Final Report

Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface

by

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ABBREVIATIONS AND ACRONYMS

BTC	Breakthrough Curves
COTS	Commercially Off-The-Shelf
CPM	Critical Path Method
DNTS	Dover National Test Site
DoD	Department of Defense
DP	Drive Point
DNAPL	Dense Non-Aqueous Phase Liquid
ESTCP	Environmental Security Technology Certification Program
FLUTe™	Flexible Liner Underground Technologies, LLC
LSC	Liquid Scintillation Counter
MCL	Maximum Contaminant Level
NAPL	Nonaqueous Phase Liquids
ND	Not Detected
NO_3	Nitrate
NTS	National Test Site
O_2	Oxygen
OSU	Oregon State University
PAM	Physical Aquifer Model
P&T	Purge And Trap
PCE	Perchloroethene
PID	Photoionization Detector
PITT	Partitioning Interwell Tracer Test
QA/QC	Quality Assurance/Quality Control
Ra	Radium-226
Rn	Radon-222
STOMP	Subsurface Transport Over Multiple Phases
TCE	Trichloroethene
U.S. EPA	United States Environmental Protection Agency

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EXECUTIVE SUMMARY

Nonaqueous phase liquids (NAPL), including chlorinated solvents, aromatic hydrocarbons, and other volatile organic chemicals (VOC), are common contaminants at Department of Defense (DoD) and other federal and non-federal sites. Residual or pooled NAPL contamination provides a long-term source of contamination as it slowly dissolves into groundwater. A major obstacle preventing cost-effective soil and groundwater cleanup at many DoD sites is the current inability to accurately and inexpensively locate and quantify NAPL contamination. This final report describes the use of naturally occurring radon-222 (Rn) as a partitioning tracer for locating and quantifying NAPL contamination in the subsurface and for monitoring changes in NAPL quantities resulting from remediation activities.

Radon-222 possesses unique physical properties that make it a useful "natural" partitioning tracer for detecting and quantifying NAPL. Rn is produced in the subsurface by the continuous decay of naturally occurring radium-226. In the absence of NAPL contamination, the aqueous Rn concentration quickly reaches a site-specific equilibrium value determined by the mineralogy and porosity of the geologic formation. In the presence of NAPL, however, the Rn concentration is substantially reduced due to partitioning of Rn into the organic NAPL phase. Moreover, the reduction in Rn concentration of groundwater in contact with a NAPL phase is quantitatively correlated with the quantity of NAPL present, as described by simple equilibrium models. Thus, the method is based on measuring Rn in groundwater samples from existing monitoring wells.

Two methods of using radon were evaluated in the study: a 1) "static" method which involves the monitoring of NAPL concentrations in groundwater samples collected spatially and temporally at a site, and 2) a "dynamic" method using single well push-pull tests, which is based on the retardation in radon transport that results from the partitioning process. The static method provides an end user with a means to easily survey NAPL contamination under subsurface conditions that are not heterogeneous with respect to parameters that dictate radon concentrations under background conditions (no NAPL present) at the site. More importantly, the static method can provide a method for monitoring the progress of remediation at a specific location. In this application the method is less sensitive to local variations in geology that affect the background Rn concentration. The "dynamic" push-pull-test method, although more complicated test to perform, potentially eliminates the complexities that result from non-homogenous subsurface conditions. In push-pull tests radon free groundwater is injected along with a conservative tracer, such as bromide, into a standard monitoring well, using the entire well screen or a packed section to probe a specific depth interval. Upon extraction at the same

location the breakthrough of bromide and the radon is monitored and then analyzed to estimated radon retardation factors, which provide estimates of NAPL saturation in the vicinity of the test well.

Physical aquifer model (PAM) studies were performed to evaluate push-pull tests under controlled laboratory conditions. Tests performed in the presence and absence of NAPL show an increase in radon retardation in the presence of TCE NAPL contamination of around 2%. Model simulations using the numerical transport code STOMP that included radon partitioning and the geometry and boundary conditions of the PAM tests did a good job in reproducing the bromide and radon breakthrough curves with a NAPL saturation similar to that emplaced in the PAM. The results show that under very controlled laboratory conditions, push-pull tests performed by injecting only radon free water containing a bromide tracer, were able to quantify NAPL saturations.

Both static and dynamic methods were used to detect changing NAPL saturations in a test cell at the Dover National Test Site. Tests were conducted in a test cell where 100 L of PCE was added to create NAPL contamination in the saturated zone. The test cell consists of fine- to medium-grade sand. Radon surveys and push-pull tests were performed in four wells that were installed near the PCE spill. Surveys performed prior to the release of PCE quantified the spatial variations in radon that resulted from geologic factors (primarily porosity and mineralogy). Upon releasing PCE, radon concentration decreased in some locations, but increased in others. Long term monitoring of radon concentrations during NAPL remediation showed increases in radon concentration that were consistent with NAPL removal. The increases occurred over a short period of time reflecting NAPL movement in the test cell in response to induced groundwater flow. Push-pull tests were performed in four of the monitoring wells at different times and at different depth intervals. For many of the tests, it was difficult to detect radon responses that would indicate retarded radon transport due to the presence of NAPL. In tests conducted during the remediation of the PCE, comparison of push-pull tests conducted over the period of eight months showed decreased radon retardation and increased radon concentration, which both indicated remediation of NAPL contamination. The results agreed with the static radon test results and indicated that decreases in NAPL residual saturation of about 1% likely occurred in response to inducing groundwater flow in the test cell. The results indicate that a combination of static and dynamic push-pull tests might be used to monitor the progress of NAPL remediation. Static tests however are much easier and less costly to employ than push-pull tests. The results indicate that the radon method is best employed when a NAPL residual saturation greater than 1 % exists, and wells for sampling exist within a NAPL source zone. The method would be best combined with other methods, such as FLUTe™ ribbon samplers, that can identify the depth intervals where NAPL exists. Long-term monitoring using the static radon method, and possibly combined with dynamic push-pull tests, can be used to estimate NAPL saturation and monitor the progress of remediation. The end user is provided with data sets and methods for potentially adopting the radon method, which might be used along with other methods for characterizing NAPL contamination and the progress of remediation efforts.

1. Background

Nonaqueous phase liquids (NAPL), including chlorinated solvents, aromatic hydrocarbons, and other volatile organic chemicals (VOC), are common contaminants at Department of Defense (DoD) and other federal and non-federal sites. Residual or pooled NAPL contamination provides a long-term source of contamination as it slowly dissolves into groundwater (Mercer and Cohen, 1990; Cohen and Mercer, 1993). Effective site remediation and monitoring programs require accurate information on the locations and volumes of NAPL contamination in the subsurface. In addition, monitoring NAPL quantities during and after remediation activities is highly desirable to quantify the extent of cleanup achieved and to verify the cost-effectiveness of the remediation method. *A major obstacle preventing cost-effective soil and groundwater cleanup at many DoD sites is the current inability to accurately and inexpensively locate and quantify NAPL contamination.*

This final report describes the use of naturally occurring radon-222 (Rn) as a partitioning tracer for locating and quantifying NAPL contamination in the subsurface and for monitoring changes in NAPL quantities resulting from remediation activities.

Section 1 (*Background)* provides an introduction to the technology, including background information on the use of partitioning tracer tests for NAPL characterization, objectives, regulatory drivers, and previous testing of the technology. Section 2 (*Technology Description)* describes the use of static and dynamic Rn sampling for detecting and quantifying NAPL contamination in the subsurface and reviews the advantages and limitations of the technology. Section 3 (*Demonstration Design*) describes the performance objectives, test site, and facilities. The performance assessment is provided in Section 4, which includes an interpretation of the results of the demonstration. The cost assessment is included Section 5, and implementation issues, such as cost and performance observations, lesson learned, and approaches to regulatory compliance and acceptance in Section 6. References are included in Section 7.

1.1 Partitioning Tracer Tests for NAPL Characterization

Traditional methods for locating and quantifying NAPL contamination consist of analyzing sediment or groundwater samples (Cohen and Mercer, 1993). However, sediment core collection is expensive and sample volumes are often small, which prevent efficient site-scale NAPL characterization by sediment sampling. Although high contaminant concentrations in groundwater samples can provide indirect evidence of the presence of NAPL, groundwater data alone cannot provide quantitative information on the quantity of NAPL that may be present.

Partitioning tracer tests provide an alternative method for quantifying NAPL contamination in the subsurface. In this type of test a suite of tracers, including both water- and NAPL-soluble compounds, is injected into the subsurface to probe for the presence of NAPL. The presence of NAPL is inferred from the difference in mobility between the injected NAPL-soluble tracers, which partition into the NAPL, and the injected water-soluble tracers, which remain in the aqueous phase. The relative mobility of the two types of tracers can be used to calculate retardation factors, from which the average NAPL saturation in the interrogated portion of the aquifer may be computed. A variety of alcohols and other organic compounds have been used as

partitioning tracers, while anions have been used as water-soluble tracers (Jin et al., 1995; Nelson and Brusseau, 1996; Annable et al. 1998; Nelson et al. 1999; Young et al. 1999). In addition to site characterization, partitioning tracer tests can be used to monitor the progress of NAPL remediation efforts. By performing partitioning tracer tests before and after remedial action, the reduction in NAPL saturation achieved by remedial action may be determined. Partitioning tracers have been shown to reliably detect the presence of NAPL contamination even in trace amounts (e.g., Jin et al., 1995). Conventional partitioning tracers, however, can be expensive, difficult to analyze for, and often require regulatory approval before they can be injected into the subsurface.

1.2. Objectives of the Demonstration

The purpose of this demonstration was to evaluate the potential of using naturally occurring Rn to quantify NAPL contamination in the subsurface and to monitor the progress of NAPL remediation. The specific objectives were:

1) To evaluate a "static method" using Rn concentration measurements to quantify NAPL contamination and monitor the progress of NAPL remediation
2) To evaluate a "dynamic" push-pull-single-well test to quantify NAPL contamination and to monitor the progress of remediation.
3) To conduct tests in both a physical aquifer model (PAM) and at a field site to both quantify NAPL contamination and to monitor the progress of remediation.

1.3 Regulatory Drivers

The target compounds for these tests were Perchloroethyene (PCE) and Trichloroethylene (TCE), which are both frequently observed subsurface contaminants existing as NAPL phases. The regulatory drivers for these environmental contaminants are maximum contaminant levels (MCLs) governed under the Safe Drinking Water Act (42 U.S.C s/s 300f et seq. 1994). The U.S. EPA has set a maximum contaminant level (MCL) of 0.005 mg/L for both PCE and TCE and (Source: http://www.epa.gov/safewater/mcl.html#3).

1.4 Stakeholder/End-User Issues

The demonstration provides information on how to conduct and perform tests using the Rn method of NAPL detection and quantification. Two methods are evaluated: a 1) "static" method which involves the monitoring of NAPL concentrations in groundwater samples collected spatially and temporally at a site, and 2) a "dynamic" method using single well push-pull tests. The static test can potentially provide an end user with a means to easily survey NAPL contamination under subsurface conditions that are not very heterogeneous with respect to parameters that dictate radon concentrations under ambient (no NAPL) present at the site. The static test method, more importantly, can provide a method for monitoring the progress of remediation at specific locations, even when heterogeneities are present.

The "dynamic" push-pull-test method is a more complicated test to perform, but potentially eliminates the complexities that result from non-homogeneous subsurface conditions and can interrogate a larger volume of the subsurface. The application of both methods would help

confirm observations at a site. The end user is provided with data sets and methods for potentially adopting the Rn method for characterizing NAPL contamination and the progress of remediation efforts.

2. Technology Description

2.1 The Natural Radon Tracer Method

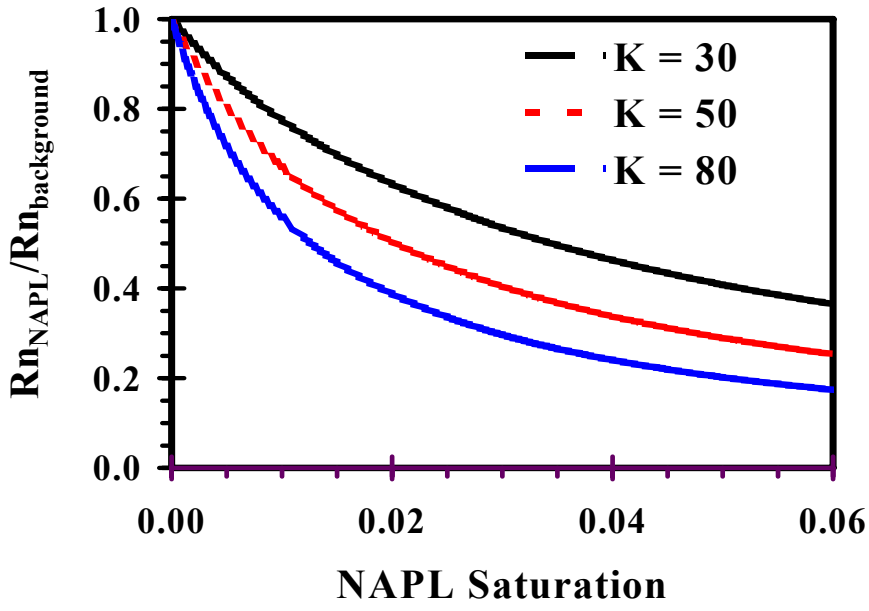
Rn possesses unique physical properties that make it useful as a partitioning tracer for detecting and quantifying NAPL, including its presence in detectable concentrations in nearly all subsurface environments and its affinity for organic liquids. Rn is produced in the subsurface by the continuous decay of naturally occurring Ra-226 (Ra). In the absence of NAPL contamination, the aqueous Rn concentration quickly reaches a site-specific equilibrium value determined by the mineralogy and porosity of the geologic formation. In the presence of NAPL, however, the Rn concentration is substantially reduced due to partitioning of Rn into the organic NAPL phase (Semprini et al. 2000). Moreover, the reduction in Rn concentration in the presence of NAPL is quantitatively correlated with the quantity of NAPL present. Thus, by measuring Rn concentration in groundwater samples from existing monitoring wells, it may be possible to identify those locations where NAPL is likely present and to obtain preliminary estimates for NAPL saturation.

The theory and capabilities of the natural radon tracer method have been previously tested in laboratory and field experiments. A simple equilibrium-partitioning model has been found to accurately describe the Rn partitioning process Semprini et al., 1993; Hopkins, 1995; Semprini et al., 2000; Davis et al. 2002):

$$\frac{Rn_{NAPL}}{Rn_{Background}} = \frac{1}{1+S_{NAPL}(K-1)} \qquad (2.1)$$

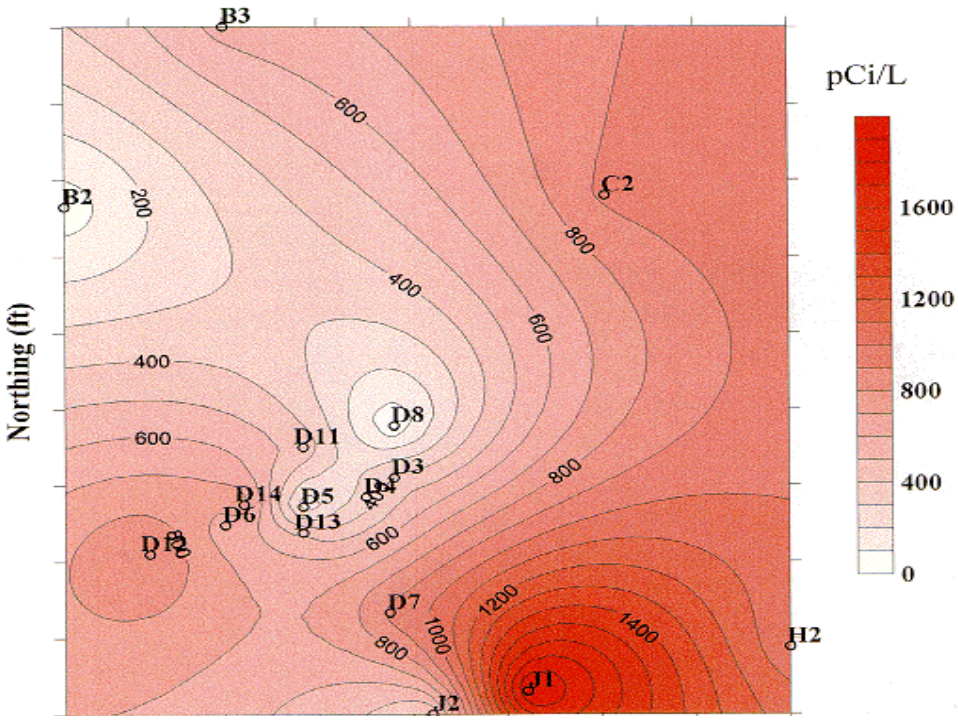
where Rn_{NAPL} is the Rn concentration (pCi/L) in a groundwater sample from a NAPL contaminated zone, $Rn_{Background}$ is the Rn concentration (pCi/L) in a "background" groundwater sample from outside the contaminated zone, S_{NAPL} is the residual NAPL saturation (NAPL volume/pore volume), and K is the Rn NAPL:water partition coefficient (dimensionless). The model predicts that as the residual NAPL saturation increases, Rn concentration in groundwater within the NAPL zone will decrease relative to Rn concentrations in adjacent uncontaminated regions (Figure 2.1). Assuming a K of 50 (typical for chlorinated solvents) (Cantaloub, 2001) and a S_{NAPL} of 0.01, the equilibrium model indicates that Rn concentrations in the NAPL contaminated zones will be only 0.67 (67 %) of the Rn concentration in a background monitoring well, which is easily detectable. Thus, the Rn method is sensitive to the presence to NAPL saturations of approximately 1% or greater.

Figure 2.1. Effect of NAPL saturation on Rn concentration in presence of NAPL relative to background Rn concentration



It may be possible to perform "static" Rn sampling to rapidly survey a site to identify locations where NAPL contamination may be present and to obtain initial estimates for NAPL saturations in contaminated zones. An example of this approach is shown in Figure 2.2, which displays a contour map of Rn concentrations obtained by sampling monitoring wells at the Building 834 operable unit of Site 300 at Lawrence Livermore National Laboratories (Semprini et al. 2000). The low Rn concentrations near wells B-2, D-5, and D-8 indicate the likely presence of NAPL. Preliminary estimates of NAPL saturation at these locations were obtained by substituting measured Rn concentrations in these wells into equation 1. For this calculation to be performed, a "background" Rn concentration from a well outside the potential NAPL zone must also be measured (e.g. well J1 in Figure 2.2).

Figure 2.2. Example results of static Rn sampling for locating NAPL



The major limitation of the static Rn sampling approach is the inherent variability in background Rn concentrations. Background Rn concentrations are determined by the mineralogy and porosity of aquifer sediments through equation 2.2:

$$C_{Rn_{background}} = \frac{C_{Ra} E \rho_b}{n} \qquad (2.2)$$

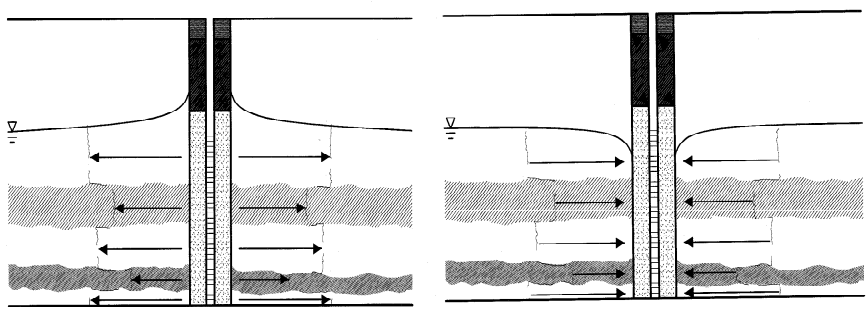
where $C_{RnBackground}$ is the radon concentration in the groundwater (pCi/L), C_{Ra} is the radium concentration of the aquifer solids (pCi/kg), E is radon emanation power (fraction of radon produced in the solids that reaches the pore fluid) of aquifers solids (-/-), ρ_b is the bulk density of the formation (kg/L), n is the porosity. Thus, natural variability in any of these factors will be reflected in variability in background Rn concentrations, which may make delineating NAPL contamination difficult using only static groundwater surveys. It should be noted that this limitation will likely not be important when the Rn method is used to monitor the progress of remediation activities, unless these results in changes in aquifer mineralogy from the remediation process.

To overcome this limitation, dynamic radon sampling can be employed by performing a partitioning tracer test, wherein Rn-free water containing a non-NAPL-partitioning (conservative) tracer is injected into the subsurface while monitoring Rn and conservative tracer concentrations at one or more points. From these data we can compute the retardation factor for Rn, which can be used to compute the average NAPL saturation in the portion of the aquifer interrogated during the test using:

$$R = \frac{V_{tracer}}{V_{radon}} = 1 + K\frac{S_{NAPL}}{S_w} \qquad (2.3)$$

where R is the retardation factor (dimensionless), V_{tracer} is the velocity of the non-partitioning tracer, V_{radon} is the Rn velocity, S_w is the water saturation (volume of water/volume of aquifer) and $S_{NAPL} + S_w = 1$. These tests must be of short duration compared to the half-life of Rn (3.83 days) so that radon emanation from the aquifer solids does not affect the results. One potential means of determining retardation factors is the use of single-well tracer tests called "push-pull" tests (Figure 2.3), which can be accomplished over short time periods.

Figure 2.3. Single-well, "push-pull" partitioning tracer test; injection phase (left), extraction phase (right)



In this push-pull partitioning tracer test, Rn-free water containing a non-partitioning tracer is injected into the saturated zone using an existing monitoring well; the injected test solution is then extracted from the same location. During the extraction phase, water samples are collected and analyzed for Rn and non-partitioning tracer and used to prepare breakthrough curves for both solutes. Test breakthrough curves are analyzed using type-curves prepared by numerical modeling (Figure 2.4) (Davis et al. 2002). In Figure 2.4, C/C_b is the ratio of a measured Rn concentration in a sample (C) to the local background concentration C_b and V_e/V_i is the ratio of the cumulative volume of water extracted at the time the sample was collected (V_{ext}) to the volume of water injected (V_{inj}). One of the assumptions of the analysis shown in Figure 2.4 is that the NAPL is uniformly distributed throughout the aquifer.

The injected test solution volume and the aquifer porosity determine the volume of aquifer interrogated during a push-pull test. The injected test solution volume is known precisely and the accuracy of this calculation depends largely on the accuracy of the porosity value. However, the shape of the interrogated zone is likely unknown because of the inevitable presence of aquifer heterogeneities that cause the injected test solution to flow further from the well along high conductivity flow paths.

Figure 2.4. Retardation is indicated by increased dispersion in a push-pull test.

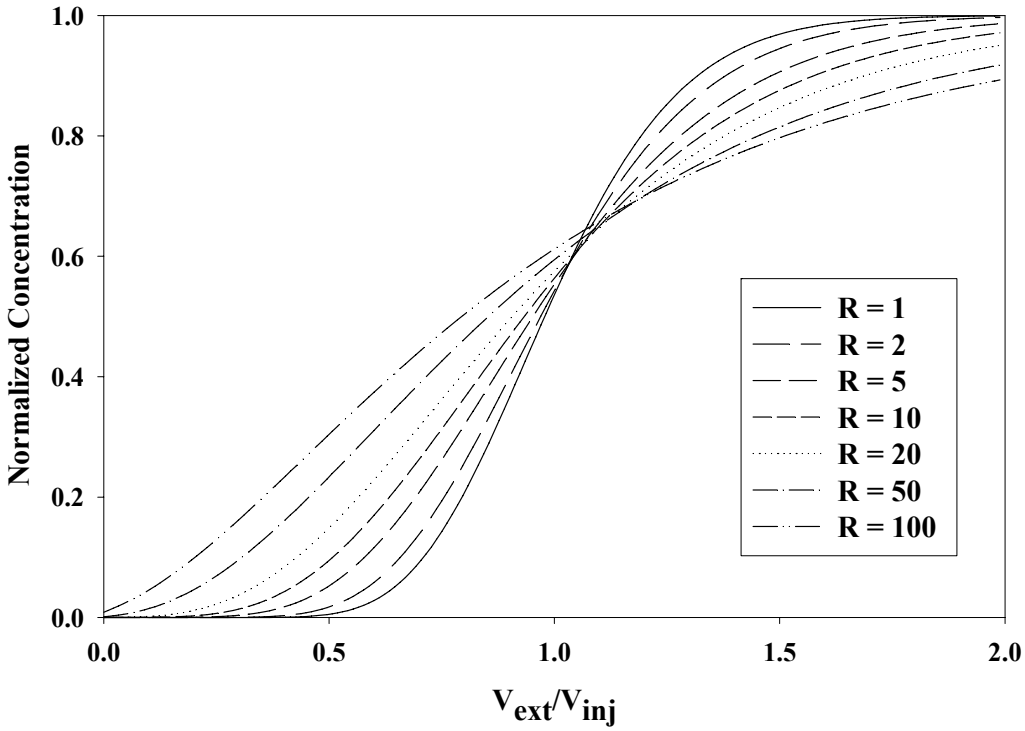


Figure 2.4 shows the effect of varying retardation factors on numerically simulated extraction phase radon breakthrough curves for push-pull tests conducted by injecting Rn-free water. In this figure V_{ext}/V_{inj} corresponds to the cumulative volume of extracted solution at a given time divided by the total volume of injected solution (i.e., dimensionless time). These simulations were performed by Schroth et al. 2000) using the Subsurface Transport Over Multiple Phases (STOMP) code (White and Oostrom, 2000). Note that normalized Rn concentrations increase during the extraction phase since a Rn-free test solution is injected. In the absence of NAPL, Rn behaves like a conservative tracer ($R = 1$); in the presence of NAPL, Rn transport is retarded ($R > 1$), resulting in an increased apparent dispersion during the extraction phase.

Previous field applications of radon as a partitioning tracer relied on observed decreases in radon concentrations in NAPL-contaminated areas relative to radon concentrations in non-contaminated areas (Hunkeler et al., 1997; Semprini et al., 2000).

In this study we evaluated using single-well, "push-pull" tracer tests using radon as a natural partitioning tracer to quantify saturations. Laboratory push-pull tests were performed in physical aquifer models using sediment prepared with and without TCE. Field push-pull tests were performed at the Dover National Test Site (DNTS) in a test cell where PCE was released. Numerical solutions to solute concentrations during the injection and extraction phases of the

push-pull test were used to estimate radon retardation factors; retardation factors were then used to calculate TCE saturations in laboratory experiments.

Our approach involved the injection of a known volume of radon-free test solution containing a conservative tracer into a single well, followed by the extraction of the test solution/groundwater mixture from the same well. TCE saturations were determined by estimating the Rn retardation factor from measured conservative tracer and radon concentrations obtained during the injection and extraction phases of the test. The retardation factor (R) for radon in a NAPL-contaminated aquifer is defined as

$$R = \frac{v_w}{v_{Rn}} \qquad (2.4)$$

where v_w is the groundwater velocity and v_{Rn} is the velocity of radon in groundwater. Assuming linear equilibrium partitioning the retardation factor for radon may be written as (Dwarakanath et al., 1999)

$$R = 1 + \frac{KS_n}{S_w} \qquad (2.5)$$

where S_n and S_w are the NAPL and water saturations in the pore space ($S_n + S_w = 1$). Once the retardation factor is known, the NAPL saturation could then be calculated via (Dwarakanath et al., 1999)

$$S_n = \frac{R-1}{R+K-1} \qquad (2.6)$$

2.2. Previous Testing of the Technology

The technology has been tested under laboratory conditions, in column studies with different degrees of NAPL saturation (Semprini et al. 2000). The results of these were modeled and showed the decrease in Rn concentration in the pore fluid resulted from an increase in NAPL saturation, consistent with the results shown in Figure 2.1. In addition, the modeling of the column studies showed the expected retardation in Rn transport due to the presence of NAPL. Limited field tests of the technology have been performed. Semprini et al. (2000), presented results from the emplace NAPL source experiments conducted at the Borden Field site in Canada. Rn concentration decreases were observed that resulted from the emplaced sources, and a Rn transport models was used to simulate the responses observed in the field. Semprini et al. (2000b) reported radon groundwater surveys at the Building 834 operable unit of Site 300 Lawrence Livermore National Laboratories Site. At this site, heavily contaminated with TCE NAPL, deficits in Rn concentration were observed that coincided with the zone of NAPL contamination (Figure 2.2).

2.3 Factors Affecting Cost and Performance

The Rn method has the advantage over other partitioning tracers in that it is naturally produced, thus it does not need to be added to the subsurface. In the simplest form of the application, Rn concentration in groundwater samples needs to be determined spatially or temporally. Samples are obtained using standard methods of sampling for Volatile Organic Analysis using VOA bottles. Rn has a half-life of 3.83 days, thus Rn samples must be processed within a few days to obtain accurate measurements. As previously discussed, spatial sampling for radon to identify NAPL contamination can be problematic due to spatial variability in subsurface geology that dictates the background radon concentration in subsurface fluids. The likely best use of the method is temporal sampling at a specific location to monitor the progress of NAPL remediation. This would be a fairly inexpensive means of monitoring remediation, since it only requires the monitoring of radon concentrations in fluids produced from areas containing NAPL. The method is best applied when the NAPL is immobile, and fluids produced are in direct contact with the NAPL phase.

Dynamic push-pull tests, where water lacking radon is injected along with a conservative tracer, such as the concentration response upon extraction is monitored. These tests would be more costly to perform. These tests might be performed in conjunction with other partitioning tests, where the partitioning tracer is added. The cost associated with adding radon analysis to these tests would be minimal, and would provide confirming data. Based on the results of our technology demonstration, the Rn method does not appear to be a stand-alone tool, but it best used in conjunction with other methods.

2.4 Advantages and Limitations of the Technology

The natural Rn tracer method has some unique properties for detecting and quantifying NAPL contamination in the subsurface. For static Rn sampling, this includes the ability to rapidly screen a field site for the presence of NAPL using only groundwater samples collected from existing monitoring wells. Sample collection protocols for radon analysis are identical to those used to collect samples for conventional VOC analyses, except that sample hold times are reduced because of Rn's short half-life. Application of the natural Rn method requires the presence of monitoring wells or other methods for injecting and/or extracting groundwater samples from the subsurface (e.g. multilevel samplers, drive-points, etc.) and detectable radon concentrations. The effectiveness of static radon sampling in detecting NAPL is in part controlled by the heterogeneity of radium content, radon emanation power, and porosity of aquifer sediments. (Equation 2.2). Static radon sampling may be less useful at sites that display heterogeneity in these properties. This limitation may not be of concern when monitoring radon concentration responses as remediation proceeds because local geologic conditions are likely not to change. For site conditions where remediation is not being implemented, or where stronger confirmation is required, this limitation might be overcome with dynamic radon sampling using either the single-well, "push-pull" test or the well-to-well test methodology. The push-pull test method has several advantages over well-to-well tracer tests including the need for only a single well, and the ability to perform tests relatively quickly using minimum volumes of injected and extracted water. A limitation of the push-pull method is that it interrogates only a small volume of the aquifer and would be more sensitive to spatial heterogeneities in NAPL saturation.

