Development of Radon-222 as a Natural Tracer for Locating and Quantifying NAPL Contamination in the Subsurface

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A rapid, low-cost method field method for locating and quantifying residual nonaqueous phase liquid (NAPL) contamination in the subsurface

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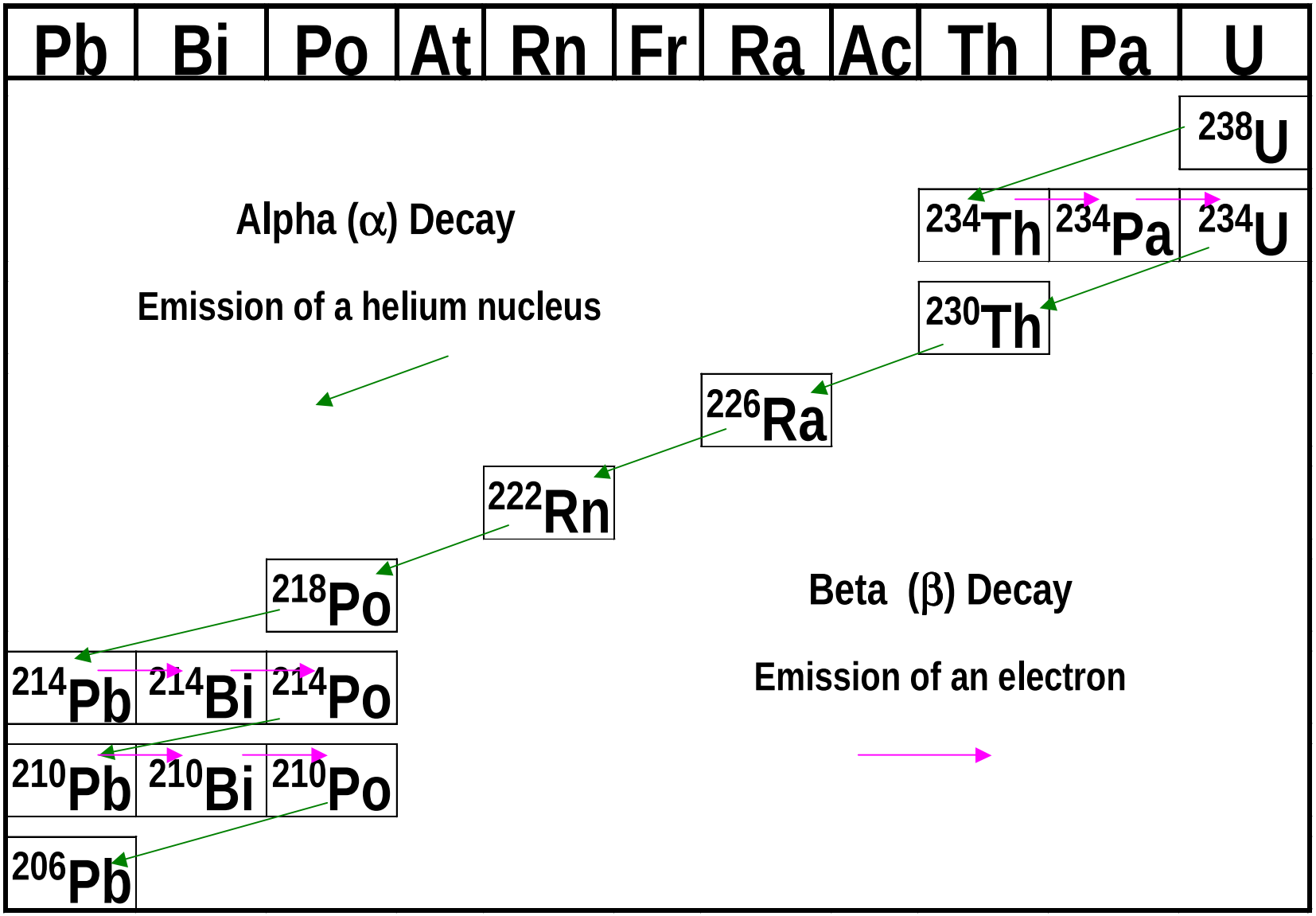
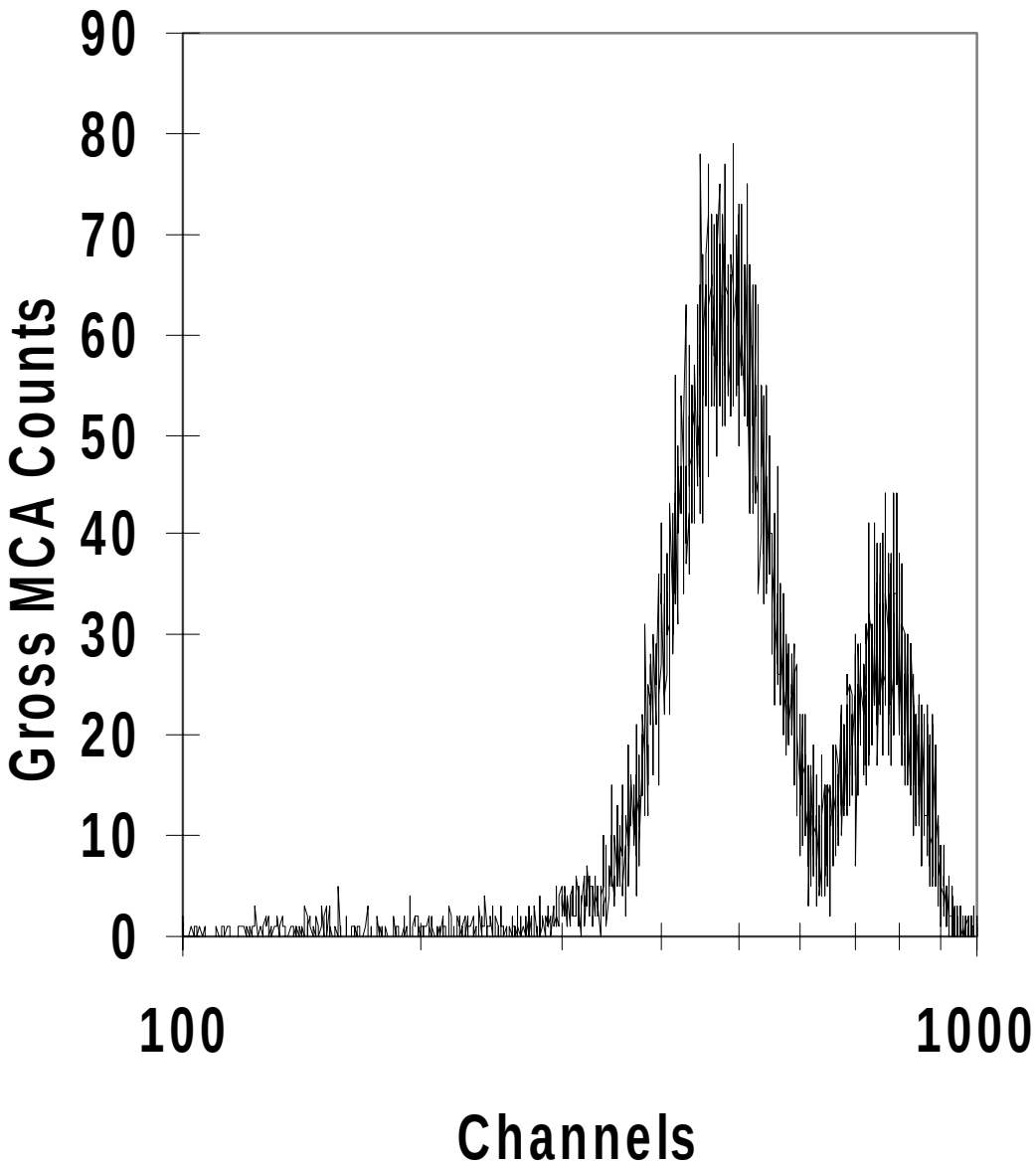
Origin of Rn in the Environment



