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Radon-222 gas has unique properties allowing it to be used as an indicator for the presence of organic phase liquids in the saturated zone. It naturally occurs in soils. It is radioactive, making quantitative detection straight forward. A noble gas, it is chemically inert and does not react with aquifer media. Finally, radon has an affinity to concentrate in nonaqueous phase liquids. A proposed linear equilibrium partitioning model was tested by batch equilibration with the pore fluid to establish the deficit in aqueous radon concentrations that results from its partitioning into the residual saturation of the organic phase (Soltrol-220). Five sets of experiments were run on columns with 0.0, 1.0, 2.5, 5.0, and 8.0 percent residual soltrol fractions. The model was found to accurately represent the partitioning process. A one-dimensional physical model was run to see if the data from the partitioning experiments could be successfully applied to predict the aqueous radon concentrations in a more complex situation. The results indicate that radon-222 has great potential to be used as a means of detecting and quantifying the presence of residual organic phase liquids in the saturated zone.

Radon-222 as an Indicator for Nonaqueous Phase Liquids in the Saturated Zone: Developing a Detection Technology

by

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorized the release of my thesis to any reader upon request.

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Omar Hopkins, Author

Acknowledgments

This thesis is dedicated to the memory of my grandfather,

Frank Snowden Hopkins

who always was interested in my work and my aspirations, who provided me with a home away from home, and who was my other father.

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Radon-222 as an Indicator for Nonaqueous Phase Liquids in the Saturated Zone: Developing a Detection Technology

Chapter 1
Introduction

Detection and monitoring of Dense Nonaqueous Phase Liquids (DNAPLs) is a serious problem in groundwater protection and remediation. Problems detecting DNAPLs occur when they fall below their residual saturation in the saturated zone. A DNAPL below its residual saturation is no longer completely contiguous and it becomes trapped in the pore spaces of the aquifer media. This makes DNAPLs difficult to extract from the aquifer material, and therefore detection by sampling of the nonaqueous phase is also problematic. Direct methods of detection and quantification are not always available, and other indirect means of sampling are required in order to aid in a subsurface investigation. This research examined the practicality of using naturally occurring radon gas as an indicator for the presence and degree of saturation of a NAPL in a saturated media.

Radon-222 gas, which will be referred to as radon, was chosen for its unique properties as an indicator for the presence of organic phase liquids. It naturally occurs in soils. It is radioactive, making its quantitative detection fairly straight forward. Radon is continuously produced from the decay of radium-226. A noble gas, it is chemically inert and will not react with the aquifer media--this means that after its production and radioactive decay are taken into consideration radon may be considered a conservative tracer. Finally, radon has an affinity to concentrate in nonaqueous organic phase liquids.

Previously, work was done by Lewis Semprini and Mike McDonald with naturally occurring radon gas to determine the presence of Dense Nonaqueous Phase Liquids in a sandy aquifer material at the Borden, Ontario site (Semprini et al., 1993). This work showed that naturally occurring radon has potential for detecting and/or in the monitoring of DNAPL concentrations in the saturated zone. Groundwater samples taken within zones of DNAPL contamination showed decreased levels of radon concentration, while samples taken from further down gradient showed radon concentrations recovering towards upgradient equilibrium levels.

Objectives

This research was conducted to: one, determine the relationship between aqueous radon concentration and the degree of NAPL saturation in groundwater systems; and two, examine the possibility that this relationship might be used to predict NAPL concentrations in the field. To that end, the research was divided into the two stages:

1. Conduct experiments to verify the linear equilibrium partitioning model that predicts decreasing aqueous radon concentrations as the residual NAPL saturation increases.

2. Run a physical one-dimensional flow model to mimic the conditions of the field study, namely; an uncontaminated zone, followed by a short contaminated zone, and finally followed by another uncontaminated zone.

In order to achieve these objectives some preliminary experiments were run to determine the characteristics of the aquifer solids used in the experiments including grain size distribution and emanation constant for radon. Interfacial properties of the NAPL used in the experiments, Soltrol-220 with various additives (hereafter soltrol), were also determined. The partitioning model was tested by a batch equilibration in the pore fluid to establish the deficit in aqueous radon concentrations that results from its partitioning into the residual saturation of the organic phase. The one-dimensional physical model was run to see if the data from the partitioning experiments could be successfully applied to predict the aqueous radon concentrations in a more complex situation.

Chapter 2
Literature Review

Introduction

There is little literature in the field on the use of radioisotopes in the detection of Nonaqueous Phase Liquids (NAPLs); some work was done in the early part of the century on the partitioning of radon gas into various organic fluids (Cleaver et al, 1979). Some literature exists on the use of radioisotopes as groundwater tracers (Hoehn, 1992, IAEA, 1989, and Semprini, 1985). A substantial amount of work has been done on the behavior of NAPLs in the subsurface environment (Parker, 1989; Mercer and Cohen, 1990; Bear, 1972; and Mackay, 1985). Substantial work has been done on radon as a health hazard--mostly on radon as an airborne contaminant and in its geographical and geological distribution (Graves, 1987).

The study of NAPL movement in the subsurface environment (unsaturated and saturated) is a relatively new development. Previous work on multiphase fluid flows in porous media has been done by petroleum engineers interested in maximizing the yield of oil from oil bearing strata (Martel, 1993) and by environmental engineers and hydrogeologists interested in NAPL recovery from contaminated subsurface sites (Abdul, 1990; Corapcioglu, 1990; Hunt, 1988; Kueper, 1991; Mercer, 1990; Parker, 1989; and Schwille, 1988). Some work has been done on water flow in the unsaturated (Vadose) zone which is conceptually similar to the case of the movement of denser than water NAPLs (DNAPLs) in the saturated zone (Reible, 1990 and Selker, 1991).

Nonaqueous Phase Liquids

NAPLs are compounds that are immiscible with, and therefore have very low solubilities in, water. A wide range of industrial activities make use of compounds that are potential NAPL groundwater contaminants. NAPLs are classified into two types: Light[er than water] Nonaqueous Phase Liquids (LNAPLs) and Dense[r than water] Nonaqueous Phase Liquids (DNAPLs). Gasoline, diesel and motor oil are examples of LNAPLs, and carbon tetrachloride, 1,1,1-trichloroethane and 1,2-dichloroethane are examples of DNAPLs.

Since LNAPLs are lighter than water, they float, and are therefore rarely found significantly below the water table. DNAPLs due to their higher density can sink through the saturated zone until they encounter an impermeable layer (Figure 2.01).

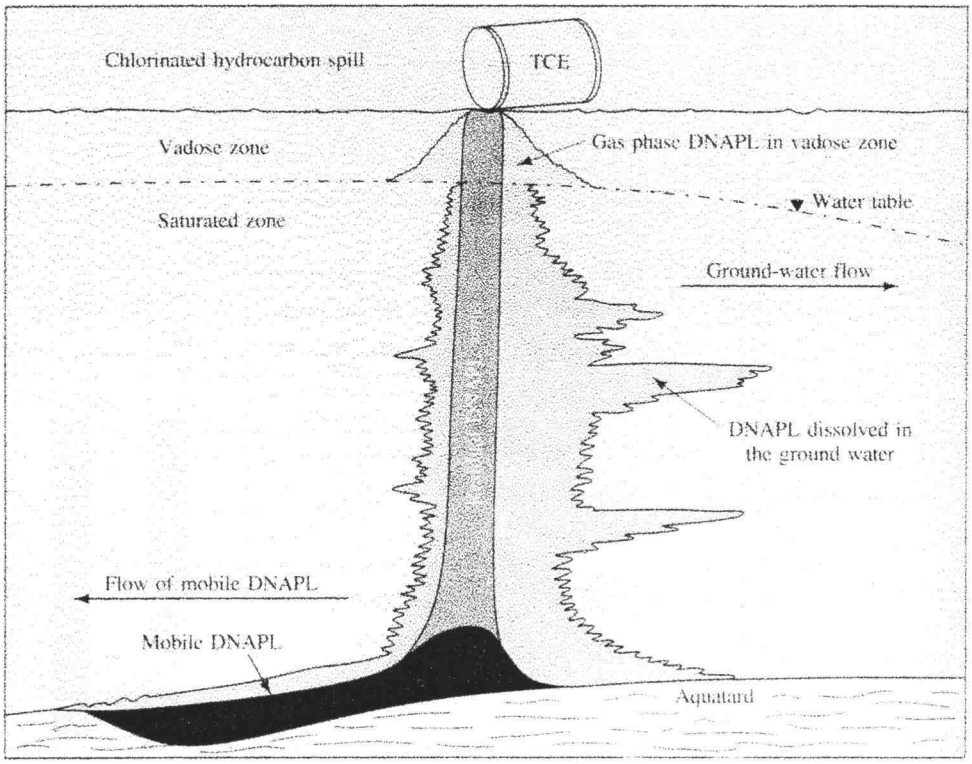

Figure 2.01 Distribution of a Dense Nonaqueous Phase Liquid in the Vadose and Saturated Zone (Fetter, 1993)

Chlorinated aliphatic hydrocarbons (CAHs) are DNAPLs of particular interest due to their widespread use, frequent presence at zones of groundwater contamination, and their toxicity. In general, the increasing chlorination of CAHs increases their nonflammability, density, viscosity, and improves their solubility in a large number of inorganic and organic materials, while decreasing their water solubility (Kroschwitz, 1993, V.5, pg. 1019). Many of these compounds are more dense and less viscous than water making them particularly difficult to recover once they enter the saturated zone.

