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Push–pull partitioning tracer tests using radon-222 to quantify non-aqueous 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 non-aqueous 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 non-aqueous 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, non-equilibrium

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radon partitioning and heterogeneous TCE distributions may affect the retardation factors and TCE saturation estimates.

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1. Introduction

Non-aqueous 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 non-aqueous 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., SF₆) 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 (Hopkins, 1995; Gottipati, 1996; Hunkeler et al., 1997; Semprini et al., 1993, 1998, 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 α -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_{Rn}) is a function of the radium content (C_{Ra}) and radon emanation power (E_p) of the mineral phase and the bulk density (ρ_b) and porosity (n) of the aquifer (Semprini et al., 2000)

$$C_{Rn} = \frac{C_{Ra}E_p\rho_b}{n} \quad (1)$$

Values of C_{Rn} are highly variable ranging from approximately 100–270,000 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

$$K = \frac{C_{Rn,n}}{C_{Rn,w}} \quad (2)$$

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., 2000). 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 an NAPL-contaminated aquifer is defined as

$$R = \frac{v_w}{v_{Rn}} \quad (3)$$

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 (Varadarajan et al., 1999)

$$R = 1 + \frac{KS_n}{S_w} \quad (4)$$

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 (Varadarajan et al., 1999)

$$S_n = \frac{R - 1}{R + K - 1} \quad (5)$$

Fig. 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 Ostrom, 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

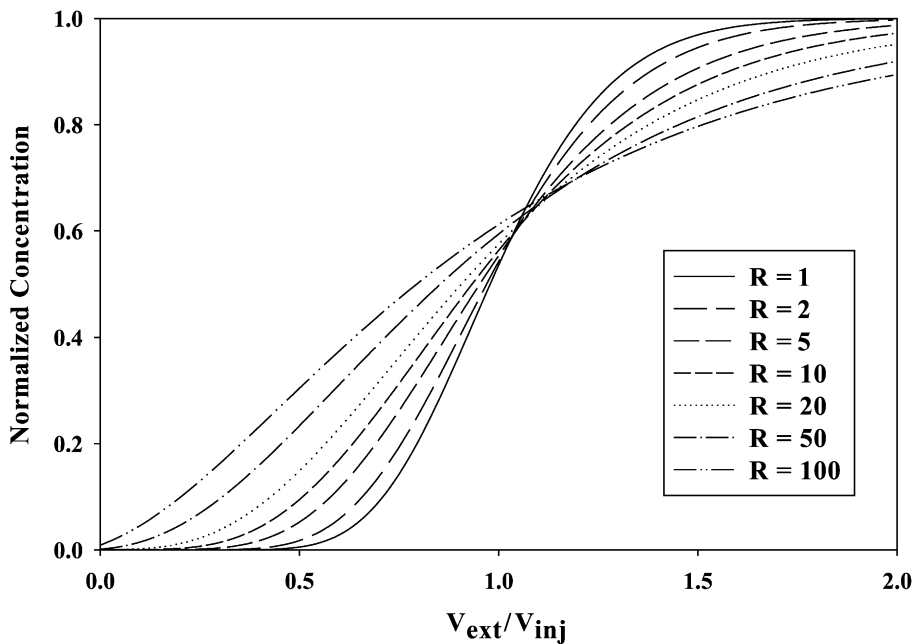


Fig. 1. Simulated push-pull test extraction phase breakthrough curves for non-retarded and retarded in situ solutes.

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.

2. Methods

2.1. 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 (Fig. 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 m³. Air-dried sediment was packed into the PAMs to a uniform bulk density (1.9 g/cm³) 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 (non-aqueous phase) TCE. This was achieved by first draining the

