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Application of a  
NAPL Partitioning Interwell Tracer Test (PITT) to  
Support DNAPL Remediation  
at the  
Sandia National Laboratories/New Mexico  
Chemical Waste Landfill

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by

James E. Studer, P.E., P.G.  
INTERA Inc.  
Albuquerque, New Mexico

Paul Mariner and Minguan Jin, Ph.D.  
INTERA Inc.  
Austin, Texas

Gary Pope, Ph.D. and Daene McKinney, Ph.D.  
The University of Texas at Austin

and

Richard Fate  
Manager, Environmental Restoration for  
Landfills and Test Areas  
Sandia National Laboratories/New Mexico

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## Abstract

Chlorinated solvents as dense non-aqueous phase liquid (DNAPL) are present at a large number of hazardous waste sites across the U.S. and world. DNAPL is difficult to detect in the subsurface, much less characterize to any degree of accuracy. Without proper site characterization, remedial decisions are often difficult to make and technically effective, cost-efficient remediations are even more difficult to obtain. A new non-aqueous phase liquid (NAPL) characterization technology that is superior to conventional technologies has been developed and applied at full-scale. This technology, referred to as the Partitioning Interwell Tracer Test (PITT), has been adopted from oil-field practices and tailored to environmental application in the vadose and saturated zones.

A PITT has been applied for the first time at full-scale to characterize DNAPL in the vadose zone. The PITT was applied in December 1995 beneath two side-by-side organic disposal pits at Sandia National Laboratories/New Mexico (SNL/NM) RCRA Interim Status Chemical Waste Landfill (CWL), located in Albuquerque, New Mexico. DNAPL, consisting of a mixture of chlorinated solvents, aromatic hydrocarbons, and PCB oils, is known to exist in at least one of the two buried pits. The vadose zone PITT was conducted by injecting a slug of non-partitioning and NAPL- partitioning tracers into and through a 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. The extracted gas stream was sampled over time to define tracer break-through curves. Soil gas sampling ports from multi-level monitoring installations were sampled to define break-through 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 utilized were perfluorocarbons and sulfur hexafluoride which are non-toxic and stable.

PITT design involved numerical modeling using a three-dimensional, multi-phase, multi-component, finite-difference simulator, UTCHEM, and laboratory batch and column studies for tracer selection. After the PITT was conducted, field data were synthesized and a preliminary evaluation

completed. Data analysis completed at the time of this writing indicates that DNAPL has penetrated non-uniformly to approximately 80 feet below ground surface (bgs), has decreased in volume with increasing depth, and has laterally spread somewhat beyond the physical limits of both pits. Detailed analysis, including method of moments and inverse modeling with UTCHEM, is in progress.

The desired final PITT results include estimates of average DNAPL saturation, and vertical and lateral extent of DNAPL, within the tested zone. The PITT results are being used as a design basis for a Voluntary Corrective Measure (VCM) aimed at cost-effectively addressing DNAPL contaminated sediment, the primary source of soil gas vapors and groundwater contamination at the site. It is anticipated that the resulting VCM design will be more readily acceptable to the various stakeholders and promote a more rapid RCRA Closure of the landfill than would otherwise be the case if the PITT had not been performed.

### Introduction

Subsurface contamination by non-aqueous phase liquids (NAPL) is a serious problem at hundreds of industrial facilities and commercial properties around the world. This is particularly the case for those sites where the NAPL consists of chlorinated solvents, creosote, and coal tars that are denser than water (referred to as DNAPL). DNAPL contaminated sites typically involve extensive groundwater contamination due to complex transport-dissolution characteristics and the persistent nature that DNAPL constituents often exhibit (Schwille, 1988). DNAPL present solely in the vadose zone can cause groundwater contamination via vapor-phase transport (Baehr, 1987).

Corrective action at many of these sites is hampered by the uncertainty of whether DNAPL is present and, if so, a lack of detailed information on the three dimensional extent and volume of DNAPL within the geologic medium. For a large number of such sites, this uncertainty about DNAPL exists principally for two reasons. First, inadequate resources are assigned to properly characterize the nature of the contamination and, second, inadequate technologies and protocols are utilized for DNAPL detection and quantification. The consequence of this situation is

ineffective or inefficient soil and groundwater cleanup operations that may be sustained for years before the eventuality of failure to meet negotiated clean-up goals is realized.

Currently available technologies such as borehole drilling, collection and analysis of soil, soil gas, and ground water samples, surface and borehole geophysical sensing, and cone penetrometry profiling do not provide reliable, spatially-integrated estimates of DNAPL presence, three-dimensional extent, and average in-situ volume. Until recently, no in-situ technology has been demonstrated to successfully detect and spatially quantify the in-situ distribution of DNAPL. DNAPL-impacted sediments have recently been detected and characterized in the saturated zone, and now in the vadose zone, using a technology referred to as the Partitioning Interwell Tracer Test (PITT).

Figure 1 presents the basic concept of a PITT, as applied to a vadose zone setting. Essentially, the PITT is based upon linear, equilibrium partitioning of tracers between the gaseous phase (soil gas) and non-aqueous organic liquid phase (Jin, et al., 1995).

Within the context of tracer pulse transport through a forced-gradient flow field, the behavior of one or more NAPL partitioning tracers is observed against that of a conservative tracer. Figure 2 illustrates tracer pulse behavior at various times of transport within a constant forced-gradient field. This flow field was created within a laboratory sand box by an injector-producer well couplet (Pickens, 1977). Five separate conservative tracer pulses are shown.

With proper attention given to tracer selection, flow field, sampling design, and data analysis strategies, it is possible to develop accurate estimates of the average NAPL saturation and physical distribution within the vadose zone test area. The basic concept of the PITT applies equally well to a saturated zone setting (Jin, et al., 1995; Annable et al., 1994).

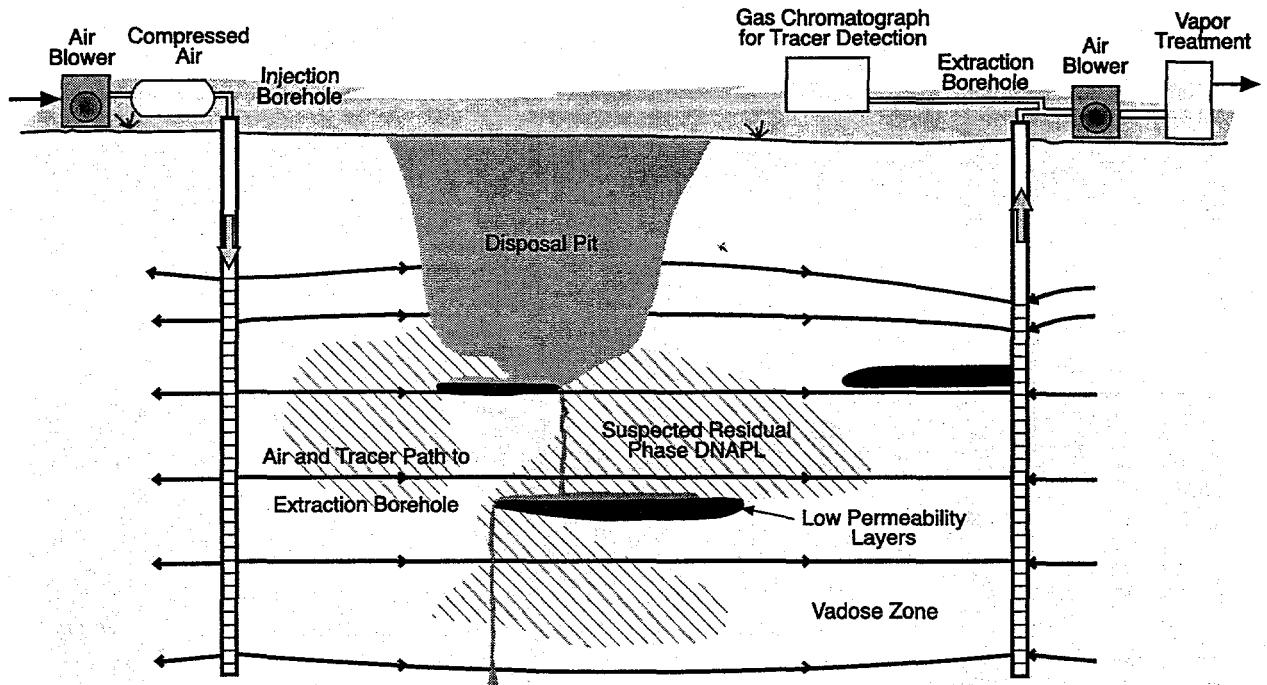


Figure 1. The Vadose Zone Partitioning Interwell Tracer Test

The use of partitioning tracers has recently been transferred and modified from oil-field application where it was first developed in the 1970's to characterize gas and oil reservoirs (Deans, 1978; Cooke, 1971). The first field test of partitioning tracers to characterize DNAPL in the saturated zone at a contaminated site was completed in 1994 at Hill Air Force Base, near Salt Lake City (Annable, et. al., 1994). The current paper describes the first full-scale demonstration/application of a PITT to characterize DNAPL in the vadose zone.

The PITT was conducted in December 1995 by University of Texas-Austin and INTERA Inc. for the Sandia National Laboratories/New Mexico (SNL/NM) Environmental Restoration (ER) Project. The site of this PITT was the RCRA Interim Status Solid Waste Management Unit known as the Chemical Waste Landfill (CWL), located in Technical Area III of SNL/NM (Figure 3). The test objectives were to 1) demonstrate the viability of the partitioning tracer technology in a full-scale vadose zone application,