Physical Properties

Understanding the particular properties of DNAPLs is important since they dictate their behavior in the environment. Some of the important properties that need to be considered are: density, viscosity, interfacial tension, wettability, spreading, and capillary characteristics.

Density: Density is one of the main driving factors in determining the rate of decent through the saturated zone. The denser the DNAPL relative to the groundwater, the greater the force applied on it by gravity, and therefore the greater its acceleration and rate of penetration into the saturated zone.

Viscosity: Viscosity is the another factor that determines how a DNAPL behaves in the saturated zone. A lower viscosity indicates a lower resistance to flow and therefore a faster rate of penetration into the saturated zone. It is also a factor in the rate of lateral spreading of the DNAPL that occurs upon contact with an impermeable layer.

Interfacial Tensions: Interfacial tensions are forces that act "at boundaries between separate phases and are tangential to the boundaries" (Corey, 1977. pg. 11). The interfacial tension is a result of unequal forces being applied to molecules at the fluid boundary. The molecules thus require additional energy to remain at the interfacial boundary (Jury et al. 1991. pp. 37 and 38). Surface tension can be affected by a range of factors including temperature and solutes.

Wetting and Nonwetting Fluids: Interfacial tensions exist at the boundary between solids and fluids but are difficult to measure. The interfacial tension at the solid boundary determines the contact angle of the two fluids at their point of contact with the solid. A wetting fluid is one that preferentially covers the solid surface, characterized by a contact angle of less than 90°. A non-wetting fluid has a contact angle greater than 90° and does not preferentially cover the solid. Figure 2.02 shows the effect of the contact angle at the meeting point of two fluids at a solid boundary (Jury et al., 1991. pg. 40). The interfacial tension between solid and fluid also affects the amount of energy required to remove the fluid from the surface, that is to say it affects the 'strength' of adhesion between the fluid and the solid (Corey, 1977. pg. 21). A media that has been previously wetted by a fluid may exhibit different behavior. A media that is "pre-wet" is one that has been previously in contact with a fluid, although that fluid no longer fills a significant fraction of the pore volume. In a media that is pre-wet with a fluid that is

less wetting than the infiltrating fluid the pre-wetting fluid may become entrapped on the particles due to their immisiblity. In general in natural systems an aquifer is pre-water wet and water is the wetting fluid.

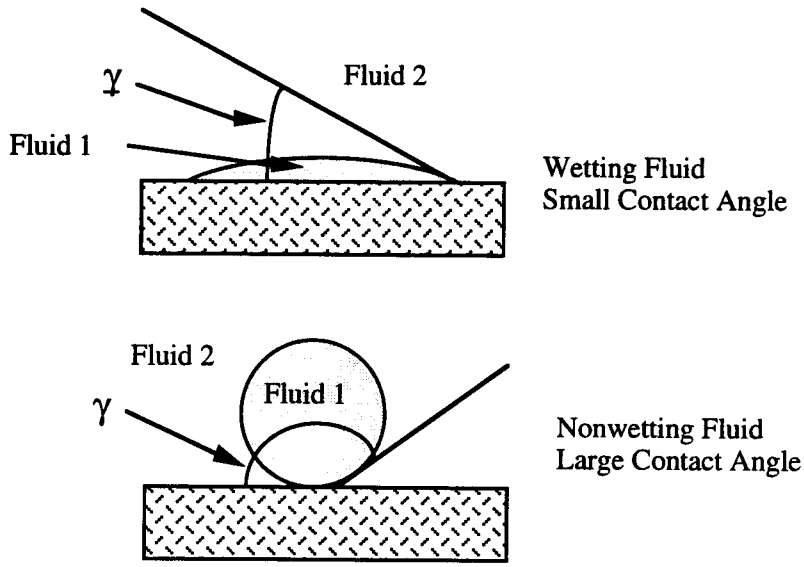

Figure 2.02 Wetting and Nonwetting Fluids

Coefficient of Spreading: A NAPL at the air-water interface will either form a lens or spontaneously spreads to a thin film. "The physical property quantifying the spreading response in an air-NAPL-water system in the spreading coefficient, C_{sp}

$$C_{sp} = \gamma_{AW} - \left(\gamma_{OW} + \gamma_{AO}\right) \qquad \textbf{Eq 2.01}$$

where γ denotes the interfacial tension; and the subscripts A, N, and W refer to air, NAPL and water respectively. If $C_{sp} < 0$ then the NAPL forms a lens; if $C_{sp} = 0$ then the NAPL spreads to a film because of gravity; and if $C_{sp} > 0$ then the NAPL spreads spontaneously because interfacial interactions enhances gravity spreading" (McBride et al., 1992). McBride documents a case where oil with a spreading coefficient > 0 was able to spread along a barrier through the capillary zone and into the saturated zone and reappear on the far side on top of the capillary zone. This indicates that NAPLs with a positive C_{sp} are also wetting fluids.

Capillarity: At the boundary between the two fluids in a porous media there is an interfacial tension; this force disequilibrium results in a fluid pressure deferential

(Jury et al. 1991. pp. 40-41 and Corey, 1977, pp. 12-22). This pressure deferential is the reason behind capillary rise. This is also the reason why smaller pore sizes in a media may act as a barrier to the flow of a DNAPL. The saturated media exerts a force on the water that holds it in place and thus effectively prevents the DNAPL from entering.

Some physical parameters for selected NAPLs are given in Table 2.01.

Table 2.01 Selected NAPLs and Their Properties
(Kroschwitz, 1993)

	density @ 20°C (g/cm^3)	viscosity @ 20°C (cP)	air-fluid tension @ 20°C (dyne/cm)	vapor pressure @ 20°C (kPa)	solubility in 100 g H2O @ 20°C (g)
1,1-DCA	1.1747	0.377	23.34	24.28	0.55
1,2-DCA	1.2529	0.84	31.28	8.5	0.869
1,1,1-TCA	1.3249	0.858	25.54	13.3	0.095
1,2-DCE-trans	1.2631	0.404	25	35.3	0.63[1]
1,2-DCE-cis	1.2917	0.467	28	24.0	0.35
TCE	1.464	0.57	29.3	7.71	0.107
CCl_4	1.48069	0.563	27.14	21.28	0.08[1]
CCl_3H	1.59472	0.965	26.77	11.94	0.822
Soltrol-220	0.809	3.3[4]	25.9[2]	>0.01 (psia)[3]	n/a

(1) at 25°C

(2) as determined during this research

(3) at 38°C

(4) McBride et al, 1992

DNAPL Behavior in the Environment

Residual Saturation: The residual saturation is the fraction of the pore volume occupied by the DNAPL which cannot be reduced by manipulation of the capillary pressure or by displacement by a second immiscible fluid. The residual saturation of a DNAPL in a media is a function of the ratio of the necks and bodies of the pore spaces. A small aspect ratio, e.g.. large bodies and small necks, will foster the entrapment of the DNAPL blobs while a large aspect ratio may only allow for a much lower residual saturation. Experimental work on the estimation of residual saturation was found to vary widely (between 1 and 50%) and is thought to be highly sensitive to the soil properties and not

particularly sensitive to the fluid properties (DNAPL Workshop Summary pg. 34). One reason might be that most soils are not uniform but have a range of particle sizes present. Clay contents as low as 2% has been found to have a substantial role in determining the residual saturation (Schwille, 1988. pp. 10-11).

