AN ABSTRACT OF THE DISSERTATION OF

Brian M. Davis for the degree of Doctor of Philosophy in Civil Engineering presented on January 30, 2003. Title: Radon-222 as an In Situ Partitioning Tracer for Quantifying Nonaqueous Phase Liquid (NAPL) Saturations in the Subsurface.

Abstract approved:

Lewis Semprini

This study investigated the use of radon-222 as an in situ partitioning tracer for quantifying nonaqueous phase liquid (NAPL) saturations in the subsurface. Laboratory physical aquifer models (PAMs), field experiments, and numerical simulations were used to investigate radon partitioning in static (no-flow) experiments and in single-well, ‘push-pull’ tests conducted in non-contaminated and NAPL-contaminated aquifers. Laboratory push-pull tests in a wedge-shaped PAM and field push-pull tests in a NAPL-contaminated aquifer showed that radon was retarded in the presence of NAPL, with retardation manifested in increased dispersion of radon extraction phase breakthrough curves (BTCs). An approximate analytical solution to the governing transport equation and numerical simulations provided estimates of the radon retardation factor ($R$), which was used to calculate NAPL saturations ($S_n$).

Laboratory static and push-pull tests were conducted in a large-scale rectangular PAM before and after NAPL contamination, and after alcohol cosolvent flushing and pump-and-treat remediation. Radon concentrations in static tests were decreased due to partitioning after NAPL contamination and increased after
remediation. Push-pull tests showed increased radon retardation after NAPL contamination; radon retardation generally decreased after remediation. Numerical simulations modeling radon as an injected or ex situ partitioning tracer were used to estimate retardation factors and resulted in overestimations of the likely $S_n$ in the PAM. Radon partitioning was sensitive to changes in $S_n$ in both static and push-pull tests. However, the test results were sensitive to test location, sample size, test design, and heterogeneity in $S_n$ distribution.

Numerical simulations of hypothetical push-pull tests conducted in a NAPL-contaminated aquifer were used to investigate the influence of homogeneous and heterogeneous $S_n$ distributions and initial radon concentrations on radon BTCs and resulting $S_n$ calculations. Both of these factors were found to affect radon BTC behavior. A revised method of plotting and interpreting radon BTCs combined with numerical simulations modeling radon as an in situ partitioning tracer (incorporating initial radon concentrations into the model as a function of $S_n$) were used to re-analyze laboratory and field push-pull test BTCs. This method reduced the overestimation of calculated $S_n$ values from laboratory tests.
Radon-222 as an In Situ Partitioning Tracer for Quantifying Nonaqueous Phase Liquid (NAPL) Saturations in the Subsurface

By

Brian M. Davis

A DISSERTATION

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Oregon State University

in partial fulfillment of

the requirements for the

degree of

Doctor of Philosophy

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.
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Radon-222 as an In Situ Partitioning Tracer for Quantifying Nonaqueous Phase Liquid (NAPL) Saturations in the Subsurface

CHAPTER 1

INTRODUCTION

Organic compounds are common groundwater contaminants at hazardous waste sites. Some of these chemicals, including trichloroethene (TCE), are suspected human carcinogens (California EPA, 2000). Organic compounds with a relatively low solubility in water are referred to as nonaqueous phase liquids (NAPLs). NAPLs with a density greater than water are referred to as dense nonaqueous phase liquids (DNAPLs), while those with a density less than water are referred to as light or LNAPLs. When released to the environment, DNAPLs can migrate through the vadose zone and below the water table to form residual contamination (i.e., ganglia) in pores (Mercer and Cohen, 1990). Physical heterogeneities in the subsurface (e.g., changes in permeability with depth) may cause DNAPL to form layers or ‘pools’ (Schwille et al., 1988; Broholm et al., 1999). LNAPLs typically migrate through the vadose zone and form a pool on the water table, leaving residual contamination in the vadose zone and smear zone. NAPLs can become long-term sources of groundwater contamination as the NAPL slowly dissolves to the aqueous phase, producing a plume of aqueous phase contamination that extends away from the NAPL ‘source zone’. The effective characterization of NAPL-contaminated sites requires the location and
quantification of NAPL saturations in the subsurface. Furthermore, the performance assessment of NAPL source zone remediation is often predicated on measured decreases in NAPL saturation. Thus accurate and cost-effective methods for locating and quantifying NAPL saturations are of critical importance when characterizing contaminated field sites and planning for and interpreting the results of various remediation alternatives.

Various in situ and ex situ, invasive and non-invasive methods have been developed to locate NAPL source zones and to quantify NAPL saturation. The most basic method involves obtaining soil cores from the subsurface using drill rigs or direct push technology. The presence of NAPL can be inferred using soil vapor analysis, hydrophobic dye shake tests, and UV fluorescence tests (Kram et al., 2001). NAPL saturations can be determined from soil cores using laboratory analysis techniques. However, adequate site characterization and remediation performance assessment requires obtaining an adequate number of core samples, thus driving up costs. Cone penetrometer (CPT) or direct-push techniques have seen increased use at contaminated sites. These in situ tests are often conducted at sites with shallow NAPL contamination and loosely consolidated sediment. Numerous characterization techniques have been incorporated into CPT methods. Membrane interface probes and hydrosparging techniques involve the partitioning of vapor phase chlorinated organics from the penetrometer to a sampling line which leads to an above ground sampling point (Kram et al., 2001; Griffin and Watson, 2002). Flexible Liner Underground Technologies Everting (FLUTe)® utilizes a hydrophobic adsorbent
ribbon that is pushed against the side of a direct-push borehole. Again, these techniques are used as general indicators for the presence of NAPL contamination and may require high sampling densities (with resultant cost increases) to obtain adequate site characterization and remediation performance assessment. Partitioning interwell tracer tests (PITTs) have been used with some success as a non-invasive, in situ method for quantifying NAPL saturations in the subsurface (Jin et al., 1995; Annable et al., 1998; Young et al., 1999; Jawitz et al., 2000). This method involves the simultaneous injection of a solution containing a partitioning tracer (commonly an alcohol) and a conservative tracer (e.g., bromide) into one well and the extraction of the test solution/groundwater mixture from a second well. The aquifer between the wells is ‘swept’ by the tracer solution and the NAPL saturation can be calculated via the difference in arrival times of the center of mass of the partitioning and conservative tracers at the extraction well. This method has the benefit of interrogating a larger volume of aquifer than is feasible using soil coring or CPT techniques, and can produce estimates of NAPL saturation in the tracer swept zone rather than simply confirming the presence or absence of NAPL. However, PITTs can be costly due to the large volume of injection solution required, the large volume of wastewater generated, and the need to install at least two pumping wells, along with monitoring wells along the flow path (if desired). In addition, regulatory approval is often required to inject alcohols into the subsurface.

The limitations of the methods outlined above, combined with the continued need to cost-effectively locate and quantify NAPL saturations, have led to the
investigation of in situ radon as a partitioning tracer (Semprini et al., 1993; Hopkins, 1995; Gottipati, 1996; Semprini et al., 1998; Semprini et al., 2000). Radon is a naturally occurring noble gas that is commonly found in groundwater; due to its non-polarity, radon will partition into NAPLs. Radon concentrations are decreased in the presence of NAPL under natural groundwater gradients due to partitioning of radon into the NAPL phase. Furthermore, radon transport is retarded due to partitioning in the presence of NAPL under the forced groundwater gradients inherent in pumping tests. As an in situ partitioning tracer, radon has the potential advantages over synthetic tracers in that it is free and does not require regulatory approval for use. Natural gradient or ‘static’ radon partitioning tracer tests hold promise for quantifying changes in NAPL saturation as a result of aquifer remediation. Forced gradient tests (i.e., ‘dynamic’ or pumping tests) incorporating radon have the potential to quantify NAPL saturations in a given volume of the aquifer and track changes in saturations resulting from remediation. In particular, the single-well ‘push-pull’ test can be used to estimate NAPL saturations in the vicinity of existing monitoring wells at a contaminated site. The push-pull test offers several advantages over PITTs such as reduced wastewater volumes, shorter test duration, and reduced costs. The combination of radon’s in situ partitioning behavior and the push-pull test offers a potentially rapid, low-cost method for quantifying NAPL saturation and tracking remediation processes.
OBJECTIVES

The main objectives of this study were:

1. To evaluate the efficacy of the push-pull test incorporating radon as an in situ partitioning tracer to estimate NAPL saturations.

2. To evaluate the efficacy of the static radon tracer method to locate NAPL contamination and quantify NAPL saturations, and to estimate changes in NAPL saturations resulting from remediation activities.

3. To evaluate the efficacy of the push-pull test incorporating radon as an in situ tracer to estimate changes in NAPL saturations resulting from remediation activities.

4. To use numerical simulations to investigate the factors influencing radon push-pull test experimental results and to further refine the radon push-pull test method using the results of these simulations.

REFERENCES


Liquids, G.B. Wickramanayake and R.E. Hinchee (Eds.). Battelle Press, Columbus, OH.


CHAPTER 2

Literature Review

CHLORINATED ALIPHATICS AND DNAPLs

Chlorinated solvents have seen prolific use in the industrialized world throughout the twentieth century. These chemicals have been utilized for numerous purposes, including metal degreasing, electroplating, semiconductor production, dry cleaning, and as a feedstock for other the production of other chemicals. Over the past 30 years the problems associated with the use and disposal of chlorinated solvents have been brought to the forefront of environmental research. Some of these chemicals, including trichloroethene (TCE), are suspected human carcinogens (California EPA, 2000). Although the health risks of chlorinated solvents are widely understood, some (e.g., TCE and perchloroethene, PCE) are still classified as a High Production Volume Chemicals by the U.S. Environmental Protection Agency (EPA), with an annual production and/or importation of over 1 million pounds (EPA HPV list, 2002). The improper use and disposal of chlorinated solvents “has given rise to many of the most serious problems of contamination encountered in hydrogeologic practice.” (Domenico and Schwartz, 1998). Sources such as leaking above ground and underground storage tanks, faulty piping systems, industrial and transportation accidents, and improper burial in landfills have led chlorinated solvents to become the
most common organic chemicals detected at contaminated sites (Broholm et al.,
1999).

Chlorinated solvents are ethanes or ethenes that have one or more hydrogen
atoms replaced by one or more chlorine atoms at various positions on the structure of
the compound. For example, TCE is an ethene with three of the four hydrogen atoms
replaced by chlorine atoms. A majority of chlorinated solvents have a density greater
than water as well as a relatively low solubility in water. For instance, TCE has a
solubility of 1100 mg/L at 20°C and 1 atm pressure, and a specific gravity of 1.46
(Domenico and Schwartz, 1998). Increasing the degree of chlorination of these
compounds generally results in an increase in their density, viscosity, and
nonflammability, while decreasing their solubility in water. These chemicals form a
dense nonaqueous phase liquid, or DNAPL, and are subsequently often referred to as
DNAPLs. When released to the subsurface, DNAPLs will volatilize in the unsaturated
zone, while in the saturated zone both volatilization and dissolution will occur. These
phenomena can produce large plumes of DNAPL-contaminated groundwater as the
DNAPL slowly dissolves to form an aqueous phase. Selected physical characteristics
of TCE, PCE, trichloromethane, and carbon tetrachloride are shown on the following
page.
Table 2.1  Selected physical characteristics of chlorinated aliphatics (Domenico and Schwartz, 1998)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Specific Gravity</th>
<th>Solubility (mg/L)</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloroethene</td>
<td>C₂HCl₃</td>
<td>1.46</td>
<td>1100</td>
<td>60</td>
</tr>
<tr>
<td>Perchloroethene</td>
<td>C₂Cl₄</td>
<td>1.63</td>
<td>150</td>
<td>14</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>CHCl₃</td>
<td>1.49</td>
<td>8200</td>
<td>160</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>CCl₄</td>
<td>1.59</td>
<td>757</td>
<td>90</td>
</tr>
</tbody>
</table>

The mechanisms controlling the migration and fate of DNAPLs in the subsurface are complex and have been the subject of extensive research (e.g., Schwille, 1988). The migration of DNAPLs in the subsurface is affected by numerous factors, including 1) the volume released, 2) the infiltration area, 3) the release duration, 4) DNAPL properties, and 5) the physical characteristics of the subsurface (Mercer and Cohen, 1990). A number of physical properties influence DNAPL behavior in the environment and are therefore critical in optimizing site characterization and remediation. These properties are briefly summarized below.
Density

The density of the DNAPL is critical in establishing the hydrostatic pressure that drives gravity flow. A greater density results in a greater hydrostatic driving force. Density is often described in terms of specific gravity, which is the ratio of the mass of a volume of substance to the mass of an equivalent volume of water at a specific temperature.

Interfacial Tension and Wettability

Interfacial tension is defined as the free surface energy at the interface between two immiscible substances (Mercer and Cohen, 1990). This energy results from the difference between the mutual attraction of like molecules in a substance and the attraction of unlike molecules across the interface between the two substances. Figure 2.1 shows a three-phase system with a Liquid 1 (L1), Liquid 2 (L2), and Solid (S).

Figure 2.1 Interfacial tensions between a solid and two liquid phases.
In Figure 2.1 the relationship between the contact angle $\theta$ (measured through the denser fluid) and the interfacial tensions ($\sigma$) is given by

$$\cos \theta = \frac{\sigma_{SL2} - \sigma_{SL1}}{\sigma_{L2L1}}$$

(2.1)

When $\theta$ is less than 90°, Liquid $L2$ will wet the solid surface, while when $\theta$ is greater than 90°, Liquid $L1$ will wet the solid surface. Since water has a lower interfacial tension with solid surfaces than many DNAPLs, water tends to wet the solid surfaces in the saturated and unsaturated zones. The interfacial tension directly influences the wettability; that is, the preferential spreading of one liquid over a solid surface in a two-liquid system (Mercer and Cohen, 1990). The wetting fluid tends to occupy smaller pores and coat the solid surfaces, while the nonwetting fluid tends to occupy larger pores and the center of those pores. Most solids are preferentially water-wet, and thus usually DNAPL forms a non-wetting fluid in the saturated and unsaturated zones.

**Viscosity**

Viscosity is defined as a liquid’s resistance to shear. As viscosity increases a DNAPL’s resistance to shear increases, potentially decreasing its rate of penetration in the saturated zone.
Capillary Pressure

Capillary pressure ($P_c$) defines the pore pressure of two liquids at the curved interface between those two liquids, as described by (Fetter, 1999)

$$P_c = \left(\frac{2\sigma}{r}\right) \cos \theta$$  \hspace{1cm} (2.2)

where $r$ is the radius of curvature of the interface between the two liquids and $\sigma$ is the interfacial tension between the two liquids. This property causes the porous media to attract the wetting liquid and repel the nonwetting liquid. Thus, the pressure that must be established for DNAPL to penetrate into a pore is directly proportional to the interfacial tension and inversely proportional to the radius of curvature. Domenico and Schwartz (1998) describe capillary pressure as “the pressure required to move a particle of nonwetting fluid into a pore filled with wetting fluid.” Small pores therefore are more resistant to DNAPL penetration than large pores (since the radius of curvature is a function of pore size), with the result that DNAPLs tend to move through coarser and more permeable mediums, may bypass less permeable mediums via gravity flow or may form ‘pools’ of DNAPL above less permeable mediums.

Relative Permeability

Relative permeability (in reference to DNAPLs) refers to the reduction of the intrinsic permeability of a given medium in the presence of water and DNAPL. As DNAPL fills pores and displaces water, the relative permeability of the medium
decreases for water and increases for DNAPL. The ratio of the volume of the pore filled with water to the volume of pore filled with DNAPL is referred to as the saturation ratio. As the pores fill with the water, the saturation ratio increases and the relative permeability of the medium to DNAPL decreases. Ultimately the DNAPL saturation is reduced to an irreducible, or ‘residual’ saturation where it is discontinuous and no longer mobile. Conversely, as the pores fill with DNAPL, the saturation ratio decreases as does the relative permeability of the medium to water. Ultimately the water saturation is reduced to a ‘residual’ saturation where it is discontinuous and no longer mobile.

DNAPL released at the surface will migrate downward due to hydrostatic pressure. In the presence of continuing hydrostatic pressure, DNAPL will continue to migrate downward, eventually passing through the water table. As it migrates, some DNAPL will spread laterally due to capillary forces and/or heterogeneity in the physical properties of the subsurface. Subsurface heterogeneity (e.g., layering) can cause DNAPL to migrate due to gravity flow along pathways distinct from the groundwater flow direction. Small ‘blobs’ or ‘ganglia’ of DNAPL will occur in pores when the DNAPL (i.e., free-phase) hydrostatic pressure is reduced below a critical level (Bedient et al., 1994). The amount of mobile DNAPL from a pulse release will therefore decrease as more and more DNAPL is ‘trapped’ in pores during downward migration. These DNAPL ganglia form a residual saturation that slowly dissolves to the aqueous phase. The end result of a DNAPL release will often be a complex distribution of residual and mobile DNAPL.
The combination of factors affecting DNAPL flow and the inherent heterogeneity of the subsurface results in many DNAPL-contaminated sites having a complex distribution of mobile and residual DNAPL. The saturation of DNAPL in the subsurface is often found to be a function of space. Broholm et al. (1999) conducted a controlled release of 5 L of mixed solvent DNAPL (TCE, PCE and trichloromethane) in an engineered ‘test cell’ in a sandy, unconfined aquifer. The DNAPL saturation was found to be highly heterogeneous when the test cell was excavated at the end of the experiment. Jawitz et al. (2000) conducted soil coring at a dry cleaner site contaminated with PCE and found a heterogeneous PCE saturation distribution using soil core analysis. A typical DNAPL-contaminated site may contain numerous zones of residual DNAPL along with DNAPL ‘pools’ of varying size and shape. Contamination at fractured bedrock sites can result in complex DNAPL saturation distributions as the DNAPL migrates along fractures of varying size and connectivity (Fetter, 1999). These phenomena present challenges to effectively locating and quantifying the distribution of DNAPL saturations in the subsurface.

The demand for effective characterization of DNAPL contamination has led to the development of numerous techniques for locating DNAPL in the subsurface. The collection of soil samples using coring devices (e.g., hollow stem augers, direct-push samplers) and subsequent analysis of those samples for DNAPL could be classified as a traditional method of obtaining subsurface DNAPL saturation data. Numerous techniques for analyzing soil samples have been developed (Cohen and Mercer, 1993). A portable organic vapor analyzer using flame ionization detection of vapor phase
organics can be used to screen samples for the potential presence of DNAPL (Griffin and Watson, 2002). Visual identification of DNAPLs in samples can sometimes be made, especially with the aid of a hydrophobic dye such as Sudan IV or Oil Red O (Kram et al., 2001). Soil/water shake tests, UV fluorescence using a field-portable light source, and laboratory-based chemical analysis of the organic phase in soil samples (incorporating phase equilibrium partitioning calculations) have been used to characterize DNAPL saturation in soil cores. Although these methods can produce direct evidence of DNAPL contamination, they typically sample small volumes of the subsurface. In order to adequately characterize a DNAPL-contaminated site, a large number of samples must be obtained; this can significantly increase the costs of site characterization (Kram et al., 2001).

Groundwater samples can be obtained from monitoring wells installed at the site. The presence of DNAPL in samples obtained from monitoring wells is obviously a direct indicator of DNAPL in the subsurface, although it cannot be reliably used to estimate the DNAPL saturation in a given volume of the subsurface. The analysis of water samples for dissolved chlorinated aliphatics can potentially locate DNAPL source zones (Broholm et al., 1999). As a rule of thumb, the presence of DNAPL is inferred if the aqueous phase concentration exceeds 1 % of the effective solubility of the DNAPL phase. However, this is not a hard and fast rule and cannot be relied on in the field to preclude the presence of DNAPL if aqueous phase concentrations are < 1 % of the effective solubility. These methods require the installation of a sufficient density of monitoring wells at a site to adequately interrogate a sufficient volume of
the subsurface. Again, the costs associated with these activities increase as the number of monitoring wells increases.

Cone penetrometer (CPT) methods involve direct push boring techniques to insert various sensors, samplers, and/or analytical devices to specified depths in the subsurface. CPT methods are best suited for relatively shallow investigations conducted in loosely compacted sedimentary deposits. More than one sensor can be mounted on a single probe to collect real-time data on sediment properties and DNAPL distributions. One of the more recent innovations in CPT technology is the membrane interface probe (MIP), which consists of a fluorocarbon polymer membrane mounted on a drive point (Griffin and Watson, 2002). The membrane is heated to 100°C to 120°C and a clean carrier gas is circulated across the internal membrane surface. Volatile organic compounds (VOCs) partition across the interface and are carried to a detector at the surface (e.g., gas chromatograph/mass spectrometer or flame ionization detector). The MIP is used as a preliminary indicator of DNAPL contamination, and positive results require obtaining confirmation samples from the area of interest. The hydrosparging technique involves the use of a CPT probe equipped with a groundwater sampling port and sparging device to sparge VOCs from the saturated zone to an above ground detection device (Kram et al., 2001). Similar to the MIP technique, the hydrosparging technique is a preliminary indicator for DNAPLs. Another CPT method incorporates Raman Spectroscopy, which enables the real time identification of specific constituents of chlorinated DNAPLs. This technique utilizes light wavelength shifts from inelastic scattering to delineate DNAPL
contamination in the subsurface. Yet another CPT technique utilizes a Waterloo Profiler, which is essentially a stainless steel, multilevel groundwater sampling device that can be pushed to a specified depth. Aqueous phase samples are obtained and analyzed for chlorinated DNAPL components. This technique is similar to obtaining groundwater samples at monitoring wells, with the advantage that numerous samples can be obtained in a relatively short amount of time from essentially temporary boreholes, thus reducing the overall sampling cost. Also, CPT coupled with a Flexible Liner Underground Technologies Everting (FLUTe)® Membrane can be used to detect the presence of DNAPL. This method utilizes a hydrophobic absorbent ribbon that is pushed against the side of the borehole at a specified depth. DNAPLs, if present, will absorb to the ribbon. The ribbon is extracted and analyzed for DNAPL components (Kram et al., 2001). Each of the CPT techniques outlined above involves the use of a direct-push device (usually truck-mounted) to advance and retract the CPT, and requires a sufficient density of sampling locations to effectively characterize DNAPL contamination at a site. The cost of CPT methods therefore is greater at larger sites and at sites where a greater sample density is desired. Also, sampling is usually limited to shallow depths and to unconsolidated materials. In addition, most of these techniques require further sampling to quantify DNAPL saturation, which adds additional costs to the initial CPT costs.
PARTITIONING INTERWELL TRACER TESTS

The need to interrogate larger volumes of the subsurface and quantify the DNAPL saturation in the interrogated volume has led to the development and application of the partitioning interwell tracer test. Partitioning interwell tracer tests involve the injection of non-reactive conservative and non-conservative (i.e., partitioning) tracers in an injection well. The tracers travel through the flow field to an extraction well, where samples are obtained for analysis. The conservative tracer will be transported at the pore water velocity. The partitioning tracer will partition between the DNAPL and water. If the DNAPL is immobile (i.e., at residual saturation), the velocity of the partitioning tracer will be retarded relative to the conservative tracer (Jin et al., 1995). The partitioning into immobile DNAPL results in a chromatographic separation of the conservative and partitioning tracers, with the degree of separation a function of the DNAPL saturation in the subsurface and the DNAPL:aqueous phase partition coefficient for the partitioning tracer ($K$), which is described by (Dwarakanath, 1999)

$$K = \frac{C_n}{C_w}$$

where $C_n$ is the concentration of the partitioning tracer in the DNAPL phase, and $C_w$ is the concentration of the partitioning tracer in the aqueous phase. Assuming linear, equilibrium partitioning, the retardation factor ($R$) is described by (Dwarakanath, 1999)
\[ R = 1 + K \frac{S_n}{S_w} \]  

(2.4)  

where \( S_n \) if the DNAPL saturation, and \( S_w \) is the water saturation (\( S_n + S_w = 1 \)). One or more partitioning tracers may be injected in an interwell partitioning tracer test, each of which may have a different DNAPL:aqueous phase partition coefficient (\( K \)). The most commonly used partitioning tracers are alcohols of varying chain length, such as 1-butanol, 1-hexanol, 1-heptanol, although SF6, a synthetic inert gas, has also been used (Wilson and Mackay, 1995).

The method of moments is used to determine the retardation factor for the partitioning tracer. This method involves calculating the zeroth \( (m_0) \) and first \( (m_1) \) temporal moments by integrating normalized conservative \( (\text{cons}) \) and partitioning \( (\text{part}) \) tracer concentrations \( (C^*) \) at the extraction well using

\[
m_0 = \int C^*(t) dt \tag{2.5}
\]

\[
m_1 = \int C^*(t) dt \tag{2.6}
\]

The retardation factor \( (R) \) is computed using

\[
R = \left( \frac{m_{1,\text{part}}}{m_{0,\text{part}}} \right) \frac{m_{1,\text{cons}}}{m_{0,\text{cons}}} \tag{2.7}
\]
Table 2.2 Partitioning interwell tracer test (PITT) descriptions.

<table>
<thead>
<tr>
<th>Test Site</th>
<th>NAPL Type</th>
<th>Partitioning Tracers</th>
<th>Method of Analysis</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>laboratory</td>
<td>PCE</td>
<td>2,3-dimethyl-2-butanol</td>
<td>method of moments, numerical simulations</td>
<td>Jin et al. (1995)</td>
</tr>
<tr>
<td>Hill AFB, Utah</td>
<td>chlorinated solvents + jet fuel</td>
<td>ethanol, hexanol, 2,2-dimethyl-3-pentanol, heptanol, octanol</td>
<td>method of moments</td>
<td>Annable et al. (1998)</td>
</tr>
<tr>
<td>Portsmouth, Ohio</td>
<td>TCE, PCE</td>
<td>3-methyl-3-pentanol, hexanol, 2,4-dimethyl-3-pentanol, heptanol</td>
<td>method of moments, numerical simulations</td>
<td>Young et al. (1999)</td>
</tr>
<tr>
<td>Jacksonville, Florida</td>
<td>PCE</td>
<td>hexanol, 2,4-dimethyl-3-pentanol, 2-ethyl-1-hexanol</td>
<td>method of moments</td>
<td>Jawitz et al. (2000)</td>
</tr>
</tbody>
</table>

The partitioning interwell tracer test (PITT) has been used in laboratory and field experiments to obtain DNAPL saturations in the volume of sediment swept by the suite of conservative and partitioning tracers. Jin et al. (1995) presented one of the first studies of the PITT using PCE-contaminated small-scale sand columns as well as 2-D numerical simulations of the Canadian Air Forces Base Borden aquifer (Table 2.2). The residual PCE saturation calculated compared favorably with residual
saturations calculated using pre- and post-contamination mass balances. Furthermore, tests conducted following surfactant remediation of the PCE showed that the PITT could be used to track remediation performance. The numerical simulations involved a complex subsurface system with a stochastic permeability field and multiple stages of PCE release, redistribution under gravity and capillary forces, and a series of PITTs conducted before and after surfactant remediation. The numerical results showed that PITTs could be used to quantify PCE saturation and track remediation. Moreover, the study highlighted the importance of selecting partitioning tracers with a $K$ value such that adequate separation of a partitioning tracer from a conservative tracer is observed without the necessity of pumping a large volume of water from the well to obtain adequate partitioning tracer mass recovery.