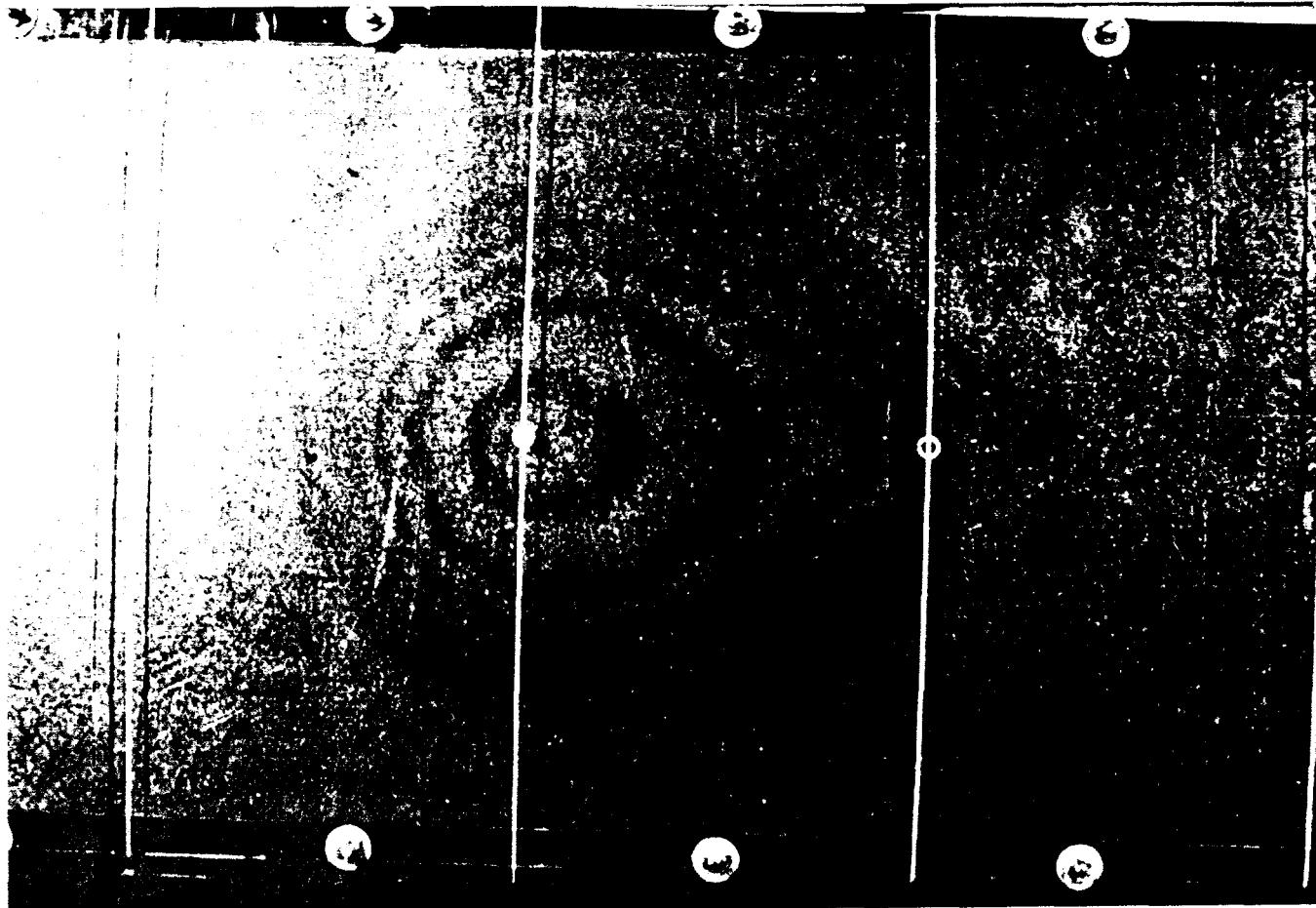
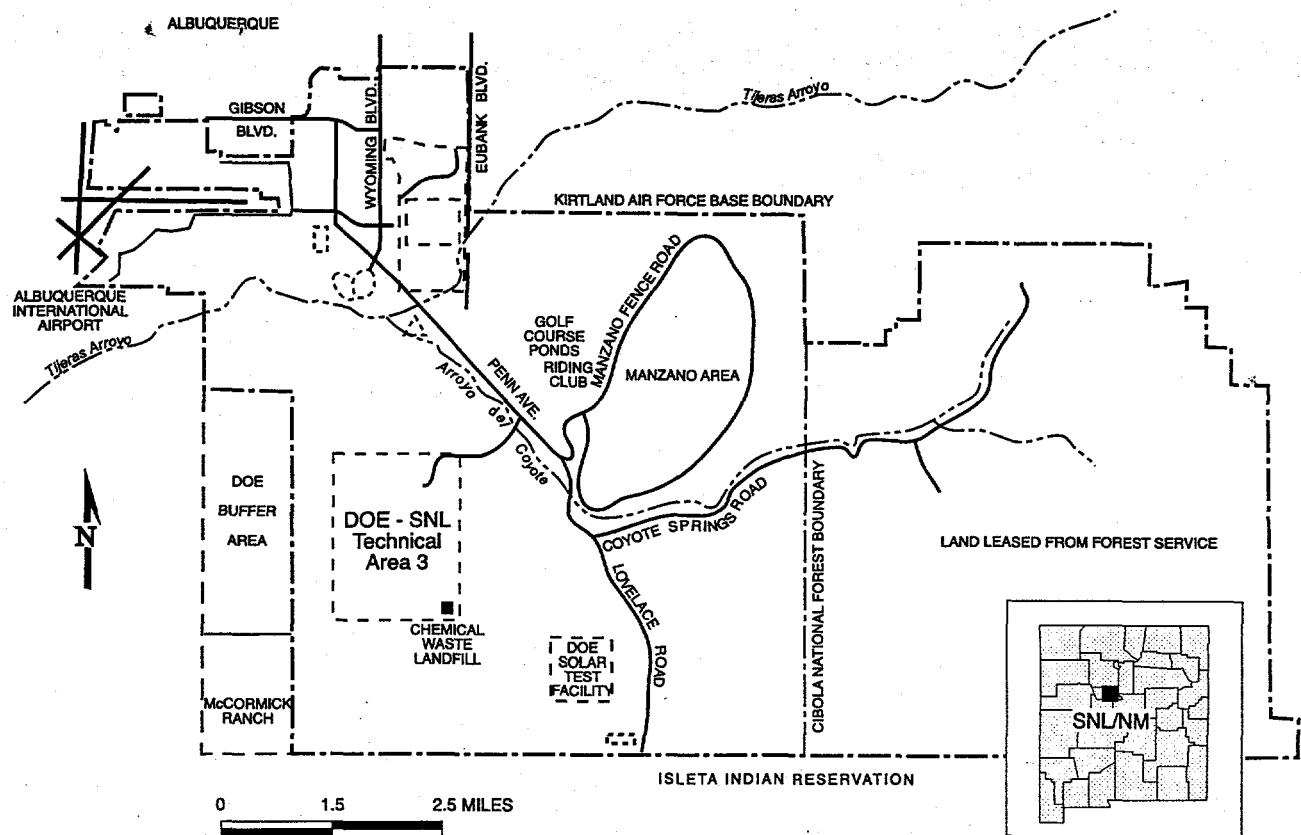


Figure 2. Composite progression of tracer pulse transport under well couplet forced-gradient flow field.

2) characterize the vertical and lateral extent of DNAPL migration within a test zone beneath two organic pits, 3) quantitatively estimate the average DNAPL saturation and the total volume of DNAPL within the test zone. The preliminary results presented in this paper indicate that the basic test objectives will be met by the PITT. The results are being used as a design basis for corrective actions that must be substantially completed before regulatory closure of the CWL can be obtained. The following sections will describe the site, the PITT design preliminary results and how the PITT results will be used in the corrective action process for the CWL.

#### Background on the Chemical Waste Landfill

The CWL is a 1.9 acre inactive landfill. The CWL was used for the disposal or storage of hazardous wastes generated at



Modified from SNL/NM

Figure 3. Site Location of Chemical Waste Landfill, SNL/NM

SNL/NM 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 (Figure 4). Wastes, in either bulk liquid or containerized form, were separated and placed according to physical properties and chemical/physical compatibility. When a pit filled, a new pit was excavated. According to waste disposal inventory records, trichloroethane (TCE) was disposed in the highest quantities. In 1981, all liquid waste disposal in unlined trenches ceased and the pits were backfilled (SNL/NM, 1992).

SNL/NM is located near the east-central edge of the Albuquerque Basin, a north-south-trending basin that is part of the Rio Grande rift zone. The Albuquerque Basin is filled with a thick sequence [up to 3,636 m (12,000 ft)] of primary and re-worked sediments eroded from the surrounding highlands or deposited by the ancestral Rio Grande. This sequence of sediments, called the Santa Fe Group, thins toward the edges of the basin and is truncated at the bounding uplifts. Basin-fill alluvial fans of the Santa Fe Group consist of channels, debris flows, flood-plain

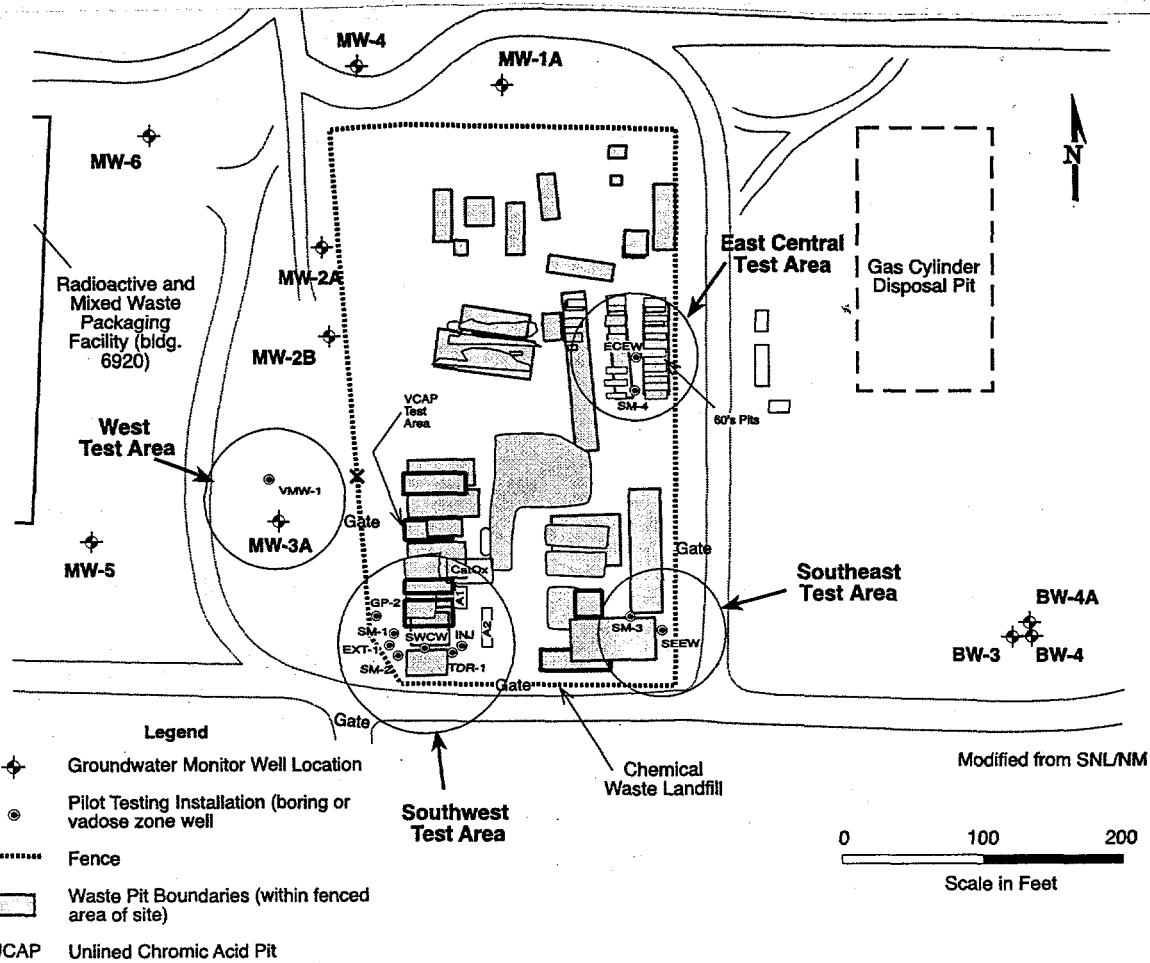


Figure 4. Site map showing known buried trench locations, monitoring wells, and the southwest pilot test area.

deposits, and eolian deposits. The upper saturated portion of the Santa Fe Group sediments within the Albuquerque Basin provides the primary source of potable water for the central Rio Grande valley. Ground water in the basin generally exists under unconfined conditions; however, confined or semi-confined conditions exist locally (Bjorklund and Maxwell, 1961).

