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

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The Problem - Residual NAPL

- One of the most formidable challenges facing the DOE's Office of Environmental Management is the significant nonaqueous phase liquid (NAPL) contamination problem at its many facilities. Scientists and facility cleanup managers are increasingly recognizing that NAPL contamination is a very serious, widespread problem, without a ready, economical solution.
- A major obstacle preventing cost-effective cleanup at many DOE sites is the current inability to accurately locate and quantify residual NAPL contamination.

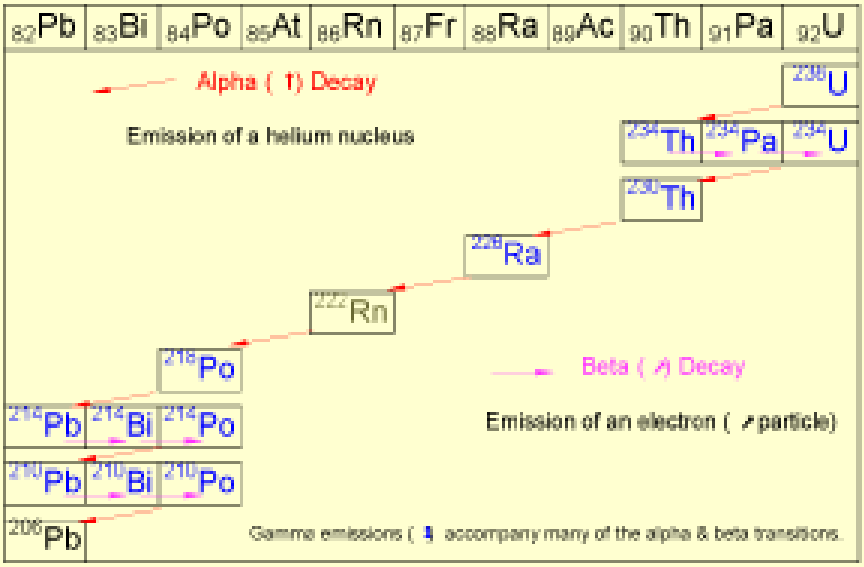
The Solution - Rn as a Tracer

The Rn Deficit Method is a new and potentially powerful partitioning tracer method for detecting and quantifying NAPL contamination in the subsurface.

Rn possesses unique qualities making it highly suitable as an indicator and tracer of NAPL contamination.

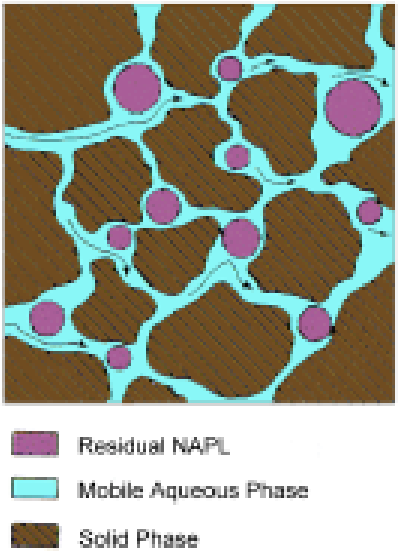
- Properties of Rn-222 as a radio-tracer
  - Natural radioactive material.
  - Non-reactive; a conservative tracer.
  - Alpha decays with 3.82 day half-life.
- Rn as a tracer for subsurface NAPLs
  - Partitions strongly into organic liquids.
  - Characteristic retardation.
  - An in situ tracer; already present.

Natural Rn in the Environment



The Rn Deficit in the Subsurface

- In the saturated zone Rn occurs in the pore fluid as a dissolved gas. In the absence of NAPL, aqueous Rn concentrations reach a site specific equilibrium value. In the presence of NAPL, the Rn concentration in pore water is substantially reduced due to the Rn partitioning into the residual NAPL. Pore fluids produced from regions with NAPL are reduced in Rn compared to adjacent (background) fluids from similar mineralogyis but without NAPL.



