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**Development of Radon as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface**

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***Introduction***

Dense non-aqueous phase liquids (DNAPLs) such as trichloroethene (TCE) and perchloroethene (PCE) present long-term challenges in terms of quantification in the subsurface at many DOE facilities. Over the past year we have continued investigating a potentially lower cost method for quantifying DNAPLs in the subsurface using naturally occurring, in situ dissolved radon as a partitioning tracer. Radon can be used as a partitioning tracer in both static (i.e., no flow) and dynamic methodologies (Semprini et al., 1993; Semprini et al., 1998; Semprini et al., 2000). The static radon method involves obtaining radon samples from DNAPL-contaminated and non-contaminated portions of the aquifer and using the change in radon concentrations to locate and quantify DNAPL saturation in the aquifer. The dynamic radon method incorporates single-well injection-withdrawal (i.e., push-pull) tests to estimate radon retardation and DNAPL saturation. These methods have the potential to provide a robust method for DNAPL saturation quantification while decreasing the costs associated with these activities.

***Research Performed Prior to 2002***

As described in the 2001 annual report, laboratory experiments have been conducted at Oregon State University to research and refine the push-pull and static radon methods. Large-scale physical aquifer models (PAMs) have been constructed to serve as models for future field application of the methods. The PAMs mimic a confined aquifer containing Hanford Formation sediment and are saturated with water (Figure 1). The push-pull method involves the injection of a solution of radon-free water containing a conservative bromide tracer into the PAM or aquifer, followed by the extraction of the solution from the same well (Davis et al., 2002; Davis et al., In Press). In the absence of DNAPL, radon is conservatively transported; in the presence of DNAPL, radon transport is retarded due to partitioning between the DNAPL and aqueous phases, resulting in an increased apparent dispersion for radon concentrations measured at the well during the pull phase of the test. The radon retardation factor ( $R$ ) is used to calculate the DNAPL saturation ( $S_n$ ) using

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

where  $K$  is radon's partition coefficient (for TCE,  $K = 50$ ). Determining the retardation factor for radon during the pull phase of the test is accomplished via numerical modeling using the STOMP code (developed and supported by Pacific Northwest National Labs).

The static method involves obtaining radon samples from DNAPL-contaminated and non-contaminated portions of the aquifer or, alternatively, from the same location in the aquifer both before and after DNAPL contamination has occurred. The change in radon concentrations from contaminated and non-contaminated portions of the aquifer (or before and after DNAPL contamination in the same location) is used to calculate the DNAPL saturation ( $S_n$ ) using

$$S_n = \frac{\left( \frac{C_{w,b}}{C_{w,NAPL}} - 1 \right)}{(K - 1)} \quad (2)$$

where  $C_{w,b}$  is the radon concentration in a water sample in a non-contaminated portion of the aquifer (or prior to DNAPL contamination), and  $C_{w,NAPL}$  is the radon concentration in a water sample from the contaminated portion of the aquifer (or after DNAPL contamination). The effect of increasing  $S_n$  on static radon concentrations (using  $K = 50$  for TCE and  $C_{w,b} = 200$  pCi/L) is shown in Figure 2. Radon concentrations decrease nonlinearly in the presence of TCE, with the greatest sensitivity to low values of  $S_n$ .

As described in the 2001 annual report, the static and push-pull tests performed in the PAMs show that the methods have the potential to quantify DNAPL saturation in the subsurface. The presence of TCE in the PAM sediment pack resulted in radon retardation during the pull phase of the push-pull test (Figure 3). Numerical modeling and an approximate analytical solution were used to estimate a radon retardation factor of 5.1, which resulted in a calculated TCE saturation of 7.4 % (equation 1). However, the actual TCE saturation ( $S_n$ ) in the PAM is 2 % (volume averaged), and thus the push-pull method is likely overestimating the radon retardation factor ( $R$ ). The overestimation of the radon retardation factor could present serious challenges to the application of this method at a contaminated field site. Also, the partition coefficient ( $K$ ) was until recently unknown for radon in TCE (and PCE). Therefore our research over the past year has focused on two main topics: 1) determining the partition coefficient ( $K$ ) for radon in TCE and PCE; and 2) refining the radon push-pull method to more accurately determine  $R$  and thus  $S_n$ .