The sediments underlying the CWL are a heterogeneous sequence of unconsolidated to semi-consolidated cobbles, gravels, very-fine to fine sands, silts, and clays of alluvial and fluvial origin. These sediments 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 a higher

percentage of clay, clayey sand, and silt layers with depth (SNL/NM, 1995a).

The upper vadose zone (upper 100 ft) is relatively heterogeneous and anisotropic with lateral layering. It consists mostly of gravelly sand, with some silty sand interbeds (SNL/NM, 1995a). Typical sediment moisture contents in this semi-arid environment range from approximately 3 to 7 percent by weight. Average infiltration and groundwater recharge rates are almost negligible (SNL/NM, 1995). Previous air permeability testing and vapor extraction tests over the upper 100 feet of the vadose zone indicate air permeabilities range approximately from 1 to 250 darcy (generally  $10^{-8}$  to  $10^{-6}$   $\text{cm}^2$ ), depending on the scale of testing method (Phelan, 1994).

At the CWL, the water table is approximately 490 ft bgs. The water table is typically encountered in unconsolidated silt, fine sands and clayey silts. Municipal pumping, including KAFB production wells located approximately 4 mi north of the CWL, have impacted the natural gradient in addition to lowering the water table elevation (Kues, 1987). Based on water-level data and aquifer testing of CWL wells, ground water flows toward the northwest at a rate of approximately 1 ft per year (SNL/NM, 1995a).

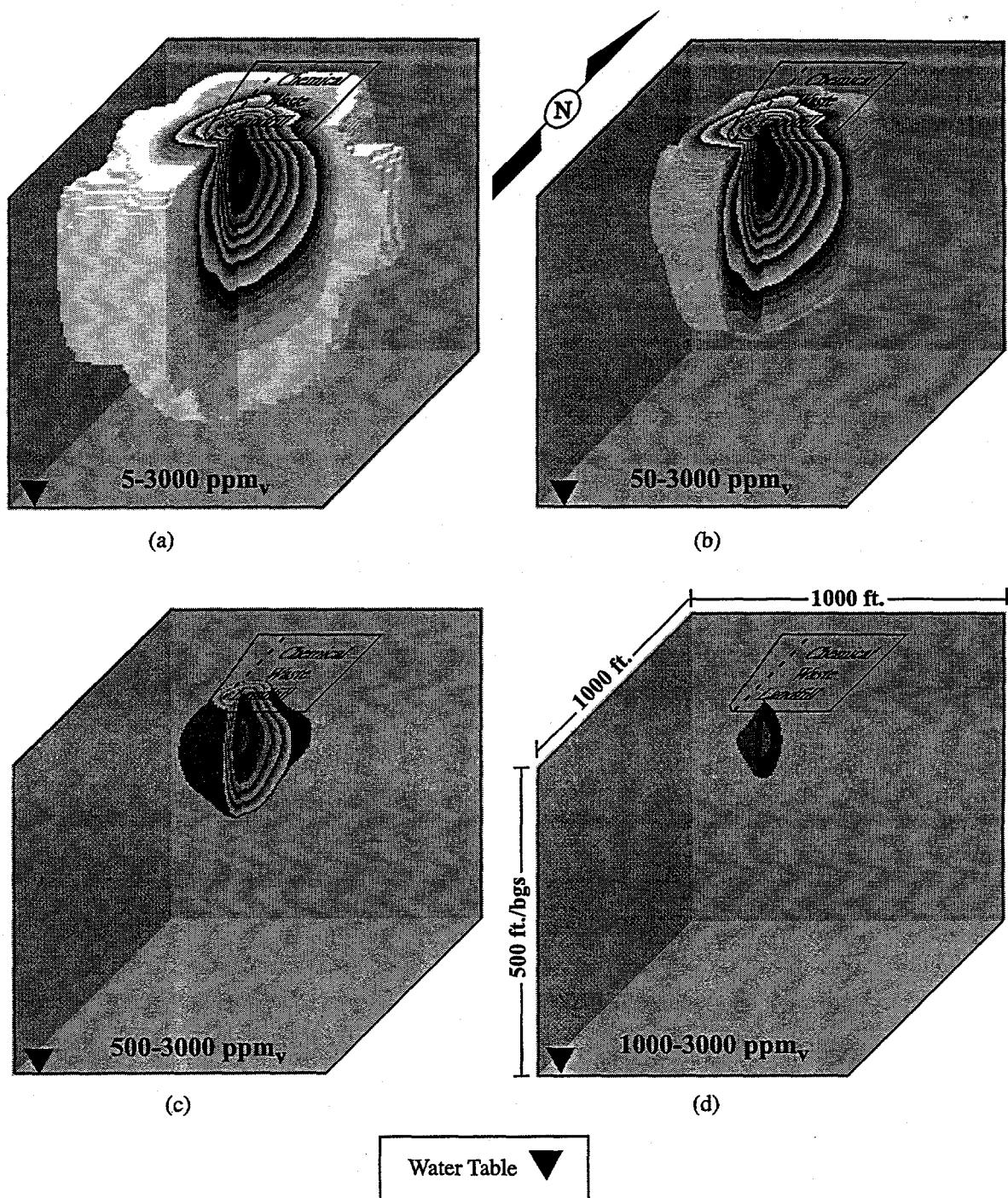
Ground-water monitoring has been performed at the CWL since 1985. Figure 4 shows the current monitoring well network. During routine ground water monitoring performed in May 1990, TCE was detected in MW-2A at a maximum concentration of 23 ppb<sub>v/v</sub>. Subsequent quarterly assessment monitoring events have routinely shown detected TCE ground water concentrations between 5 and 15 ppb<sub>v/v</sub> in wells MW-2A, MW-2B, MW-3A, MW-5, and MW-6. Other volatile organic constituents (VOCs) such as tetrachloroethene (PCE) and 1,1,1-trichloroethane (TCA) have been detected at concentrations lower than detected TCE concentrations. These data indicate that a ground water plume is present beneath and downgradient of the CWL (SNL/NM, 1995).

The ground water plume is likely caused by a soil gas VOC vapor plume beneath and around the CWL. It encompasses approximately 15 acres in area and extends to the groundwater surface at 490 ft bgs. VOCs contained in the

soil gas vapor plume come in contact with, and partition into, the groundwater (SNL/NM, 1993 and 1995). The source of the soil vapor plume is VOCs that were disposed in pits during the time the landfill was in operation. These contaminants are present as containerized or residual NAPL in certain organics disposal pits or as residual NAPL in the pore spaces beneath some of these pits. The VOCs that have migrated into the groundwater appear to have originated primarily from two disposal pits located in the southwest quadrant of the CWL.

In 1992 and 1993, shallow and deep soil-vapor surveys (SVS) were performed within and around the CWL to define the source locations and the extent of five target VOCs (TCE, TCA, PCE, carbon tetrachloride, and dichloromethane) in soil vapor. The shallow SVS was conducted at depths of 10, 30 and 50 ft bgs. The deep SVS was conducted to depths ranging between 130 and 200 ft bgs. The highest concentration of total target VOCs in soil and soil gas were detected near the southwest corner of the CWL (SNL/NM, 1993). The highest total target VOC concentration detected in soil was 9,500 ppm<sub>v/v</sub> at 6.5 ft in a boring next to two organics disposal pits. This high concentration was associated with an oily DNAPL encountered at 6.5 ft during drilling of this boring. The DNAPL was sampled and analyzed to determine major components. Besides TCE, other chlorinated and aromatic compounds were detected. Results of the SVS confirmed the presence of a vapor plume that extends outside the CWL fenced area to the southwest and southeast. The highest detected TCE soil vapor concentration was 2,928 ppm<sub>v/v</sub> taken at a depth of 18 bgs from a boring next to the same two organics pits. Soil gas analyses indicated the potential presence of DNAPL as deep as 50 feet bgs at one location beneath these two organics pits (SNL/NM, 1993).

Figure 5 presents three-dimensional cut-aways of the soil gas vapor plume at various TCE concentration ranges. These illustrations were produced using concentrations derived from numerical modeling of vapor-phase transport at the CWL. These results are in agreement with the field-derived SVS sampling data collected in the upper 220 feet of the vadose zone (Elmer Klavetter, personal communication, 1996). The modeling results are also in good agreement with soil vapor concentration data collected during the period 1992 to 1995



*Note: vertical to horizontal scale ratio = 2:1*

Figure 5. Four perspectives of the soil gas TCE vapor plume developed from vapor-phase modeling results with a TCE DNAPL source beneath southwest organics pits. (a) at 5 to 300 ppm<sub>v/v</sub>; (b) 50 to 3000 ppm<sub>v/v</sub>; (c) 500 to 3000 ppm<sub>v/v</sub>; (d) 1000 to 3000 ppm<sub>v/v</sub>.

from above the water table through packer-isolated monitoring well screens. As a point of reference, soil gas containing TCE vapor at a concentration of 5 ppm<sub>v/v</sub> can cause (per Henry's constant) a ground water concentration of greater than 5 ppb TCE.

- The SNL/NM ER Project is responsible for completing corrective actions at the CWL and obtaining final regulatory closure (SNL/NM, 1992). The schedules for corrective action and final closure are highly interdependent and strongly influenced by the soil gas vapor plume and ground water plume. Consequently, although no imminent threats to human health exist because of the CWL, SNL/NM is initiating voluntary corrective measures (VCMs) to expedite reductions in the VOC sources, i.e., the vapor plume and the NAPL source(s). A vapor extraction VCM and a focused excavation/stabilization VCM are in the planning stages. Expected benefits include reduced long-term risks, enhanced future land-use options, reduced over-all costs, and enhanced public perception. Through enhancement of our understanding of DNAPL occurrence at the CWL, the PITT will help ensure successful outcomes for both VCM.

#### PITT Design and Execution

The theoretical and experimental foundation for partitioning interwell tracer testing for NAPL characterization in either the saturated zone or vadose zone has been published elsewhere (Jin, et. al., 1995; Pope, et. al., 1995). A properly designed PITT will provide quantitative information on average NAPL saturation and total NAPL volume, in addition to the basic information about NAPL presence or absence in the test zone that can be obtained from a cursory review of tracer breakthrough curves. This volumetric information is derived from the break-through curves through application of method of moments.

The details of the method of first moment theory for the NAPL partition interwell tracer test can be found in Jin et al. (1995) and Jin (1995). We only give some pertinent equations which relate to the estimation of NAPL volume here.

For a partitioning interwell tracer test with variable injection and production rates, multiple injectors and producers, and open test boundaries, the volume of NAPL in the swept pore volume of producer  $i$  ( $V_i$ ) is calculated as,

$$V_i = \frac{m_i (\bar{v}_p - \bar{v}_n)}{M K}$$

where  $M$  is the total mass of tracer injected,  $m_i$  is the total mass of tracer produced from the producer  $i$ .  $K$  is the partition coefficient of the partitioning tracer defined as the ratio of the tracer concentration in NAPL phase to that in air phase,  $v_n$  and  $v_p$  are the first moments of the nonpartitioning and partitioning tracers, respectively, and obtained by integrating the corresponding tracer response curve over the total volume of air injected ( $v$ ) as

$$\bar{v} = \frac{\int_0^{v_f} v C(v) dv}{\int_0^{v_f} C(v) dv} - \frac{v_s}{2},$$

where  $v_f$  is the total volume of air injected at tracer test cutoff time and  $v_s$  is the total volume of air injected at the end of tracer slug injection.