As the retardation response is reflected mainly by increased dispersion (Figure 2.4), the retardation by advection observed in well-to-well tests is lost. Another limitation of the radon method is that dilution by native groundwater with high radon concentrations can interfere with the decreases in radon that result from the partitioning into the NAPL. Thus when NAPL contamination occurs over small spatial scales, the radon sampling must also occur over similar scales. As with a half-life of 3.83 days, the radon rapidly equilibrates to background levels away from the NAPL source zone. Thus the method applies to samples obtained mainly from direct contact with the NAPL zone. The partitioning to the NAPL limits the detection with radon to NAPL saturations of approximately 1% or greater. Thus the method would be of use in cases of high NAPL saturation.

3. Demonstration Design

3.1 Performance Objectives

The primary performance objective of this study was to demonstrate Rn as a natural partitioning tracer for locating and quantifying NAPL contamination in the saturated zone. A combination of field tests were performed, including spatial and temporal surveys, called "static tests," and dynamic "push-pull-tests." In addition, push-pull tests were performed in a laboratory physical aquifer model (PAM) to evaluate the radon push-pull test method under controlled conditions. Performance objectives, performance criteria, expected performance, and actual performance are presented in Table 3.1.

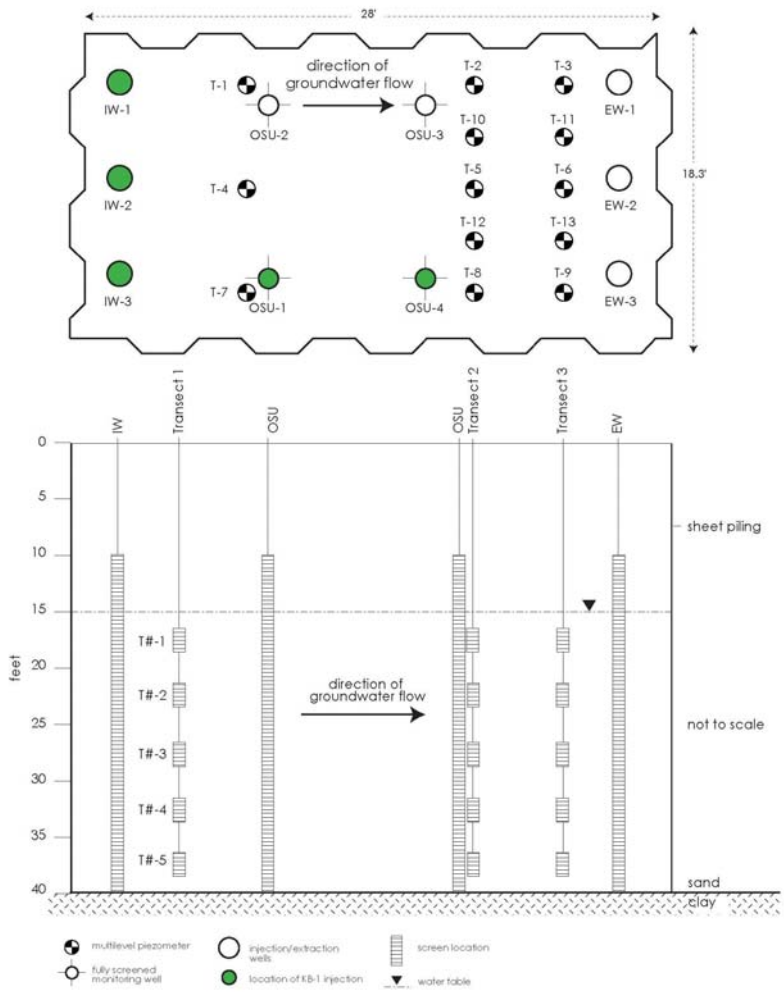
Table 3.1: Performance Objectives

Type of Performance Objective	Primary Performance Criteria	Expected Performance	Actual Performance
Quantitative	Estimate NAPL saturation with push-pull tests performed in laboratory Physical Aquifer Model (PAM).	Observed retardation can be used to estimate NAPL saturation.	Numerical model used to simulate observations. Reasonable measurements of NAPL saturation were achieved.
Quantitative	Spatial surveys of radon concentration in the Dover tests cell to quantify NAPL saturation.	Decreases in radon concentration spatially could be use to locate and quantify NAPL saturation.	Radon concentrations were variable and appeared to result from geologic variability. Geophysical methods tested by others were unable to locate or quantify the NAPL contamination.
Quantitative	Temporal survey of radon concentration at select locations in the Dover test cell.	Increases in radon concentration at specific locations could be used to monitor the progress of remediation.	Concentrations increases appeared to be linked with NAPL transport as a result of flow of groundwater.
Quantitative	Push-pull tests conducted to estimate NAPL saturation.	Retarded response in radon transport could be use to estimate NAPL saturation.	Retarded response observed in push-pull tests was used to estimate NAPL saturation.

3.2 Selecting the Test Site

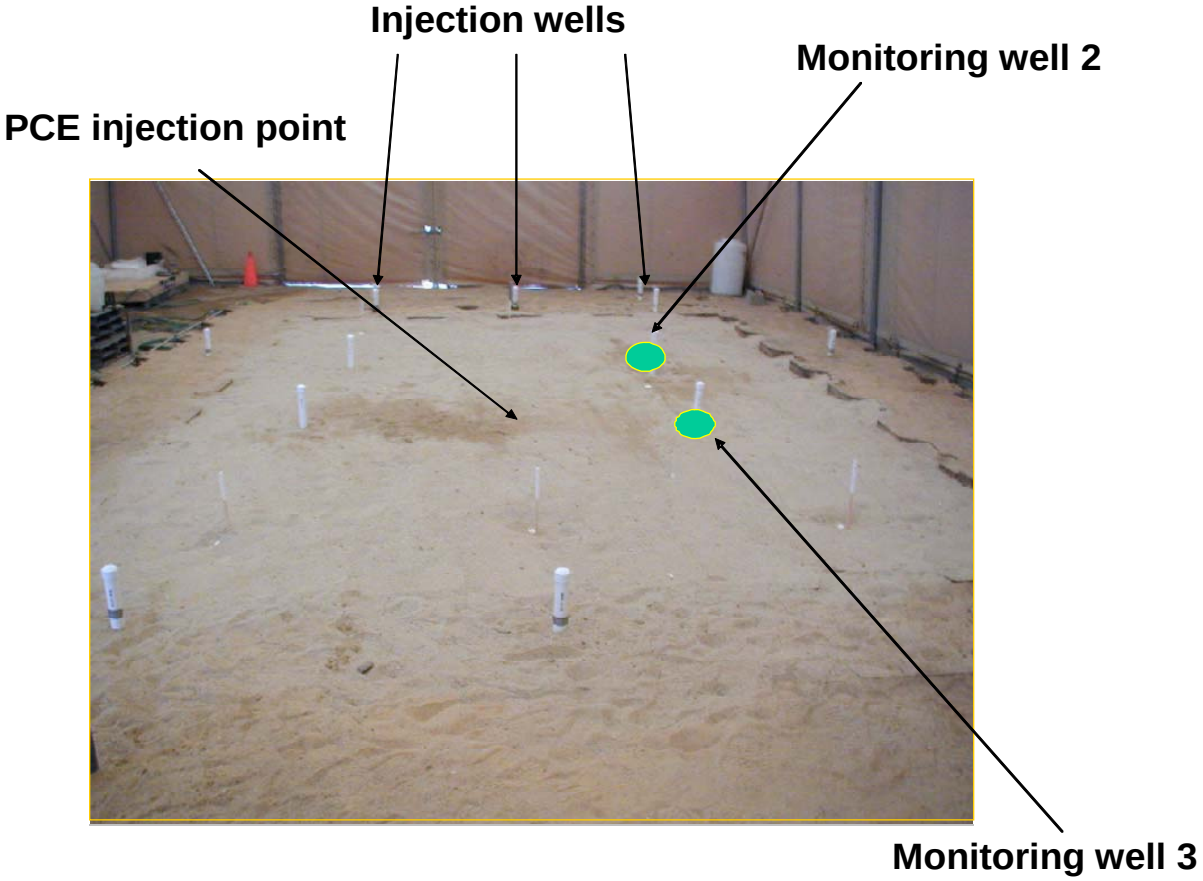
Field tests were conducted in a test cell located at the Dover National Test Site (DNTS) at Dover Air Force Base, Dover, Delaware. At the DTNS site, NAPL contamination resulted from a controlled release of perchloroethene (PCE) into the test cell. The test cell at the site also underwent active remediation using enhanced in situ bioremediation. The PCE released into the test cell was also to be investigated by others using geophysical methods. This test cell consists of native sandy aquifer material surrounded by double-walled sheet piling. The test cell is 27 ft long, 18 ft wide, and is underlain by a clay aquitard approximately 40 ft below grade. Figure 3.1 is a schematic of a test cell used in the demonstration. At each end of the test cell, a gallery of wells permits groundwater to be injected at one end and extracted at another to create induced gradient conditions. Monitoring wells are located in the interior of the test cell.

Figure 3.1 Test cell used at DNTS for the static and dynamic tests. Tests were performed in OSU wells 1-4.



(Figure is provided courtesy of GeoSyntec Consultants)

Figure 3.2. Test cell used in the demonstration and well used for long term monitoring



Shown in Figure 3.2 is a photo of the test cell used in the demonstration and the long-term monitoring locations during the bioremediation study. Injection wells pumped radon-free water into the test cell; extraction wells removed the water from the opposite end. Two monitoring wells aligned with the flow gradient are used to obtain radon samples. The test cell is equipped with four monitoring wells arranged in an 8 ft by 8 ft square pattern surrounding the location of the NAPL release. The monitoring wells were slotted in the saturated zone over an interval of 10 to 40 ft below ground surface. In July 2001 approximately 100 L of perchloroethene DNAPL (PCE) was released into the test cell.

GeoSyntec Consultants began an interwell tracer test in the test cell on March 22, 2002, using a conservative chloride tracer. The tracer test solution consisted of test cell groundwater that is treated for aqueous phase organics using a carbon adsorption system. Chloride was added before injection of the solution into the south end of the test cell through three injection wells. Three extraction wells were located at the north end of the test cell. The wells were pumped at a constant rate, thus creating a uniform flow field within the test cell.

Two multilevel samplers for collecting groundwater samples for radon analysis were installed prior to the tracer test. These samplers were capable of sampling three depth intervals: 17-20, 23-26, and 29-32 ft below grade. Each depth interval was bounded by non-inflatable packers in order to create a barrier to flow contribution from other depth intervals. One multilevel sampler was located in well OSU-2, while the other is located in well OSU-3. These two wells were parallel with the flow direction in the test cell, with well OSU-2 located upgradient from well OSU-3. For push-pull tests, an inflatable packer system was used that permitted tests to be performed over two-foot slotted intervals of the well screens. The inflatable packer system was also used to obtain samples from different depth intervals prior to the push-pull test.

3.3 Pre-Demonstration Testing and Analysis

Pre-demonstration testing at the Dover field test site involved a survey of wells to determine the background Rn concentrations. The survey helped determine whether the Rn concentrations were high enough to be measured by the liquid scintillation counting methods that were to be used in the demonstration. The results determined the spatial variability in the Rn concentration as a result of geologic variability in the test cell. The survey results are presented in Table 3.2. Radon concentrations were easily measured using the liquid scintillation method that will be described. The concentrations ranged from 55 to 302 pCi/L. The concentrations tended to be lower at depth with the lowest concentrations observed 36 to 39 ft below grade. The highest concentrations were at the depth range of 27 to 33 ft below grade, and depth average concentration was about a factor of three greater than the lowest depth averaged concentrations. The results show that there is a fair amount of variability in background radon concentrations at the site. Concentrations vary by over a factor of five within the test cell. Thus radon surveys to detect NAPL would be problematic at this site based on spatial measurements alone.

Table 3.2. Result of the radon survey at the OSU monitoring wells in the Dover Test Cell

Depth (ft below grade)	Well OSU1 (pCi/L)	Well OSU2 (pCi/L)	Well OSU3 (pCi/L)	Well OSU4 (pCi/L)	Depth Ave. (pCi/L)	STD ± (pCi/L)
39-42	54.4	86.6	78.6	87.9	76.9	15.51
36-39	70.9	76.8	76.0	108.8	83.1	17.32
33-36	108.5	225.4	98.0	155.1	146.8	58.00
30-33	133.5	176.1	302.7	231.5	210.9	73.12
27-30	215.6	165.4	221.9	218.5	205.4	26.77
24-27	217.9	140.2	183.6	181.1	180.7	31.81
21-24	148.8	190.5	243.8	158.3	185.3	42.84
18-21	129.1	140.6	172.5	160.9	150.8	19.54
15-18	163.9	104.4	139.2	182.7	147.5	33.86

In addition, batch radon emanation experiments were performed from a core sample from the test cell to estimate variability in the radon source term. The batch emanation measurements were performed as follows. Sediment samples were to be dried at 105° C before use, and a 100 g sample was added to a 125 ml batch bottle that was capped with a Teflon-lined septum. Note that sediment samples used in emanation studies contained no NAPL. The bottle was evacuated to remove air, and then filled with tap water. A 30-day incubation period was used to allow Rn concentrations in the sample to reach secular equilibrium with emanation from the sediment. The bottles were then sampled (5 to 10 ml), and analyzed using the scintillation method described in Section 3.4. The results from the emanation study are presented in Table 3.3. Estimates of the groundwater concentration are based on equation 3.1, using a bulk density value of 1.885 kg/L and an aquifer porosity of 0.3.

Table 3.3 Results from the emanation study with aquifer solids from different depths from the DNTS test cell.

Depth Interval Ft Below grade	Radon Emanation	[1]Estimated Groundwater Radon Concentration
	pCi/kg	pCi/L
17.5 - 18.2	55	338
19.5 – 20.1	41	255
21.5 – 22.1	47	290
25.5 – 26.2	23	143
27.5 – 28.2	22	134
31.5 – 32.2	45	277
33.3 – 34.2	48	294
35.5 – 36.2	34	207

The results show variability in radon emanation from the aquifer solids. All tests were run in duplicate, and were very reproducible. Emanation from the aquifer solids varied by about a factor of 2.5, from 22 to 55 pCi/kg of solids. It is interesting to note that a similar variation in groundwater concentration was observed (Table 3.2).

Several investigators have found that measured Rn concentrations in groundwater are in good agreement with values predicted from emanation studies using aquifer minerals (Andrews and Wood, 1972; Heaton, 1984; Smith et al., 1978; Semprini, 1987; Semprini et al., 1998), especially for aquifers in sedimentary deposits. Emanation measurements on core samples can provide estimates of the background Rn concentrations to be expected in the absence of NAPL. The background Rn concentration is given by:

$$Rn_{Background} = \frac{C_{ra} E_p \rho_b}{\theta} \qquad (3.1)$$

where $Rn_{Background}$ is the Rn concentration in groundwater (pCi/L), C_{ra} is the Ra-226 content of the aquifer material (pCi/kg); E_p is the emanation power; ρ_b is the aquifer bulk density (kg/L); θ is the porosity; and ρ_w is the groundwater density (kg/L). Emanation studies measure the product $C_{ra}E_p$ and values are given of a pCi/Kg basis (Table 3.3). If the aquifer porosity, bulk density, and fluid density are known, the expected equilibrium concentration in the subsurface fluid can be computed.

Equation 3.1 was used to estimate groundwater radon concentration and emanation values provided in Table 3.3. These estimates were based on a porosity of 0.30 and a bulk density of aquifer solids of 1.885 kg/L. The estimated background radon concentration in groundwater (in the absence of NAPL) was in the range of values measured in the groundwater samples. The results support our observations of spatial variations in groundwater radon concentration resulting from of geologic conditions at the site. The results also indicate the maximum concentrations that might be expected in groundwater at the site would be in the range of 300 pCi/L, consistent with maximum concentrations measured in groundwater samples. However, there was not a strong correlation between depth averaged radon groundwater concentrations (Table 3.2) and the estimated values from the emanation studies (Table 3.3). Groundwater measurement tended to yield lower radon concentrations than the estimates from core emanation tests.

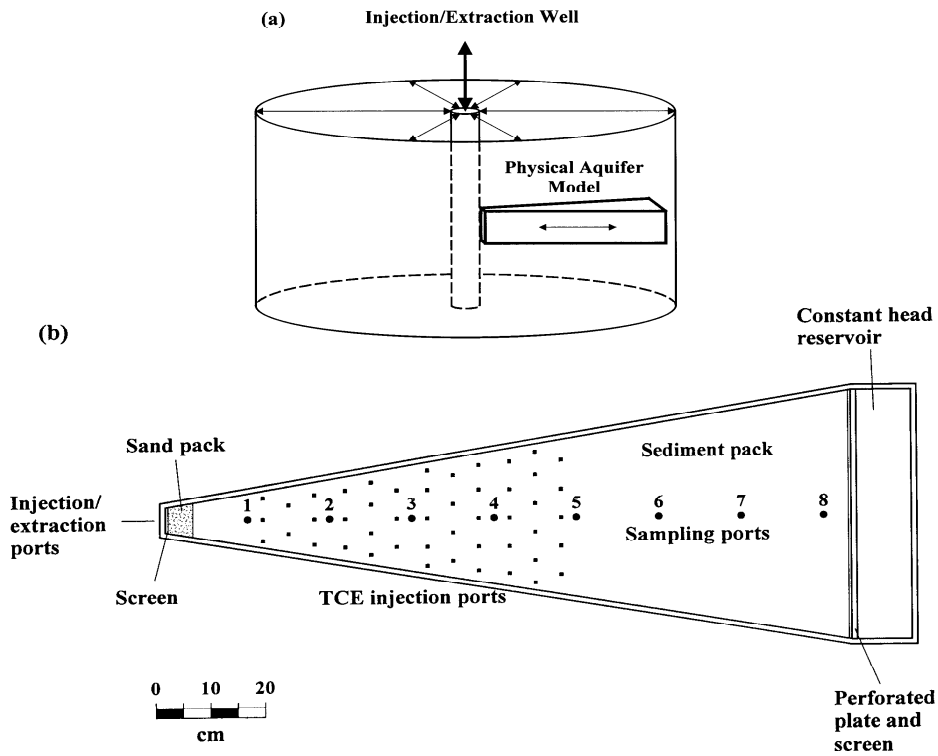
3.4 Testing and Evaluation Plan

The demonstration activities consisted of a combination of laboratory and field studies. Laboratory studies involved using laboratory physical aquifer models (PAMs). The studies used existing facilities and equipment available at Oregon State University. Field studies used facilities and services used in routine groundwater sample collection at the DNTS. We will first describe the test plan used in the PAM study. We will then describe the plan for the DNTS demonstration studies.

3.4.1 Testing in the Laboratory Physical Aquifer Model

Laboratory studies were conducted to evaluate push-pull tests in a controlled laboratory setting. Laboratory push-pull tests were performed in physical aquifer models (PAMs) constructed in a wedge shape to simulate the radial flow field near an injection/extraction well during a push-pull test (Figure 3.3).

Figure 3.3 (a) Physical aquifer model design (b) plan view



The PAMs were constructed with polypropylene with interior dimensions of 5 cm (width at narrow end), 50 cm (width at wide end), 125 cm (length), 20 cm (height), and a total internal volume of 0.069 m^3. Air-dried sediment was packed into the PAMs to a uniform bulk density (1.9 g/cm^3) and calculated porosity (0.35).

The PAMs were packed using the method of Istok and Humphrey (1995) with sediment from the Hanford Formation, an alluvial deposit of sands and gravels of mixed basaltic and granitic origin (Lindsey and Jaeger, 1993). The sediment was collected as a single batch from an outcrop at a quarry near Pasco, WA. The sediment was homogenized by manual mixing, air-dried to a water content between 2 and 3 wt %, and sieved to remove particles > 2 cm in diameter (which were < 0.01 % of the original outcrop material). The sieved sediment is a sand with approximately 30% fine gravels and less than 5 % silt and clay. The sediment contains less than 0.001 wt % organic matter. Tap water was used as the synthetic groundwater in all laboratory experiments. The sediment packs were saturated with tap water and a lid containing eight sampling ports was installed.

For experiments involving TCE NAPL contamination, the sediment pack contained a known initial quantity of liquid (nonaqueous phase) TCE. This was achieved by first draining the

sediment pack and then slowly injecting aliquots of TCE at depths between 2.5 and 17.5 cm through 52 injection ports bored through the model lid between sampling ports 1 and 5 (Figure 3.3). A total of 304 g (208 mL) of TCE was uniformly injected through the injection ports, which represents a TCE saturation equivalent to ~ 2 % of the total pore volume within the contaminated zone. After TCE injection, the sediment pack was re-saturated and then flushed for ~ 24 h with tap water to remove mobile TCE from the injection/extraction ports and to entrap TCE within the pore space. No TCE was observed in the water removed from the sediment pack during the tap water flush.

Push-pull tests were performed under confined conditions. Each push-pull test was preceded by a three-week equilibrium period during which radon concentrations reached > 95 % of their secular equilibrium value as a result of concurrent radon emanation from sediment and decay. During the injection phase, flow was directed from the injection/extraction ports at the narrow end of the PAM toward the constant head reservoir at the PAM's wide end. During the extraction phase, flow was reversed. The constant head reservoir was supplied with water from a second PAM containing the same sediment (without TCE) to provide a source of water with a similar and constant radon concentration. For each experiment, 8 to 16 L of test solution was injected and 16 to 32 L was extracted.

Test solutions were injected and extracted using a piston pump (Fluid Metering, Oyster Bay, NY). The volumes of test solution injected were selected to ensure that no injected test solution left the PAM through the constant head reservoir. The test solution consisted of tap water containing ~ 100 mg/L bromide, prepared from sodium bromide (Fisher Scientific, Fair Lawn, NJ) to serve as a conservative tracer. Dissolved radon was removed by bubbling compressed air through the test solution prior to injection. The extraction phase began within 30 minutes after the end of the injection phase. Injection and extraction pumping rates were constant at ~ 106 mL/min. Water samples were obtained by connecting a 20 mL Luer-Lock plastic syringe (Becton-Dickinson, Franklin Lakes, NJ) to a syringe needle or a valve. During the injection phase water samples were collected from the sediment pack by inserting a stainless steel syringe needle into brass 'well' screens that fully penetrated the sediment pack beneath each sampling port. During the extraction phase water samples were collected from a valve located between the pump and the PAM injection/extraction ports.

3.4.2. Dover Site Series of Tests

Push-pull Tests

Push-pull tests were performed in OSU test wells that were installed surrounding the NAPL spill zone in the DNTS test cell. For each test, 30 to 80 L of test solution was injected. The test solution consisted of site groundwater containing ~ 100 mg/L bromide, prepared from sodium bromide (Fisher Scientific, Fair Lawn, NJ) to serve as a conservative tracer. The solution was prepared in a large plastic carboy (500-L). Dissolved radon was removed by bubbling compressed nitrogen through the test solution prior to injection. Nitrogen was typically sparged for 24 hours prior to injecting the test solutions. The nitrogen sparing also served to completely mix the test solution. Several tests were performed by injecting groundwater over the complete

slotted interval of the well. In other tests, inflatable straddle packers were used to isolate 3-ft. depth intervals of the well screen for testing. Test solutions were injected using a peristaltic pump (Cole-Parmer, Vernon Hills, IL) and the test solution/groundwater mixture was extracted using the same peristaltic pump. For each test approximately double the amount of solution that was injected was extracted (50 to 500 L of injected solution and groundwater was removed from the well). The injected groundwater was allowed to reside in the aquifer for several hours prior to extracting the groundwater. Details of the test procedures are provided below.

Push-pull tests at the DNTS field followed similar procedures as the laboratory PAM tests, but involved conducting tests in the complete screened interval, or a packed section of a screened interval, to investigate a specific depth interval. The tests were performed with typical equipment used in groundwater monitoring. These included a source of electric power for either the peristaltic pump, a container to collect well purge water prior to sample collection, suitable purge water disposal system, VOA bottles for sample collection, coolers and ice packs for shipping samples to the analytical laboratory, and site-appropriate personal protection equipment. Push-pull tests also required a large tank for test solution preparation. The tests were performed by a single field technician. Monitoring consisted of collecting samples of test solution during the injection phase of push-pull tests and collecting groundwater samples during the extraction phase using standard sampling protocols established for VOC sample collection. Since the groundwater table was shallow in the test cell, peristaltic pumps were used to bring groundwater from the aquifer to the surface. A sampling valve was used to obtain groundwater samples from the pump discharge line. The valve contained a Luer-Lock syringe fitting. Water samples were obtained by attaching a plastic 20 mL Luer-Lock syringe to the valve, opening the valve and slowly withdrawing ~ 20 mL, taking care to avoid trapping air bubbles in the syringe barrel or exposing the sample to the atmosphere. The syringe was then removed from the sampling line and a 0.45 μm Millipore filter and a 12 gauge, 2 inch stainless steel syringe needle attached to the syringe. The needle was inserted into the bottom of a pre-weighed 20 mL borosilicate scintillation vial that contained 5 mL of scintillation "cocktail."

Figure 3.1 shows a schematic of the DNTS test cell used for the demonstration test. Push-pull tests were conducted in four wells surrounding the PCE NAPL spill (OSU-1, OSU-2, OSU-3, OSU-4). Push-pull tests were performed prior to the addition of PCE to the test cell and after PCE addition. Tests were also performed without and with groundwater flow being induced. The induced flow experiment included tests as NAPL remediation proceeded via enhanced reductive dehalogenation, which was initiated in the spring of 2002.

Although many conservative (i.e., nonreactive) tracers have been used in groundwater studies, bromide at a concentration of 100 mg/L was used as a conservative tracer for push-pull tests. This concentration was selected as a compromise between analytical detection limits (~ 1 mg/L for Br^- by ion chromatography) and the desire to avoid injecting test solutions with densities substantially larger than that of site groundwater. Bromide is added as potassium bromide (KBr).

The Static Test Method

The static method refers to measuring the radon concentration in the groundwater temporally and spatially in the test cell to evaluate spatial changes that occur due the presence of NAPL, or temporal changes at a given sampling location to monitor the progress of remediation. The method requires the groundwater samples be collected to ensure minimal loss occurs due to volatilization of the Rn from the sample. Thus, methods for sampling VOAs in groundwater were employed.

Two different static methods were employed. One method employed sampling many depth intervals at the four OSU wells that surrounded the NAPL source zone. These surveys were conducted several times when the test crew from OSU was present at the DNTS to conduct push-pull tests. Prior to conducting the push-pull tests, discrete three-foot depth intervals were sampled using inflatable packers to seal the desired depth interval of the well. The wells were surveyed over eight depth intervals ranging from 12-15 to 36-39 ft. Duplicate groundwater samples were collected for each depth interval. The samples were collected using a peristaltic pump. Three well volumes were purged prior to collecting a sample. Samples for radon analysis were added on-site to scintillation vials, as previously described. Samples were shipped on ice overnight to OSU for analysis.

Long term temporal monitoring was performed with groundwater samples obtained from monitoring wells OSU-2 and OSU-3 on a weekly basis. These wells are located in line with the flow direction in the test cell, with well OSU-3 located approximately 8 ft upgradient from well OSU-2. Radon samples were obtained from multilevel sampling lines that use 'packers' to isolate the 17' - 20', 23' - 26', and 29' - 32' intervals in the aquifer. Technical staff from the DNTS obtained the weekly samples using the same procedures as previously described. Groundwater samples were added to 40-ml VOA bottles and shipped to OSU overnight. 10-ml samples of groundwater for radon analysis were added to the scintillation vials upon being received at OSU. The remainder of the sample was used for PCE analysis.

METHODS

Determination of Bromide by Ion Chromatography

Concentrations of Br^- were determined with a Dionex DX-500 (Sunnyvale, CA) ion chromatograph equipped with electrical conductivity detector and a Dionex AS14 column. The eluent consisted of 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ and the eluent flow rate was 1.5 mL/min. A 0.6-mL sample was transferred to Dionex Polyvials ™ with filter caps for auto-sampler injection; the auto-sampler was programmed to deliver an injection volume of 50 µL. Run time was approximately 10 minutes. External calibration was performed using five standards with anion concentrations between 5 and 100 mg/L; the approximate quantitation limit was 0.5 mg/L.

Radon Analysis

The measurement of radon in groundwater is based on a standard method for radon in water using liquid scintillation counting (see Method 7500-Rn in *Standard Methods for the Analysis of Water and Wastewater, supplement to the 19th Ed.*). The same method was used in both the laboratory PAM tests, the field push-pull tests and static monitoring tests. The cocktail was manufactured by Packard Instruments and carries the brand name Ultima-Gold F (UGF). UGF contains both an "extractant" (99%) and a "detector" (1%). The extractant is an organic chemical that aids in extracting Rn from the aqueous phase into the cocktail. Radon, being a non-polar substance, partitions into the less polar cocktail from the more polar water sample. In UGF the extractant is diisopropylnaphthalene (DIN). The detector (i.e., scintillator) was composed of a scintillating (i.e., light-emitting) substance that emits photons as a result of direct interaction with alpha and beta decay particles or as an indirect result of interaction with excited DIN molecules.

The groundwater sample was added by inserting the tip of the needle into the scintillation cocktail and dispensing 10 to 15 mL of sample. The vial was then sealed and slowly mixed for approximately 5 minutes on a rotary mixer to allow for equilibrium partitioning of radon between the aqueous phase, the cocktail, and the small volume of headspace in the vial. The location, time, and date of sample collection are recorded and the sample is stored in the dark and on ice until analyzed.

Due to Rn's short half-life, sample analysis had to be completed within approximately 5 days after sample collection. Each vial was weighed to determine the exact mass of water sample. Counting was performed with a Packard 2500 TR/AB Liquid Scintillation Counter (LSC). This instrument counts the number of radioactive decay events (i.e., counts) as the number of photons emitted from the vial over a given total count time. Each photon is associated with an alpha (a helium nucleus) or beta (an electron) decay event. The photons emitted by the scintillator are intercepted by a photomultiplier tube, which converts the energy of the photon into an electric impulse. The LSC is able to use the energy of each decay event (i.e., each energy "pulse") to distinguish between alpha and beta decays, each of which has different characteristic energies. Radon-222 decays into an alpha particle and an atom of polonium-218. Polonium-218 decays via 2 alpha decays and 2 beta decays into a series of short-lived bismuth, polonium and lead daughters and finally to lead-210 (which has a half-life of 22.3 years), thus leading to three alpha decays from radon and its daughter products. Because each radon atom emits one alpha particle, the number of alpha counts originating from radon atoms is an accurate estimate of the number of radon atoms in the sample. The water sample was permitted to equilibrate for at least three hours prior to counting in order to permit the build-up to the daughter products.