Annable et al. (1998) provided results of the first PITT test applied at a field site (Table 2.2). The tests were performed in a 4.3 m (width) by 3.5 m (width) by 6.1 m (depth) test cell that was isolated from the surrounding aquifer by sheet piling and a clay aquitard. The test cell was equipped with injection wells and extraction wells located on opposite sides of the cell. A NAPL saturation of 4.6 % was estimated in the tracer swept region of the test cell. A log-linear extrapolation of the other partitioning tracer data (necessitated due to poor mass recovery) was used to estimate a NAPL saturation of 5.4 %. These results compared favorably with NAPL saturations of 3.0 and 4.6 % from soil cores. In addition, ethanol, pentanol, and hexanol showed evidence of biodegradation during the PITT, showing a potential limitation to using alcohols as partitioning tracers.
The Portsmouth Gaseous Diffusion Plant in Ohio was the site of another field application of the PITT technique (Young et al., 1999; Table 2.2). In this case the PITT results were used in conjunction with planning and analyzing the results of a remedial surfactant flood. Numerical simulations were used to optimize the PITTs in terms of test duration, mass of tracer, injection and extraction rates, and mass recovery estimates. PITTs conducted prior to surfactant flooding were used to determine the average residual DNAPL saturation in the tracer swept zone of the aquifer. Tracer concentrations from monitoring wells set at different depths between the injection and extraction wells showed spatial variability in DNAPL saturations, with an average value of 0.1 to 0.2 %. A post-remediation PITT showed a decrease estimated DNAPL saturation to 0.06 %.

Annable et al. (1998) used an adsorbing interfacial tracer in conjunction with a partitioning alcohol tracer in PITTs to estimate NAPL saturations and NAPL-water interfacial areas. Jawitz et al. (2000) used a series of PITTs to characterize and track the remediation of a PCE contaminated former dry cleaner site (Table 2.2). Wilson and Mackay (1995) conducted tests using sand-packed columns containing DNAPL to investigate SF₆ as a partitioning tracer in the laboratory. Nelson and Brusseau (1996) applied the method at a field site to investigate SF₆ as a detector of TCE saturation, as opposed to quantifying saturation. The results showed the presence of TCE in samples taken from monitoring wells along the tracer flowpath. Further evidence of the presence of TCE was supported by constant aqueous phase TCE concentrations at
the extraction well during the flushing of 71 pore volumes through the tracer swept region of the aquifer.

Although PITTs have been applied with some success, some concerns remain regarding the factors that can influence the efficacy of the tests. A study by Rao et al. (2000) discussed the potential for DNAPL saturation underestimation in PITTs due to 1) constraints on the accessibility of low hydraulic conductivity zones to partitioning tracers, and 2) the effect of nonequilibrium tracer mass transfer between the DNAPL and aqueous phases. These effects are magnified at field sites with low DNAPL saturations, highly heterogeneous physical and DNAPL saturation characteristics, or DNAPL ‘pools’. Tracer breakthrough curves (BTCs) can be highly skewed (i.e., have long ‘tails’) in such situations, which can lead to low tracer mass recoveries and greater errors in DNAPL saturation estimation. A study by Nelson et al. (1999) highlighted the effect of physical and DNAPL heterogeneity and sampling method on PITT results in laboratory flow cell experiments. The flow cell contained two zones of differing permeability and TCE saturation emplaced in a sand matrix. Experimental results showed that the PITT was less effective in characterizing TCE saturation in the zone of lower intrinsic and relative permeability, likely as a result of preferential flow around this zone and nonequilibrium partitioning (i.e., mass transfer limited partitioning). The PITT was especially poor in characterizing TCE saturation from samples taken from vertically-integrated sampling ports, since these ports intercepted a large fraction of streamlines that were not in contact with the TCE-contaminated
portions of the test cell. These results gave weight to the argument that the PITT is a better ‘detector’ than ‘quantifier’ of DNAPL saturation.

The PITT is a useful test for detecting and quantifying DNAPL saturation in the subsurface. However, in addition to the issues relating to preferential flow, mass transfer limitations, and DNAPL heterogeneity outlined above, the economic feasibility of conducting multiple PITTs at contaminated sites is hampered by two factors: 1) large volumes of contaminated wastewater are produced, and must be remediated to remove aqueous phase chlorinated solvents and alcohol tracers; and 2) the tests require the installation of at least two pumping wells, plus monitoring wells if desired. Although the PITT can be used to interrogate a much larger volume of aquifer than can be sampled using coring or CPT techniques, it is still a potentially costly and time consuming endeavor. The single-well injection-withdrawal tracer test, or ‘push-pull’ test, offers the ability to conduct more numerous, smaller scale partitioning tracer tests at a lower cost.

PUSH-PULL TESTS

The push-pull test has its origins in the investigation of the mixing of injected water and groundwater for the purposes of artificial groundwater recharge (Sternau et al., 1967). Hoopes and Harleman (1967) investigated dispersion in radial flow from a recharge well. Their study included an analytical solution for a conservative tracer in a homogeneous, isotropic, confined aquifer which was tested against experimental and
numerical results. Gelhar and Collins (1971) developed an approximate analytical solution to the advective-dispersive equation in radial coordinates tests whereby longitudinal dispersivity is treated as a variable for nonuniform, steady flow. In this manner conservative tracer data from the well during the pull phase can be used to determine the longitudinal dispersivity of the aquifer. This approximate solution was later investigated by Schroth et al. (2000) and Davis et al. (2002) using empirically-derived data and numerical simulations (see below and Chapter 3). The application of the push-pull test incorporating reactive, partitioning tracers was investigated by Tomich et al. (1973) for the purposes of determining residual oil saturation in petroleum reservoirs. This application involved a novel technique of injecting a partitioning tracer (ethyl acetate) that hydrolyzed to a conservative tracer (ethanol) in the reservoir. The presence of residual oil saturation was indicated by a delay in the arrival times at the extraction well of the two tracers during the pull phase of the test (incorporating a rest period before the extraction to allow for hydrolysis of ethyl acetate).

Recently the push-pull test has been applied to a variety of environmental topics including: investigating microbial activities in a petroleum contaminated aquifer (Istok et al., 1997); determining first-order reaction rate coefficients (Haggerty et al., 1998); investigating sorption of surfactants to natural aquifer sediment (Istok et al., 1999); and characterizing the solubilization of TCE using surfactant remediation (Field et al., 1999). Additional studies have been published on topics such as: investigating TCE and TCFE transport and anaerobic biotransformation in an aqueous
phase TCE-contaminated aquifer (Hageman et al., 2001); and investigating the immobilization and remobilization of uranium (Senko et al., 2002).

The use of the push-pull test incorporating a partitioning tracer to quantify DNAPL saturation is a novel application of the methodology. Like the PITT, the partitioning tracer push-pull test has the ability to interrogate larger volumes of an aquifer for DNAPL location and quantification than is typically feasible using traditional coring or CPT methods. However, the push-pull test has advantages over the PITT in terms of reducing costs as a result of: 1) the need for only a single well to conduct a test; 2) the use of smaller volumes of water, with resultant decreases in test water remediation costs; 3) rapidity of test completion, with a single test often requiring less than one day from start to finish; and 4) the ease of conducting a test, since less equipment, and less costly equipment, is required. A potential disadvantage of the push-pull test is the inability to use the method of moments to estimate retardation and NAPL saturation.

Unlike the PITT, the push-pull test utilizes a single well for both the injection and extraction phases of the test. A specified volume of test solution containing known concentrations of both conservative (e.g., bromide) and partitioning tracers (e.g., alcohols) is injected into the subsurface through a well at a specified flowrate. During the injection or push phase of the test the solution is transported radially outward from the well in a nonuniform flow field to a radial distance that is a function
of the volume of solution injected, aquifer thickness, effective porosity of the aquifer, and the well radius (Figure 2.2). The test solution can be injected across the entire well screen or through a selected screen interval through the use of inflatable straddle packers. The conservative tracer will be transported at the pore water velocity, while the partitioning tracer (in the presence of DNAPL) will be transported at a lesser velocity due to partitioning between the aqueous and DNAPL phases. The injection solution interrogates an approximately cylindrical volume of aquifer; however, the exact shape of the interrogated region is a function of aquifer heterogeneities (e.g., heterogeneity in hydraulic conductivity), DNAPL saturation heterogeneities (e.g., heterogeneity in relative permeability), and the injection rate (which can affect the dispersion of the tracer front).

![Figure 2.2](image)

Figure 2.2 Radial positions \( r \) (defined as a normalized concentration = 0.5) of conservative \( r_{inj} \) and partitioning tracers \( r_{sol} \) during the injection phase \( (inj) \), at the end of the injection phase \( (max) \), and during the extraction \( (ext) \) phases. Well radius is denoted by \( r_w \), and \( Q \) is pumping rate (Schroth et al., 2000).
The pull phase begins upon the completion of the push phase, reversing the nonuniform flow field and causing the injected tracers, which are now mixed with groundwater, to flow back toward the well (Figure 2.2). Tracer samples are taken at the extraction well during the pull phase of the test. Again, the partitioning tracer will be transported at less than the pore water velocity due to partitioning. Unlike a PITT, however, the conservative and partitioning tracers arrive simultaneously at the well; this means that partitioning tracer retardation is not manifested in a delay in arrival time of the partitioning tracer vs. the conservative tracer (Schroth et al., 2000). The manner in which retardation is manifested is a function of the dispersion coefficient \( D \), which is described by

\[
D = \alpha_L v
\]

(2.8)

where \( \alpha_L \) is dispersivity (assumed to be constant) and \( v \) is pore water velocity. In nonuniform flow the pore water velocity \( v \) is a function of radial distance from the well \( r \) as described by (Schroth et al., 2000)

\[
v(r) = \frac{Q}{2\pi bnR}
\]

(2.9)

where \( Q \) is pumping rate, \( b \) is aquifer thickness, \( n \) is porosity, and \( R \) is the retardation factor (equation 2.4). For the partitioning tracer \( R > 1 \), resulting in a decreased velocity. This results in the partitioning tracer undergoing greater dispersion than the conservative tracer due to its longer residence time in the higher velocity region near the well. The effect of greater dispersion on the partitioning tracer is evident in a pull phase concentration times series, or breakthrough curve (BTC) plot of the
conservative \((R = 1)\) and partitioning tracers \((R > 1)\) as shown in a numerical simulation of injected tracers using the Subsurface Transport Over Multiple Phases (STOMP) code (Figure 2.3). Note that \(C\) is normalized concentration and \(V_e/V_i\) is dimensionless time, where \(V_e\) is the volume extracted at the time a sample was obtained during the pull phase and \(V_i\) is the total volume injected during the push phase.

![Graph showing BTCs for conservative \((R = 1)\) and partitioning \((R > 1)\) tracers, showing greater dispersion of the partitioning tracer in the presence of DNAPL.](image)

Assuming linear equilibrium partitioning, equation 2.10 can be used to calculate the DNAPL saturation if the partition coefficient \((K)\) and retardation factor \((R)\) are known:

\[
S_p = \frac{R - 1}{R + K - 1}
\] (2.10)
However, $R$ must be estimated from the dispersion of the partitioning tracer BTC relative to the conservative tracer BTC in order to calculate a value for DNAPL saturation (see Chapters 3, 4, and 5).

The reliable estimation of $R$ is therefore a critical step in quantifying $S_n$. Schroth et al. (2000) conducted an investigation of a simplified approach to estimating retardation factors for partitioning tracers during the pull phase of push-pull tests. This approach built upon the approximate analytical solutions developed by Geihar and Collins (1971) and was tested against numerical simulations for ideal and nonideal conditions, the latter utilizing a Langmuir isotherm for nonlinear equilibrium conditions and first-order mass transfer coefficients for linear nonequilibrium conditions. Also, linear equilibrium simulations were performed using a physically heterogeneous aquifer in 2-D. A data set of $^{131}$I (conservative) and $^{85}$Sr (partitioning) tracers from a radial injection dual-tracer test conducted by Pickens et al. (1981) was used to investigate the approximate solution in a field application.

The linear equilibrium simulations revealed that the approximate solution provided a good estimate of $R$ at low values of $R$, but that the estimate was less reliable as $R$ increased. The decrease in reliability is due to the fact that the approximate solution is accurate only if (Schroth et al., 2000)

$$\left(\frac{\alpha_L}{L_0}\right)^{\frac{1}{2}} \ll 1$$

where $\alpha_L$ is dispersivity and $L_0$ is the total radial distance traveled by the partitioning tracer solute front ($L_0 = 2r_{max}$). Assuming that $\alpha_L$ is constant, as $R$ increases, $L_0$
decreases and the likelihood of violating equation 2.11 becomes greater. Thus for solutes with greater values of $K$, or for systems with greater $S_n$, the radial distance $L_o$ must be increased (i.e., a longer push phase) in order for the approximate solution to provide a reliable estimate of $R$. The effect of varying porosity and aquifer thickness on $R$ was also investigated and found to be minimal since both the retarded and conservative solutes are equally affected by changes in these parameters. Overall, the approximate solution revealed errors $\leq 14\%$ between estimated and simulated $R$ values for values ranging from 1 to 100 where equation 2.11 was not violated. The approximate solution was found to provide poor estimates of $R$ under conditions of nonlinear equilibrium and linear nonequilibrium sorption. However, a general trend was found where the partitioning tracer BTC crossed the conservative tracer BTC at greater values of dimensionless time ($V_e/V_i$) as 1) concentration increased in nonlinear equilibrium conditions, and 2) the mass transfer coefficient decreased in linear nonequilibrium conditions. Thus the push-pull test may serve to qualitatively indicate the existence of nonideal transport (e.g., mass transfer limited partitioning) in aquifers.

In the 2-D simulations the presence of heterogeneity in hydraulic conductivity resulted in the approximate solution seriously underpredicting $R$, largely as a result of the spatial variability in dispersion due to the velocity differences between layers of varying hydraulic conductivity. The field application of the method to the data set of Pickens et al. (1981) resulted in an estimated $R = 11.4$ for the retarded tracer $^{85}$Sr. Using the provided values of porosity and bulk density, a solid:aqueous phase partition coefficient ($K_d$) = 2.33 mL/g was calculated, which closely matched the values
measured by Pickens et al. (1981). This showed the ability of the approximate solution to accurately estimate \( R \) in a field application. Schroth et al. (2000) concluded that the push-pull test and approximate solution could provide reasonably accurate estimates of \( R \) under certain aquifer and test conditions.

A recent article by Istok, Field, Schroth, Davis, and Dwarakanath (2002) investigated the ability of the push-pull test method to quantify NAPL saturation in laboratory and field applications. In this study the partitioning tracer push-pull test method was combined with the use of conservative and partitioning alcohols. 1-pentanol was used as the conservative tracer, while 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol were used as the partitioning tracers. The laboratory tests were conducted in a TCE-contaminated physical aquifer model (PAM) described in Chapter 3, with samples being obtained during the push phase (from sampling ports along the long axis of the PAM) and the pull phase (from a sampling port at the injection/extraction well). Field tests were conducted in a LNAPL-contaminated aquifer at a former petroleum refinery. The experimental results were numerically simulated in order to estimate a value for \( R \) and calculate \( S_n \) (equation 2.10).

Results from a laboratory test performed in the PAM prior to TCE contamination showed slight sorption of the partitioning tracers to the sediment, while the tests performed in the contaminated PAM showed clear evidence for much greater retardation due to partitioning into TCE. The simulations provided good fits to the 1-pentanol and 1-hexanol data at the sampling ports, with the sorption-adjusted \( R = 1.3 \) yielding a calculated \( S_n = 1.6 \). This value is in agreement with the estimated \( S_n = 2 \% \)
in the PAM. However, the simulation fits were poor for 1-heptanol and 2-ethyl-1-hexanol at the sampling ports due to BTC tailing, with calculated values of $S_n = 1.7$ for 1-heptanol and 0.7 for 2-ethyl-1-hexanol. The pull phase data were also poorly fit by the simulations, with evident tailing of the BTCs. This is possibly due to rate limited mass transfer between the aqueous and DNAPL phases. Another test was conducted at a lower flowrate to reduce the effects of mass transfer limitation. Interestingly, the simulations failed to provide better fits to the data in this test. Tailing of BTCs was evident in the push and pull phases, with calculated values of $S_n$ increasing vs. the previous test and ranging from 1.1 to 4.7 %. The increased values possibly reflect a decrease in the effects of rate limited mass transfer of the partitioning tracer as a result of the lower flowrate. The field test resulted in a calculated $S_n$ ranging from 1.4 to 2.0 %, which is in agreement with previously determined $S_n$ values ranging from 1.7 to 2.1 % from PITTs, sediment coring, and CPT tests conducted at the site.

This study showed that the push-pull test could be applied in laboratory and field settings using injected partitioning tracers (i.e., alcohols). In the field tests, costs were reduced in terms of time, equipment needs, and wastewater treatment relative to PITTs conducted at the site. Also, large volumes of the aquifer were interrogated relative to the volumes interrogated using coring and CPT methods. However, the use of an alcohol tracer is a potential hindrance to this method since regulatory approval may be required to use these tracers in the field.
RADON AS AN IN SITU PARTITIONING TRACER

The use of in situ partitioning tracers in push-pull tests provides a way to avoid the potential regulatory hurdle. Radon is well suited to serve as an in situ partitioning tracer. Radon (atomic number 86, chemical symbol: Rn) is the largest of the Group VIII noble gases, and is chemically inert due to the complete filling of its electron valence shells: \([\text{Xe}]4f^{44}5d^{10}6s^2p^6\). It is nonreactive and does not form an ionized or solid phase at earth surface temperatures and pressures. Radon is part of the uranium/thorium decay series. Like all elements with an atomic number > 82, the radon nucleus is unstable and undergoes radioactive decay. There are three naturally occurring radon isotopes: \(^{222}\text{Rn}\), originating from \(^{238}\text{U}\); \(^{224}\text{Rn}\), originating from \(^{232}\text{Th}\), and \(^{219}\text{Rn}\), originating from \(^{235}\text{U}\). Since \(^{238}\text{U}\) is the most abundant of the three parents, \(^{222}\text{Rn}\) (hereafter referred to as radon) is the most abundant of the three isotopes. The relatively long half-life of radon (3.83 days) results in its being commonly found in the vadose and saturated zones. It is continuously produced in the subsurface via the \(\alpha\)-decay of its parent, radium-226 (half-life of 1600 years) that is contained within the structure of aquifer minerals and/or exists as secondary mineral coatings. Radon is released (i.e., emanated) from the aquifer matrix via \(\alpha\)-decay. The mechanism for the emanation of radon from solids is understood to involve a combination of (Rama and Moore, 1984; Semkow and Parekh, 1990; Maraziotis, 1996): 1) direct recoil of the radon atom from the solid surface to the pore fluid; 2) diffusion of the radon atom from the crystal lattice of the mineral to the grain surface; and 3) recoil of the radon
atom within the crystal lattice to a dislocation plane or connected intragranular pore and diffusion to the grain surface. The emanation power is the fraction of radon produced that escapes from the solids into the pore water. Radon emanation is expressed in terms of pCi (1 pCi = 2.22 disintegrations per minute, or DPM) of radon emanated per unit mass (kg) of sediment. Radon that migrates to the pore water is available for measurement through aqueous sampling. Aqueous radon concentrations are expressed in pCi/L of water.

Radon is constantly emanating from radium-bearing aquifer solids and is also constantly decaying; thus the radon concentration in the pore water is determined by the secular equilibrium between radon emanation and decay as described by (Adloff and Guillaumont, 1993)

$$C_{Rn} = C_{Rn,\infty} (1 - e^{-kt}) + C_{Rn,0} e^{-kt}$$

(2.12)

where $C_{Rn}$ is the radon concentration (pCi/L) in the pore water at time $t$, $C_{Rn,\infty}$ is the equilibrium radon concentration, $C_{Rn,0}$ is the radon concentration in the pore water at the time the water is removed from the pore, and $k$ is radon's decay constant (0.181 days$^{-1}$). The secular equilibrium radon concentration is reached when the rate of radon emanation is equal to the rate of radon decay. Using radon's decay constant and equation 2.12 shows that 25 days are required for a parcel of radon-free water to obtain a radon concentration that is 99% of the equilibrium radon concentration. The equilibrium radon concentration is also a function of the bulk density and porosity of the aquifer. Thus the equilibrium radon concentration can be described by (Semprini et al., 2000)
where $C_{Ra}$ is the radium concentration in the aquifer solids (pCi/kg), $E_p$ is emanation power, $\rho_b$ is bulk density, and $n$ is porosity. Radon is moderately volatile, with a dimensionless Henry's coefficient of 3.9 (pCi/L/air/ pCi/L/liquid) at 20°C (Clever, 1979).

The environmental occurrence and behavior of radon has been investigated in numerous studies across a wide range of disciplines. Radon has been used to investigate: the thermodynamic, geologic and transport properties of geothermal reservoirs (Semprini, 1986); groundwater recharge rates (Hamada and Komae, 1998); groundwater residence times (Snow and Spalding, 1997); and groundwater discharge to the ocean (Cable et al., 1996). Additional studies have been performed using radon to: quantify groundwater flow rates in fractured bedrock aquifers (Cook et al., 1999); to investigate surface water mixing with groundwater (Bertin and Bourg, 1994); and to infer the bedrock geology underlying Quaternary aquifers (Morland et al., 1998). However, fewer studies have been performed relating to the phase partitioning behavior of radon. The ability of radon to partition from the aqueous phase into the DNAPL phase makes radon a candidate for locating and quantifying DNAPL contamination in the subsurface.

**Steady-State Partitioning Theory**

Semprini et al. (2000) presents the equations describing steady-state or equilibrium radon partitioning in the presence of DNAPL (these equations also apply
to LNAPLs). Radon has an affinity for partitioning into DNAPL; the linear partition coefficient \( K \) for radon is described by

\[
K = \frac{C_n}{C_{w,n}} \tag{2.14}
\]

where \( C_n \) is the concentration of radon in the DNAPL phase, and \( C_{w,n} \) is the concentration of radon in the aqueous phase in the presence of DNAPL. A value of \( K = 50 \) for radon in the presence TCE was determined using the methodology of Cantaloub (2001).

The steady-state or 'static' method involves calculating DNAPL saturations from a comparison of radon concentrations in groundwater samples obtained from DNAPL-contaminated and non-contaminated portions of the same aquifer. This method assumes secular equilibrium between radon emanation and decay, equilibrium radon partitioning between the water and DNAPL phases, and a constant background radon concentration. In the presence of DNAPL, radon will be distributed between the water and DNAPL phases as described by

\[
C_n S_n + C_{w,n} S_w = \frac{C_{Ra} E_p \rho_b}{n} \tag{2.15}
\]

Assuming linear equilibrium radon partitioning of radon between DNAPL and water, equation 2.15 can be rearranged as

\[
C_{w,n} = \frac{C_{Ra} E_p \rho_b / n}{1 + S_n (K - 1)} \tag{2.16}
\]

which can be further rearranged to solve for the DNAPL saturation...
where $C_{w,bkg}$ (the equivalent of $C_{Rn}$ in equation 2.13) is the radon concentration in groundwater in a ‘background’ zone outside of the DNAPL-contaminated zone or in the aquifer before DNAPL contamination has occurred. The sensitivity of radon to small DNAPL saturations is evident when equation 2.16 is used to plot radon concentration as a function of $S_n$ (Figure 2.4).

The plot shows that radon concentrations are sensitive to changes in $S_n$, especially at smaller values of $S_n$. Thus radon has the potential to quantify DNAPL saturations and changes in saturations, with greater efficacy at smaller saturations.
Also, radon’s short half-life and constant emanation from aquifer solids result in rapid re-equilibration of radon concentrations in pore water following changes in DNAPL saturation.

Dynamic Partitioning Theory

Semprini et al. (2000) also developed a 1-D advective-dispersive equation to describe radon transport (i.e., dynamic partitioning) in a DNAPL-contaminated matrix. The final form of this 1-D equation, incorporating radon transport, linear equilibrium partitioning as described by equation 2.4, emanation, and decay, is

\[
\frac{\partial C_{w,n}}{\partial t} = \frac{1}{S_w n R} \left[ D n S_w \frac{\partial^2 C_{w,n}}{\partial x^2} - \nu \frac{\partial C_{w,n}}{\partial x} + E \lambda \rho_b \right] - \lambda C_{w,n} \tag{2.18}
\]

where \( E = E_p \times C_{Ra} \) and \( \lambda \) is the first-order decay rate for radon (0.00754 hours\(^{-1}\)). This equation can be solved numerically using a finite difference technique to show temporal and spatial changes in radon concentration (Tasker, 1995). Equation 2.18 reduces to equation 2.16 under steady-state conditions. The steady-state and dynamic partitioning equations have been investigated in laboratory and field settings to determine the efficacy the method for locating and quantifying DNAPL contamination.
Radon as an Indicator of DNAPL Contamination

The static and dynamic methods have been investigated in the laboratory (Hopkins, 1995; Gottipati, 1996; Semprini et al., 1998, 2000) and in the field (Semprini et al., 1993, 1998, 2000; Hunkeler et al., 1997). Hopkins (1995) performed column studies using aquifer solids from the Canadian Air Forces Base Borden and Soltrol 200® as a NAPL. The columns were constructed with residual NAPL saturations of 0 to 8 % and were allowed 2-4 weeks for radon concentrations to reach equilibrium. After equilibration the columns were exchanged with radon-free water and the radon concentrations measured at the column outlet. Numerical simulations were performed for each column test and the results plotted as a function of the volume exchanged in the column. The results showed an inverse relationship between the maximum NAPL saturation in the column and the maximum radon concentration measured at the outlet. In addition, as NAPL saturation increased, so did the volume of radon-free water required for the outlet concentration to reach a radon concentration = 0 pCi/L. This is due to retarded transport of radon-free water. These results are in agreement with the steady-state and dynamic equations presented above. Numerical simulations provided good fits to the experimental data (Semprini et al., 2000).

Gottipati (1996) constructed soil columns containing sand and residual NAPL saturations ranging from 0 to 8 % using Soltrol 220® which were then remediated using a surfactant (Triton® X-100). The columns were constructed to contain 1, 5, and 8 % residual NAPL saturation and were flushed with sequential batches of surfactant.
to solubilize and remove the NAPL from the columns. Outlet radon concentrations were tracked to investigate the influence of NAPL solubilization and removal on the changes in the radon BTC (as defined by the “breakthrough” concentration of 0.5 when normalized to the initial radon concentration in the columns). The results showed that after surfactant remediation 1) the maximum measured radon concentrations in the columns increased, and 2) the time to the “breakthrough” concentration decreased. Thus the change in NAPL saturation in the columns was reflected in the behavior of the partitioning radon tracer, showing that radon could be used to track changes in NAPL saturation during remediation. Further evidence of the ability of radon to track changes in DNAPL saturation in PAMs using surfactant flooding was presented by Semprini et al. (1998). Using the static partitioning method, these experiments showed that radon concentrations in the contaminated portion of the PAM decreased after TCE contamination. Radon samples taken after surfactant remediation showed little change from pre-remediation samples, which was consistent with a mass balance on TCE recovered from the injection/extraction well showing that insufficient TCE had been removed to cause a change in radon concentrations.