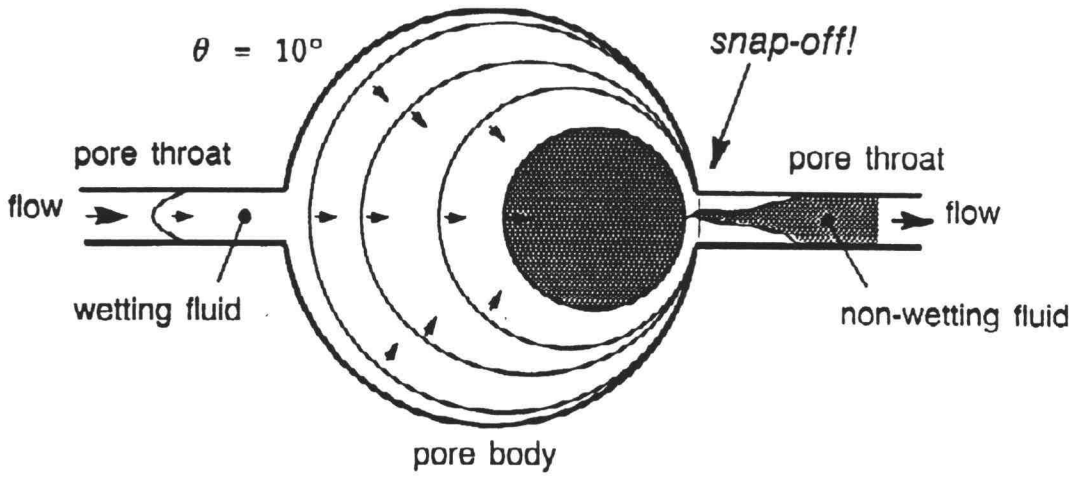

Figure 2.03 Entrapment of a DNAPL Blob
(Wilson, 1990)

Flow in Porous Media: Homogeneous fluid flows in a saturated porous medium can be described by Darcy's Law when the intrinsic soil properties, gradient, and the fluid properties are known. When the saturated system contains two phases, the problem gets significantly more complicated. This is due to the fact that fluid movement in a porous medium is based on a continuum approach, where the liquids are continuous throughout the medium. As the percentage of the pore space occupied by a particular fluid decreases the tortuosity of the continuous phase increases significantly and eventually may become discontinuous. The aqueous phase conductivity decreases rapidly as the fraction of pore space occupied by the DNAPL increases, and the reverse is also true (Figure 2.04). Due to the wetting nature of water, below a residual saturation the flow of DNAPL stops. This is a result of the water being trapped by capillary forces in the necks of the pores. Recent work suggests that the DNAPL forms blobs in the bodies of the pore spaces around which the aqueous phase flows (Dense Nonaqueous Phase Liquids, EPA, 1991). Since water is the wetting fluid it advances around the DNAPL along the pore body sides and at the neck joins together to close the pore exit.

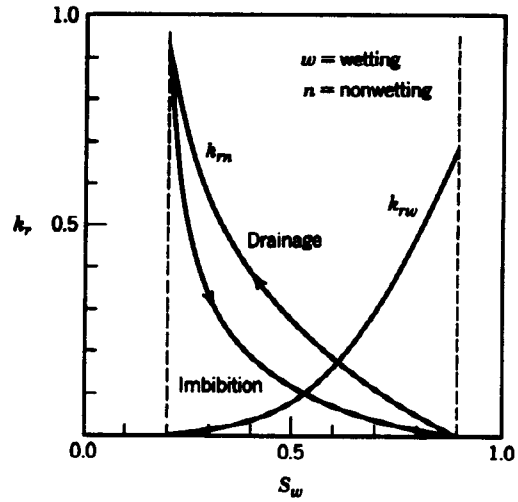

Figure 2.04 Permeabilities of Water and a Nonwetting Fluid as a Function of the Relative Saturation (Domenico and Schwartz, 1990)

Soil Properties: Properties of a porous media have a very significant effect on DNAPL movement in the subsoil. If the DNAPL is present in 100% of the pore volume then the hydraulics of the system may be analyzed as a homogeneous fluid using the fluid properties and the intrinsic permeability of the soil. The size of the pore spaces plays a significant role in determining the capillary force exerted on the fluid and in determining the residual fraction remaining after the bulk of the DNAPL has passed. Soils with a hydraulic conductivity of less than 10^{-4} m/s show significant resistance to penetration by DNAPLs (Schwille, 1988). This is due to the strong capillary force that holds the water to the soil particles and the interfacial tension that holds the DNAPL together.

Site Characterizations: Determining the location and extent of a spill is of primary importance for remediating contaminated sites. Wells and other intrusive testing schemes may potentially aggravate the extent of contamination by creating pathways by which the DNAPLs might rapidly migrate (i.e., down around the casing of a well). Direct sampling of groundwater will not detect a NAPL when it is below its residual saturation. The use of exploratory borings will provide accurate data on the degree of contamination, but its cost may be quite high (EPA, DNAPL Workshop, 1992). Other detection techniques are not entirely reliable in detecting the presence of DNAPLs in the saturated zone. Ground Penetrating Radar and dielectric methods are best suited for determining changes in the saturated zone, but may lack the resolution to pinpoint the presence of

DNAPLs, or to detect them at low residual saturation concentrations (Chudyk, 1987 and Kurtovich, 1987). Soil Gas Surveys are a valuable tool in the determination of the approximate location of volatile DNAPL spills; however, their use may be more limited in the saturated zone (EPA, DNAPL Workshop, 1992).

NAPL Summary

This discussion serves to provide a brief overview of the nature of DNAPL contamination of groundwaters. Understanding how NAPLs behave in the saturated zone was essential in order to properly design the experiment. In these experiments a less toxic substance, Soltrol-220, was substituted for CAHs. Understanding the similarities and differences between soltrol and CAHs was critical in making that substitution.

Radon

Radon, atomic number 86, is a noble gas. It is radioactive and has three main isotopes: Rn-219, Rn-220, and Rn-222. The first two radon isotopes are rare and have very short half-lives that make their measurement and detection quite difficult. Rn-222 has a half-life of 3.83 days. The characteristics that make Rn-222 useful as an indicator for NAPLs are: its chemical inertness, its radioactivity, and its solubility in organic phase liquids.

Chemical Properties of Radon-222: Radon as a member of the noble gas family is highly inert. The inertness is due to the filled outer electron shell of the atom. This inertness is an important quality since it allows radon to be considered a conservative tracer (with consideration for its radioactive properties) in an aquifer medium since it will not become bound up chemically with other elements or molecules.

Radioactivity: Radon-222 is an intermediate daughter product of the Uranium-238 decay sequence, as shown in Table 2.02.

Table 2.02 The Uranium-238 Decay Sequence:
(CRC Handbook of Chemistry and Physics, 1990)

Parent	Daughter	Type of Decay	Half-Life
Uranium-238	Thorium-234	Alpha	4.46 billion years
Thorium-234	Protactinium-234	Beta	24.1 days
Protactinium-234	Uranium-234	Beta	6.70 hours
Uranium-234	Thorium-230	Alpha	245,000 years
Thorium-230	Radium-226	Alpha	75,400 years
Radium-226	Radon-222	Alpha	1,599 years
Radon-222	Polonium-218	Alpha	3.823 days
Polonium-218	Lead-214	Alpha	3.11 minutes
Lead-214	Bismuth-214	Beta	26.8 minutes
Bismuth-214	Polonium-214	Beta	19.9 minutes
Polonium-214	Lead-210	Alpha	163 microseconds
Lead-210	Bismuth-210	Beta	22.6 years
Bismuth-210	Polonium-210	Beta	5.01 days
Polonium-210	Lead-206	Alpha	138.4 days

The rate of decay of a radioactive element is given by Equation 2.02 (Nuclear Chemistry, 1980):

$$C = C_0 e^{-\lambda t} \qquad \textbf{Eq 2.02}$$

where C_0 is the original number of atoms present

C is the number of atoms currently present

λ is the decay constant

t is the time during which decay occurs

In systems where radioactive elements are not being removed by means other than decay, an equilibrium will establish itself between a parent-daughter pair. This equilibrium can be expressed by the following equation (Nuclear Chemistry, 1980):

$$\lambda_{\text{Parent}} N_{\text{Parent}} = \lambda_{\text{Daughter}} N_{\text{Daughter}} \qquad \textbf{Eq 2.03}$$

which states that at equilibrium, the rate of production of an element (the decay rate of its parent, where λ is the decay constant and N is the number of atoms) is equal to the rate with which it decays.