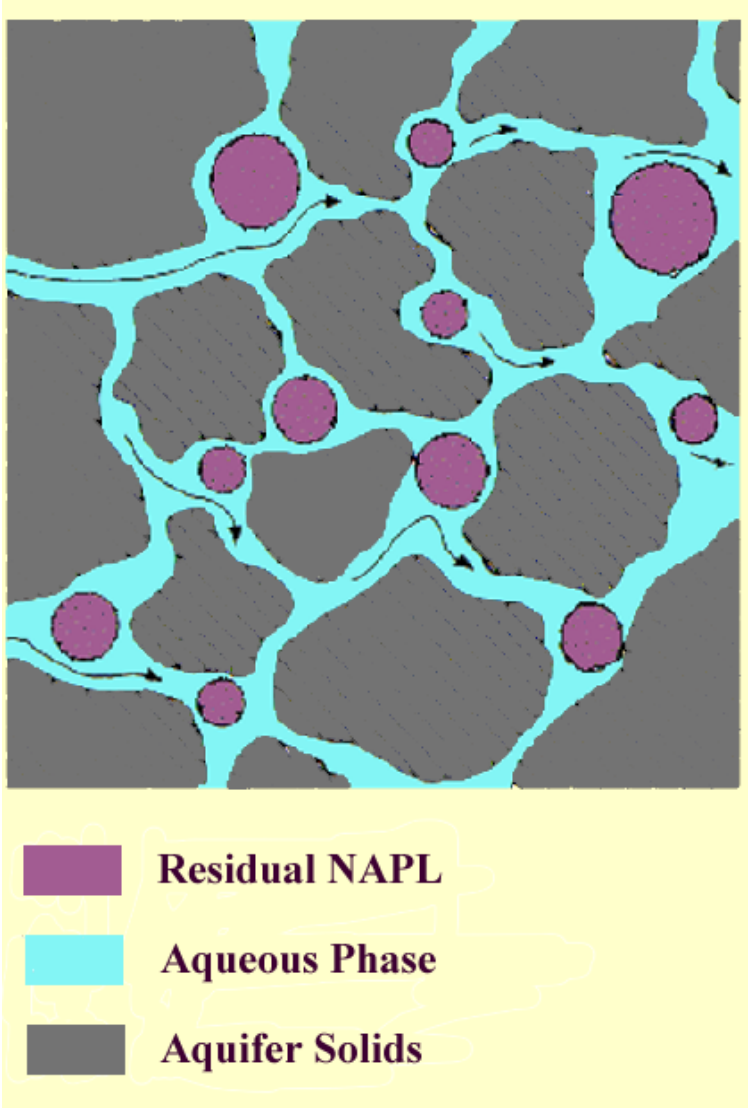
Rn Measurement

- Spectra for Rn-222 and decay daughters obtained with a Packard TriCarb2500 alpha/beta liquid scintillation analyzer.

- The larger peak is the sum of the ^{222}Rn (5.5 MeV) and ^{218}Po (6.0 MeV) alpha decays. The smaller peak is ^{214}Po (7.6 MeV) alpha.



