, the rates were increased to obtain complete breakthrough curves at all locations within 15 days. Although higher flow rates increase the possibility of nonequilibrium partitioning, they do not affect the first moment (retardation factor) of a partitioning tracer breakthrough curve (*6*). Instead, they affect the spreading and skew of the breakthrough curve, i.e., the second and third moments (related to the Peclet and Damkohler numbers), which do not affect the NAPL or water saturation calculation. In practice, however, severe nonequilibrium conditions should be avoided in a PITT because they may result in long breakthrough curve tails at low concentrations that are difficult to measure precisely or are below detection limits.

Results and Discussion

The results of the initial CF_4 conservative tracer test revealed that mean residence times were much lower than expected, particularly in the intermediate zone. Previous studies in the immediate area had indicated much lower air permeability. In addition, large differences in mean residence times were evident between the shallow, intermediate, and deep zones. Consequently, not only were the flow rates reduced for the PITT but flow rates into each zone were adjusted to equalize, as much as possible, the mean residence times between the three zones. This adjustment allowed the two online gas chromatographs to collect sufficient breakthrough data at each sampling location. It also provided more residence time for tracers sweeping highly permeable zones. For the PITT, a 2:1:3 flow rate ratio for the shallow, intermediate, and deep zones was used to equalize the mean residence times.

The PITT required a total of 15 days. Below-freezing weather on several nights resulted in water condensation inside sample lines, causing the online gas chromatographs to malfunction temporarily. Nevertheless, sufficient data were collected over the course of the test to provide useful breakthrough curves. SF_6 and C_9F_{18} provided the most reliable nonpartitioning and DNAPL-partitioning tracer data. The results for each monitor location are presented in Table 1.

First moment analysis indicated that TCE DNAPL was present in the shallow zone. The average TCE DNAPL saturation in the shallow zone (3 to 11 m depth interval) was estimated to be 0.11 ± 0.02%. The shallow zone extraction well breakthrough curves are shown in Figure 2. At this location, C_9F_{18} migration was retarded by a factor of 1.2 ± 0.04. One monitor point at a depth of 3.05 m indicated a local TCE DNAPL saturation of 0.21 ± 0.05%, corresponding to a retardation factor of approximately 1.4 ± 0.09 (Figure 3). The monitor well data, as well as the extraction well data, show that TCE DNAPL decreased in volume with increasing depth. For an approximated shallow zone swept pore space volume of 620 m^3, the measured saturation is equivalent to approximately 680 ± 120 L of TCE. No DNAPL was detected in the intermediate or deep zones; breakthrough curves in these zones showed no chromatographic separation of tracers. The NAPL detection limit depends on the tracers used and the NAPL targeted. In this PITT, the estimated quantification limit for average NAPL saturation was approximately 0.05%.

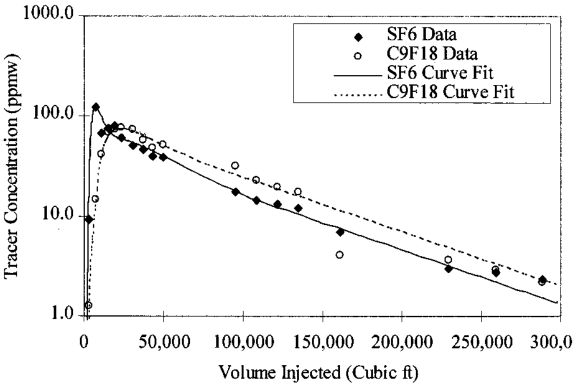

FIGURE 2. SF_6 and C_9F_{18} tracer breakthrough curves at EXT-1-shallow. The timing and peak SF_6 concentrations at the shallow monitor well locations attest to the timing and peak SF_6 concentration measured for EXT-1-shallow.

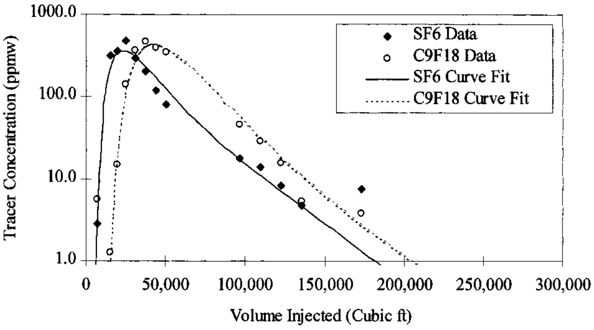

FIGURE 3. SF_6 and C_9F_{18} tracer response at shallow monitor point SM2-10, located 3.0 m below ground surface.

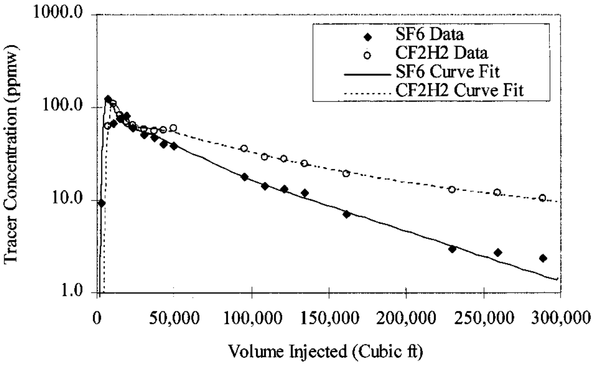

FIGURE 4. Breakthrough curves of shallow zone SF_6 and CF_2H_2 indicate 23 ± 2.0% water saturation.

Average water saturations were estimated from first moment analysis of SF_6 and CF_2H_2 breakthrough curves. The breakthrough curves for the shallow zone are displayed in Figure 4. Results indicate that average water saturations at the time of the PITT decreased with depth. For the shallow, intermediate, and deep zones, the measured average water saturations were 23 ± 2.0, 13 ± 1.2, and 10 ± 1.9%, respectively.

The results of this PITT had important implications for DNAPL remediation efforts at the site. The PITT measurements of average DNAPL saturation, DNAPL volume, and spatial distribution provided crucial information for predicting the amount of time necessary to remove the TCE by a soil vapor extraction system which was subsequently designed and operated. In addition, the results indicated that TCE DNAPL at the site was confined to the top 9 m and that the observed concentrations of TCE in deep groundwater more likely resulted from another process, such as the migration of a dense vapor plume. These results ultimately led to the decision that a combination of soil excavation and vapor extraction would satisfy site cleanup objectives.

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