Semprini et al. (1993; 2000) conducted two field applications of the methodologies at the Canadian Air Forces Base Borden. The first test involved the release of a mixed DNAPL (trichloromethane, trichloroethene, and tetrachloroethene) source into a shallow sand aquifer. The mixture was allowed to slowly dissolve under natural gradient conditions. Radon samples were obtained upgradient, within, and
downgradient of the DNAPL source zone. The radon concentrations in the DNAPL zone decreased by a factor of 2 to 3 vs. the upgradient zone, and rebounded to upgradient zone concentrations within a few meters of the source zone. A numerical simulation of the experimental data (using equation 2.18) showed good agreement between the data sets, with a DNAPL saturation of 4.5 % predicted by the simulation (the measured DNAPL saturation was 3.8 %). A second experiment was performed in a physically isolated test cell at the site in which 5 L of DNAPL was injected. The DNAPL was allowed to distribute itself in the test cell, forming an irregular DNAPL zone. Injection and extraction wells at opposite ends of the test cell created a groundwater velocity of 10.1 cm/day within the test cell. Steady-state radon concentrations were obtained by allowing the flow to continue for 1 month prior to radon sampling. Radon samples were then obtained at sampling wells upgradient and downgradient of the DNAPL source. The experimental data showed the presence of a DNAPL source between 0.5 and 1 m in length, with a residual DNAPL saturation of 4.5 to 7.8 %. Numerical simulations were found to be in good agreement with the experimental data. Excavation of the test cell later confirmed the presence of DNAPL in the predicted location. These studies showed that radon could be applied as a partitioning in situ tracer in the field to locate and quantify DNAPL saturation.

Hunkeler et al. (1997) performed a laboratory and field study of the method at a diesel fuel (LNAPL)-contaminated site in central Switzerland. The partition coefficient ($K$) for radon in diesel fuel was determined 1) using bottles containing tap water and diesel fuel, yielding a $K = 40$, and 2) in batch experiments with sand-filled
separatory funnels containing varying saturations of diesel fuel and tap water, yielding
\( K = 45 \). Two columns in series were used to model radon partitioning in an aquifer,
with the first column containing clean sand and the second column containing diesel
fuel. Flow rates were adjusted such that steady-state radon concentrations were
achieved as the radon left the first column, thus providing a source of radon-
equilibrated water for the second (contaminated) column. The calculated LNAPL
saturation in the column was 1.0 \%, which was in good agreement with the actual
measured value of 1.4 \%. The field experiment involved sampling radon
centrations under natural gradient conditions in monitoring wells upgradient and
downgradient from a diesel LNAPL contamination zone in a shallow sandy aquifer.
Nearly all wells containing aqueous phase hydrocarbons showed a decrease in radon
centrations relative to background concentrations. A LNAPL saturation of 1.5 \%
was calculated using the radon data, using \( K = 45 \) from the batch experiments. This
value was in agreement with the value of 1.9 \% measured in a core sample taken from
the contaminated zone.

Semprini et al. (1998) provided further evidence for the field applicability of
the method at a LNAPL and DNAPL-contaminated site at Lawrence Livermore
National Laboratory. Radon samples were obtained from 17 monitoring wells at the
site, with concentrations varying from 8 to > 1500 pCi/L. Since the background radon
centration was estimated to be 820 pCi/L (based on sediment emanation studies), it
was likely that radon samples with concentrations well below background values were
obtained from NAPL-bearing zones of the aquifer. Very low radon concentrations
were measured in locations where diesel and TCE were known to have spilled. Moreover, high radon concentrations were measured in locations with high aqueous TCE concentrations, providing evidence for the transport of aqueous TCE away from a DNAPL source zone. Thus the method was able to provide evidence for both the presence of DNAPL in one location and the absence of DNAPL in a second location.

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CHAPTER 3

Push-Pull Partitioning Tracer Tests Using Radon-222 To Quantify Nonaqueous Phase Liquid Contamination

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ABSTRACT

Naturally occurring radon in groundwater can be used as an in situ partitioning tracer for locating and quantifying nonaqueous phase liquid (NAPL) contamination in the subsurface. When combined with the single-well, push-pull test, this methodology has the potential to provide a low-cost alternative to inter-well partitioning tracer tests. During a push-pull test, a known volume of test solution (radon-free water containing a conservative tracer) is first injected ("pushed") into a well; flow is then reversed and the test solution/groundwater mixture is extracted ("pulled") from the same well. In the presence of NAPL radon transport is retarded relative to the conservative tracer. Assuming linear equilibrium partitioning, retardation factors for radon can be used to estimate NAPL saturations. The utility of this methodology was evaluated in laboratory and field settings. Laboratory push-pull tests were conducted in both non-contaminated and trichloroethene NAPL (TCE)-contaminated sediment. The methodology was then applied in wells located in non-contaminated and light nonaqueous phase liquid (LNAPL)-contaminated portions of an aquifer at a former petroleum refinery. The method of temporal moments and an approximate analytical solution to the governing transport equations were used to interpret breakthrough curves and estimate radon retardation factors; estimated retardation factors were then used to calculate TCE saturations. Numerical simulations were used to further investigate the behavior of the breakthrough curves. The laboratory and field push-pull tests demonstrated that radon retardation does occur in the presence of TCE and
LNAPL and that radon retardation can be used to calculate TCE saturations. Laboratory injection phase test results in TCE-contaminated sediment yielded radon retardation factors ranging from 1.1 to 1.5, resulting in calculated TCE saturations ranging from 0.2 to 0.9%. Laboratory extraction phase test results in the same sediment yielded a radon retardation factor of 5.0, with a calculated TCE saturation of 6.5%. Numerical simulation breakthrough curves provided reasonably good matches to the approximate analytical solution breakthrough curves. However, nonequilibrium radon partitioning and heterogeneous TCE distributions may affect the retardation factors and TCE saturation estimates.

INTRODUCTION

Nonaqueous phase liquids (NAPLs) are common groundwater contaminants at hazardous waste sites (Mercer and Cohen, 1990; Cohen and Mercer, 1993). Due to their high toxicity and low solubility in water, NAPLs can become long-term sources for dissolved contaminants in groundwater. Thus effective remediation requires the accurate location and quantification of NAPL saturations in the subsurface. This is particularly true for dense nonaqueous phase liquids (DNAPLs) because their high density causes them to migrate below the water table and move along pathways distinct from water flow (Schwille, 1988; Nelson and Brusseau, 1996).

A number of methods have been employed to characterize NAPL distribution at contaminated sites including soil coring, cone penetrometer testing, soil gas
analysis, and aqueous phase sampling. However, these methods can be costly and they typically interrogate relatively small aquifer volumes. Partitioning tracers including alcohols (e.g., 1-heptanol, 1-hexanol) and synthetic inert gases (i.e., SF$_6$) have been used to locate and quantify NAPL contamination in a variety of laboratory and field experiments (Jin et al., 1995; Wilson and Mackay, 1995; Nelson and Brusseau, 1996; Annable et al., 1998; Nelson et al., 1999; Young et al., 1999). In this approach, retardation factors for injected partitioning tracers are determined by measuring tracer concentrations in one or more monitoring wells. NAPL saturations are then computed from the retardation factors. Because partitioning tracer tests can be designed to sample much larger aquifer volumes (e.g., compared to sediment coring) they have the potential to accurately locate and quantify NAPL contamination.

Previous studies have suggested that naturally occurring radon-222 (hereafter referred to as radon) can be used as a partitioning tracer (Semprini et al., 1993; Hopkins, 1995; Gottipati, 1996; Hunkeler et al. 1997; Semprini et al., 1998; Semprini et al., 2000). Radon is a naturally occurring, radioactive, inert isotope that occurs in groundwater as a dissolved gas. Radon is part of the uranium-238 decay series and has a half-life of 3.83 days. It is continuously produced in the subsurface via the $\alpha$-decay of its parent, radium-226 (half-life of 1600 years) that is contained within the structure of aquifer minerals and/or exists as secondary mineral coatings. The steady-state radon concentration in groundwater ($C_{\text{rn}}$) is a function of the radium content ($C_{\text{Rad}}$) and radon emanation power ($E_r$) of the mineral phase and the bulk density ($\rho_b$) and porosity ($n$) of the aquifer (Semprini et al., 2000)
Values of $C_{Rn}$ are highly variable ranging from approximately 100 to 270,000 pCi/L in groundwater (National Research Council, 1999).

Radon is moderately volatile, with a dimensionless Henry's coefficient of 3.9 at 20° C (Clever, 1979). Due to its non-polarity radon has a high affinity for partitioning into NAPLs. The linear partition coefficient ($K$) for radon is defined as

$$K = \frac{C_{Rn,n}}{C_{Rn,w}}$$

(3.2)

where $C_{Rn,n}$ is the concentration of radon in the NAPL phase, and $C_{Rn,w}$ is the concentration of radon in the aqueous phase. The $K$ value for radon in the presence of trichloroethene DNAPL (hereafter referred to as TCE) has not been determined. An estimate of $K$ for radon in TCE can be determined using the Ostwald coefficient, which is defined as the ratio of the concentration of gas per unit volume of liquid phase to the concentration of gas per unit volume of gas phase (Clever, 1979). A $K = 58$ for radon in trichloromethane is estimated by dividing the Ostwald coefficient for radon in trichloromethane vs. radon in air by the Ostwald coefficient for radon in water vs. radon in air. In this study we assume a $K = 58$ for radon in TCE based on the estimate for trichloromethane. For light NAPLs (LNAPLs) measured values of $K$ for radon range from 37 (o-xylene) to 61 (cyclohexane) (Cantaloub, 2001).

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.,
In this study we evaluate the use of single-well, "push-pull" tracer tests using radon as a natural partitioning tracer to quantify TCE saturations. During a push-pull test, a known volume of test solution (radon-free water containing a conservative tracer) is first injected ("pushed") into a well; flow is then reversed and the test solution/groundwater mixture is extracted ("pulled") from the same well (Schroth et al., 2000). Laboratory push-pull tests were performed in physical aquifer models using sediment prepared with and without TCE. Field push-pull tests were performed in LNAPL-contaminated and non-contaminated portions of an aquifer at a former petroleum refinery. An approximate analytical solution to solute concentrations during the injection and extraction phases of the push-pull test was used to estimate radon retardation factors; retardation factors were then used to calculate TCE saturations in laboratory experiments. Numerical simulations were performed to investigate the validity of the approximate solution.

Our approach involves 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 are determined by estimating the radon 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

$$ R = \frac{v_w}{v_{Rn}} \quad (3.3) $$
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)

\[
R = 1 + \frac{KS_n}{S_w} \tag{3.4}
\]

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 can then be calculated via (Dwarakanath et al., 1999)

\[
S_n = \frac{R - 1}{R + K - 1} \tag{3.5}
\]

Figure 3.1 Simulated push-pull test extraction phase breakthrough curves for non-retarded and retarded in situ solutes.

Figure 3.1 shows the effect of varying retardation factor on numerically simulated extraction phase radon breakthrough curves for push-pull tests conducted by injecting radon-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 radon concentrations increase during the extraction phase since a radon-free test solution is injected. In the absence of NAPL, radon behaves like a conservative tracer ($R = 1$); in the presence of NAPL, radon transport is retarded ($R > 1$), resulting in an increased apparent dispersion during the extraction phase.

METHODS

Laboratory Push-Pull Tests

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 3.2). 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 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 3.2). 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 rest 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.

Following these tests the sediment pack was drained and excavated in sequential 5 cm thick layers to determine the vertical distribution of TCE contamination. For each 5 cm thick layer triplicate sediment samples (~ 100 g) were collected from a single location and placed in 125 mL glass jars. Each jar was then filled with ~ 65 mL of tap water, sealed, placed on a mechanical shaker for 30 minutes, and allowed to sit overnight. A 2 mL water sample was collected by inserting a syringe needle through a septum in the jar lid and analyzed for aqueous phase TCE.
Field Push-Pull Tests

Push-pull tests were performed at a former refinery in the Ohio River Valley. The aquifer is formed in glacial outwash deposits consisting primarily of sands and gravels. Portions of the site are contaminated with LNAPL, consisting primarily of jet fuel and gasoline. Tests were conducted in wells located within non-contaminated and contaminated portions of the site. For each test, ~250 L of test solution was injected. 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. Straddle packers were used to isolate 1.5 m long depth intervals of the well screen for testing. Intervals were chosen based on the inferred presence or absence of LNAPL within the aquifer as determined by soil coring during well installation and subsequent aqueous sampling. Test solutions were injected using a peristaltic pump (Cole-Parmer, Vernon Hills, IL) and the test solution/groundwater mixture was extracted using a submersible pump (Grundfos, Bjerringbro, Denmark). Approximately 500 L of injected solution and groundwater was removed from the well. Water samples were collected for bromide and radon analyses using a sampling line and syringe.
Analytical Methods

Bromide concentrations were determined using a Dionex Model DX-120 ion chromatograph equipped with an electrical conductivity detector (Sunnyvale, CA). Aqueous radon samples were filtered through a 0.45 μm filter (Millipore, Bedford, MA) attached to a syringe and a 1.5 inch steel needle (Becton-Dickinson, Franklin Lakes, NJ). The filtered sample (15 ± 0.5 mL) was then dispensed into the bottom of a pre-weighed 20 mL borosilicate scintillation vial containing 5 mL of Ultima Gold F scintillation “cocktail” (Packard Instruments, Meriden, CT). The exact mass of filtered sample added was determined by mass difference. Counting was performed with a Packard 2500 TR/AB Liquid Scintillation Analyzer (LSA) as described by Cantaloub (2001). Aqueous TCE was quantified using a Waters HPLC using the method described by Field and Sawyer (2000).

Data Analysis

Data analysis was performed using normalized concentrations. The normalized concentration for bromide is defined as $C^* = 1 - C/C_0$ where $C$ is the measured bromide concentration in a sample and $C_0$ 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.

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

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

$$m_1 = \int C^*(t) dt$$

The retardation factor for radon was then computed using

$$R = \begin{pmatrix} m_{1,Br^-} \\ m_{0,Br^-} \end{pmatrix} \over \begin{pmatrix} m_{1,Br^-} \\ m_{0,Br^-} \end{pmatrix}$$

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

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

(3.9)

where $r$ is radial distance from the injection well, $\alpha_L$ 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

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

(3.10)

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

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

(3.11)

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

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

(3.12)

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

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

(3.13)
where $r_{\text{max}}$ 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 $V_{\text{inj}}$ is the total volume of test solution injected.

For the laboratory tests, sampling port data from the injection phase were analyzed by using a minimized least-squares procedure to fit equation 3.9 to the normalized bromide data to obtain an estimate for $a_L$. Then another minimized least-squares procedure was used to fit equation 3.9 to the normalized radon data to obtain estimates for $R$ using the value of $a_L$ estimated from the bromide data.

For the laboratory and field tests, extraction phase normalized bromide data were fit to equation 3.11 using a minimized least-squares procedure to obtain another estimate for $a_L$. Then another minimized least-squares procedure was used to fit equation 3.11 to the normalized radon data to obtain an estimate for the maximum travel radius of the radon-free water. The retardation factor was then computed using

$$R = \left( \frac{r_{\text{max,Br}}}{r_{\text{max,Rn}}} \right)^2$$

Field test normalized breakthrough curve results were adjusted for the bromide data by dividing $V_{\text{ext}}/V_{\text{inj}}$ by the bromide mass fraction recovery achieved in the test. For the radon data, $V_{\text{ext}}/V_{\text{inj}}$ was divided by 1 - the mass fraction of bromide recovered during the test. This calculation was performed because only 42 to 57 % of the bromide injected was recovered during the field tests. The calculation assumes that dilution effects are uniform for bromide and radon; that is, any loss of test solution to the aquifer is matched by an equal gain in groundwater from the aquifer.
calculation served to force the bromide $C^* = 0.5$ value through $V_{ext}/V_{inj} = 1$; this simplified the comparison of the bromide and radon breakthrough curves and best-fit approximate solutions. The extraction phase approximate solution was then fit to the normalized bromide and radon data as described above.

The validity of the approximate analytical solution was evaluated using numerical simulations performed with the STOMP code (White and Oostrom, 2000). STOMP is a fully implicit volume-integrated finite difference simulator for modeling one-, two- and three-dimensional flow and transport, which has been extensively tested and validated against published analytical solutions as well as other numerical codes (Nichols et al., 1997). The computational domain consisted of a line of 250 nodes with a uniform radial node spacing of $\Delta r = 1.0$ cm. Initial conditions were a constant hydraulic head for the aqueous phase and $C = 0$ for all solutes. Time-varying third-type flux boundary conditions were used to represent pumping at the injection/extraction ports; constant head and zero solute flux boundary conditions were used to represent aquifer conditions beyond the radius of influence of the well. Bromide and radon transport were simulated using PAM sediment pack properties, best-fit $\alpha_l$ values obtained from the extraction phase approximate solution, and estimated $R$ values from the injection phase and extraction phase approximate solutions.
RESULTS

Laboratory Tests

Results for sampling ports 1 and 2 from the push phase of Test 1 conducted in the absence of TCE are shown in Figures 3.3a and 3.3b. Breakthrough curves are displayed as normalized concentration ($C^*$) versus dimensionless pore volume ($V_{\text{inj}}/V_{\text{pore}}$) for bromide and radon. In these figures $V_{\text{inj}}$ is the cumulative volume of injected test solution at the time the sample was collected, and $V_{\text{pore}}$ 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 3.9), with best-fit $\alpha_L$ values of 3.8 cm for port 1 and 6.6 cm for port 2 (Table 3.1). 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 3.1). 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 at port 2.
Figure 3.3a Injection phase breakthrough curves for lab Test 1, port 1 in the absence of TCE.

Figure 3.3b Injection phase breakthrough curves for lab Test 1, port 2 in the absence of TCE.
Retarded radon transport was not very apparent in extraction phase breakthrough curves for Test 1 (Figure 3.3c) where normalized concentration ($C^*$) is plotted as a function of the ratio $V_{\text{ext}}/V_{\text{inj}}$, where $V_{\text{ext}}$ is the cumulative volume of water extracted at the time the sample was collected and $V_{\text{inj}}$ 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 3.11), with a best-fit $\alpha_L$ of 3.2 cm (Table 3.1). A best-fit value of $R = 1.1$ was obtained for radon (Table 3.1). 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 3.1 Radon retardation factors \((R)\), adjusted retardation factors for the effect of trapped gas \((in\ italics)\), approximate solution best-fit dispersivities \((\alpha_L)\), and TCE saturations \((S_n)\) from push-pull tests.

<table>
<thead>
<tr>
<th>Injection Phase Approx. Solution</th>
<th>Extraction Phase Approx. Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R) (\alpha_L) (S_n) (\text{(cm)}) (\text{(%)})</td>
<td>(R) (\alpha_L) (S_n) (\text{(cm)}) (\text{(%)})</td>
</tr>
<tr>
<td>Test 1 Port 1</td>
<td>1.0 - -</td>
</tr>
<tr>
<td>Test 1 Port 2</td>
<td>1.2 - -</td>
</tr>
<tr>
<td>Test 1 Injection/Extraction Ports</td>
<td>- - -</td>
</tr>
<tr>
<td>Test 2 Port 1</td>
<td>1.4/1.4 - 0.7</td>
</tr>
<tr>
<td>Test 2 Port 2</td>
<td>1.7/1.5 - 0.9</td>
</tr>
<tr>
<td>Test 2 Injection/Extraction Ports</td>
<td>- - -</td>
</tr>
<tr>
<td>Field Test No LNAPL</td>
<td>- - -</td>
</tr>
<tr>
<td>Field Test With LNAPL</td>
<td>- - -</td>
</tr>
</tbody>
</table>

Radon transport was retarded during the push phase of Test 2 conducted in the presence of 2 % TCE (Figures 3.4a and 3.4b). The data were well fit by the injection phase approximate solution, with best-fit \(\alpha_L\) values of 3.4 cm at port 1 and 2.1 cm at port 2 (Table 3.1). 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 3.1). 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 3.4a Injection phase breakthrough curves for lab Test 2, port 1 with 2 % TCE.

Figure 3.4b Injection phase breakthrough curves for lab Test 2, port 2 with 2 % TCE.
Retarded radon transport was apparent in extraction phase breakthrough curves for Test 2 (Figure 3.4c). 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 $\alpha_e$ of 4.0 cm (Table 3.1). An estimated value of $R = 5.1$ was obtained for radon using the extraction phase approximate solution (Table 3.1). 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.
Field Tests

Radon retardation was investigated using extraction phase breakthrough curves from two wells at the field site. Radon transport was slightly retarded in Test 1 conducted in the absence of LNAPL (Figure 3.5a). Normalized concentrations increased smoothly as the test solution was extracted from the aquifer. However, the shapes of the extraction phase breakthrough curves differed from those in the laboratory tests. This is likely due to a greater apparent dispersion and/or heterogeneity in hydraulic conductivity in the natural sediment. The best-fit $\alpha_L$ was 38.6 cm (Table 3.1). The radon data were well fit by the extraction phase approximate solution; the estimated retardation factor for radon was 1.6 (Table 3.1).

Radon transport was retarded in Test 2 conducted in the presence of LNAPL (Figure 3.5b). Again, the shape of the extraction phase breakthrough curves differed from those from the laboratory tests. The best-fit $\alpha_L$ was 20.3 cm (Table 3.1). The bromide data were well fit by the extraction phase approximate solution, but the radon data were poorly fit by the extraction phase approximate solution; the estimated retardation factor for radon was 7.3 (Table 3.1).
Figure 3.5a  Extraction phase breakthrough curves for field Test 1 with no LNAPL.

Figure 3.5b  Extraction phase breakthrough curves for field Test 2 with LNAPL.
DISCUSSION

Laboratory Tests

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

\[ R = 1 + H_{cc} \frac{S_g}{S_w} \]  

(3.15)

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 3.15 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

\[ R_{adj} = R_{test2} - (R_{test1} - 1.0) \]  

where \( R_{adj} \) is the adjusted retardation factor, \( R_{test2} \) is the retardation factor from Test 2, and \( R_{test1} \) 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 3.1).

Table 3.2. Aqueous TCE as a function of depth in the PAM sediment pack.

<table>
<thead>
<tr>
<th>Depth Interval (cm)</th>
<th>TCE (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 5</td>
<td>3.9</td>
</tr>
<tr>
<td>5 – 10</td>
<td>9.8</td>
</tr>
<tr>
<td>10 – 15</td>
<td>77.2</td>
</tr>
<tr>
<td>15 – 20</td>
<td>273.2</td>
</tr>
</tbody>
</table>

Using equation 3.5, adjusted injection phase retardation factors, and \( K = 58 \), calculated TCE saturations ranged from 0.2 to 0.9 % (Table 3.1), which is less than the volume-averaged TCE saturation of 2 % in the sediment pack. This underestimation may be due to nonequilibrium 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 3.2), 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. However, uncertainties in radon’s \( K \) in TCE would also result in a miscalculation of \( S_n \) in the sediment pack, with a smaller value of \( K \) providing a larger calculated TCE saturation. The extraction phase adjusted radon retardation factor was 5.0 (Table 3.1). 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. The reasons for the greater estimated retardation factor during the extraction phase are unclear. Because the extraction phase approximate solution closely matches the numerical solution (Figure 3.4c), the overestimation of the retardation factor and thus TCE saturation is not likely due to an error in the extraction phase approximate solution. A possible reason for the greater estimated retardation factor may be that the contact time between the test solution and the TCE is greater for samples taken during the extraction phase of the test. This may be explained as follows. For a sample taken during the injection phase, the test
solution is subject to partitioning from the time the solution enters the PAM to when a sample is removed from a sampling port. In contrast, for a sample taken during the extraction phase the test solution is subject to partitioning from the time the solution enters the PAM, through the completion of the injection phase and flow reversal (the extraction phase) and, ultimately, until sampling of the solution at the injection/extraction ports. This could result in a more retarded radon breakthrough curve during the extraction phase relative to the injection phase.

Numerical simulations using STOMP were used to check the validity of the approximate solution by running simulations using the values of $a_L$ that were best-fit by the extraction phase approximate solution for the $R$ values estimated by the injection and extraction phase approximate solutions. The numerical simulation results show that $a_L$ is adequately estimated by the extraction phase approximate solution; this is evident in the moderately good match between the extraction phase approximate solution and numerical simulation breakthrough curves (Figures 3.3c and 3.4c).

For Test 1, the best-fit values of $a_L$ for the injection phase approximate solution were 3.8 cm at port 1 and 6.6 cm at port 2, while the best-fit value of $a_L$ for the extraction phase approximate solution was 3.2 cm. (Table 3.1). The higher best-fit value of $a_L$ at port 2 is a result of the more dispersed bromide breakthrough curve (Figure 3.3b). The reason for the more dispersed bromide breakthrough curve at port 2 is unclear. This resulted in the numerical simulations providing a poor match to the injection phase approximate solution at port 2. However, the numerical simulations
provided a moderately good match to the injection phase approximate solution at port 1. For Test 2, the best-fit values of $a_L$ for the injection phase approximate solution were 3.4 cm at port 1 and 2.1 cm at port 2. The difference between the port 2 best-fit values of $a_L$ between Tests 1 and 2 is possibly due to the presence of TCE in Test 2. The injection of TCE into the sediment pack may have reduced the pore size distribution through which water could flow, thus reducing $a_L$. The best-fit value of $a_L$ for the Test 2 extraction phase approximate solution was 4.0 cm. The numerical simulations provided a moderately good match to the injection phase approximate solution at ports 1 and 2.

Field Tests

The minimal radon retardation observed in Test 1 (Figure 3.5a) may be attributed to partitioning of radon between the pore water and trapped gas present in the aquifer. Radon was significantly retarded in Test 2 conducted in the LNAPL-contaminated portion of the site (Figure 3.5b), with an adjusted retardation factor of 6.7 (Table 3.1). Retardation in Test 2 is attributed to partitioning of radon between the injected test solution, LNAPL, and trapped gas in the aquifer. In Test 2 the extraction phase approximate solution provides a poor fit to the radon breakthrough curve, and thus the adjusted $R = 6.7$ has a high uncertainty. Note that for the radon breakthrough curve, $C^* = 0.5$ passes through $V_{ext}/V_{inj} = 2$. This may have resulted from a heterogeneous LNAPL distribution and/or nonideal transport (i.e., nonequilibrium
partitioning) during the test. Schroth et al. (2000) found that simulated push-pull tests with linear nonequilibrium partitioning resulted in the partitioning tracer \( C^* = 0.5 \) passing through \( V_{\text{ext}}/V_{\text{inj}} \) at values greater than 1. Nonequilibrium partitioning can occur in the presence of NAPL pools. Pools can create a mass transfer limitation to partitioning that may account for the tailing in the radon breakthrough curve and its poor fit to the extraction phase approximate solution. In this case LNAPL pools could inhibit the equilibrium partitioning of radon between the LNAPL and the test solution during the timescale of the push-pull test. In this test, nonideal radon breakthrough curve behavior limited the applicability of the method in accurately determining the LNAPL saturation.