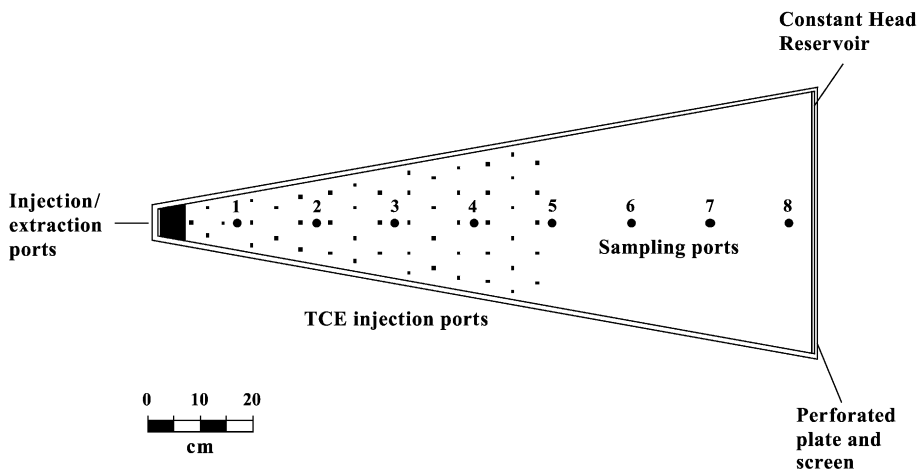


Fig. 2. Plan view of physical aquifer model (PAM) used in laboratory push–pull tests, showing dimensions and sampling locations.

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 (Fig. 2). A total of 304 g (208 ml) of TCE was uniformly injected through the injection ports, which represents a TCE saturation equivalent to $\sim 2\%$ 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 3-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, 8–16 l of test solution was injected and 16–32 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 min 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 min, 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.

2.2. 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 contami-

nated 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) 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.

2.3. 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-in. steel needle (Becton-Dickinson). 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).

2.4. 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 h 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

$$m_0 = \int C^*(t)dt \quad (6)$$

$$m_1 = \int C^*(t)t dt \quad (7)$$

The retardation factor for radon was then computed using

$$R = \frac{\left(\frac{m_{1,Rn}}{m_{0,Rn}}\right)}{\left(\frac{m_{1,Br^-}}{m_{0,Br^-}}\right)} \quad (8)$$

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

$$C^* = \frac{1}{2} \operatorname{erfc} \left\{ (r^2 - r_{inj}^2) / \left[\frac{16}{3} \alpha_L (r_{inj}^3 - r_{well}^3) \right]^{\frac{1}{2}} \right\} \quad (9)$$

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

$$r_{inj} = \left(\frac{Q_{inj} t_{inj}}{\pi b n R} + r_{well}^2 \right)^{\frac{1}{2}} \quad (10)$$

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

$$C^* = \frac{1}{2} \operatorname{erfc} \left\{ (r^2 - r_{ext}^2) / \left[\frac{16}{3} \alpha_L (2r_{max}^3 - r_{ext}^3 - r_{well}^3) \right]^{\frac{1}{2}} \right\} \quad (11)$$

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

$$r_{ext} = \left(r_{max} + \frac{Q_{ext} t_{ext}}{\pi b n R} \right)^{\frac{1}{2}} \quad (12)$$

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

$$r_{max} = \left(r_{well} + \frac{V_{inj}}{\pi b n R} \right)^{\frac{1}{2}} \quad (13)$$

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

For the laboratory tests, sampling port data from the injection phase were analyzed by using a minimized least-squares procedure to fit Eq. (9) to the normalized bromide data to

obtain an estimate for α_L . Then another minimized least-squares procedure was used to fit Eq. (9) to the normalized radon data to obtain estimates for R using the value of α_L estimated from the bromide data.

For the laboratory and field tests, extraction phase normalized bromide data were fit to Eq. (11) using a minimized least-squares procedure to obtain another estimate for α_L . Then another minimized least-squares procedure was used to fit Eq. (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

$$R = \left(\frac{r_{\max, \text{Br}^-}}{r_{\max, \text{Rn}}} \right)^2 \quad (14)$$

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 42–57% 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. The calculation served to force the bromide $C^* = 0.5$ value through $V_{\text{ext}}/V_{\text{inj}} = 1$; 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 α_L values obtained from the extraction phase approximate solution, and estimated R values from the injection phase and extraction phase approximate solutions.