Each sample vial was counted by the LSC for 60 minutes. The LSC provided the gross count of alpha particles (gross alpha CPM); the background alpha CPM detected by the LSC via sample blanks was subtracted from the gross alpha CPM value to determine a net alpha CPM value. The half-life of radon (3.3 days) was then used to back-calculate the net alpha CPM value in the sample at the time and date of sampling. The result of this calculation was a time corrected net alpha CPM. Table 3.4 presents results from a typical calculation of Rn concentrations.

Table 3.4. Typical values to determine radon concentrations analysis in a groundwater sample.

Sample Number (#)	Mass of Vial and Cocktail (g)	Mass of Vial, Cocktail and Water Sample (g)	Sample Volume (ml)	Date and Time Sampled (m:d:yr hr:m)	Date and Time Counted (m:d:yr hr:m)	Gross Alpha Count (cpm)	Net Alpha Count (cpm)	Time Corrected Alpha Count (cpm)	Aqueous Alpha (cpm/ml)	Aqueous [Rn] (dpm/ml)	Aqueous [Rn] (pCi/L)
24	21.66	36.91	15.25	8/3/99 2:11 PM	8/5/99 5:22 PM	24.4	24.239	35.56	2.33	1.05	473.4

The natural radon tracer method uses entirely "commercially off-the-shelf" (COTS) components such as sampling pumps, VOA bottles, and scintillation cocktail, vials and liquid scintillation counter. No proprietary technologies were used.

Determination of PCE Concentrations by Gas Chromatography

Test samples were collected in 40-mL VOA vials with a Teflon/neoprene septum and a polypropylene-hole cap (Supelco, Bellefonte, PA). Samples for PCE analysis were preserved with acid. The same sample for radon analysis was divided and used for PCE determination. Samples for laboratory analysis were stored at 4 ºC and analyzed within one week. For push-pull tests, OSU personnel on-site would transfer the groundwater sample directly on-site into scintillation cocktail. For long term monitoring of well DNTS personnel collected groundwater samples in 40-ml VOA bottles, that were shipped to OSU. Sample were then placed in a scintillation cocktail at OSU.

PCE was determined by a modified EPA 8000 purge and trap GC analysis. A 1 or 5 mL aqueous sample was taken from a VOA vial using a S. G. E. gas tight luer lock syringe (Supelco Co, Bellefonte, PA). The sample was then added into a purge tube installed in HP 7695 Purge & Trap. A Tenax/silica gel/charcoal trap was used as a purge trap (Supelco, Bellefonte, PA). A sample purge time of 5 min was used. Chromatographic separation was achieved with a 30-m megabore GSQ-PLOT column from J&W Scientific (Folsom, CA) installed on a HP6890 series GC connected to a photo ionization detector (PID) followed by a flame ionization detector (FID) operated at 250 °C. The GC was operated at the following conditions: initial oven temperature, 40 °C for 3 min; 4 °C/min up to 70 °C; 5 °C/min up to 220 °C. The GC was operated in the splitless inlet mode with a carrier gas (He) flow of 15 mL/min, a H_2 flow to detectors of 35 mL/min, an air flow to the detectors of 165 mL/min and a FID detector makeup gas (He) flow of 15 mL/min. Calibration curves for the compounds were developed using external standards.

Data Analysis

Push-Pull Tests

Data analysis for push-pull tests was performed using normalized concentrations. The normalized concentration for bromide is defined as $C^* = 1 - C/C_o$ where C is the measured bromide concentration in a sample and C_o is the bromide concentration in the injected test

solution (~ 100 mg/L). This calculation is performed to facilitate the comparison of bromide and radon breakthrough curves. Bromide is an injected tracer, and thus its concentrations increase with time during the injection phase and decrease with time during the extraction phase. Radon, in contrast, is an in situ tracer and thus its concentrations decrease with time during the injection phase (of radon-free water) and increase with time during the extraction phase. The normalized concentration for radon is defined as $C^* = C/C_b$, where C is the measured radon concentration and C_b is the background (equilibrium) radon concentration in the sediment pack or aquifer. Push-pull tests were performed over a time period of < 8 hours so that radon emanation from aquifer sediments during the test was negligible.

For the laboratory PAM test, breakthrough curves at interior sampling ports were available, permitting retardation estimates to be made. Injection phase data for the sampling ports in laboratory push-pull tests were interpreted using the method of temporal moments (Cunningham and Roberts, 1998), the approximate analytical solution of Gelhar and Collins (1971) as further described by Schroth et al. (2000), and numerical modeling. The zeroth (m_0) and first (m_1) temporal moments were computed by integrating normalized bromide and radon concentrations at the sampling ports using

$$m_0 = \int C^*(t)dt \qquad (3.2)$$

$$m_1 = \int C^*(t)tdt \qquad (3.3)$$

The retardation factor for radon was then computed using

$$R = \frac{\left(\dfrac{m_{1,Rn}}{m_{0,Rn}}\right)}{\left(\dfrac{m_{1,Br^-}}{m_{0,Br^-}}\right)} \qquad (3.4)$$

Laboratory and field push-pull test data were interpreted using an approximate analytical solution to the advection–dispersion equation for solute transport during a push-pull test as presented by Schroth et al. (2000). The solution gives normalized concentration (C^*) as a function of time and radial distance from the injection well. For the injection phase the solution is

$$C^* = \frac{1}{2} erfc\left\{\left(r^2 - r_{inj}^{\ 2}\right) \Big/ \left[\frac{16}{3}\alpha_L\left(r_{inj}^{\ 3} - r_{well}^{\ 3}\right)\right]^{\frac{1}{2}}\right\} \qquad (3.5)$$

where r is radial distance from the injection well, α_L is the dispersivity, r_{well} is the well radius and r_{inj} (the radial distance of the $C^* = 0.5$ tracer front at time t_{inj}) is given by

$$r_{inj} = \left(\frac{Q_{inj} t_{inj}}{\pi b n R} + r_{well}^{\ 2} \right)^{\frac{1}{2}} \qquad (3.6)$$

where Q_{inj} is the injection phase flowrate, t_{inj} is time, b is the saturated thickness, n is the porosity, and R is the retardation factor. For the extraction phase the solution is

$$C^* = \frac{1}{2} erfc \left\{ \left(r^{\ 2} - r_{ext}^{\ 2} \right) \Big/ \left[\frac{16}{3} \alpha_L \left(2 r_{\max}^{\ 3} - r_{ext}^{\ 3} - r_{well}^{\ 3} \right) \right]^{\frac{1}{2}} \right\} \qquad (3.7)$$

where r_{ext} (the radial distance of the $C^* = 0.5$ tracer front at time t_{ext}) is given by

$$r_{ext} = \left(r_{\max} + \frac{Q_{ext} t_{ext}}{\pi b n R} \right)^{\frac{1}{2}} \qquad (3.8)$$

where Q_{ext} is the extraction phase pumping rate, t_{ext} is time, and r_{max} is defined by

$$r_{\max} = \left(r_{well} + \frac{V_{inj}}{\pi b n R} \right)^{\frac{1}{2}} \qquad (3.9)$$

where r_{max} is the maximum radial distance traveled by the $C^* = 0.5$ tracer front at the end of the injection phase (corresponding to the radius of influence of the tracer) and V_{inj} is the total volume of test solution injected.

Both static and push-pull methods using radon as a partitioning tracer can be used to quantify NAPL contamination. The static method involves calculating NAPL saturations from a comparison of radon concentrations in groundwater samples obtained from NAPL-contaminated and non-contaminated portions of the same aquifer, or by changes that occur over time. This method assumes secular equilibrium between radon emanation and decay, equilibrium radon partitioning between the water and NAPL phases, and a constant background radon concentration (Semprini et al., 2000). In the presence of NAPL, radon will be distributed between the water and NAPL phases as described by:

$$C_n S_n + C_{w,n} S_w = \frac{C_{Ra} E_p \rho_b}{n} \qquad (3.10)$$

where S_n and S_w are the NAPL and water saturations in the pore space ($S_n + S_w = 1$). Assuming linear equilibrium radon partitioning of radon between NAPL and water, equation 3.10 can be rearranged as

$$C_{w,n} = \frac{C_{Ra} E_p \rho_b / n}{1 + S_n (K - 1)} \qquad (3.11)$$

which can be further rearranged to solve for the NAPL saturation

$$S_n = \left(\frac{C_{w,bkg}}{C_{w,n}} - 1 \right) \left(\frac{1}{(K-1)} \right) \qquad (3.12)$$

where $C_{w,n}$ is the radon concentration in groundwater in the NAPL contaminated zone and $C_{w,bkg}$ is the radon concentration in groundwater in a 'background' zone outside of the NAPL contaminated zone or in the aquifer before NAPL contamination has occurred and K is the solvent/water partition coefficient.

The push-pull method consists of the injection (push) of a known volume of radon-free test solution containing a conservative tracer (i.e., bromide) into a single well, followed by the extraction (pull) of the test solution/groundwater mixture from the same well (Schroth et al., 2000). Previous studies have shown that pull phase radon breakthrough curves show an increased dispersion relative to bromide due to retardation resulting from mass transfer of radon between NAPL and the test solution (Davis et al., 2002). NAPL saturations are determined by estimating the radon retardation factor (R) during the pull phase of the test, where $R > 1$ in the presence of NAPL. Assuming linear equilibrium partitioning the retardation factor for radon is (Dwarakanath et al., 1999)

$$R = 1 + \frac{KS_n}{S_w} \qquad (3.13)$$

Once the retardation factor is known, the NAPL saturation can then be calculated via (Dwarakanath et al., 1999)

$$S_n = \frac{R-1}{R+K-1} \qquad (3.14)$$

Temporal changes in static radon concentrations are used to estimate changes in PCE saturations in the test cell at DNTS. Radon retardation factors obtained from push-pull tests are used to estimate PCE saturations to estimate the efficacy of remediation.

Numerical Simulations of Laboratory Tests Results

Simulations were also performed with the STOMP code (White and Oostrom, 2000), a fully implicit volume-integrated finite difference simulator for modeling one-, two- and three-dimensional groundwater flow and transport. STOMP has been extensively tested and validated against analytical solutions and other numerical codes (Nichols et al., 1997). Simulations were based on a hypothetical push-pull test conducted in a 5 cm diameter well over a 91.4 cm long screened interval of an aquifer. The model aquifer is based on an aquifer composed of sediment from the Hanford Formation, an alluvial deposit of sands and gravels of mixed basaltic and granitic origin (Lindsey and Jaeger, 1993) used in the laboratory push-pull tests. A solid density (ρ_s) = 2.9 g/cm^3, porosity (n) = 0.35, calculated bulk density (ρ_b) = 1.89 g/cm^3 and longitudinal

dispersivity (α_L) = 4.0 cm were used in all the simulations. Simulations incorporated injection and extraction volumes used in the PAM tests. Injection and extraction pumping rates were constant at 1 L/min with no rest period between the injection and extraction. The computational domain consisted of a line of 500 nodes with a uniform radial node spacing of Δr = 1.0 cm. The model geometry and injection volumes resulted in the injection solution traveling 48 cm from the well, as measured by the travel distance to half the solution injection concentration of the conservative tracer (C/C_o = 0.5) assuming plug flow of a conservative tracer. Simulations were performed using time-varying third-type flux boundary conditions to represent pumping at the well, with a constant hydraulic head. Constant head and zero solute flux boundary conditions were used to represent aquifer conditions at r = 500 cm.

Specified NAPL saturations were modeled using TCE with a value of K = 50 for radon (Davis et al., 2003). To simplify the modeling procedure NAPL saturations (S_n) were incorporated into the model using solid:aqueous phase partition coefficients. First, equation 3.11 was used to determine a retardation factor (R) for a given ratio of S_n to water saturation (S_w). Second, this calculated R value, the sediment porosity, and bulk density were used to determine a solid:aqueous phase partition coefficient (K_d),

$$K_d = (R-1)\left(\frac{n}{\rho_b}\right) \qquad (3.12)$$

Simulations were performed with specified S_n values from 0 to 15.25 %, which corresponds to retardation factors (R) ranging from 1 to 10, respectively. The effects of initial radon concentrations and S_n heterogeneity on simulation results were investigated with three sets of simulations, with NAPL extending homogeneously from 1) r ≤ 500 cm, 2) r ≤ 48 cm (corresponding to the maximum travel radius of a conservatively transported tracer, as defined by plug flow), and 3) r ≤ 24 cm (corresponding to half the maximum travel radius of a conservatively transported tracer), where r is the radial distance from the injection/extraction well. An initial radon concentration = 200 pCi/L (corresponding to S_n = 0 %) was emplaced at r > 48 cm for the second set of simulations and at r > 24 cm for the third set of simulations. Each simulation utilized 1) an injection radon concentration = 0 pCi/L, which corresponds to the true radon injection concentration in laboratory and field push-pull tests and negates the need for "inverting" concentrations as was performed in the previous modeling analysis, and 2) an initial radon concentration in the model that varied in space as a function of S_n. All simulations and PAM push-pull tests were performed over time periods such that the effects of radon emanation and decay on radon concentrations could be neglected (i.e., V_e/V_i = 2 was obtained in ≤ 12.5 hours.

4. Performance Assessment

The performance assessment provides an evaluation of the demonstration of the radon method for quantifying NAPL contamination in the subsurface. Both the demonstration in the laboratory PAM and at the DNTS are included. The demonstration consisted of both static testing, which represented the monitoring of radon concentrations, and dynamic testing using single-well, push-pull tests. Presented in Tables 4.1 and 4.2 are performance criteria, expected performance, and performance confirmation methods for the demonstration. A summary of the study results from both sites was presented in Section 4.1 through 4.3, followed by a data assessment presented in Section 4.4, and a technology comparison in Section 4.5.

4.1 Results of PAM Tests

Push-pull tests were conducted in laboratory PAMs (shown in Figure 3.3) using the methods described in Section 3.5. Test 1 was conducted in the absence of TCE NAPL contamination, while Test 2 was conducted with 2% residual TCE emplace. Prior to each push-pull test, radon was permitted to emanate for at least 25 days so that radon concentration in the PAM would reach secular equilibrium. Push-pull tests were conducted as described in section 3.5 by injecting radon free water along with bromide as a conservative tracer. In the laboratory tests breakthrough curves at interior sampling ports 1 and 2 were monitored during the push (injection phase) of the test. During the extraction phase, the concentrations were monitored at the (injection/extraction) well.

Results for sampling ports 1 and 2 from the push phase of Test 1 conducted in the absence of TCE are shown in Figures 4.1a and 4.1b. Breakthrough curves for bromide and radon are displayed as normalized concentration (C^*) versus dimensionless pore volume (V_{inj}/V_{pore}). In these figures V_{inj} is the cumulative volume of injected test solution at the time the sample was collected, and V_{pore} is the pore volume between the injection/extraction ports and the sampling port. At each sampling port normalized concentrations decreased smoothly as the test solution penetrated further into the sediment pack.

Radon transport was somewhat retarded relative to bromide. The data were well fit by the injection phase approximate solution (Equation 3.5), with best-fit α_L values of 3.8 cm for port 1 and 6.6 cm for port 2 (Table 4.3). Estimated radon retardation factors for ports 1 and 2 were 1.0 and 1.2 using the method of temporal moments and 1.1 and 1.4 using the injection phase approximate solution (Table 4.3). Numerical simulations using STOMP were also conducted for the injection phase data using R = 1.0 and 1.1 at port 1 and R = 1.0 and 1.4 at port 2. The simulated breakthrough curves matched the injection phase approximate solution moderately well at port 1, but did not match the results at port 2.

Table 4.1. Performance Criteria

Performance Criteria	Description	Primary or Secondary
Spatial variations in radon concentration can result from geologic variability prior to NAPL addition	Groundwater radon concentrations were determined at 8 different depths in four monitoring wells at DNTS cell.	Primary
DNTS Spatial changes in radon concentration can result from the NAPL addition to the test cell	Groundwater radon concentrations were determined at 8 different depths in four monitoring wells at DNTS cell.	Primary
Spatial variability in radon emanation for aquifer core samples show geologic variability in Rn source term	Radon emanation from aquifer core samples was measured at eight different depths with cores from four monitoring wells at DNTS	Secondary
Radon concentration in GW can be predicted from radon emanation values from core materials	Compare groundwater concentration to estimates from core samples for DNTS cell	Secondary
Temporal changes in radon concentration result from NAPL remediation	Monitor groundwater radon concentrations at three different depths in monitoring wells at the DNTS cell.	Primary
Retardation in radon transport can be used to estimate NAPL saturation.	Compare Rn concentration breakthroughs to that of bromide as a conservative tracer in PAM during the injection phase of push-pull tests.	Primary
Response in single well push-pull tests can be used to estimate NAPL saturation in PAM tests	Compare radon concentration breakthroughs to bromide in the extraction phase of the PAM push-pull tests.	Primary
Response in single well push-pull tests can be used to estimate NAPL saturation at the DNTS	Compare radon concentration breakthroughs to bromide in the extraction phase in single-well push-pull tests conducted at the DNTS	Primary
Factors affecting the technology performance	Geologic variability in radon concentrations NAPL saturation and distribution Spatial resolution in GW sampling Packer performance Ability to estimate background radon concentrations	Primary
Reliability	Reproducibility of push-pull tests Ability to perform at different sites.	Secondary
Ease of Use	Number and skills of people required to perform tests	Primary
Versatility	Use at several locations. Use with different types of geology Use with different types of NAPL contamination	Primary
Scale-up Constraints	Spatial resolution in sampling	Secondary

Table 4.2. Expected Performance and Performance Confirmation Methods

Performance Criteria	Expected Performance Metric	Performance Confirmation Method	Actual
Spatial variations in radon concentration can result from geologic variability prior to NAPL addition	Measured Rn concentrations will vary significantly spatially	Repeated measurements show similar results	Significant differences in radon concentration were observed as a function of depth prior to the NAPL releases
DNTS Spatial changes in radon concentration can results from the NAPL addition to the test cell	Radon concentrations would decrease as a result of NAPL being present	Measurement of Rn concentration in groundwater before and after NAPL is releases at different depths in monitoring wells	Concentrations decreased in some locations and decreased in others.
Spatial variability in radon emanation for aquifer core samples show variations in radon source term	Spatial variations in radon source term are observed	Emanation measurements are reproducible	Emanation of radon from core material was found to vary spatially.
Radon concentration in GW can be predicted from radon emanation values from core materials	Correlation between estimated and predicted values	Correlation analysis	A strong correlation did not exist between estimated and measured values
Temporal changes in radon concentration result from NAPL remediation	Radon concentration increase as NAPL remediation proceeds	PCE concentration in groundwater decrease	Radon concentrations increased with time
Retardation in radon transport can be used to estimate NAPL saturation.	Retardation in radon transport is expected compared to bromide as a conservative tracer	Compare saturation estimates based on retardation with actual saturation,	Saturations estimated from radon retardation agreed reasonable well with emplaced NAPL saturations
Response in single well push-pull tests can be used to estimate NAPL in PAM tests	Extraction phase radon concentrations can be modeled to estimate NAPL saturation in PAMs	Estimated saturation compared with actual saturations in PAMs	Estimated saturations compared well with actual saturations in PAMs
Response in single well push-pull tests can be used to estimate NAPL saturation at the DNTS	Extraction phase radon concentrations can be modeled to estimate NAPL	Compare the mass of PCE added to test cell with estimated saturation	Estimated saturations difficult to compare with saturation emplace since emplaced distribution was not known.
Factors affecting the technology performance	Similar metrics as above	Similar metrics as above	Important factors: The amount and spatial distribution of NAPL; spatial resolution of GW sampling; geological variability in radon concentrations; closeness of monitoring locations to the NAPL
Ease of Use	Personnel required; tests conducted per day. Reproducibility of the tests. High spatial resolution needed	Number and training of personnel	Required at less one high trained technician with field expertise and analytical skills. Tests often difficult to reproduce; high spatial resolution needed when limited NAPL is present.
Versatility	Similar metrics as above	Similar metrics as above	Work was performed only at one site. Similar issues with use at other sites.
Scale-up Constraints	Conducted at full scale	Conducted at intermediate scale	Spatial resolution at full scale

Figure 4.1a Injection phase breakthrough curves for lab Test 1, port 1 in the absence of TCE.

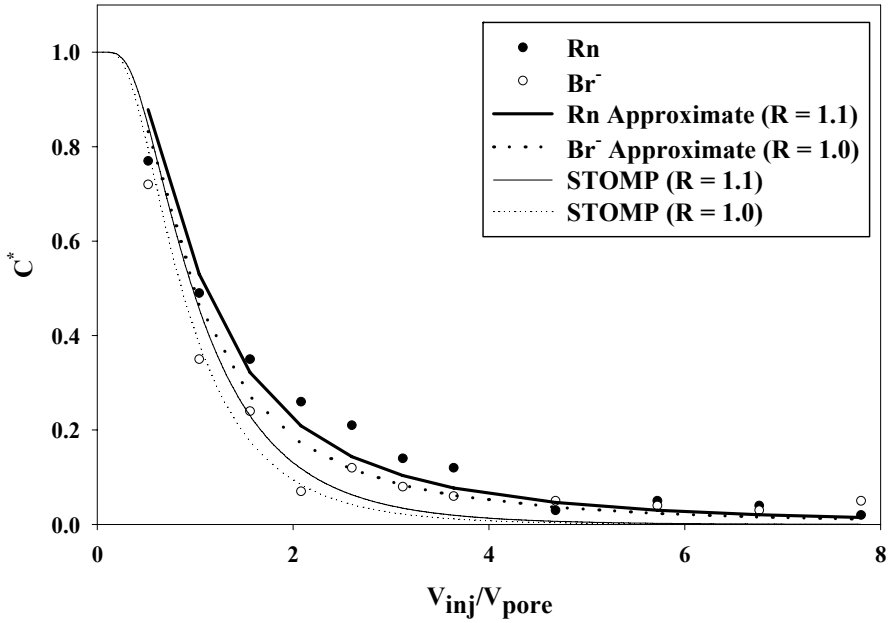


Figure 4.1b Injection phase breakthrough curves for lab Test 1, port 2 in the absence of TCE.

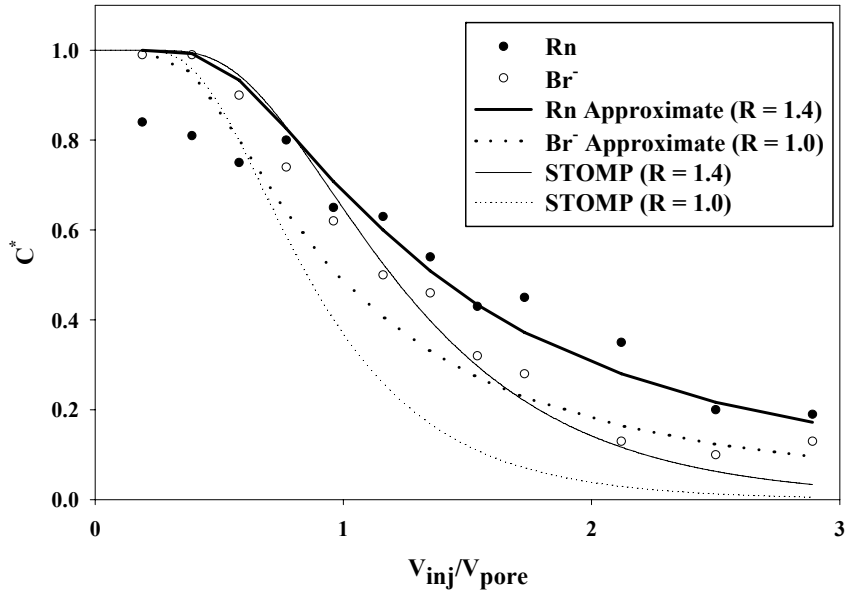
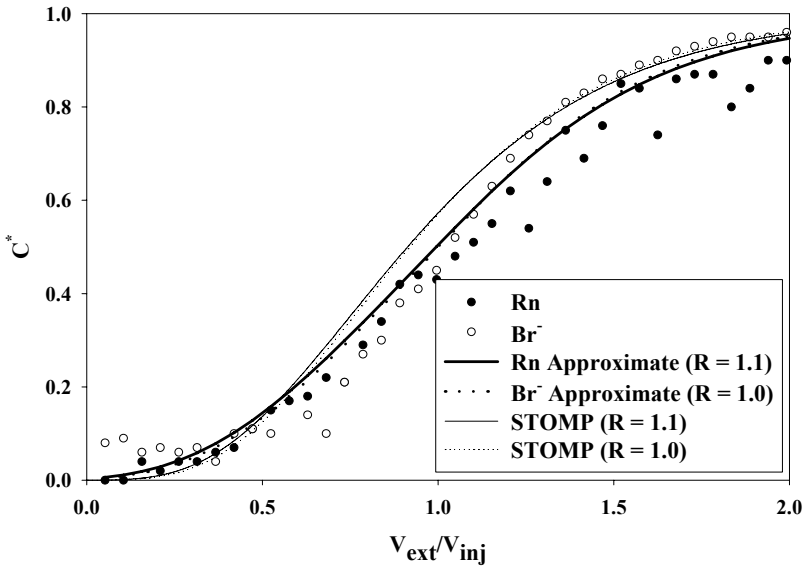


Figure 4.1c Extraction phase breakthrough curves for lab Test 1 in the absence of TCE.



Retarded radon transport was not very apparent in extraction phase breakthrough curves for Test 1 (Figure 4.1c) where normalized concentration (C^*) is plotted as a function of the ratio V_{ext}/V_{inj}, where V_{ext} is the cumulative volume of water extracted at the time the sample was collected and V_{inj} is the volume of injected test solution. Normalized concentrations increased smoothly as the test solution was extracted from the sediment pack. The data were well fit by the extraction phase approximate solution (equation 3.7), with a best-fit α_L of 3.2 cm (Table 4.3). A best-fit value of R = 1.1 was obtained for radon (Table 4.3). Numerical simulations using STOMP were also conducted for the extraction phase data using R = 1.0 and R = 1.1. The simulated breakthrough curves matched the extraction phase approximate solution moderately well.

Table 4.3 Radon retardation factors (*R*), adjusted retardation factors for the effect of trapped gas (*in italics*), approximate solution best-fit dispersivities (α_L), and TCE saturations (S_n) from push-pull tests.

	Method of Moments R α_L S_n (cm) (%)	Injection Phase Approx. Solution R α_L S_n (cm) (%)	Extraction Phase Approx. Solution R α_L S_n (cm) (%)
Test 1 Port 1	1.0 - -	1.1 3.8 -	- - -
Test 1 Port 2	1.2 - -	1.4 6.6 -	- - -
Test 1 Injection/Extraction Ports	- - -	- - -	1.1 3.2 -
Test 2 Port 1	1.4/*1.4* - 0.7	1.4/*1.3* 3.4 0.5	- - -
Test 2 Port 2	1.7/*1.5* - 0.9	1.5/*1.1* 2.1 0.2	- - -
Test 2 Injection/Extraction Ports	- - -	- - -	5.1/*5.0* 4.0 6.5

Radon transport was retarded during the push phase of Test 2 conducted in the presence of 2% TCE (Figures 4.2a and 4.2b). The data were well fit by the injection phase approximate solution, with best-fit αL values of 3.4 cm at port 1 and 2.1 cm at port 2 (Table 4.3). Estimated radon retardation factors for ports 1 and 2 were 1.4 and 1.7 using the method of temporal moments and 1.4 and 1.5 using the injection phase approximate solution (Table 4.3). Numerical simulations using STOMP were conducted for the injection phase data using R = 1.0 and R = 1.4 at port 1 and R = 1.0 and R = 1.5 at port 2. The simulation breakthrough curves provided a reasonable match to the injection phase approximate solution.

Figure 4.2a Injection phase breakthrough curves for lab Test 2, port 1 with 2 % TCE.

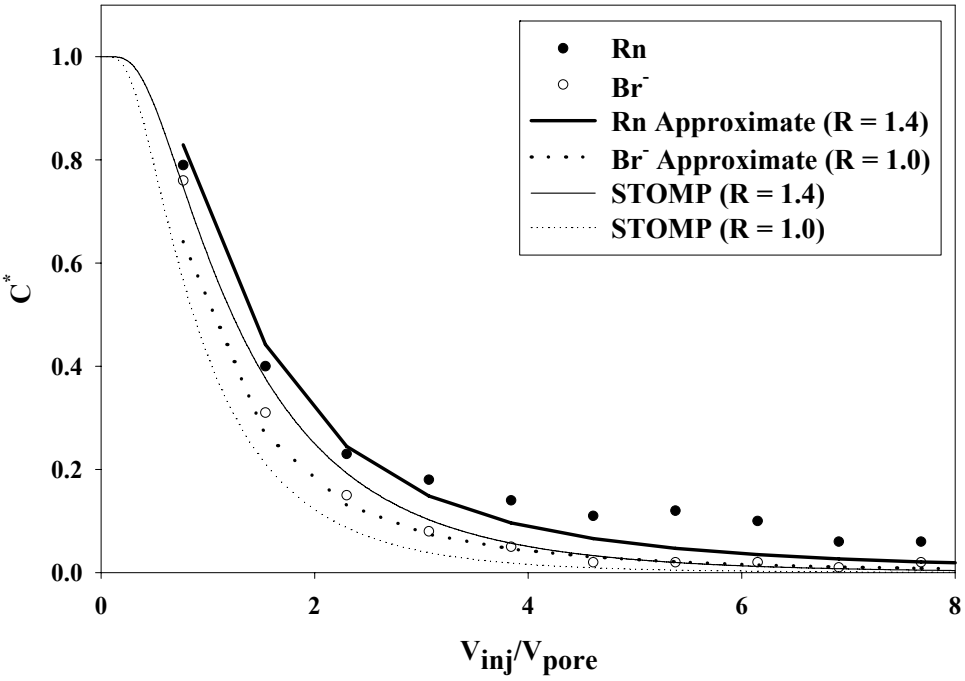


Figure 4.2b Injection phase breakthrough curves for lab Test 2, port 2 with 2 % TCE.