The total volume of NAPL ( $V_N$ ) is the summation of the volumes estimated from each producer and is given by

$$V_N = \sum_{i=1}^{N_p} V_i$$

where  $N_p$  is the total number of extractors.

For an unsaturated zone partitioning interwell tracer test, the retardation factor  $R_f$  is related to the partition coefficient and average NAPL saturation  $S_N$  by

$$R_f = 1 + \frac{KS_N}{1 - S_{wr} - S_N} = \frac{\bar{v}_p}{\bar{v}_n},$$

where  $S_{wr}$  is the residual water saturation.

In order to estimate the NAPL volume accurately, the tracer response curves should be complete, because much of the information is contained in the tail of the response curves. Unfortunately, the tracer response curves are often incomplete either due to the dilution of the tracer concentration below the detectable limit or to the limitation of the duration of the tracer tests, or for some other reason. However, the tracer response curves can be extrapolated with an exponential function provided the duration of the test is sufficient to establish this decline.

The practical full-scale implementation of the partitioning theory and experimental background required consideration of the test site subsurface conditions including geology, vadose zone hydrology and hydraulics, geometry of waste pits, DNAPL and soil vapor plume characteristics. These considerations formed important bases for the PITT design. The PITT design included these important design parameters: general orientation of forced-gradient flow field in relation to pits and underlying contaminated sediment; number, spacing and depth of injection and extraction wells; injection and extraction well screen interval geometry, tracer pulse composition and mass of individual tracer; mean pulse velocity (i.e., mean residence time stated in pore volumes) and overall PITT duration; ground surface cover; soil gas monitoring device type, spacing and depth; soil gas sampling frequency; and analytical quantification issues including procedures for minimizing interferences due to background vapor contamination.

The following list represents the general phases of the PITT design:

- development of PITT objectives and conceptualization of test lay-out,
- numerical modeling to establish basic test conditions

and the relative sensitivity of the basic design to various site and hydrogeologic features (e.g., surface infiltration potential, permeability anisotropy, DNAPL distribution),

- selection of tracers via laboratory column studies followed by numerical model confirmation,
- finalization of preliminary detailed field test configuration and system construction, and
- completion of pre-PITT conservative tracer tests (CTT) designed to test the preliminary design and field set-up, followed by updating of conceptual and numerical models using the CTT field results to finalize the PITT design.

All of these phases are crucial to a successful outcome. However, as experience is gained from completion of PITTs in different settings, it is anticipated that the need for laboratory testing for tracer selection will diminish, and the overall design process will become more streamlined.

UTCHEM, a three-dimensional, multi-phase, multi-component, finite-difference, chemical compositional simulator developed at the University of Texas for enhanced oil recovery applications and recently adapted to model surfactant remediation and other related subsurface transport in permeable media problems (Brown, et al. 1995, Delshad, et al. 1996), was the numerical simulator used for this PITT design. Numerical modeling was conducted at specific stages of the PITT design and served as the initial design scoping tool and integrator of all subsequent design phases. Project and laboratory information was rapidly and quantitatively synthesized as it became available and field results from the pre-PITT conservative tracer tests were modeled as soon as the individual tests were completed. Final PITT design details (in particular flow rates and test duration) were based upon the CTT history-matching and mean residence time optimization modeling. Simulation modeling prior to the realization of the PITT in the field was used to gain insight into some pertinent design parameters. The parameters include: such the selection of tracers with an appropriate range of partitioning coefficients, amount of tracers needed, and injection and extraction pattern and

rates. Each of these design parameters affect the duration of the tracer test and the test outcome.

In order to establish a near-optimum design prior to performing pre-PITT field tests using conservative tracers, a number of sensitivity study cases were simulated using UTCHEM. These sensitivity study cases included evaluation of the following parameters: the injection and extraction rates, the amount and distribution of DNAPL contamination, the amount of tracer injected, the permeability field, the top surface boundary (closed or open), and the screen interval of the injector (Jin, 1995). Based upon the results of these sensitivity studies and other project constraints, a preliminary operation design was chosen. A near-optimum design was completed after the CTT sequence was performed and evaluated. The most important design features and the rationale behind the chosen design are as follows.

The choice of injection and extraction well location and screen intervals: Two wells were chosen for the partitioning interwell tracer test, one injection well and one extraction well. The intent was to create a forced-gradient flow field within a well couplet configuration (similar to that shown in 2). The well couplet was designed for a 55 ft spacing and development of a forced-gradient flow field over an approximate 70 feet vertical section of the vadose zone, from 10 to 80 ft bgs. This geometry satisfied the basic project objective of creating a flow field that would allow thorough contact of tracer with DNAPL-containing sediment potentially present below the subject disposal pits. The extraction well also served the dual purpose of a pilot well to allow for concurrent vapor extraction pilot testing in the southwest test area.

Both wells were designed and constructed to have identical features. Nominal five inch schedule 40 PVC casing and slotted screen were specified. Well screen intervals were selected so that three zones within the overall 70 feet 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 vertically-segmented injection and extraction scheme was chosen based on the site lithology and

simulation results suggesting that vertical-cross flow would not be highly significant (less than 10 percent cross flow due to dispersion in a horizontal flow field). This configuration would allow estimation of the total volume of the NAPL within the 70 feet zone. With adequate sampling of each isolated tracer-soil gas effluent stream, independent estimation of NAPL volume within each of the three zones would also be possible.

The choice of monitoring point location and depth: If average DNAPL saturation and total DNAPL volume within a test volume are the only questions that need to be answered, an injection/extraction well couplet is all that is necessary. Vertical segmentation of the test zone as described above is not required. For our test, the important additional objectives of developing more accurate information on the vertical and lateral extent of DNAPL migration drove the decision to segment the well couplet vertically and to design and install multi-level soil gas monitoring installations. UTCHEM modeling results suggested that one multi-level monitoring installation located approximately 10 feet to either side of the extraction well would allow for sampling from individual stream-tubes without significantly disrupting the overall sampling and analysis frequency. Taking this approach, it is possible to independently investigate the presence or absence of DNAPL within individual streamtubes of unique depth and unique spatial orientation relative to the physical limits of the pits themselves.

The choice of tracers: There are a number of tracer performance criteria that must be met for field applications. Some of these are environmental acceptability, chemical and biological stability, insensitivity to the precise composition of all pertinent fluids, low detectable limits, cost effectiveness and reasonable market availability. Perfluorocarbon tracers (PFTs) utilized in the vapor phase for oil reservoir studies (Senum, et al., 1992) were screened for use in our tracer test (Whitley, et al., 1995). These tracers are very stable, inert, available at low cost, have highly desirable properties, and are not present even in very low quantities in the contaminated zone. Sulfur hexafluoride was another tracer screened as a nonpartitioning tracer. Although it does partition into the organic phase, its partition

coefficient is not large enough to be noticeably retarded under our test conditions.

The tracers and their experimentally determined partitioning coefficients are shown in Table 1. These tracers were selected based on laboratory batch and column experiments (Whitley, et al., 1995). These experiments included tests on various mixtures of TCE, and volatile and semi-volatile aromatics. Table 1 includes values for TCE only. The partitioning behavior of these tracers has been shown to be very similar for other chlorinated aliphatics, and aromatics like benzene.

Table 1  
Tracers used in the CTTs or PITT.  
Partition coefficients are relative to TCE.

Tracer	Partition Coefficient, K
helium (He)	0
tetrafluoromethane (CF <sub>4</sub> )	0
sulfur hexafluoride (SF <sub>6</sub> )	1
octafluorocyclobutane (C <sub>4</sub> F <sub>8</sub> )	7.5
dodecafluorodimethylcyclobutane (C <sub>6</sub> F <sub>12</sub> )	15
perfluoro-1,3-dimethylcyclohexane (C <sub>8</sub> F <sub>16</sub> )	73
perfluoro-1,3,5-trimethylcyclohexane (C <sub>9</sub> F <sub>18</sub> )	160

The UTCHM simulations were able to test the suitability of these tracers for the CWL partitioning tracer test. The partition coefficients of the partitioning tracers should be within a certain range such that the resulting retardation factor is in the range from 1.2 to 4. The sensitivity studies indicate that the resulting retardation factors for C<sub>6</sub>F<sub>12</sub>, C<sub>8</sub>F<sub>16</sub>, and C<sub>9</sub>F<sub>18</sub> are in this range and meet the criterion.

The choice of number of tracers used in the PITT: Another important parameter in the design of a NAPL PITT is the number of tracers to be used. Theoretically, at least two tracers, one nonpartitioning and one partitioning, are required for the interwell test. Practically, however, two partitioning tracers and one nonpartitioning are preferred to improve the estimation accuracy because each pair of

tracers can give an independent estimate of the residual NAPL saturation. When there is a large range of uncertainty in the quantity and distribution of the NAPL such as the case here, even more than two partitioning tracers can be used. If the residual saturation 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 partitioning coefficients. If the residual saturation is lower than expected, the tracers with larger partition coefficients can ensure good separation of the tracer response curves. We, therefore, chose three partitioning tracers ( $C_6F_{12}$ ,  $C_8F_{16}$ ,  $C_9F_{18}$ ) and two nonpartitioning tracers ( $SF_6$  and  $C_4F_8$ ) shown in Table 1 as the tracers used in PITT.

The choice of mass of each tracer: The sensitivity studies indicate that the produced tracer concentrations are directly proportional to the mass of tracer injected. The amount of each tracer can be reduced only if the detection limit is reduced proportionally. Because the concentration of each tracer can be accurately measured to about 1 to 10 ppmw, 1 kg of each tracer was needed for the tracer test according to the simulation results.

The choice of extraction and injection rates: The conservative tracer test results indicated that a zone of high conductivity exists in the 40 to 60 feet bgs intermediate zone. As a result, the mean residence time in the intermediate zone was much lower than those of the shallow and deep zones. History matches of the CTTs indicated that a 2:1:3 flow rate ratio between the shallow, intermediate, and deep zones, respectively, was required to balance the mean residence times in the three zones. The other consideration in our selection of the injection and extraction rate involved tracer local equilibrium partitioning between phases. In order to achieve both a sufficient residence time [a minimum of 15 hours based on the lab column experiments (Whitley, et al., 1995; Whitley, 1996)], and a tracer test duration of at most 15 days, a variable injection and extraction rate was needed. An initial flow rate of 7.5 scfm was chosen for the first two days. The total flow rate was incremented to 12, 24, 48, and 56 scfm after 2, 4, 6, and 8 days. The 2:1:3 flow ratio was maintained for the entire test duration of 15 days.