In the case of Radium-226 due to its very long half life (1,600 years) relative to that of Radon-222 (3.823 days) the number of Radium-226 atoms is so much larger than the number of Radium-226 decayed to radon over any experimental period that it may be considered to be a constant. Thus, in these experiments, the source term for radon is considered to be constant.

The build up of radon in a closed system is given by Eq 2.04,

$$\frac{C}{C_\infty} = 1 - e^{-\lambda t} \qquad \textbf{Eq 2.04}$$

Another important equation is one that relates the decay constant and the actual observed disintegrations to the number of atoms of the parent compound. This relationship can be expressed as follows:

$$-\frac{dN}{dt} = \lambda N \qquad \textbf{Eq 2.05}$$

which states that the number of disintegrations divided by the time in which they occurred is equal to the number of atoms multiplied by the decay constant.

<u>Emanation of Radon from Solids:</u> The radium atom disintegrates into a helium nucleus and a radon atom. Momentum must be conserved, therefore, the ejection of the helium nucleus means that the radon atom also has a velocity. It has been shown that the recoil distance may vary from 10E-6 to 10E-3 cm depending on the medium. The probability of radon escaping from a solid particle is proportional to $1/d^{-1/2}$, where d is the diameter of the particle. This suggests that the coefficient of radon emanation is strongly relating to the size and/or surface area of the particle (Davis et al, Graves Ed, 1987).

<u>Radon in Groundwaters</u>: In the saturated zone radon will emanate from the solids and enter the pore volume. The rate of emanation will be dependent on the concentration of radium-226 (C_{Ra}) in the aquifer solids and on the emanation power (E_p), which is the fraction of radon produced that enters the pore volume. The equilibrium concentration of radon in the saturated zone is given by,

$$C_{Rn} = \left[\frac{C_{Ra} E_p \rho_b}{e} \right] \qquad \textbf{Eq 2.06}$$

where,

C_{Rn}	is the aqueous radon concentration, pCi/L
C_{Ra}	is the radium concentration, pCi/kg
E_p	is the emanation power
ρ_b	is the bulk density of the aquifer solids, kg/L
e	is the aquifer porosity

Solubility of Radon-222 in Organic Phase Liquids: Some work has been done to establish the partitioning of radon between air and various liquids, including several nonaqueous phase liquids (Cleaver et al, 1979). The Ostwald coefficient is given by,

$$L = \frac{(\text{pCi Rn/ml})_{\text{liquid}}}{(\text{pCi Rn/ml})_{\text{air}}} \qquad \textbf{Eq 2.07}$$

Thus the Ostwald Coefficient is the ratio between the concentrations in the air and liquid phases. The partition coefficient, K, between two liquid phases can be estimated by using the Nerst Distribution Law (Denbigh, 1971), which states that the partition coefficient is equal to the ratio of the Ostwald coefficients. The Ostwald coefficients (Cleaver, 1979) and estimated organic-water partitioning for several compounds are given in Table 2.03.

Table 2.03 Ostwald Coefficients and Estimated Organic-Water Partitioning Coefficients for Radon-222

Compound	L	K
Water	0.285	- -
CS_2	23.14	81
$CHCl_3$	15.08	53
Benzene	12.82	45
Toluene	13.24	46
Hexane	16.56	58
Di-ethyl-ether	15.08	53
Petroleum	9.01	32
1-pentanol	10.6	37
2-butanol	7.58	26
methanol	5.4	19
xylene	15.4	54

Partitioning and Retardation

Radon distributes itself unequally between aqueous and nonaqueous phases. A linear partitioning model was used in this work. The linear model is appropriate due to the very low concentration of radon in both phases (Semprini, personal communication). The model assumes that there is always a local equilibrium between the partitioning compound and the two competing partitioning sites.

The Linear Sorption Isotherm is expressed by (Fetter, 1993),

$$C_N = KC_W \qquad \textbf{Eq 2.08}$$

where, C is the radon concentration in the phase, pCi/L
K is the partition coefficient
W is the aqueous phase
N is the nonaqueous phase

Retardation, R, is the rate at which a contaminant moves in the aquifer relative to the groundwater, and can be expressed as (Fetter, 1993),

$$R = \frac{V_{Groundwater}}{V_{Rn}} \qquad \textbf{Eq 2.09}$$

where V is the velocity

since the retardation is a function of the ratio of the amount of compound sorbed or otherwise immobilized to the amount in water is can also be expressed by (Class Notes CE 516),

$$R = \frac{[Rn]_{Voids}}{[Rn]_W} \qquad \textbf{Eq 2.10}$$

where the numerator represents the concentration of radon in the total pore space and denominator represents the concentration of radon in water.

In a system where two immiscible fluids are present in the pore space, radon will partition between the two phases as can be shown by modifying Equation 2.06,

$$S_N C_N + S_W C_W = \frac{C_{Ra} E_p \rho_b}{e} \qquad \textbf{Eq 2.11}$$

where, S is the volumetric phase saturation, L/L

If we assume that the partitioning relationship is linear than the concentration can be expressed by,

$$C_N = KC_W \qquad \textbf{Eq 2.08}$$

From Equations 2.08 and 2.11 we can develop an expression that relates the aqueous radon concentration to the emanation power of the solids, the amount of NAPL present, and the partitioning coefficient (Semprini et. al., 1993),

$$C_W = \frac{\left(C_{Ra}E_p\rho_b\right)/e}{1 + S_N\left(K - 1\right)} \qquad \textbf{Eq 2.12}$$

Two assumptions are made in order to use this model: one, the linear model is appropriate; and two, emanation is not affected by the fluid occupying the pore volume.

From Equation 2.12 a theoretical graph (Figure 2.05) showing the impact of NAPLs with various partition coefficients on the aqueous radon concentration.

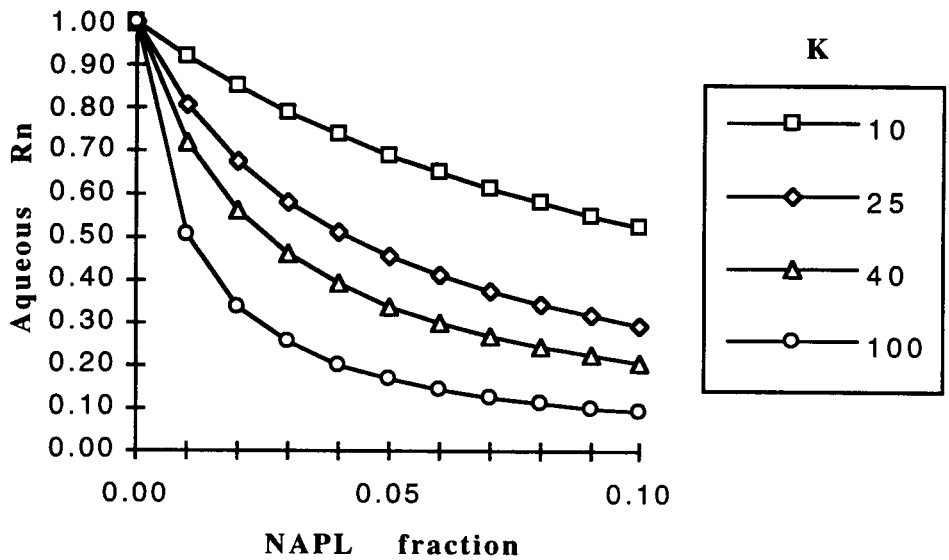

Figure 2.05 Predicted Reductions in Aqueous Radon Concentration as a Function of Residual NAPL Fraction and the Partition Coefficient

The partitioning values of various fluids (10, 25, 40, and 100--the compounds presented in Table 2.03 range from 45 to 81) are used to calculate the impact that various residual saturations would have on the aqueous radon concentration.

The Borden Field Experiments

Previous work on the use of Radon as an indicator for the presence and extent of DNAPLs was done at the Borden Test Site in Ontario, Canada (Semprini et al., 1993b). This previous work had both laboratory and field components.