### ***Determining 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 ( $S_n$ ) using equations 1 and 2. We performed experiments during 2002 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 light or LNAPLs and DNAPLs. This “sequential extraction” technique enabled the determination of the partition coefficient ( $K$ ) for TCE or PCE. The concentration of radon in the NAPL after the  $n$ th extraction is equal to

$$C_{NAPL,n} = K \left( \frac{V_w}{KV_{NAPL} + V_w} \right)^n C_{w,0} \quad (3)$$

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

extraction vessel prior to the experiment, and  $V_w$  and  $V_{NAPL}$  are the volumes of the water and NAPL phases. A plot of the log form of equation 3 for an experiment with PCE is shown in Figure 4. The slope of this plot is used to determine  $K$ . The results of the experiments (done in triplicate for TCE and PCE) are shown in Table 1. The values of  $K$  for TCE and PCE are similar, which is not surprising since both are chlorinated aliphatics.

Table 1. Partition coefficients ( $K$ ) for dissolved radon in aqueous solution in the presence of TCE or PCE.

	Mean $K$	95 % confidence	Mean $r^2$
<b>TCE</b>	50.02	1.78	0.9953
<b>PCE</b>	48.42	0.94	0.9954

### ***Numerical Modeling to Investigate and Refine the Push-Pull Method***

The STOMP code was used to create a 1-D simulated aquifer containing saturated Hanford Formation sediment and a 2" diameter well. To mimic a typical field test the simulation was performed over a 3' long interval of the simulated aquifer. Similar to previous modeling efforts, the simulated aquifer was contaminated with varying saturations ( $S_n$ ) of TCE to observe the effect of TCE on radon retardation during a simulated push-pull test. These tests were conducted with an injection (push) volume of 250 L and an extraction (pull) volume of 500 L, with pumping rates constant at 1 L/min. The injection solution was radon-free (i.e., 0 pCi/L). However, unlike previous modeling efforts, the initial concentration of radon in the aquifer before the push-pull test was simulated as a function of  $S_n$  using equation 2,  $K = 50$  for TCE, and a 'background' radon concentration of 200 pCi/L (previously measured in our laboratory with Hanford Formation sediment). A series of simulations was performed for aquifers containing spatially varying values of  $S_n$ . The simulations produced breakthrough curves (BTCs) showing radon concentrations as a function of dimensionless time ( $V_e/V_i$ ), where  $V_e$  is the cumulative volume of solution pulled from the well at the time a sample was obtained, and  $V_i$  is the volume of solution pushed into the aquifer (which in this case is 250 L).

The results of the simulations showed that the radon push-pull method is sensitive to the initial radon concentration in the model domain and, therefore, these initial radon concentrations must be incorporated into the simulations. In addition, the sensitivity of the method is greatest at low values of  $S_n$ , similar to the sensitivity of the static radon method in the presence of TCE (Figure 2). Figure 5 shows radon BTCs (pCi/L) vs. dimensionless time ( $V_e/V_i$ ) in a simulated aquifer for a series of simulations with TCE  $S_n$  values varying from 0 to 15.25 % (corresponding to radon retardation factors of 1 to 10, respectively). For each of these simulations, the TCE extended to the maximum radius of the injected solution, beyond which the sediment was non-contaminated. The  $R = 1$  BTC shows the conservative transport behavior of radon in the absence of TCE, while the BTCs with  $R > 1$  show that as  $S_n$  and  $R$  increase, radon retardation increases, with the greatest sensitivity at low values of  $S_n$ .

These simulations were used to develop a new, more sensitive, and more accurate method for interpreting radon BTCs from laboratory and field push-pull tests. The

method for estimating  $S_n$  utilizing non-normalized radon BTCs requires obtaining a ‘background’ radon concentration from the contaminated aquifer. Such a sample could be obtained from a non-contaminated well screened in the same aquifer as the contaminated well(s). Using this sample as a ‘background’ concentration assumes homogeneity in porosity and radon emanation between the well chosen for the ‘background’ radon sample and the well with suspected DNAPL contamination where the push-pull test is conducted. A push-pull test is then conducted in the well with suspected DNAPL contamination using an injection solution of radon-free water (sparged with air to remove dissolved radon gas) containing a conservative bromide tracer. Samples of the injection solution are obtained to determine the actual bromide concentration and to ensure that the solution is indeed radon-free. Pull phase samples are obtained for radon and bromide, with the pull phase proceeding until  $V_e/V_i = 2$ . Radon and bromide samples are analyzed and the results plotted in concentration units (pCi/L for Rn and mg/L for Br<sup>-</sup>) as a function of  $V_e/V_i$ . The y-axis of the plot shows radon concentrations ranging from 0 at the origin (assuming the injection solution is radon-free) 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 experimental radon and bromide BTCs to overlap. Numerical simulations are then performed using existing values of sediment porosity and bulk density 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 value for sediment dispersivity ( $a_L$ ). The best-fit  $a_L$  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 2 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 1 is then used to calculate the value of  $S_n$  that corresponds to the best-fit  $R$  value.