3. Results

3.1. 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 Fig. 3a and b. Breakthrough curves are displayed as normalized concentration (C^*) vs. dimensionless pore volume ($V_{\text{inj}}/V_{\text{pore}}$) for bromide and radon. In these figures, V_{inj} is the cumulative volume of injected test solution at the time

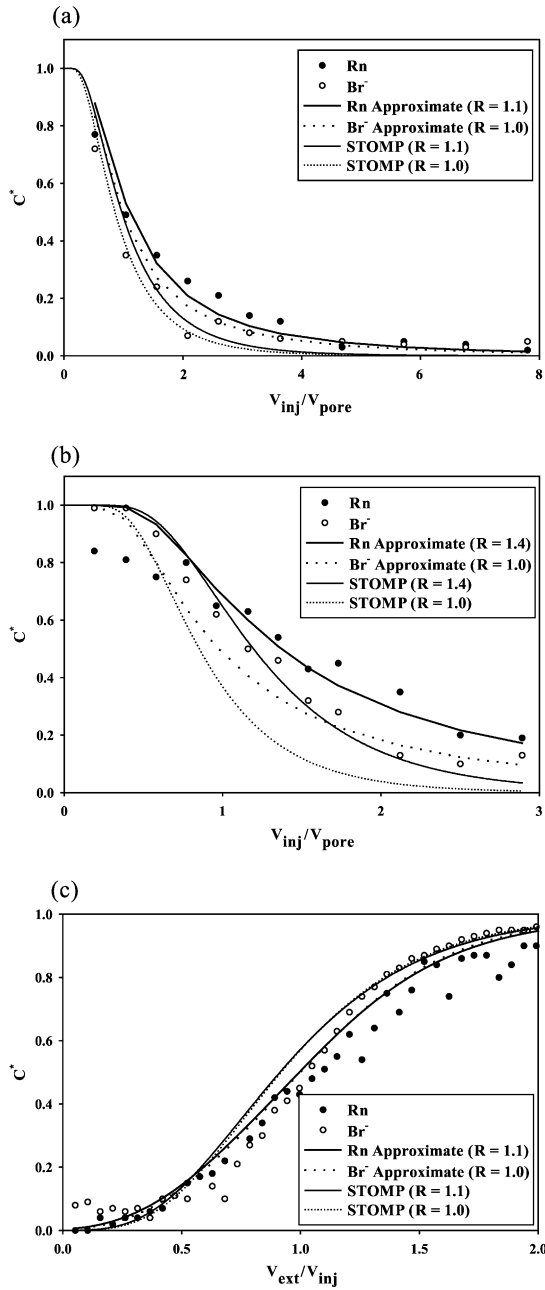


Fig. 3. (a) Injection phase breakthrough curves for lab Test 1, port 1 in the absence of TCE. (b) Injection phase breakthrough curves for lab Test 1, port 2 in the absence of TCE. (c) Extraction phase breakthrough curves for lab Test 1 in the absence of TCE.

the sample was collected, and V_{pore} is the pore volume between the injection/extraction ports and the sampling port. At each sampling port normalized concentrations decreased smoothly as the test solution penetrated further into the sediment pack. Radon transport was somewhat retarded relative to bromide. The data were well fit by the injection phase approximate solution (Eq. (9)), with best-fit α_L values of 3.8 cm for port 1 and 6.6 cm for port 2 (Table 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 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.

Retarded radon transport was not very apparent in extraction phase breakthrough curves for Test 1 (Fig. 3c) where normalized concentration (C^*) is plotted as a function of the ratio $V_{\text{ext}}/V_{\text{inj}}$, where V_{ext} is the cumulative volume of water extracted at the time the sample was collected and V_{inj} is the volume of injected test solution. Normalized concentrations increased smoothly as the test solution was extracted from the sediment pack. The data were well fit by the extraction phase approximate solution (Eq. (11)), with a best-fit α_L of 3.2 cm (Table 1). A best-fit value of $R=1.1$ was obtained for radon (Table 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.

Radon transport was retarded during the push phase of Test 2 conducted in the presence of 2% TCE (Fig. 4a and b). The data were well fit by the injection phase approximate solution, with best-fit α_L values of 3.4 cm at port 1 and 2.1 cm at port 2 (Table 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 1). Numerical simulations using STOMP were conducted for the injection phase data using $R=1.0$ and

Table 1

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

	Method of moments			Injection phase approx. solution			Extraction phase approx. solution		
	R	α_L (cm)	S_n (%)	R	α_L (cm)	S_n (%)	R	α_L (cm)	S_n (%)
Test 1, port 1	1.0	–	–	1.1	3.8	–	–	–	–
Test 1, port 2	1.2	–	–	1.4	6.6	–	–	–	–
Test 1, injection/ extraction ports	–	–	–	–	–	–	1.1	3.2	–
Test 2, port 1	1.4/1.4	–	0.7	1.4/1.3	3.4	0.5	–	–	–
Test 2, port 2	1.7/1.5	–	0.9	1.5/1.1	2.1	0.2	–	–	–
Test 2, injection/ extraction ports	–	–	–	–	–	–	5.1/5.0	4.0	6.5
Field test, no LNAPL	–	–	–	–	–	–	1.6	38.6	–
Field test, with LNAPL	–	–	–	–	–	–	7.3/6.7	20.3	–