The laboratory studies established that the Borden solids have an emanation coefficient of 0.025 ± 0.005 pCi/g. With an aquifer porosity (e) of 0.30 and a bulk density of 1750 g/L Semprini et al. (1993b) estimated that the Borden groundwater had a radon concentration of 145 pCi/L. Several column studies were run in which a column was filled with the Borden aquifer material and a synthetic groundwater and allowed to equilibrate. The maximum radon concentration in these columns (e = 0.42) was found to be 110 pCi/L. In a similar column with 1% powdered activated carbon, which was used to mimic the partitioning into a NAPL, the radon level was found to be "greatly attenuated."

The field studies occurred in a small section in which 5 liters of a DNAPL mixture (Chloroform, Trichloroethene, and Perchloroethene) was injected via a well below the water table. Radon depleted groundwater was injected two meters up gradient from the DNAPL injection well. The groundwater flowed through the NAPL zone at approximately 10 cm/day. As can be seen from Figure 2.07, immediately down gradient from the DNAPL injection well, the radon concentrations are 50% of the values found two meters further down gradient. The wells between these point appear to show the type of recovery that is predicted by the radon transport theory. This seems to indicate that the radon is indeed partitioning into the NAPL and as it passes beyond the NAPL zone there is a recovery to background levels due to emanation from the aquifer solids.

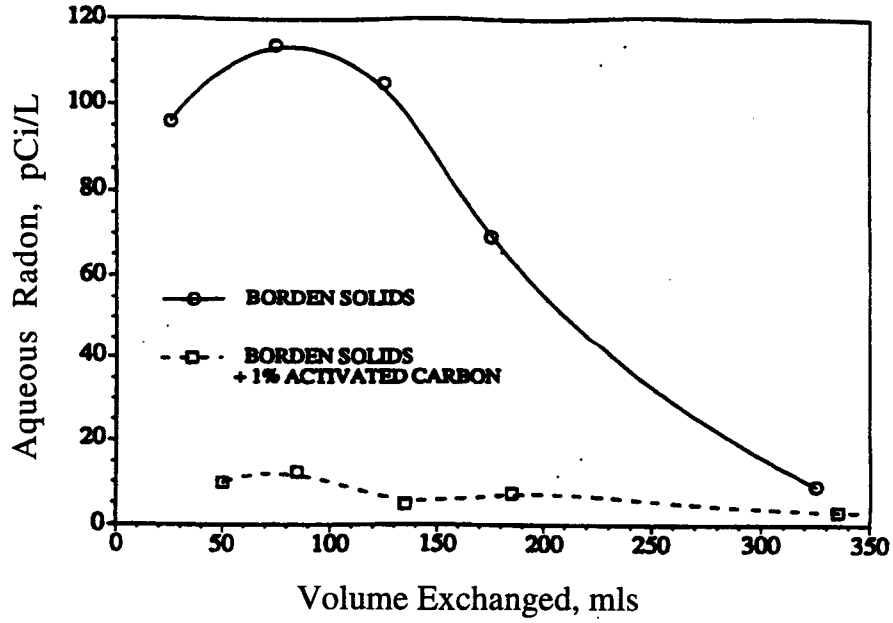

Figure 2.06 Batch Exchange Column Study (Semprini, 1993b)

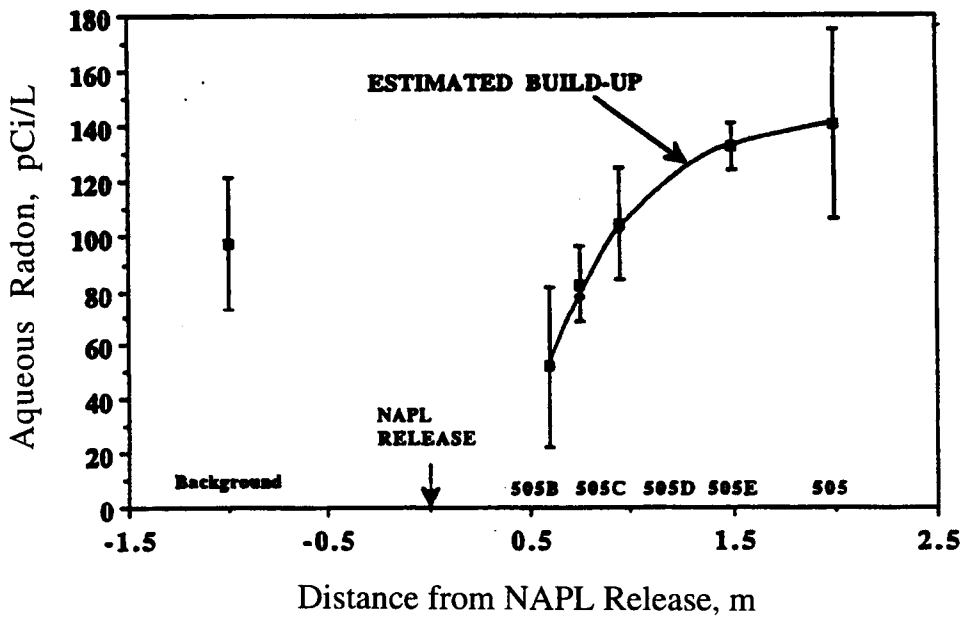

Figure 2.07 Radon Observations in the Field (Semprini, 1993b)

The Borden Field Studies indicated that using radon as an indicator for the detection of NAPLs in an aquifer is feasible and that it is sensitive over small distances and might thus be used to accurately determine the bounds of a NAPL contaminated zone. As suggested by Figure 2.07 sampling points would have to spaced with approximately every 2 meters in order to detect a plume boundary.

Chapter 3
Materials Characterizations: Methods and Results

The preparatory steps involved in achieving the two goals of this work were: (1) determine sand characteristics; (2) select a NAPL and find a means of immobilizing it in the sand matrix so that an accurate means of constructing columns with known residual NAPL saturations could be achieved.

A grain size analysis was run and the results were compared to previous characterizations of Borden sand (Ball, 1989), which allowed us to incorporate their more extensive characterization data in this report. The rate of radon emanation from the Borden sands was also measured.

A NAPL, Soltrol-220™ (soltrol), was selected for use in these experiments for its low, toxicity, vapor pressure, and solubility. To ensure that the exact NAPL fraction in every column was known, the soltrol had to be modified in order to immobilize it in the column. This was done by altering the soltrol with the addition of 0.5% by weight Lubrizol™ and 0.01% by weight Sudan III dye (McBride et al., 1992). This addition altered the spreading characteristics of the soltrol sufficiently to ensure that it was a wetting fluid. Prewetting of the sand particles with the soltrol prior to saturating the column with water also helped to ensure that the soltrol was attached to sand grains and not free floating. This is contrast to the conditions in an aquifer with a DNAPL spill where the DNAPL would be free floating blobs in the centers of the pore bodies.

Sand Characterization

Grain Size Analysis

A grain size analysis on the Borden material was run in order to determine not only the physical characteristics of the matrix material but also to permit comparisons with the other researchers' results, to therefore see if this material is reasonably representative of the Borden aquifer sands.

The grain size analysis procedure used is outlined in ASTM D421 and D422 (ASTM, 1980), with the modifications recommended by Bowles (Bowles, 1986). The results from the trials are presented below in tabular form in Table 3.01. A fines analysis was run and the results are presented in Table 3.02.

Table 3.01 Grain Size Distributions; Dry Sieve Method

Sieve #		8	16	30	50	100	200	pan
Opening Size, microns		2380	1180	600	300	150	75	0
Trial 1	Retained, gms	0	1.2	3.8	33.1	472.2	433.9	67.9
	% Passed	100	100	100	96	50	7	0
Trial 2	Retained, gms	0	1.0	3.7	33.2	623.3	312.4	65
	% Passed	100	100	100	96	36	3	0
Trial 3	Retained, gms	0	1.5	3.9	34.6	769.6	199.8	71.2
	% Passed	100	100	100	96	25	7	0
Trial 4	Retained, gms	0	1.8	4.8	38.7	809.5	101.6	49.7
	% Passed	100	100	99	95	15	5	0
% Passed	Averages	100	100	100	96	32	5	0
Summary	Highs	100	100	100	96	50	7	0
	Lows	100	100	99	95	15	3	0

Table 3.02 Total Grain Size Distribution; Dry Sieve and Hydrometer Methods

Size, microns	Percent Passing
2380	100.00
1180	99.90
600	99.55
300	96.35
150	36.34
75	6.26
35	1.21
25	0.96
18	0.84
13	0.84
9	0.71
7	0.71
5	0.59
1	0.46

Radon Emanation from Borden Solids

Eight 125 ml serum vials were filled with approximately 100 gms of Borden solids and topped off with synthetic Borden groundwater (Appendix B Preparation of Synthetic Borden Groundwater). The vials were sparged with helium for 5 minutes and then crimped shut with an aluminum sealed PTFE backed red-rubber septa (Kimble Corporation, Kimble No. 73823-20). The vials were stored inverted (mouth down) for a month to permit radon build up before being testing for radon content (Appendix D Extraction, Transfer, and Counting of a Radon Sample). See Appendix A (Emanation Experiments) for details. The samples were not all sealed for equal amounts of time, thus the results were normalized to equilibrium radon concentrations. The build up of radon is given by the equation,

$$\frac{C}{C_\infty} = 1 - e^{-\lambda t} \qquad \textbf{Eq 3.01}$$

In order to have comparable results, all the calculations for radon were normalized by dividing by the fraction equilibrium concentration achieved during the experiment. The normalized results are presented in Table 3.03.

