Cost Proposal

Using Partitioning Interwell Tracer Tests to Characterize Carbon Tetrachloride DNAPL Beneath the Z-9 Crib

Hanford, Washington

Prepared for:

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EXECUTIVE SUMMARY

Numerical modeling simulations were conducted by Duke Engineering & Services (DE&S) to provide a preliminary design for partitioning interwell tracer tests (PITTs) in both the vadose zone and ground-water zones beneath the Z-9 Crib area. The primary objective of the simulations was to develop a feasible PITT design and detailed cost estimate for conducting PITTs in the vadose zone between the caliche layer and the water table. A secondary objective was to briefly examine the design and cost implications for conducting ground-water PITTs in the vicinity of the Z-9 Crib. ITRD is interested in the use of PITTs at the Z-9 Crib area to detect and measure the amount (i.e., volume and saturation) of carbon tetrachloride present in the subsurface as a dense non-aqueous phase liquid (DNAPL).

The initial conceptual plan for a vadose-zone PITT, referred to as Scenario D, was provided to DE&S by the ITRD committee. Scenario D specified the use of existing well locations to investigate the vadose-zone of the Ringold Formation directly beneath the Z-9 Crib and to include the area adjacent and immediately north of the crib. PITT simulations were conducted with the UTCHEM modeling code to test the feasibility of conducting a PITT with the Scenario D wellfield configuration. The simulation results showed that the interwell distances in Scenario D were too large to achieve acceptable PITT results (i.e., sensitivity and accuracy in the detection and measurement of the volume of DNAPL) given the site-specific conditions and the large pore volume to be investigated by a Scenario D PITT. Therefore, DE&S proposed dividing Scenario D into two smaller-scale PITTs, referred to as D1 and D2, in order to investigate the same zone as the original Scenario D, yet increase the sensitivity of the test to measure DNAPL in the swept pore volume of interest. Simulations were conducted with an average DNAPL saturation of 1% in the model grid. PITT simulations indicate that it is feasible to design PITTs for Scenarios D1 and D2.

Simulation results provided the design basis (i.e., flow rates, test duration, and tracer mass required) for a detailed cost estimate to conduct two PITTs for Scenarios D1 and D2. The DE&S cost estimate for all tasks, from design and planning to implementation and final reporting, is $696,971. PNNL estimated costs to provide project management and integration support (including laboratory and field analytical services) is $201,989. Therefore, the combined cost estimate for both DE&S and PNNL to complete both VZ-PITTs (D1 and D2) is $898,960.

PITT simulations were also conducted to evaluate the feasibility of conducting ground-water PITTs in the shallow and deep ground-water zone of the Ringold Formation in the vicinity of the Z-9 Crib. The initial scenario provided by ITRD for evaluation was a two-well test beneath the crib, using existing wells with an interwell distance of approximately 170 feet. PITT simulations showed that such a PITT scenario would provide poor results for detecting and measuring DNAPL in the swept pore volume because the interwell distance is too great for a two-well PITT with such a narrow screened interval. Subsequent PITT simulations for a two-well PITT with an interwell distance of 50 feet show that such a well configuration is about the maximum distance for a two-well PITT under the site specific conditions at this location. Finally, PITT simulations were conducted to evaluate a three-well PITT in the ground-water zone beneath the Z-9 Crib, utilizing the original wells proposed by ITRD to be used as extraction wells, and with a slant well installed beneath the crib as a mid-point injection well. Such a wellfield configuration would test the same 170-ft interwell zone originally proposed by ITRD. Simulation results showed that the three-well (divergent flow) configuration is vastly superior for conducting a PITT beneath the crib. A rough cost estimate for the ground-water PITT is not included herein but will follow later.

1 INTRODUCTION

Duke Engineering & Services is providing this proposal in support of the Innovative Treatment Remediation Demonstration (ITRD) Program's need for a remedial design basis with respect to carbon tetrachloride in the subsurface at the Z-9 Crib, 200 Area West, Hanford, Washington. The specific objective of the proposal is to evaluate several investigative scenarios with respect to the design of partitioning interwell tracer tests[1] (PITTs). ITRD is interested in the use of PITTs to detect and quantify carbon tetrachloride that is suspected to be present as a dense non-aqueous phase liquid (DNAPL) in the sediments beneath the Z-9 Crib. The primary focus of this proposal is to provide a preliminary (i.e., 50%) PITT design, along with a detailed cost estimate for PITTs in the vadose zone (Scenario D) of the Ringold Formation between the caliche layer and the water table in the Z-9 Crib area. PITT design simulations were conducted using the UTCHEM simulator to model the necessary flow rates and the tracer mass required, and to estimate the swept pore volume and duration for the two VZ-PITT scenarios. A second, lower-priority focus of this proposal was to conduct initial design simulations for two ground-water, or saturated-zone, PITTs in the Z-9 Crib area. Several ground-water PITT scenarios were simulated to evaluate the feasibility and preliminary cost implications of a shallow ground-water PITT (i.e., just below the water table). A deeper ground-water PITT scenario in the Ringold Formation in the vicinity of the Z-9 Crib area was also considered.