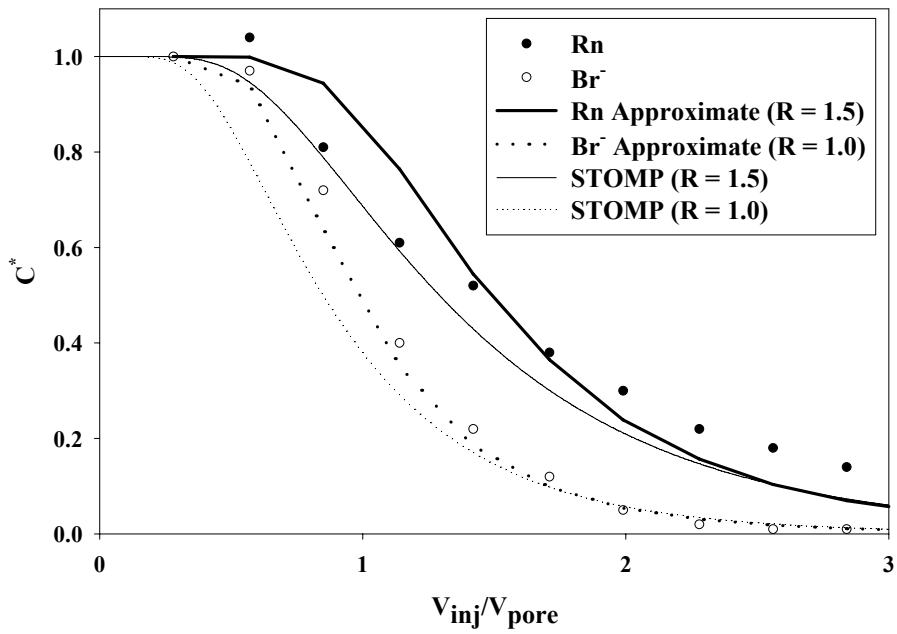
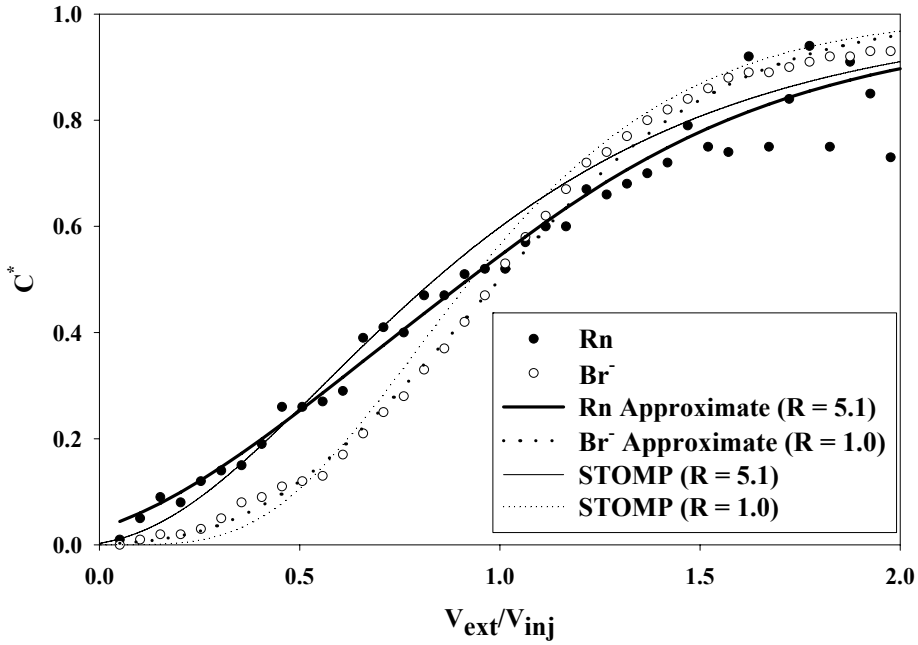


Figure 4.2c Extraction phase breakthrough curves for lab Test 2 with 2 % TCE.



Retarded radon transport was apparent in extraction phase breakthrough curves for Test 2 (Figure 4.2c). Normalized concentrations increased smoothly as the test solution was extracted from the sediment pack. The data were well fit by the extraction phase approximate solution, with a best-fit αL of 4.0 cm (Table 4.3). An estimated value of $R = 5.1$ was obtained for radon using the extraction phase approximate solution (Table 4.3). Numerical simulations using STOMP were also conducted for the extraction phase data using $R = 1.0$ and $R = 5.1$. The simulation breakthrough curves provided a good match to the extraction phase approximate solution.

Using retardation factor estimates can be made of the NAPL saturation. The slight radon retardation observed during Test 1 may be attributed to the partitioning of radon between the pore water and trapped gas present in the sediment pack. Retarded transport of dissolved gases in the presence of trapped gas has been observed in previous column and PAM experiments in our laboratory (Fry et al., 1995; Fry et al., 1996). Assuming equilibrium partitioning between the trapped gas and aqueous phases, the retardation factor for a dissolved gas can be written as

$$R = 1 + H_{cc} \frac{S_g}{S_w} \qquad (4.1)$$

where H_{cc} is the dimensionless Henry's coefficient and S_g is the trapped gas saturation. Fry et al. measured gas saturations of 11% in column experiments and between 7 and 22 % in PAM experiments conducted with the same sediment used in the laboratory push-pull tests. Using equation 4.1 and a value of $H_{cc} = 3.9$ for radon (Clever, 1979) the estimated gas saturation in our PAM sediment pack ranges from 0 to 9.3 % using radon retardation factors obtained from ports 1 and 2 during the injection phase. The higher gas saturation observed at port 2 is a function of the greater retardation factor estimated at that port (R = 1.4 for the injection phase approximate solution). The radon retardation factor of 1.1 obtained for the extraction phase approximate solution estimates a trapped gas saturation of 2.5 %.

During Test 2 radon was retarded due to 1) radon partitioning between TCE and the aqueous phase, and 2) radon partitioning between trapped gas and the aqueous phase. In order to estimate the portion of radon retardation due to TCE partitioning, retardation factors were adjusted to account for trapped gas partitioning using

$$R_{adj} = R_{test2} - \left(R_{test1} - 1.0\right) \qquad (4.2)$$

where R_{adj} is the adjusted retardation factor, $R_{test\ 2}$ is the retardation factor from Test 2, and $R_{test\ 1}$ is the retardation factor from Test 1. For example, in Test 1 the method of moments retardation factor at Port 2 is 1.2, while in Test 2 the retardation factor is 1.7, yielding an adjusted retardation factor of 1.5. Adjusted retardation factors were used to calculate TCE saturations (Table 4.3).

Table 4.4. Aqueous TCE as a function of depth in the PAM sediment pack.

Depth Interval (cm)	TCE (mg/L)
0 – 5	3.9
5 – 10	9.8
10 – 15	77.2
15 – 20	273.2

Using equation 3.12, adjusted injection phase retardation factors, and K = 50, calculated TCE saturations ranged from 0.2 to 0.9 % (Table 4.3), which is less than the volume-averaged TCE saturation of 2% in the sediment pack. This underestimation may be due to non-equilibrium radon partitioning and the heterogeneous distribution of TCE in the sediment pack. A heterogeneous TCE distribution with pooling toward the bottom of the sediment pack could result in underestimated radon retardation factors because of the reduced interfacial area between the TCE and the test solution. NAPL pools can create a mass transfer limitation to partitioning because of the long length scales of pooled NAPL relative to the scale of diffusion over the test time (Willson et al., 2000), thus violating the assumption of equilibrium partitioning. Aqueous TCE concentrations increased with depth upon the excavation of the PAM (Table 4.4), indicating that the TCE partially sank to the bottom of the sediment pack, which could account for the low retardation factors estimated during the injection phase. The extraction phase adjusted radon retardation factor was 5.0 (Table 4.3). This corresponds to a TCE saturation of 6.5 %, which is larger than the TCE saturations obtained from the port data and is an overestimation of the volume-averaged TCE saturation of 2 % in the sediment pack.

Reanalysis of the extraction phase radon data using STOMP

Although the above simulations of the extraction phase using STOMP accounted for radon partitioning between the NAPL and aqueous phases during the push-pull test, they did not account for radon partitioning into NAPL prior to the test. Radon concentrations are decreased in the presence of NAPL, with the equilibrium radon concentration being a non-linear function of S_n (Figure 2.1). Furthermore, these simulations assumed that NAPL saturation was spatially homogeneous in the PAM. However, a non-uniform NAPL distribution existed in the PAM (Figure 3.3) where the S_n ~2% extended to 74 cm from the narrow end of the PAM, beyond which S_n=0%. This non-uniform distribution affects initial radon concentrations and partitioning behavior during the push-pull test and can affect estimations of R and S_n. Additional STOMP simulations were performed to examine two factors that can influence interpretation of radon data from push-pull tests and resulting estimations of S_n: 1) the influence of NAPL on initial radon concentrations, and 2) Non-uniform NAPL saturation distributions. A revised interpretation of radon the extraction phase radon breakthrough curves (BTC) presented that reduces overestimation and results in an increase in sensitivity of the estimation method at small values of S_n. The initial conditions at the start of the simulations were set so that radon concentration was in equilibrium with emanation from the aquifer solids and the radon was

partitioned between the NAPL and aqueous phase based on Eq. 3.11, and the non-uniform distribution was that emplaced in the PAM as described above. The model was validated by comparing steady-state simulation with no flow to the analytical solution given in Eq. 2.1.

The revised method was applied to the results of the extraction phase radon breakthrough curves shown in Figures 4.1c and 4.2c. These push-pull tests were performed in clean sediment (Test 1, Figure 4.1) and TCE-contaminated sediment (Test 2, Figure 4.2c), with the contaminated zone ($S_n \sim 2$ %) of Test 2 extending 74 cm from the narrow end of the PAM, beyond which $S_n = 0$ %. The tests were originally modeled using normalized BTCs without the incorporation of initial radon concentrations in the model domain, and resulted in overestimates of R and the likely S_n in the PAM (Table 4.3).

Test 1 was modeled using the revised method, with an average initial radon concentration = 197.6 pCi/L (measured in 4 sampling ports in this PAM before the test). The bromide data are well fit by a simulated R = 1 BTC, with a best-fit $\alpha_L = 1.9$ cm, and the radon data are best-fit by a simulated R = 1.3 BTC (Figure 4.3). Similar to the previous analysis the radon retardation in Test 1 is attributed to partitioning of radon between the trapped gas. Using Eq. 4.1, a R = 1.3 yields an estimated $S_g = 7.1$ %. These values are similar to those provided in Table 4.3. The best-fit R = 1.3 also compares favorably to the retardation factors measured in sampling ports 1 and 2 (located 15 and 30 cm from the narrow end of the PAM) during the injection phase of Test 1, which ranged from 1.0 to 1.4 (Table 4.3).

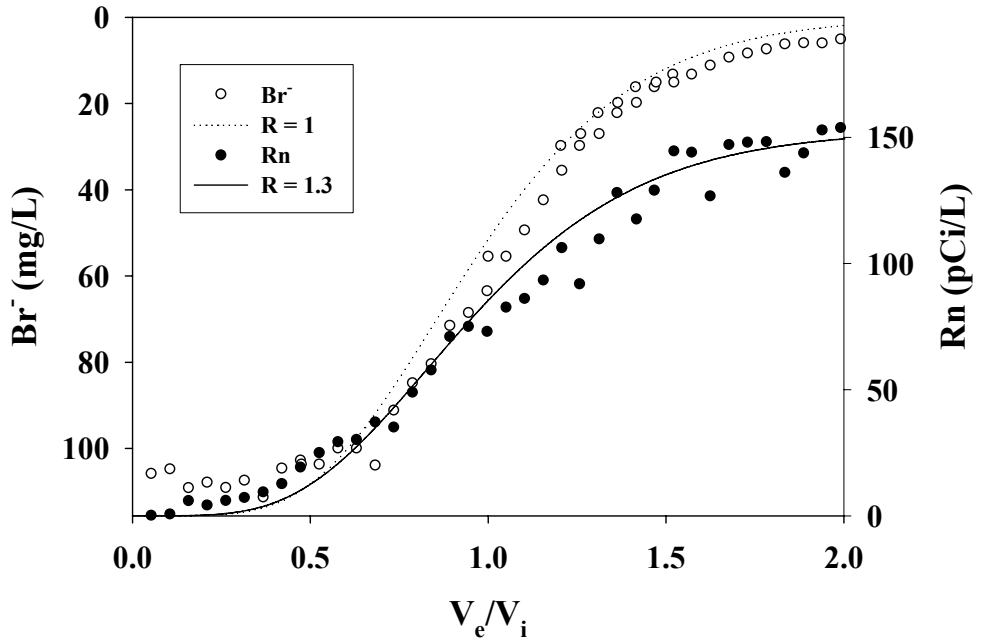
Table 4.5 Radon retardation factors (R), adjusted retardation factors for the effect of trapped gas (in italics), best-fit dispersivities (αL), and calculated TCE saturations (Sn) from push-pull tests. Results from Davis et al. (2002) are shown on the left, while results using the revised method are shown on the right. A value of K = 50 was used to calculate Sn in the presence of TCE.

	From Table 4.5 (α_L best-fit using approximate solution)			Using revised method (α_L best-fit using STOMP)		
	R	α_L (cm)	S_n (%)	R	α_L (cm)	S_n (%)
Test 1, no TCE	1.1	3.2	-	1.3	1.9	-
Test 2, with TCE	5.1/5.0	4.0	7.4	2.2/1.9	3.7	1.8

Test 2 was also modeled using the revised method, with an average initial radon concentration = 262.1 pCi/L (measured in 4 sampling ports in this PAM prior to TCE contamination). A simulation was performed in which TCE contamination extended to 74 cm, with uncontaminated sediment at > 74 cm. The bromide data are well fit by a simulated R = 1 BTC, with a best-fit $\alpha_L = 3.7$ cm, and the radon data are best-fit by a simulated R = 2.2 BTC (Figure 4.7). The radon retardation in Test 2 is attributed to partitioning of radon between 1) the trapped gas and aqueous phase, and 2) the TCE and aqueous phase. The portion of radon retardation due to TCE partitioning was determined by adjusting R to account for trapped gas partitioning using Eq. 4.2 An adjusted R value of 1.9 is calculated using Eq. 4.2, which results in an estimated $S_n = 1.8$ % (Table 4.5). The best-fit $\alpha_L = 3.7$ cm compares favorably with the best-fit $\alpha_L = 4.0$ in Table 4.3,

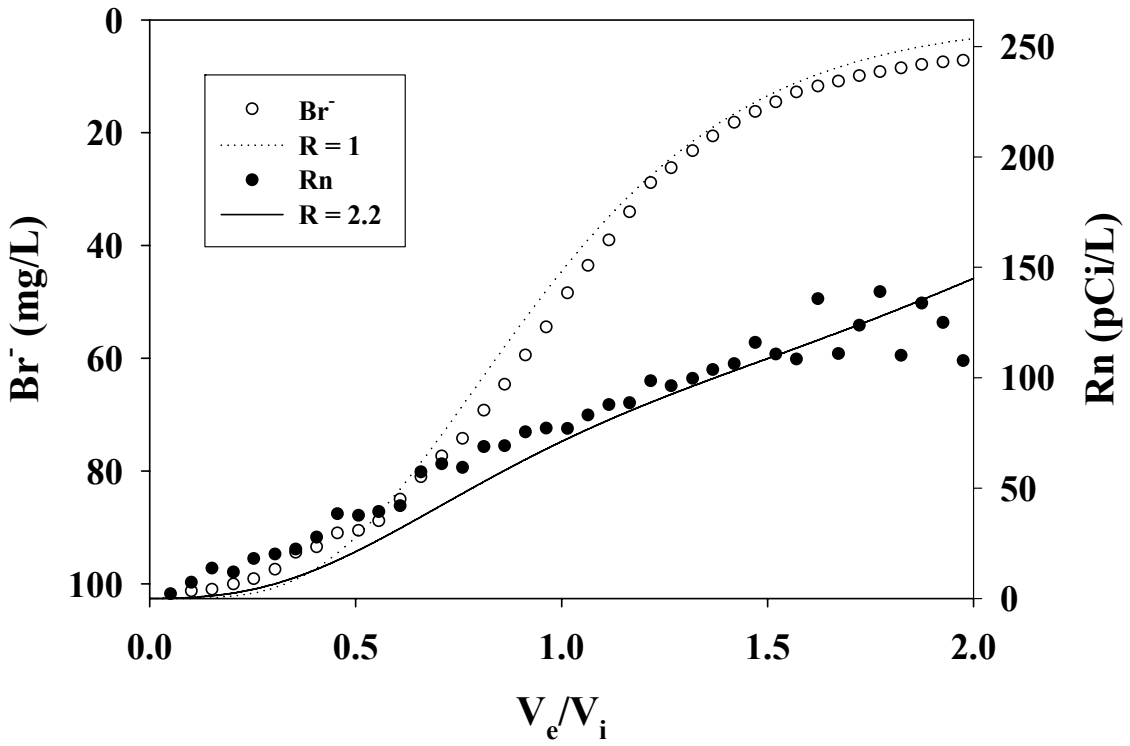
while the estimated S_n = 1.8 % is a more reasonable estimate of the TCE saturation in the sediment pack (~ 2 %) than is the estimated S_n = 7.4 % (Table 4.3) determined previously.

Figure 4.3 Radon (pCi/L) and bromide (mg/L) experimental and simulated (R = 1 and R = 1.3) breakthrough curves during the extraction phase of a push-pull test performed in a non-contaminated physical aquifer model (Test 1).



The adjusted R = 1.9 compares favorably with the adjusted retardation factors measured in sampling ports 1 and 2 during the injection phase of Test 2, which ranged from 1.1 to 1.5 (Table 4.3). Thus the revised method results in better agreement of extraction and injection phase estimated R values and subsequent estimations of S_n. The new estimate of S_n = 1.8 % is also in agreement with S_n values ranging from 0.7 to 1.6 % from partitioning alcohol push-pull tests performed in this PAM (Istok et al., 2002).

Figure 4.4 Radon (pCi/L) and bromide (mg/L) experimental and simulated (R = 1 and R = 2.2) breakthrough curves during the extraction phase of a push-pull test performed in a TCE-contaminated physical aquifer model (Test 2).



The revised simulations provided estimates for S_n in the PAM test closer to the emplaced saturation of 2%. The simulations more accurately represented the true condition of in situ radon partitioning both prior to and during the push-pull test. The method shows promise in providing estimates for S_n and showing changes in S_n over time as, for example, source zone remediation is affected.

The PAM tests showed that partitioning responses are manifested in push-pull extraction phase breakthrough curves under the very controlled laboratory setting of the push-pull tests. Tests conducted at the DNTS will evaluate whether similar observations can be made under the less controlled conditions in the field.

4.2 Push-Pull Test Results for the Dover Test Cell

Over the course of a two-year period, sixteen push-pull tests were completed in the test cell at the DNTS. (Table 4.6 provides a summary of the tests conducted in four wells and one drive point well. The wells surround the location where NAPL was injected; see Figure 3.2). The tests were conducted either over the complete screened section of the well or over a specific depth interval. The May and August 2001 tests were performed over the complete screened interval, and one test in OSU-2 was conducted over a three-foot interval. Later tests were performed over specific depth intervals in an attempt to quantify NAPL contamination over a specific depth interval. Push-pull tests were conducted over specific depth intervals by packing off a three-foot section of test well using inflatable packers. Later, April and September 2002 tests were repeated on the different dates over similar depth intervals to study changes in NAPL saturation that may have resulted at specific locations in response to remediation.

Varying amounts of radon-depleted groundwater were injected in the push-pull tests along with bromide as a conservative tracer. For tests conducted over the complete screened interval, 250 L of groundwater was injected and 500 L was extracted. For tests conducted over a three-foot section of well screen, typically less groundwater was injected or extracted.

Table 4.6 Summary of Push-Pull Test Conducted at the DNTS.

Date	**Well**	**Interval Tests**	**Volume Injected and Volume Extracted**	**Bromide Recovery**	**Average Radon Concentration of Last Five Samples**
		Ft bgs	L and L	Percent	pCi/L
May 01	OSU-1	Full Interval	250 and 500	86	191
May 01	OSU-2	34.5 -37.5	250 and 500	70	265
May 01	OSU-3	Full Interval	250 and 500	80	280
May 01	OSU-4	Full Interval	250 and 500	64	176
August 01	OSU-1	Full Interval	250 and 250	69	175
August 01	OSU-2	15.5-18.5	250 and 350	56	220
August 01	OSU-3	13.5-16.5	200 and 350	52	143
August 01	OSU-4	20.5-23.5	125 and 240	35	197
Nov. 01	OSU-3	21-24	109 and 350	84	181
Nov. 01	OSU-4	28.5-31.5	109 and 220	88	248
Feb. 02	OSU 03	22.5 Full Interval	280 and 390	68	268
April 2002	OSU-2	19.5-22.5	75 and 153	79	196
April 2002	OSU-3	18.5 -21.5	75 and 150	62	168
April 2002	OSU DP	20-22	30 and 50	93	256
Sept 2002	OSU-2	19.5 to 22.5	94 and 187	73	289
Sept 2002	OSU-3	21 and 24	94 and 187	65	290

Bromide recovery varied in the tests. Low bromide recovery was often obtained when the system packer system failed during the tests. Recoveries of less than 60% indicated a leaky packer system. Recoveries of less than 70% might also indicate packer leakage. The highest bromide recovery of 93% was achieved in a test conducted in a two-foot drive point well that did not use a packer system to isolate the well. A significant problem with a leaky packer system is high radon concentrations in background groundwater could dilute the signal of lower radon concentrations that result from partitioning into a NAPL phase.

The average groundwater radon concentrations at the latter stages of the extraction phase are also reported in Table 4.6. These concentrations are important since they are representative of background conditions and how radon concentrations are changing over extended time periods. For example, an increase in radon concentration would indicate the remediation of NAPL contamination.

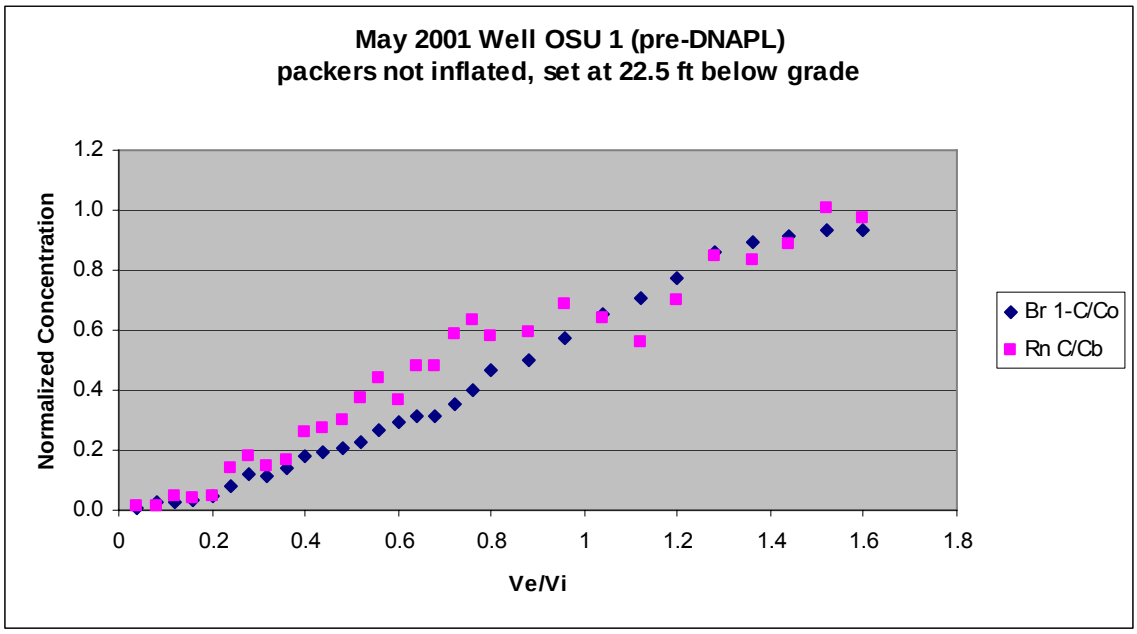
Tests conducted prior to August 2001 were before NAPL was added to the test cell. Tests conducted prior to April 2002 were before groundwater flow was initiated in the test cell. The tests conduced in April 2002 and September 2002 were performed after groundwater flow was started in the test cell for the remediation experiments. The push-pull tests will be discussed in order of the sequence in which they were performed.

Push-Pull Tests, May 2001

Push-pull tests were conducted in all four OSU DNTS wells in May 2001. The tests were performed over the full-screened section of the wells except for OSU-2, which was tested over a depth interval of 34.5-37.5 ft. Bromide recovery ranged from 64% in well OSU-4 to 86% in OSU-1. In the OSU-2 well, the extraction well bromide breakthrough curves showed normalized extraction concentrations (C/Co) at the end of the test that never reaching 1.0, indicating dilution by water that did not contain bromide and suggesting the packer was leaking. The average radon concentrations of the last five samples ranged from 176 to 280 pCi/L, showing spatial variations in the radon concentration within the test cell (Table 4.6).

Based on the extraction breakthrough curves (Figures 4.5a and 4.6), there was no evidence showing retardation, which was expected since NAPL had not been released into the test cell. Well OSU-1 had the best recovery of bromide (86%). The extraction phase radon concentrations for this well were normalized based on a background concentration (C_b), where C_b was determined from the radon concentration in the last five samples of the extract breakthrough curve. Based on this normalization, retardation is not obvious. Similar responses were observed at the other wells. Well OSU-4 showed some difference in radon breakthrough behavior with minor retardation in radon compared to bromide. This well also showed sporadic concentration behavior during the early portion of the test. The bromide mass balances also indicate the poorest recovery in this well. In general the results of the push-pull tests suggest little retardation in the radon. Since these tests were conducted prior to the NAPL release into the test cell phase, little retardation was expected.

Figure 4.5. Results of May 2001 push-pull tests conducted in wells OSU-1 and OSU-2.



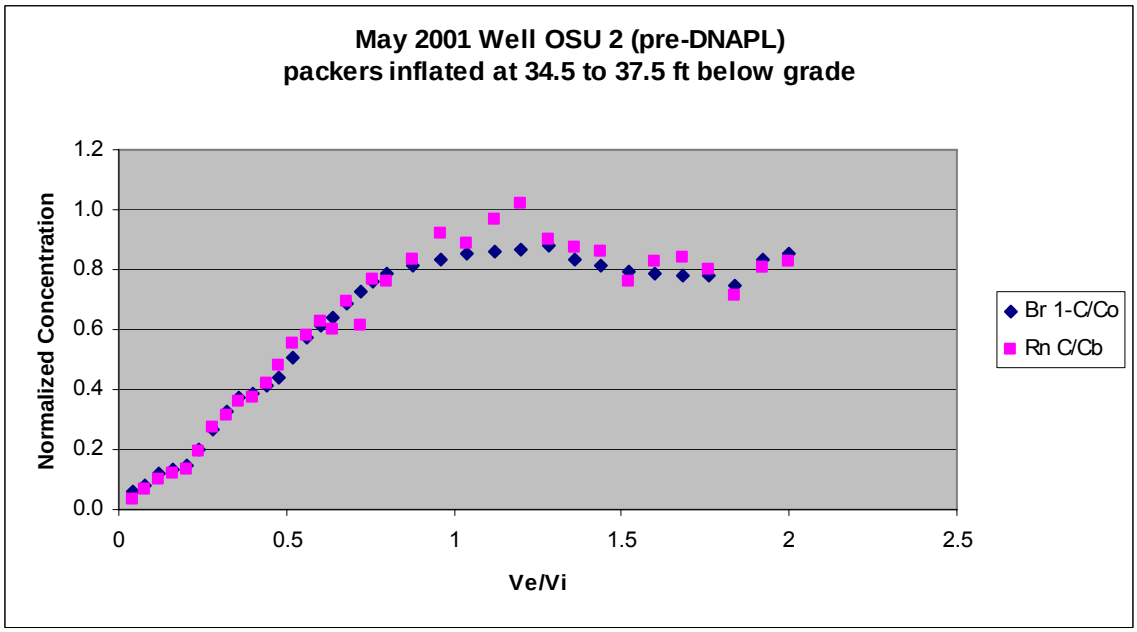
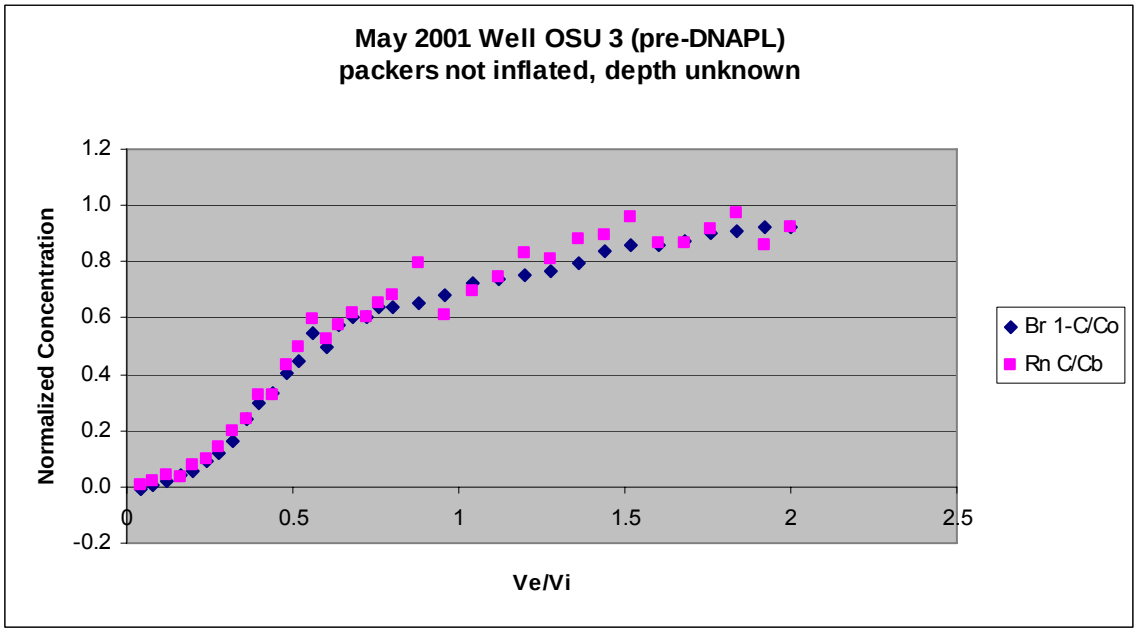
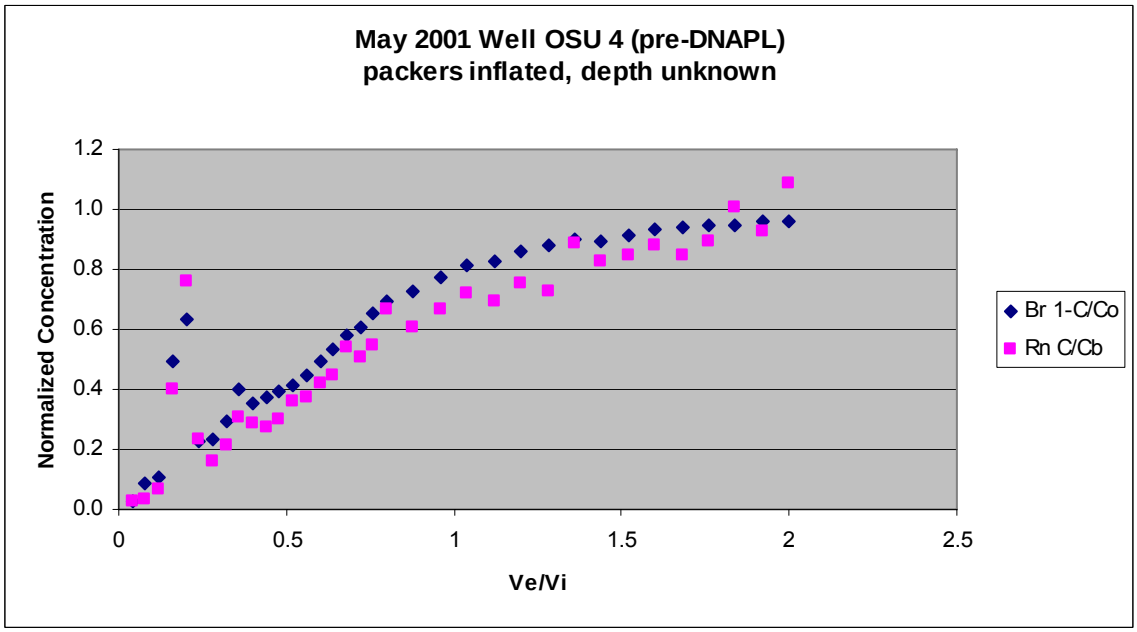


Figure 4.6. Results of push-pull tests conducted in May 2001 in OSU-3 and OSU-4.