Table 3.03 Radon Emanation of Borden Solids

Trial No.	Mass of Solids gms	Normalized Radon pCi	Emanation pCi/gm
1	101.3	5.026	4.96E-02
2	107.6	4.079	3.79E-02
3	103.0	5.248	5.10E-02
4	107.6	3.061	2.85E-02
5	101.0	3.187	3.16E-02
6	98.0	3.576	3.65E-02
7	100.0	3.676	3.68E-02
8	100.0	3.865	3.86E-02

From this data the estimated average value of the emanation coefficient of radon-222 from the Borden solids is 0.033 ± 0.008 pCi/gm.

Emanation was also measured for ranges of particle sizes. If one assumes that the radium, the radon parent, is distributed randomly through out the solid particle that the primary means of radon emanation is due to alpha recoil (Davis, Graves Ed, 1987), then

it follows that the rate of emanation is a function of the particle size. A procedure identical to the bulk solids emanation was used except that all the material was used was from the material trapped on each sieve. The results are presented in Table 3.04.

Table 3.04 Radon Emanation as a Function of Particle Size

	Emanation Coefficient (pCi/g)			
Particle Size, microns	Trial 1	Trial 2	Trial 3	Mean
less than 75	9.95E-2	n/a	n/a	9.95E-2
75 to 150	1.57E-2	3.04E-2	2.71E-2	2.44E-2
150 to 300	2.04E-2	2.07E-2	2.39E-2	2.17E-2
300 to 600	4.35E-2	n/a	n/a	4.35E-2

Although the expected trend is not found, using the values from Table 3.02 (Grain Size Distribution) and Table 3.04 (Radon Emanation as a Function of Grain Size) the estimated value for the bulk emanation coefficient is 0.030 pCi/g which agrees with the value measured directly for the bulk samples of 0.033 pCi/gm.

Surface and Interfacial Tension

A series of experiments was run to determine the interfacial tension between water and various Soltrol based fluids in order to determine what, if any, effect the addition of a Sudan III dye (0.01% by weight) and/or the addition of Lubrizol (0.5% by weight) would have on the interfacial tensions. For the measurement of surface tensions (air-fluid interfaces) the procedure as outlined in the Operating Instructions of the CSC-DuNouy Tensiometer, CSC No. 70535 was followed. We initially tested distilled water to determine the approximate degree of accuracy that we might expect. As indicated in the results our surface tension values for distilled water were within 0.7 dynes/cm of the commonly cited value of 72.7 dynes/cm (Jury et al., 1991).

The operating instructions indicated the use of a clean evaporating dish or beaker with a diameter of approximately 4.5 cm in the experiment--this was found to be too small for the experiments measuring interfacial tensions between two fluids. The meniscus resulting at the interfacial boundary was sufficiently curved to affect the results. This was due to the fact that the ring tended to slide away from the center and, therefore, the

force being applied was not vertical and perpendicular at the interfacial boundary. We therefore used an 8 cm diameter culture dish were the curvature of the meniscus was considerably less, and the resulting data were more reproducible. The pore water in these experiments was the eluent from a water and Ottawa sand mixture that had been in contact for several weeks. All the interfacial tension measurements between the immiscible fluids were measured after one minute of contact time (Schroth, M., personal communication, 1993). Table 3.05 summarizes the data from these experiments.

Table 3.05 Interfacial and Surface Tension Data (dynes/cm)

	Trial 1	Trial 2	Trial 3	Average
Distilled water and air				
	72.2	72.0	71.9	72.0
Soltrol-220 and air				
	26.1	25.7	25.8	25.9
Soltrol-220 with 0.55% Lubrizol and air				
	25.7	25.3	25.7	25.6
Soltrol-220 with 0.01% Sudan III and air				
	25.9	26.0	25.7	25.9
Soltrol-220 and distilled water				
	45.6	45.7	48.5	46.6
Soltrol-220 with 0.01% Sudan III and distilled water				
	46.9	48.4	47.8	47.7
Soltrol-220 with 0.5% Lubrizol with 0.01% Sudan III and distilled water				
	21.5	22.0	22.0	21.9
Soltrol-220 with 0.01% Sudan III and pore water				
	45.8	45.6	44.0	45.1
Soltrol-220 with 0.5% Lubrizol with 0.01% Sudan III and pore water				
	19.2	18.3	18.6	18.7

Discussion

Grain Size Analysis: The grain size distribution of the Borden sands used in this research was found to correlate closely to the grain size distribution of the Borden sands described by Ball (1989)--Figure 3.01 and Figure 3.02. Since both samples where from the Borden site and the grain size distributions were essentially identical, the other properties of the material were also assumed to be identical. Based on Ball's analysis, the sand consists of primarily quartz and feldspar. The sand solids have a density of 2.71 g/cm^3. Organic carbon content is 0.018% ± 0.006%.