The Rn Deficit Model

- Equilibrium Partitioning Model

$$[Rn]_{NAPL} \approx \frac{[Rn]_{Bkgd}}{1 + S(K - 1)}$$

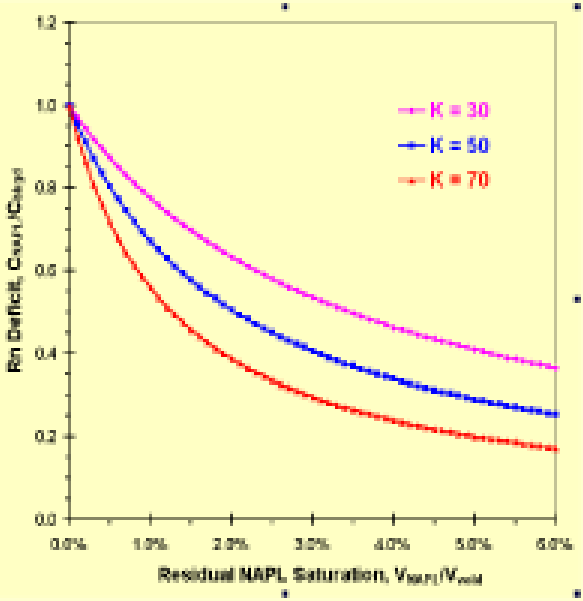
$[Rn]_{NAPL}$ = Aqueous Rn conc. in NAPL zone (pCi/L)

$[Rn]_{Bkgd}$ = Aqueous Rn conc. in non-NAPL zone (pCi/L)

S = Residual NAPL saturation (V_{NAPL}/V_{void})

K = NAPL:water Rn partition coefficient (unitless)

The Rn Deficit vs NAPL Saturation

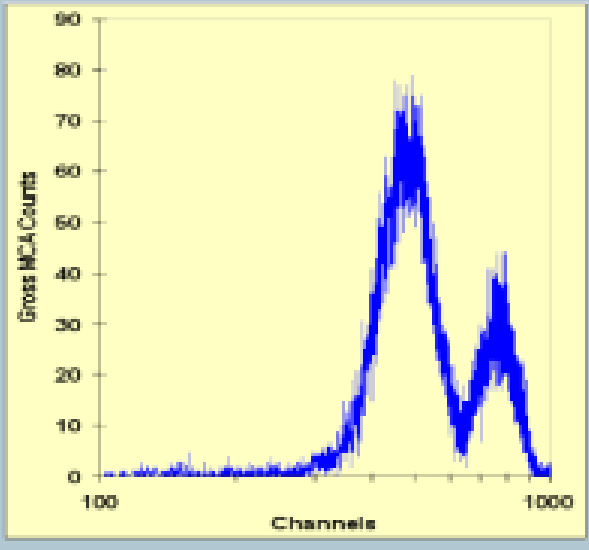


- The Rn Deficit
  - Most sensitive at residual NAPL which are < 5%.
  - Small changes in Rn signal once residual NAPL > 6%.
  - Values of K range from 30-70.
  - K = 50 typical for chlorinated solvents(?)

Rn Analysis by LSC

- Liquid Scintillation Counting (LSC)
  - Highly specific for Rn in aqueous samples.
  - Fast sample preparation; automated counting; low detection limits.
- The Liquid Scintillation Method
  - Add aqueous sample to vial containing the LS 'cocktail' - a solution of scintillators in an organic solvent, normally aromatic.
  - Rn is extracted into the organic cocktail.
  - 4 hrs for Rn and daughter equilibrium.
  - Count sample on liquid scintillation analyzer. Analyze combined alpha/beta spectra of all decay particles or only the alpha spectra from Rn and daughters.
- Highly sensitive analysis
  - Units of radioactivity - Curie (Ci).
  - 1 Ci = 3.7×10^{10} decays per second.
  - Lab and field samples give ~ 4.0 counts per minute (cpm)/ml yielding atto M (10^{-18}M) Rn concentrations.