The simulation results provided a PITT design basis for cost estimation purposes. Detailed cost estimates are provided herein for completion of the design, execution and analysis of vadose-zone PITTs that would investigate the area proposed in Scenario D. A rough cost estimate is also provided for a ground-water PITT, as well as recommendations for an improved wellfield configuration for a ground-water PITT.

The cost estimates for PITT scenarios presented in this proposal are based on the simulation results of the UTCHEM simulator. UTCHEM is a multi-component, multiphase, three-dimensional chemical flood reservoir simulator developed at the University of Texas at Austin. It was originally developed to simulate the surfactant/polymer enhanced oil recovery process (Pope and Nelson, 1978; Datta-Gupta et al., 1986; Saad et al., 1990). In the past nine years, enhancements have been made to adapt UTCHEM to simulate both PITTs and surfactant-enhanced aquifer remediation (SEAR) processes (Delshad et al., 1996). UTCHEM represents the current state of the art for PITT and SEAR design, and has been successfully used by DE&S to design numerous PITTs, surfactant, and surfactant/foam flood field demonstrations (e.g DE&S, 1998, RICE et al, 1997, USAF 1998a-d, 1999). UTCHEM modeling was used in this proposal to gain insight into pertinent design parameters that affect the sensitivity of a given PITT scenario to detect and measure DNAPL in the subsurface, as well as to provide a design basis for developing cost estimates for a PITT scenario. A general background of PITTs is also provided which includes a discussion of the theory behind the PITT technology, the laboratory protocol to be utilized, and the detection limit and error typically associated with an estimate of NAPL volume and saturation as measured by a PITT.

[1]US Patents 5,905,036 and 6,003,365, assigned to the University of Texas at Austin and Duke Engineering & Services

2 PITT SIMULATIONS

The UTCHEM simulator (Delshad et al., 1996) is used by DE&S for PITT design. The usual approach for PITT design typically proceeds in the following sequence:

- Construction of a geosystem model which incorporates site-specific information: stratigraphy, formation properties (permeability, heterogenity, water saturation, and natural organic carbon content), NAPL composition, and NAPL properties; then
- PITT simulations are conducted in an iterative manner to optimize the wellfield geometry and flow rates with respect to the zone of investigation (i.e., swept pore volume), tracer signal at the extraction wells, tracer recovery (i.e. hydraulic control), and duration of the test.

The goal of this design approach is to maximize the technical merits of the PITT technology while minimizing costs to conduct a PITT.

However, the design approach was modified, by necessity, for the proposed PITT scenarios in the Z-9 Crib area. Due to the high cost of installing new wells at Hanford, DE&S was tasked with designing PITTs with the design constraint of using existing well locations. Therefore, the first simulations were conducted to test the feasibility of conducting a PITT with the Scenario D wellfield configuraton. Scenario D was devised to meet the dual needs of ITRD for: (1) large-scale DNAPL-zone characterization across the areas of greatest immediate concern; and (2) to minimize well installation costs to conduct a PITT. The simulation model was developed with the use of site stratigraphic data, and porous media and fluid physical properties contained in technical reports prepared by Westinghouse Hanford Company (1994) and Bechtel Hanford, Inc. (1997). A number of sensitivity simulations were run to evaluate the performance of each PITT scenario under different conditions. These sensitivity studies included varying the injection and extraction rates, well locations (using existing wells), well screen intervals, and carbon tetrachloride NAPL saturation and distribution.

3 SCENARIO D

PITT simulations for Scenario D were conducted using UTCHEM. Scenario D involves injecting tracer at well W15-82 and extracting from wells W15-8L, W15-84, W15-219L, and W15-218L, as shown in Figure 1.

PITT simulation results indicate several major problems with Scenario D. First, the distance between injection well W15-82 and extraction well W15-219L is approximately 237 feet. This results in several problems:

- There is a large disparity in interwell distances (i.e., 145, 190, and 174 foot interwell distances for wells W15-8L, W15-84, and W15-218L, respectively) so that the long interwell distance to W15-219L dictates both the required tracer mass and test duration.

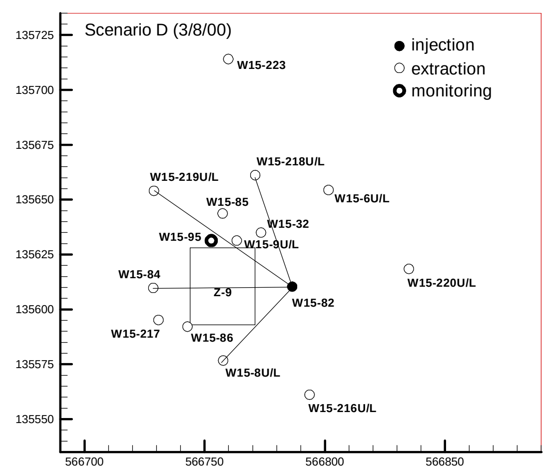

Figure 1. Scenario D

- In a heterogeneous system, there is a good chance that there will be little or no communication between wells W15-82 and W15-219L.
- The long distance, when coupled with a non-uniform NAPL distribution, results in low retardation factors (i.e. <1.2, which is the minimum recommended by Jin et al., (1997) for accurate PITT results). Low retardation factors result in relatively high errors in the calculated NAPL volume.
- There is little chance of obtaining useful information from the proposed mid-point monitoring well at W15-95 given the length scale in Scenario D.