CONCLUSIONS

Overall, the laboratory test results show that the methodology is capable of detecting and quantifying NAPL saturations. Using radon as a partitioning tracer requires only the injection of radon-free water containing a conservative tracer, while the single-well, push-pull test requires smaller water volumes compared to inter-well tracer tests. These factors can reduce the costs of determining NAPL saturations. However, future research is needed to investigate the reasons for the differences between injection and extraction phase retardation factors. The influence of nonequilibrium radon partitioning on breakthrough curve behavior and the role of heterogeneous NAPL distributions (i.e., layered systems) need to be determined.
Numerical modeling should be employed to investigate the role of these phenomena in influencing injection and extraction phase retardation factors and calculated NAPL saturations. More detailed field investigations using the radon push-pull method described here are also needed where detailed information on residual NAPL saturations is available.

ACKNOWLEDGEMENTS

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REFERENCES


CHAPTER 4

Static and push-pull methods using radon-222 to characterize dense nonaqueous phase liquid saturations

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Ground Water

In Press
ABSTRACT

Naturally occurring radon in ground water can potentially be used as an in situ partitioning tracer to characterize dense nonaqueous phase liquid (DNAPL) saturations. The static method involves comparing radon concentrations in water samples from DNAPL-contaminated and non-contaminated portions of an aquifer, while the push-pull method involves the injection (push) and extraction (pull) of a radon-free test solution from a single well. In the presence of DNAPL, radon concentrations during the pull phase are retarded, with retardation manifested in greater dispersion of radon concentrations relative to a conservative tracer. The utility of these methods was investigated in the laboratory using a physical aquifer model (PAM). Static and push-pull tests were performed before and after contamination of the PAM sediment pack with trichloroethene (TCE), and after alcohol cosolvent flushing and pump-and-treat remediation. Numerical simulations were used to estimate the retardation factor for radon in push-pull tests. Radon partitioning was observed in static and push-pull tests conducted after TCE contamination. Calculated TCE saturations ranged up to 1.4 % (static test) and 14.1 % (push-pull test). Post-remediation tests showed decreases in TCE saturations. The results show that radon is sensitive to changes in DNAPL saturation in space and time. However, the methods are sensitive to DNAPL saturation heterogeneity, test location, sample size, and test design. The influence of these factors on test results, as well as the apparent
overestimation of the retardation factor in push-pull tests, warrant further investigation.

INTRODUCTION

The release of nonaqueous phase liquids (NAPLs) to the subsurface environment can create long-term sources of ground water contamination as the NAPL slowly dissolves into ground water (Mercer and Cohen, 1990; Cohen and Mercer, 1993). Effective remediation of subsurface NAPL contamination requires that NAPL be accurately located and saturations quantified. This is particularly important for dense nonaqueous phase liquids (DNAPLs) since their high density causes them to migrate below the water table and move along pathways distinct from water flow (Schwille, 1988; Nelson and Brusseau, 1996).

Laboratory and field studies have shown that partitioning tracers can be used to locate and quantify NAPL contamination (Jin et al., 1995; Wilson and Mackay, 1995; Nelson and Brusseau, 1996; Annable et al., 1998; Nelson et al., 1999; Young et al., 1999). Partitioning tracers have the advantage of interrogating larger aquifer volumes compared to traditional coring techniques. These studies have typically involved the injection of a suite of conservative and partitioning tracers at one well, followed by the measurement of the tracers at one or more monitoring wells (i.e., an interwell tracer test). An alternative approach involves the use of single well “push-pull tests” in which the tracers are injected and extracted from the same well (Schroth et al., 2000;...
Davis et al., 2002). Retardation factors for injected partitioning tracers are determined from concentration breakthrough curves and, assuming linear equilibrium partitioning, NAPL saturations are calculated (see below).

Naturally occurring radon-222 (hereafter referred to as radon) can be used in lieu of injected partitioning tracers for locating and quantifying NAPL contamination. Radon is a naturally occurring, radioactive, inert isotope that occurs in ground water as a dissolved gas. A part of the uranium-238 decay series, radon has a half-life of 3.83 days and is continuously produced through the α-decay of radium-226 (half-life of 1600 years) that is contained within the structure of aquifer minerals and/or exists as secondary mineral coatings.

Radon has previously been used to investigate ground water recharge rates (Hamada and Komae, 1998), ground water residence times (Snow and Spalding, 1997), and ground water discharge to the ocean (Cable et al., 1996). Studies have shown that radon can be used as a partitioning tracer to locate and quantify NAPL contamination (Semprini et al., 1993; Hopkins, 1995; Gottipati, 1996; Hunkeler et al., 1997; Semprini et al., 1998; Semprini et al., 2000; Davis et al., 2002). In ground water, the equilibrium or ‘background’ radon concentration ($C_{w,bkg}$) is a function of the radium content ($C_{Ra}$) and radon emanation power ($E_p$) of the mineral phases and the bulk density ($\rho_b$) and porosity ($n$) of the aquifer (Semprini et al., 2000)

$$C_{w,bkg} = \frac{C_{Ra} E_p \rho_b}{n}$$

(4.1)

Values of $C_{w,bkg}$ are highly variable ranging to 270,000 pCi/L or more in public water supplies (Hess et al., 1985; National Research Council, 1999). Radon is moderately
volatile, with a dimensionless Henry's coefficient ($H_{cc}$) of 3.9 at 20° C (Clever, 1979). Radon has an affinity for partitioning into NAPL; the linear partition coefficient ($K$) for radon is defined as

$$K = \frac{C_n}{C_{w,n}}$$ (4.2)

where $C_n$ is the concentration of radon in the NAPL phase, and $C_{w,n}$ is the concentration of radon in the aqueous phase in the presence of NAPL.

Both static and push-pull methods using radon as a partitioning tracer can be used to locate and quantify NAPL contamination. The static method involves calculating NAPL saturations from a comparison of radon concentrations in ground water samples obtained from NAPL-contaminated and non-contaminated portions of the same aquifer. 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

$$C_nS_n + C_{w,n}S_w = \frac{C_{Ra} E_p \rho_b}{n}$$ (4.3)

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 4.2), equation 4.3 can be rearranged as

$$C_{w,n} = \frac{C_{Ra} E_p \rho_b / n}{1 + S_n (K - 1)}$$ (4.4)

which can be further rearranged to solve for the NAPL saturation
\[ S_n = \left( \frac{C_{w,bkg}}{C_{w,n}} \right) - 1 \left( \frac{1}{(K-1)} \right) \]  

(4.5)

where \( C_{w,n} \) is the radon concentration in ground water in the NAPL-contaminated zone and \( C_{w,bkg} \) is the radon concentration in ground water in a 'background' zone outside of the NAPL-contaminated zone or in the aquifer before NAPL contamination has occurred. 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/ground water 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)

\[ R = 1 + \frac{KS_n}{S_w} \]  

(4.6)

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

\[ S_n = \frac{R-1}{R+K-1} \]  

(4.7)

In this study we evaluate the use of static and push-pull methods using radon as an in situ partitioning tracer to estimate TCE DNAPL (hereafter referred to as TCE)
saturations in a laboratory physical aquifer model (PAM) after TCE contamination and remediation. Spatial and temporal changes in static radon concentrations are used to estimate changes in TCE saturations, and push-pull test radon retardation factors are used to estimate TCE saturations as a function of space and time and to estimate the efficacy of remediation.

METHODS

Experimental Methods

Static and push-pull tests were performed in selected portions of a large-scale rectangular PAM (Figures 4.1 and 4.2; experimental timeline shown in Table 4.1). The PAM consists of an aluminum box with interior dimensions of 4 m (length), 2 m (width), and 0.2 m (depth). Constant head reservoirs are located at each end of the PAM. Perforated aluminum plates covered with stainless steel screens separate the sediment pack from the reservoirs. The water height in the reservoirs is controlled by standpipe/overflow systems. An array of fully penetrating wells is fitted into the bottom of the PAM. The PAM is covered with an aluminum lid that is clamped to a flange around the perimeter. Sampling ports are located in the lid; these ports consist of a brass fitting through which a needle can be inserted into the sediment pack below. A more extensive description of the PAM can be found in Humphrey (1992).
The PAM was 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 clean sand with approximately 30 % fine gravels and less than 5 % silt and clay. The sediment contains less than 0.001 wt % organic matter, and has a uniform bulk density (after packing) of 1.72 g/cm³ and calculated porosity of 0.39. After sediment packing the PAM was saturated with tap water from the constant head reservoirs, which was used as the synthetic ground water in all laboratory experiments.

Figure 4.1 Photograph of physical aquifer model (PAM) used in laboratory tests.
For some tests, a portion of the sediment pack contained a known initial quantity of liquid TCE. This was achieved by slowly injecting aliquots of neat TCE at depths between 2.5 and 17.5 cm through 18 ports in the PAM lid (these ports do not correspond to the sampling ports described above) using a 10 mL glass syringe (SGE, Ringwood, Australia) connected to a 12 gauge stainless steel needle (Aldrich Chemical, Milwaukee, WI). A total of 210.2 g (144 mL) of TCE was injected to create concentric zones of 6 % and 3 % TCE saturation (Figure 4.5). Following TCE injection, a push-pull test (described below) was conducted through the fully penetrating well to entrap TCE within the pore space (water samples were not obtained during this test).

Static and push-pull tests were performed under confined conditions. Each test was preceded by at least a three week rest period during which radon concentrations reached > 95 % of their equilibrium value as a result of concurrent radon emanation from sediment and decay (Adloff and Guillaumont, 1993). Static tests were performed under no-flow conditions by extracting 20 mL water samples through PAM sampling ports using a 20 mL plastic syringe (Becton-Dickinson, Franklin Lakes, NJ) attached to a 12 gauge stainless steel needle that was inserted into the sediment pack through a sampling port.

Push-pull tests were performed 1) in a fully penetrating well located in the center of the TCE-contaminated portion of the PAM (Figure 4.2), and 2) in sampling ports using a 12 gauge stainless steel needle inserted into the sediment pack. For the fully penetrating well tests, 10 L of test solution were injected and 20 L were
extracted, while for the sampling port tests 1.2 L were injected and 2.4 L were extracted. Test solutions were injected and extracted using a piston pump (Fluid Metering, Oyster Bay, NY). 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. Injection and extraction pumping rates were constant at ~50 mL/min for the fully penetrating well tests and ~40 mL/min for the sampling port tests. Pull phase water samples were obtained using a 20 mL plastic syringe connected to a valve in a sampling line.

Figure 4.2 Plan view of portion of PAM used in laboratory tests, showing dimensions, fully penetrating well (x), sampling ports (●), and static radon concentrations prior to contamination of the PAM with TCE. Samples were obtained at a depth of 10 cm.

Time series concentration profiles of aqueous TCE and radon in the sediment pack after TCE contamination were obtained using a 15 L pull test (i.e., with no push
phase preceding the pull phase) performed in the fully penetrating well. Water samples were obtained at depths of 7.5, 10 and 17.5 cm within the TCE-contaminated portion of the sediment pack using 20 mL plastic syringes and 12 gauge stainless steel needles. Also, the fully penetrating well was used to obtain depth-integrated samples over the entire sediment pack.

Following a series of static and push-pull tests, ethanol cosolvent and tap water flushes were used to solubilize and remove TCE from the sediment pack. A 75 % denatured ethanol (Fisher Scientific, Fair Lawn, NJ) solution was injected into the sediment pack (with four piston pumps) through four 12 gauge stainless steel needles set within the TCE-contaminated portion of the PAM. The injection rate was 5 mL/min for each of the pumps. Another piston pump was used to simultaneously extract the ethanol solution/PAM water mixture through the fully penetrating well located at the center of the TCE-contaminated portion of the PAM. This pump was calibrated at 20 mL/min to create a steady-state flow regime in the PAM. A total of 89 L of ethanol solution were injected into the TCE-contaminated zone of the PAM. Following the ethanol flushes, approximately 1150 L of tap water (~ 2 pore volumes) were flushed through the PAM from the constant head reservoirs through the fully penetrating well. Water samples were obtained during the ethanol and tap water flushes using a 5 mL glass syringe (SGE, Ringwood, Australia) connected to a valve located in a sampling line. Static and push-pull tests were performed after remediation of the sediment pack.
The sediment pack was then drained and four core samples were obtained adjacent to the fully penetrating well. Each core sample was divided into three sections of equal length and each section placed in a 125 mL glass jar. Each jar was then filled with ~ 95 mL of methanol (Fisher Scientific, Fair Lawn, NJ), sealed, and placed on a mechanical shaker for 30 minutes. A 2 mL sample was collected by inserting a syringe needle through a septum in the jar lid and analyzed for methanol-extracted TCE.

Analytical Methods

Bromide concentrations were determined using a Dionex Model DX-120 ion chromatograph equipped with an electrical conductivity detector (Sunnyvale, CA). Aqueous radon samples were filtered through a 2.0 μm filter (Millipore, Bedford, MA) attached to a syringe and a 1.5 inch steel needle (Becton-Dickinson, Franklin Lakes, NJ). The filtered sample (~ 15 mL) was then dispensed into the bottom of a pre-weighed 20 mL borosilicate scintillation vial containing 5 mL of Ultima Gold F scintillation “cocktail” (Packard Instruments, Meriden, CT). Counting was performed with a Packard 2900 TR Liquid Scintillation Analyzer (LSA) as described by Cantaloub (2001). Aqueous TCE was quantified using a Waters HPLC using the method described by Field and Sawyer (2000), with a detection limit of 1 mg/L. The methodology of Cantaloub (2001) was used to determine the partition coefficient (K) for radon in the presence of TCE (Appendix D). This methodology incorporates a
sequential liquid-liquid extraction technique using aqueous radium-226 and TCE. The radium-226 is used to generate radon-222. For each sequential extraction, an aliquot of TCE was added to a glass centrifuge tube containing aqueous radium-226, the solution was thoroughly mixed, and the TCE (now containing a proportion of the radon generated from the radium-226) removed. The TCE was then added to a liquid scintillation vial for counting. A value of $K = 50$ was determined, compared to a value of $K = 58$ for radon in the presence of trichloromethane (Clever, 1979).

**Data Analysis**

Static radon data were used to calculate TCE saturations ($S_n$, equation 4.5) after TCE contamination of the sediment pack, and after remediation. Radon and aqueous TCE concentrations and calculated values of $S_n$ were plotted using the Surfer® software package (Golden Software, Golden, CO).

Push-pull test data analysis was performed using normalized bromide and radon concentrations. The normalized bromide concentration is defined as $C^* = 1 - \frac{C}{C_0}$, where $C$ is the measured bromide concentration in a sample and $C_0$ is the bromide concentration in the injected test solution ($\sim 100$ mg/L). This calculation is performed to facilitate the comparison of bromide and radon breakthrough curves. The normalized radon concentration is defined as $C^* = \frac{C_w}{C_b}$, where $C_w$ is the measured radon concentration and $C_b$ is the background radon concentration in the sediment pack, which was measured prior to each push-pull test. Push-pull tests were
performed within < 8 hours so that radon emanation could be neglected. For each push-pull test, pull phase normalized radon and bromide concentrations were plotted as a function of dimensionless time $V_e/V_i$, where $V_e$ is the volume of solution extracted from the sediment pack at the time a water sample was obtained, and $V_i$ is the total volume of solution injected into the sediment pack. Pull test radon and aqueous TCE concentrations were plotted as a function of the volume of solution extracted from the sediment pack at the time a sample was obtained.

Numerical simulations were performed with the Subsurface Transport Over Multiple Phases (STOMP) code, a fully implicit volume-integrated finite difference simulator (White and Oostrom, 2000). Solute transport was simulated using PAM sediment pack properties for a range of retardation factors ($R$). The longitudinal dispersivity of the sediment pack was estimated for each push-pull test by fitting the experimental normalized bromide breakthrough curve to an approximate analytical solution for the pull phase of the test (Gelhar and Collins, 1971; Schroth et al., 2000) as described by Davis et al. (2002). This dispersivity value was then used in the simulation of each push-pull test for a range of retardation factors ($R$) using STOMP, thus producing a series of simulated breakthrough curves. A least-squares method was used to determine which simulated breakthrough curve (corresponding to a specific value of $R$) best fit the experimental normalized radon breakthrough curve for each push-pull test. The value of $S_n$ for the best fit value of $R$ was then calculated using equation 4.7.
RESULTS

Prior to TCE contamination, static radon concentrations from samples obtained at a depth of 10 cm ranged from 181 to 224 pCi/L (Figure 4.2), with this variability likely due to heterogeneity of porosity and radon emanation in the sediment pack. Results from the pull phase of a push-pull test conducted prior to TCE contamination at a depth of 10 cm in sampling port 3 (location shown in Figure 4.2) are shown in Figure 4.3. Breakthrough curves are displayed as normalized concentration ($C^*$) versus dimensionless time ($V_e/V_i$) for bromide and radon. Normalized concentrations increased smoothly as the test solution was extracted from the sediment pack, and radon transport was slightly retarded relative to bromide. The normalized bromide concentration data were well fit by a simulated $R = 1$ breakthrough curve, while the normalized radon concentration data were best fit by a simulated $R = 1.2$ breakthrough curve (Table 4.1). Additional push-pull tests performed under the same conditions at different sampling ports (data not shown) showed results similar to Figure 4.3. Following these tests TCE was injected into the PAM sediment pack as described above.
Figure 4.3 Pull phase breakthrough curves for a push-pull test conducted in sampling port 3 prior to contamination of the PAM with TCE. The test was conducted at a depth of 10 cm.

Two months after TCE contamination a push-pull test was conducted in the fully penetrating well. Normalized concentrations increased smoothly as the test solution was extracted from the sediment pack, and radon transport was retarded relative to bromide with the radon retardation manifested as greater dispersion relative to bromide (Figure 4.4). The normalized bromide concentration data were well fit by a simulated $R = 1$ breakthrough curve while the normalized radon concentration data were best fit by a simulated $R = 9.4$ breakthrough curve (Table 4.1). Another static test was then performed with radon samples again being obtained from a depth of 10 cm (Figure 4.5).
Figure 4.4 Pull phase breakthrough curves for the first push-pull test conducted in the fully penetrating well after contamination of the PAM with TCE.

Figure 4.5 Plan view of static radon concentrations after contamination of the PAM with TCE. Samples were obtained at a depth of 10 cm.
Table 4.1 Experimental timeline and push-pull test results, showing best fit radon retardation factors ($R$), adjusted retardation factors, and TCE saturations ($S_n$).

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Months after TCE contamination</th>
<th>Figure</th>
<th>Test Location</th>
<th>Depth of Test (cm)</th>
<th>Volume injected (L)</th>
<th>Adjusted $R$</th>
<th>$S_n$ (%)</th>
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Radon concentrations ranged from 166 to 225 pCi/L. The radon retardation in the previous push-pull test, combined with the negligible change in static radon concentrations at the 10 cm depth relative to pre-contamination concentrations (Figure 4.2) supported a hypothesis that TCE had sunk to the bottom of the sediment pack. A second push-pull test was conducted in the fully penetrating well 8 months after TCE contamination. Normalized concentrations increased smoothly as the test solution was extracted from the sediment pack, although the radon data exhibited some unexplained tailing at the end of the test (Figure 4.6). Radon transport was retarded relative to bromide, but to a lesser extent than the earlier test (Figure 4.4). The normalized bromide concentration data were well fit by a simulated \( R = 1 \) breakthrough curve while the normalized radon concentration data were best fit by a simulated \( R = 3.8 \) breakthrough curve (Table 4.1), compared to the larger best fit \( R = 9.4 \) for the first push-pull test in the fully penetrating well. The decrease in \( R \) between the two tests indicated a change in TCE saturation and is consistent with the hypothesis that TCE had sunk.

A 15 L pull test was then conducted to further investigate the TCE distribution in the sediment pack. Time series concentration profiles show that radon concentrations decreased with depth with the exception of the 7.5 cm depth (Figure 4.7a), where partitioning to a gas phase at the top of the sediment pack probably resulted in reduced concentrations. The decrease in radon concentrations between 3 and 5 L at the 17.5 cm depth likely results from water originating from a zone of high TCE saturation toward the bottom of the sediment pack. Aqueous TCE concentrations
increased with depth and approached the solubility limit (~ 1000 mg/L) at 17.5 cm (Figure 4.7b), which correlates well with decreasing radon concentrations with depth to indicate that TCE had sunk to the bottom of the sediment pack.

Figure 4.6 Pull phase breakthrough curves for the second push-pull test conducted in the fully penetrating well after contamination of the PAM with TCE.
Figure 4.7a Time series concentration profile of radon concentrations (pCi/L) for a pull test conducted after contamination of the PAM with TCE. Samples were obtained from the fully penetrating well (average = 157.7, standard deviation = 9.1), and from needles located at depths of 7.5 cm (average = 170.1, standard deviation = 10.6); 10 cm (average = 197.0, standard deviation = 9.6); and 17.5 cm (average = 147.5, standard deviation = 11.3).

Figure 4.7b Time series concentration profile of aqueous TCE concentrations (mg/L) for a pull test conducted after contamination of the PAM with TCE. Samples were obtained from the fully penetrating well (average = 334.1, standard deviation = 39.4), and from needles located at depths of 7.5 cm (average = 66.7, standard deviation = 11.5); 10 cm (average = 120.8, standard deviation = 22.1); and 17.5 cm (average = 779.6, standard deviation = 65.3).
Following the 15 L pull test another static test was performed, with radon and aqueous TCE samples obtained at a depth of 19.5 cm. This depth was chosen to further investigate the hypothesis that TCE had sunk to the bottom of the sediment pack. Unfortunately, radon samples were not collected from this depth prior to TCE contamination. Due to partitioning into TCE, radon concentrations were reduced in the sediment pack, ranging from 120 to 217 pCi/L (Figure 4.8a), compared to the previous static test conducted at a depth of 10 cm (Figure 4.5). The greatest radon concentration reductions occurred in the vicinity of the concentric zones of 6 % and 3 % TCE saturation. Aqueous TCE concentrations ranged from 251 mg/L to the solubility limit, with the highest concentrations located in the 6 % and 3 % TCE saturation zones (Figure 4.8b). Calculated TCE saturations ($S_n$) show a maximum value of 1.4 % (Figure 4.8c) in the vicinity of both the lowest radon concentrations and the highest aqueous TCE concentrations.
Figure 4.8a  Plan view of static radon concentrations after contamination of the PAM with TCE. Samples were obtained from a depth of 19.5 cm.

Figure 4.8b  Plan view of static aqueous TCE concentrations after contamination of the PAM with TCE. Samples were obtained from a depth of 19.5 cm.
Figure 4.8c Plan view of calculated TCE saturations ($S_n$) after contamination of the PAM with TCE. Samples were obtained from a depth of 19.5 cm.

The TCE in the sediment pack was then remediated using a series of ethanol cosolvent and tap water flushes. Gross mass balance TCE calculations were performed using aqueous TCE data from the remediation activities and the 15 L pull and push-pull test immediately preceding remediation. These calculations showed that roughly 50% of the injected TCE was removed over the course of these experiments. However, the actual amount of TCE removed is likely greater than 50% since additional push-pull tests were performed where aqueous TCE was not sampled. The remediation was followed by a three week rest period to allow for the equilibration of radon concentrations in the pore water. Another static test was then performed at a depth of 19.5 cm. Radon concentrations increased across portions of the PAM and decreased in other locations (ranging from 140 to 219 pCi/L, Figure 4.9a) and aqueous
TCE concentrations were decreased (ranging from $< 1$ to 19 mg/L, Figure 4.9b). Calculated TCE saturations ($S_n$) show a maximum value of 1.3 % in the vicinity of the lowest radon concentrations (Figure 4.9c), although aqueous TCE concentrations were $< 5$ mg/L in this portion of the PAM.

Figure 4.9a Plan view of static radon concentrations after PAM remediation. Samples were obtained from a depth of 19.5 cm.
Figure 4.9b  Plan view of static aqueous TCE concentrations after PAM remediation. Samples were obtained from a depth of 19.5 cm.

Figure 4.9c  Plan view of calculated TCE saturations ($S_n$) after PAM remediation. Samples were obtained from a depth of 19.5 cm.
Another push-pull test was then performed in the fully penetrating well. Normalized concentrations increased smoothly as the test solution was extracted from the sediment pack, although there is no clear evidence for radon retardation relative to bromide (Figure 4.10). The normalized bromide concentration data were not well fit by a simulated $R = 1$ breakthrough curve. The normalized radon concentration data were best fit by a simulated $R = 1$ breakthrough curve, although the fit is poor (Table 4.1). The normalized bromide and radon concentration data show increased dispersion compared to identical push-pull tests conducted before remediation (Figures 4.4 and 4.6), making breakthrough curve interpretation difficult.

Push-pull tests were then performed at a depth of 19.5 cm in sampling ports 1 (located in the TCE injection zone) and 2 (located outside the TCE injection zone, Figure 4.9a). These ports were chosen based on static sampling data (Figure 4.9c).
which indicated that the sediment pack near sampling port 1 was contaminated with TCE, while there was a decreased likelihood of TCE contamination near sampling port 2. Unfortunately, push-pull tests were not performed in these sampling ports before remediation, which would have enabled a comparison of pre- and post-remediation radon retardation factors. For both push-pull tests normalized concentrations increased smoothly as the test solutions were extracted from the sediment pack (Figures 4.11 and 4.12). Radon transport was retarded relative to bromide in sampling port 1, and slightly retarded in sampling port 2. The normalized bromide concentration data were well fit by a simulated $R = 1$ breakthrough curve for both tests. The normalized radon concentration data were best fit by a simulated $R = 7$ breakthrough curve in sampling port 1 and simulated $R = 1.4$ breakthrough curve in sampling port 2 (Table 4.1). Following these push-pull tests the PAM was drained and four core samples were obtained adjacent to the fully penetrating well. All core samples showed methanol-extracted TCE concentrations below detection limits (1 mg/L).
Figure 4.11 Pull phase breakthrough curves for a push-pull test conducted in sampling port 1 after PAM remediation. The test was conducted at a depth of 19.5 cm.

Figure 4.12 Pull phase breakthrough curves for a push-pull test conducted in sampling port 2 after PAM remediation. The test was conducted at a depth of 19.5 cm.
DISCUSSION

Partitioning of radon between the pore water and trapped gas present in the sediment pack is likely the cause of the slight radon retardation observed in the push-pull test conducted prior to TCE contamination (Figure 4.3). This phenomenon has been observed in previous laboratory push-pull tests using the same sediment (Davis et al., 2002). Assuming equilibrium partitioning between the trapped gas and aqueous phases, the retardation factor for a dissolved gas can be written as (Fry et al., 1995)

\[ R = 1 + H_{cc} \frac{S_g}{S_w} \] (4.8)

where \( H_{cc} \) is the dimensionless Henry’s constant and \( S_g \) is the trapped gas saturation. Using equation 4.8, a value of \( H_{cc} = 3.9 \) for radon (Clever, 1979), and the best fit \( R = 1.2 \) for radon from the push-pull test, the estimated gas saturation in the sediment pack is 5%.

Radon retardation during the push-pull tests conducted after TCE contamination was likely 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, best fit \( R \) values were adjusted to account for partitioning of radon into the trapped gas using

\[ R_{adj} = R_{post-TCE} - (R_{pre-TCE} - 1.0) \] (4.9)

where \( R_{adj} \) is the adjusted retardation factor, \( R_{post-TCE} \) is the retardation factor from a push-pull test conducted after TCE contamination, and \( R_{pre-TCE} \) is the retardation factor
from the push-pull test conducted prior to TCE contamination \((R = 1.2, \text{ Figure 4.3})\).