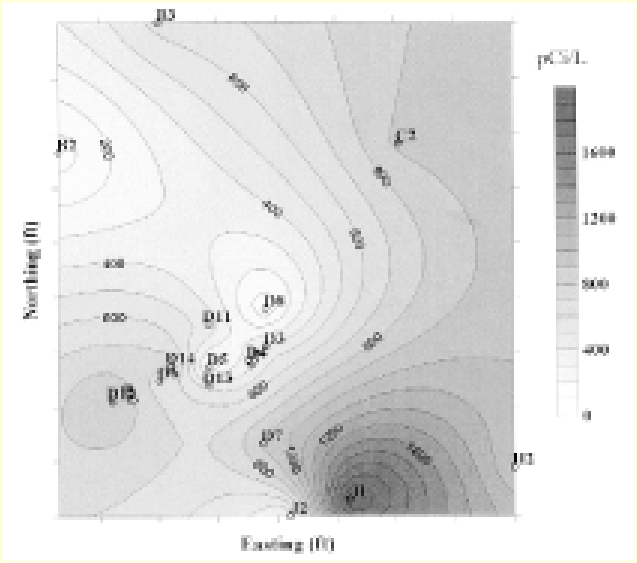
The figure below shows the Rn-222, Po-218 and Po-214 alpha spectra. The larger peak is the combined Rn-222 and Po-218 signal.



Field Evaluations - LLNL

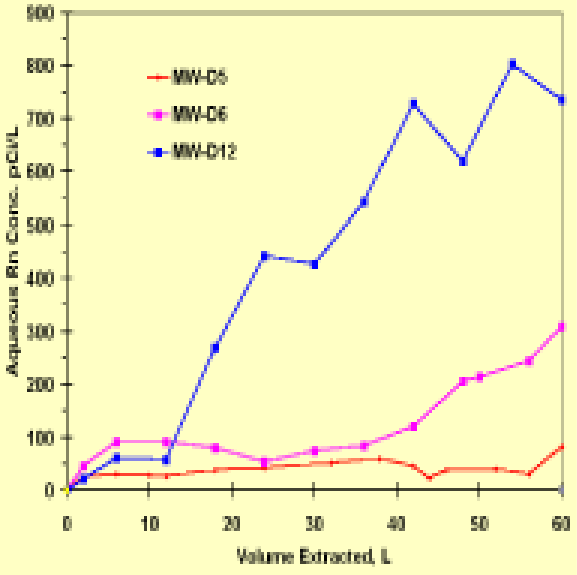
- Site 300, Building 834 Complex at Lawrence Livermore National Lab.
  - Preliminary groundwater Rn surveys conducted to identify suitable test wells.
- Initial Rn tracer ëpush-pullí field tests.
  - Performed at three existing monitoring wells; MW D-5, MW D-6, MW-D12 having low, intermediate and high aqueous Rn concentrations.
  - Rn free, site water with a Br ´ tracer injected in the well, followed by extraction.
  - Tests were first of a kind ëpush-pullsí utilizing Rn as an in situ tracer.
- Tests were incorporated into current site monitoring and remediation demonstration activities at the site.

LLNL Site 300 Rn Field Survey



Monitoring wells D5, D6 and D12 were selected for push-pull tests based on the results of this Rn field survey.

Field Push-Pull Evaluations



Well Comparison

MW-D5: Very low Rn levels; high NAPL contamination.

MW-D6: Rn levels indicate NAPL, but not as much as at MW-D5.

MW-D12: Rn levels indicative of little or no residual NAPL contamination.

Values consistent with previous survey.

Field Results - Implications

- Rn partitioning behavior observed in the test wells was similar to that seen in the PAMs , and consistent with transport theory.
  - Aqueous Rn levels from the three test wells agreed with the site Rn survey performed six months earlier.
  - Rapid increase in Rn levels in the NAPL free well.
  - Depressed, constant Rn signal from the well having higher residual NAPL contamination.
- The Rn tracer test was quick and inexpensive.
  - Rn free (degassed) site water with a Br tracer.
  - No special chemical tracers required.
  - Use of existing monitoring facilities.
  - Injection and extraction from a single existing well.