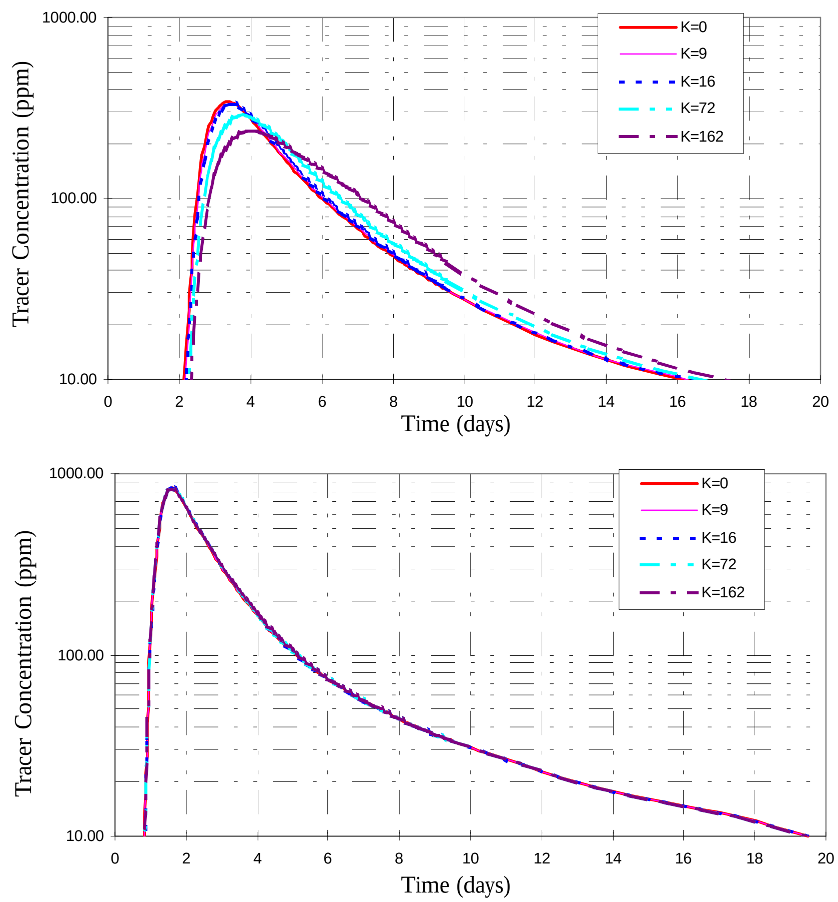

Figure 2. Simulated tracer response curves for Scenario D well W15-219L (above) and well W15-218L (below).

In addition to these problems, it is very difficult to achieve a balanced flow of tracers to each well when using four extraction wells in a fan-shaped wellfield configuration (i.e., single injector with multiple extraction wells fanning out from the injector). In such a wellfield configuration, a relatively balanced tracer flow is more likely to occur with three extraction wells than with four extraction wells.

Figure 2, above, shows examples of the simulated tracer breakthrough curves for extraction wells W15-218L and W15-218L. There is insufficient tracer separation, i.e., tracer retardation, under Scenario D to provide a robust PITT data analysis. Given the problems associated with this scenario, we recommend pursuing an alternative approach, with the use of existing wells, that would provide a much higher-quality PITT with respect to detection and measurement of the volume of DNAPL beneath the Z-9 Crib area.

The average DNAPL saturation in Figure 2 is assumed to be 1%, which is confined to the unsaturated zone beneath the Z-9 pad. No DNAPL is assumed present outside the footprint of the pad.

4 RECOMMENDED ALTERNATIVE

In order to meet ITRD's objective to test the zone directly beneath the Z-9 Crib, as well as the area north/adjacent to the crib, we recommend splitting the proposed Scenario D PITT into two PITTs. Splitting the test area into two smaller-scale wellfields, and using three rather than four extraction wells per PITT will increase the sensitivity of the PITTs to detect and quantify DNAPL. Therefore we suggest Scenarios D1 and D2, which use existing wells to test the same zone of interest as originally proposed in Scenario D. In both scenarios, the average DNAPL saturation is 1% in the vadose zone and extending beyond the footprint of the Z-9 pad.

4.1 SCENARIO D1

Scenario D1 involves injecting gaseous partitioning tracers at well W15-82 and extracting soil gas at wells W15-8L, W15-84, and W15-95, as shown in Figure 3. This wellfield configuration reduces the interwell distances to 145, 190, and 130 feet, respectively. An injection rate of 500 cfm was used for the entire test in the simulations. Cumulative extraction rates summed to 500 cfm for the three extraction wells and were weighted with respect to each interwell distance in order to achieve a relatively balanced breakthrough of tracers at each well.