The new method was used to re-model the original laboratory push-pull test results (shown in Figure 3) from the PAM (shown in Figure 1). The results of the re-modeling (Figure 6) show that bromide is conservatively transported in the PAM, while radon transport is retarded due to partitioning of radon between the aqueous and DNAPL (TCE) phases. The bromide BTC is best-fit by a simulated  $R = 1$  BTC (with a best-fit  $a_L = 4.7$  cm), while the radon BTC is best-fit by a simulated  $R = 2$  BTC. A previous test performed in this PAM prior to TCE contamination showed slight radon retardation due to partitioning of radon between the aqueous phase and a trapped gas phase in the sediment pack. This effect was accounted for by subtracting the best-fit radon  $R$  value from the ‘clean’ test (data not shown; this  $R$  value was also determined using the new modeling method) from the best-fit  $R$  value from the test shown in Figure 6. This resulted in a final best-fit radon  $R = 1.8$ . Using equation 1 and  $K = 50$ , this value of  $R$  corresponds to a TCE  $S_n = 1.6$  %. Considering that the actual volume-averaged  $S_n$  in the PAM is 2 %, the new method produces a much more reasonable value for  $S_n$  in the sediment pack compared to the  $S_n$  value of 7.4 % obtained using the old modeling method (Figure 3).

This new modeling approach holds promise for further application of the push-pull method at DNAPL and LNAPL-contaminated field sites, provided that accurate 'background' radon concentrations can be obtained from non-contaminated portions of the aquifer that is being interrogated. The new method enhances the ability of the radon push-pull test to provide more accurate estimates for  $S_n$  at contaminated sites, with a greater sensitivity to low values of  $S_n$ . In addition, the method shows promise in showing changes in  $S_n$  over time as, for example, source zone remediation is effected.

### ***Conclusions***

Research during 2002 has concentrated on 1) determining partition coefficients ( $K$ ) for radon in the presence of TCE and PCE, and 2) refining the push-pull method to more accurately determine  $R$  and estimate  $S_n$ . These activities have been successfully accomplished. With regards to further research activities, field trials of the radon push-pull method at contaminated sites in various geologic settings would be useful in determining if the method can be consistently and accurately applied to estimate DNAPL saturations at field sites. An article was published in the Journal of Contaminant Hydrology Journal (Davis et al. 2002) based on the results of the project work performed the previous year. Another journal article has been accepted for publication in Ground Water (Davis et al. In Press)

### ***References***

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## Figures

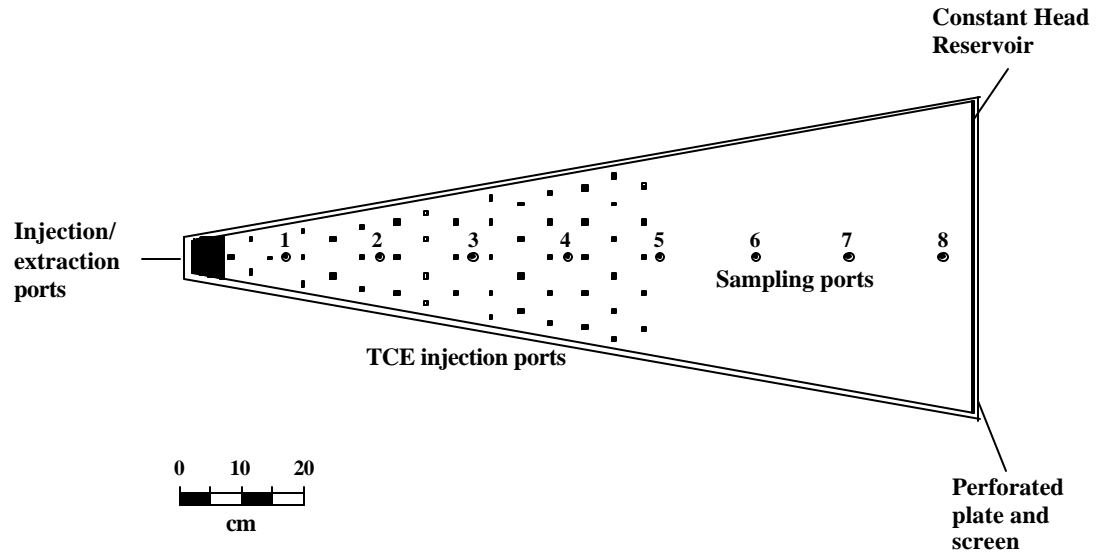


Figure 1. Plan view of PAM used in push-pull tests.