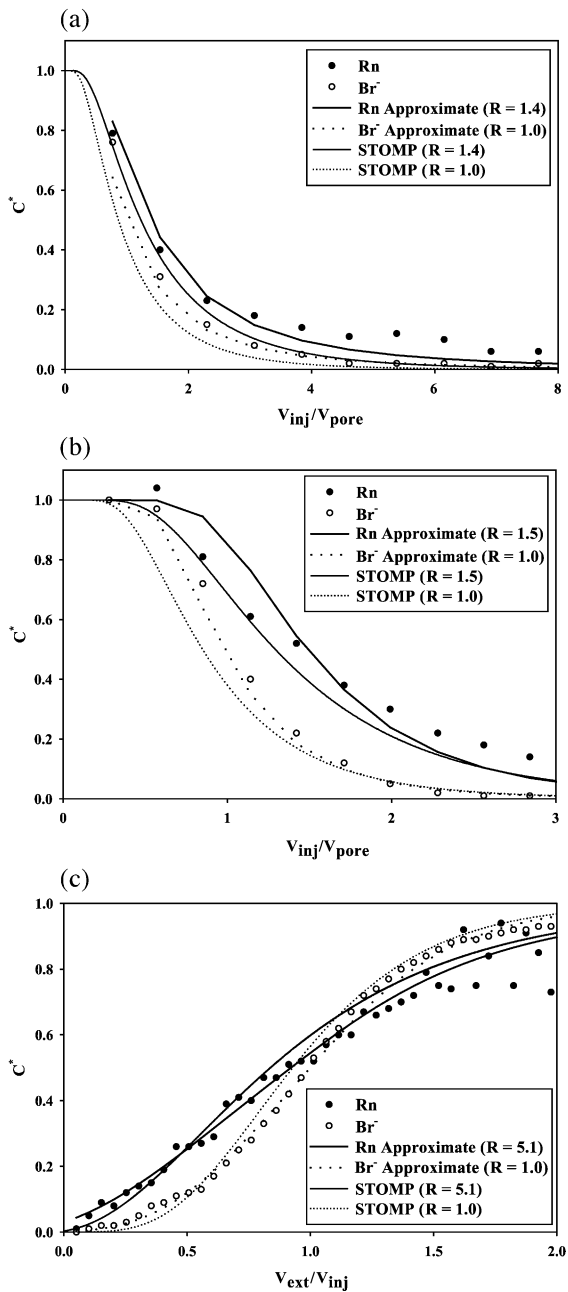


Fig. 4. (a) Injection phase breakthrough curves for lab Test 2, port 1 with 2% TCE. (b) Injection phase breakthrough curves for lab Test 2, port 2 with 2% TCE. (c) Extraction phase breakthrough curves for lab Test 2 with 2% TCE.

$R=1.4$ 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.

Retarded radon transport was apparent in extraction phase breakthrough curves for Test 2 (Fig. 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 α_L of 4.0 cm (Table 1). An estimated value of $R=5.1$ was obtained for radon using the extraction phase approximate solution (Table 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.