Adjusted retardation factors were used to calculate TCE saturations \((S_n, \text{ Table 4.1})\).

The best fit \(R = 9.4\) for the push-pull test conducted after TCE contamination (Figure 4.4) is therefore adjusted to a value of \(R = 9.2\). Using equation 4.7, the adjusted retardation factor, and \(K = 50\), the calculated \(S_n = 14.1\%\). This value overestimates the volume-averaged TCE saturation of 1.2 % in the sediment pack, where the TCE saturation is averaged over the approximate 20 cm radius of influence of this push-pull test. The reasons for this overestimation are unclear, especially in light of the subsequent static and push-pull tests that indicated that TCE sank to the bottom of the sediment pack. A heterogeneous TCE distribution with pooling toward the bottom of the sediment pack would more likely result in smaller radon retardation factors because of the reduced interfacial area between the TCE and the injection solution. This reduced interfacial area due to the geometry of the pools would limit mass transfer and could violate the assumption of equilibrium partitioning (Chrysikopoulos and Kim, 2000; Willson et al., 2000). In addition, push-pull tests conducted in the fully penetrating well interrogated the entire 0 to 20 cm thickness of the PAM. Thus with a heterogeneous TCE distribution, the contribution of radon from layers of the sediment pack with either a lower TCE saturation or no TCE would serve to “dilute” the retarded radon response from layers contaminated with TCE, thus decreasing \(R\).

Static radon samples obtained from a depth of 10 cm after TCE contamination (Figure 4.5) showed little change relative to pre-contamination radon concentrations (Figure 4.2), indicating that TCE had sunk below the 10 cm depth. The second push-
pull test in the fully penetrating well (Figure 4.6) showed an adjusted $R = 3.6$, with a calculated $S_n = 4.9 \%$ (Table 4.1). The decrease in adjusted $R$ values between these two push-pull tests indicates that additional TCE sank in the 6 months between the tests (Table 4.1). Although the push-pull tests may tend to overestimate $S_n$, the tests show that changes in retardation may indicate changes in TCE saturation distribution over time.

Results from the 15 L pull test following TCE contamination (Figures 4.7a and 4.7b) support the hypothesis that the TCE sank. The lowest radon and highest aqueous TCE concentrations were observed at a depth of 17.5 cm. The likely existence of a zone of greater $S_n$ is shown by the decrease in radon concentrations between 3 and 5 L (Figure 4.7a). Assuming a cylindrical geometry, this zone is located approximately 11 to 14 cm from the well. Radon concentrations then increased as water from zones of lesser $S_n$ was extracted. The decrease in radon concentrations at 7.5 cm (Figure 4.7a) is attributed to radon partitioning to a gas phase at the top of the sediment pack, which is consistent with a decrease in aqueous TCE concentrations at this depth. During the 15 L pull experiment it was determined that the upper 3 to 4 cm of the sediment pack was not water saturated; this was remedied by adjusting the PAM standpipe/overflow systems.

Static radon and aqueous TCE samples obtained after the 15 L pull test were obtained from a depth of 19.5 cm to account for the sinking of TCE. Radon concentrations were decreased after TCE contamination, with the greatest decreases occurring near the concentric zones of 6 % and 3 % TCE saturation (Figure 4.8a).
Due to the sinking of injected TCE it is unlikely that these predicted TCE saturations were realized in the sediment pack. For example, a water sample obtained from the bottom of the sediment pack after TCE contamination contained neat TCE, supporting the hypothesis that TCE sank to the bottom of the sediment pack. The TCE injection scheme likely resulted in the highest TCE saturations in the 6 % zone, with lower saturations in the 3 % zone and the lowest saturations outside of the 3 % zone. The highest aqueous TCE concentrations (Figure 4.8b) were observed in the vicinity of the lowest radon concentrations. Although aqueous TCE concentrations approaching the solubility limit were measured in these zones, calculated values of $S_n$ (Figure 4.8c) were $\leq 1.4 \%$, which were lower than expected. This is possibly due to the relationship between diffusion and the volume of water obtained from the sediment pack for each static sample (i.e., 20 mL). A radon sample obtained from directly adjacent to the TCE would have a decreased concentration (relative to the pre-TCE contamination concentration) due to partitioning of radon into TCE. However, as the sampling point moves away from the TCE, the emanation of radon from the sediment attenuates the effect of radon partitioning. A 20 mL sample interrogates a radius of approximately 2.3 cm, assuming a spherical shape. If TCE were not present within this sample radius, or if only a portion of the interrogated sediment was contaminated, the effect of partitioning on the observed radon concentration would be lessened. The non-linear relationship between radon concentration and $S_n$ (equation 4.4) could also result in an underestimation of $S_n$. For example, a decrease in radon concentration in a sampling port from 200 to 100 pCi/L after TCE contamination would result in a
calculated $S_n = 2.0\%$. However, if the sample containing radon at 100 pCi/L contained two equal volumes of water with 50 and 150 pCi/L, respectively, then calculating $S_n$ individually for each of the volumes would result in calculated $S_n$ values of 6.0 and 0.67\%, with an average $S_n = 3.3\%$. These phenomena could result in an underestimation of the TCE saturation in the sediment pack, as is evident in Figure 4.8c. The static method is therefore sensitive to sample size in a heterogeneous DNAPL distribution.

Figures 4.8a and 4.9a show that static radon concentrations at 19.5 cm increased in some locations after remediation, with the greatest increases occurring near the concentric zones of injected TCE. However, radon concentrations also decreased in some portions of the sediment pack. Aqueous TCE concentrations were decreased after remediation (Figure 4.9b), with concentrations < 5 mg/L across the majority of the PAM. A comparison of calculated $S_n$ (Figures 4.8c and 4.9c) shows a decrease after remediation in the zones of highest $S_n$ prior to remediation. Also noted is an increase in $S_n$ in the vicinity of $x = 20$ cm, $y = 40$ cm. The decrease in radon concentrations and resulting increased values of $S_n$ in this vicinity could be due to the movement of TCE (during remediation). However, the presence of relatively low (< 5 mg/L) concentrations of aqueous TCE in this vicinity may indicate a change in sediment pack physical properties during remediation causing localized decreases in radon concentrations. The creation of localized preferential flow paths during remediation could increase porosity and reduce the equilibrium radon concentration (equation 4.4).
A change in sediment pack physical properties is indicated by a comparison of the results from the push-pull tests conducted in the fully penetrating well before (Figures 4.4 and 4.6) and after remediation (Figure 4.10). The normalized bromide breakthrough curves from the post-remediation test have a greater dispersion than those from the pre-remediation tests, possibly due to the creation of preferential flow paths resulting from the pumping of over 1200 L of tap water and ethanol solution through the sediment pack during remediation. Preferential flow paths and a resulting increase in porosity could decrease the travel distance of the injection solution during the push-pull test, which would result in increased dispersion in pull-phase breakthrough curves (Schroth et al., 2000). The simulation results provided poor fits to the post-remediation push-pull test normalized bromide and radon breakthrough curves, likely resulting from preferential flow paths. However, even with the increased dispersion of the normalized bromide and radon breakthrough curves, radon retardation was not evident in this push-pull test. This supports the contention that the majority of the TCE was removed by the end of the remediation activities.

The static test results after remediation, methanol-extracted TCE concentrations < 1 mg/L from core samples obtained adjacent to the fully penetrating well, and the gross mass balance on TCE provide additional evidence that the majority of the TCE was removed from the sediment pack by the end of remediation. However, two push-pull tests conducted at a depth of 19.5 cm in sampling ports 1 and 2 (Figures 4.11 and 4.12) highlight the influence of sample size and location on push-pull test results and the continued presence of TCE at the bottom of the sediment pack.
after remediation. These two push-pull tests had a radius of influence of approximately 9 cm. For sampling port 1 the adjusted $R = 6.8$ resulted in a calculated $S_n = 10.4\%$ (Table 4.1), indicating the existence of a ‘pocket’ of higher $S_n$ that was not detected by the push-pull test conducted in the fully penetrating well after remediation. Conversely, for sampling port 2 the adjusted $R = 1.2$ resulted in a calculated $S_n = 0.4\%$, indicating that little TCE remained in the vicinity of this sampling port.

These results show that push-pull test location in a heterogeneous TCE distribution can be critical in the calculation of $S_n$. Moreover, a comparison of the push-pull test conducted in the fully penetrating well after remediation with the push-pull test conducted in sampling port 1 highlights the sensitivity of the method to both sample size (i.e., volume of injection solution) and test design. In this case the two tests used different volumes of injection solution (10 L vs. 1.2 L). In addition, the test in the fully penetrating well interrogated the entire thickness of the PAM, while the test in sampling port 1 was focused at the bottom of the sediment pack. The two tests, although conducted within a horizontal distance of 5 cm of each other, interrogated different volumes of the sediment pack, with the 10 L push-pull test not showing clear evidence for any remaining ‘pockets’ of TCE. In contrast, the 1.2 L push-pull test, by nature of its location at the bottom of the sediment pack and smaller volume of injection solution, interrogated a smaller portion of the sediment pack with a greater $S_n$. 
CONCLUSIONS

The results of the laboratory and modeling studies show that static and push-pull methods using naturally occurring radon as a partitioning tracer have the potential to characterize DNAPL saturations in the subsurface. These methods can be applied at contaminated field sites using existing monitoring wells. Radon has the potential benefit of being an in situ partitioning tracer and can be easily sampled using standard sampling techniques and liquid scintillation analysis. However, the application of these methods to characterizing field sites with heterogeneous DNAPL distributions is complicated by the methods’ sensitivity to test location, sample size, and test design. The static method is influenced by spatial changes in aquifer properties and DNAPL saturations. Sample size can also critically influence results from static and push-pull tests. If DNAPL is heterogeneously distributed in the aquifer, static samples with different volumes may provide different estimates of DNAPL saturation. Similarly, a push-pull test conducted with a smaller volume of injection solution may yield a radon retardation factor different from a test conducted with a larger volume of injection solution at the same location. Test design can also influence push-pull test results through the selection of a specified thickness of an aquifer over which to conduct the test. When DNAPL is heterogeneously distributed (e.g., in a layered aquifer), push-pull tests can be performed using inflatable packers to isolate a suspected zone of DNAPL contamination. Tests conducted over the entire saturated thickness of the aquifer in the same well could yield a lesser retardation factor due to the contribution
of higher radon concentrations from less contaminated portions of the aquifer. The sensitivity of the static and push-pull methods to these factors presents challenges to the application of these methods at field sites. The static and push-pull methods have the potential to provide quantitative information on changes in DNAPL saturations as a result of remediation. However, further study of the influence of these factors on the ability of the methods to quantify DNAPL saturations is warranted.

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REFERENCES


CHAPTER 5

Numerical Simulations of Radon as an In Situ Partitioning Tracer for Quantifying NAPL Contamination Using Push-Pull Tests

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Naturally occurring radon in groundwater can be used as an in situ partitioning tracer in push-pull tests to quantify nonaqueous phase liquid (NAPL) contamination in the subsurface. A push-pull test consists of the injection (push) of a known volume of solution consisting of radon-free water and a conservative bromide tracer into a well, followed by the extraction (pull) of the test solution/groundwater mixture from the same well. The presence of NAPL is manifested in the greater dispersion of the radon breakthrough curve (BTC) relative to the bromide BTC during the extraction phase of the test as a result of radon partitioning into the NAPL phase. Laboratory push-pull tests in a NAPL-contaminated physical aquifer model (PAM) indicated that the modeling approach previously used to estimate the radon BTC retardation factor (which was used to calculate the NAPL saturation, $S_n$) resulted in the overestimation of the likely $S_n$ in the PAM. The numerical simulations presented here investigated the influence of 1) initial radon concentrations, which vary as a function of $S_n$, and 2) heterogeneity in $S_n$ distribution within the radius of influence of the push-pull test. The simulation results showed that these factors influence radon BTCs and resulting estimates of $S_n$. A revised method of plotting and interpreting radon BTCs is presented which takes into account initial radon concentrations and uses non-normalized radon BTCs. This revised method produces greater radon BTC sensitivity at small values of $S_n$ and was used to re-analyze the results from the laboratory push-pull tests reported in Davis et al. (2002). The re-analysis resulted in a more accurate
estimate of $S_n$ (1.8 %) vs. a previously estimated value (7.4 %). The revised method was then applied to results from a push-pull test conducted in a LNAPL-contaminated aquifer at a field site, resulting in an estimated $S_n = 4.1$ %. The revised method improves upon the efficacy of the radon push-pull test to estimate NAPL saturations. A limitation of the revised method is that ‘background’ radon concentrations from a non-contaminated well in the NAPL-contaminated aquifer are needed to accurately estimate NAPL saturation. The method has potential as a means of monitoring the progress of NAPL remediation.

INTRODUCTION

Partitioning interwell tracer tests have been used to quantify nonaqueous phase liquid (NAPL) saturations in laboratory and field settings (Jin et al., 1995; Nelson and Brusseau, 1996; Annable et al., 1998; Nelson et al., 1999; Young et al. 1999). Recently, single-well ‘push-pull’ partitioning tracer tests have been used to quantify NAPL saturations (Davis et al., 2002; Istok et al., 2002). In a push-pull test, an injection solution containing partitioning and conservative tracers is injected (‘pushed’) into an aquifer through a well. The solution/groundwater mixture is then extracted (‘pulled’) from the same well. These tests have involved the use of both ‘ex situ’ (i.e., injected) and ‘in situ’ (i.e., naturally occurring radon) partitioning tracers. For the ex situ tracer method, partitioning and conservative (e.g., bromide) tracers are injected into the aquifer, while for the in situ tracer method, a radon-free injection
solution (containing a conservative bromide tracer) is injected into the aquifer. In both cases the presence of NAPL is indicated by a greater dispersion of the extraction phase breakthrough curve (BTC) for the partitioning tracer relative to a conservative tracer (Schroth et al., 2000).

In situ radon has been used as a partitioning tracer for locating and quantifying NAPL in field and laboratory settings (Semprini et al., 1993; Hunkeler et al. 1997; Semprini et al, 1998; Semprini et al., 2000; Davis et al., 2002). The steady-state or 'background' radon concentration in groundwater ($C_{w,bkg}$) is a function of the radium content ($C_{Ra}$) and radon emanation power ($E_{p}$) of the mineral phase and the bulk density ($\rho_b$) and porosity ($n$) of the aquifer as described by (Semprini et al., 2000)

$$C_{w,bkg} = \frac{C_{Ra} E_{p} \rho_b}{n}$$  \hspace{1cm} (5.1)

The partition coefficient ($K$) for radon is defined as

$$K = \frac{C_n}{C_{w,n}}$$  \hspace{1cm} (5.2)

where $C_n$ is the concentration of radon in the NAPL phase, and $C_{w,n}$ is the concentration of radon in the aqueous phase. Partition coefficients may be determined using the methodology of Cantaloub (2001) and range from 37 (o-xylene) to 50 (trichloroethene, or TCE) to 61 (cyclohexane). In the presence of NAPL, radon will partition between the water and NAPL phases as described by

$$C_n S_n + C_{w,n} S_w = C_{w,bkg}$$  \hspace{1cm} (5.3)
where \( S_n \) and \( S_w \) are the NAPL and water saturations in the pore space \((S_n + S_w = 1)\).

Assuming linear radon partitioning between NAPL and water (equation 5.2), equation 5.3 can be rearranged as

\[
C_{w,n} = \frac{C_{w,bkg}}{1 + S_n (K-1)}
\]  

(5.4)

where \( C_{w,n} \) is a non-linear function of \( S_n \) and \( K \) (shown in Figure 5.1 using \( C_{w,bkg} = 200 \) pCi/L and \( K = 50 \)). Equation 5.4 can be further rearranged to solve for the NAPL saturation in an aquifer under natural gradient conditions

\[
S_n = \left( \frac{C_{w,bkg}}{C_{w,n}} - 1 \right) \left( \frac{1}{(K-1)} \right)
\]  

(5.5)

Radon retardation during transport can be used to determine NAPL saturation. The retardation factor for a partitioning tracer is given by (Dwarakanath et al., 1999)

\[
R = 1 + \frac{KS_n}{S_w}
\]  

(5.6)

which can be solved for \( S_n \)

\[
S_n = \frac{R - 1}{R + K - 1}
\]  

(5.7)

Push-pull tests using radon as a partitioning tracer were performed in laboratory physical aquifer models (PAMs) containing TCE (Davis et al., 2002). Experimental conservative (bromide) tracer and radon extraction phase BTCs were fit to an approximate analytical solution of the governing transport equations in order to estimate a value for \( R \), which was then used to calculate \( S_n \). Numerically generated BTCs using the Subsurface Transport Over Multiple Phases (STOMP) code were used
to investigate the validity of the approximate analytical solution, and provided good matches to the experimental and approximate analytical solution BTCs. However, this approach resulted in overestimations of $S_n$ compared to injection phase BTC results and the estimated TCE saturation in the PAM. In this approach, radon transport during a push-pull test was modeled assuming to behave similarly to an injected tracer. These simulations used a step input of radon (during the injection phase) into radon-free, saturated PAM sediment. An initial concentration $= 0$ for all solutes in the model domain was used with an injection solution concentration ($C_o$) = 1 (i.e., normalized). The extraction phase concentration results ($C$) from the simulations were converted to 'inverted' concentrations ($C^*$) using $C^* = 1 - C/C_o$ to mimic the behavior of radon in a push-pull test, since 1) a radon-free solution is injected in laboratory and field push-pull tests, and 2) radon concentrations increase with time during the extraction phase of the test. Extraction phase BTCs were plotted as a function of dimensionless time $V_e/V_i$, where $V_e$ is the volume of solution extracted from the aquifer at the time a sample was obtained at the well and $V_i$ is the total volume of solution injected into the aquifer. In addition, these models incorporated NAPL throughout the domain (infinite distribution), while the laboratory push-pull tests interrogated sediment beyond the NAPL-contaminated zone in the PAM.

Although these simulations 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 $S_n$ (Equation 5.4; Figure 5.1). Furthermore, these simulations assumed that NAPL saturation was spatially homogeneous in the PAM. A heterogeneous NAPL distribution will affect initial radon concentrations and partitioning behavior during the push-pull test and can affect estimations of $R$ and $S_n$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_1.png}
\caption{Aqueous phase radon concentrations ($C_{w,n}$) as a function of NAPL saturation, plotted using equation 4 with a background radon concentration ($C_{w,bkg}$) = 200 pCi/L and $K = 50$.}
\end{figure}

The goal of this study was 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) heterogeneous NAPL saturation distributions. A revised method of interpreting radon BTCs is presented that reduces overestimation and results in an increase in sensitivity of the estimation method at small values of $S_n$. This method is then used to re-estimate values of $S_n$ in
previously conducted laboratory push-pull tests and to estimate $S_n$ from field push-pull test data.

METHODS

Simulations were performed with the STOMP code (White and Oostrom, 2000), a fully implicit volume-integrated finite difference simulator for modeling one-, two- and three-dimensional flow and transport, which has been extensively tested and validated against published analytical solutions as well as 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) previously used in laboratory push-pull tests. A solid density ($\rho_s$) of 2.9 g/cm$^3$, porosity ($n$) = 0.35, calculated bulk density ($\rho_b$) = 1.89 g/cm$^3$ and longitudinal dispersivity ($\alpha_L$) = 4.0 cm were used in all simulations. Simulations incorporated an injection volume of 250 L and an extraction volume ranging from 500 to 2000 L. Injection and extraction pumping rates were constant at 1 L/min with no rest phase between the injection and extraction phases. The computational domain consisted of a line of 500 nodes with a uniform radial node
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spacing of $\Delta r = 1.0$ cm. The model geometry and injection volumes resulted in the injection solution traveling 48 cm from the well, 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 and its $K = 50$ for radon. NAPL saturations ($S_n$) were incorporated into the model using solid:aqueous phase partition coefficients. First, equation 5.6 and $K = 50$ were used to solve for 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 solve for a solid:aqueous phase partition coefficient ($K_d$)

$$K_d = (R - 1) \left( \frac{n}{\rho_s} \right)$$  \hspace{1cm} (5.8)

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) $r \leq 500$ cm, 2) $r \leq 48$ cm (corresponding to the maximum travel radius of a conservatively transported tracer, as defined by plug flow), and 3) $r \leq 24$ 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 described above, and 2) an initial radon concentration in the model that varied in space as a function of $S_n$. The simulations involving the PAM and field tests are described below.

RESULTS AND DISCUSSION

Injection Phase Results

The end of the injection phase of a simulated push-pull test (corresponding to $V_e/V_i = 0$) with $S_n = 0\%$ for $r \leq 500$ cm results in conservative radon transport as shown in a radon concentration profile from $r = 0$ to $100$ cm (Figure 5.2). The radon-free injection solution is transported to $r = 48$ cm, as measured by half the initial radon concentration at the injection well. In contrast, when $S_n \neq 0\%$ over a specified portion of the model domain, radon transport is retarded. For the simulation where $S_n = 4\%$ for $r \leq 500$ cm (i.e., a homogeneous NAPL distribution), the initial radon concentration in the model = 67.6 pCi/L (equation 5.4) and when $V_e/V_i = 0$, the radon-free injection solution is transported only to $r = 26$ cm as measured by half the initial radon concentration at the injection well (Figure 5.2).
Figure 5.2 Simulated radon concentration profiles ($C_{wn}$) at the end of the injection phase of push-pull tests with no NAPL ($S_n = 0\%$ to 500 cm); heterogeneous NAPL saturation ($S_n = 4\%$ to 48 cm) and ($S_n = 4\%$ to 24 cm); and homogeneous NAPL saturation ($S_n = 4\%$ to 500 cm).

The decrease in the transport distance of the radon-free injection solution is due to radon retardation resulting from partitioning between the injection solution and NAPL during transport. For the simulation where $S_n = 4\%$ for $r \leq 48$ cm and $S_n = 0\%$ for $r > 48$ cm (i.e., a heterogeneous NAPL distribution), when $V_e/V_i = 0$, the radon-free injection solution is again transported only to $r = 26$ cm (Figure 5.2). The mixing of radon-free injection solution, water with an initial radon concentration = 67.6 pCi/L for $r \leq 48$ cm, and water with an initial radon concentration = 200 pCi/L for $r > 48$ cm, combined with radon partitioning prior to the test and during transport, results in a complex, two-step radon concentration profile. For the simulation where $S_n = 4\%$ for $r \leq 24$ cm and $S_n = 0\%$ for $r > 24$ cm (i.e., a heterogeneous NAPL distribution), when $V_e/V_i = 0$, the radon-free injection solution is transported only to $r = 29$ cm (Figure
5.2). The change in the transport distance of the injection solution (vs. the previous simulation) is due to the mixing of radon-free injection solution, water with an initial radon concentration = 67.6 pCi/L for \( r \leq 24 \) cm, and water with an initial radon concentration = 200 pCi/L for \( r > 24 \) cm, combined with radon partitioning prior to the test and during transport. Thus when the portion of the model domain containing NAPL decreases, radon transport distance increases (i.e., radon retardation is lessened). These simulations show that both homogeneous and heterogeneous NAPL distributions result in radon retardation. Radon concentration profiles are influenced by both radon partitioning between the aqueous and NAPL phases prior to the push-pull test, and radon partitioning between the injection solution and NAPL during the test. Heterogeneity in NAPL distribution can affect injection phase radon concentration profiles due to the partitioning processes described above and mixing of water with different initial radon concentrations during the test.

**Extraction Phase Results – Concentration Profiles**

The extraction phase of a simulated push-pull test (beginning with \( V_e/V_i = 0 \) and continuing through \( V_e/V_i = 4 \) where \( S_n = 4 \% \) for \( r \leq 500 \) cm (i.e., a homogeneous NAPL distribution) shows that radon concentrations increase with time as the injection solution/groundwater mixture is extracted from the well (Figure 5.3a). In this simulation the initial radon concentration is 67.6 pCi/L for \( r \leq 500 \) cm (equation 5.4). The radon concentration measured at the well \(( r = 0 \) cm\) is 62.7 % of the initial radon
concentration at \(\frac{Ve}{Vi} = 1\), 88.6 % at 2, and 96.2 % at 3. Thus as the extraction phase of the test proceeds, radon concentrations at the well approach but do not exceed the initial radon concentration at the well. This holds true for any simulation with a homogeneous NAPL distribution.

Figure 5.3a Simulated radon concentration profiles \((C_{w,n})\) during the extraction phase of a push-pull test, with a homogeneous NAPL saturation \((S_n = 4 \% \text{ for } r \leq 500 \text{ cm})\).

Figure 5.3b Simulated radon concentration profiles \((C_{w,n})\) during the extraction phase of a push-pull test, with a heterogeneous NAPL saturation \((S_n = 4 \% \text{ for } r \leq 48 \text{ cm}; S_n = 0 \% \text{ for } r > 48 \text{ cm})\).
Figure 5.3c Simulated radon concentration profiles ($C_{w,n}$) during the extraction phase of a push-pull test, with a heterogeneous NAPL saturation ($S_n = 4\%$ for $r \leq 24$ cm; $S_n = 0\%$ for $r > 24$ cm).

The extraction phase of a simulated push-pull test (beginning with $V_e/V_i = 0$ and continuing through $V_e/V_i = 8$) where $S_n = 4\%$ for $r \leq 48$ cm and $S_n = 0\%$ for $r > 48$ cm (i.e., a heterogeneous NAPL distribution) shows that radon concentrations increase with time as the injection solution/groundwater mixture is extracted from the well (Figure 5.3b). In this simulation the initial radon concentration is 67.6 pCi/L for $r \leq 48$ cm and 200 pCi/L for $r > 48$ cm (equation 5.4). The radon concentration measured at the well ($r = 0$ cm) is 63.4 % of the initial radon concentration at $V_e/V_i = 1$, 102.5 % at 2, and 153.4 % at 3, and increases to 291.1 % at 8. As the extraction phase of the test proceeds, radon concentrations at the well exceed the initial radon concentration at the well at approximately $V_e/V_i = 2$. This is due to the influx of water with a radon concentration = 200 pCi/L from $r > 48$ cm, where $S_n = 0\%$. Such a
response in push-pull tests might be utilized in identifying heterogeneous NAPL distributions.

The extraction phase of a simulated push-pull test (beginning with $V_e/V_i = 0$ and continuing through $V_e/V_i = 8$) where $S_n = 4\%$ for $r \leq 24\text{ cm}$ and $S_n = 0\%$ for $r > 24\text{ cm}$ (i.e., a heterogeneous NAPL distribution) shows that radon concentrations increase more quickly with time as the injection solution/groundwater mixture is extracted from the well (Figure 5.3c) compared to the previous simulation (Figure 5.3b). In this simulation the initial radon concentration is 67.6 pCi/L for $r \leq 24\text{ cm}$ and 200 pCi/L for $r > 24\text{ cm}$ (equation 5.4). The radon concentration measured at the well ($r = 0\text{ cm}$) is 91.6\% of the initial radon concentration at $V_e/V_i = 1$, 216.6\% at 2, and 273.4\% at 3, and increases to 295.9\% at 8. As the extraction phase of the test proceeds, radon concentrations at the well exceed the initial radon concentration at the well just after $V_e/V_i = 1$. This is due to the influx of water with a radon concentration $= 200\text{ pCi/L}$ from $r > 24\text{ cm}$, where $S_n = 0\%$. Thus as NAPL is concentrated closer to the well, radon concentrations more rapidly exceed initial values at the well as the extraction phase proceeds. Conversely, if NAPL saturations were greater farther from the well, radon concentrations would possibly not approach initial values at the well.
Extraction Phase Results – Breakthrough Curves

Although radon concentration profiles provide useful information on radon transport behavior, usually the only radon concentration data available at field sites is obtained from the well in which the push-pull test is being conducted. To investigate radon BTC behavior, 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 5.4a), with each value of $R$ corresponding to a value for $S_n$. The initial radon concentration was a function of $S_n$ (equation 5.4), 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 decrease is due to the increase in dispersion 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 5.1).
Figure 5.4a Simulated radon breakthrough curves during the extraction phases of six push-pull tests with homogeneous NAPL saturations ($S_n = 0$ to 15.25 % for $r \leq 500$ cm).