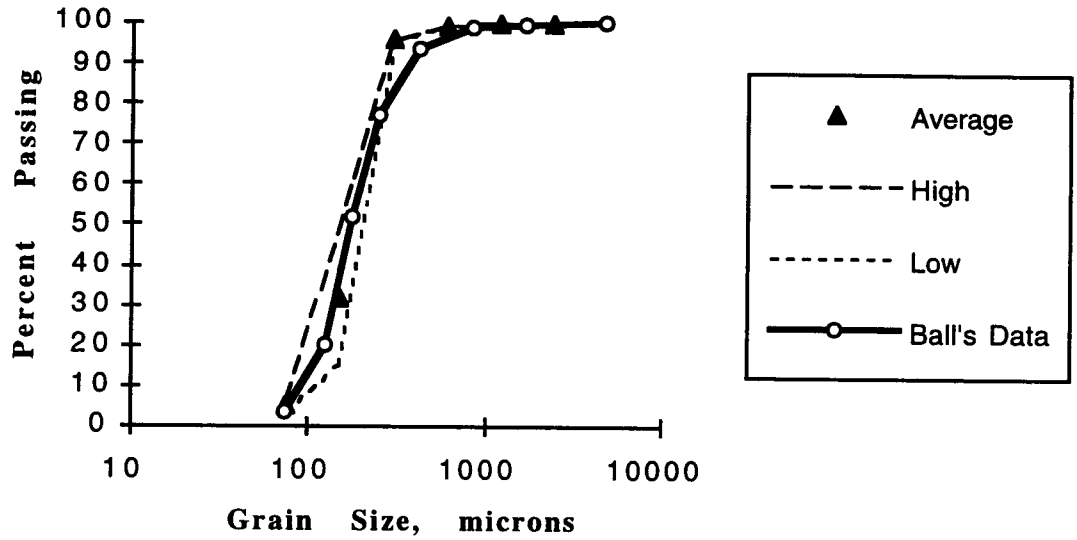

Figure 3.01 Grain Size Distributions

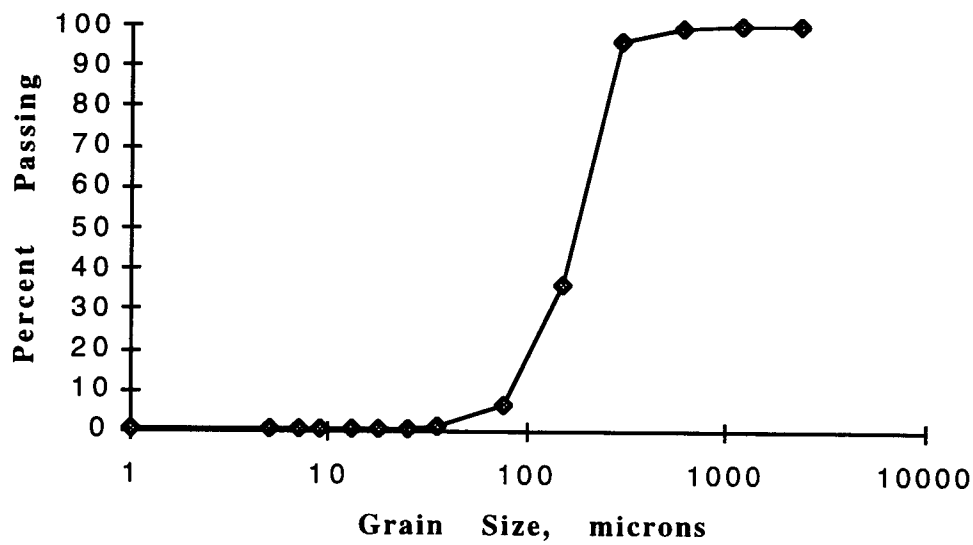

Figure 3.02 Total Grain Size Distribution

Radon Emanation from Borden Solids

Ball states that the coarse and the very fine materials have higher specific areas than the particle of median size--Table 3.06. This is also reflected in the emanation rates,

where the very fine and the very course had the highest rates of emanation. Note that these results contradict the literature which states that emanation is related to $d^{1/2}$ (Graves, 1987). While the data used in this report is not conclusive, it is indicative of the trend found by Ball--Figure 3.03, and suggests the possibility that radon might be used to characterize aquifer material.

Table 3.06 Data from Ball on Specific Surface Vs Particle Size

Screen Sizes	Particle Size (mm)	Specific Surface Area (m^2/g)
-12+20	1.7-0.85	1.92 ± .01
-20+40	0.85-0.42	0.88 ± .37
-40+80	0.42-0.25	0.40 ± .12
-60+80	0.25-0.18	0.36 ± .10
-80+120	0.18-0.125	0.51 ± .07
-120+200	0.125-0.075	0.36 ± .05
-200	< 0.075	0.90 ± .01
bulk	0.160	0.42 ± .20

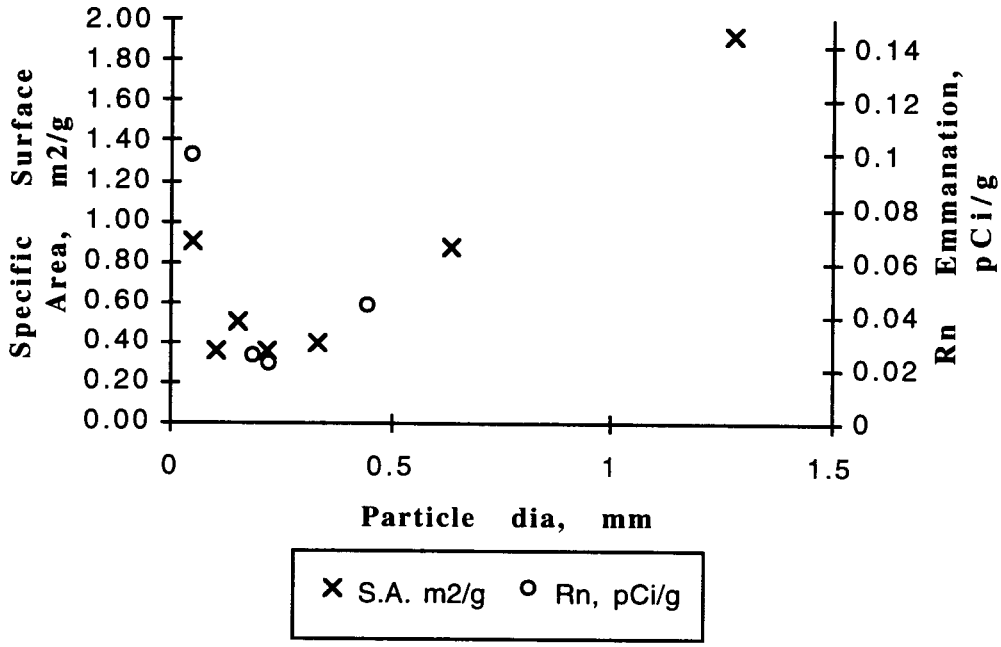

Figure 3.03 Specific Surface Area and Radon Emanation Vs Particle Size

Surface and Interfacial Tension

From the data presented in Table 3.05 it is clear that the addition of Lubrizol (at 0.5% by weight) significantly reduces the NAPL-water interfacial tension. This is significant since in an air-NAPL-water system with a $C_{sp} < 0$ the NAPL forms a lens on water whereas when $C_{sp} > 0$ the NAPL spreads over the water. Based on the discussion in Chapter 2,

$$C_{sp} = \gamma_{AW} - \left(\gamma_{OW} + \gamma_{AO}\right) \qquad \textbf{Eq 3.02}$$

We can see that the C_{sp} for Soltrol and water is $C_{sp} = 71.5 - \left(46.6 + 25.9\right) = -1.0$ or lens forming. When Lubrizol is added, the $C_{sp} = 71.5 - \left(21.9 + 25.6\right) = 24.0$ or highly spreading. McBride et. al. (1992) reported similar results: a $C_{sp} = 3$ for pure soltrol and "pore water"; and a $C_{sp} = 22$ for soltrol with 0.5% Lubrizol and "pore water". By having a highly spreading NAPL and by prewetting the soil particles with the NAPL, the NAPL was successfully immobilized on the sand and could be used to mimic an immobilized DNAPL in the saturated zone. This permitted the construction of soil columns with known residual saturations of soltrol.

With the sand characterizations and the ability of immobilize the NAPL to the sand media the groundwork had been done for the experiments on the relationship between residual NAPL saturations and aqueous radon concentrations, which will be discussed in Chapter 4.

Chapter 4
Radon NAPL-Water Partitioning: Methods and Results

The first objective of this thesis was to verify the equilibrium partitioning model presented in Chapter 2 that predicts decreasing aqueous radon concentrations as the residual NAPL saturation increases. To this end, five sets of soil column experiments were run to determine the aqueous radon concentrations at residual soltrol saturations of 0.0, 1.0, 2.5, 5.0, and 8.0 percent, after equilibrating with radon emanating from the Borden solids.

Methods

Columns were packed in lifts of dry sand and soltrol (each sand lift was approximately 1/8 of the column volume and each soltrol lift approximately 1/7 of the total soltrol used), starting and ending with sand. After 3 or 4 lifts of sand, and for every subsequent lift of sand, the column was mixed with a combination of end-over-end and rotational movements. Once the column was packed it was placed in a vertical position. A deaired water source was attached to the bottom and a vacuum line was attached to the upper port. A vacuum was applied to the column until maximum evacuation had been achieved throughout the length of the column. The vacuum port was then sealed and the bottom port was opened to allow de-aired water to flood the column. In the case of columns with 5 and 8 percent NAPL concentrations some problems achieving a good vacuum were encountered and the column was flooded with CO_2 and then filled with de-aired water. De-aired water was then passed through the column until all the CO_2 bubbles had dissolved (about 10 pore volumes). Appendix C Batch Exchange Experiments has the complete protocol.

The principal behind this experiment is to allow a column packed with the Borden sand, synthetic Borden groundwater, and a known amount of residual NAPL to reach a radon-222 equilibrium or close to it (approximately ten days). This time allows for the build up of radon to approximately 84% of the equilibrium value (Eq 2.04). This period also allows for the radon in the pore spaces to partition and equilibrate between the two immiscible liquid phases. The columns were then flushed with deaired (radon free)

synthetic groundwater. The equilibrated pore fluid was collected for analysis. Initially all the water exiting the column would be the equilibrated water, relatively high in dissolved radon. Eventually the displacing water will exit, resulting in a diminution in the effluent radon concentration. In the present study the plot of aqueous radon concentration against the volume of groundwater exchanged is referred to as the breakthrough curve. The peak of the curve was determined by averaging the maximum aqueous radon concentration for all the exchanges run for a particular saturation. The breakthrough point was where the aqueous radon equaled 50% of the maximum value.