Dissolved Rn Concentrations as an Indicator of NAPL Contamination

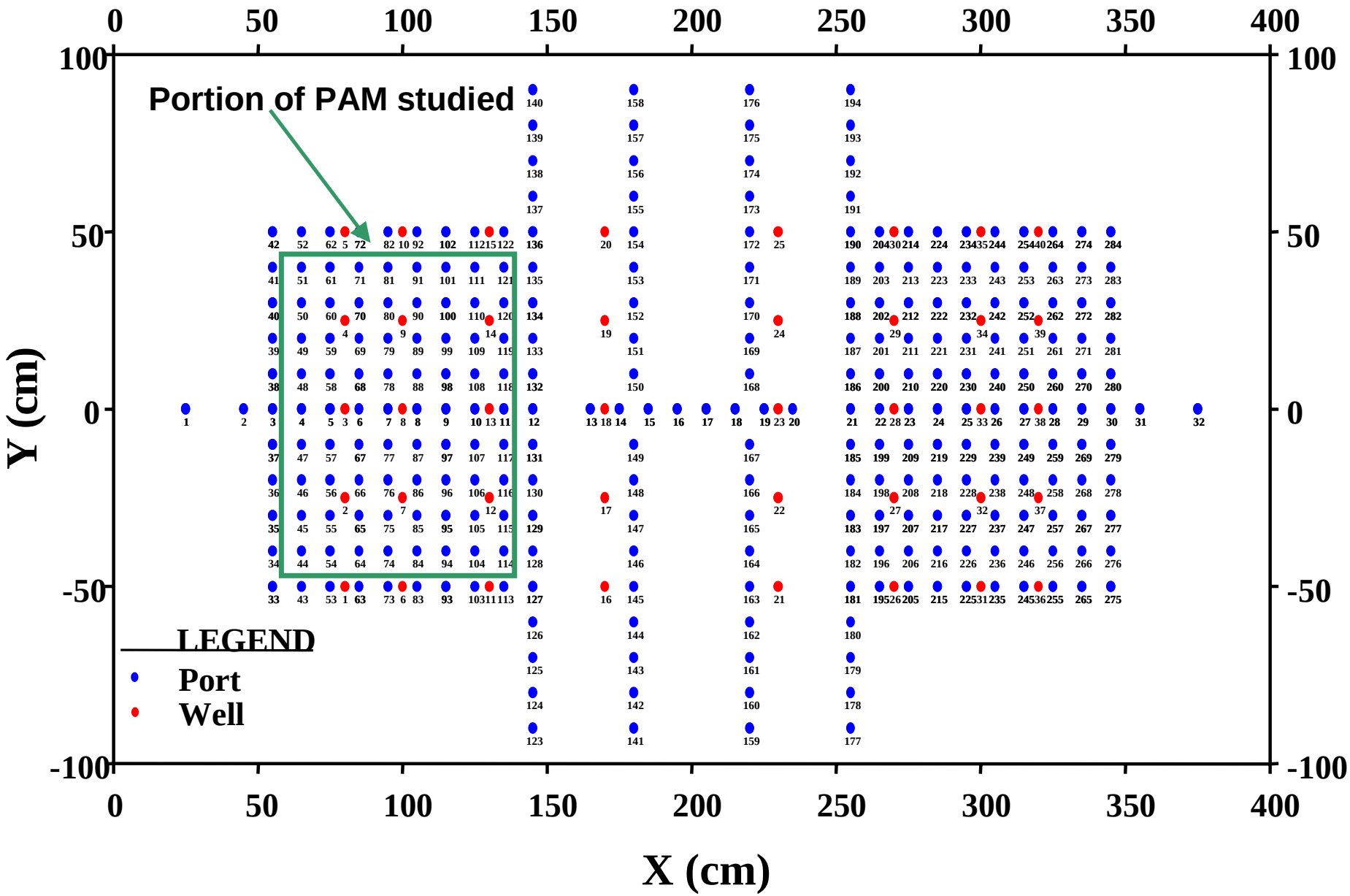


- **Rn-222 is a naturally occurring radioisotope, which occurs in groundwater as a dissolved gas.**
- **In the absence of NAPL, Rn concentrations reach a site-specific equilibrium value.**
- **In the presence of NAPL, Rn concentrations are decreased as Rn partitions into NAPL.**
- **This decrease is called the *Rn deficit.***

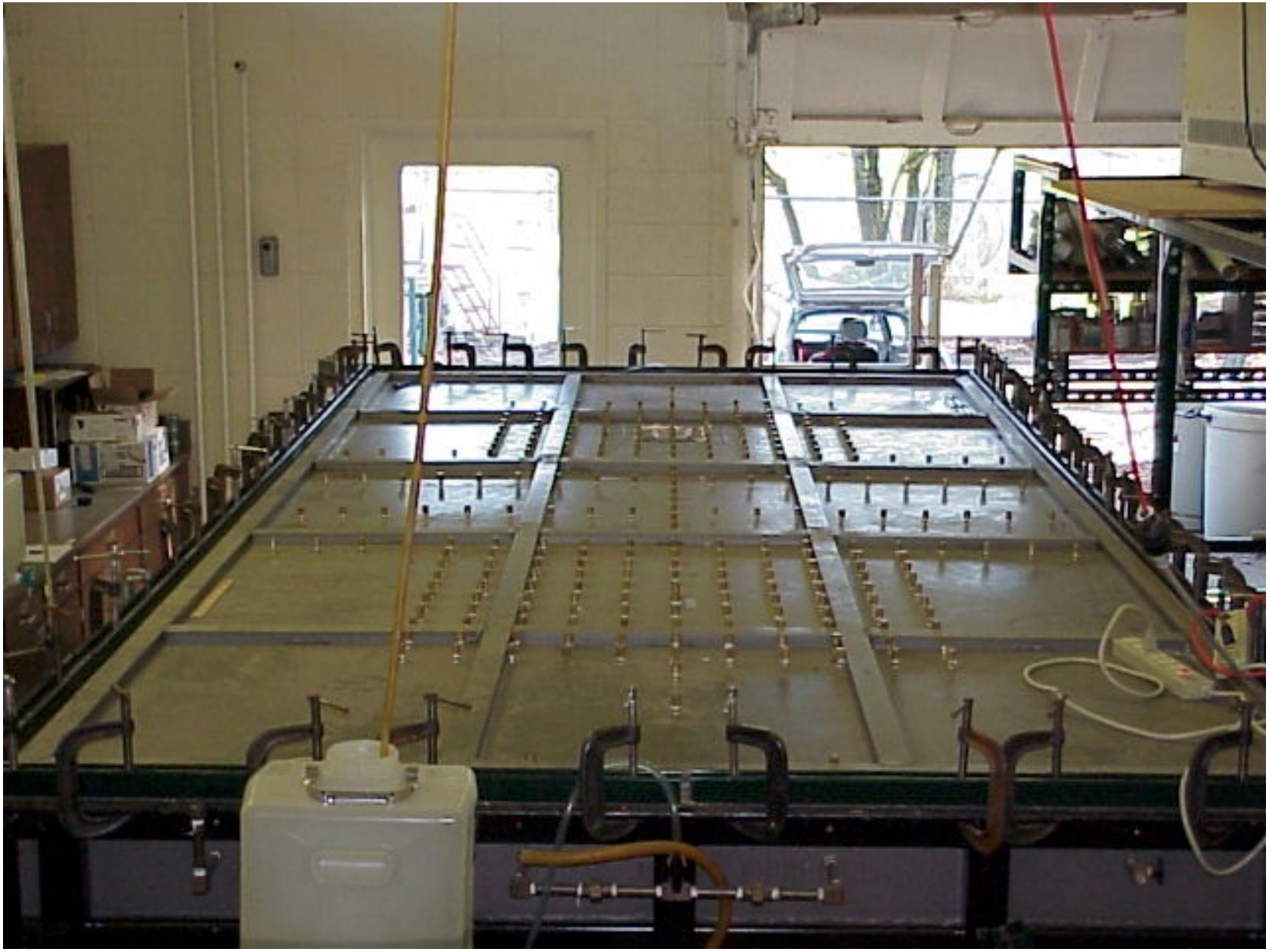
TCE NAPL Experiments in PAM

- ***Description of Physical Aquifer Models (PAMs)***
  - **4 m long, 2 m wide, and 20 cm deep**
  - **Packed with saturated medium Hanford sand**
  - **284 sampling ports drilled into top of PAM**
  - **40 wells emplaced in bottom of PAM (fully screened)**
- ***Experimental Methods:***
  - **Conduct push-pull tests to determine Rn initial concentrations and non-retarded Rn breakthrough curve (BTC).**
  - **Emplace a known volume of TCE NAPL to create concentric zones of 6% and 3% residual saturation in PAM.**
  - **Conduct additional push-pull tests to observe the retardation of Rn in the breakthrough curve and determine residual saturation of TCE NAPL.**