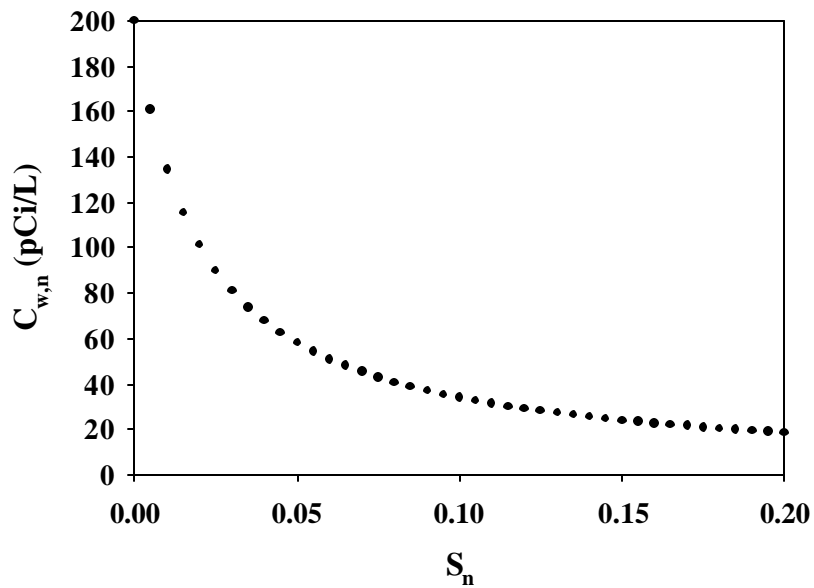


Figure 2. Aqueous phase radon concentrations as a function of TCE saturation ( $S_n$ ), using a ‘background’ radon concentration = 200 pCi/L and  $K = 50$ .

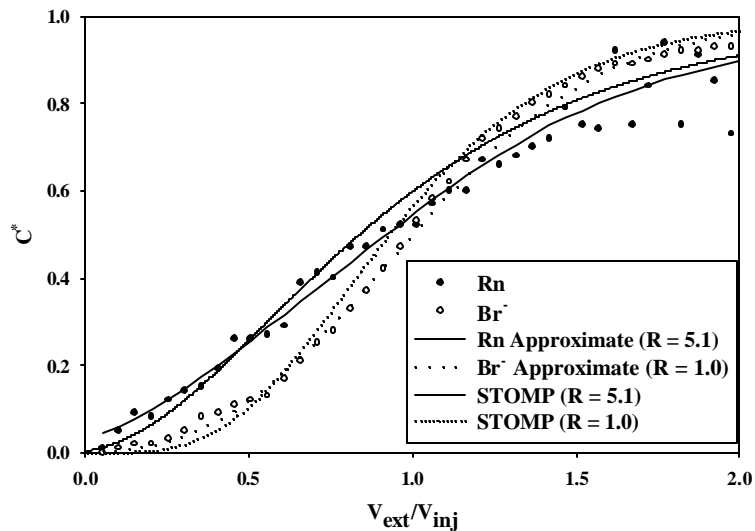


Figure 3. Pull phase radon and bromide breakthrough curves (BTCs) at the narrow end of the PAM after TCE contamination.

#### Sequential Extraction Technique Using PCE

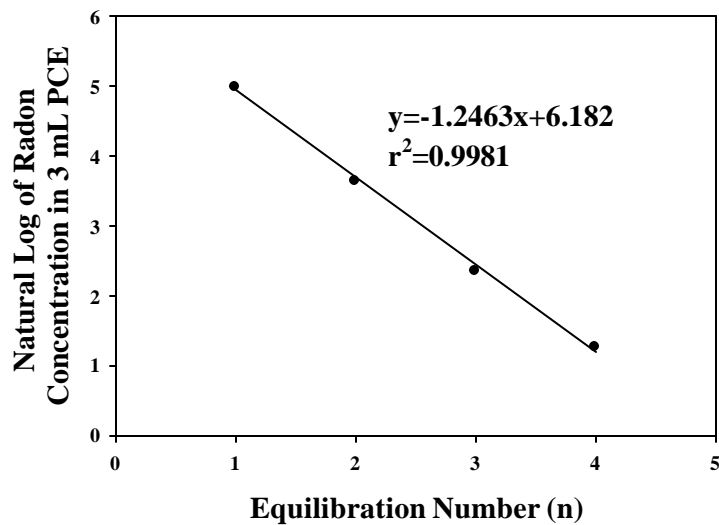


Figure 4. Plot of natural log of radon concentration in each 3 mL sequential extraction of PCE vs. equilibration number.