The choice of closed top surface boundary: The sensitivity studies indicate that a major factor affecting the tracer test duration and estimation accuracy (especially for the shallow zone) is the top surface boundary. With a closed surface boundary, the simulated tracer recovery from the extraction well (shallow isolated screen interval) increases by a factor of 3, the minimum detectable tracer concentration needed to obtain good estimates increases by a factor of 5, tracer swept pore volume increases by a factor of 2, and the duration of the tracer test decreases by a factor of 2. Consequently a decision was made to cover the ground surface around the injection and extraction wells using 10 mil thick polyethylene sheeting with weighting material. The plastic sheeting also reduced the potential for an increase in soil moisture content during the test due to possible precipitation.

Our sensitivity studies indicated that the design and analysis of the tracer test was insensitive to fluid and soil properties such as relative permeability to water, capillary pressure functions, densities, and viscosities. This is a reasonable conclusion as the transport of both the conservative and partitioning tracers will be similarly influenced by these properties, and we are only interested in the partitioning and shape of break-through curves. This is a fortunate circumstance since these same properties may not always be accurately known at the time of tracer test design. In such cases, fluid and soil properties based on analogy to similar materials and site settings can be used in the PITT design.

Many aspects of the final test design and field set-up during the CTTs and PITT are depicted in Figure 6. A significant portion of the field equipment and monitoring installations were already on-site and being utilized for the soil vapor extraction pilot tests conducted before, during, and after the tracer tests. This is an important attribute in that this tracer characterization technology can be readily integrated into other pilot tests or full-scale remedial actions.

As can be seen in Figure 6, the injection well (INJ-1) and extraction well (EXT-1) are located 55 feet apart and to the east and west, respectively of the two disposal pits.

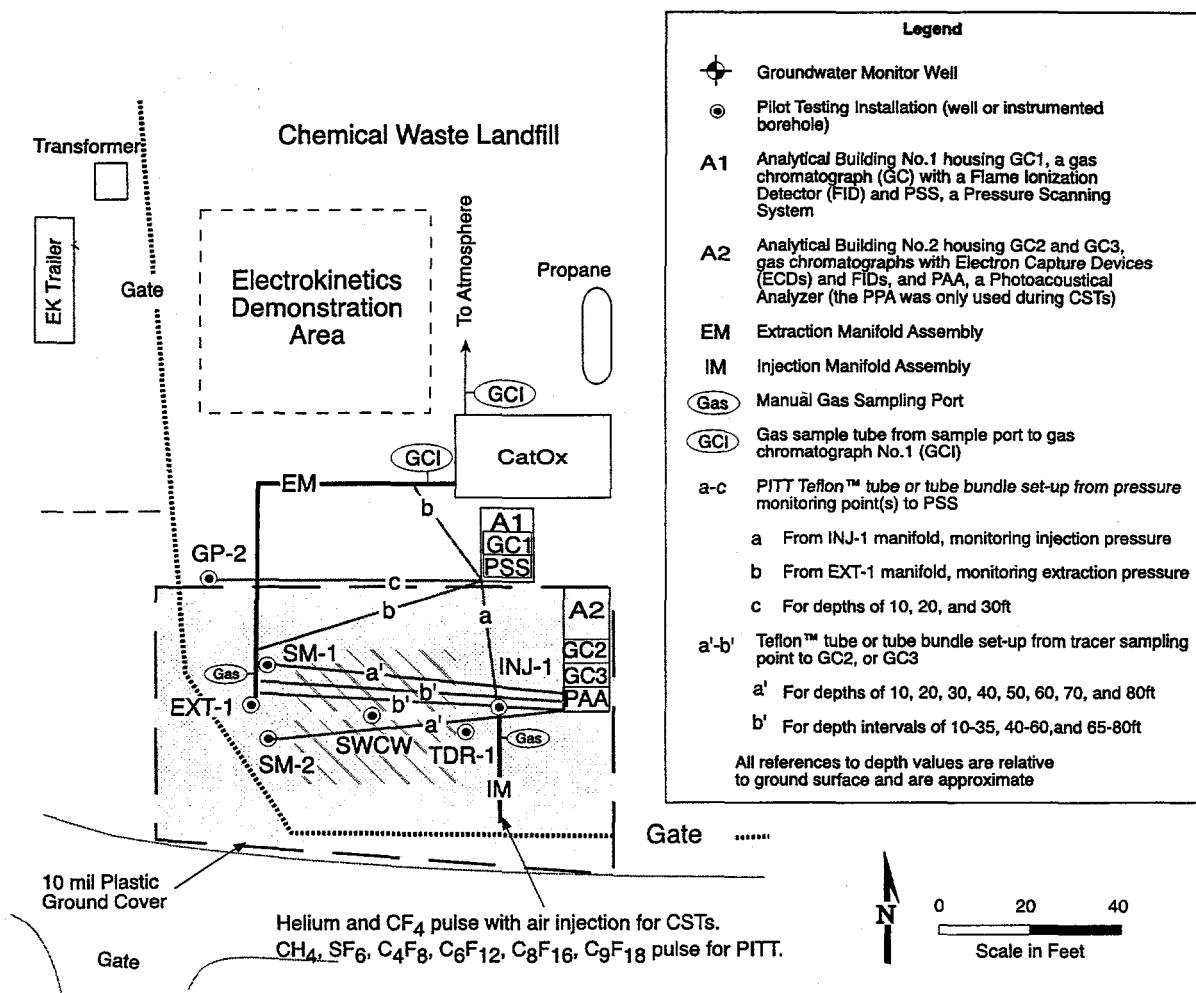


Figure 6. Site Layout During CTTs and PITT

Effluent created by applying a vacuum to EXT-1 was directed through an instrumented extraction pipe manifold system to a vacuum blower/catalytic oxidizer system. Air and tracer pulses were introduced to the subsurface at INJ-1 through an instrumented injection piping manifold system. A process diagram showing some of the basic components for the extraction and injection manifold systems is presented in Figure 7.

To provide for discrete, multi-level soil gas sampling and analysis, SEAMIST™ membranes were designed and installed in borings drilled 10 feet to the northeast (SM-1) and southeast (SM-2) of EXT-1 (Figure 6). The general construction of these two monitoring installations is shown

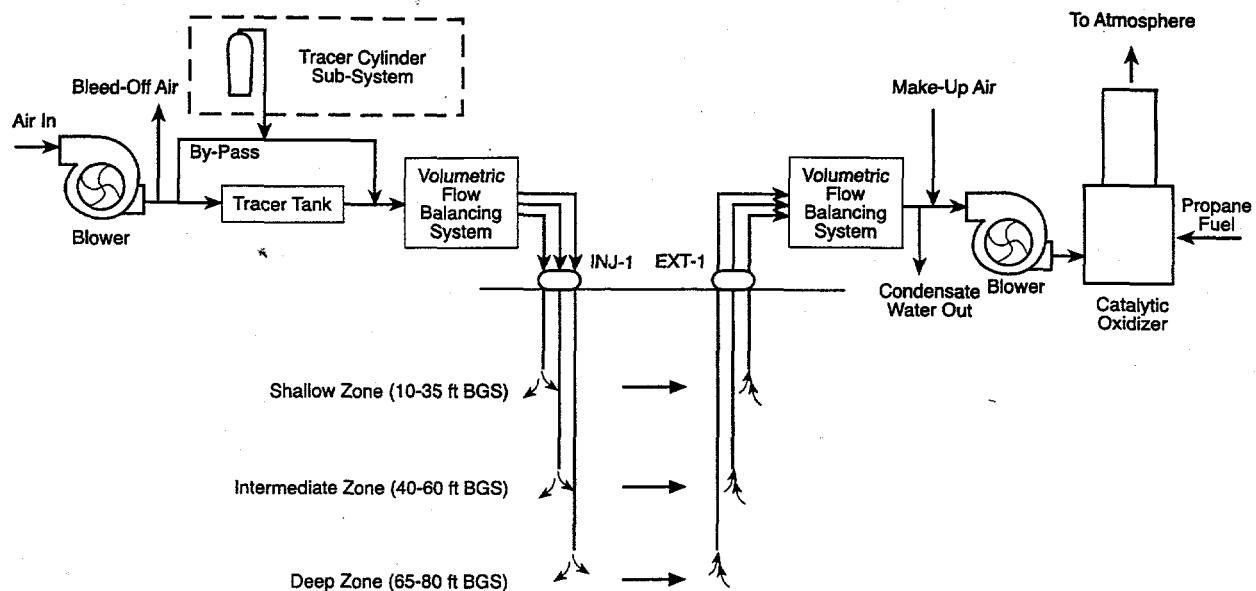
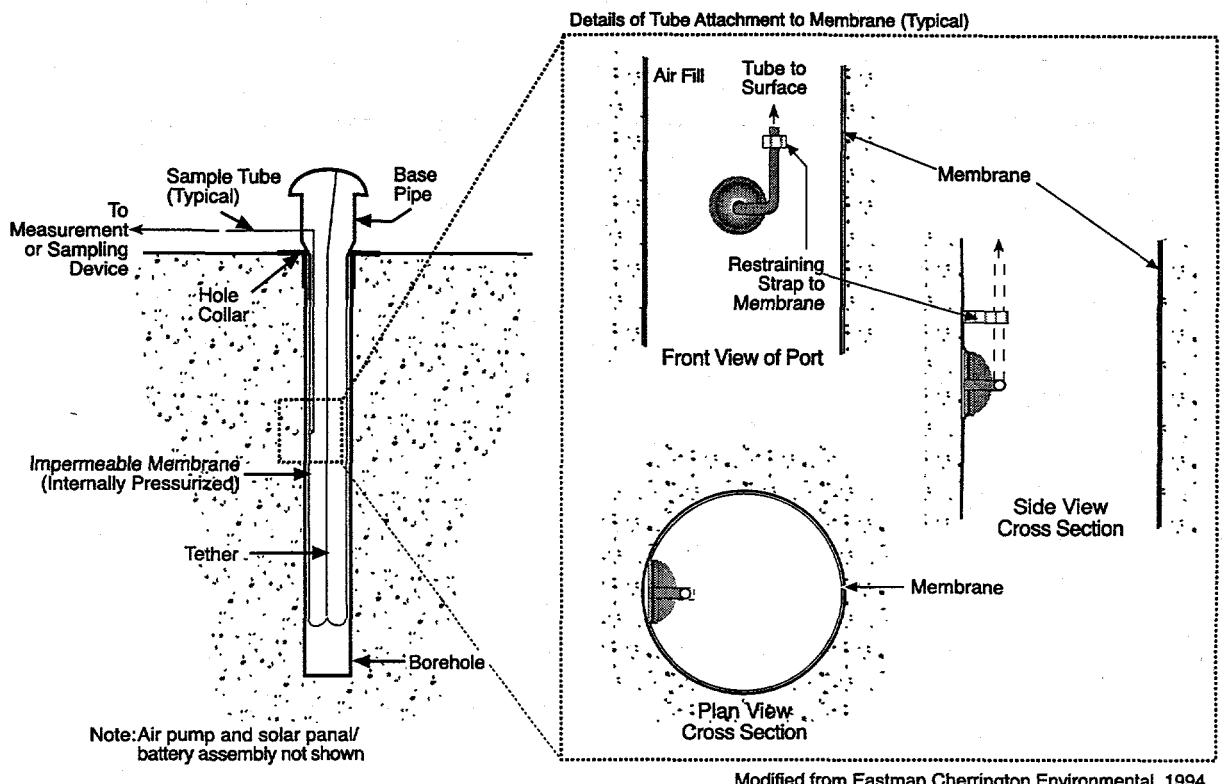


Figure 7. Process Flow Diagram for Air/Tracer Injection and Extraction System

in Figure 8. Small diameter flexible tubes convey soil gas (or pressure state) from the immediately adjacent formation through the SEAMIST™ membrane and up to the ground surface to couplings for manual and automated sampling. Our design for SM-1 and SM-2 consisted of nominal 80 feet long, 10 inch diameter membranes with 8 tubes connected to membrane ports spaced approximately 10 feet apart over the interval 10 to 80 feet bgs. Each membrane was internally pressurized to between 0.5 and 1.5  $p_{sig}$  using one diaphragm air pump system powered by a common solar cell/rechargeable battery system.