4.2 SCENARIO D2

Scenario D2 involves injecting tracers at well W15-218L and extracting soil gas at wells W15-219L, W15-95, and W15-82, as shown in Figure 4. This reduces the interwell distances to 135, 115, and 174 feet, respectively. Extraction rates summed to 500 cfm and were weighted with respect to interwell distance for a balanced breakthrough of tracers at each well.

The simulation results for Scenarios D1 and D2 were much more promising than for the original Scenario D. The shorter interwell distances used in D1 and D2 result in better communication between injection and extraction wells and a shorter test duration. Most importantly, by decreasing the interwell distance with respect to the anticipated length scale of the DNAPL zone, separation between conservative and partitioning tracer responses was observed earlier and more uniformly throughout the test. This will lead to an increased sensitivity for the detection of DNAPL and improved accuracy of the test results. The simulation results show that by using three extraction wells with comparable distances from the injection well, a more balanced flow of tracers is distributed to each well. The result is that no single well dictates the overall test duration and tracer mass required in the PITT design. In addition, the alternative scenarios D1 and D2

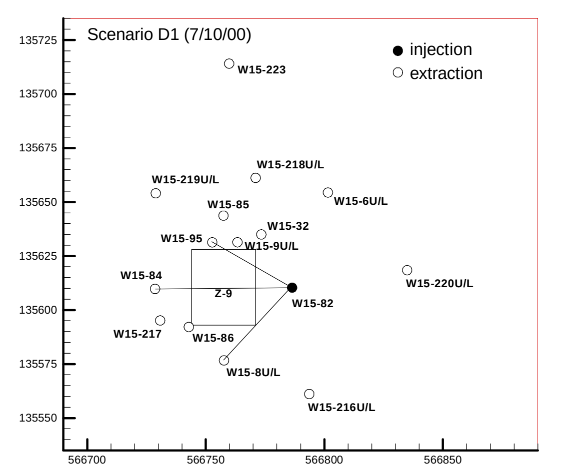

Figure 3. Scenario D1

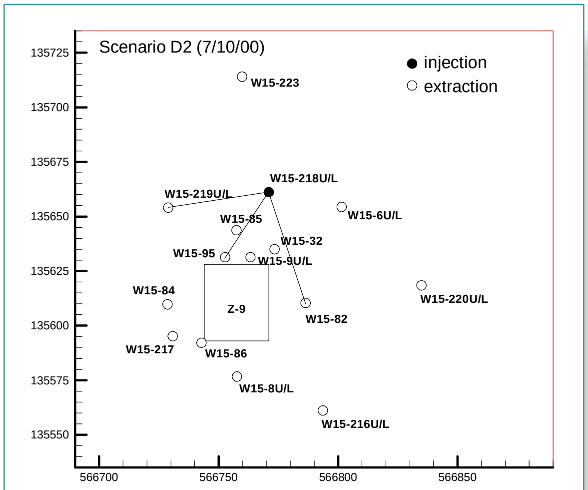

Figure 4. Scenario D2

required less tracer mass per test in order to ensure extracted tracer concentrations above the detection limits throughout the test. Simulated tracer response curves in Figure 5 show greater tracer separation for Scenarios D1 and D2 than for the Scenario D (Figure 2). The results of the preliminary design simulations are summarized in Table 1, below, to allow a comparison of the primary PITT design parameters for Scenarios D, D1, and D2.