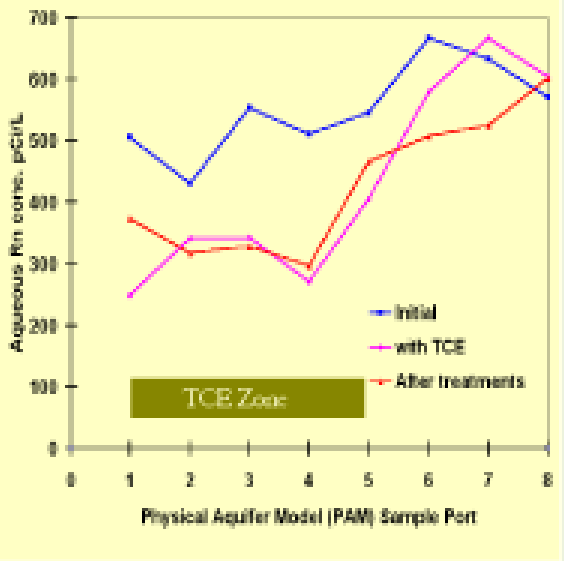
Current & Planned Research

- NAPL remediation assessment
  - A 2-D PAM packed with aquifer solids obtained near the DOE Hanford Site.
  - Evaluations performed in conjunction with a new set of surfactants (Aerosol MA 80-I; Istok & Field).
  - Incorporation of regional flow field.
- Further development of Rn as an in situ partitioning tracer using the single-well ëpush-pullí test.
- A small scale field test at an Oregon site contaminated with NAPL.
- Development of computer models to simulate and predict static and dynamic Rn partitioning behavior.
- Continued development of Rn sampling and analysis protocols.

PAM Expít . -Static Rn Profile

Surfactant Treatment

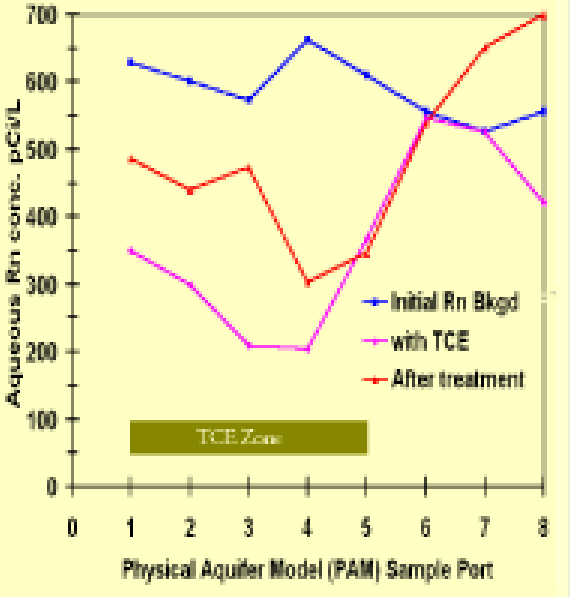
- TCE - 5% saturation between Ports 1 -5.
- Initial Rn deficit correlates well with TCE placement.
- Surfactant injection.
  Push-Pull w/DOWFAX surfactant.
- Rn signal after treatment agrees w/TCE mass balance: low TCE removal.



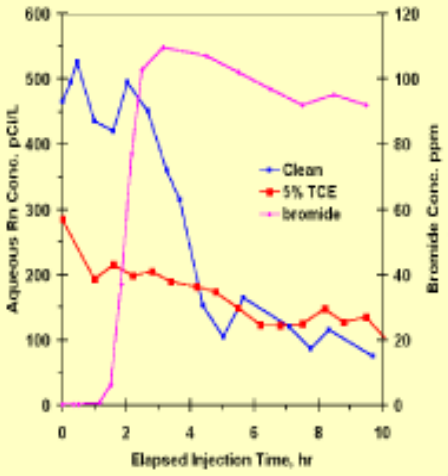
PAM Expít . - Static Rn Profile

In situ Oxidation

- TCE - 5% saturation between Ports 1 -5.
- Initial Rn deficit correlates well with TCE placement.
- $KMnO_4$ injection.
- Rn signal after treatment indicates less TCE, especially in narrow end of PAM. Mass balances indicate 30-35% TCE oxidation.



PAM Expít . -Dynamic Rn Tracer Test



Rn Partitioning

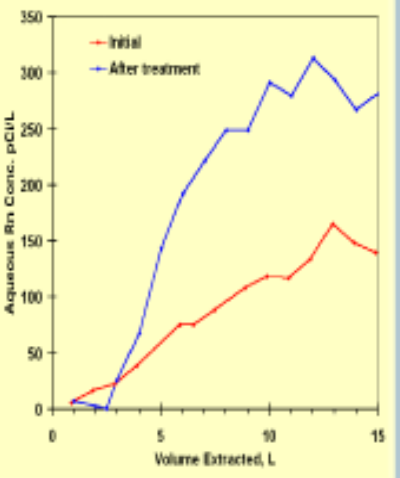
- Tracer tests performed in PAMs with and w/out TCE NAPL (5% residual).
- Injection of Rn free water (w/Br tracer).
- Rn measured at port 2 during injection.
- Retardation of Rn breakthrough in the presence of TCE, Br tracer unaffected by presence of TCE.