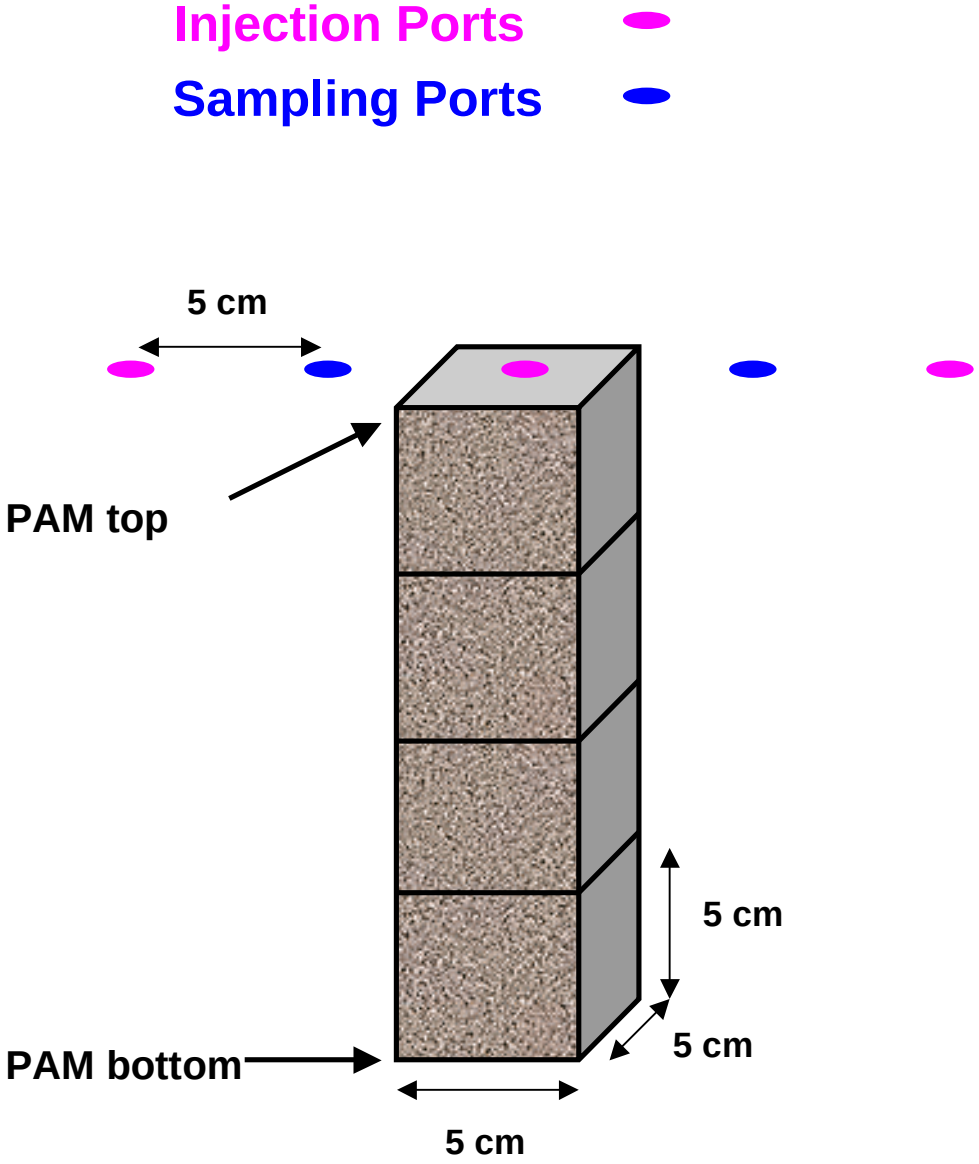
Plan View of PAM



PAM



Emplacement of TCE NAPL



- Each port contains four 125 cm^3 "cubes".
- Each cube injected with sufficient TCE NAPL to obtain either 6% or 3% residual saturation.
- 6 injection ports with 6% residual TCE NAPL saturation (total cubes = 24)
- 12 injection ports with 3% residual TCE NAPL saturation (total cubes = 48)
- Cubes are arranged to create inner zone of 6% and outer zone of 3% residual saturation.

Retardation of Transported Dissolved Rn as an Indicator of NAPL Contamination

In presence of NAPL, dissolved Rn concentrations are retarded during *transport,* creating a Rn deficit in water:

$$R = 1 + \frac{K_c S_{NAPL}}{S_W}$$

R = Retardation factor

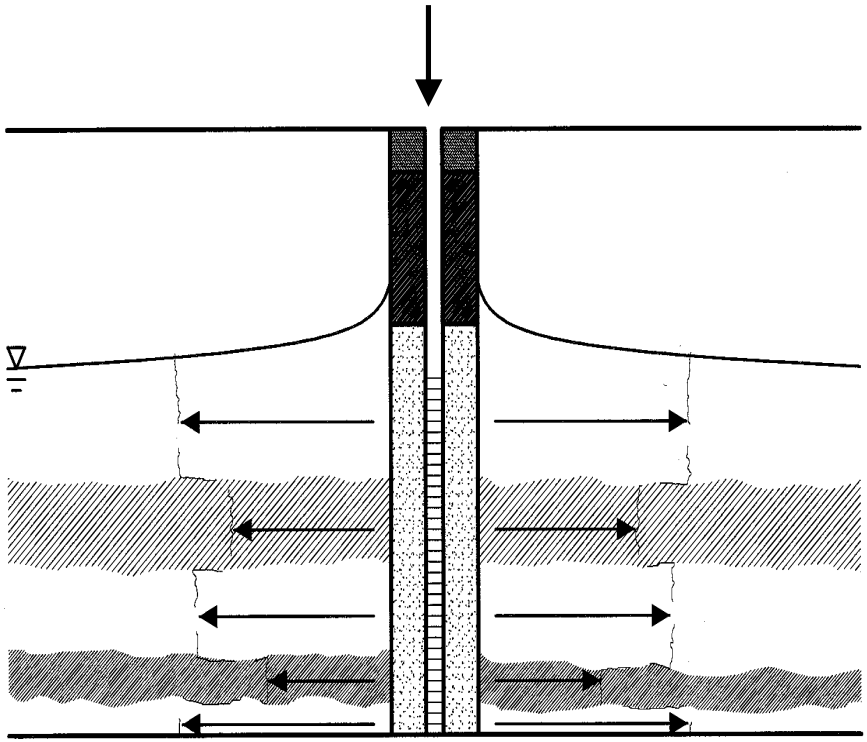
S_{NAPL} = Residual saturation of NAPL in pores