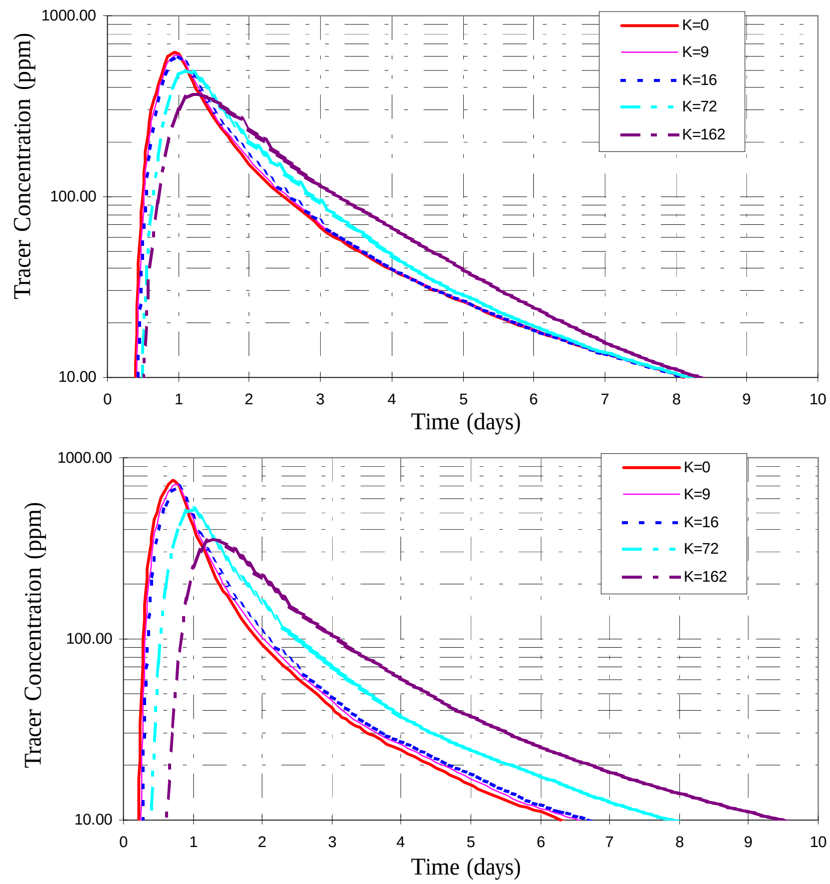

Figure 5. Examples of simulated tracer response curves for Scenario D1 (above) and Scenario D2 (below).

As can be seen in Table 1, there is no significant difference between the tracer mass required and the test duration in Scenario D compared to the combined Scenarios D1/D2. Therefore, the overall costs required to field two smaller PITTs is only marginally higher than that required to conduct one large PITT. The incremental costs required to conduct two smaller PITTs are primarily associated with increased labor for test design and analysis of two CITTs and PITTs, increased test plan preparation, and additional reporting. These relatively small incremental costs are, however, offset by significantly improved sensitivity of the recommended

Table 1. Summary of vadose-zone PITT scenarios

Scenario	Interwell Distance (ft)	Pore Volume (million ft³)	Test Duration (days)	Tracer Mass (kg/tracer)	Flow Rate (cfm/well)	Recovery (%)
D	145–237	2	20	50	125 (ext) 500 (inj)	81
D1	130–190	1.2	10	20	~167 (ext) 500 (inj)	73
D2	115–174	1.1	10	20	~167 (ext) 500 (inj)	78

PITTs for DNAPL detection and improved accuracy of the DNAPL saturation and volume estimates for the area to be tested by the PITT technology. This approach greatly improves the ability of the PITT technology to provide the necessary remedial design information with respect to DNAPL site characterization that is needed for the Z-9 Crib area.

5 GROUND-WATER PITTS

Simulations were conducted using UTCHEM to estimate the cost of a shallow groundwater PITT and a deep groundwater PITT. The proposed shallow groundwater PITT scenario involved tracer injection in well W15-86 and extraction in well W15-32 screened between depths of 195-235 ft bgs and 194-235 ft bgs, respectively. With the water table at a depth of 216.5 ft bgs, this resulted in an 18.5 ft screened interval. Based on input from BHI, a sustainable flow rate of 25 gpm of water injection and extraction was assumed. Due to the large interwell distance (172.7 ft) and the lack of hydraulic control (i.e., constraining the flow paths between injection and extraction wells) this scenario resulted in an excessively long test duration (months). For this scenario, additional simulations with pumping rates as high as 100 gpm still predicted a test duration in excess of 30 days. Furthermore, simulations indicated that the lack of hydraulic control would result in a very dispersed, diluted tracer response, thereby decreasing the sensitivity of the test in this scenario.

Although the specific wells for the deep groundwater PITT are to be determined, the interwell distance was assumed to be comparable to that of the shallow groundwater PITT. While the shallow groundwater PITT was somewhat constrained in the vertical direction by the water table (i.e., an overlying boundary constraint for the PITT), the deep groundwater PITT had one more degree of freedom with respect to boundary conditions. This translates into a larger swept pore volume, even more dispersion and therefore a lower degree of sensitivity for the deep groundwater PITT scenario. Based on these limitations to both proposed scenarios, alternative PITT scenarios were investigated for the saturated zone.

6 ALTERNATIVE SCENARIOS FOR GROUND-WATER PITTS

By shortening the interwell distance, both the test duration and dispersion are reduced. To evaluate a feasible distance at which a PITT could be conducted with acceptable sensitivity and accuracy, a simulation was conducted with the interwell distance reduced to 50 ft. The wells were assumed to be completed with 30-ft screened intervals in the saturated zone with sustainable flow rates of 100 gpm and a DNAPL saturation of 1%. The simulations indicate a much stronger tracer response (i.e., greater difference between peak and tail concentrations) for a smaller mass of tracer. This translates into a PITT design with much greater sensitivity by using the shorter interwell distance.