3.2. 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

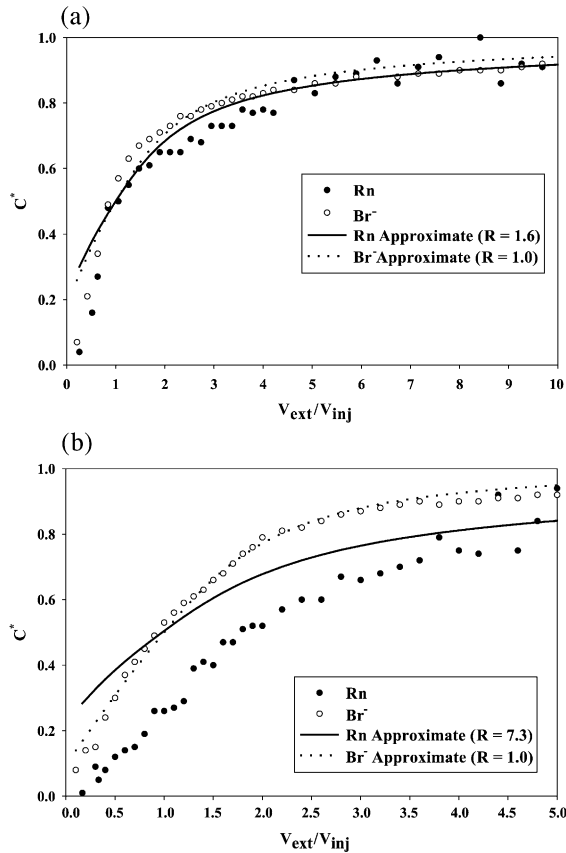


Fig. 5. (a) Extraction phase breakthrough curves for field Test 1 with no LNAPL. (b) Extraction phase breakthrough curves for field Test 2 with LNAPL.

absence of LNAPL (Fig. 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 α_L was 38.6 cm (Table 1). The radon data were well fit by the extraction phase approximate solution; the estimated retardation factor for radon was 1.6 (Table 1).

Radon transport was retarded in Test 2 conducted in the presence of LNAPL (Fig. 5b). Again, the shape of the extraction-phase breakthrough curves differed from those from the laboratory tests. The best-fit α_L was 20.3 cm (Table 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 1).

4. Discussion

4.1. 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, 1996). Assuming equilibrium partitioning between the trapped gas and aqueous phases, the retardation factor for a dissolved gas can be written as

$$R = 1 + H_{cc} \frac{S_g}{S_w} \quad (15)$$

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 Eq. (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

$$R_{adj} = R_{test\ 2} - (R_{test\ 1} - 1.0) \quad (16)$$

where R_{adj} is the adjusted retardation factor, $R_{test\ 2}$ is the retardation factor from Test 2, and $R_{test\ 1}$ is the retardation factor from Test 1. For example, in Test 1 the method of moments retardation factor at Port 2 is 1.2, while in Test 2 the retardation factor is 1.7, yielding an

adjusted retardation factor of 1.5. Adjusted retardation factors were used to calculate TCE saturations (Table 1).

Using Eq. (5), adjusted injection phase retardation factors, and $K = 58$, calculated TCE saturations ranged from 0.2% to 0.9% (Table 1), which is less than the volume-averaged TCE saturation of 2% in the sediment pack. This underestimation may be due to non-equilibrium radon partitioning and the heterogeneous distribution of TCE in the sediment pack. A heterogeneous TCE distribution with pooling toward the bottom of the sediment pack could result in underestimated radon retardation factors because of the reduced interfacial area between the TCE and the test solution. NAPL pools can create a mass transfer limitation to partitioning because of the long length scales of pooled NAPL relative to the scale of diffusion over the test time (Willson et al., 2000), thus violating the assumption of equilibrium partitioning. Aqueous TCE concentrations increased with depth upon the excavation of the PAM (Table 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 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 (Fig. 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 α_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 α_L is

Table 2
Aqueous TCE as a function of depth in the PAM sediment pack

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

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 (Figs. 3c and 4c).

For Test 1, the best-fit values of α_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 α_L for the extraction phase approximate solution was 3.2 cm. (Table 1). The higher best-fit value of α_L at port 2 is a result of the more dispersed bromide breakthrough curve (Fig. 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 α_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 α_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 α_L . The best-fit value of α_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.

4.2. Field tests

The minimal radon retardation observed in Test 1 (Fig. 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 (Fig. 5b), with an adjusted retardation factor of 6.7 (Table 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 $V_{\text{ext}}/V_{\text{inj}}=2$. This may have resulted from a heterogeneous LNAPL distribution and/or non-ideal transport (i.e., non-equilibrium partitioning) during the test. Schroth et al. (2000) found that simulated push–pull tests with linear non-equilibrium partitioning resulted in the partitioning tracer $C^*=0.5$ passing through $V_{\text{ext}}/V_{\text{inj}}$ at values greater than 1. Non-equilibrium 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, non-ideal radon breakthrough curve behavior limited the applicability of the method in accurately determining the LNAPL saturation.

5. 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 non-equilibrium 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.

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