Autonomously operated pressure scanning and vapor sampling and analysis systems allowed for 24 hour continuous operation of injection and extraction systems, the catalytic oxidizer, and for on-line collection and real-time gas chromatograph (GC) analysis of a large number of vapor samples. Daily site visits were made to ensure that site conditions were safe, equipment was functioning properly, GCs were calibrated, and certain manual readings and computer memory checks were periodically completed.



Modified from Eastman Cherrington Environmental, 1994

Figure 8. Seamist™ Membrane Configuration for Tests

Table 2 summarizes the tracers used, tracer mass injected, pulse injection duration, and flow rates for the four CTTs and the PITT. The initial conservative tracer test, #2a, involved injecting helium in air at three percent concentration into the isolated intermediate zone of INJ-1 to measure the amount of vertical spreading that might be expected during the PITT as a result of forced-gradient vapor-phase flow from INJ-1 to EXT-1. A MARK Helium detector was used for sampling and analyzing the three exit streams from EXT-1. The intermediate zone breakthrough was rapid which indicated that the intermediate zone had a higher permeability than anticipated. Spreading was only noticeable to the deep zone as helium concentrations in EXT-1 deep rose slightly above background (the detection limit was 0.01 percent in air).

Figure 9 shows the results of the conservative tracer test #2b. The initial injection and extraction flow rates for

Table 2  
Summary of Test Conditions

Test	Tracers	Tracer Mass Injected (kg)	Pulse (min)	Flow Rate
Conservative Tracer Tests				
2a	He	1 (into intermediate zone only)	260	25 cfm @ zone, 6 hours
2b	CF <sub>4</sub>	0.47	54	7 cfm @ zone, 1 day 14 cfm @ zone, 1 day 25 cfm @ zone, 2 days
2c	CF <sub>4</sub>	0.19	21	2:1:3 ratio for shal:int:deep zones 30 cfm total, 1 day 45 cfm total, 3 hours 60 cfm total, 1 day
2d	CF <sub>4</sub>	0.32	25	2:1:3 ratio for shal:int:deep zones 7.5 cfm total, 2 days
Partitioning Interwell Tracer Test				
3	SF <sub>6</sub> C <sub>4</sub> F <sub>8</sub> C <sub>6</sub> F <sub>12</sub> C <sub>8</sub> F <sub>16</sub> C <sub>9</sub> F <sub>18</sub>	1 1 1 1 1	120	2:1:3 ratio for shal:int:deep zones 7.5 cfm total, 2 days 12 cfm total, 2 days 24 cfm total, 2 days 48 cfm total, 2 days 56 cfm total, 6 days

each zone were balanced at 7 scfm and a total of 0.16 kg CF<sub>4</sub> was injected into each of the three isolated screen intervals. The test flow rates were adjusted per Table 2.

The results show that there is a zone of higher permeability in the intermediate zone between the two wells, and that the intermediate zone as a whole is more permeable to air than the shallow and deep zones. They also indicate that the overall permeability is higher than we had

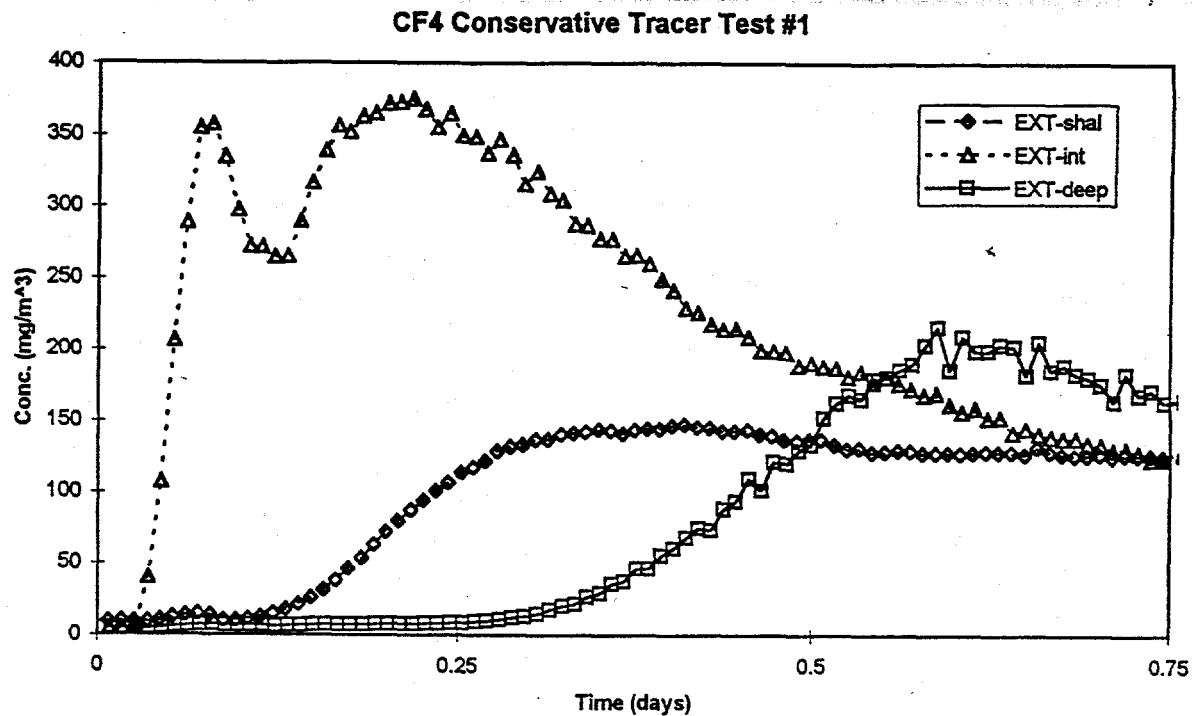


Figure 9. Results from CTT #2B Using CF<sub>4</sub>

expected. In order to obtain an adequate frequency of sample data at the sample points during the PITT and to increase the residence time of the tracers, the flow rates required adjustment. Post-CTT modeling using these results indicated that a 2:1:3 ratio of flow rates for the shallow, intermediate and deep zones, respectively, would approximately balance the mean residence times in all zones. Conservative tracer test #2c confirmed that this ratio would adequately balance the mean residence times, and the final CTT, #2d, which was performed after low flow rate meters were installed, confirmed that the very low initial flow rates specified would allow for sufficient capture of the tracers.

#### PITT Results

Data obtained during the PITT include time-series concentrations of the tracers (SF<sub>6</sub>, C<sub>4</sub>F<sub>6</sub>, C<sub>6</sub>F<sub>12</sub>, C<sub>8</sub>F<sub>16</sub>, and

$C_9F_{18}$ ) for EXT-1 shallow, intermediate, and deep screen intervals and the eight sampling point depths of SM-1 and SM-2. Also collected were data on contaminant emissions for 10 VOCs from EXT-1 combined flows, and pressure/vacuum and temperature states. Because of time constraints, only preliminary  $C_4F_8$  and  $C_9F_{18}$  data are presented. No calculations of retardation, NAPL saturation, and NAPL volume have yet been performed pending completion of data processing and quality control checks on the data.

Figure 10 presents three graphs of  $C_4F_8$  and  $C_9F_{18}$  tracer concentrations versus cumulative volume soil gas extracted from EXT-1 zone. The upper graph is for EXT-1 shallow zone, and EXT-1 intermediate and deep zones correspond to the middle and lower graphs. Use of  $C_4F_8$  instead of  $SF_6$  for these preliminary graphs appears to be acceptable as  $C_4F_8$  has such a low partition coefficient that its retardation during the PITT was essentially negligible ( $SF_6$  and  $C_4F_8$  break-through occurred at the same time).

Figures 11 and 12 provide similar type graphs for selected SM-1 and SM-2 monitoring points. Preliminary findings are:

- The separation of peaks observed in EXT-1 shallow indicates the significant presence of NAPL in the shallow zone. The separations are best displayed in the break-through curves for SM1-10 and SM2-10. In comparison, separation is much reduced in SM1-30 and SM2-30.
- The break-through curves at SM2-50 indicate that this monitoring location is partially connected to the relatively high permeability feature discussed earlier that is believed to exist in the intermediate zone. This feature appears to be laterally continuous in the test area and is positioned between 40 and 50 feet, or 50 and 60 feet.
- The high permeability channel in the intermediate zone caused an early initial breakthrough of  $C_4F_8$  and  $C_9F_{18}$  in EXT-1 intermediate, even though the injection and extraction flow rates in the intermediate zone were the lowest. Significant separation in the tracer peaks is not evident for EXT-1 intermediate and SM1-40, but a