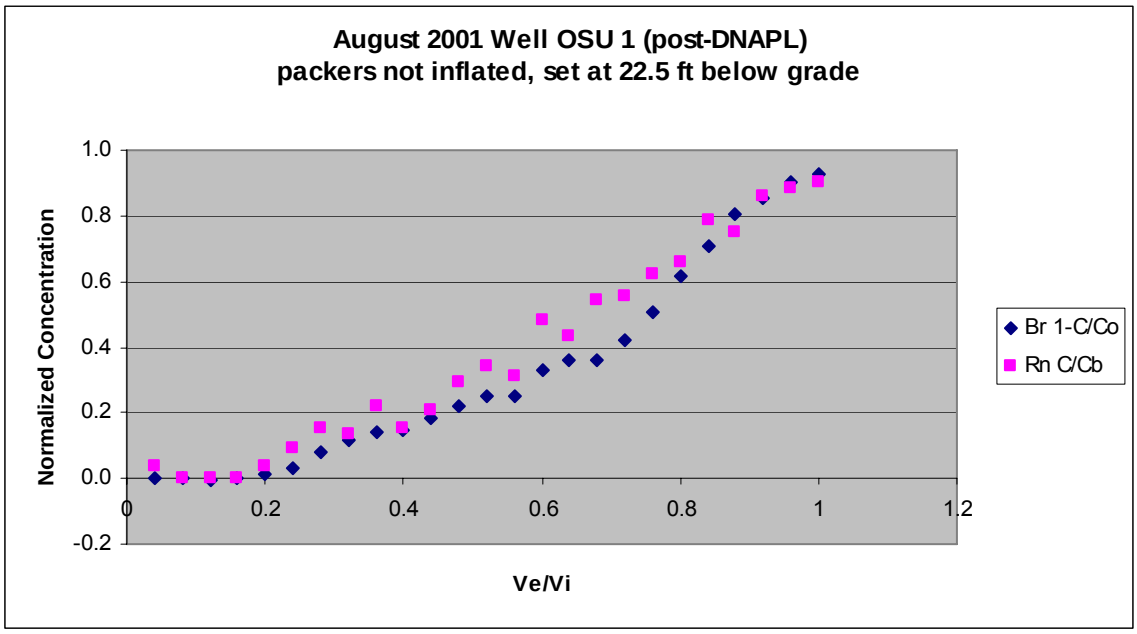
Push-Pull Tests, August 2001

Another series of push-pull tests were conducted in August 2001 after the test cell was contaminated with 100 L of PCE. PCE concentrations in the wells ranged from 0 to over 150 mg/L. The tests were repeated using essentially the same procedures as the previous tests conducted in May 2001 (prior to PCE addition). Like the May test, the test in OSU-1 was conducted over the entire screen interval of the well. The tests in the other wells were conducted over a three-foot packed interval to probe for NAPL contamination at specific depths. Problems were encountered in the tests, since good bromide mass recoveries were not achieved. Bromide recoveries ranged from 35 to 69%, indicating problems with leaking packers. These recovery problems are indicated by the results of the bromide and radon extraction well breakthrough curves shown in Figure 4.5 and 4.8. Erratic behavior in normalized radon and bromide concentrations were observed in wells OSU-2, OSU-3, and OSU-4. Low bromide recovery was observed in all three push-pull tests. None of the tests truly reproduced the earlier test results on recovery of bromide. Radon concentrations observed at the end of the tests also differed and tended to be lower (Table 4.6).

The test in OSU-1 was the most comparable to the test performed in May. Both tests were performed by injecting 250 L of radon free groundwater over the complete screened interval of the well. In the August test, however, only 250 L of groundwater was extracted (1 injection volume) compared to 500 L in the May test. It is interesting to note that with up to 1 injection volume extracted, little difference was observed in the response at OSU-1 between the August and May tests (Figures 4.5 and 4.7). The results of this test, when compared to the May test, would not indicate a significant increase in retardation, despite the addition of PCE to the test cell. The results would indicate that a push-pull test conducted over complete slotted interval of the well was unable to detect NAPL contamination.

Based on the erratic concentration responses in well OSU-2, OSU-3, OSU-4, it is difficult to determine if any retardation in radon was observed. A significant difference in retardation of radon between the tests was not evident.

Figure 4.7. Results of push-pull tests conducted in August 2001 in OSU-1 and OSU-2.



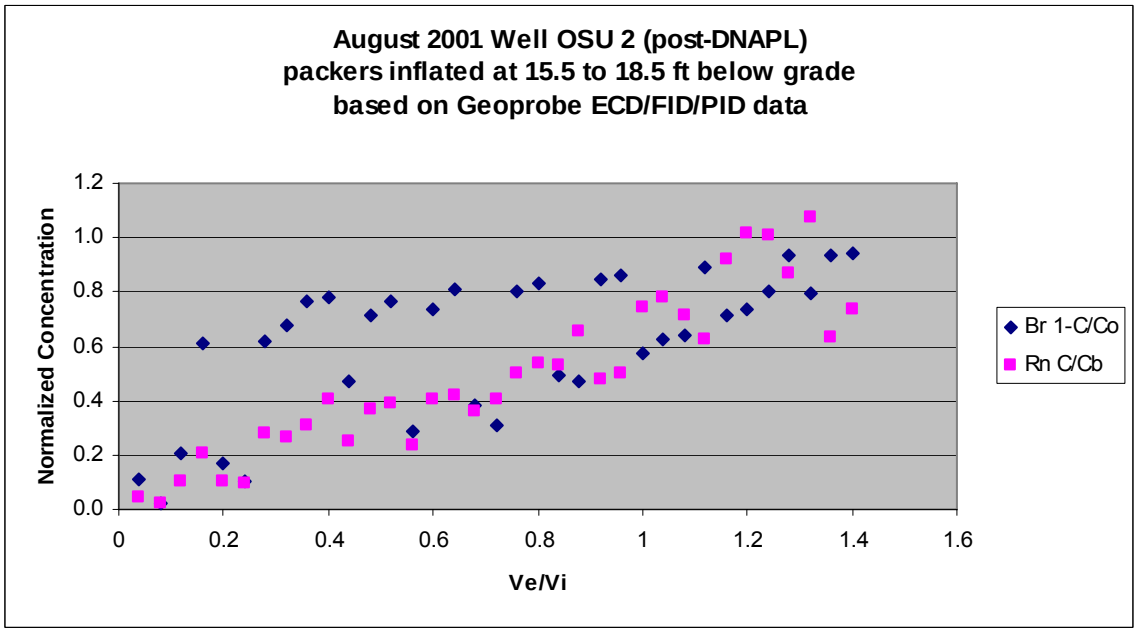
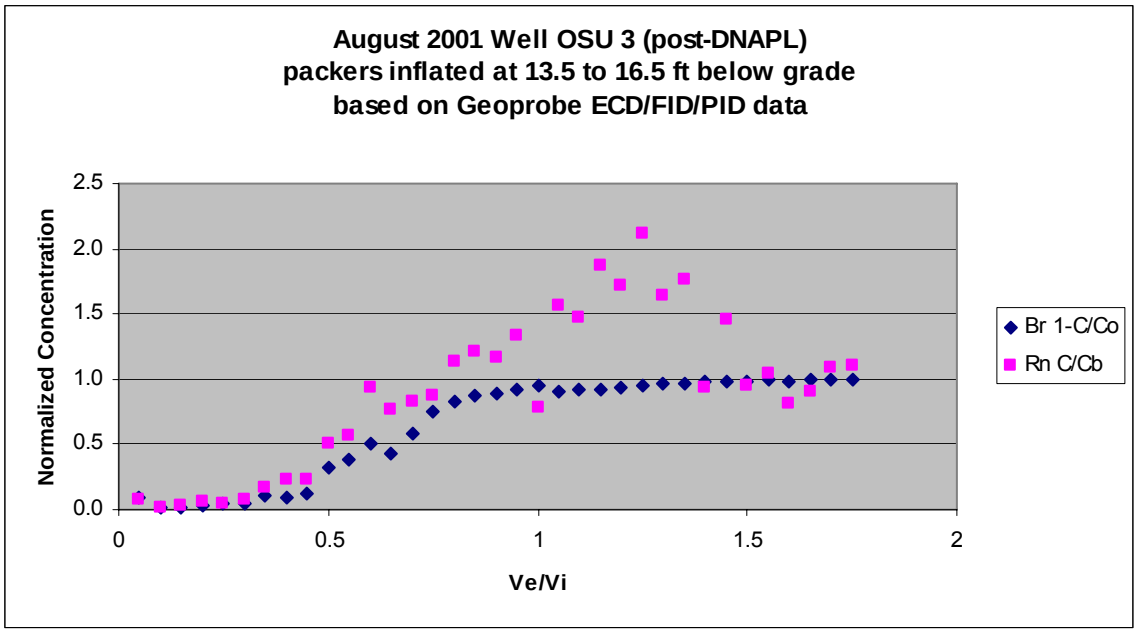
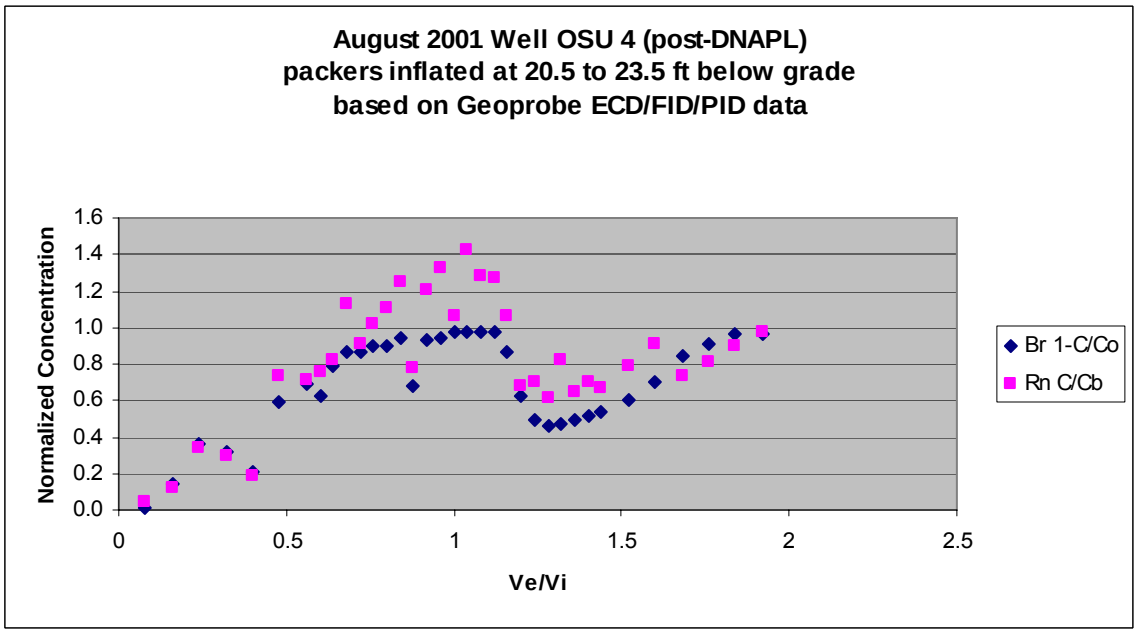


Figure 4.8. Results of push-pull tests conducted in August 2001 in OSU-3 and OSU-4.





Push-Pull Tests, November 2001

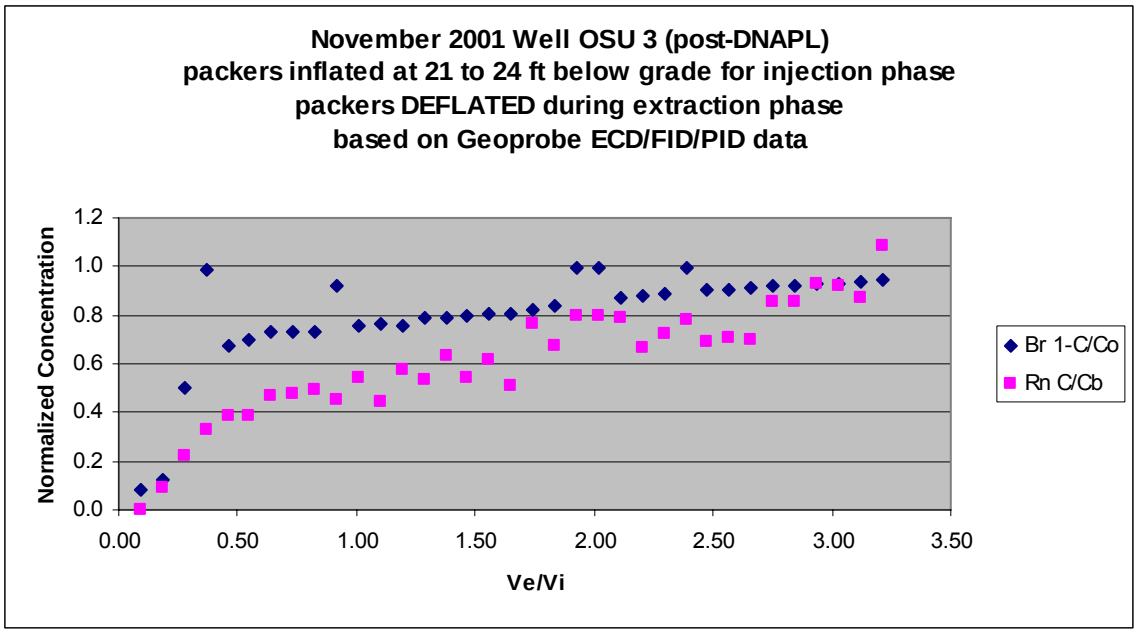
Push-pull tests were conducted in November 2001 in wells OSU-3 and OSU-4 over three-foot packed intervals. The intervals were chosen to probe for NAPL contamination at select depths, based on prior background radon concentration measurements at specific depth intervals (Table 4.7). Static groundwater samples from the 21-24 ft depth interval showed a decrease in radon concentration by 42% in the August 2001 sampling compared to the May 2001 sampling, possibly indicating a response due to the presence of NAPL. At the depth interval of 27-30 ft in well OSU-4, only a 2.5% change was observed, possibly indicating NAPL was not present at this depth near OSU-4. Thus a retarded response would be expected in well OSU-3 at the 21-24 ft. interval, while little retardation would be expected in the 27-30 ft. interval in well OSU-4.

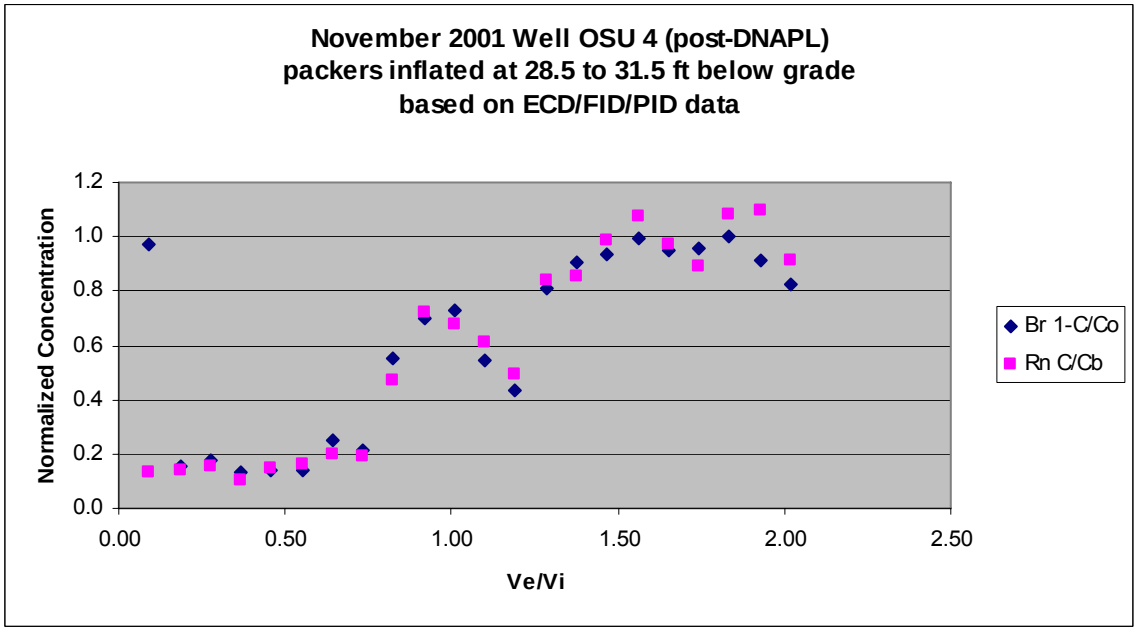
Both push-pull tests were successful in that good bromide mass recovery was achieved, thus problems with leaky packers were resolved. Bromide recovery of 84 and 88% was achieved in well OSU-3 and OSU-4, respectively. These tests represent some of the best tests, with respect to bromide recovery.

The results of the push-pull tests are shown in Figure 4.9. Well OSU-3 results showed evidence of retardation, while those from well OSU-4 do not. The results for OSU-3 were obtained from a packed interval of 21 to 24 ft. The background radon samples (average of samples at the end of the extract phase) were 181 pCi/L. In contrast, the tests at OSU-4 were performed at the 27 to 30 ft interval and had a background concentration of 248 pCi/L. The higher background concentration in OSU-4 would indicate that less NAPL was present, consistent with the results of the push-pull tests.

The results of specific depth-interval sampling of the background radon concentrations prior to the tests are provided in Table 4.7. The groundwater radon concentrations in the November sampling at the 21-24 ft depth interval in OSU-3 deceased by 72% compared to May. The concentrations decreased from 244 pCi/L in May to 69 pCi/L in November. In contrast, the concentrations at the 27-30 ft in the well OSU-4 interval decreased by only 17% over the same time interval, from 219 to 180 pCi/L. These results support the retardation observed in OSU-3 and the lack of retardation in OSU-4.

Figure 4.9. Results of push-pull tests conducted in November 2001 in OSU-3 and OSU-4.





Results of Radon Concentration Surveys: May, August, November 2001
Surveys of the background radon concentration in groundwater samples from different depth intervals in OSU-1, OSU-2, OSU-3, and OSU-4 were obtained prior to conducting the push-pull tests. The samples were obtained by packing a 3-ft. section of well screen at a specific depth and pumping three well volumes prior to collecting a sample. Attempts were made to sample ten depth intervals from 12-15 ft to 39-42 ft. On several sampling events the shallowest levels could not be sampled due to a lowering of the groundwater table inside the test cell.

The results of three surveys conducted in May, August, and November 2001 are provided in Table 4.7 and 4.8. The May survey was performed prior to the addition of 100-L of PCE to the test cell, while the August and November surveys were conducted after PCE addition.

The May survey confirmed earlier observations that a broad range of radon concentrations exist in the test cell as a result of geologic factors. Radon concentrations ranged from 31 to 303 pCi/L in groundwater. Lower concentrations tend to be deeper in the test cell (39-42 ft interval) and higher concentrations tend to be at the depth interval of around 30 – 33 ft. Depth average concentrations were made for intervals where samples were obtained over all three sampling events, providing 6 to 8 depth levels to be averaged for each well. In the May survey depth well, depth-averaged values ranged from 127 to 195 pCi/L (Table 4.8).

Table 4.7. Dover AFB Static Rn Samples 2001

Well	Depth Interval (ft. below grade)	May-01 Rn pre-DNAPL (pCi/L)	Aug-01 Rn post-DNAPL(pCi/L)	% Change Aug vs. May	Nov-01 Rn post-DNAPL (pCi/L)	% Change Nov vs. May	% Change Nov vs. Aug
OSU 1	12-15	30.3	125.0		n.a.		
	15-18	163.9	150.2	-8.3	84.6	-48.4	-43.7
	18-21	129.1	136.1	5.4	n.a.		
	21-24	148.8	121.3	-18.5	103.2	-30.7	-14.9
	24-27	217.9	133.8	-38.6	131.2	-39.8	-1.9
	27-30	215.6	143.2	-33.6	115.6	-46.4	-19.2
	30-33	133.5	132.3	-0.9	131.2	-1.7	-0.9
	33-36	108.5	112.0	3.2	140.3	29.4	25.3
	36-39	70.9	56.6	-20.1	133.2	87.9	135.3
	39-42	54.4	n.a.		n.a.		
OSU 2	12-15	n.a.	121.3		125.2		3.2
	15-18	104.4	137.3	31.6	89.8	-13.9	-34.6
	18-21	140.6	139.2	-1.0	n.a.		
	21-24	190.5	120.9	-36.5	48.3	-74.6	-60.0
	24-27	140.2	121.6	-13.3	159.5	13.8	31.2
	27-30	165.4	120.7	-27.0	120.8	-26.9	0.1
	30-33	176.1	126.3	-28.3	161.7	-8.2	28.0
	33-36	225.4	123.5	-45.2	195.0	-13.5	57.9
	36-39	76.8	128.9	67.9	174.4	127.1	35.3
	39-42	86.6	n.a.		n.a.		
OSU 3	12-15	n.a.	112.2		106.8		-4.8
	15-18	139.2	123.6	-11.2	129.9	-6.7	5.1
	18-21	172.5	114.8	-33.4	78.5	-54.5	-31.7
	21-24	243.8	132.2	-45.8	68.9	-71.7	-47.8
	24-27	183.6	123.1	-33.0	108.7	-40.8	-11.7
	27-30	221.9	128.4	-42.1	135.0	-39.2	5.1
	30-33	302.7	104.8	-65.4	148.7	-50.9	41.9
	33-36	98.0	53.3	-45.7	161.5	64.7	203.2
	36-39	76.0	n.a.				
	39-42	78.6	n.a.				
OSU 4	12-15	n.a.	n.a.		182.5		
	15-18	182.7	n.a.		295.2	61.6	8.6
	18-21	160.9	n.a.		277.8	72.7	7.1
	21-24	158.3	176.3	11.4	194.6	22.9	-25.4
	24-27	181.1	220.4	21.7	142.6	-21.3	-19.6
	27-30	218.5	223.9	2.5	180.0	-17.6	-35.3
	30-33	231.5	235.7	1.8	175.7	-24.1	10.4
	33-36	155.1	215.1	38.7	230.3	48.5	
	36-39	108.8	193.8	78.2	210.5	93.5	
	39-42	87.9	n.a.				

Table 4.8. Depth averaged groundwater radon concentrations.

Well	May, 01	August 01	November 01
	Depth Average Rn (pCi/L)	Depth Average Rn (pCi/L)	Depth Average Rn (pCi/L)
OSU-1	151	104	105
OSU-2	127	108	135
OSU-3	195	111	104
OSU-4	176	210	189

Depth Intervals Averaged
OSU-1 and OSU-2 15-18ft; 21-24 ft; 24-27 ft; 27-30ft; 30-33 ft; 33-36 ft; 36-39 ft.
OSU-3 - 15-18ft;18-21 ft; 21-24 ft; 24-27 ft; 27-30ft; 30-33 ft; 33-36 ft.
OSU4 - 21-24 ft; 24-27 ft; 27-30ft; 30-33 ft; 33-36 ft; 36-39 ft.

The August survey represents results after PCE had been added to the test cell. The survey shows radon concentration decreasing at some locations by as much as 65%. However, radon was also observed to increase by a much a 78% at one location. While a decrease in radon concentration would be associated with the presence of NAPL, we have had no logical explanation for an increase in radon concentration.

Well OSU-3 showed the greatest decreases at specific depth intervals. The radon concentrations decreased at all locations between the May and August surveys. The greatest decrease was 65% at the 30-33 ft interval. In the November sampling the greatest decrease was observed at the 21-24 ft interval. The radon concentration shows a progressive decrease at this location.

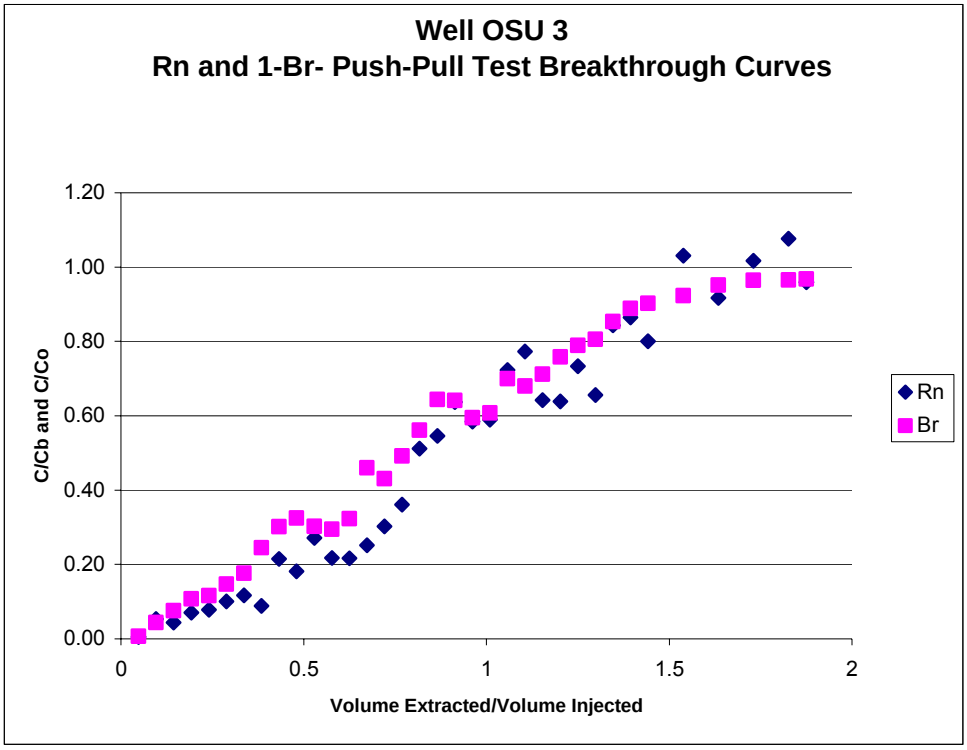
The results from the surveys show definite variations in radon concentration from May to November. At OSU-1 and OSU-3, depth-averaged radon concentrations decreased after NAPL was added (Table 4.8). The most dramatic decrease was observed in OSU-3, where the depth-averaged concentrations decreased from 195 pCi/L in the May survey to 104 pCi/L in the August survey. This rapid response is consistent with what we would expect if the NAPL upon release was rapidly transported to regions near this well.

Results of Push-Pull Test, February 2002

In February, a single push-pull test was conducted in well OSU-3. For this test the packer was broken and a test was conducted by injecting radon-free groundwater at the 21 ft level without packers in place. This test therefore does not represent conditions of the prior November 2001 test, which was conducted over the packer interval of 21-24 ft. The bromide recovery in this test was 68%, a significant reduction over the test in November. 2001, and less than the 80% recovery observed in May 2001, when injection was performed over the entire thickness.

The results of the test are presented in Figure 4.10. A significant retardation in Rn was not observed. The background radon concentration was 268 pCi/L, which was higher than observed in the November 2001 test (181 pCi/L). The range of that observed in the May 2001 test (280 pCi/L) prior to radon addition, and when injection and extraction was performed over the complete interval. It is also of interest to note that the background concentration was much higher than the depth-average values determined in the November survey (Table 4.8). The reason for this difference is not known. The results would indicate that if NAPL were present, it may be localized over a specific depth interval, and not the complete saturated thickness of the aquifer. For example, the November 2001 test that showed retardation was indicated over the 21-24-ft. depth interval.

Figure 4.10. Push-pull tests conducted in well OSU in Feb 2002. Fluid was injected at the 22 ft. interval with no packer present.



April/May 2002

GeoSyntec consultants began an interwell tracer test in the test cell in March 2002 using a conservative chloride tracer. The tracer test solution consisted of test cell groundwater that was treated for aqueous phase organics using a carbon adsorption system. Samples showed radon was effectively removed by the activated carbon system, thus groundwater that lacked radon was injected to the test cell. Radon then accumulated in the groundwater as a result of emanation from the aquifer solids during transport through the test cell. The residence time of groundwater in the test cell was greater than 20 days, permitting secular equilibrium of radon to be achieved. Chloride was added before injection of the solution into the south end of the test cell through three injection wells. Three extraction wells were located at the north end of the test cell. The wells pumped at a constant rate, thus creating a uniform flow field within the test cell.