Another alternative was investigated which attempted to maximize the use of existing wells while circumventing the shortcomings of the proposed PITT scenario. This alternative involved using wells, W15-32 and W15-86 (the same wells in the original scenario) as extraction wells plus one additional well installed at the center point between the two wells. The center well would, of course, have to be installed as a slant well in order to obtain a screened interval beneath the Z-9 Crib. The wells were assumed to be completed with 30 ft screened intervals in the saturated zone and a sustainable extraction rate of 100 gpm and an injection rate of 200 gpm. Because the sustainable extraction rate is the limiting factor, this well configuration allows the total injection and extraction rates to be doubled, thereby decreasing the test duration. In addition, the decreased interwell distance also results in a shorter test duration and decreased dispersion. Finally, using two extraction wells placed on opposite sides of the injector results in a divergent-line drive flow field, which results in a substantial increase in the percent of tracer mass recovered. All these factors indicate that the three-well, divergent line drive well configuration provides a much more robust tracer test design. The results of the shallow groundwater zone PITT simulations are summarized in Table 2. A review of the results tabulated in Table 2 is very instructive for comparison of PITT wellfield configurations. Alternative 2 clearly shows the highest performance in terms of the pore volume investigated, test duration, tracer mass required, and tracer recovery. Tracer recovery is particularly notable for comparison of Alternative 2 to the original scenario since both use the same overall interwell distance. The vastly increased tracer recovery and significantly shorter test period in Alternative 2 yield a much stronger tracer signal at the extraction wells. While both of these PITTs test a similar pore volume of aquifer, the Alternative 2 scenario greatly increases the sensitivity of the PITT to measure DNAPL.

Table 2. Summary of ground-water PITT scenarios

Scenario	Interwell Distance (ft)	Pore Volume (million ft^3)	Test Duration (days)	Tracer Mass (kg/tracer)	Flow Rate (cfm/well)	Recovery (%)
Original Scenario	173	1.70	>30	>500	100	29
Alternative 1	50	0.38	20	300	100	67
Alternative 2	86 (x2)	2.20	20	300	100 (ext) 200 (inj)	75

7 APPLICABILITY OF PITTS AT HANFORD

The applicability of PITTs to estimate NAPL saturations is well documented in literature (Jin et al., 1995, 1997; Annable et al., 1998; Mariner et al., 1999). In general PITTs are excellent tools to characterize the volume and extent of NAPL in the pore space being tested. For NAPL saturations above 0.1%, and using tracers with good detectability to concentrations two orders of magnitude below the peak concentration will result in an uncertainty of around 10%. Furthermore, PITTs are a non intrusive technology and and have the distinct advantage in being able to test a large pore volume for the presence of NAPL.

One of the main challenges associated with the implementation of PITTs are the selection of tracers with an appropriate range of partition coefficients as well as detection limits. A high partition coefficient and low detectability will be required to detect low NAPL saturations. High partition coefficients and low detectability will also reduce the uncertainty associated with the detection and quantification of NAPL. Another challenge is to characterize the effect of variability in NAPL composition on the estimates of NAPL saturation. The paper by Dwarakanath et al. (1999) discusses the effect of variability in NAPL composition on the error in the estimate of NAPL saturations and estimated the error due to the variation in composition of the trichloroethene-rich Hill DNAPL was 7%. The equivalent alkane carbon number approach developed by Dwarakanath and Pope (1998) and the approach presented in Dwarakanath et al., (1999) may be used to estimate the effect of variable NAPL composition on the resulting NAPL estimation by a PITT at Hanford.

Additional background on PITT theory and methods is presented in Section 9. The laboratory studies that are proposed for the vadose-zone PITTs are described in Section 10, and a discussion of the errors associated with PITTs is included in Section 11.

8 COST ESTIMATE FOR THE VADOSE-ZONE PITTS

A detailed cost estimate, for designing and conducting two vadose-zone PITT's, D1 and D2, is included in Appendix A. The cost estimate is based upon a partnering effort that has been developed between Bechtel Hanford, Inc (BHI), Pacific Northwest National Laboratory (PNNL) and DE&S, as described in the PITT Guidance Document (DE&S, 2000). The DE&S cost estimate include a list of assumptions that were used as the basis for costing. The assumptions are generally related to the partnering of tasks that was developed in the PITT Guidance Document. The PNNL costs required to support the project are presented in Appendix B. BHI costs associated with this proposed project are not included herein.

A generalized schedule is shown in Appendix C, based upon the commencement of planning and design activities on September 1, 2000. The tentative total duration of proposed activities necessary to complete the D1 and D2 VZ-PITTs is approximately 300 days. A Pert chart is currently in preparation and will be distributed electronically under a separate cover. The Pert chart will show the relationship of various tasks throughout the project and to identify critical path tasks.

9 PITT THEORY AND METHOD

The partitioning interwell tracer test involves setting up a flow field in the subsurface between injection and extraction wells to measure the amount of NAPL contamination in the interwell zone. Partitioning and nonpartitioning tracers are introduced simultaneously in the injection wells, with subsequent measurement of the tracer concentrations in the extraction wells. The partitioning tracer is distributed between the mobile phase and the NAPL and is retarded relative to the nonpartitioning tracer, which remains in the mobile phase only. The mobile phase for a saturated zone PITT is water, while the mobile phase for a vadose zone PITT is air. The chromatographic separation of a partitioning tracer from the nonpartitioning tracer is directly proportional to the volume of NAPL contacted and the NAPL-water or NAPL-air tracer partition coefficient.