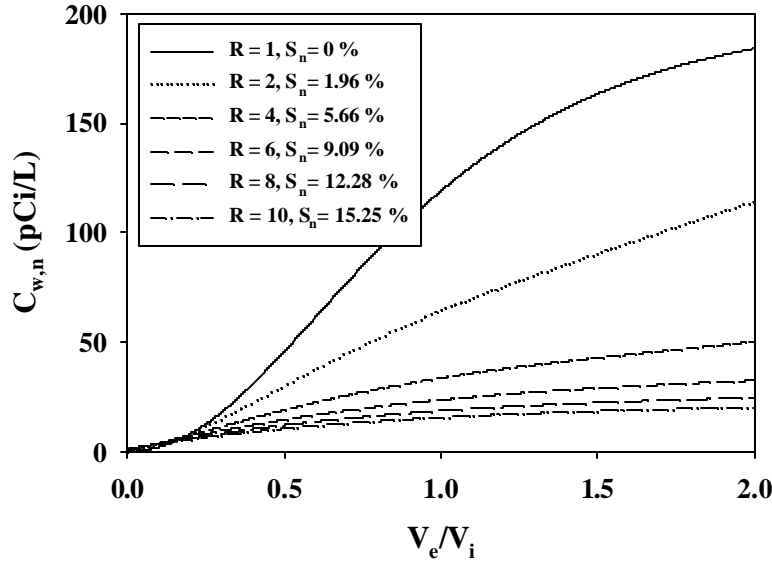


Figure 5. Radon breakthrough curves (BTCs) during the pull phase of a simulated push-pull test at varying retardation factors ( $R$ ) and corresponding values of  $S_n$  (TCE).

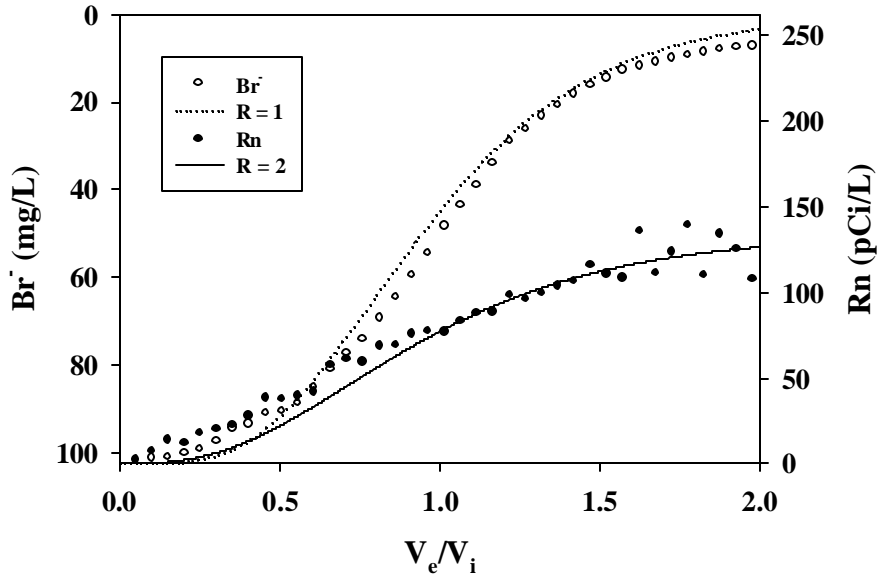


Figure 6. Radon (pCi/L) and bromide (mg/L) experimental and simulated ( $R = 1$  and  $R = 2$ ) BTCs during the pull phase of a push-pull test performed in a physical aquifer model (PAM). This test was conducted in the TCE-contaminated PAM shown in Figure 1. Y-axis radon concentrations range from 0 to 262.1 pCi/L, and y-axis bromide concentrations range from 102.6 to 0 mg/L.