A series of push-pull tests were conducted with flow occurring for comparison with the tests performed earlier in the absence of flow. In addition, a drive point (DP) sampling well was installed in the center of the Dover test cell at the 20' -22' depth interval for a push-pull test. The placement of the drive point well was close to the zone where NAPL was released the previous summer. The April and May push-pull tests were performed in the DP well, and the OSU-2 and OSU-3 at the depth interval (19.5 to 22.5 ft) (18.5 to 21.5), respectively, using the same procedures previously discussed. For the DP well, the volume injected and extracted was much lower than for OSU-2 and OSU-3, since the interval was shorter. It is interesting to note that a higher recovery of bromide was achieved in the DP well compared to OSU-2 and OSU-3 (Table 4.6). The radon concentrations in final samples collected (background) show a range of values from 168 pCi/L in OSU-3 to 256 pCi/L in the DP well, despite similar depth intervals being sampled. This spatial difference existing in the test cell might be caused by distributions in DNAPL saturation. The background samples in well OSU-3 were in the range observed in the November 2001 tests of a similar packed interval. The bromide recovery, however, was lower in the April 2002 test than in the November test for well OSU-3.

Results from the push-pull tests are provided in Figures 4.11a and 4.11b. The results show no direct evidence of retardation in radon transport in any of the wells. The results were similar to those obtained under no-flow conditions, except there appears to be less retardation observed in well OSU-3 in April with flow occurring than in the November 2001 test without flow. Less bromide was recovered in the April 2002 test at well OSU-3 compared to the November 2001 test, thus the tests are not directly comparable. The results potentially indicate a change in NAPL saturation around the 18 to 21 ft interval of OSU-3 as a result of induced groundwater flow. It is possible that with the introduction of flow in the test cell, the NAPL became mobile and saturations decreased.

Figure 4.11a. Results of April/May 2002 push-pull tests.

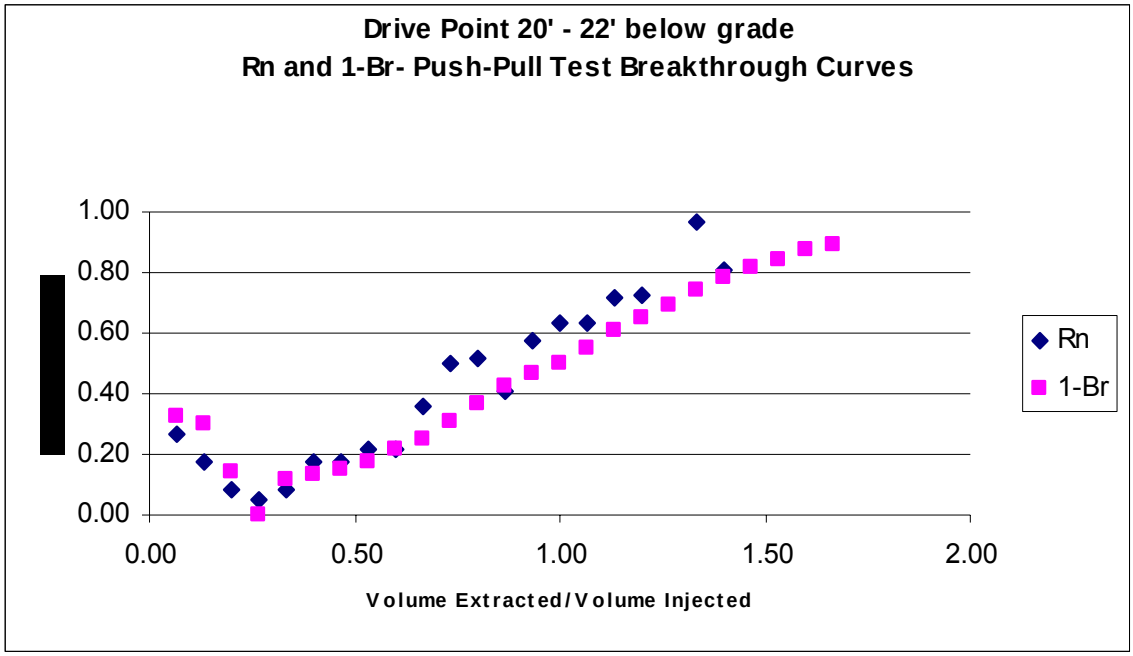
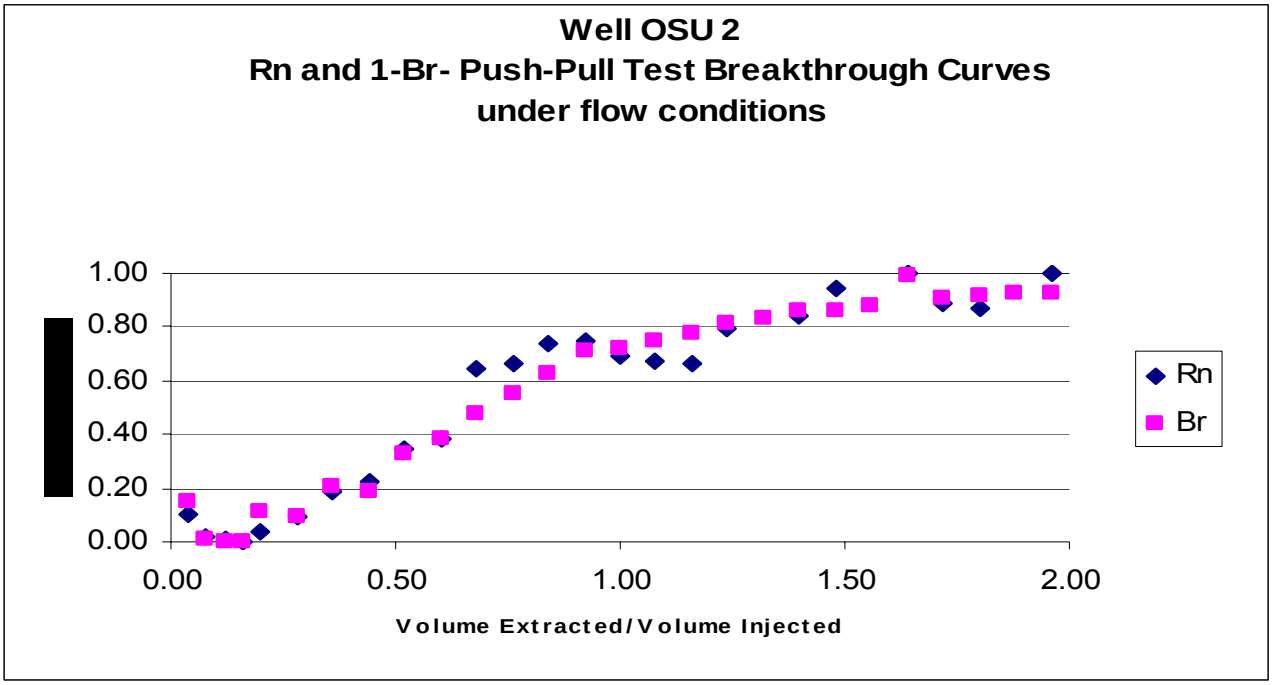
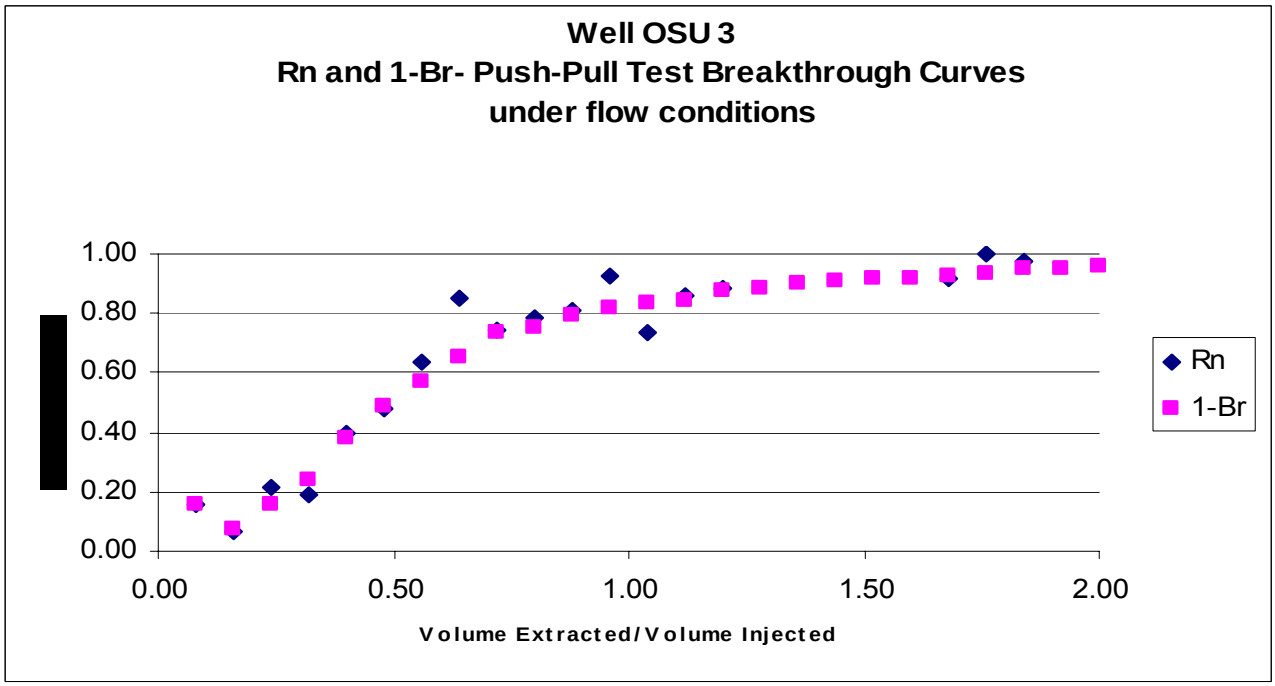


Figure 4.11b. Results of push-pull tests conducted in April/May 2002 in OSU-2 and OSU-3.





Push-Pull Tests, September 2002
A final series of push-pull tests were conducted in wells OSU-2 and OSU-3 in September 2002, seven months after flow was induced in the test cell. The tests permit comparisons between test results obtained in April 2002. The tests were conducted over similar depth intervals. Bromide was recovered in both wells to a similar percentage as achieved in the April tests. The background radon concentrations increased in the OSU-2 and OSU-3 wells, from 196 to168 pCi/L in April to 289 to 290 pCi/L, respectively.

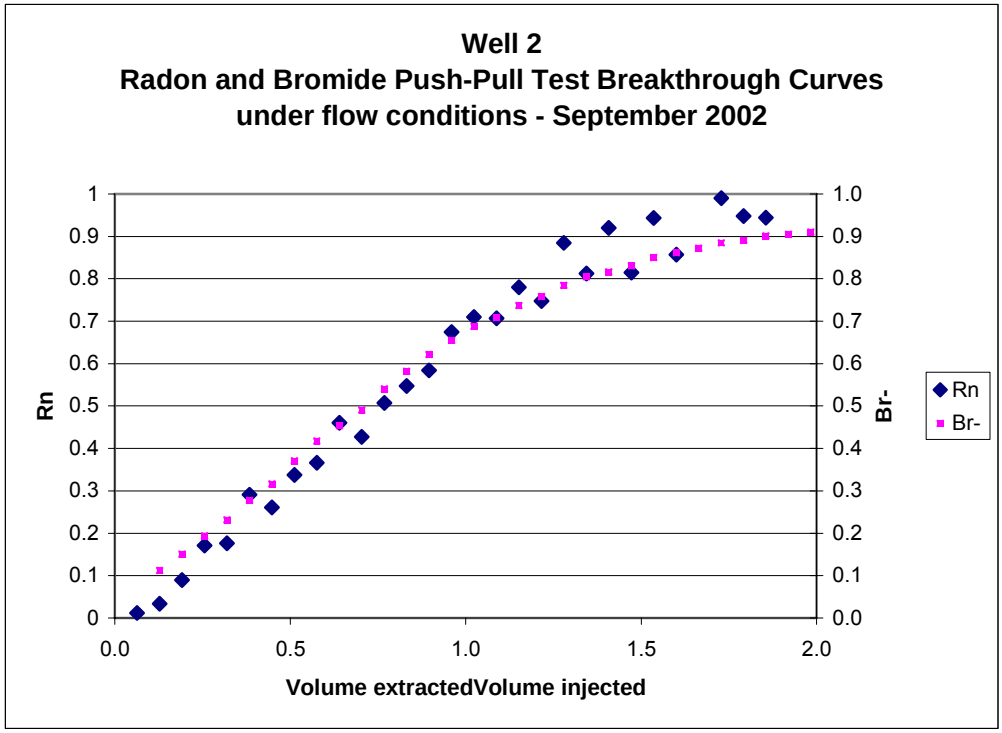
Results from the normalized plots are shown in Figure 4.12. Little evidence for retardation is shown for well OSU-2, while some evidence for retardation is shown in well OSU-3. The results indicate slightly more retardation in OSU-3 in the September 2002 test than was observed in April 2002. The result is inconsistent with the increase in the background radon concentration from 168 pCi/L to 290 pCi/l, observed in the well at this depth interval.

Analysis of the push-pull tests using actual measured concentrations
The analysis of the laboratory PAM push-pull tests indicated that analyzing the push-pull test results using actual measured radon concentration, instead of normalized concentrations, provides a more sensitive means of evaluating responses. Results from the PAM tests along with a modeling analysis are shown in Figure 4.13 and 4.15. The results show both the increase in retardation and a decrease in radon concentration that resulted from the presence of NAPL.

For conditions of generalized push-pull tests, model simulations were performed over a range of saturations using the STOMP numerical code. A complete description of these simulations is provided by Davis et al. (2005). Shown in Figure 4.13 are results of simulations where PCE or TCE NAPL is uniformly distributed in an aquifer with different degrees of saturation. The simulations were performed to illustrate expected behavior and representative breakthrough curves of radon response that might be used in analyzing the results form the Dover Tests.

To investigate radon breakthrough responses during the extraction phase of the push-pull tests, a set of six simulations was performed for a homogeneous NAPL distribution. Each simulation utilized a single value of S_n for $r \leq 500$ cm (Figure 4.13), with each value of R corresponding to a value for S_n. The initial radon concentration was a function of S_n (equation 3.11, for example), and ranged from 200 pCi/L for the first simulation ($S_n = 0$ %, R = 1) to 23.6 pCi/L for the sixth simulation ($S_n = 15.25$ %, R = 10). As the extraction phase approaches $V_e/V_i = 2$, for homogeneous NAPL distributions, radon concentrations approach but do not exceed their initial value at the well. For the simulation where $S_n = 0$ %, radon concentrations reach 92.1 % of their initial value at the well. In contrast, for the simulation where $S_n = 15.25$ %, radon concentrations reach 86.3 % of their initial value at the well. This percentage decrease is due to retardation of the radon BTC as S_n increases (Schroth et al., 2000). Radon BTCs show the greatest sensitivity at small values of S_n, which is due to the non-linear relationship between S_n and the initial radon concentration (Figure 2.1).

Figures 4.12. Results of push-pull tests conducted in September 2002 in OSU-2 and OSU-3.



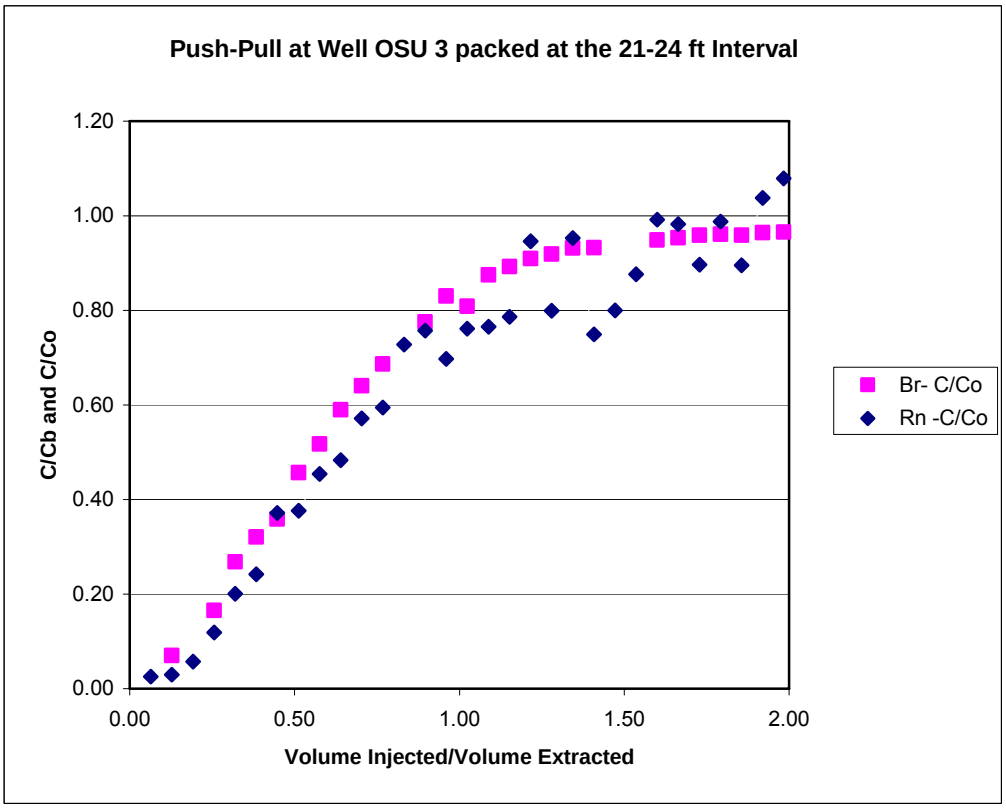


Figure 4.13 Simulated radon breakthrough curves during the extraction phases of six push-pull tests with homogeneous NAPL saturations (S_n = 0 to 15.25 % for r ≤ 500 cm).

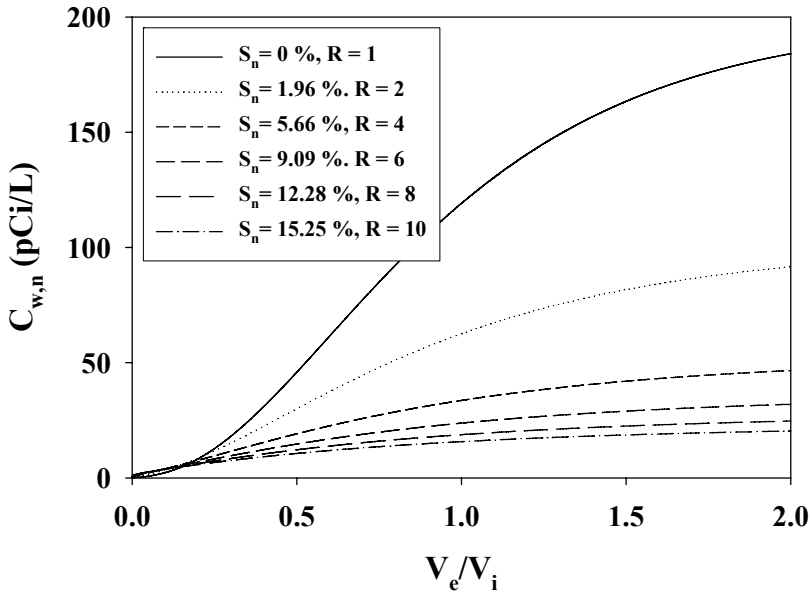


Figure 4.14 Simulated radon breakthrough curves during the extraction phases of six push-pull tests with heterogeneous NAPL saturations (S_n = 0 to 15.25 % for r ≤ 48 cm; S_n = 0 % for r > 48 cm).

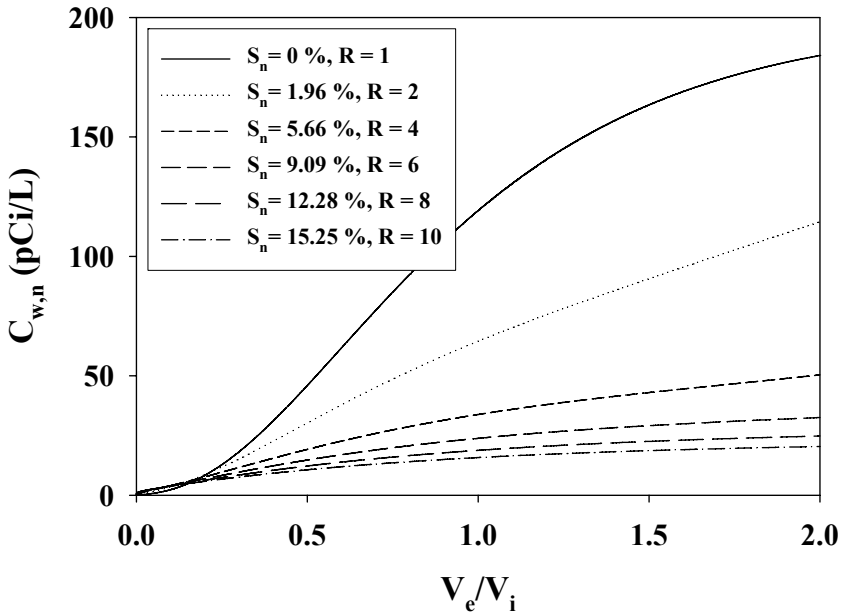
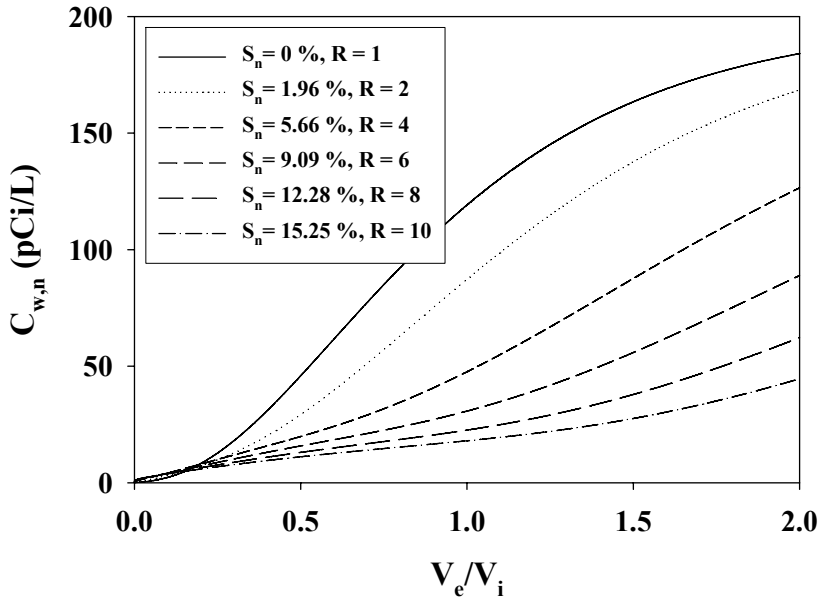


Figure 4.15 Simulated radon breakthrough curves during the extraction phases of six push-pull tests with heterogeneous NAPL saturations (S_n = 0 to 15.25 % for r ≤ 24 cm; S_n = 0 % for r > 24 cm).



A second set of six simulations was performed for a heterogeneous NAPL distribution with a homogeneous value of S_n for r ≤ 48 cm and S_n = 0 % for r > 48 cm (Figure 4.14). The initial radon concentration was a function of S_n (Equation 3.11), and for r ≤ 48 cm ranged from 200 pCi/L for the first simulation (S_n = 0 %, R = 1) to 23.6 pCi/L for the sixth simulation (S_n = 15.25 %, R = 10), while for r > 48 cm, the initial radon concentration = 200 pCi/L for each of the six simulations. As the extraction phase approaches V_e/V_i = 2, radon concentrations approach (and for S_n = 1.96 % exceed) their initial value at the well. For the simulation where S_n = 0 %, radon concentrations reach 92.1 % of their initial value at the well. These percentages vary as a function of S_n, reaching 112.3 % for S_n = 1.96 %, 95.1 % for S_n = 5.66 %, and 86.4 % for S_n = 15.25 %. The presence of S_n = 0 % for r > 48 cm produces greater radon concentrations for each simulation at V_e/V_i = 2 (Figure 4.14) as compared to when S_n is constant for r ≤ 500 cm (Figure 4.13). However, the shapes of the radon BTCs are similar at early times for the two sets of simulations (Figures 4.13 and 4.14), and again radon BTCs show the greatest sensitivity at small values of S_n.

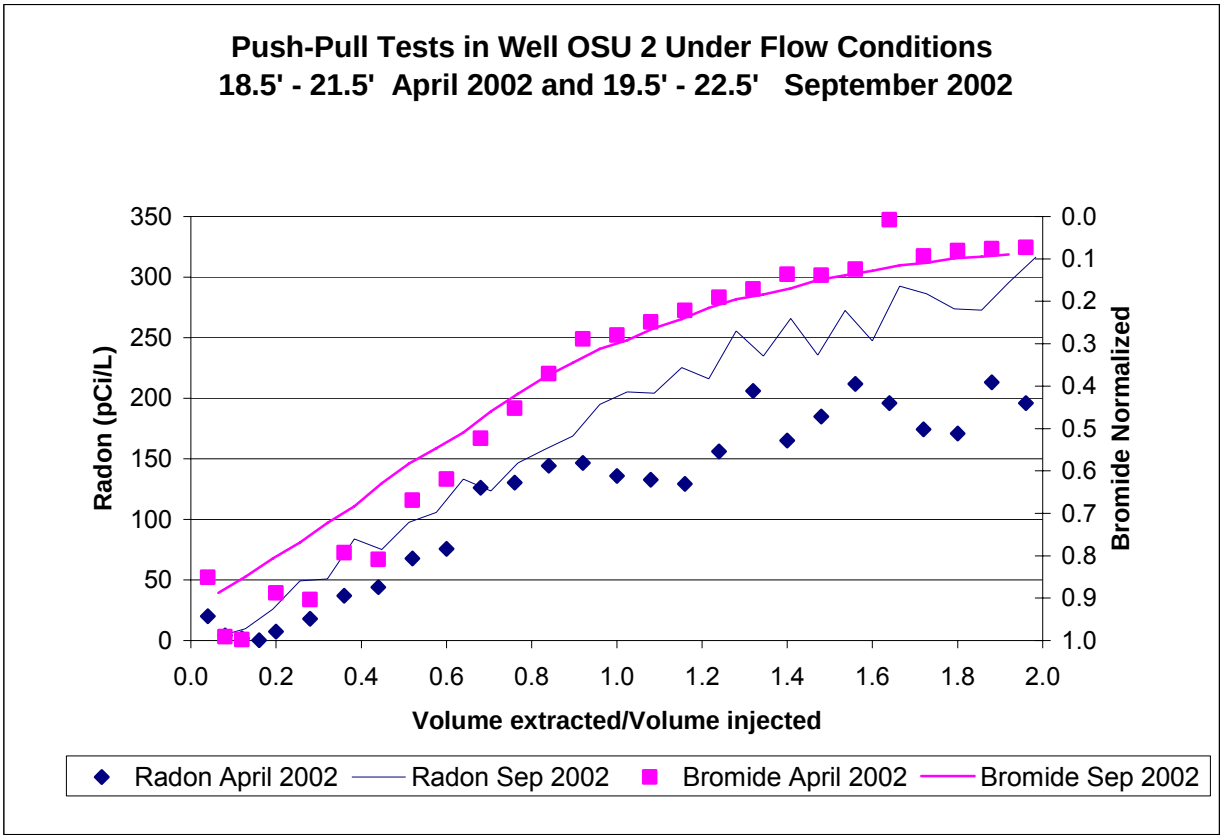
A third set of six simulations was performed for a heterogeneous NAPL distribution with a homogeneous value of S_n for r ≤ 24 cm and S_n = 0 % for r > 24 cm (Figure 4.15). The initial radon concentration was a function of S_n (Equation 3.11), and for r ≤ 24 cm ranged from 200 pCi/L for the first simulation (S_n = 0 %, R = 1) to 23.6 pCi/L for the sixth simulation (S_n = 15.25 %, R = 10), while for r > 24 cm, the initial radon concentration = 200 pCi/L for each of the six simulations. As the extraction phase approaches V_e/V_i = 2, radon concentrations approach and exceed their initial value at the well to a greater degree than when NAPL extends to 48 cm. These percentages vary as a function of S_n, reaching 165.2 % of the initial value at the well for

S_n = 1.96 %, 238.7 % for S_n = 5.66 %, and 188.9 % for S_n = 15.25 %. The presence of S_n = 0 % for r > 24 cm produces greater radon concentrations for each simulation at V_e/V_i = 2 (Figure 4.15) as compared to when S_n > 0 % for r ≤ 48 cm (Figure 14) or when S_n is constant for r ≤ 500 cm (Figure 4.13). Radon concentrations would continue to increase beyond the initial radon concentration for S_n > 0 % if V_e/V_i progressed beyond 2, as shown in the radon concentration profiles for S_n = 4 % for r ≤ 24 cm and S_n = 0 % for r > 24 cm (Figure 4.15). The influence of S_n = 0 % at r > 24 cm results in greater slopes for radon BTCs compared to the previous simulations (Figures 4.13 and 4.14). These results show that the shape of the radon BTCs and a comparison of initial radon concentrations at the well vs. late time concentrations could potentially be used to investigate heterogeneity in NAPL distribution. It also shows the difficulty in predicted saturations from the field responses in the field when heterogeneous NAPL distributions likely exist.

Shown in Figure 4.16 are the combined results of the April and September 2002 tests for well OSU-2 plotted in a form similar to the modeling analysis shown in Figures 4.13-4.15. The bromide tracer tests results show very reproducible normalized bromide concentration curves. The results indicate fairly reproducible transport conditions in the two tests. Radon was more retarded and the maximum concentrations are lower in the April tests. Radon transport in the latter tests is behaving more like bromide, although there still may be some retardation. The response of radon indicate that NAPL saturation decreased from April to September as a result of the initiation of flow conditions. The shape of the response curves are similar to those of the numerical simulations shown in Figure 4.13. The results would indicate that the NAPL saturation in April was in the range of 2%, if homogeneous NAPL saturations existed.

The push-pull test results for OSU-3 are shown in Figure 4.17. The results are similar to those observed in the OSU-2 well. Bromide concentration breakthrough curves are very reproducible between the tests and show similar transport conditions during the tests. The radon response is shown to be more retarded in the April test, and the maximum concentration achieved was also lower. Radon concentration increases are less retarded in the September test. Like the OSU-2 well tests, the tests in OSU-3 are similar in shape to the simulated responses shown in Figure 4.13. The result indicates a NAPL saturation of around 2%, if a uniform distribution of NAPL existed, as was used in the simulations shown in Figure 4.13.