S_W = Water saturation in pores

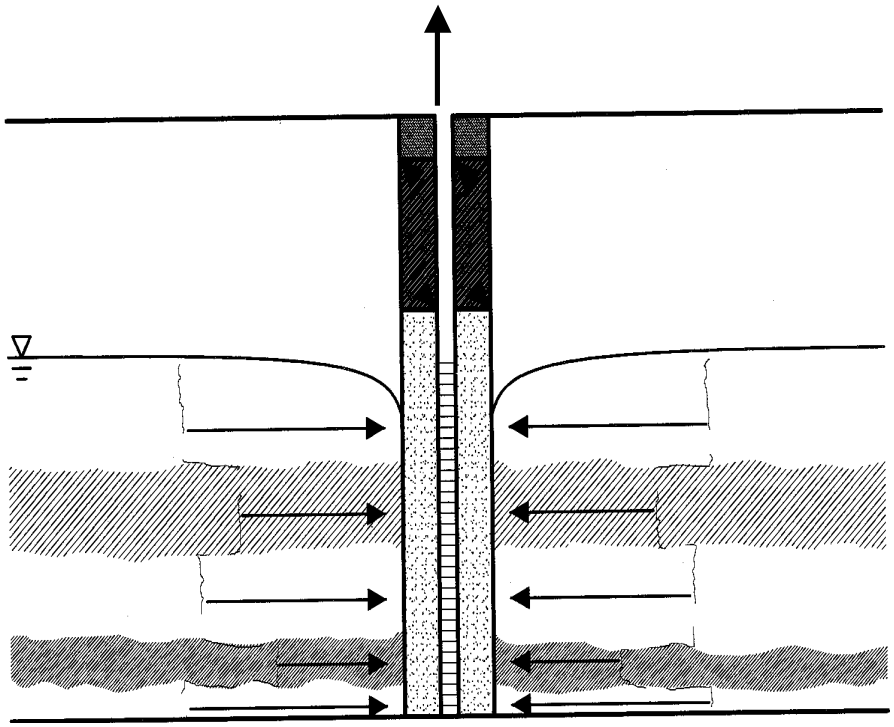
K_c = NAPL:water partition coefficient

Retardation of Solutes is Determined with a "Push-Pull" Test

During the *injection phase*, a prepared test solution containing Br^- tracer and Rn-free water is injected into the saturated zone using an existing monitoring well

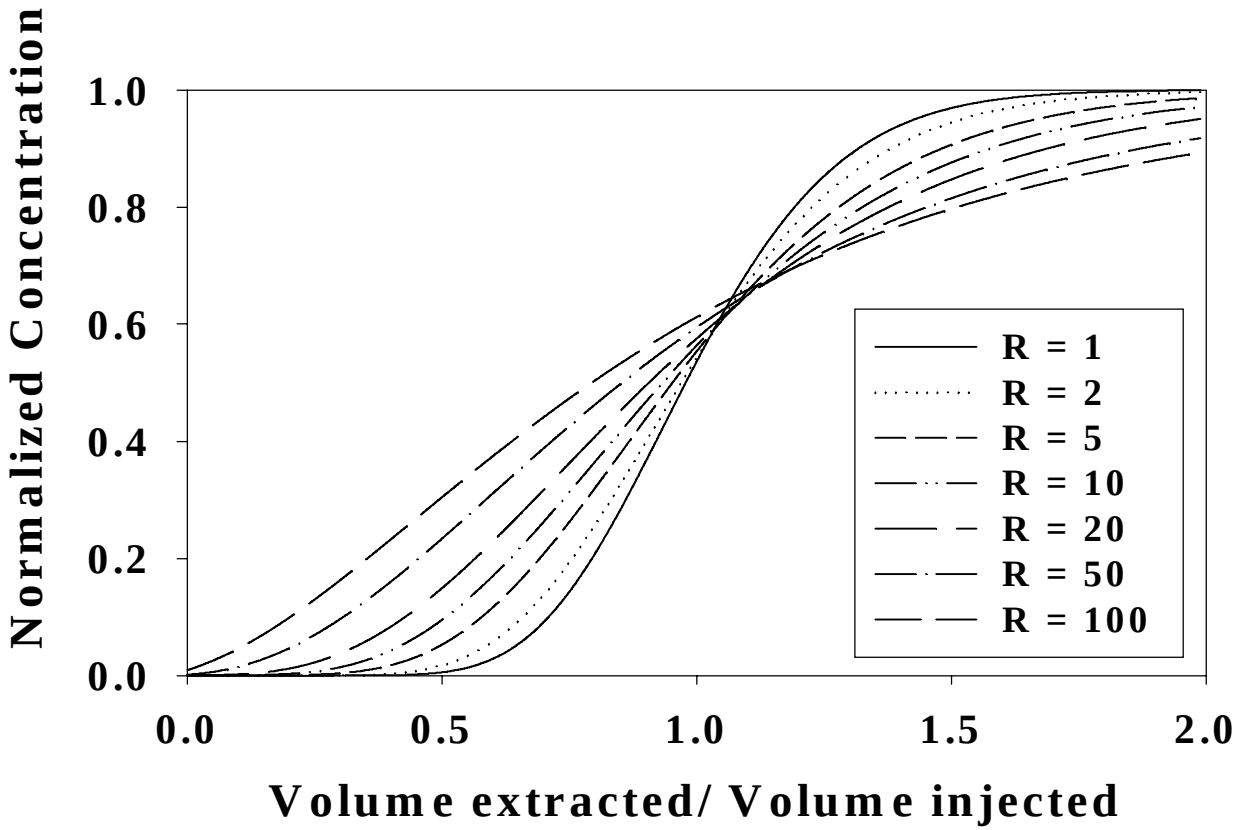


During the *extraction phase*, flow is reversed and samples of test solution/groundwater are collected and analyzed to develop breakthrough curves for all solutes