Figure 5.4b Simulated radon breakthrough curves during the extraction phases of six push-pull tests with heterogeneous NAPL saturations ($S_n = 0$ to 15.25 % for $r \leq 48$ cm; $S_n = 0$ % for $r > 48$ cm).
Figure 5.4c Simulated radon breakthrough curves during the extraction phases of six push-pull tests with heterogeneous NAPL saturations ($S_n = 0$ to 15.25 % for $r \leq 24$ 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 $r \leq 48$ cm and $S_n = 0$ % for $r > 48$ cm (Figure 5.4b). The initial radon concentration was a function of $S_n$ (equation 5.4), and for $r \leq 48$ 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 5.4b) as compared to when $S_n$ is constant for $r \leq 500$ cm (Figure 5.4a). Radon concentrations would 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 $r \leq 48$ cm and $S_n = 0$ % for $r > 48$ cm (Figure 5.3b). However, the shapes of the radon BTCs are similar at early times for the two sets of simulations (Figures 5.4a and 5.4b), 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 $r \leq 24$ cm and $S_n = 0$ % for $r > 24$ cm (Figure 5.4c). The initial radon concentration was a function of $S_n$ (equation 5.4), and for $r \leq 24$ 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 5.4c) as compared to when $S_n > 0$ % for $r \leq 48$ cm (Figure 5.4b) or when $S_n$ is constant for $r \leq 500$ cm (Figure 5.4a). 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 $r \leq 24$ cm and $S_n = 0\%$ for $r > 24$ cm (Figure 5.3c). The influence of $S_n = 0\%$ at $r > 24$ cm results in greater slopes for radon BTCs compared to the previous simulations (Figures 5.4a and 5.4b). 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.

**Extraction Phase Results – Normalized Breakthrough Curves**

The normalization of each of the radon BTCs for the homogeneous NAPL distribution (Figure 5.4a) to the initial concentrations at the well results in radon BTCs that approach but do not exceed a normalized concentration = 1 at $V_c/V_i = 2$ (Figure 5.5a). The effect of increasing dispersion as $S_n$ increases is apparent (Schroth et al., 2000). This figure applies to any idealized homogeneous NAPL distribution and by inverting the concentrations is analogous to the ex situ tracer test, since this set of simulations utilizes a step input during the injection phase into a model domain with a spatially constant initial condition. A drawback to normalizing to the initial radon concentration is the decrease in sensitivity of the radon BTCs to small values of $S_n$ compared to the non-normalized method (Figure 5.4a). This drawback is a concern when fitting experimental radon BTCs to simulated BTCs in order to determine a best-fit value of $R$ in order to estimate $S_n$. 
Figure 5.5a  Simulated radon breakthrough curves during the extraction phases of six push-pull tests with homogeneous NAPL saturations ($S_n = 0$ to $15.25\%$ for $r \leq 500$ cm). Radon concentrations are normalized to the initial radon concentrations at the well for each value of $S_n$.

Figure 5.5b  Simulated radon breakthrough curves during the extraction phases of six push-pull tests with heterogeneous NAPL saturations ($S_n = 0$ to $15.25\%$ for $r \leq 48$ cm; $S_n = 0\%$ for $r > 48$ cm). Radon concentrations are normalized to the initial concentrations at the well for each value of $S_n$. 
Figure 5.5c Simulated radon breakthrough curves during the extraction phases of six push-pull tests with heterogeneous NAPL saturations ($S_n = 0$ to 15.25% for $r \leq 24$ cm; $S_n = 0$% for $r > 24$ cm). Radon concentrations are normalized to the initial concentrations at the well for each value of $S_n$.

Radon BTC normalization for the heterogeneous NAPL distribution where $S_n = 0$% for $r > 48$ cm (Figure 5.4b) results in radon BTCs that approach a normalized concentration = 1 at $V_e/V_i = 2$ (Figure 5.5b). Normalized radon BTCs deviate from those in the homogeneous set of simulations (Figure 5.5a) as $V_e/V_i$ approaches 2, and for $S_n = 1.96$% the normalized concentration is $> 1$.

Radon BTC normalization for the heterogeneous NAPL distribution where $S_n = 0$% for $r > 24$ cm (Figure 5.4c) results in radon BTCs that exceed a normalized concentration = 1 at approximately $V_e/V_i = 1$ (Figure 5.5c). Comparing Figure 5.5c with Figures 5.5a and 5.5b shows that as the proportion of $S_n = 0$% in the model domain increases, normalizing to the initial radon concentration results in greater deviations in radon BTCs, with normalized concentrations $\geq 2.5$ at $V_e/V_i = 2$. Thus
the interpretation of normalized radon BTCs becomes more difficult as heterogeneity in $S_n$ increases. Moreover, the shape of normalized BTCs is influenced by the radon concentration to which BTCs are normalized.

**Revised Method for Radon BTC Interpretation**

The simulation results show that non-normalized radon BTCs (Figures 5.4a, 5.4b, and 5.4c) have a greater sensitivity to small values of $S_n$ than the corresponding normalized radon BTCs (Figures 5.5a, 5.5b, and 5.5c). Furthermore, these simulations also show that heterogeneity in $S_n$ can result in extraction phase normalized radon concentrations $> 1$. Conversely, a reversal of the simulated $S_n$ distributions such that $S_n$ increased with distance from the well would result in extraction phase normalized radon concentrations $< 1$. Thus heterogeneity in $S_n$ can introduce uncertainties in the applicability of the initial radon concentration at the well as a normalization value. The use of non-normalized radon BTCs to estimate $S_n$ provides two advantages over normalized radon BTCs: 1) the sensitivity of non-normalized radon BTCs to small values of $S_n$ can be utilized; and 2) the effect of heterogeneity in $S_n$ on the shape of radon BTCs can be lessened.

The revised method for estimating $S_n$ utilizing non-normalized radon BTCs requires obtaining a ‘background’ radon concentration ($C_{w,bkg}$; equation 5.1) from a non-contaminated portion of the contaminated aquifer. Using this sample as a ‘background’ concentration assumes homogeneity in porosity and radon emanation...
between the non-contaminated location chosen for the ‘background’ radon sample and the location with suspected NAPL contamination where the push-pull test is conducted. Extraction phase radon and bromide results are plotted in concentration units (pCi/L for Rn and mg/L for Br) as a function of $V_e/V_i$. The y-axis of the plot shows radon concentrations ranging from 0 at the origin to a maximum value equal to the ‘background’ concentration. Bromide concentrations are plotted on a secondary y-axis with concentrations ranging from the injection solution concentration to 0 mg/L, with the injection solution concentration at the origin and 0 mg/L at the maximum or ‘background’ radon concentration. This inverts the bromide concentrations and causes the radon and bromide BTCs to overlap. Numerical simulations are then performed to best-fit (using a least-squares procedure) the experimental bromide BTC to a non-retarded simulated BTC (i.e., with $R = 1$) by varying the sediment dispersivity ($\alpha_L$). The best-fit $\alpha_L$ value is then used in subsequent simulations to best-fit (using a least-squares procedure) the experimental radon BTC to a simulated BTC corresponding to a particular value of $R$. For each simulated BTC, equation 5.4 is used to input the initial radon concentration in the model as a function of $S_n$ and $K$. The initial radon concentration can be input into the model as a homogeneous or heterogeneous $S_n$ distribution. Equation 5.7 is then used to calculate the value of $S_n$ that corresponds to the best-fit $R$ value.
PAM push-pull tests re-analysis

The revised method was applied to existing radon and bromide extraction phase data from push-pull tests performed in wedge shaped physical aquifer models (PAMs) by Davis et al. (2002). These push-pull tests were performed in clean sediment (Test 1) and TCE-contaminated sediment (Test 2), with the contaminated zone ($S_n \approx 2\%$) 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 5.1).

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 5.6). The radon retardation in Test 1 is attributed to partitioning of radon between the trapped gas and aqueous phases, as described by Fry et al. (1995)

$$R = 1 + \frac{H_{cc} S_g}{S_w}$$

(5.9)

where $H_{cc}$ is radon’s dimensionless Henry’s coefficient and $S_g$ is the trapped gas saturation. Using equation 5.9, $H_{cc} = 3.9$ (Clever, 1979), and $R = 1.3$, the estimated $S_g$ = 7.1 %. These values are similar to those from Davis et al. (2002) (Table 5.1), who reported a best-fit $\alpha_L = 3.2$ cm, $R = 1.1$, and estimated $S_g$ ranging up to 9.3 %. 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 (Davis et al., 2002).

Table 5.1 Radon retardation factors ($R$), adjusted retardation factors for the effect of trapped gas (in italics), best-fit dispersivities ($\alpha_L$), and calculated TCE saturations ($S_n$) 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 $S_n$ in the presence of TCE.

<table>
<thead>
<tr>
<th>From Davis et al. (2002) ((\alpha_L) best-fit using approximate solution)</th>
<th>Using revised method ((\alpha_L) best-fit using STOMP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R)</td>
<td>(\alpha_L) (cm)</td>
</tr>
<tr>
<td>Test 1, no TCE</td>
<td>1.1</td>
</tr>
<tr>
<td>Test 2, with TCE</td>
<td>5.1/5.0</td>
</tr>
</tbody>
</table>

Figure 5.6 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).
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 5.7). 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 (Davis et al., 2002)

\[
R_{adj} = R_{test\ 2} - (R_{test\ 1} - 1.0)
\]  
(5.10)

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. Using equation 5.10, an adjusted \( R \) value of 1.9 is calculated, which results in an estimated \( S_n = 1.8 \% \) (Table 5.1). The best-fit \( \alpha_L = 3.7 \) cm compares favorably with the best-fit \( \alpha_L = 4.0 \) cm from Davis et al. (2002), 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 \( S_n = 7.4 \% \) from Davis et al. (2002) (using \( K = 50 \)). 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 (Davis et al., 2002). 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 5.7 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).](image)

**Field push-pull test application**

The revised method was applied to radon and bromide BTCs from a field test performed at a former petroleum refinery in the Ohio River valley. As further described in Davis et al. (2002) and Istok et al. (2002), the site consists of glacial outwash deposits that are contaminated with a mixture of petroleum light or LNAPLs including gasoline, heating oil, and jet and aviation fuel. Radon samples from a non-contaminated well showed a maximum concentration of 788.5 pCi/L. This value was used as the 'background' concentration for radon. A push-pull test was performed in a contaminated well in which LNAPL has been detected. Radon concentrations
increased and bromide concentrations decreased smoothly as the test solution/groundwater mixture was extracted from the aquifer, with the radon BTC being retarded relative to the bromide BTC (Figure 5.8). Numerical simulations were performed for this test with LNAPL assuming to extend far beyond the radius of influence of the test. The simulation results fit the bromide BTC to a simulated $R = 1$ BTC using a best-fit $\alpha_L = 11$ cm. This value is less than the best-fit $\alpha_L = 20.3$ cm from the approximate analytical solution used to fit the normalized bromide BTC by Davis et al. (2002), where the BTC was adjusted to intersect a normalized concentration $= 0.5$ at $V_e/V_i = 1$. Using the revised method and $\alpha_L = 11$ cm, the radon BTC was best-fit by a simulated $R = 2.7$ BTC. Using the best-fit $R = 2.7$, a value of $S_n = 4.1\%$ was calculated using equation 7 and a value of $K = 40$ for radon in the presence of diesel fuel, as reported by Hunkeler et al. (1997). The relatively poor fits of the simulated BTCs to the experimental BTCs likely are a result of heterogeneities in hydraulic conductivity and porosity in the aquifer. In addition, the use of a $K$ value for radon in the presence of diesel fuel adds uncertainty to the value of $S_n = 4.1\%$, since the actual LNAPL composition at the site is a mixture of LNAPLs. However, the method does provide an estimate for the LNAPL saturation in the vicinity of the well. Furthermore, a series of similar push-pull tests could be conducted in this well over time to track the efficacy of remediation and source zone removal.
CONCLUSIONS

The revised method enhances the ability of the radon push-pull test to provide estimates for $S_n$ at NAPL-contaminated sites. The effect of heterogeneity in $S_n$ on radon BTCs is lessened, and a greater sensitivity to smaller values of $S_n$ is realized. Also, the revised method more accurately represents 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 effected. However, the revised method is potentially constrained by the need to obtain a ‘background’ radon sample from a non-contaminated well in the contaminated aquifer. Geologic properties with respect to radon emanation and porosity must be similar between the contaminated and non-
contaminated wells. This may or may not be the case at a field site. The collection of radon samples from additional non-contaminated wells emplaced in the NAPL-contaminated aquifer could provide a range of 'background' values which could be used in conjunction with the revised method to provide a range of estimated values of $S_n$. Also, it should be noted that estimated values of $S_n$ represent a volume-averaged value, and may or may not be representative of the true value of $S_n$ at a given location within the radius of influence of the push-pull test. These uncertainties highlight our view that push-pull test results provide an estimate of NAPL saturation in the immediate vicinity of the well in which the test was conducted.

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REFERENCES


CHAPTER 6

Engineering Significance and Conclusion

ENGINEERING SIGNIFICANCE

Overall, the laboratory, modeling, and field studies presented in this dissertation show that the static and push-pull methods using radon as a partitioning tracer have the potential to quantify NAPL saturations in the subsurface. These methods also have the potential to be applied at field sites where various remediation techniques are being implemented (e.g., cosolvent flushing, bioremediation, surfactant enhanced aquifer remediation). Here the techniques could be applied to detect changes in NAPL saturation over time as remediation proceeds. The benefits of the methods are numerous. Radon is a free, in situ partitioning tracer and does not require injection into the subsurface or regulatory approval for use at field sites. Radon can be easily analyzed using liquid scintillation counting techniques, while bromide (for push-pull tests) can be analyzed using ion chromatography. Both the static and push-pull methods involve the use of existing monitoring wells; no additional soil coring or well installation is required, but could be implemented at a field site to increase sampling density, if desired. One of the advantages of the static and push-pull methods is the ability to sample larger aquifer volumes in a single test than is possible using soil coring or direct push techniques (e.g., membrane interface probes). This
results in NAPL saturation estimates made over a larger volumes of the aquifer, as opposed to saturation estimates from the smaller aquifer volumes inherently sampled in soil coring and direct push techniques. In addition, these methods have an advantage over partitioning interwell tracer tests (PITTs) in that smaller volumes of water are required for the tests, resulting in less wastewater being generated and less time required per test; this translates to a lower cost per test. Furthermore, radon is most sensitive at small NAPL saturations for both the static and push-pull methods, which is advantageous when the remediation of residual saturation in a NAPL source zone is being attempted.

The static method is easily applied in the field, requiring only a pump, sampling lines, and vials for collecting groundwater samples for radon analysis. However, the application of the method to determine NAPL saturations requires knowledge of the ‘background’ radon concentration in the aquifer. Since samples from a NAPL-contaminated well cannot be obtained prior to contamination, radon samples obtained from the same aquifer (from a non-contaminated well) must be collected and assumed to represent ‘background’ radon concentrations in the contaminated well. This requires the assumption of homogeneity in porosity and radon emanation between the wells. In any case, test results should be considered to be an estimate of NAPL saturation. Moreover, the static method is sensitive to sample size. For example, a larger sample will interrogate a larger aquifer volume than a smaller sample. If NAPL is heterogeneously distributed, the saturation estimates from the two samples may not be the same. Furthermore, the accurate measurement of
radon’s partition coefficient for a given NAPL must be known in order to calculate saturation values. Contaminated field sites may contain a mixture of NAPLs, which would require laboratory partitioning tests in order to determine radon’s partition coefficient for a given NAPL mixture. However, the caveats described here do not negate the static method’s potential to provide estimates of NAPL saturation and changes in saturation over time. The static method is a non-destructive, low cost method that has the potential to be of use for characterizing NAPL saturation at contaminated field sites.

The push-pull method is also easily applied in the field, requiring a pump, sampling lines, vials for collecting groundwater samples for radon and bromide analysis, and storage containers for injection solution and wastewater containment. Inflatable packers and an air tank are required if the test is to be conducted over a specified interval of the aquifer where NAPL contamination is suspected (for example, at and above a layer of fine-grained sediment). The push-pull method can be used to estimate NAPL saturations and track changes in saturations over time as a result of remediation activities. Push-pull tests can be performed repeatedly in the same well, and different tests can incorporate varying volumes of injection solution in order to interrogate varying aquifer volumes. The tests can be typically performed in < 8 hours and involve the use of existing monitoring wells, which makes the push-pull test cost advantageous over PITTs. Again, the application of the push-pull method requires knowledge of the ‘background’ radon concentration in the aquifer, which requires the assumption of homogeneity of porosity and radon emanation between contaminated
wells and a well outside of the zone of contamination where a 'background' radon sample(s) can be obtained. The push-pull method is influenced by sample size and test design. A heterogeneous NAPL distribution can result in varying saturation estimates in a given well if different volumes of injection solution are used in successive tests. A test conducted using packers may produce a different estimate of NAPL saturation than a test conducted over the entire screened interval of the same well, since each test may sample a zone of potentially different NAPL saturation. Also, the radon retardation signal may be 'diluted' by the influx of groundwater with higher radon concentrations from zones of lower NAPL saturation. In addition, the potential for injection solution to bypass regions of greater NAPL saturation (and lower relative permeability to water) must be considered, especially where NAPL 'pools' are suspected to exist. However, this caveat is inherent in all partitioning tracer tests, including PITTs, as are the influences of sample size and test design. The push-pull method, although not without drawbacks, is nevertheless a potentially robust and low-cost method for estimating NAPL saturations in the subsurface and tracking saturation changes over time.

CONCLUSIONS

In summary, the research in this dissertation supports the following conclusions:
1. Laboratory results show that the static method using radon as a partitioning tracer has the ability to detect changes in radon concentrations as a result of partitioning of radon into NAPL and can be used to estimate NAPL saturations.

2. Laboratory results show that the static method can be used to track changes in NAPL saturation arising from alcohol cosolvent and pump-and-treat remediation.

3. Heterogeneity in NAPL saturations, including pooling, combined with the sensitivity of the static method to test sample size, can influence static method estimates of NAPL saturation.

4. Laboratory push-pull tests using radon as a partitioning tracer show that radon is minimally retarded in the absence of NAPL and that retardation is greater in the presence of NAPL as a result of partitioning of radon between the NAPL and aqueous phases. The radon retardation factor from push-pull tests can be used to estimate NAPL saturations.

5. Laboratory tests show that the push-pull method is sensitive to NAPL migration and remediation, with these processes being manifested in changes in radon retardation over time in tests conducted in the same well.

6. The laboratory tests show that the push-pull method is sensitive to sample size (i.e., volume of solution injected) and test design in heterogeneous NAPL distributions, and that these factors can influence measured retardation factors and resulting estimates of NAPL saturations.
7. The push-pull method can be applied in the field in order to provide an estimate of NAPL saturation.

8. Modeling studies show that in order to realistically model radon push-pull tests, initial radon concentrations must be incorporated into numerical model domains.

9. Modeling studies also show that the sensitivity of the push-pull method to smaller retardation factors (and smaller NAPL saturations) is enhanced by not normalizing radon pull-phase concentrations.

**FUTURE WORK**

Future work should concentrate on field and modeling investigations of the static and push-pull methods. The ultimate goal of future research should be the acceptance of the methods as a valid tool for NAPL characterization at contaminated field sites. To that end, additional studies are needed at field sites that are characterized by different hydrogeological characteristics and are suspected to have different NAPL distributions. These studies could be performed at sites with high anisotropy and heterogeneity in hydraulic conductivity. Ideally, such studies should be performed at sites where other NAPL characterization techniques are being used, as this would enable comparisons between methods to be made. Furthermore, studies could be performed at sites where various remediation activities are being implemented, such as in situ chemical oxidation, surfactant flushing, alcohol cosolvent
flushing, and augmented bioremediation. Studies at such sites could then incorporate the potential effects of remediation activities on radon test results, as well as serving the purpose of tracking changes in NAPL saturation over time.

Additional modeling studies of the push-pull method are needed, for both hypothetical and field trials of the method. The incorporation of 2-D and 3-D simulations could allow for better interpretation of radon extraction phase breakthrough curves, and may result in more accurate estimates of NAPL saturation. Also, the incorporation of radon emanation and decay into non-steady state models could allow for a more accurate representation of push-pull tests conducted over longer time periods. The effect of NAPL saturation heterogeneity on test results could be incorporated into these modeling studies. Such studies could go a step further through the incorporation of NAPL pools into the models. The effect of rate-limited mass transfer of radon between the NAPL and aqueous phases could be modeled with NAPL pools using a non-equilibrium numerical code. This could prove especially useful for interpreting push-pull test results from field sites where NAPL pooling is known or suspected. The combination of additional field studies and modeling advances could serve to increase the efficiency and utility of the methods, which could lead to the acceptance and application of the methods at field sites by the environmental regulatory and consulting community.
BIBLIOGRAPHY


APPENDICES
APPENDIX A: Radon Sampling Methodology

This methodology is applicable for obtaining radon samples in the laboratory and field. The primary consideration is that radon samples are analyzed via liquid scintillation counting (LSC) within one half life (3.82 days) of being collected.

A1: COLLECTING SAMPLES DIRECTLY IN LSC VIALS

Supplies Needed:

- 20 mL borosilicate LSC vials containing 5 mL of Ultima Gold F LSC cocktail (Packard Bioscience catalog nos. 6001050 and 6013179), pre-weighed with weights recorded
- 20 mL plastic syringe(s) with Luer-Lock hub (available at OSU Chemstores)
- Millipore 0.45 μm syringe prefilter with Luer-Lock hub (Fisher Science catalog no. SLAP 02550)
- Becton-Dickinson 18 ga 1.5 in disposable needle (available at OSU Chemstores)
- Radon mixing device (stored at OSU Groundwater Lab)

1. Attach 20 mL plastic syringe to Luer-Lock hub sampling valve in sampling line. If line does not contain a sampling valve, attach an 18 ga needle to the syringe and insert the needle directly into the water flow at the end of the sampling line to avoid withdrawing air into the syringe.

2. Slowly withdraw syringe plunger and fill syringe with water.
3. Remove syringe from sample valve or, if line did not contain a sampling valve, remove the 18 ga needle from the syringe.

4. Record date, time and sample source in a notebook for later entry into radon spreadsheet. Do not attach label to side of LSC vial, as this will interfere with the liquid scintillation counting process.

5. Within 1 minute of completing step 3, attach a 0.45 μm syringe prefilter and 18 ga 1.5 in disposable needle to the syringe.

6. In order to remove air from syringe prefilter and needle, depress syringe plunger and waste approximately 1 mL of water through pre-filter and needle into a waste container.

7. Insert needle to bottom of pre-weighed LSC vial containing 5 mL of Ultima Gold F cocktail and slowly fill vial with approximately 15 mL of water from syringe. Fill the vial to just below the beginning of the curvature at the neck of the vial.

8. Immediately cap LSC vial snugly. Gently shake vial to disperse cocktail into sample, and place vial on radon mixing device for at least 5 minutes.

9. While vial is mixing, dispose of remaining water in syringe into waste container. Rinse syringe, prefilter and disposable needle for re-use with a triple rinse of clean tap water or deionized water. Be certain that all rinse water has been removed from prefilter before repeating the sampling process. Prefilters can be reused until resistance to flow is encountered.

10. Remove vial from radon mixing device and set into cooler for transport to OSU for liquid scintillation counting.
A2: ALTERNATE METHOD: COLLECTING SAMPLES IN 40 mL VOAs

Supplies Needed:

- 40 mL non-preserved VOA vials and labels
- 6 in 18 ga stainless steel needles
- Supplies noted in Section A1 above

1. Place end of sampling line into bottom of 40 mL non-preserved vial and fill vial with sample water. Allow the vial to overflow and fill after approximately 2 vial volumes have overflowed from the vial.

2. Remove sampling line from vial and carefully cap vial to create a “zero headspace” vial.

3. Record time, date and sample source in notebook and on vial label.

4. Place vial in cooler for transport to OSU.

5. After returning to OSU, place the 40 mL vials in a fume hood along with all supplies.

6. Attach an 18 ga 6 in needle to a plastic syringe.

7. Insert the tip of an 18 ga 1.5 in disposable needle into the top of a 40 mL vial to create a vent line.

8. Insert the syringe with attached 18 ga 6 in needle to the bottom of the vial, then slowly withdraw syringe plunger and fill with water.

9. Remove the syringe and attached needle and the vent line needle from the 40 mL vial.
10. Within 1 minute of completing step 9, attach a 0.45 μm syringe prefilter and 18 ga 1.5 in disposable needle to the syringe.

11. In order to remove air from syringe prefilter and needle, depress syringe plunger and waste approximately 1 mL of water through pre-filter and needle into a waste container.

12. Insert needle to bottom of pre-weighed LSC vial containing 5 mL of Ultima Gold F cocktail and slowly fill vial with approximately 15 mL of water from syringe. Fill the vial to just below the beginning of the curvature at the neck of the vial.

13. Immediately cap LSC vial snugly. Gently shake vial to disperse cocktail into sample, and place vial on radon mixing device for at least 5 minutes.

14. While vial is mixing, dispose of remaining water in syringe into waste container. Rinse syringe, prefilter and disposable needle for re-use with a triple rinse of clean tap water or deionized water. Be certain that all rinse water has been removed from prefilter before repeating the sampling process. Prefilters can be reused until resistance to flow is encountered.

15. Remove LSC vial from radon mixing device.

A3: LIQUID SCINTILLATION COUNTING USING THE PACKARD 2500 TR LSC IN MERRYFIELD HALL

1. Make 3 LSC vial “blanks” containing deionized or tap water which has been sparged with air for approximately 15 minutes using steps 1 – 10 in Section A1. Make
sure vials are free of dirt and fingerprints. Use Kimwipes and methanol to clean vials if necessary.

2. Weigh all LSC vials on the same analytical balance that was used to determine LSC vial weights before filling them with sample water. Record weights in notebook.

3. Place LSC vials in sequential order, starting with the three blanks from step 1, in black LSC vial “cassettes” located below the 2500 TR LSC. Note: In order for radon and its daughter products to reach equilibrium, at least 4 hours must elapse from time that radon sample is obtained in the lab or field and when it is counted on the LSC.