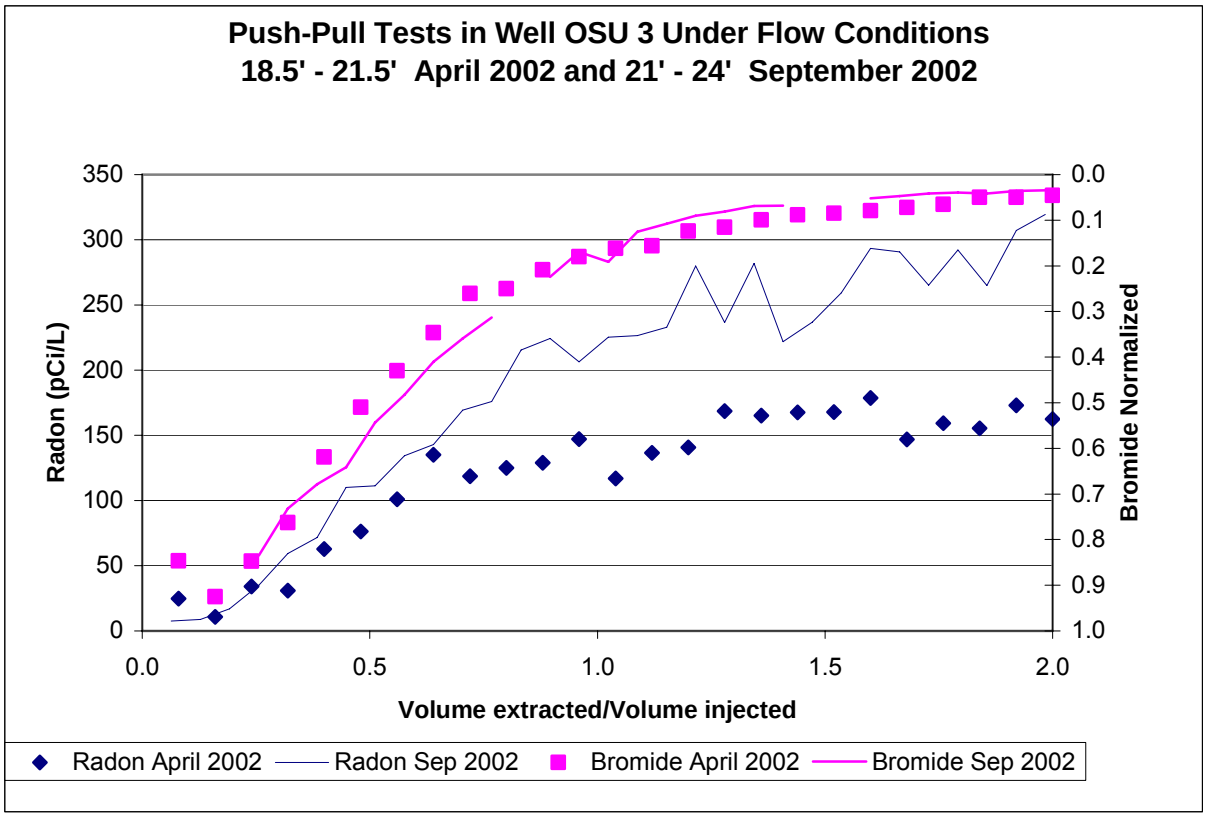
Figure 4.16. Comparison of push-pull tests conducted in April 2002 and September 2002 in well OSU-2.



The results from the April and September tests appear to provide stronger evidence that NAPL presence decreased with continuous groundwater flow through the test cell over a six-month period. The method of plotting actual radon concentrations, presented in Figure 4.16 and 4.17, compared to normalized concentrations, appears to be a more sensitive means of analyzing the results.

The amount of groundwater that was flushed through the test cell was likely not enough to dissolve the emplaced NAPL. A more likely scenario is that the NAPL became mobilized with the initiation of flow in the test cell.

Figure 4.17. Comparison of push-pull tests conducted in the OSU-3 well in April 2002 and September 2002.



Estimates of changes in NAPL saturations

Based on the April and September push-pull tests, estimates of the changes in NAPL saturation can be made. Equation 2.1 can be used to determine changes in saturation that results from changes in radon concentration. Equation 2.1 can be rearranged to yield equation 4.3.

$$\nabla S_n = \left(\frac{C_{w,1}}{C_{w,2}} - 1 \right) \left(\frac{1}{(K_{PCE} - 1)} \right) \qquad 4.3$$

Where $C_{w,1}$ and $C_{w,2}$ are the groundwater radon concentrations at two different samplings, and a K_{PCE} of 48 was used, as measured by Davis (2003). For these estimates we will use the observed radon concentrations after 2 pore volumes of fluid are extracted.

Table 4.9. Estimated changes in saturations based on radon test results.

	April Rn (pCi/L) *	Sept. Rn (pCi/L)	change in S_n
OSU-2	200	300	-0.007
OSU-3	150	300	- 0.020

* concentrations at the end of the tests were used for the estimates.

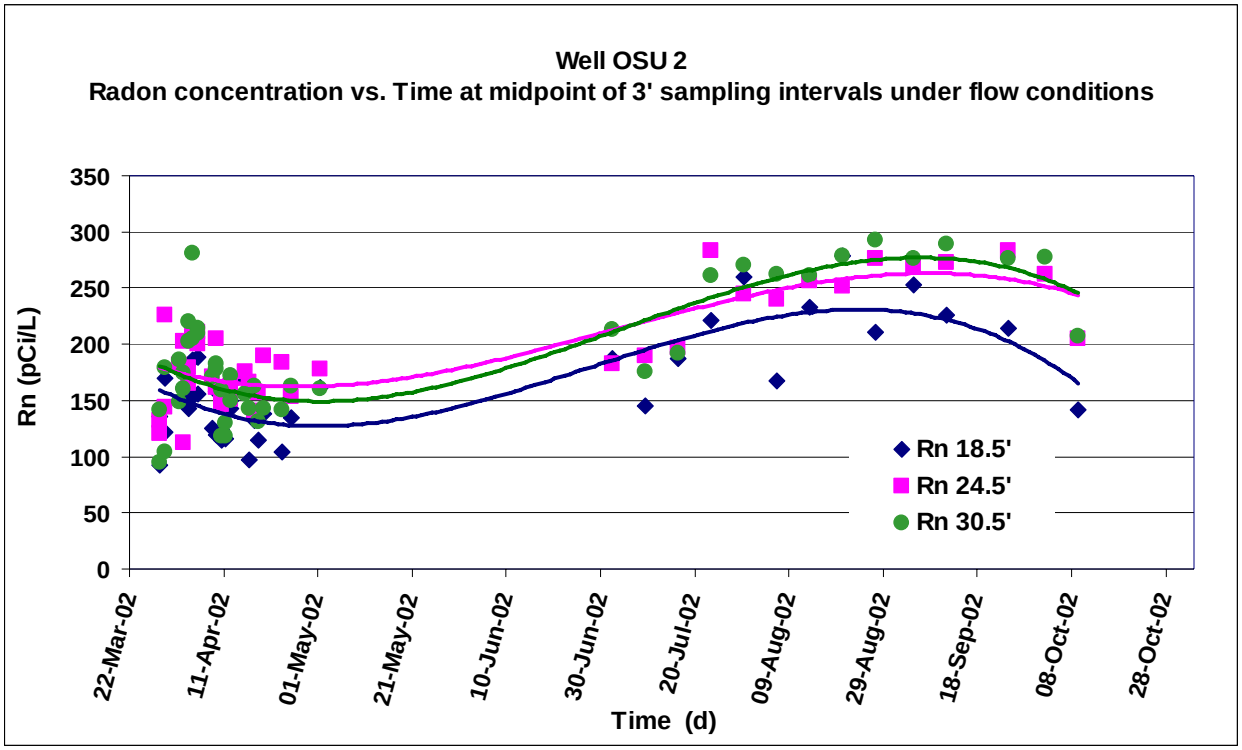
The results of the analysis are provided in Table 4.9 Based on the increases in radon concentration, a decrease in saturation of about 0.007 (0.7%) and 0.02 (2%) was predicted. The results are consistent with decreases in retardation, shown in Figures 4.16 and 4.17, and the results of model simulations shown in Figure 4.12.

Static Tests Results

Long-term monitoring of radon concentrations in groundwater samples from OSU-2 and OSU-3 were performed using two multi-level samplers. These multi-level samplers were capable of sampling three different depth intervals: 17-20, 23-26, and 29-32 ft below grade. Each depth interval was bounded by non-inflatable packers in order to create a barrier to flow contribution from other depth intervals. These two wells are parallel with the flow direction in the test cell, with well OSU-2 located upgradient from well OSU-3. Samples in 40-ml VOA vials using procedures previously described were obtained weekly by the staff of the DNTS and shipped overnight to OSU for radon analysis.

Results from the surveys at OSU-2 from March 2002 through September 2002 are shown in Figure 4.18. The results represent conditions afte/r flow was initiated in the test cell. Increases in radon concentration were observed at all locations, based on the mean and standard deviations determined for data collected in the spring grouped as one set and the summer fall as another set. No data were collected May through June, since the packer system failed as a result of PCE dissolving some of the packer's plastic fittings. A new packer system was installed at the same depth intervals for the later monitoring. The greatest increases were observed at the 24.5-ft and the 30.5-ft depth intervals. The statistical analyses of these results are presented in Table 4.10, and indicate significant differences in the mean values. Whether the changing of the packer system was responsible for some of the change in radon concentrations is not known.

Figure 4.18. Groundwater radon concentrations in OSU-2 at three depth intervals from weekly monitoring events. The solid curves are a 3 point polynomial fit to the data.



Results from the surveys at OSU-3 from March through September 2002 are shown in Figure 4.19. Increases in radon concentrations were observed at all three depth intervals. Again most of the increases occurred between July and September. The greatest increases again occurred at the 24.5-ft and the 30.5 ft depth intervals.

A summary of the results of the surveys in OSU-2 and OSU-3 over this period are presented in Tables 4.10 and 4.11. Statistically significant increases in radon concentration were observed at all locations during the surveys. The greatest percentage increase from 125 to 237 pCi/L was observed at the 24.5-ft level in well OSU-3. Estimates of the change in NAPL saturation were performed using Equation 4.3. Decreases in NAPL saturation were estimated to range from 0.65% at 24.5-ft interval of well OSU-2 to 1.00% at the 24.5-ft level at OSU-3. These changes in saturation are consistent with the estimates for well OSU-3 and OSU-2 based on push-pull test results (Figures 4.16 and 4.17), and surveys conducted at the times of the push-pull tests (Table 4.9).

Figure 4.19 Groundwater radon concentrations in OSU-2 at three depth intervals from weekly monitoring events. The solid curves represent a 3 point polynomial fit to the data.

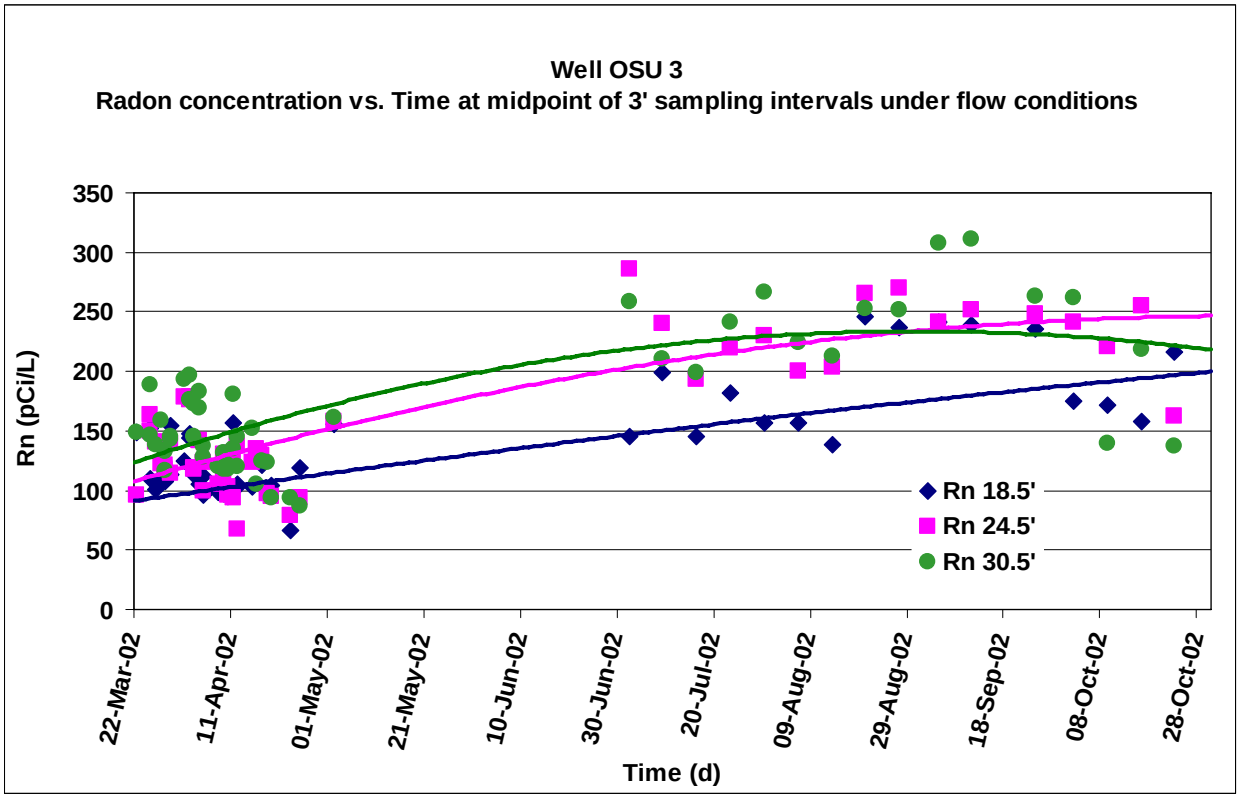


Table 4.10. Summary of the radon survey in Well OSU-2 and estimated changes in saturation based on equation 4.3.

Well OSU 2	18.5'	24.5'	30.5'
Spring 2002 Mean	142.8	170.2	164.5
Standard Deviation	26.0	27.5	38
Summer/Fall 2002 Mean	215.5	245.6	254
Standard Deviation	38.9	36.7	38.6
Calculated Student's t value	7.12	7.34	6.91
99 % t value	2.7	2.7	2.7
Change in PCE Saturation	-0.71%	-0.65%	-0.74%

Table 4.11. Summary of the radon survey in Well OSU-3 and estimated changes in saturation based on equation 4.3.

Well OSU 3	18.5'	24.5'	30.5'
Spring 2002 Mean	115.9	124.7	142.8
Standard Deviation	21.0	27.8	29.6
Summer/Fall 2002 Mean	193.4	237.4	249.9
Standard Deviation	44.0	29.1	35.6
Calculated Student's t value	8.16	12.04	10.33
99 % t value	2.69	2.69	2.69
Change in PCE Saturation	-0.85%	-1.00%	-0.90%

Monitoring of OSU-2 and OSU-3 continued until May 2004 at the three different depth levels. This time period coincided with the biological remediation through the addition of lactate as a substrate (ESTCP Project –CU-0116 Remediation of Dense Non-Aqueous Phase Liquids through Sequential In-Situ Chemical Oxidation and Bioaugmentation)**.** Results of the continuous monitoring are shown in Figure 4.20 and 4.21. Anaerobic conditions were observed as indicated by the presence of iron in groundwater samples. Reductive dechlorination of PCE to TCE, Cis-DCE, VC, and ethylene were observed on samples taken after August 2003 (data not shown). PCE aqueous concentrations ranged from 10 mg/L to 30 mg/L, which is substantially lower than the PCE solubility limit values of 150 mg/L.

Results from long-term monitoring of radon concentrations showed an increase in radon concentrations over time from March 2002 to May 2004 (Figures 4.20 and 4.21). With the beginning of remediation activities (lactate addition) radon concentrations decreased as PCE concentrations decreased. PCE concentration likely decreased due to reductive dechlorination of aqueous PCE (Figure 4.22). Radon concentration decreased or remained the same at all sampled depths in both wells (Figures 4.18, 4.19, 4.20 and 4.21). These results are contrary to the expected increase in radon concentrations if PCE NAPL saturations decreased.

The dramatic decreases in radon are shown in well OSU-3 from March 2003 to July 2003 (Figure 4.21). The decrease was observed when discoloration of the groundwater sample occurred as a result of iron being present. We realized that the presence of iron was likely interfering with the radon scintillation counting method, resulting in low radon concentration measurements. We therefore developed a method to remove the color. The groundwater samples in the VOA bottles were treated with hydrogen peroxide to oxidize ferrous iron (Fe^{++}) to ferric iron (Fe^{+++}). This resulted in an iron hydroxide flock being formed. The flock was allowed to settle, and the groundwater was filtered through a 2 micron inline filter that was attached to the tip of the syringe. The filtered groundwater sample was added to the scintillation cocktail, and

radon was measured as previously described. The treatment process removed the color in the sample and eliminated the interference in scintillation counting.

The new method of pre-treating the groundwater sample was initiated in mid-July 2003. An immediate increase in radon concentration was observed compared with levels measured prior to March 2003. The results illustrate the care that must be taken in measuring radon concentrations using the scintillation method.

The results of the prolonged monitoring indicated that little change in radon occurred despite the application of the bioremediation process. This is in agreement with the PCE concentration, which was always below its solubility limit (Figure 4.18). Some decrease in PCE concentration occurred as a result of the remediation process. For example, at OSU- 2 at the 24.5-ft level, the radon concentrations remained essentially constant, while PCE concentration decreased from about 20 mg/L to 10 mg/L. The results indicate that the residual saturation of PCE NAPL remaining in the test cell was low during the period of the test when anaerobic treatment was being applied. Radon concentrations remained essentially constant for a period of over a year after they had increased over a short period of time in August 2002.

The results indicate that the rapid increase in radon concentration observed around August 2002 may have been associated with the movement of NAPL in the test cell in response to the initiation of groundwater flow through the test cell. The radon results indicate that low residual saturations of PCE were likely present. This result is consistent with PCE monitoring results, which show PCE concentrations below the solubility limit that existed in the test cell.

Figure 4.20. Long term monitoring of radon in groundwater from OSU-2

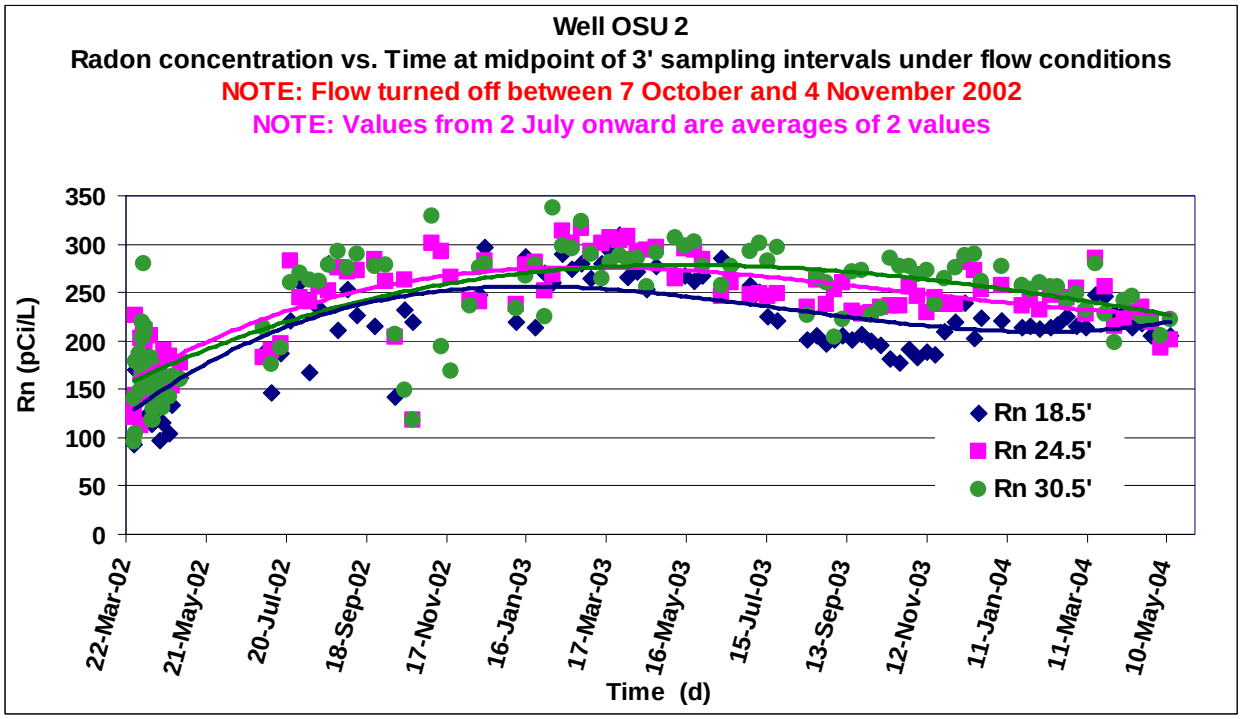


Figure 4.21. Long term monitoring of radon in groundwater from OSU-3

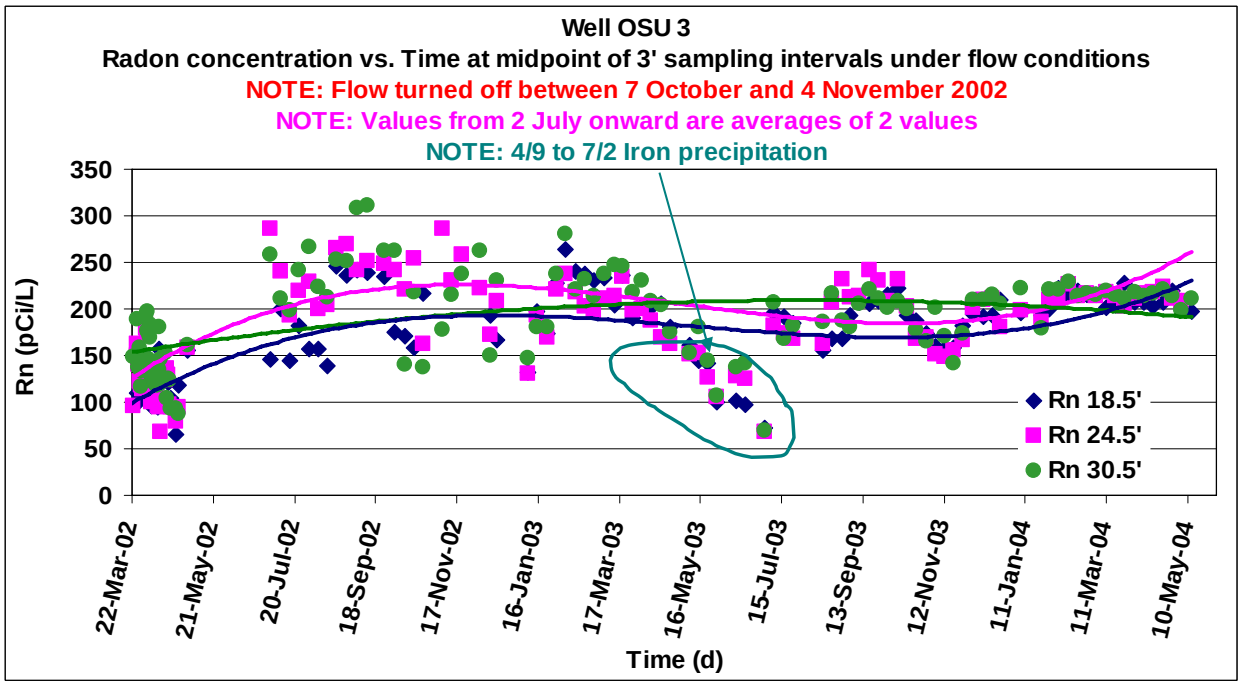
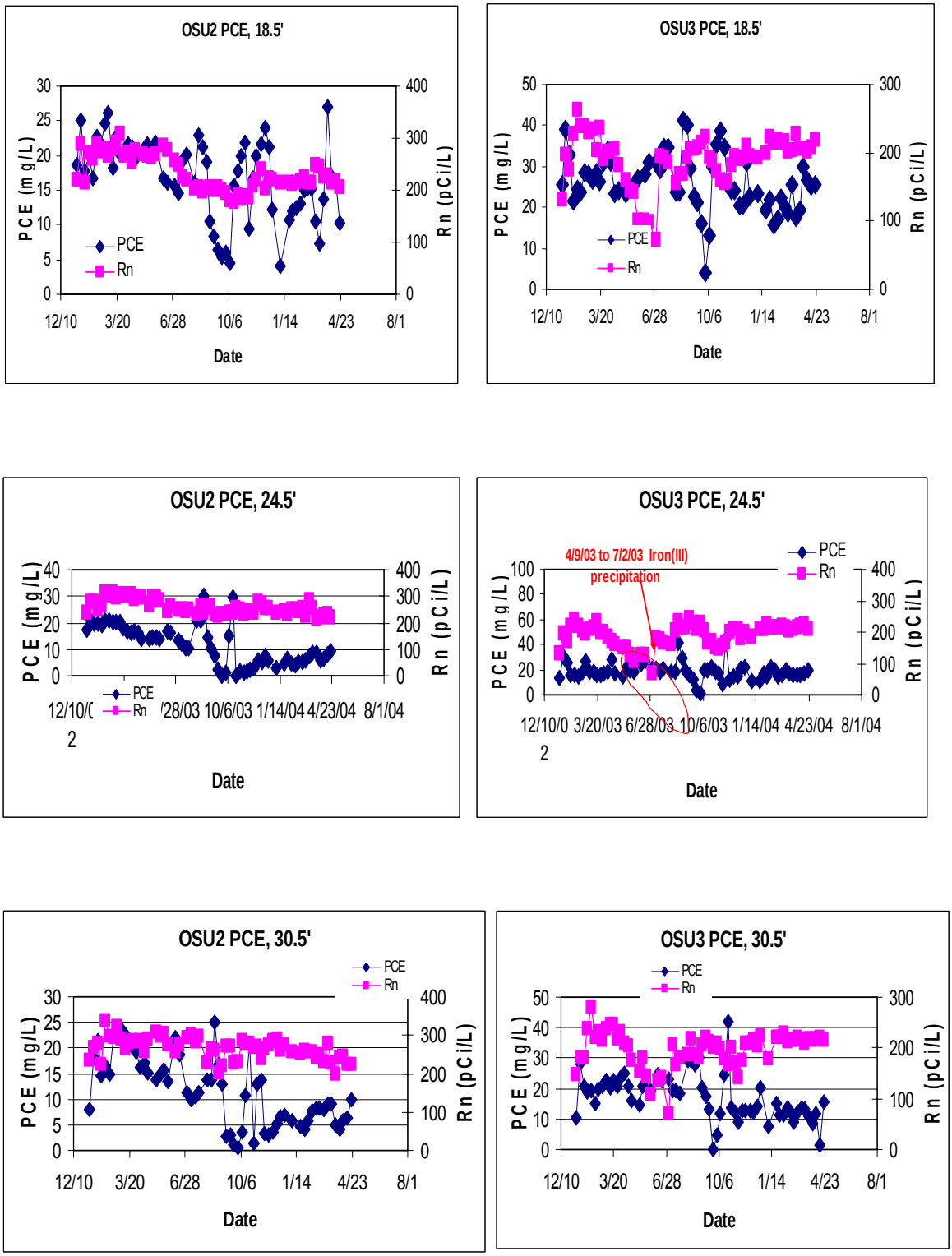


Figure 4.22. Radon concentration measurements and corresponding PCE concentrations at three different depth intervals in OSU-2 and OSU-3 from December 2002 though August 2004.



4.3. Summary of Results for the DNTS Study

The results from the Dover test cell illustrate some of the complications of using the radon method at the field scale for detecting and monitoring NAPL remediation. Variations in background radon concentrations were observed that must be considered in evaluating radon concentration distribution. These spatial variations in radon concentration could potentially mask the decreases in radon concentration that can result from the presence of NAPL.

Temporal changes in radon concentration at specific locations are a more effective means of using radon as a natural tracer and might be used as one measure of how NAPL remediation is progressing. In the Dover test cell, radon concentrations were measured before and after PCE was added as a DNAPL. In general Rn concentration decreased after PCE was added, but at several locations Rn concentration increased, which cannot be easily explained.

Push-pull tests proved difficult to interpret, and convincing evidence for retarded transport was obtained only in a few tests. Graphing the measured radon concentration instead of normalized concentrations provided for better means of interpreting test results. A series of push-pull tests, conducted after groundwater flow was initiated, showed an increase in background radon concentration and a decrease in retardation consistent with the response that is expected when NAPL saturations are decreasing.

The long term monitoring indicated that radon concentration increased at three different depth intervals in two wells that surrounded the area were NAPL was released. The increases occurred abruptly over a period of about of about two months, after groundwater flow was initiated in the test cell. The results indicate the NAPL PCE may have moved during this time period.

The results from spatial radon monitoring and push-pull tests indicate the NAPL saturation was low in the test cell, in the range of 2% or less. This low amount of saturation appears to be near the detection limit of the radon method. Thus it is difficult to draw strong conclusions from the different radon tests that were performed. Studies should be repeated in a field setting were higher NAPL saturations are present.

The sensitivity of the radon method strongly depends on the partition coefficient for partitioning of radon into the NAPL phase. As shown in Figure 2.1, for a partition coefficient for TCE and PCE in the range of 50, a 1% NAPL saturation would decrease radon concentrations by about 30% from background levels. To increase the sensitivity we need to verify such changes on radon concentration have occurred. This might be accomplished by processing larger size groundwater to establish higher counting rates and to make measurements in triplicate, and use mean values of triplicate measurements. However, obtaining a larger sample may be a drawback because at many locations acquiring large volumes of groundwater may be difficult. Also the processing of the larger sample volumes for radon analysis would require a non-standard analytical method.

Obtaining groundwater samples over more discrete depth intervals would help prevent the mixing of groundwater for zones with no NAPL that can have high radon concentration, with those from NAPL zones that are depleted in radon concentrations.

4.4 Data Assessment

The data collected under controlled laboratory conditions in the PAMs showed increased retardation of radon in push-pull tests conducted with TCE NAPL of around 2%. Numerical model simulations were in agreement with results from the PAM tests (Figures 4.3 and 4.4).

Results from the DNTS test cell were much more difficult to interpret. Spatial variations in radon concentration were observed in the absence of the NAPL release as a result of geologic variations. The results for the spatial survey are consistent with measured variations for radon emanation of core materials obtained from the test cell.

Temporal changes in radon concentration at specific depth interval after radon was added to the test cell were observed, as well as both increases and decreases in radon concentration (Table 4.7). While decreases in radon concentration are expected due to partitioning into the NAPL, increases are more difficult to explain. Radon is volatile and can be lost during sampling. It is possible that in early tests low radon concentrations were measured due to losses during sampling. Concentration then increased in later tests. It is also possible that the packer isolating the depth interval was not working correctly and the groundwater that was sampled came from different depths. Radon concentrations did vary with depth (Table 3.2), thus the mixing groundwater from different depths could have caused changes in concentration. It is also possible that the interval of pumping could cause some change in radon concentration, if geologic properties vary spatially within a given depth interval. The results demonstrate the care that must be taken when sampling for radon: keep variables constant, such as pumping rate, depth interval and time of sampling.