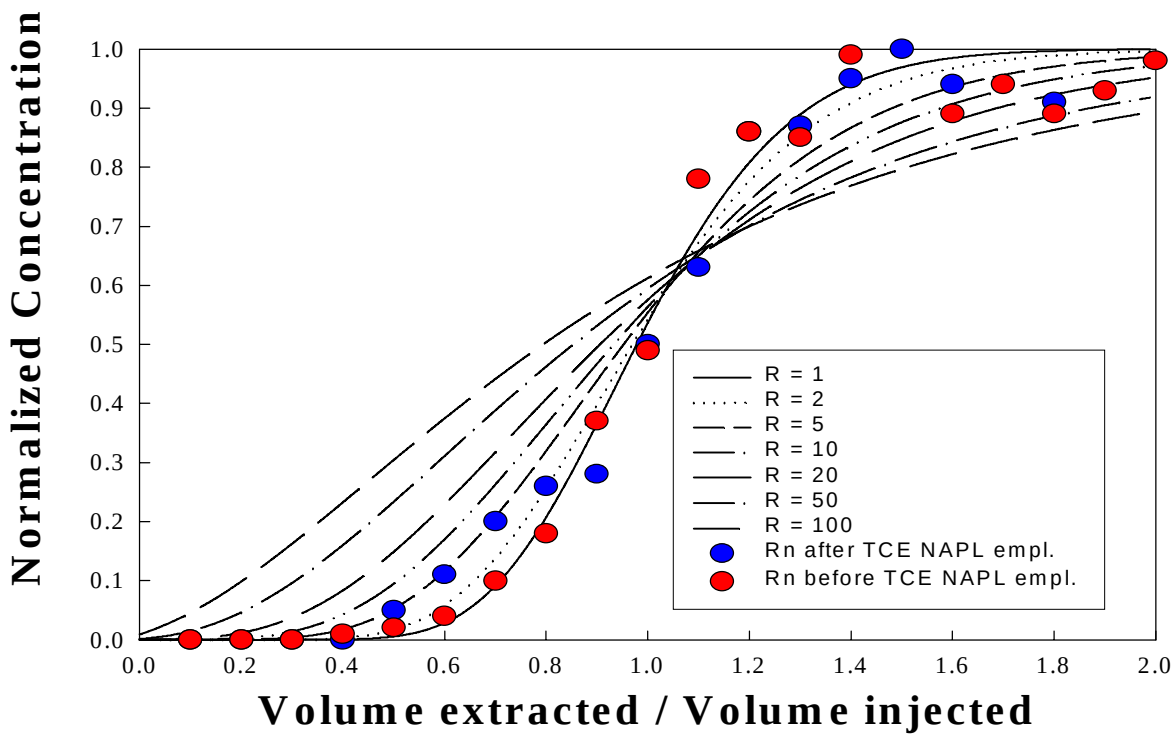
Type Curve Data Interpretation

- Retardation "type curves" have been developed from simulated push-pull tests using the STOMP code.
- Rn breakthrough curves (BTCs) from lab/field tests can be modified and compared to type curves to determine retardation factors and estimate NAPL saturation



Results of Push-Pull Tests Before and After TCE NAPL Emplacement

- Tests conducted through a well emplaced in the middle of the future TCE NAPL zone.
- Pre-Emplacement Rn BTC follows R = 1 type curve.
- Post-Emplacement Rn BTC follows R = 5 type curve .



Determining Area-Averaged Residual TCE NAPL Saturation

- **The actual area-averaged NAPL saturation (in the NAPL-contaminated portion of the PAM) = 4%.**
- **The push-pull test shows R = 5. The radius of influence of our push-pull test equals the radius of the TCE NAPL emplacement (~14 cm; also the radius of bromide tracer).**
- **However, the radius of travel of Rn, the retarded solute, is equal to the bromide radius/R, or (14 cm/5), which is 2.8 cm. This places the radon BTC response wholly within the 6% NAPL saturation zone.**
- **Now use observed retardation factor (R=5) and the retardation equation to calculate an area-averaged TCE NAPL residual saturation.**
- **Our result = 7.4% TCE NAPL residual saturation (using K = 50).**

Determining Residual TCE NAPL Saturation via Analytical Curve Fitting

A curve fitting method can also be used to determine the residual saturation for NAPL (Schroth, Istok and Haggerty; in review).

- **Conduct push-pull test with Br^- and Rn tracers.**
- **Calculate the radius of the Br^- tracer:**

$$r_{\max} = \left(\frac{V}{\pi b n R} + r_w^{\,2} \right)^{\frac{1}{2}}$$

- **Fit an analytical solution to the extraction phase of the push-pull test to the *bromide data* by varying the dispersivity (α):**

$$\frac{C}{C_o} = \frac{1}{2} erfc \left\{ \left(\frac{V_{ext}}{V_{inj}} - 1 \right) \Bigg/ \left[\frac{16}{3} \frac{\alpha_L}{\hat{r}_{\max}} \left(2 - \left| 1 - \frac{V_{ext}}{V_{inj}} \right|^{1/2} \left(1 - \frac{V_{ext}}{V_{inj}} \right) \right) \right]^{1/2} \right\}$$

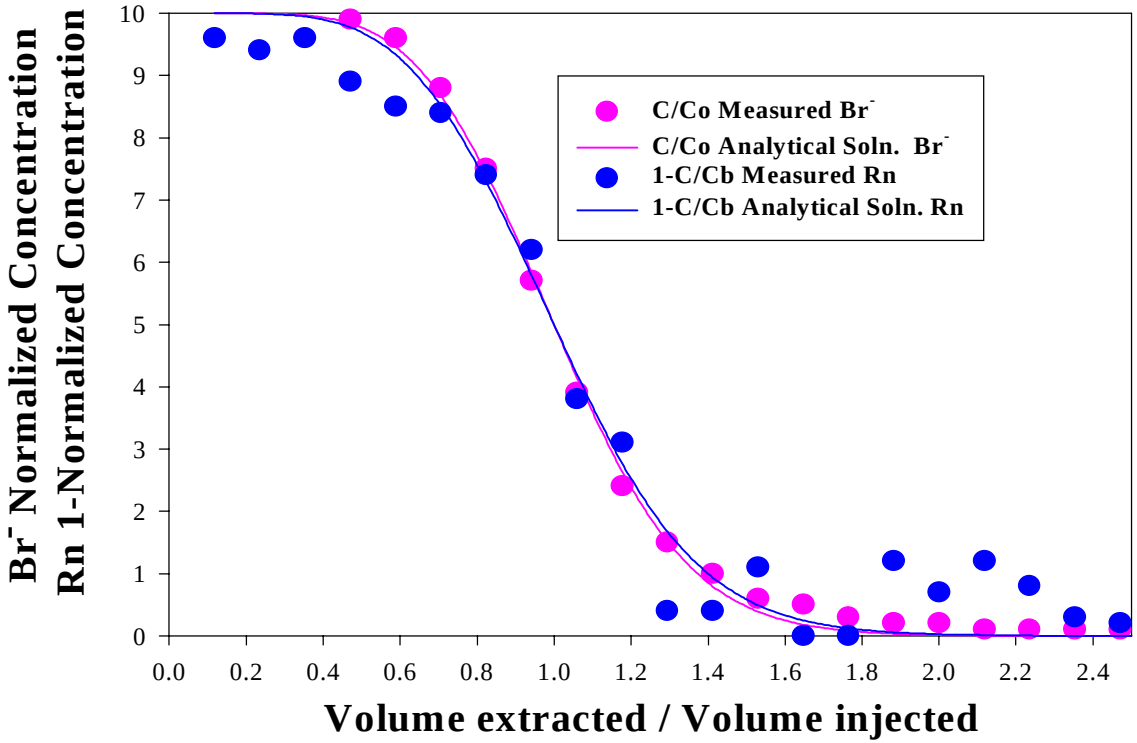
- **Keeping the dispersivity constant, fit the analytical solution to the extraction phase of the push-pull test to the *radon data* by varying the radius term "r_{max}" in the analytical solution.**