The simplest and most robust method for using PITT data to calculate the volume of NAPLs is the method of moment equations, using the first temporal moments of the tracer response data (Jin et al., 1995). A classical derivation of the method of moments theory applied to packed bed reactors can be found in work by Himmelblau and Bischoff (1969). The partition coefficient for tracer *i* between the NAPL phase and the mobile phase *j* is

$$K_i = \frac{C_{i,N}}{C_{i,j}} \tag{1}$$

where $C_{i,N}$ is the concentration of tracer i in the NAPL phase, while $C_{i,j}$ is the concentration of tracer i in mobile phase j.

The retardation factor for a partitioning tracer 2 relative to a nonpartitioning tracer 1 is given by

$$R_f = \frac{\overline{V}_2}{\overline{V}_1} \tag{2}$$

where

$$\overline{V}_i = \frac{\int_0^\infty C_i V dV}{\int_0^\infty C_i dV} - 0.5V_s \tag{3}$$

In Equation (3), V_s is the volume of the injected tracer slug, and V is the cumulative volume of fluid injected. For the case of multiple extraction wells or open test boundaries, the swept volume is calculated for each extraction well from

$$V_k = \frac{m_k}{M} \frac{\overline{V}_1}{1 - S_N} \tag{4}$$

where m_k is the tracer mass extracted from well k and M is the total tracer mass injected.

The retardation factor is related to the average NAPL saturation by

$$R_f = 1 + \frac{S_N K_2}{S_j} \tag{5}$$

where S_j is the saturation of the flowing phase. For saturated-zone PITTs, the flowing phase is water, and $S_j = 1 - S_N$. For unsaturated-zone PITTs, the flowing phase is air and $S_j = 1 - S_N - S_W$.

The NAPL volume in the swept volume of extraction well k ($V_{N,K}$) is calculated by

$$V_{N,K} = \frac{m_k}{M} \frac{\overline{V}_2 - \overline{V}_1}{K_2} \tag{6}$$

The total volume of NAPL (V_N) is the summation of the volume estimated from each extraction well and is given by

$$V_N = \sum_{K=1}^{Np} V_{N,K} \tag{7}$$

where N_p is the number of extraction wells.

The partition coefficient of a partitioning tracer can be measured by performing static partition coefficient experiments and/or soil column experiments. Static partition coefficient experiments are essentially partitioning isotherm experiments. A fixed volume of NAPL (V_{NAPL}) is mixed with a fixed volume of tracer solution (V_W) over a wide range of initial tracer concentrations. The NAPL-tracer solution is mixed and allowed to equilibrate. The initial concentration ($C_{i,ini}$) and equilibrium concentration ($C_{i,equ}$) of the tracer are measured using a gas chromatograph, and the concentration of the tracer in the NAPL ($C_{i,N}$) is calculated from a mass balance using the following equation:

$$C_{i,N} = \frac{V_W}{V_{NAPL}} \bullet (C_{i,ini} - C_{i,equ}) \tag{8}$$

The concentration of the tracer in the NAPL is plotted against the concentration of the tracer in the mobile phase, and the slope of this isotherm is the static partition coefficient. Performing partitioning isotherm experiments with gas phase tracers is very difficult and typically associated with a high level of error. Therefore, another means of measuring partition coefficients is to perform a PITT in a column with a known NAPL saturation. In these experiments a fixed mass of NAPL is added to a column. A PITT is conducted and the response of the partitioning tracers is used to determine their temporal moments. Equation (5) and the computed temporal moments are used to estimate the tracer partition coefficient. Such an estimate of the partition coefficient is defined as the dynamic partition coefficient (Dwarakanath et al., 1999). This technique has been extensively tested to estimate NAPL-air tracer partition coefficients (Whitley et al., 1999; Mariner et al. 1999; Deeds et al., 2000).

10 LABORATORY PROTOCOL

A total of four experiments will be conducted to determine the dynamic partition coefficients of the various candidate tracers. Two partitioning tracer experiments will be conducted in soil columns packed with Ottawa sand and containing a fixed volume of NAPL. The NAPL saturation will be set between 4% and 8%. The experimental procedures followed will be similar to those discussed in Whitley et al., (1999) and Deeds et al., (2000). In these experiments, methane will be used as the conservative tracer and perfluoro1,3-dimethylcyclohexane, perfluoro1,3,5-trimethylcyclohexane, and perfluorodecalin will be used as the partitioning tracers. The tracer concentrations will be monitored using a gas chromatograph. The temporal moments of the conservative and partitioning tracers and the NAPL volume will be used to estimate the partition coefficients.

Once the partition coefficients are measured, one experiment will be conducted in a column packed with uncontaminated aquifer material from the Ringold formation. This experiment will quantify the retardation of the partitioning tracers by the organic material present in the soil. Using the retardation factors observed in uncontaminated aquifer material and the measured partition coefficients the apparent NAPL volume estimated due to soil organic matter can be estimated. These estimates can be used later, if necessary, to correct the volume of NAPL determined during the PITT.