The temporal monitoring at specific locations was the simplest method to apply and gave as much information as the more complicated push-pull tests. Radon concentration increased as remediation proceeded, which was consistent with the expected response. Comparison of average values computed over a specific time interval, and using a t-statistical test, indicates significant changes occurred. The changes in radon concentration indicated that NAPL saturations were low in the test cell in the range of 2% or less. This level of saturation appears to be in the range of the detection limit of the method.

4.5. Technology Comparison

There are numerous approaches to use for NAPL source zone assessments, and comparisons to the different technologies are beyond the scope of this work. The National Research Council study of "Contaminants in the Subsurface: Source Zone Assessment and Remediation" (2004) provides a review of different technologies that are employed for source zone assessment. Over sixteen assessment methods are listed and discussed. Kram et al. (2001; 2002) compare about eighteen different technologies, with the radon method being one of the technologies evaluated. The radon method differs significantly from all the methods discussed, since it is a natural tracer

method. The most closely related test was a partitioning tracer test, where a tracer or suit of tracers is added to the subsurface and their transport breakthrough is monitored in monitoring wells. The most common form of the test is the partitioning interwell tracer test (PITT) for estimating the mass and distribution of DNAPL over volumes larger than achieved by soil sampling. The NCR reports that this method has been applied to over 50 sites with good success.

The PITT method involves the use of, for example, hydrophobic chemicals, such as higher-weight alcohols as partitioning tracers, and is injected through the contaminated zone along with a conservative tracer. Partitioning tracer transport is retarded compared to the conservative tracer, and the degree of retardation can be used to determine NAPL saturation. Kram et al. (2002) rated the PITT test as the most expensive test to perform, followed by the radon test method. Part of the higher costs for these tests was associated with the installation of wells needed to conduct the tests. The costs estimates also included using other screening methods for NAPL contamination prior to conducting the radon tests.

The radon method, being a natural tracer, is shown to have some advantages over the PITT method, and thus addition is not required. This results in a lower cost, especially when the static monitoring method is being applied. The radon method, however, is limited to a single partition coefficient, and is more subject to dilution effects. Due to the half-life of radon of 3.83 days, sampling wells must be very close to the area of NAPL contamination. Provided below (Table 4.12) is a comparison of the PITT tests and the radon test method.

Table 4.12. Comparison PITT versus Radon Method Test (+ less of an advantage; +++ more of an advantage)

PITT	Rank	Radon Method	Rank
Injection of an partitioning tracer required	+	Injection of partitioning tracer not required	+++
Interwell tests can be performed	+++	Interwell test can be performed but residence time of < 2 days	+
Push-pull tests can be performed	+++	Push-pull tests can be performed	+++
Several tracers can be added with different partition coefficients	+++	Radon has a fixed partition coefficient	+
Mass transfer issues must be resolved	+	Mass transfer less of an issue with radon partitioned into the NAPL	+++
Dilution effects less of a problem	+++	Dilution effects more of a problem	+
Aquifer heterogeneities less of an issue	+++	Aquifer heterogeneities more of an issue	+
Samples a larger volume of aquifer	+++	Samples a smaller volume of aquifer	+
Temporal monitoring of the tracer required	+	Continuous monitoring of radon not required	+++
Higher cost	+	Lower cost	++
Usually conducted at a single location	+	Can be conducted at multiple locations	++
More amendable to modeling	++	Less amenable to modeling	+

5. Cost Assessment

Implementation costs for the test at DNTS are shown in Table 5.1. The total cost was $237,300, with the fixed cost ($50,000) representing 21% of the total cost, while the variable costs ($187,300) representing 79%. 40% of the fixed costs were associated with mobilization and demobilization, 24% for planning and preparation, and start-up and equipment costs were 36%. For the variable costs the labor for conducting the field tests represented 11%, travel 6%, rentals and consumables 3%, analytical 66%, and data analysis and report writing 14%. A major cost was the analytical costs, which represented about 52% of the total cost. The analytical costs and the number of samples are provided in the footnote. Groundwater radon analysis costs were based on several vendor price quotes found in a Web search. Costs for PCE and bromide analysis were based on a price quote from a local analytical laboratory for single compound analysis for these compounds. The costs are based on the long term monitoring that included the push-pull test analysis.

Several scenarios have been determined for using commercial vendor cost analysis. These are presented in Table 5.2, 5.3, and 5.4. The cost analysis presented in Table 5.2 is based on a site where quarterly monitoring analysis is performed over a three-year period where twelve locations are selected for long-term radon monitoring. The case represents the monitoring of a NAPL remediation project. Triplicate samples are analyzed for radon analysis and singlet samples for CAH analysis. For these long-term monitoring tests the estimated total cost is $113,800, or 100% lower than OSU costs. The fixed cost ($41,500) represents 37% of the total cost, while the variable costs ($71,780) represent 63%. A significant reduction in cost was achieved by eliminating the push-pull tests, and monitoring on a quarterly basis. The fixed costs are reduced from $50,000 (OSU) to $41,500 (vendor). In addition, equipment costs such as peristaltic pumps, packers, and carboys are around $10,000. The fixed costs of mobilization and demobilization as well as planning and preparation result in the only 20% reduction in Capital Costs of the vendor estimates compared to the OSU study. A large difference in the costs between the OSU and the vendor is a reduction in analytical costs with the elimination of the push-pull tests, as well as performing quarterly monitoring, which was much less frequent than the weekly OSU sampling. Triplicate quarterly radon samples were replaced by singlet weekly samples in the OSU study. The analytical costs in Table 5.2 represent 30% of the variable compared to 66% for the case presented in Table 5.1

Table 5.3 presents an analysis for a smaller site compared to that given in Table 5.2, but having the same quarterly monitoring program. For this site the sampling locations have been reduced to six, compared to 12 location presented in Table 5.2. The total cost was reduced to $80,610 compared to $113,280, or about a 30% reduction. Thus a 50% reduction in the sample locations results in only a 30% reduction in costs because of only a 15% reduction in the Capital Costs. The main saving of about 37% results from lower testing and analytical costs. The fixed cost ($35,750) represents 44% of the total cost, while the variable costs ($44,860) represent 54%. The analysis indicates that as the number of monitoring locations is reduced the fixed cost percent of the total cost increases.

Table 5.4 presents the same quarterly scenario as presented in Table 5.2, but included now are yearly push-pull tests at each of the12 test locations, so the cost of conducting 36 push-pull tests are now included. The approach here would be to perform push-pull tests at the beginning, during, and at the end of a NAPL remediation project. This scenario would provide the additional information for estimating the change in saturation using the change in retardation factors as remediation proceeds. The addition of the push-pull tests added about 600 radon and

600 bromide samples to be analyzed, which include about 12 samples per test, and including some duplicates and background samples. In order to include the push-pull tests along with the quarterly monitoring, the total cost would increase from $113,280 (Table 5.2) to 171,210 (Table 5.4) per site. The main increase would occur in the testing and analytical, from $71,780 to $128,208. The cost analysis is based on reducing the number of samples taking during a push-pull from 25 used on the OSU tests to 12 in the vendor tests. We believed that precise breakthrough curves can be obtained with 12 samples. The cost analysis also assumed that the push-pull tests would be conducted during site trips for quarterly monitoring. The duration of the trips would be extended to permit the push-pull tests to be performed. For this case the direct costs were 25% of the total cost, again showing the trend that as the total cost increases, the variable cost become a great percentage of the total costs.

In all the cases, mobilization and demobilization, site planning and preparation are fixed costs that do not change much from case to case. These costs may be reduced once a vendor has experience using the radon method at a number of different sites. Other fixed costs include equipment costs. Savings could be realized in equipment costs by using the same equipment at several sites with only the cost for maintenance. Purchase of equipment requires a large initial investment, but long-term savings are realized over time as the equipment is used at all of the sites. The major variable costs include labor of the technician doing the sampling, travel cost, the analytical costs for radon, CAH, and bromide analysis, and for data analysis and reporting. Analytical costs tend to increase directly with the number of samples analyzed. Travel costs, especially for the distance sites, were significant (about 10% of the variable costs), assuming the technician needs to travel out of state, e.g. to the DNTS site, or if equipment has to be hauled back and forth if no storage is established at the site, e.g. at the Fort Lewis site, which is closer to OSU and where we have done field work for much lower cost. Costs could also reduced in practice if local on-site personnel are used and if travel and shipping costs can be reduced. The labor costs and analytical costs will scale with the number of observation locations for the monitoring approach and the number of push-pull tests performed. Data analysis costs and report preparation costs may be reduced once a vendor has experience analyzing the data and developing reports on the findings.

Estimation of cost saving to DoD using the radon method of DNAPL detection is difficult to determine based on the many different potential characterization methods available, the type of applications it is used for, and specifics of the individual sites. Kram et al. (2002) did an independent cost evaluation of nine different methods used to detect and delineate DNAPL, including the radon method. Their estimates for using the radon method, although based on different assumptions than ours, were similar to ours and ranged from $70,870 to $104,425 per site. Their baseline approach, which required collecting core samples through drilling and chemical analysis, ranged from $46,160 to $59,440 per site. In order for fair comparisons for the different methods, they assumed that the sites being investigated had no wells for sampling, and thus if a characterization method needed wells, as the radon method does, the cost well installation was included in the estimates. Thus, if appropriate wells for sampling already existed at a site the radon method costs would be lower.

Table 5.1 Implementation costs for the test at DNTS

Cost Category	Sub Category	Costs ($)
FIXED COSTS		
1. CAPITAL COSTS	Mobilization/demobilization	$10,000
	Planning/Preparation[a]	$10,000
	Site investigation and testing[b] - Field work preparation - Other	 $ 5,000 $ 2,000
	Equipment Cost - Peristaltic Pumps - Packer Systems	 $2,500 $3,000
	Start-up and Testing	$5,000
	Other - Carboys, Tubing - Chemicals, Gas supplies - Sampling vials, labels	 $4,500 $5,000 $3,000
Sub-Total $50,000		
VARIABLE COSTS		
2. TESTING, ANALYTICAL, AND REPORTING COSTS	Labor - Field personnel[c] - Travel[d] - Lodging[e]	 $ 20,000 $ 6,000 $ 5,000
	Materials and Consumables	$ 2,000
	Utilities and Fuel	$ 1,000
	Equipment Rentals - Trailer - Analytical tank rentals - Other rentals	 $1,500 $1,000 $500
	Performance Testing/Analysis - Radon analysis (IC)[f] - CAHs analyses (GC)[g] - Bromide[h] - Data analysis[i] - Report preparation[j] - Other	 $66,000 $37,500 $20,000 $15,500 $10,500
	Other direct costs	$800
Sub-Total: $187,300		
TOTAL COSTS: $237,300		
Unit Cost: $237,300/Site		

[a] Planning/Preparation: 118 hr @ $85/hr for Environmental Engineer;
[b] Field work preparation and Other 156 hr @ $45/hr for Technician
[c] Field personnel: Technician 444 hr @ $45/hr for Technician
[d] Travel: 10 trips @ 600/trip
[e] Lodging 10 trips @ 500/trip
[f] Cost of Radon Analysis $22/sample (3,000 samples analyzed in the study)
[g] Cost of CAH analysis $ 75/sample (500 samples analyzed during the study)
[h] Cost of Br analysis $35/sample (1000 samples analyzed in the study
[i] Data Analysis 176 hr @ $85/hr for Environmental Engineer
[j] Report preparation 124 @ $85/hr for Environmental Engineer

Table 5.2 Estimated Demonstration Costs by Commercial Vendor (Long-Term Quarterly Monitoring for Three Years at 12 Sample Locations at the Site)

Cost Category	Sub Category	DNTS Costs ($)
1. CAPITAL COSTS	Mobilization/demobilization	$10,000
	Planning/Preparation[a]	$10,000
	Site investigation and testing[b] - Field work preparation - Other	 $5,000 $2,000
	Equipment Cost Peristaltic Pumps Packer Systems	 $2,500 $3,000
	Start-up and Testing	$5,000
	Other - Carboys, Tubing - Chemicals, Gas supplies - Sampling vials, labels	 $2,500 $0,000 $1,500
Sub-Total $41,500		
2.TESTING, ANALYTICAL, AND REPORTING COSTS	Labor - Field personnel[c] - Travel[d] - Lodging[e]	 $17,280 $7,200 $6,000
	Materials and Consumables	$2,000
	Utilities and Fuel	$ 1,000
	Equipment Rentals - Trailer - Analytical tank rentals - Other rentals	 $ 0,00 $1,000 $500
	Performance Testing/Analysis - Radon analysis[f] - CAHs analyses[g] - Data analyses[h] - Report preparation[i] - Other	 $10,000 $11,400 $5,000 $ 7,500 $2,500
	Other direct costs	$400
Sub-Total: $71,780		
TOTAL COSTS: $113,280		
Unit Cost: $113,280/site		

[a] Planning/Preparation: 118 hr @ $85/hr for Environmental Engineer;
[b] Field work preparation and Other 156 hr @ $45/hr for Technician
[c] Field personnel: Technician 384 hr @ $45/hr for Technician
[d] Travel: 12 trips @ 600/trip
[e] Lodging 12 trips @ 500/trip
[f] Cost of Radon Analysis $22/sample (454 samples) (triplicate samples)
[g] Cost of CAH analysis $ 75/sample (152 samples) (single samples)
[h] Data Analysis 59 hr @ $85/hr for Environmental Engineer
[i] Report preparation 88 hr @ $85/hr for Environmental Engineer

Table 5.3 Estimated Demonstration Costs by Commercial Vendor Long-term Quarterly Monitoring for Three Years at 6 Locations at a Site

Cost Category	Sub Category	DNTS Costs ($)
1. CAPITAL COSTS	Mobilization/demobilization	$10,000
	Planning/Preparation[a]	$ 5,000
	Site investigation and testing[b] - Field work preparation - Other	 $5,000 $2,000
	Equipment Cost Peristaltic Pumps Packer Systems	 $2,500 $3,000
	Start-up and Testing	$5,000
	Other - Carboys, Tubing - Chemicals, Gas supplies - Sampling vials, labels	 $ 2,500 $ 0,000 $ 750
Sub-Total $35,750		
2. TESTING, ANALYTICAL, AND REPORTING COSTS	Labor - Field personnel[c] - Travel[d] - Lodging[e]	 $ 12,960 $ 7,200 $ 4,800
	Materials and Consumables	$1,000
	Utilities and Fuel	$ 500
	Equipment Rentals - Trailer - Analytical tank rentals - Other rentals	 $ 0,00 $1,000 $500
	Performance Testing/Analysis - Radon analysis[f] - CAHs analyses[g] - Data analyses[h] - Report preparation[i] - Other	 $ 5,000 $ 2,500 $ 2,500 $ 5,000 $ 1,500
	Other direct costs	$400
Sub-Total: $44,860		
TOTAL COSTS: $80,610		
Unit Cost: $80,610/site		

[a] Planning/Preparation: 118 hr @ $85/hr for Environmental Engineer;
[b] Field work preparation and Other 156 hr @ $45/hr for Technician
[c] Field personnel: Technician 178 hr @ $45/hr for Technician
[d] Travel: 7 trips @ 600/trip
[e] Lodging 7 trips @ 500/trip
[f] Cost of Radon Analysis $22/sample (227 samples)
[g] Cost of CAH analysis $ 75/sample (33 samples)
[h] Data Analysis 29 hr @ $85/hr for Environmental Engineer
[i] Report preparation 59 hr @ $85/hr for Environmental Engineer

Table 5.4 Estimated Demonstration Costs by Commercial Vendor
Long-Term Quarterly Monitoring for Three Years at 12 Sample Locations at a Site, Plus Yearly Push-pull Tests at Each Location

Cost Category	Sub Category	DNTS Costs ($)
1. CAPITAL COSTS	Mobilization/demobilization	$10,000
	Planning/Preparation[a]	$10,000
	Site investigation and testing[b] - Field work preparation - Other	 $5,000 $2,000
	Equipment Cost - Peristaltic Pumps - Packer Systems	 $2,500 $3,000
	Start-up and Testing	$5,000
	Other - Carboys, Tubing - Chemicals, Gas supplies - Sampling vials, labels	 $2,500 $1,500 $1,500
Sub-Total $43,000		
2. TESTING, ANALYTICAL, AND REPORTING COSTS	Labor - Field personnel[c] - Travel[d] - Lodging[e]	 $25,920 $7,200 $9,600
	Materials and Consumables	$4,000
	Utilities and Fuel	$ 2,000
	Equipment Rentals - Trailer - Analytical tank rentals - Other rentals	 $ 1,500 $1,000 $ 500
	Performance Testing/Analysis - Radon analysis[f] - CAHs analyses[g] - Br- analysis[h] Data analyses[i] - Report preparation[j] - Other	 $23,188 $11,400 $21,000 $ 9,000 $ 9,000 $2,500
	Other direct costs	$400
Sub-Total: $128,208		
TOTAL COSTS: $171,208		
Unit Cost: $171,208/site		

[a] Planning/Preparation: 118 hr @ $85/hr for Environmental Engineer;
[b] Field work preparation and Other 156 hr @ $45/hr for Technician
[c] Field personnel: Technician 576 hr @ $45/hr for Technician
[d] Travel: 12 trips @ 600/trip
[e] Lodging 12 trips @ 800/trip
[f] Cost of Radon Analysis $22/sample (1054 samples) (triplicate samples)
[g] Cost of CAH analysis $ 75/sample (152 samples) (single samples)
[h] Cost of Br analysis $35/sample (600 samples analyzed in the study)
[i] Data Analysis 106 hr @ $85/hr for Environmental Engineer
[j] Report preparation 106 hr @ $85/hr for Environmental Engineer

6. Implementation Issues

6.1 Cost Observations

Factors that affected project costs were performing the study at the DNTS sites. At DNTS the depth of groundwater in sampling wells was about 40 ft, which did not required special pumps; only peristaltic pumps were required to conduct the temporal sampling and the push-pull tests. Monitoring wells at DNTS were provided, as well as logistical support, including personnel of the sampling for the long-term monitoring.

A big factor driving costs was conducting the push-pull tests at the site. These tests drive personnel cost as well as analytical costs, and it is not clear whether the information they provide is worth the additional cost. Much lower costs would be achieved by applying the static radon method to monitor the progress of site remediation of NAPL contamination. Temporal monitoring on a monthly basis would also result in a significant reduction in the cost of applying the method. For example the cost analysis provided in Table 5.2, where push-pull tests were eliminated, show about a 60 % reduction compared to the OSU study that included push-pull tests. Not conducting the push-pull tests, however, would eliminate the information obtained on retardation. Thus an independent means of estimating saturation would be lost. Changes in radon concentration with time would be the only means of estimating changes in NAPL saturation. Temporal changes in radon concentration would be as sensitive as changes in retardation factors in estimating saturations. However users would need to determine the benefits versus costs of conducting push-pull tests to provide and an additional means for estimating saturation. Having two different radon methods to determine changes in NAPL saturation may in some cases be worth the additional costs.

Kram et al. (2002) estimated the cost of using the radon flux survey for a site using the radon method as described by Semprini et al. (1998). The survey involved methods such as the static radon sampling described here and not push-pull tests. The screening approach includes collecting multi-depth samples from 65 to 100 ft depth as five locations. Prior to radon sampling, a survey using the ribbon NAPL sampler FLUTe™ method was implemented during conventional drilling to help identify zones of NAPL contamination and to direct the radon survey. Confirmation included collection of analysis of six samples from two locations to a total depth of 75 ft. Five wells were needed to be installed for the analysis. The cost per site including reporting was 80 to 110 K using commercial vendors. This is in a similar range as the estimates for our study provided in Table 5.2.

The Kram et al. (2002) study also made estimates for the Partitioning Interwell Tracer Tests (PITT), and the cost ranged from $113,580 to $144,740, which are about 60% higher than the radon method. The higher cost of the PITT method results from the assumptions used in the analysis by Kram et al. (2002), which are summarized in Appendix I of their paper. The PITT method required more wells to be installed (8 versus 5 for the radon method). The PITT method also included costs for laboratory tests prior to the field tests in order to select the partitioning tracers to be used. The PITT tests also resulted in higher labor costs due to the need to conduct well-to-well transport tests, while the radon tests were based on surveys which are less labor intensive. The inclusion of the push-pull tests with the radon method would increase the costs and make the costs more comparable.

However, as indicated in Table 4.12, are some advantages to the PITT method over the radon method, and thus cost alone can not be the criteria for selecting one method over another. If the long-term monitoring approach using the radon method fit the needs for monitoring, then significant saving might be achieved compared to the PITT method.

6.2 Performance Observations

This study evaluated using radon to try to locate NAPL saturation, quantify the amount of NAPL saturation emplaced, and monitor the progress of NAPL remediation. The types of approaches evaluated included monitoring spatial and temporal radon concentrations in groundwater, as well as more dynamic single-well, "push-pull" tests. The method requires only simple components for groundwater sampling, such as pumps, to extract groundwater from the test wells, plastic tanks and carboys to hold prepared test solutions, and standard groundwater sampling equipment. Temporal monitoring at selected special locations was fairly straight forward to employ, while push-pull tests required more expertise and are more complicated to interpret.

In the laboratory PAM, push-pull tests demonstrated that retardation in radon was observed as a result of NAPL being present. Results of numerical simulations showed the response observed could be well simulated with a NAPL saturation of about 1.8 percent, which was in reasonable agreement with the amount emplaced in the PAM of 2%.

The tests conducted in the DNTS site were less conclusive. Natural spatial variations in radon concentrations in groundwater from the test cell were observed, with concentration ranging by about an order of magnitude. Thus using spatial concentration of radon alone to local NAPL contamination would prove to be problematic. Observing temporal changes in concentrations at specific sampling locations normalizes for spatial variations in radon concentration, as long as the radon source term in the aquifer material does not change over time. The temporal sampling indicates radon concentration increased at some locations and decreased at others after NAPL PCE was added to the test cell. Concentrations were expected to decrease or remain constant as a result of NAPL addition. More important are the observations of changes in radon concentration as a result of remediation activities. Radon concentrations increased after groundwater flow was initiated in the test cell. The monitoring of radon groundwater concentrations at three depth intervals in two wells indicated that abrupt increases in radon concentration were observed, which is more consistent with NAPL movement than slow dissolution as a result of the remediation process that was being applied.

Push-pull tests permitted investigation of the presence of NAPL at specific depth intervals of wells. The tests proved difficult to perform and interpret. When normalizing concentrations to background concentrations, it was difficult to determine what represented a true background level. Radon concentrations at the end of the test were available for use for normalization procedures. Unfortunately radon concentrations were usually not obtained at the depth level of the push-pull test prior to conducting the test. For push-pull tests conducted in April 2002 and September 2002, conditions of the tests were consistent enough for comparisons to be made among the tests. Groundwater flow was occurring in both tests, similar amount of fluid were injected and extracted, and the tests were performed at similar depth intervals. The analysis of the results from these tests, especially when the actual radon concentrations are compared, support decreases PCE NAPL saturations as remediation proceeded (Figures 4.16 and 4.17).

Unfortunately the remediation study was still ongoing when the radon project ended. Independent measurements of core samples could not be obtained, as it would have disrupted the remediation study. Thus mapping of the NAPL presence using an independent method was not possible.

6. 3 Scale-Up

The field tests were performed at the scale that they would be implemented in practice. Depth interval surveys over three-ft depth intervals seem reasonable for field scale tests. Push-pull tests could be easily modified to inject more groundwater, if probing larger radial distances was of interest. A limitation, however, is that the volume required increases with r^2, thus probing greater radial distances required large volumes of water to be injected. Costs might be reduced by making radon survey part of a standard monitoring program since sampling by standard methods for volatile organics is required. Kram et al. (2002) provide costs and sampling for Rn-flux estimates for applying the method at the field scale.

6.4. Lessons Learned

The long term monitoring approach and the depth interval surveys seem to provide as much, if not more, information than the push-pull tests. Obtaining more replicate samples throughout the course of the study would have been helpful as well as obtaining a complete history of PCE aqueous concentrations.

Methods to better determine if a packer was not working properly would have been useful. Several push-pull tests had low bromide recovery. Since, in the absence of NAPL, radon concentrations would be higher in the background groundwater, sampling of higher radon concentration water would dilute the signal of the reduced radon concentration as a result of NAPL being present. Thus a leaky packer would be problematic.

More efforts should have been put into determining background radon samples prior to conducting the push-pull tests. After the packer was set at the desired test interval a series of groundwater samples should have been collected for determining background radon concentrations. Basing background concentrations on the final samples collected in a push-pull tests assumed that background levels have been reached, which may not have been the case. Normalizing concentrations based these samples affects the normalized breakthrough curves.

Push-pull tests should be conducted at specific depth intervals and not over the complete screened intervals of the wells. The potential of dilution of the tests by groundwater of higher radon concentration is more likely when tests are conducted over complete intervals. Tests should also be repeated over the same depth intervals throughout the course of the study, once a depth likely containing NAPL has been identified. This would permit comparisons in changes over time at specific locations. More tests should have been repeated using the drive point sampler that was installed in the test cell, since the best bromide recovery was achieved in this well.

The aqueous phase concentrations of PCE or TCE, or other NAPLs of interest, should have been monitored at the depth interval for the complete temporal history of the test. This would have permitted comparisons between changes in radon concentration with changes in PCE

concentration. In the latter part of the test, when we began to monitor PCE the concentration, the major increases in radon concentration had already occurred.

The test cell at Dover had a limited amount of PCE added, about 100 liters. Calculation estimates indicate that this amount of PCE would contaminate a radial volume of about 0.8 m over the 10-meter saturated thickness of the aquifer, if a uniform NAPL saturation of 2% was achieved. The spacing between the OSU observation wells was 2 meters. These calculations indicate that the amount of PCE released was fairly limited, and the amounts of NAPL estimated from the radon method were in the range of those expected from this very simple calculation. However, we had no control over the amount of PCE to be added to the test cell. The saturation of PCE that results was near the detection limit of the radon method.

Care must be taken when using the radon scintillation method if samples are colored or other interferences are present. We found that the scintillation method gave too low of values when iron was present. Iron had to be removed from the sample for accurate radon concentration to be achieved.

The radon test method appears to be most appropriately used to monitor the remediation of NAPL contamination. It would likely be more successfully applied where gross NAPL contamination is present, and where a remediation method, such as six phase heating, is being employed that removed large amounts of the NAPL phase. It was our objective to perform such a study in subsequent tests of this technology. However funds to the project were terminated prior to those tests.

6. 5 End-User Issues

The method of measuring temporal changes in radon concentration over time appears to be the most straightforward application of this technology. Standard methods for groundwater sampling can to be applied for sampling VOAs in groundwater. Commercial laboratories for radon analysis actually use standard VOA bottles for customers to collect groundwater samples for analysis. Radon concentrations measurements can therefore be performed by standard commercial laboratories. As discussed above, care must be taken to ensure the interfering compounds, such as iron, is not present in the sample.

A standard approach would be to determine radon and dissolved phase of the chlorinated solvent concentrations over specific depth intervals in monitoring wells. A three-ft packed interval, as was used in this study, might be appropriate. Both sampling for radon and the dissolved of the chlorinated solvent would employ the same sampling methods. Decreases in the concentration of the chlorinated solvent and increases in radon would be expected if NAPL saturations were decreasing. The radon method is meant for use where gross contamination with chlorinated solvents is present. Concentration of the chlorinated solvent, for example, should be in the range of its solubility limit in water. If concentration of the chlorinated solvent is much lower that the solubility limit, then too much dilution of background groundwater is likely occurring to see a detectable reduction in radon concentration. For example, Figure 4.22 shows that radon concentrations remained fairly constant, while PCE concentration decreased from 25 to 10 mg/L. The results indicate that the radon method did not detect a decrease in NAPL saturation, if one was occurring.

The method also works best if the NAPL is immobile and is not present in groundwater samples. The presence of a NAPL phase would complicate the analysis since radon that partitions into the NAPL would be in the sample. Users may consider using passive samplers that would result in sampling of only the dissolved phase.

Spatial measurements of radon concentrations alone is not a good approach for using this method, due to likely heterogeneities in geology conditions that would cause radon concentration to vary. Monitoring temporal changes in concentration as remediation proceeds is a better use of the technology, since heterogeneities in geology would be less important.
Push-pull tests provide more detailed information than can be obtained from temporal sampling alone. If push-pull tests are employed, they should be performed over specific depth intervals and repeated at these depth intervals. Changes in breakthrough curves, such as those shown in Figure 4.16 and 4.17, would be most useful for interpretation. Care must be taken in injecting radon free groundwater, and test must be conducted over short time intervals so radon does not build up in the injected groundwater. Bromide was an effective non-partitioning tracer, and should be applied in the tests.

The radon method would be best employed while using other methods. For example, in the cost estimation calculations of Kram et al. (2002) they used the radon flux method in combination with the FLUTe™ ribbon sampling methods.

Based on the observations of our demonstration, estimation of changes in NAPL saturation of less that 1% would provide to be difficult using the radon method. Since the response is non-linear (see Figure 2.1) the method is more sensitive to changes in saturation a low level of saturation than (0 to 1%) than high levels (5% to 6%), for example. However, at very low levels of NAPL saturation (less than 0.5%), reliable detection of NAPL saturation and changes in NAPL saturation would not be achieved.

6.6 Approach and Regulatory Compliance and Acceptance

The demonstration, although showing some promise for using the radon method, was not conclusive enough for an end-user to seek regulatory compliance for it being a method to locate and quantify NAPL contamination. However, it is an easy method to implement and apply with other methods, such as monitoring the chlorinated solvents concentration in groundwater samples. The best use of the method would be as a monitoring method where changes in radon concentration in groundwater samples could be tracked over time as a means of monitoring the progress of remediation.

The radon method is a potentially useful tool to be employed for assessing the monitored natural attenuation (MNA) of chlorinated solvent DNAPL contamination. The monitoring-based radon method would require only obtaining temporal samples at specific locations, which fits well with protocols for MNA. Unlike partitioning tracers, tracers need not be added, thus disturbances to the MNA processes that might result from the injection of tracers would not occur using the radon method.

Future demonstrations should be directed to sites where gross NAPL contamination is present, and concentrations of the solvents at specific locations are near the solubility limit in water. The most appropriate application of the technology would be for sites where large amounts of NAPL are being removed.

7. References

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8. Points of Contact

Table 8.1. Points of Contact

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