PAM Expít . -Remediation Assessment

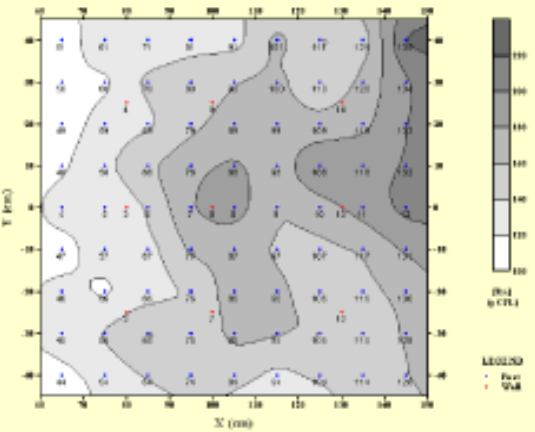
Remediation Monitoring: Rn push-pull tests were performed periodically on the PAM undergoing permanganate treatment.

Initial Extraction : Low Rn levels indicative of residual NAPL.

After treatment : Higher Rn conc . during extraction. Increased Rn signal due to the removal of some TCE. Rn signal does not indicate complete TCE removal.



Rn Profile for Grid 1 of the 2-D PAM



Rn contour plot showing the spatial variation in Rn concentration for a "clean", fully saturated PAM packed with solids obtained near the DOE Hanford Site.

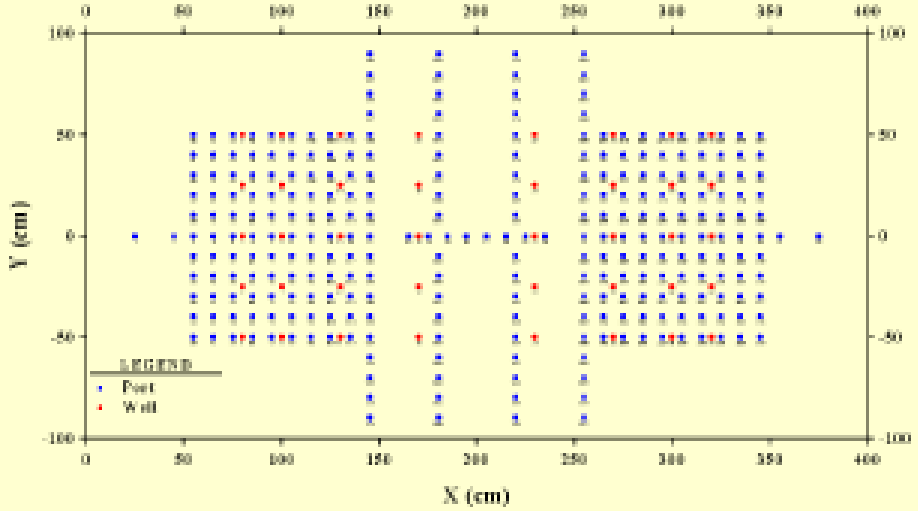
Laboratory Results

- The static Rn profiles were consistent with, and accurately reflected, the changing residual NAPL signal within the PAMs.
- In situ tracer studies show Rn breakthrough is retarded in the presence of NAPL. Retardation factors (R) of 1.5 to 4.5 observed for residual NAPL from 1 to 8%.
- The ëpush-pullí tests show the Rn concentration responses changing during the course of the PAM remediation.
- The results from the remediation PAM studies clearly demonstrate the potential for using Rn to monitor the progress of NAPL remediation.

EMSP Project Summary

- Successful remediation of a NAPL contaminated site requires accurate knowledge of the NAPL presence and spatial distribution.
- The laboratory and field results to date, indicate the natural Rn tracer method has the potential to provide a rapid, low-cost, method for routine use in quantifying residual NAPL in the subsurface.
- The Rn methodís simplicity and compatibility with present research lends itself well to DOEís and EMís mission of reducing the time and costs in evaluating and conducting environmental remediation.

Physical Aquifer Model for Future Tests



Plan view of the large 2-D PAM for future Rn tracer investigations. The PAM contains 280 sampling ports & 40 injection ports. Additionally, the PAM allows for establishment of a flow gradient.