4. Attach a protocol “flag” (located in a box below the LSC) to the left side of the first LSC cassette and push the flag to the left. Place this cassette into the rear of the right side of the LSC. Then place the next cassette in the right side of the LSC in front of the cassette with the protocol flag, and repeat until all cassettes are in the LSC. Note: The SNC cassette always stays in the LSC and can be in any location inside the LSC (except between the cassettes for a single protocol).

5. Press the spacebar on the keyboard to activate the monitor above the LSC. Then press the F1 key “Edit Protocol” to create a protocol to analyze the LSC vials.

6. Note that all entries on every highlighted line must be followed by pressing the Return key.

7. Enter the number of the protocol that you wish to Edit, coinciding with the number on the protocol flag on the cassette.
8. Press the F2 key “Protocol ID”. This opens up a window within which the protocol can be identified. Enter the protocol name, user ID, and, if you wish, additional heading, remembering to press the Return key after each line’s entry. When finished, press the F1 key to exit “Protocol ID”.

9. Press the F3 key “Count Conditions”. This opens up a window in which the LSC counting instructions will be provided to the computer. For radon counting, the following entries should be made:

Count time: 60 min

Cycles: 1

Data Mode: Alpha/Beta

Radionuclide: Manual

Press the F2 key when this field is highlighted to make sure that the Beta Region A has an LL of 0 and UL of 2000 (keV), and the Alpha Region has a LL of 250 and an UL of 900 (keV), and that the A/B Discriminator setting is 170. The Beta Region B should have an LL and UL of 0. Exit the Radionuclide window by pressing the F1 key.

Count Termination: No

Background Subtract: No

Quench Indicator: tSIE

ES Terminator: 60 sec (choose by pressing the F6 key)

Half Life Correction: No

Special Conditions: Use Exist.
Press the F4 key “View/Edit” and choose the following:

Luminescence Correction: No
Heterogeneity Monitor: No
Low Level Count Mode: No
Static Controller: Yes
Coincidence Time: 18
Delay Before Burst: Normal

Exit the Special Conditions window by pressing the F1 key.

When finished, press the F1 key to exit “Count Conditions”.

10. Press the F4 key “Sample Order”. This opens up a window in which the sample counting details are defined. The following entries should be made:

1st Vial Background: No
% of Reference: No
# Counts/Sample Vial: 1
# Vials/Sample: 1

When finished, press the F1 key to exit “Sample Order”.

11. Press the F5 key “Printer Output”. If you do not wish to print the counting results on the dot matrix printer, and use only the disk file output to transfer the results to another computer, press F2 “No”. If you wish to print the results, press the F3 “Use Exist” key, and then press the F4 “View/Edit” key to open a window where the results to be printed are chosen. Using the list on the left, choose the following result fields by placing numbers 1,2, etc. next to the field: P# (protocol number), PID (positive i.d.,
giving the number of the cassette each sample is located in), S# (sample number),
TIME (the total count time), CPMa (counts per minute alpha), a:2S% (the second
standard deviation of CPMa, in %), CPMA (counts per minute beta), A:2S% (the
second standard deviation of CPMA, in %), FLAG (to flag samples for warning
messages), tSIE (the transformed spectral index of the external standard, a quench
number where 0 = totally quenched and 1000 = unquenched, normally falls between
450 and 750), {CR-LF} (carriage return – line feed, to advance the printer). These
items can be chosen to occur in any order.

12. Press the F7 key “Disk File Output”. This information in provided in this
window controls where your data is stored and what is contained in your data. The c:
drive is used for all data storage. Remember that in a DOS program such as this, the
maximum number of characters in a directory or filename is 8 and the maximum
number of characters in the extension is 3 (e.g., filename.dat).
Under Protocol Data? Enter the name under Count Data?, located just below. The name will be chosen by the computer to by SDATA_.DAT, with the space corresponding to the number of the protocol and protocol flag. Under Drive & Path, for both Protocol Data and Count Data, enter a directory name where you would like the results to be stored (e.g., RICHMOND.OCT).
For Output Type, select Sample.
For Header, select Yes.

13. For Output Cells, press F3 “Use Exist” and then F4 “View/Edit” to open a
window where the results to be saved to the c: drive are chosen. Using the list on the
left, choose the following result fields by placing numbers 1, 2, etc. next to the field:
P# (protocol number), PID (positive i.d., giving the number of the cassette each sample is located in), S# (sample number), TIME (the total count time), CPMa (counts per minute alpha), a:2S% (the second standard deviation of CPMa, in %), CPMA (counts per minute beta), A:2S% (the second standard deviation of CPMA, in %), FLAG (to flag samples for warning messages), tSIE (the transformed spectral index of the external standard, a quench number where $0 = $ totally quenched and $1000 = $ unquenched, normally falls between 450 and 750), {CR-LF} (carriage return – line feed, to advance the printer). These items can be chosen to occur in any order.

For Spectrum Data, select Yes and then enter the same Drive & path that was entered for Protocol Data and Count Data.

The software will now save the counting results in a file named SDATA_.DAT in the c: drive in the directory you named above. Also, after each sample is counted a Spectrum File will be created for each sample’s alpha and beta results, showing the CPM results as a function of energy channel, ranging from 0 to 1000 keV in 0.5 keV increments.

14. The LSC is equipped with a refrigeration unit to keep the samples cool. Prior to beginning counting leave the samples in the LSC for approximately 4 hours to allow for temperature equilibration in the vials. Do not remove the SNC cassette from the LSC (read the manual for information about its purpose, if interested).

15. The protocol has now been created and, assuming the samples are in the LSC and the instructions above have been followed, the LSC can be started. Press the
green button on the keyboard and the LSC will start. Counting will take approximately 1 hour per vial.

16. A few important details about the LSC software: On the 2500 TR, the samples can be re-counted with a different energy window without the samples being present in the LSC. This can be accomplished in the F5 key “Replay” window. Read the blue Packard manual for details on this procedure. The sample changer in the LSC can be manually controlled (e.g., stopped, started, paused, etc.) using the alt-F2 key “SC Control”. Again, consult the manual regarding this operation. The F10 key “etc” can be pressed to show additional keys at the bottom of the screen. Consult the manual regarding the function of these keys.

17. The computer clock runs a bit slow, so every few weeks the F4 key “Date/Time” should be pressed and the correct time entered.

18. Over time the directory should be emptied of old directories and files in order to make room for new data.

19. The LSC is equipped with a battery backup to prevent it from shutting down during very short power outages. Power outages that last more than a few seconds will cause the LSC to shut down, requiring the computer to be re-booted or, if that does not work, the LSC and computer to be turned off and then on again. The sample data for samples that have already been counted will be saved in the directory that you have chosen. However, to begin counting again you must change the directory name (in step 12) so that the new data after the re-start is not saved over the old data from
before the re-start. If this is not done the new data will be written over the data from before the re-start. Hence an edit of the protocol is necessary.

20. The refrigeration unit empties its condensate into a cooler on the left side of the LSC. Empty the cooler every month and make sure that the drainage line is not cramped shut by the cooler lid after emptying the cooler.

21. After the samples have finished counting, the counting data can be obtained from the 2500 TR. The data fields chosen for “Printer Output” in step 11 and/or “Disk Output” in step 12 can be obtained from the printout from the dot matrix printer and from the LSC’s c: drive. The file containing the data is located in the directory chosen in step 12 and has the filename SDATA_.DAT, where the space corresponds to the number of the protocol and protocol flag. To obtain this file, press the F5 key “DOS Exit” to exit the Packard software. Then type ‘cd c:\’ to change directories to the c: drive, followed by typing ‘cd c:\directory name’ to access the directory chosen in step 12. Type ‘dir /p’ to view the directory contents. At the bottom of the list of contents should be a file named SDATA_.DAT. Place a floppy disk into the a: drive, and then type ‘copy SDATA_.DAT a:\’ to copy that file to the floppy disk. Then go to step 22.

22. The date and time each sample was counted on the LSC must be known in order to back-calculate the radon concentration to the time the sample was obtained in the lab or field. The LSC creates a Spectrum file at the time each sample is finished counting and stores each file, one for the alpha spectrum and one for the beta spectrum, in the same directory as is located the SDATA_.DAT file. Use the instructions in step 21 to access the directory containing the SDATA_.DAT file. Type
‘dir /p’ at the DOS command and a series of similar looking files will be shown, with the filename p_s00_.a01 (the alpha spectrum file) and p_s00_.001 (the beta spectrum file). The first space in the filename corresponds to the protocol and protocol flag number, while the second space in the filename corresponds to the sample number. To the right of each filename is the file size and date and time the file was created, corresponding to when the sample finished counting. This entire directory can be converted to a file and saved to the floppy disk. In this way a file will be created showing exactly what is on the monitor, and, like the SDATA_.DAT file discussed in the previous step, can be easily entered into an Excel spreadsheet. To convert the directory to a file, at the DOS command type ‘dir > times’. This will convert the directory to a file named times, although any name can be chosen for this file. To copy the times file to the floppy disk, type ‘copy times a:\’. If you have followed steps 21 and 22 directory, the floppy disk now contains a file named SDATA_.DAT and a file named times. These files contain all of the data needed to determine the radon concentrations in the samples. To obtain a printed copy of the directory, in lieu of a file named times, the directory can be printed by using the print screen key on the upper right of the keyboard. This key will print only what is on the screen, so you will have to advance through the directory and print each screen if there are a large number of samples and, hence, a large directory filled with a large number of Spectrum files.

23. Remove the floppy disk from the LSC computer. To return to the Packard software type ‘cd c:\’, then type ‘cd Packard’, then type ‘Exit’. Remove the cassettes
from the LSC and remove the vials from the cassettes. Place the vials in a labeled box to the right of the LSC. When approximately 1000 vials have accumulated, contact Environmental Health & Safety for disposal. These vials are not radioactive vials, but do contain scintillation cocktail and, depending on the water source, may contain carcinogens such as trichloroethene (TCE). Remove the protocol flag from the first cassette and place it back in the box underneath of the LSC. Place the cassettes back into their storage area underneath the LSC. The LSC is now ready for the next set of samples for counting. Please go to APPENDIX B: Radon Data Reduction to convert the data to radon concentrations.

A4: LIQUID SCINTILLATION COUNTING USING THE PACKARD 2900 TR LSC IN THE GROUNDWATER RESEARCH LAB

1. Make 3 LSC vial “blanks” containing deionized or tap water which has been sparged with air for approximately 15 minutes using steps 1 – 10 in Section A1. Make sure vials are free of dirt and fingerprints. Use Kimwipes and methanol to clean vials if necessary.

2. Weigh all LSC vials on the same analytical balance that was used to determine LSC vial weights before filling them with sample water. Record weights in notebook.

3. Place LSC vials in sequential order, starting with the three blanks from step 1, in black LSC vial “cassettes” located to the right of the 2900 TR LSC. Note: In order for radon and its daughter products to reach equilibrium, at least 4 hours must elapse
from time that radon sample is obtained in the lab or field and when it is counted on
the LSC.

4. Attach a protocol “flag” to the left side of the first LSC cassette and push the
flag to the left. The flags are located in a box to the right of the LSC. Place this
cassette into the rear of the right side of the LSC. Then place the next cassette in the
right side of the LSC in front of the cassette with the protocol flag, and repeat until all
cassettes are in the LSC. Note: The SNC cassette always stays in the LSC and can be
in any location inside the LSC (except between the cassettes for a single protocol).

5. Under File on the toolbar in the upper portion of the monitor, select New
Assay, then select Alpha/Beta. This begins the creation of an assay that can be linked
to the protocol that has the same number as the protocol flag from step 4.

6. Under the Assay Parameters window, type the name of the assay author and an
assay description.

7. Next, under the Count Conditions window, for Radionuclide Name select AB
Manual, the press OK within this Alpha Beta Nuclides subwindow. The AB Manual
nuclide has already been defined to have a Beta lower energy level = 0 keV and an
upper energy level = 2000 keV, and an Alpha lower energy level = 250 keV and an
upper energy level = 900 keV, with a Discriminator Setting = 170.

8. Also in the Count Conditions window, choose the following: Count Mode:
Normal
Quench Indicator: tSIE
External Std. Terminator: 60 sec
Pre-Count Delay (min): 0.00
Count Time (min): 60.00
Assay Count Cycles: 1
Repeat Sample Count: 1
#Vials/Sample: 1
do not check any other boxes in the Count Conditions window

9. Next, under the Count Corrections window, choose the following:
   Static Controller: checked
   Coincidence Tie (nsec): 18 (should be pre-set)
   Delay Before Burst (nsec): 75 (should be pre-set)
   Do not check half-life correction

10. Next, under the Report Definition window, press Rename to change the name of the report to one of your choosing. In Report Fields, use the mouse to check the following boxes: P# (protocol number), PID (positive i.d., giving the number of the cassette each sample is located in), S# (sample number), COUNT TIME (the total count time), CPMa (counts per minute alpha), C:2S% (the second standard deviation of CPMa, in %), CPMA (counts per minute beta), A:2S% (the second standard deviation of CPMA, in %), MESSAGES (for warning messages), tSIE (the transformed spectral index of the external standard, a quench number where 0 = totally quenched and 1000 = unquenched, normally falls between 450 and 750), DATE (gives the date the sample finished counting), TIME (gives the time the sample finished
counting) These items can be chosen to occur in any order by using the arrow keys at the bottom of the screen.

11. Next, under the Report Output window, check the box marked Output to Printer (if a printed report is desired) and check Data File. Under File Type choose Excel (a .csv file), and under File Name change the name to the report name that was used in step 10. An Excel file with this name will be created during and at the end of counting containing the counting results using the parameters specified in step 10. Make sure the Output per Sample is dotted, and check Include Column Header.

12. Next, under the Special Files window, check Spectra Files (individual). This will create 2 spectrum files for each sample showing the alpha and beta CPM results as a function of energy channel, ranging from 0 to 1000 keV in 0.5 keV increments.

12. Press Save As to save the assay, and select a name for the assay. The assay will be saved as a .las file in the path c:\Packard\TriCarb\Assays\assay name.lsa

13. Now the assay can be associated with the protocol number that is on the flag on the first cassette of samples (from step 4). Use the trackball to highlight the protocol flag # on the left side of the screen corresponding to the protocol flag number on the cassette. Then select File, and then select Associate Assay. Open the assay that was saved in step 12, and for User ID select Brian Davis. Now look at the output data path. Add to the path so that it reads c:\packard\TriCarb\Results\Brian Davis\assay name\report name (The report name was defined in step 10). This path is where the counting data, in the form of the Excel file (.csv), will be saved. Write the path down in a notebook for future reference.
14. Prior to beginning counting, allow the vials to sit in the LSC for 4 hours so that the temperature of the vials equilibrates with the refrigerated interior of the LSC. Do not remove the SNC cassette from the LSC (read the manual for information about its purpose, in interested).

15. To begin counting press the green flag in the upper left corner of the screen. Counting will take approximately 1 hour per vial.

16. When sample counting is finished, a checkered flag will appear next to the protocol flag in the window next to the assay in the window on the left side of the screen.

17. The computer clock runs a bit slow, so every few weeks the date and time should be updated by clicking on the clock in the lower right of the screen.

18. The LSC is equipped with a battery backup to prevent it from shutting down during very short power outages. Power outages that last more than a few seconds will cause the LSC to stop counting, but the computer will re-boot automatically. The sample data for samples that have already been counted will be saved in the directory that you have chosen. However, to begin counting again you must change the output data path (in step 13) so that the new data after the re-start is not saved over the old data from before the re-start. If this is not done the new data will be written over the data from before the re-start. Hence an edit of the assay and re-association with the protocol flag is necessary. Remember to periodically re-fill the printer with paper.

19. After the samples have finished counting, the counting data can be obtained from the 2900 TR. The printed data will be sitting in the tray of the printer located to
the right of the LSC. To obtain the data on a floppy disk, place a floppy disk in the a: drive. Using Windows Explorer, go to the directory that was defined in step 13. The Excel file containing the count data should be located in this directory with an extension of .csv.

Simply copy and paste this file to the a: drive and remove the floppy disk from the a: drive.

20. Close Windows Explorer and return to the Packard software. Highlight the protocol flag of your protocol on the left side of the screen, then go to File. The go to Disassociate Assay to disassociate the assay from the protocol flag.

21. Remember that this assay can be re-used an unlimited number of times by simply changing the report name and output data path as described above (if this is not done, the data stored in the computer will be overwritten with new data).

22. Remove the cassettes from the LSC and remove the vials from the cassettes, placing the vials on the counter to the right of the LSC. When approximately 1000 LSC vials have accumulated, contact Environmental Health and Safety for disposal. These vials are not radioactive vials, but do contain scintillation cocktail and, depending on the water source, may contain carcinogens such as trichloroethene (TCE). Remove the protocol flag from the first cassette and place it back in the box to the right of the LSC. Place the cassettes back into their storage area to the right of the LSC. The LSC is now ready for the next set of samples for counting. Please go to APPENDIX B: Radon Data Reduction to convert the data to radon concentrations.
APPENDIX B: Radon Data Reduction

This methodology is for reducing LSC counting data to radon concentrations (pCi/L) using an Excel spreadsheet. Please refer to the Excel spreadsheet at the end of this appendix when referring to these instructions. The cells where data must be entered by hand or copied from a disk file are highlighted in grey. These instructions are written for obtaining radon concentration data from a push-pull test. Some of the steps (marked by an asterisk) can be skipped if the radon samples originate as static samples. Spend some time going through a copy of this spreadsheet on your computer so that you thoroughly understand the equations prior to entering data into a spreadsheet for the first time.

1. Open a radon Excel spreadsheet similar to the one in this Appendix. Using the methodology outlined in Appendix A, obtain LSC counting data from the 2500 TR or 2900 TR in printed or disk form. For disk files, place the floppy disk in the a: drive of the computer you are working on. For disk files from the 2500 TR, open the SDATA_.DAT and Times files in Excel. For disk files from the 2900 TR, open the .csv file in Excel.

2. *By hand, Enter the time “Mixing Begins” for the injection solution (i.e., sparging to remove radon), as well as the “Injection Start Time” and “Injection Stop Time” (referring to the push phase).
3. By hand, Enter the “Sample Mass (i)” and “Sample Mass (f)”, referring to the LSC vial weights with ~ 5 mL cocktail and with ~ 5mL cocktail + ~ 15 mL water sample, respectively.

4. By hand, Enter the “Sample Location”, referring to the location the sample was obtained from.

5. By hand, enter the “Real Time Sampled”, referring to the time the radon sample was obtained in the field (format = 5/25/02  1:45:00 PM) Note that the times are automatically converted by Excel to the (format = 5/25/02 13:45:00), or military time. Be sure these data are in Pacific time.

6. Copy and paste the “Sample Counted” from the Times file (2500 TR) or the .csv file (2900 TR) into the radon spreadsheet. The format may have to be converted to the time format shown in step 5 by hand. Use the Find and Replace option to speed this process. There is more than one way to do this, so use the method that suits you best. These data can also be entered by hand from a printout.

7. Copy and paste the “Gross Count” (CPMa) from the SDATA_.DAT file (2500 TR) or the .csv file (2900 TR) into the radon spreadsheet. These data can also be entered by hand from a printout.

8. Copy and paste the “Quench Indicator (tSIE)” from the SDATA.DAT file (2500 TR) or the .csv file (2900 TR) into the radon spreadsheet. These data can also be entered by hand from a printout.

9. *Copy the “Gross Count” and “Quench Indicator (tSIE)” data from the rows of the spreadsheet where the injectate samples are located into the small “Injectate
Background” table at the top of the spreadsheet. In the “Net Count” column, make sure to change the equation in the appropriate rows (your discretion) so that the average of the “Injectate Background” is subtracted from the “Gross Count” (e.g., for the pull phase samples until the volume extracted/volume injected > 1).

10. Copy the “Gross Count” and “Quench Indicator (tSIE)” data from the rows of the spreadsheet where the blank samples are located into the small “Interval Inst. Background” table at the top of the spreadsheet. In the “Net Count” column, make sure that the equation for the samples not referred to in step 9 takes into account this average background value for CPMa.

11. Make sure that the following values are located in the “Alpha conversion efficiency” cell in the upper right corner of the spreadsheet: for the 2500 TR: 0.74; for the 2900 TR: 0.712. These are the calculated efficiencies of the two LSCs as determined by Mike Cantaloub and Brian Davis using radium-226 standards.

12. The LSC counting data has now been converted to radon concentration data in picoCuries per liter (pCi/L), as shown on the right side of the spreadsheet. Note that the bottom right corner of the spreadsheet contains a few potentially useful conversions for units of radioactivity.
Table B.1 Radon data reduction spreadsheet

Title: Push-Pull on well 1

Purpose: Develop Rn and Br breakthrough curves for single-well push-pull test

Injectate Background

<table>
<thead>
<tr>
<th>Quench</th>
<th>Time</th>
<th>Proto DPM</th>
<th>Count</th>
<th>Count Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>0.05</td>
<td>60</td>
<td>705.51</td>
<td>0.2</td>
</tr>
<tr>
<td>0.15</td>
<td>0.05</td>
<td>60</td>
<td>699.59</td>
<td>0.18</td>
</tr>
<tr>
<td>0.27</td>
<td>0.07</td>
<td>60</td>
<td>718.12</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Data

<table>
<thead>
<tr>
<th>Start Time</th>
<th>Stop Time</th>
<th>Interval</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/30/2002 7:27</td>
<td>4/30/2002 8:41</td>
<td>at least 2 days before test</td>
<td>Develop Rn and Br breakthrough curves for single-well push-pull test</td>
</tr>
</tbody>
</table>

GRL LSC

Approx. Mixing Time 2+ days

<table>
<thead>
<tr>
<th>Number</th>
<th>Sample Mass(i)</th>
<th>Sample Mass(II)</th>
<th>Sample Volume</th>
<th>Sample Location</th>
<th>Real Time</th>
<th>Sample Counted</th>
<th>Sample Elapsed</th>
<th>Sample Location</th>
<th>Gross Count</th>
<th>Error Count</th>
<th>Corrected Count</th>
<th>Error Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.81</td>
<td>37.60</td>
<td>15.79</td>
<td>well 1</td>
<td>4/30/2002 9:37</td>
<td>5/2/20 19:08</td>
<td>60 57.2</td>
<td>well 1</td>
<td>12.05</td>
<td>0.45</td>
<td>11.52</td>
<td>0.44</td>
</tr>
<tr>
<td>2</td>
<td>21.78</td>
<td>37.26</td>
<td>15.46</td>
<td>well 1</td>
<td>4/30/2002 9:34</td>
<td>5/2/20 20:11</td>
<td>60 58.1</td>
<td>well 1</td>
<td>11.92</td>
<td>0.45</td>
<td>11.47</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>21.92</td>
<td>37.09</td>
<td>15.77</td>
<td>well 1</td>
<td>4/30/2002 9:47</td>
<td>5/2/20 21:15</td>
<td>60 58.9</td>
<td>well 1</td>
<td>11.82</td>
<td>0.44</td>
<td>11.39</td>
<td>0.44</td>
</tr>
<tr>
<td>4</td>
<td>21.83</td>
<td>36.66</td>
<td>14.75</td>
<td>well 1</td>
<td>4/30/2002 9:54</td>
<td>5/2/20 22:16</td>
<td>60 59.9</td>
<td>well 1</td>
<td>11.56</td>
<td>0.43</td>
<td>11.09</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>21.80</td>
<td>37.33</td>
<td>15.47</td>
<td>well 1</td>
<td>4/30/2002 9:58</td>
<td>5/2/20 23:19</td>
<td>60 60.9</td>
<td>well 1</td>
<td>13.75</td>
<td>0.48</td>
<td>13.29</td>
<td>0.48</td>
</tr>
<tr>
<td>6</td>
<td>21.69</td>
<td>37.28</td>
<td>15.39</td>
<td>well 1</td>
<td>4/30/2002 10:04</td>
<td>5/3/20 12:22</td>
<td>60 73.8</td>
<td>well 1</td>
<td>0.74</td>
<td>0.40</td>
<td>0.78</td>
<td>0.40</td>
</tr>
<tr>
<td>7</td>
<td>21.64</td>
<td>36.35</td>
<td>14.71</td>
<td>well 1</td>
<td>4/30/2002 10:10</td>
<td>5/3/20 1:25</td>
<td>60 62.8</td>
<td>well 1</td>
<td>11.11</td>
<td>0.43</td>
<td>10.68</td>
<td>0.43</td>
</tr>
<tr>
<td>8</td>
<td>21.76</td>
<td>37.32</td>
<td>15.58</td>
<td>injectate</td>
<td>4/30/2002 10:31</td>
<td>5/3/20 2:27</td>
<td>60 63.4</td>
<td>injectate</td>
<td>0.17</td>
<td>0.05</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>9</td>
<td>21.76</td>
<td>36.84</td>
<td>15.09</td>
<td>injectate</td>
<td>4/30/2002 10:40</td>
<td>5/3/20 3:30</td>
<td>60 64.3</td>
<td>injectate</td>
<td>0.16</td>
<td>0.05</td>
<td>0.15</td>
<td>0.08</td>
</tr>
<tr>
<td>10</td>
<td>21.73</td>
<td>36.68</td>
<td>14.95</td>
<td>injectate</td>
<td>4/30/2002 10:51</td>
<td>5/3/20 4:33</td>
<td>60 65.2</td>
<td>injectate</td>
<td>0.27</td>
<td>0.07</td>
<td>0.25</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calibration Data:

<table>
<thead>
<tr>
<th>Vial</th>
<th>DPM in vial</th>
<th>CPM measured</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1250.13</td>
<td>899.46</td>
<td>0.706</td>
</tr>
<tr>
<td>2</td>
<td>921.35</td>
<td>662.31</td>
<td>0.719</td>
</tr>
</tbody>
</table>

Quadruplicate 60 minute counts for each sample. Average count rate (cpm) for the two samples. Total count time of 4 hr.

Pulse Decay Discriminator Setting of 170 nanoseconds.

Alpha efficiency should remain constant. Potential shift in spectrum reanalysis at wider window; lower window of 200 or 175.