- **Compute the retardation factor R via:**

$$R = \left(\frac{\hat{r}_{\max,\ Br^-}}{\hat{r}_{\max,\ Rn}} \right)^2$$

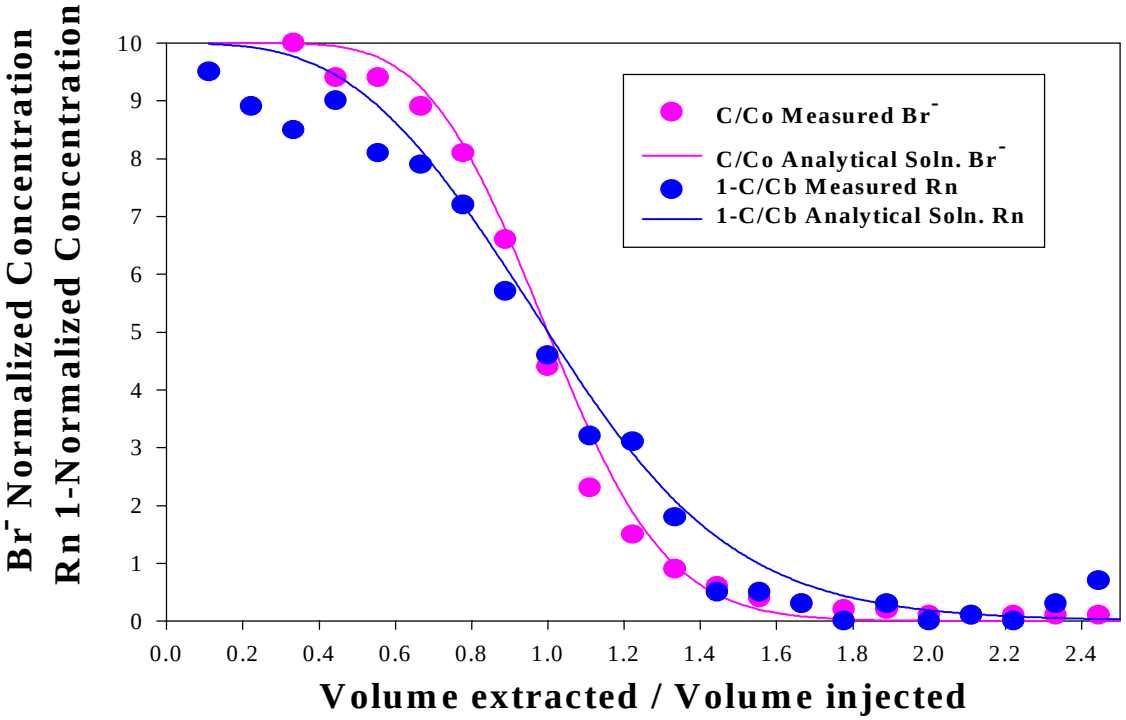
Pre-TCE NAPL Emplacement Results from Analytical Curve Fitting

- The Br^- C/Co curves and Rn 1-C/Cb curves were fit to their respective analytical solutions as shown below.
- R = 1.3, proving that no NAPL was present.



Post-TCE NAPL Emplacement Results from Analytical Curve Fitting

- The Br^- C/Co curves and Rn 1-C/Cb curves were fit to their respective analytical solutions as shown below.
- R = 6.53, with S_{NAPL} = 9.97%.



Field Application at a Contaminated Industrial Site

- ***Description of Site***
  - A former chemical manufacturing plant in the San Francisco Bay Area
  - Aquifer contaminated with aqueous-phase TCE
  - Presence of TCE NAPL not certain
  - Goal of Tests: Verify presence of TCE NAPL

- ***Experimental Methods:***
  - Conduct push-pull tests in aqueous-phase TCE contaminated wells to observe the retardation of Rn in the breakthrough curve and determine residual saturation of TCE NAPL.
  - Use the type curve method (*not* analytical curve fitting) to determine the residual saturation of TCE NAPL.