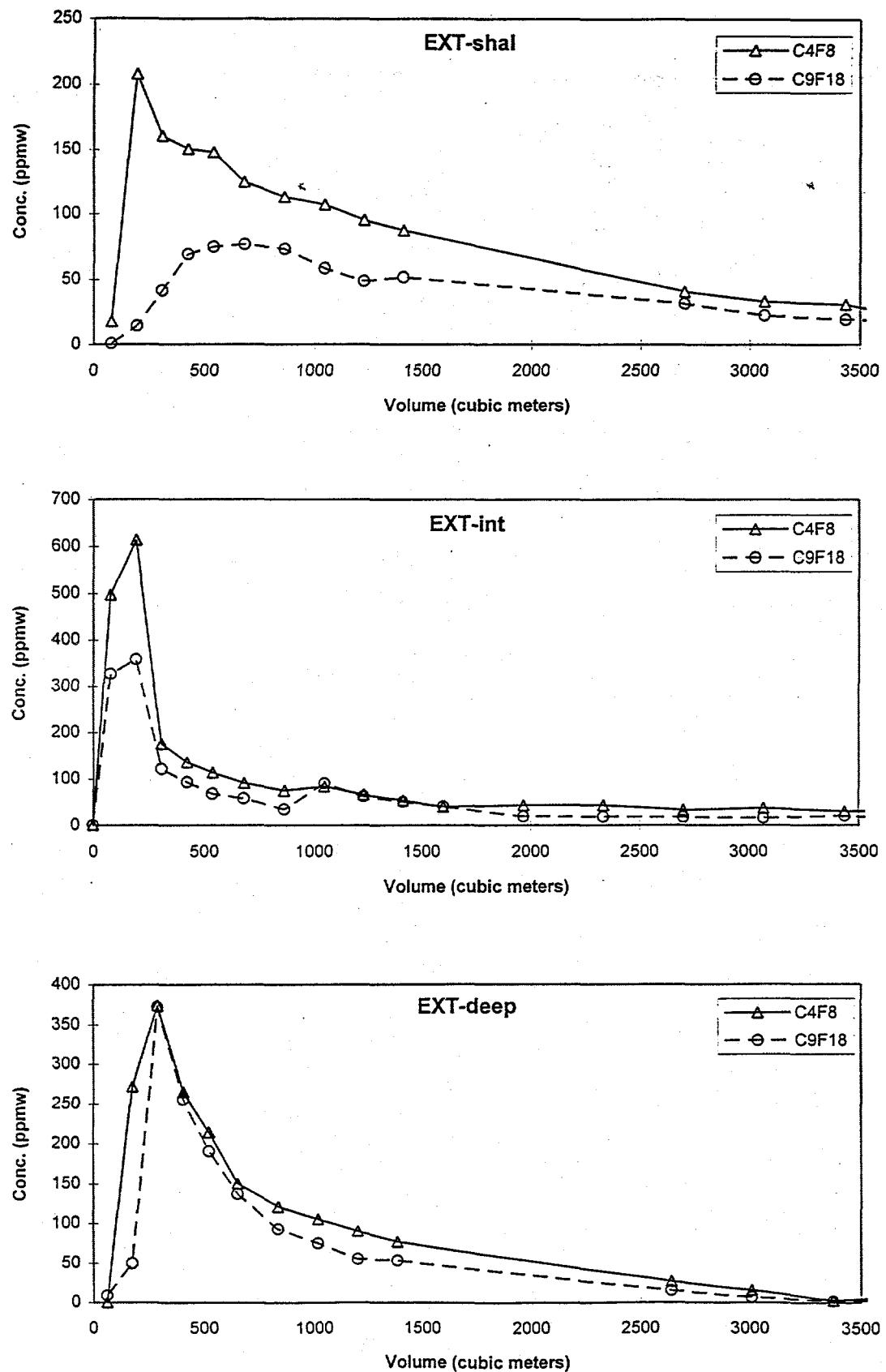


Figure 10. PITT break-through curves, C<sub>4</sub>F<sub>8</sub> and C<sub>9</sub>F<sub>18</sub>.  
 Extraction Well EXT-1 (a) shallow zone;  
 (b) intermediate zone, and (c) deep zone

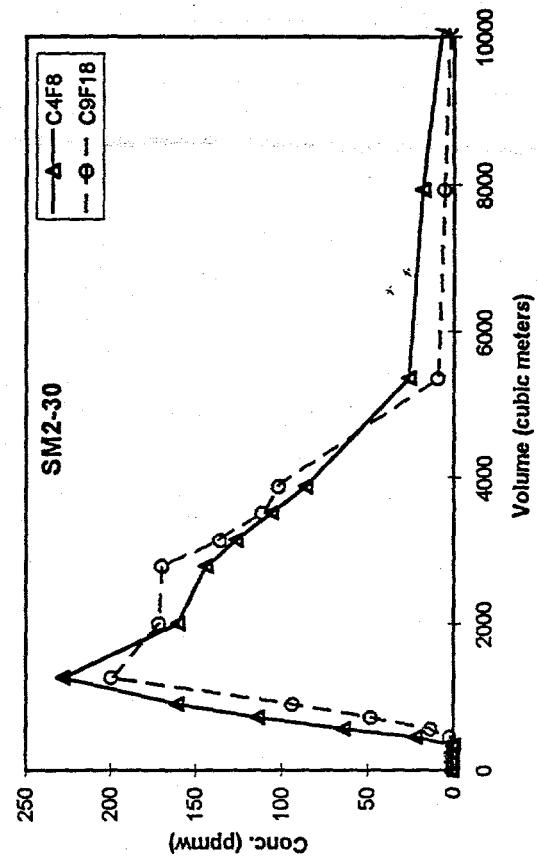
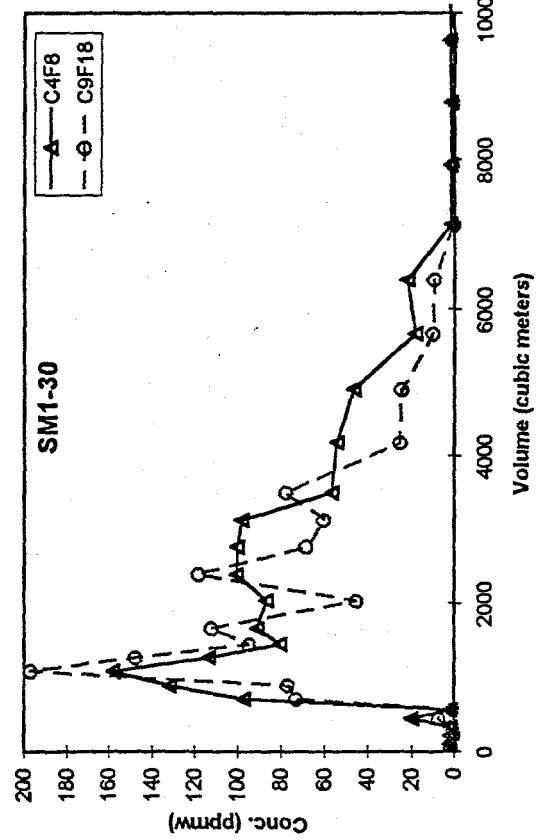
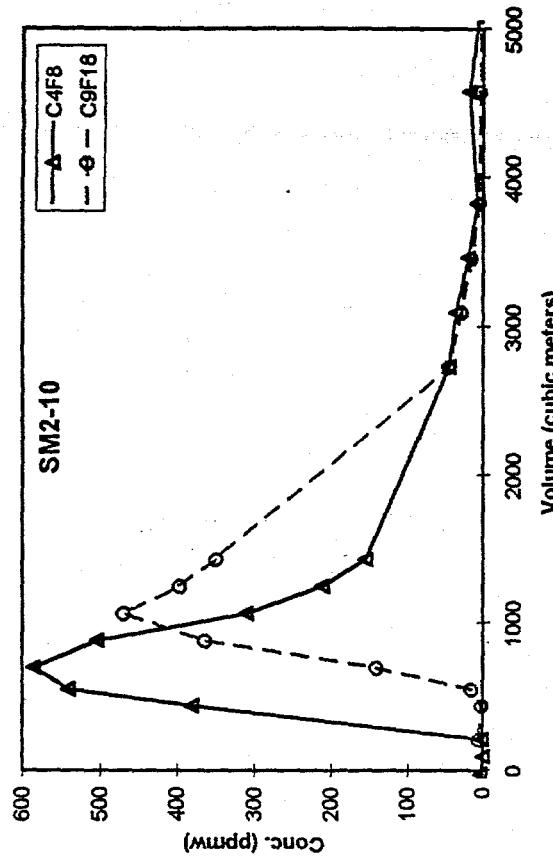
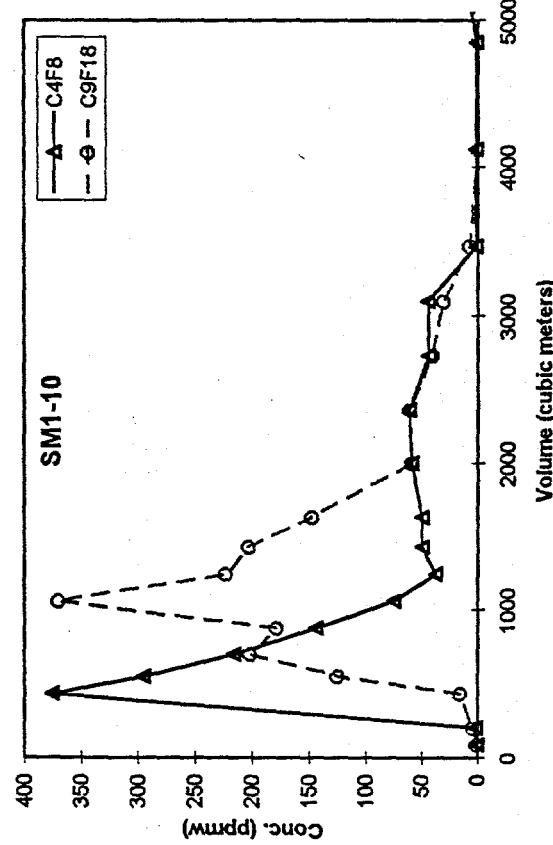


Figure 11. Pitt break-through curves,  $C_4F_8$  and  $C_9F_{18}$ .  
 (a) at SM1-10 ft bgs; (b) SM2-10 ft bgs;  
 (c) SM1-30 ft bgs; (d) SM2-30 ft bgs