One final confirmatory experiment will be conducted in a soil column packed with sediments from the Ringold Formation, containing a known volume of NAPL to determine the accuracy of the partitioning tracers to estimate NAPL saturation.

11 ERRORS ASSOCIATED WITH PITTS

The errors in PITT measurement and analysis can be divided into two broad categories, systematic errors and random errors. Systematic errors usually occur in the measurement of fluid volumes and tracer concentration whereas random errors are usually associated with the measurement of partition coefficient and tracer retardation factors. The error associated with the measurement of tracer partition coefficients and retardation factors are typically the largest and most common errors associated with PITTs. There are other possible sources of systematic error that are site specific in some cases, or that can be eliminated or minimized with appropriate design of the PITT, or in some cases corrected with appropriate laboratory measurements under site specific conditions. An example of such an error is the adsorption of the tracers on the soil, that can result in a false positive i.e. a false detection of NAPL. In some laboratory experiments, tracers with high partition coefficients such as 1-heptanol (K=35) showed an apparent retardation on the order 1.12 in uncontaminated clay-rich soil from MCB Camp Lejeune, which translated into an apparent NAPL saturation of 0.4% PCE-rich DNAPL (Dwarakanath et al., 1999). However, conduct of several laboratory partitioning tracer experiments in uncontaminated soil can quantify the effect of retardation by the aquifer material and determine the appropriate correction factors that can be used to interpret the field PITTs. A detailed discussion of systematic and random errors is given in Dwarakanath et al., (1999).

In general for a well designed PITT with good analytical measurement of the tracer concentrations, the error in estimating the NAPL volumes is on the order of 10%. However for most field PITTs where a wide variation is observed in the NAPL saturations, the error in estimating NAPL saturations is between 10% - 25%. Typically for higher NAPL saturations, between 0.1% to 1%, or higher, the uncertainty of saturation measurement could be lower, i.e., in the range of 10 to 15%. However, if the NAPL saturation is low, such as in the range 0.01% to 0.1% or lower, the uncertainty could be considerably higher, sometimes even >> 50%. The higher uncertainty associated with the detection of low NAPL saturations is due to small retardation factors as the retardation factors are directly proportional to the NAPL saturation (see Equation 5).

Theoretically speaking, a PITT can detect any volume of NAPL as long as there is NAPL present in the flow path of the partitioning tracer. Once the partitioning tracer contacts NAPL in its flow path, the tracer will partition into the NAPL, which will consequently result in some retardation. The uncertainty in estimating NAPL is therefore due to the experimental error associated with the measurement resulting in a practical NAPL saturation that a PITT can estimate with certainty. Other factors that affect the uncertainty in NAPL estimation using partitioning tracers include limitations on the test duration, potential tracer biodegradation, and the physical properties of the tracers. Geosystem factors such as the NAPL distribution and aquifer heterogeneity also affect the accuracy of PITT detection. The influence of most of these factors can be compensated for by a robust tracer test design. As a rule of thumb, however, an average NAPL saturation as low as 0.05% can be measured with more than 50% certainty with a well-designed PITT and a GC quantification limit at least two orders of magnitude lower than the peak tracer concentration. Finally, the estimation error is higher if free phase NAPL is present (Jin et al., 1997).

12 LIST OF SYMBOLS

$C_{i,j}$ = Concentration of tracer *i* in phase *j* (ML^{-3})

$C_{i,I}$ = Initial concentration of tracer *i* in water for partition coefficient experiments (ML^{-3})

$C_{i,N}$ = Equilibrium concentration of tracer *i* in the NAPL for batch partition coefficient experiments (ML^{-3})

$C_{i,W}$ = Equilibrium concentration of tracer *i* in water for batch partition coefficient experiments (ML^{-3})

K_i = Partition coefficient of tracer *i* (ML^{-3}/ML^{-3})

m_k = Mass of tracer recovered in extraction well *k* (M)

m_t = Mass of tracer injected (M)

M = Total mass of tracer injected (M)

Q = Total injection rate (L^3T^{-1})

R_f = Retardation factor

S_j = Saturation of flowing phase *j*

S_N = Saturation of NAPL

S_w = Saturation of water

V_1 = First moment of volume of the nonpartitioning tracer (L^3)

V_2 = First moment of volume of the partitioning tracer (L^3)

V_N = Volume of NAPL (L^3)

V_S = Volume of injected tracer solution (L^3)

V_W = Volume of water (L^3)

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APPENDIX A

COST ESTIMATE FOR THE VADOSE-ZONE PITTS

APPENDIX B

PNNL COSTS FOR Z-9 VADOSE-ZONE PITTS

The material contained herein is submitted for informational purposes only and is not binding on Battelle. Binding commitments can only be made by the submission of a formal proposal which sets forth a specific Statement of Work, estimated cost, and contract documents, and which is signed by a Battelle duly authorized contracting representative.

APPENDIX C

PROJECT SCHEDULE