Field-Scale Push-Pull Tests

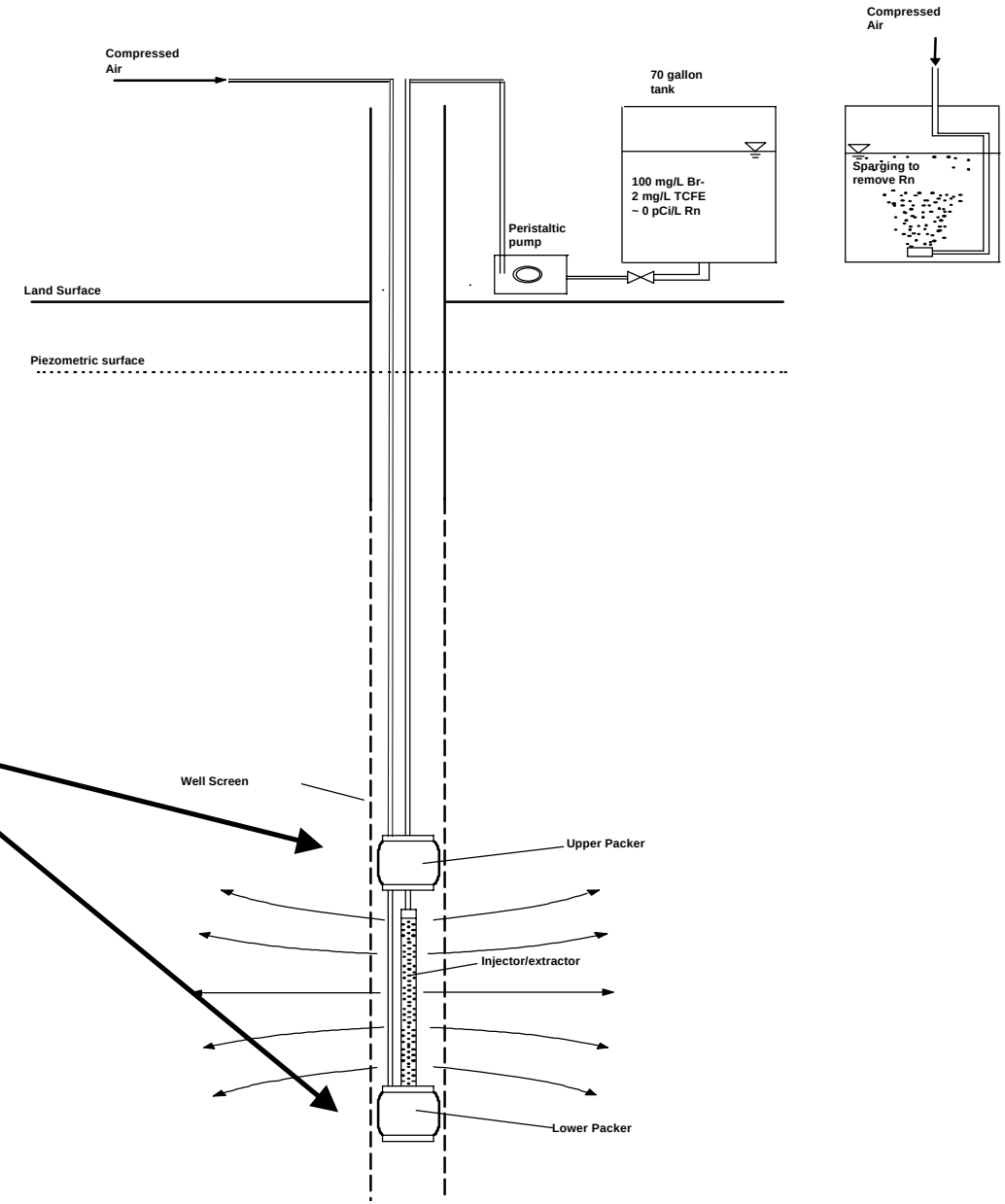
The push-pull test is easily applied to the field:

Supplies needed: a pump, a tracer mixing tank, tubing, and a "straddle packer"

What is a "straddle packer"?

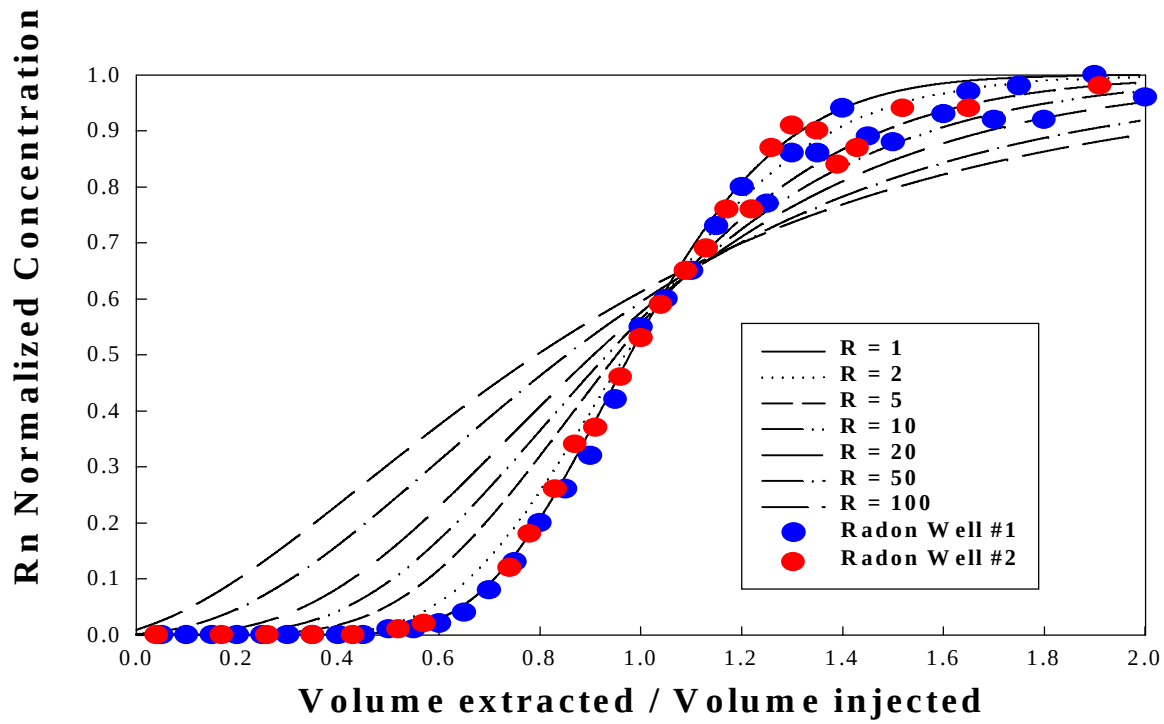
The well screen located between a set of inflatable bladders, or "packers"

This seals the well screen between the packers and allows for the interrogation of a specific depth interval of the aquifer



Results of Push-Pull Tests and Type Curve Analysis

- Tests conducted through wells emplaced in aqueous-phase TCE contaminated aquifer.
- Straddle packers used to isolate a 5 ft length of the aquifer.
- No TCE NAPL exists in the interrogated portion of the aquifer.



Conclusions

The natural Rn tracer method has the potential to provide a rapid, low-cost method for routine use in locating and quantifying residual NAPL.

- **Push-pull tests can be used at both the laboratory and field scale.**
- **The type curve method or the analytical curve fitting method can be used to determine the Rn retardation factor from BTCs.**
- **The retardation factor can be used to determine the residual saturation of NAPL in the aquifer.**

Forthcoming research

- **Exact determination of TCE K factor**
- **Additional field tests**
- **Numerical modeling of Rn transport and partitioning**