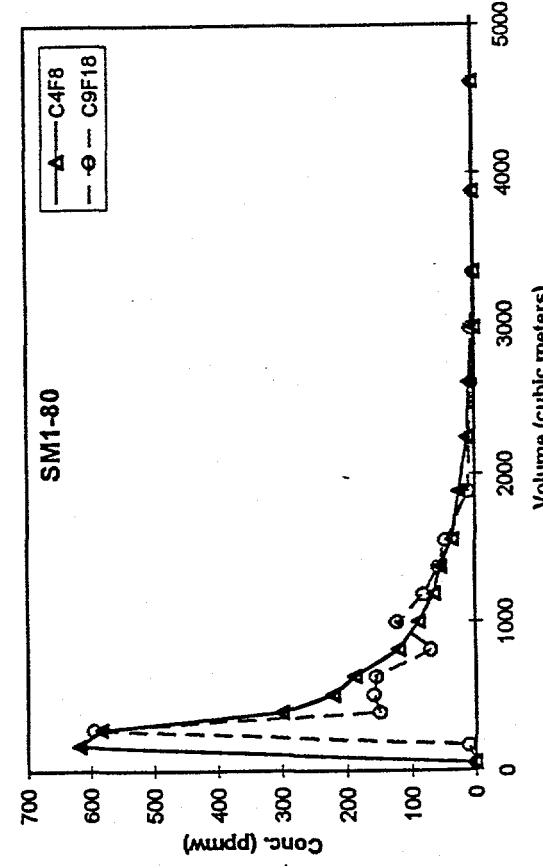
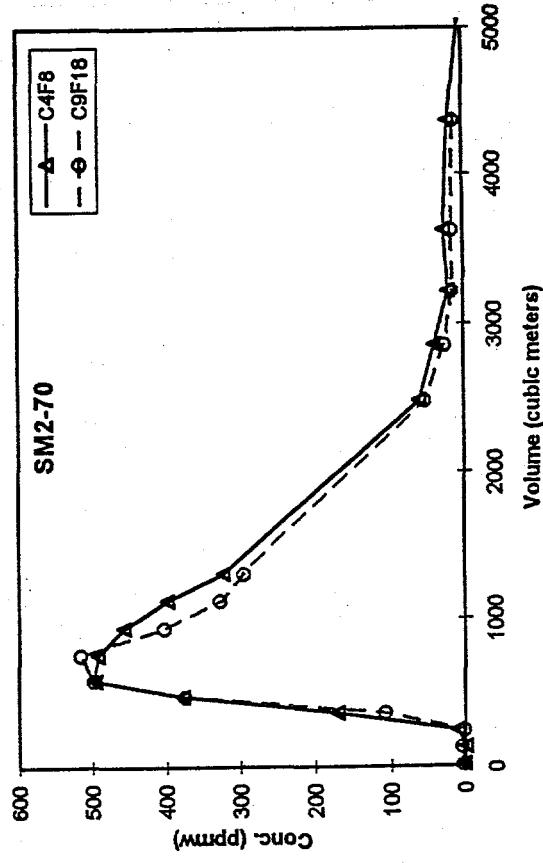
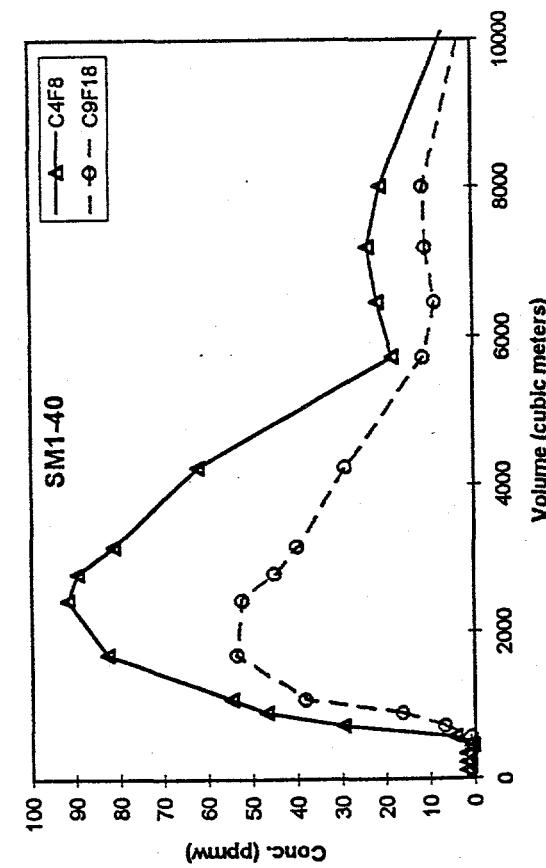
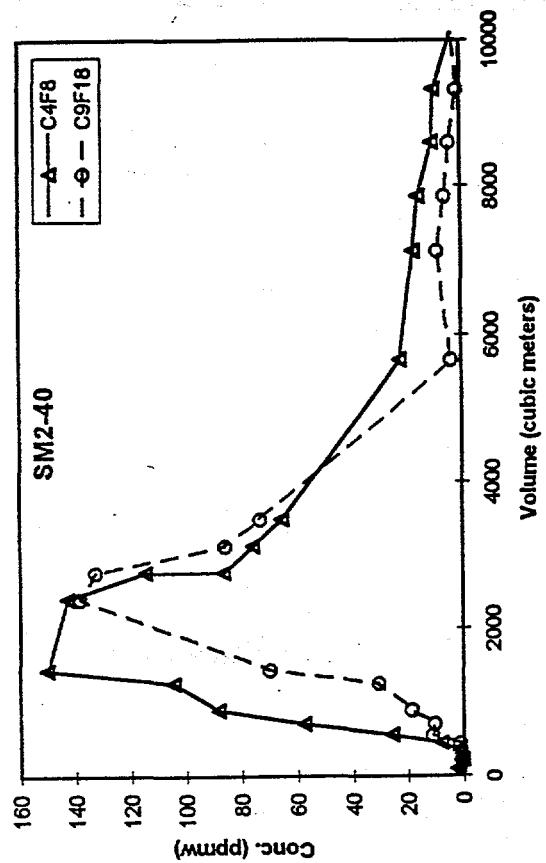


Figure 12. Pitt break-through curves,  $C_4F_8$  and  $C_9F_{18}$ .  
 (a) SM1-40 ft bgs; (b) SM2-40 ft bgs  
 (c) SM1-80 ft bgs; (d) SM2-70 ft bgs

significant separation is seen for SM2-40. This suggests that both the streamtube intersecting SM1-40 contains low or negligible amounts of NAPL, while the streamtube intersecting SM2-40 (in the relatively lower permeability portion of the intermediate zone) contains a significant amount of NAPL. Because EXT-1 intermediate should capture the streamtubes that the SM-1 and SM-2 40 feet and 50 feet sampling tubes capture, the EXT-1 intermediate peaks should show some separation. Because the high permeability channel appears to be relatively NAPL-free, the tracer separations which occurred in the intermediate zone will most likely be seen in the tails of the breakthrough curves as measured at EXT-1 intermediate.

- A slight delay in the  $C_9F_{18}$  break-through curve is apparent in the EXT-1 deep data, indicating that some NAPL has penetrated into the 65 to 80 feet bgs zone. The SM1-80 data confirm that NAPL has penetrated to at least 80 feet into sediment coincident with the streamtube it intersects. The SM2-70 data, however, indicate no detectable NAPL in the streamtube it intersects.

Although this tracer data presentation is preliminary and is only a fraction of the total amount of data collected, it is apparent that the break-through curves are not as smooth and well-defined as we would have liked. While they are certainly good enough to dramatically reduce the uncertainty about the presence of NAPL and the approximate saturations in different zones and streamtubes, smoother curves would provide more accurate estimates.

The primary reasons for the scatter in the tracer break-through data are related to the dynamics of gaseous tracer testing versus aqueous-phase tracer testing, and the autonomous on-line collection and analysis of gas samples. An on-line method was chosen because collecting gas samples for later analysis would have been prohibitively expensive (e.g., inexpensive sorptive collection tubes could not be used because conservative tracers do not sufficiently sorb). Water condensation in sample lines on cold nights and fluctuations in GC performance, although easy to monitor, were difficult to avoid. Adding to the difficulty was the requirement that the on-line GCs be calibrated for ranges of concentration of at least four orders of magnitude, i.e.,

dilutions are not possible. Finally, the GCs could analyze only one sample every 45 minutes, considerably reducing the frequency at which each sample location could be sampled. Increased sampling frequency relative to mean residence time and improved methods of sampling and analysis are being integrated into upcoming vadose zone PITTs to improve tracer break-through curves.

#### Implications for DNAPL Remediation and Landfill Closure

The PITT has had a significant impact on strategic planning for corrective action at the CWL. The PITT preliminary results show that a significant volume of NAPL is present in the shallow zone between 5 and 30 feet bgs. NAPL migration has occurred to at least 80 feet bgs beneath and around the subject pits. Consistent with current state of knowledge about NAPL migration mechanisms in vadose zone settings, NAPL distribution beneath these pits is not uniform. Preferential DNAPL flow with stabilized ganglia stringers are probably prevalent in some portions of the test zone (and the larger pore openings of those zones) while volumes of sediment that contain no DNAPL are likely intermingled between these zones.

Based on this information, a more integrated VCM approach is contemplated. Two VCMs are planned for the near future. The focused excavation VCM will concentrate on a principal source of VOCs feeding the existing vapor-phase plume, the DNAPL contained in the southwest pits and below these pits. The Vapor Extraction VCM will concentrate on the soil gas vapor-phase plume and the vapor plume interaction with the ground water. The VE VCM objectives are now being modified because of the PITT to include a focus on removing VOCs in DNAPL existing below approximately 25 feet bgs. As mentioned, DNAPL above approximately 25 feet bgs will likely be addressed through surface excavation techniques. Previously contemplated deep excavation techniques may not prove to be cost-effective due to the non-uniform nature of the NAPL at depth.

Final PITT results will include average saturation and total volume of NAPL in each zone. These results will be useful in estimating the level of effort and time required to remove VOCs in NAPL that would otherwise continue to feed the soil gas vapor plume. A higher density of extraction and

air inlet wells, or heated vapor extraction techniques, might be applied to speed the removal, if significant VOC-containing NAPL is projected below 25 feet bgs.

Remediation waste volume estimates associated with projected VCM and final corrective actions can now be updated to reflect the more accurate understanding of DNAPL presence. Accurate waste volume estimates for the CWL are critical inputs to the ER Project efforts to complete corrective actions at all SNL/NM solid waste management units, cost-effectively and in a timely manner.

#### Acknowledgements

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#### Author Biographic Sketches

Mr. James E. Studer is a senior engineer with INTERA Inc., a subsidiary of Duke Engineering and Services, Charlotte, NC. He holds B.S and M.S. degrees in Geological Engineering from the University of Missouri-Rolla. Mr. Studer is a registered professional engineer and geologist. He has 12 years of professional experience with national and international consulting and remediation firms. He specializes in site characterization and remediation of hazardous waste sites and is currently the corrective action project manager for the CWL at Sandia. Mr. Studer is also leading a design team to develop aspects of a proposed Corrective Action Management Unit (CAMU) for a DOE facility.

Mr. Paul Mariner is a Project Hydrogeochemist with INTERA Inc. and specializes in the chemical behavior of organic and inorganic compounds in geologic systems. His work has involved hydrogeochemical modeling, forensic analysis of contaminated media, and development of computer models for quantitative assessments at NAPL-contaminated sites. Mr. Mariner has a M.S. degree in Hydrology and a B.A. in Environmental Science.

Dr. Minquan Jin staff consultant with the Austin office of INTERA Inc. He received his M.S. and Ph.D. degrees in Petroleum and Geosystems Engineering from The University of Texas at Austin. He is experienced in modeling of multiphase flow in porous media and has done extensive studies in the areas of surfactant-enhanced aquifer remediation and

partitioning interwell tracer testing for non-aqueous phase liquid characterization.

Dr. Gary A. Pope is Professor of Petroleum Engineering at The University of Texas at Austin, where he does research in the areas of flow and transport in porous media, properties of surfactant and polymer solutions, surfactant-enhanced aquifer remediation, reservoir simulation, reservoir characterization using tracers, enhanced oil recovery processes and ground water modeling. He has 25 years of experience with the experimental investigation of surfactants, co-solvents and water-soluble polymers with applications to both oil recovery and the clean up of organic wastes from aquifers. He and his colleagues and students at The University of Texas have developed a three-dimensional multicomponent, multiphase numerical simulator (UTCHEM) that is widely used to solve a variety of flow in permeable media problems. Since 1992, this simulator has been adapted and applied to ground water modeling problems with a special focus on the remediation of dense non-aqueous phase liquids in the ground water and the development and application of the use of partitioning tracers to locate and quantify NAPLs in the subsurface.

Dr. Daene McKinney is an Assistant Professor of Civil Engineering at The University of Texas at Austin where he conducts research in developing and applying numerical methods for simulation, optimization, and uncertainty analysis of water resources management problems, and the development of laboratory and field experimental techniques for the characterization and remediation of aquifer and groundwater contamination. Before his employment at UT Austin, Dr. McKinney was an environmental Engineer and hydrogeologist with the USEPA. He has a Ph.D. in Civil Engineering from Cornell University.

Mr. Richard Fate has a B.S. from West Point, and holds a M.S. in Mechanical Engineering and a Master of Business Administration from New Mexico State University. He has been with the Environmental Restoration Project with Sandia National Laboratories for the last 5 years. Mr. Fate is currently the manager for environmental restoration of landfills and test areas.