Groundwater Lab LSC

Calibration performed on October 23 and 24 2000

Total extraction volume

152.96

Average volume

15.30

Std deviation

0.40

Little significant effect from quench difference between calibration sets. Calibration performed on October 23 and 24 2000.
Table B.1 Radon data reduction spreadsheet

<table>
<thead>
<tr>
<th>Time</th>
<th>Quench</th>
<th>Alpha conversion efficiency (cpm/µl)</th>
<th>4/30/2002 Title: Push-Pull on well 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cpm) ± 0.06</td>
<td>60</td>
<td>707.26</td>
<td></td>
</tr>
<tr>
<td>(cpm) ± 0.05</td>
<td>60</td>
<td>739.83</td>
<td>Single point calibration used rather than linear regression.</td>
</tr>
<tr>
<td>(cpm) ± 0.07</td>
<td>60</td>
<td>740.67</td>
<td>Volume Injected: 30 L</td>
</tr>
<tr>
<td>Average 0.06</td>
<td>60</td>
<td>732.247</td>
<td>Volume Extracted: 50 L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rn Activity</th>
<th>Relative Concent.</th>
<th>Error (%)</th>
<th>Quench Indicator (ISIE)</th>
<th>Well (location)</th>
<th>Elapsed Sample Time (min)</th>
<th>Aqueous alpha (cpm/ml)</th>
<th>Aqueous Rn (dpm/ml)</th>
<th>Aqueous Rn (pCi/L)</th>
<th>Aqueous Rn (aM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15</td>
<td>0.09</td>
<td>8%</td>
<td>662.65</td>
<td>well 1</td>
<td>0</td>
<td>1.15</td>
<td>0.540</td>
<td>243</td>
<td>7.12</td>
</tr>
<tr>
<td>1.17</td>
<td>0.09</td>
<td>8%</td>
<td>702.38</td>
<td>well 1</td>
<td>0</td>
<td>1.17</td>
<td>0.547</td>
<td>247</td>
<td>7.22</td>
</tr>
<tr>
<td>1.15</td>
<td>0.09</td>
<td>8%</td>
<td>683.56</td>
<td>well 1</td>
<td>0</td>
<td>1.15</td>
<td>0.537</td>
<td>242</td>
<td>7.09</td>
</tr>
<tr>
<td>1.17</td>
<td>0.09</td>
<td>8%</td>
<td>738.18</td>
<td>well 1</td>
<td>0</td>
<td>1.17</td>
<td>0.547</td>
<td>246</td>
<td>7.22</td>
</tr>
<tr>
<td>1.38</td>
<td>0.10</td>
<td>7%</td>
<td>707.08</td>
<td>well 1</td>
<td>0</td>
<td>1.38</td>
<td>0.648</td>
<td>292</td>
<td>8.55</td>
</tr>
<tr>
<td>1.08</td>
<td>0.09</td>
<td>9%</td>
<td>705.78</td>
<td>well 1</td>
<td>0</td>
<td>1.08</td>
<td>0.503</td>
<td>227</td>
<td>6.65</td>
</tr>
<tr>
<td>1.19</td>
<td>0.10</td>
<td>8%</td>
<td>728.35</td>
<td>well 1</td>
<td>0</td>
<td>1.19</td>
<td>0.556</td>
<td>250</td>
<td>7.34</td>
</tr>
<tr>
<td>0.00</td>
<td>0.02</td>
<td>1563%</td>
<td>705.31</td>
<td>injectate</td>
<td>0</td>
<td>0.00</td>
<td>0.000</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>0.00</td>
<td>0.02</td>
<td>1520%</td>
<td>668.58</td>
<td>injectate</td>
<td>0</td>
<td>0.00</td>
<td>0.001</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>0.00</td>
<td>0.02</td>
<td>481%</td>
<td>718.12</td>
<td>injectate</td>
<td>0</td>
<td>0.00</td>
<td>0.002</td>
<td>1</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Conversion Factors:

\[ \lambda = \ln(2)/T_{1/2} \]

where \( \lambda \) is the decay constant, \( T_{1/2} \) is the half-life, and \( \lambda = 0.001 \text{ day}^{-1} \)

\[ \text{Conversion:} \]

1 dpm \( \alpha \) = 0.333 dpm Rn

1 dpm Rn = 0.450 pCi Rn

1 ml = 0.001 L

1 pCi/L = 0.029 aM = 1.0 \times 10^{-9} \text{ M}
APPENDIX C: STOMP Numerical Code Helpful Hints

This appendix is intended to supplement the User’s Guide for STOMP: Subsurface Transport Over Multiple Phases, a numerical groundwater modeling code developed and supported by Pacific Northwest National Laboratory. An example Input file at the end of this appendix is used to highlight the various components of this Input file. The user should consult the User’s Guide for further guidance on the use of the code and interpretation of results (White and Oostrom, 2000).

In order to run STOMP, the program must be installed in a directory in your engr account. The program is named stomp1_bd.f. In addition to this program, the following files must be installed in the same directory: Input, Parameters, and Commons. Note that these files do not have extensions after their names. A numerical simulation is organized and defined in the Input file as described below. Note that all changes to the Input file must be performed in Microsoft Notepad; do not use Microsoft Word for these changes, as it can add miscellaneous hidden characters to the Input file that will cause STOMP to fail to run.

The example Input file is based on a radon push-pull test conducted in water saturated, NAPL-contaminated sediment. This 1-D radial flow simulation is performed over a 500 cm long domain, with a uniform node spacing $\Delta r = 1.0$ cm. The injection solution consists of radon-free water. The initial radon concentration in the sediment is a function of the NAPL saturation as defined in equation 3.4, with an assumed porosity ($n$) of 0.35, bulk density ($\rho_b$) of 1.89 g/cm$^3$, and $K = 50$ (for radon in
TCE). The simulated push-pull test involves the push of 250 L and pull of 500 L of solution over a 3 ft interval of a 2 in diameter well. Push and pull pumping rates are constant at 1 L/min. The Input file is structured as a series of "cards" that each define various input parameters for the simulation. Each card in the Input file is named and ordered as follows: Simulation Title Card, Solution Control Card, Grid Card, Rock/Soil Zonation Card, Mechanical Properties Card, Hydraulic Properties Card, Saturation Function Card, Aqueous Relative Permeability Card, Solute/Fluid Interaction Card, Solute/Porous Media Interaction Card, Initial Conditions Card, Boundary Conditions Card, Output Control Card, Surface Flux Card. The basic components of each card as represented in the example Input file are described below; however, the user should read section 4.0 "Input File" in the STOMP User's Guide in conjunction with these descriptions in order to further understand the nuances of the card.

The Simulation Title Card consists of twelve lines. The first line defines the version of STOMP that is being used (1). The second through sixth lines contain the title of the simulation, user name, university name, date, and time. The seventh line defines the number of subsequent description lines in the Card. The eighth through twelfth lines provide a user-defined, detailed description of the simulation. Changes can be made to these lines, but the total number of lines should not be changed.

The Solution Control Card consists of seven lines. Note that lines beginning with a # symbol are comment lines. The first line defines the execution mode of the program (Normal), and the second line the operational mode of the program (Water
w/TVD Transport). The third line defines the number of Execution Periods for the program, which is 2 for a push-pull test (one for the push phase and one for the pull phase). The fourth line defines the first execution period start (0.0) and stop (15580) time in seconds, along with the initial time step (10), maximum time step (10), time step acceleration factor (1), maximum number of Newton-Rhapson iterations (8), and convergence criterion (1.e-06). The fifth line repeats the criteria for the fourth line for the second execution period (i.e., for the pull phase). The sixth line defines the maximum CPU time (46740) in seconds, maximum clock time (46740) in seconds, and maximum number of time steps (4674). Make sure to end that the maximum CPU and clock times end on a number ending with 0. The last line defines the number of interfacial averaging variables (0).

The Grid Card consists of five lines. The first line defines the coordinate system for the simulation (Cylindrical). The second line defines the number of radial direction nodes (500), the number of azimuthal direction nodes (1), and the number of z direction nodes (1). The third line defines the well radius (2.54) in cm, and the number of radial direction nodes and node spacing (500@1.0) in cm. The fourth line defines the number of degrees over which flow is occurring through the well screen (in this case over the entire 360° of the well). The fifth line defines the z direction length of the well (91.4) in cm.

The Rock/Soil Zonation Card consists of four lines. The first line defines the number of different soils in the simulation. Each of the following three lines defines one of the three soils, with the user-defined name of the soil (m, n, or p), beginning
and ending radial direction nodes for each soil (ranging from 1 to 500), and beginning and ending azimuthal and z direction nodes for each soil (corresponding to 1 for a 1-D simulation). Note that soil m ranges from nodes 1 to 24, soil n ranges from nodes 25 to 48, and soil p ranges from nodes 49 to 500.

The Mechanical Properties Card consists of three lines. On each line the mechanical properties of one of the three soils named in the Rock/Soil Zonation Card are defined. Each line defines the rock/soil name (m, n, or p), the particle density (2900) in kg/m^3, the total porosity (0.35), the diffusive porosity (0.35), and tortuosity function option (Millington and Quirk).

The Hydraulic Properties Card consists of three lines. On each line the hydraulic conductivity of one of the three soils named in the Rock/Soil Zonation Card is defined (14.0) in cm/min.

The Saturation Function Card consists of five lines. On the first three lines the saturation-capillary pressure function for each of the three soils named in the Rock/Soil Zonation Card is defined. Each line defines the rock/soil name (m, n, or p), the saturation function option (Nonhysteretic van Genuchten), the \( \alpha \) parameter (0.025) in 1/cm, the \( n \) parameter (3.0), and the minimum saturation (0.05). These parameters do not need to be changed for saturated system simulations. The last two lines are comment lines.

The Aqueous Relative Permeability Card consists of three lines. On each line the relative permeability saturation function for each of the three soils named in the Rock/Soil Zonation Card is defined. Each line defines the rock/soil name (m, n, or p).
and the relative permeability function (Mualem). These parameters do not need to be changed for saturated system simulations.

The Solute/Fluid Interaction Card consists of seven lines. The first line defines the number of solutes in the simulation (5). Each of the next five lines defines the user-defined solute name (a, b, c, d, or e), the effective diffusion option (Conventional), the aqueous phase molecular diffusion coefficient (1.0E-30) in m^2/sec, the solute partition option (Continuous), and the radioactive half-life (1.0E10) in years. The last line defines the number of reactions (0).

The Solute/Porous Media Interaction Card consists of three sets of six lines each. This card is where the degree of partitioning for a particular solute is defined. The first line defines the rock/soil name (m, n, or p), and, for a given soil, the longitudinal dispersivity (4.00) in cm and the transverse dispersivity (0.4) in cm. For a 1-D simulation recall that the transverse dispersivity is unimportant. Each of the next five lines defines the partition coefficient for each of the five solutes (a, b, c, d, and e) named in the Solute/Fluid Interaction Card. The partition coefficient is defined via equation 4.8. Please refer to the discussion accompanying that equation for a description of how NAPL saturations are converted to solid:aqueous phase partition coefficients. On each of the five lines the solute name is followed by the soil:aqueous phase partition coefficient (a five digit number) in cm^3/g. This six line grouping is then repeated twice, once for soil n and once for soil p. Thus partition coefficients are defined for each solute for each particular rock/soil name.
The Initial Conditions Card consists of three lines followed by three sets of five lines (eighteen total lines). The first line defines the initial saturation option (Gas Pressure, Aqueous Pressure). The second line defines the number of initial condition domains (16). The third line defines the variable name option (Aqueous Pressure) and the aqueous pressure (102450.9) in Pascals. A series of six commas follows, followed by the domain over which the aqueous pressure initial condition is defined (1,500) for the radial nodes, (1,1) for the azimuthal nodes, and (1,1) for the z direction nodes. Next are three sets of five lines. Each set of five lines is associated with a particular soil (m, n, or p) as defined on the Rock/Soil Zonation Card. Each line in a five line set refers to one solute (a, b, c, d, or e) and defines the variable name option (Solute Aqueous Conc.), the solute name (a, b, c, d, or e), the initial radon concentration for that particular solute as defined by equation 4.5 (assuming a 'background' radon concentration of 200 pCi/L), the solute concentration units (1/cm^3), a series of six commas, and the domain over which the solute initial concentration is defined (1 to 24, 48, or 500) for the radial nodes, (1,1) for the azimuthal nodes, and (1,1) for the z direction nodes. Note that the nodes 1,24 are associated with soil m, the nodes 25,48 are associated with soil n, and the nodes 49,500 are associated with soil p as defined in the Rock/Soil Zonation Card.

The Boundary Conditions Card consists of a series of lines (fifteen total) in which the boundary conditions at each end of the domain are defined separately for the push and pull phases of the push-pull test. The domain has two ends, one named West (at node 1, where the well is located) and one named East (at node 500, at the
opposite end of the domain). The first line of the card defines the number of boundary condition domains (4). This line is followed by four sets of lines, with each set consisting of four (the first two sets) or three (the last two sets) of lines; each set defines the boundary condition at one end of the domain for either the push or pull period of the push-pull test. The first set of lines defines the boundary condition for the West end of the domain during the push phase. The first line defines the end of the domain (West), the boundary condition for aqueous flux (Neumann Aqueous), and the boundary condition for each of the five solutes (Inflow Aqueous). The second line defines the radial (1,1), azimuthal (1,1) and z direction nodes (1,1) for this boundary condition, and the number of boundary condition times (2). The third line defines the starting time for the boundary condition (0.0) in seconds, the aqueous flux (0.69) in cm/mm (this is defined by dividing the volumetric flow rate by the area of the well screen, or Q/A), and the inflow concentrations of solutes a, b, c, d, and e (0.0) in 1/cm^3. The fourth line defines the same parameters as the third line for the end of the push phase (15580) in seconds. The second set of lines defines the boundary condition for the East end of the domain during the push phase. The first line defines the end of the domain (East), the boundary condition for aqueous flux (Dirichlet Aqueous), and the boundary condition for each of the five solutes (Outflow). The second line defines the radial (500,500), azimuthal (1,1) and z direction nodes (1,1) for this boundary condition, and the number of boundary condition times (2). The third line defines the starting time for the boundary condition (0.0) in seconds, the aqueous pressure (102450.9) in Pascals, followed by a series of 10 commas. The fourth line
defines the same parameters as the third line for the end of the push phase (15580) in seconds. The third set of lines defines the boundary condition for the West end of the domain during the pull phase. The first line defines the end of the domain (West), the boundary condition for aqueous flux (Neumann Aqueous), and the boundary condition for each of the five solutes (Outflow). The second line defines the radial (1,1), azimuthal (1,1) and z direction nodes (1,1) for this boundary condition, and the number of boundary condition times (1). The third line defines the starting time for the boundary condition (15580.0) in seconds, the aqueous flux (-0.69) in cm/min (this is defined by dividing the negative volumetric flow rate by the area of the well screen, or Q/A), followed by a series of 10 commas. The fourth set of lines defines the boundary condition for the East end of the domain during the pull phase. The first line defines the end of the domain (East), the boundary condition for aqueous flux (Dirichlet Aqueous), and the boundary condition for each of the five solutes (Zero Flux). The second line defines the radial (500,500), azimuthal (1,1) and z direction nodes (1,1) for this boundary condition, and the number of boundary condition times (1). The third line defines the starting time for the boundary condition (15580.0) in seconds, the aqueous pressure (102450.9) in Pascals, followed by a series of 10 commas.

The Output Control Card consists of a series of lines (twenty-five total) where the output data for the simulation results is chosen. Output data takes the form of 1) time series concentration data sets at a given node(s) (called Output files), and 2) concentration profiles at given times (called Plot files). The first part of the Output
Control Card deals with 1). The first line defines the number of reference nodes where output data is desired (6). The second through seventh lines define the location (radial, azimuthal, and z direction) of those six nodes where the output data is desired. The eighth line defines the reference node screen output frequency (10), the reference node output file frequency (1), the output time units (s), the output length units (cm), a comma, the screen significant digits (4), the output file significant digits (4), and the plot file significant digits (4). The ninth line defines the number of solutes for which output file data is desired (5). The tenth through fourteenth lines define for each solute the reference node variable option (Solute Aqueous Conc.), the solute name (a, b, c, d, or e), and the solute concentration units (1/cm^3). The second part of the Output Control Card (beginning on the fifteenth line) defines the number of times for which concentration profiles (Plot files) are desired (4). The sixteenth through nineteenth lines define those times and time units (s). The twentieth line defines the number of solutes for which concentration profiles are desired (5), and the twenty-first through twenty-fifth lines define the plot file variable option (Solute Aqueous Conc.), the solute name (a, b, c, d, or e), and the solute concentration units (1/cm^3). STOMP will this generate these data files, which can then be opened and manipulated in Excel. It is important to note that Output files are generated in relation to the well screen. That is, an output file generated at (24,1) will be located 24 cm from the well screen. Conversely, Plot files are generated without regard to the well screen. That is, the Plot file incorporates the well radius in its data, and thus the 0 to 2.54 cm distance in the Plot file includes the well, and from 2.54 cm onward includes the soil domain.
The Surface Flux Card governs how solute concentrations at the well during the push and pull phase are determined. This data is generated as a Surface file. The card consists of twelve lines. The first line defines the number of surface flux inputs (11). The second line defines the surface flux type option (Aqueous Volumetric Flux), flux units (cm^3/hr), length units (cm), the surface location (West) and the radial (1,1), azimuthal (1,1), and z direction (1,1) node locations of that surface. The third through seventh lines define the surface flux type option (Solute Flux), solute name (a, b, c, d, or e), units (1/hr), a comma, the surface location (West), and the radial (1,1), azimuthal (1,1), and z direction (1,1) node locations of that surface. This surface corresponds to the well screen. The eighth through twelfth lines define the surface flux type option (Solute Flux), solute name (a, b, c, d, or e), units (1/hr), a comma, the surface location (East), and the radial (500,500), azimuthal (1,1), and z direction (1,1) node locations of that surface. This surface corresponds to the edge of the domain (at node 500). The Surface file thus contains the aqueous flux as well as the solute fluxes for the five named solutes at each end of the model domain. This file can be opened in Excel. To obtain the flux-averaged concentration (in units of 1/cm^3) at the well for a given solute, the column in the Excel file for a given solute flux at the well (the West surface) must be divided by the column in the Excel file for the aqueous volumetric flux. All Aqueous Volumetric Flux and Solute Flux data are given in the Surface file for each second of the simulation.
After the input file is complete, it must be saved in the engr directory with the name Input and without a file extension of any kind. The Commons file (which is never altered) and Parameters file must also be contained in this engr directory. The Parameters file is required to compile and execute STOMP and is used to allocate memory for the storage of variables. This file contains simple numeric variables that must be altered if certain changes are made to the Input file (for example, changing the number of solutes). Please refer to Chapter 5 of the STOMP User’s Guide for information on changing the Parameters file. Like changes made to the Input file, changes made to the Parameters file must be performed in Microsoft Notepad. The Parameters file must then be saved (with no file extension) in the engr directory with the Input, Commons, and stomp1_bd.f files. The next step is to compile the program and create an executable file. Compiling is performed on the engr UNIX system computer named “wa”. Use Telnet to access this computer using your existing engr account name and password. To access Telnet, press the Start button at the bottom right corner of the Microsoft Windows screen, select Run, type telnet, and press OK. Then type:

```
open wa.engr.orst.edu
```

The server will ask for your engr user name and password. Once you have accessed your engr account, go to the directory containing stomp1_bd.f, Input, Commons, and Parameters. Compile the program by typing the following:

```
/opt/fortran90/bin/f90 stomp1_bd.f
```
The program will compile and create two new files in the engr directory: 1) stomp1_bd.o, and 2) a.out, which is the executable file. To execute STOMP simply type a.out and the program will run. If there are errors in the Input file the program will not run, but will generate an error message stating the error type and the Input file Card where the error is located. Please refer to the STOMP User’s Guide for error troubleshooting information. The data generated by STOMP will be placed in the engr directory and will include Output, Plot, and Surface files (as mentioned previously). These files are then opened using Excel to obtain the desired solute concentration data.

STOMP Input File

```plaintext
# ~Simulation Title Card
# ~-----------------------------------
# 1,
 SOLUTE RETARDATION IN A RADIAL FLOW FIELD,
 Brian M. Davis,
 Oregon State University,
 27 August 2002,
 9:00 am PDT,
 5,
 field simulation,
 simulate solute with homogeneous NAPL,
 with R's 2,4,6,8,10 and in situ tracer injection,
 diffusion set to 10^-30; soils m,n,p, solutes a to e,
 use TVD transport option, time step of 10s,

# ~Solution Control Card
# ~-----------------------------------
 Normal,
 Water w/TVD Transport,
 2,
```
# Grid Card
Cylindrical, 500,1,1, 2.54,cm,500@1.0,cm, 0,deg,360.,deg, 0,cm,91.4,cm,

# Rock/Soil Zonation Card
3, m,1,24,1,1,1,1, n,25,48,1,1,1,1, p,49,500,1,1,1,1,

# Mechanical Properties Card
m,2900,kg/m^3,0.35,0.35,,,Millington and Quirk, n,2900,kg/m^3,0.35,0.35,,,Millington and Quirk, p,2900,kg/m^3,0.35,0.35,,,Millington and Quirk,

# Hydraulic Properties Card
m,14.0,hcm/min,,, n,14.0,hcm/mm,,, p,14.0,hcm/mm,,, 

# Saturation Function Card
m,Nonhysteretic van Genuchten,0.025,1/cm,3.0,0.05,, n,Nonhysteretic van Genuchten,0.025,1/cm,3.0,0.05,, p,Nonhysteretic van Genuchten,0.025,1/cm,3.0,0.05,, # Soil numbers are fake so far, but not important # for saturated groundwater flow.

# Aqueous Relative Permeability Card
m,Mualem,,
n, Mualem,
p, Mualem,

# --------------------------------------------------------
~Solute/Fluid Interaction Card
# --------------------------------------------------------
5,
a, Conventional, 1.0E-30, m^2/s, Continuous, 1.0E10, yr,
b, Conventional, 1.0E-30, m^2/s, Continuous, 1.0E10, yr,
c, Conventional, 1.0E-30, m^2/s, Continuous, 1.0E10, yr,
d, Conventional, 1.0E-30, m^2/s, Continuous, 1.0E10, yr,
e, Conventional, 1.0E-30, m^2/s, Continuous, 1.0E10, yr,

# --------------------------------------------------------
~Solute/Porous Media Interaction Card
# --------------------------------------------------------
m, 4.00, cm, 0.4, cm,
a, 0.1857, cm^3/g,
b, 0.5570, cm^3/g,
c, 0.9284, cm^3/g,
d, 1.2997, cm^3/g,
e, 1.6711, cm^3/g,
n, 4.00, cm, 0.4, cm,
a, 0.1857, cm^3/g,
b, 0.5570, cm^3/g,
c, 0.9284, cm^3/g,
d, 1.2997, cm^3/g,
e, 1.6711, cm^3/g,
p, 4.00, cm, 0.4, cm,
a, 0.0000, cm^3/g,
b, 0.0000, cm^3/g,
c, 0.0000, cm^3/g,
d, 0.0000, cm^3/g,
e, 0.0000, cm^3/g,

# --------------------------------------------------------
~Initial Conditions Card
# --------------------------------------------------------
Gas Pressure, Aqueous Pressure,
16,
Aqueous Pressure, 102450.9, Pa,
Solute Aqueous Conc., a, 102.000, 1/cm^3,
Solute Aqueous Conc., b, 53.000, 1/cm^3,
Solute Aqueous Conc., c, 36.700, 1/cm^3,
Solute Aqueous Conc., d, 28.500, 1/cm^3,
Solute Aqueous Conc., e, 23.600, 1/cm^3,
# Boundary Conditions Card

## Output Control Card
4, 0.0, Solute Aqueous Conc., a, 1/cm^3, 15580.0, Solute Aqueous Conc., b, 1/cm^3, 31160.0, Solute Aqueous Conc., c, 1/cm^3, 46740.0, Solute Aqueous Conc., d, 1/cm^3, Solute Aqueous Conc., e, 1/cm^3,

# ~Surface Flux Card

Aqueous Volumetric Flux, cm^3/hr, cm^3, West, 1, 1, 1, 1, 1, 1,
Solute Flux, a, 1/hr, West, 1, 1, 1, 1, 1, 1,
Solute Flux, b, 1/hr, West, 1, 1, 1, 1, 1, 1,
Solute Flux, c, 1/hr, West, 1, 1, 1, 1, 1, 1,
Solute Flux, d, 1/hr, West, 1, 1, 1, 1, 1, 1,
Solute Flux, e, 1/hr, West, 1, 1, 1, 1, 1, 1,

Solute Flux, a, 1/hr, East, 500, 500, 1, 1, 1, 1,
Solute Flux, b, 1/hr, East, 500, 500, 1, 1, 1, 1,
Solute Flux, c, 1/hr, East, 500, 500, 1, 1, 1, 1,
Solute Flux, d, 1/hr, East, 500, 500, 1, 1, 1, 1,
Solute Flux, e, 1/hr, East, 500, 500, 1, 1, 1, 1,
APPENDIX D: Radon Partition Coefficients in TCE and PCE

The partition coefficient for aqueous phase radon in the presence of TCE or PCE ($K$) must be known in order to calculate DNAPL saturations ($S_n$). Experiments were performed to determine these values. Radon partitioning experiments were performed using an adaptation of the methodology described by Cantaloub (2001). This method involves the sequential extraction of radon-enriched NAPL from a mixing vessel, and can be used for both LNAPLs and DNAPLs. A radium chloride solution of known activity was obtained and diluted to an activity of 40 pCi/mL. The radium chloride solution provided a means to generate radon-equilibrated water with a known activity equal to the radium chloride activity. Glass centrifuge tubes (50 mL) were filled with radium chloride solution, capped with a septum-equipped screw cap, and allowed to rest for 30 days to allow for secular equilibrium (i.e., the equilibration of radon concentrations). The exact mass of water and thus the exact radon activity in each centrifuge tube was determined by weighing using a 4-digit analytical balance.

For each centrifuge tube, a known volume and mass of water (3 mL) was removed using a syringe and vent line. A known volume and mass of TCE or PCE (3 mL) was then injected into the centrifuge tube, which was then vigorously mixed for 30 minutes. The 3 mL of TCE or PCE was then removed from the centrifuge tube using a syringe and vent line, and was immediately injected into a 20 mL LSC vial containing 17 mL of scintillation cocktail. A fresh 3 mL aliquot of TCE or PCE was then injected into the centrifuge tube, and the process repeated. This “sequential
extraction" technique enabled the determination of the partition coefficient \( K \) for TCE or PCE as follows:

The fraction of radon remaining in the aqueous solution (in the centrifuge tube) after each extraction of 3 mL of TCE or PCE is described by

\[
\frac{C_w V_w}{C_{NAPL} V_{NAPL} + C_w V_w}
\]  

(D.1)

where \( C_w \) is the concentration of radon in aqueous solution (pCi/L), \( V_w \) is the volume of aqueous solution in the centrifuge tube (L), \( C_{NAPL} \) is the concentration of radon in the NAPL (either TCE or PCE, pCi/L), and \( V_{NAPL} \) is the volume of NAPL (L).

Assuming a linear equilibrium partition coefficient \( K = C_{NAPL}/C_w \), equation D.1 can be rewritten as

\[
\frac{V_w}{K V_{NAPL} + V_w}
\]  

(D.2)

The concentration of radon in the NAPL after the \( n \)th extraction is equal to

\[
C_{NAPL,n} = K \left( \frac{V_w}{K V_{NAPL} + V_w} \right)^n C_{w,0}
\]  

(D.3)

where the bracketed term is the fraction of radon remaining in aqueous solution after the \( n \)th extraction, and \( C_{w,0} \) is the initial concentration of radon in aqueous solution in the centrifuge tube prior to the experiment. Equation D.3 can be rewritten as

\[
\ln(C_{NAPL,n}) = n \ln \left( \frac{V_w}{K V_{NAPL} + V_w} \right) + \ln(C_{w,0} K)
\]  

(D.4)

Thus a plot of extraction number \( n \) vs. the natural log of the radon concentration in each 3 mL NAPL sample can be obtained. The bracketed term in equation D.4 is
equal to the slope of the line. By knowing the precise values for $V_{NAPL}$ and $V_w$, and determining the natural log of the radon concentration in each sequentially extracted 3 mL volume of TCE or PCE, the partition coefficient $K$ can be determined. The results of the experiments (done in triplicate for TCE and PCE) are as follows: for TCE, mean $K = 50.02$, 95 % confidence = 1.78; for PCE, mean $K = 48.42$, 95 % confidence = 0.94.