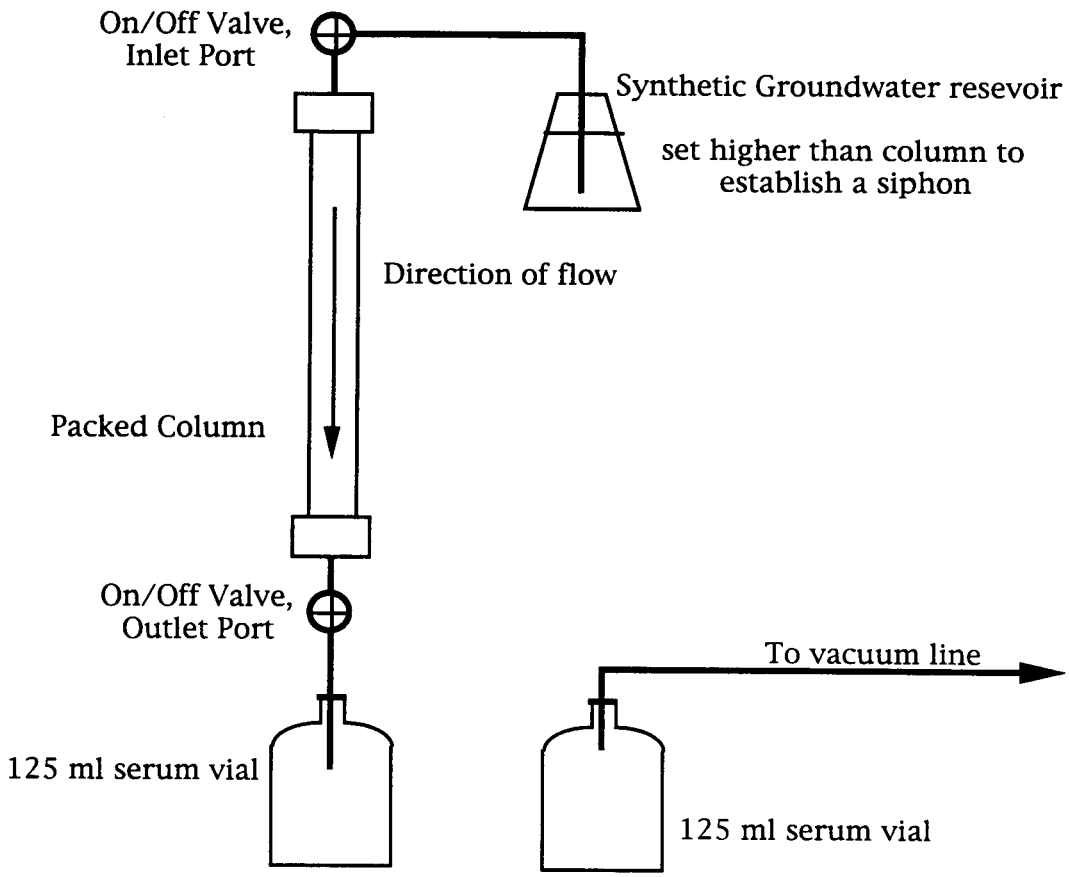

Figure 4.01 Diagram for Batch Exchange Set Up

Each column has a total volume of 1060 mls and when packed with the Borden sand has a pore volume of approximately 445 mls (based on an estimated porosity of e = 0.42). Six samples of approximately 100 mls were collected with sufficient water wasted (but measured for volume) in between each sample to ensure that data for the entire breakthrough curve was collected.

Six 125 ml serum vials were prepared for sample collection by crimping a PTFE backed red rubber septa and filling with helium (to minimize any atmospheric radon). The vials were evacuated immediately prior to collecting the sample. Each of the vials and a beaker was tared to determine their empty weight. Figure 4.01 shows a schematic of the experimental set up. Collecting samples was done by attaching a de-aired synthetic groundwater source to the inlet port. The groundwater source was elevated above the top of the column to ensure that water was always flowing out of the reservoir, down through the column, and exiting the outlet port. Direct transfer of the sample from the column to the vial was done by means of copper and tygon tubing and a needle used to perforate the vial septa. Each sample was approximately 90 mls. Some extracted water was wasted between each sample. The sample point was set at the midpoint of the sample volume. See Appendix E (Calculating Radon Concentration) for details on calculations. Each vial was reweighed after collecting the sample. The waste water beaker was also reweighed after each filling. The amount of sample or wasted water was determined by subtracting the tare weight. After the column sampling was completed, the vials were stored in an inverted position to minimize the amount of radon escaping from the vials. The vials were then taken to extract and transfer the radon into the scintillation flasks for counting.

The protocol for the transfer of radon from the aqueous solution to the scintillation flask and its counting is presented in Appendix D (Stoker and Kruger, 1975).

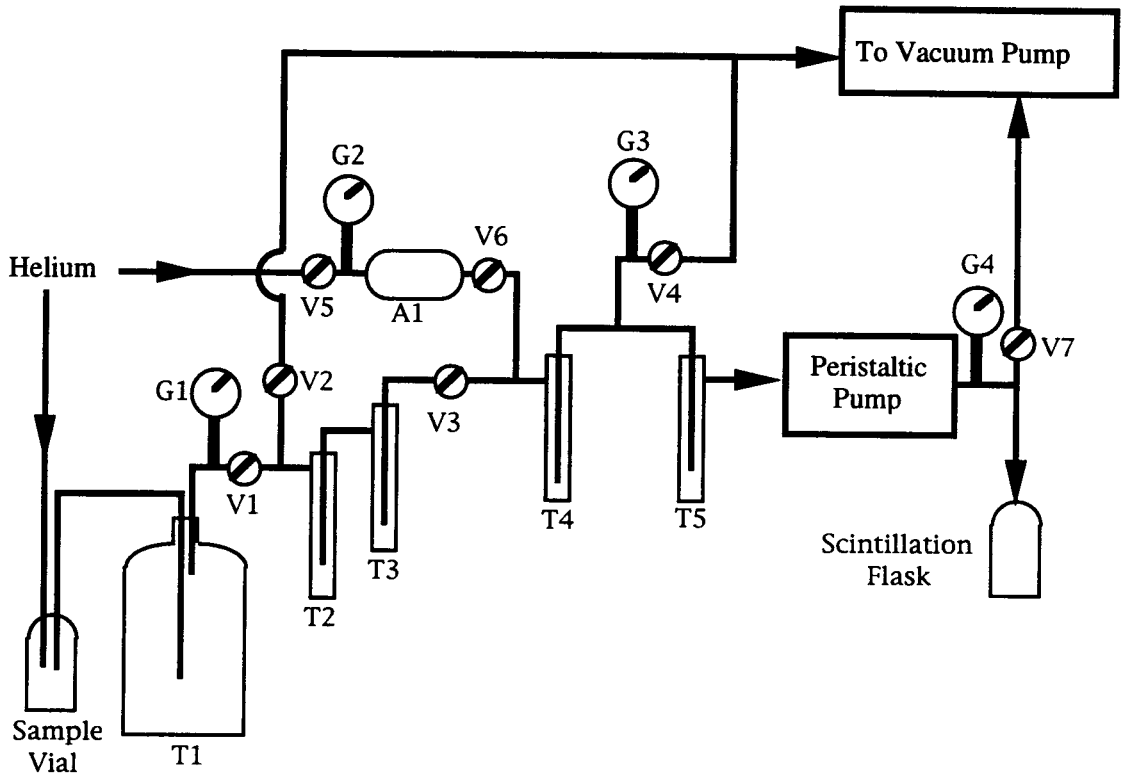

Figure 4.02 Schematic of Extraction and Transfer Equipment

A schematic of the transfer apparatus is shown in 4.02.

T1 through T5 are traps.

V1 through V7 are stopcock valves.

G1 through G4 are vacuum gages.

A1 is the helium aliquot.

The apparatus is constructed of glass except for the vacuum lines (vacuum line tubing), the helium lines (tygon tubing), a short 15" section of tygon tubing connecting the evacuating needle from the sample vial to the first trap (T1), and a short 1" length of tygon tubing connecting the scintillation flask needle to the apparatus.

The first step in transferring the radon to the scintillation flask is to open V1, V2, V3, V4, and V6 (all others closed) to evacuate the apparatus. V2 and V6 are then closed to ensure that the gas stream flows through traps T1 to T4 before being exhausted into the atmosphere. The sample containing the aqueous radon is attached by a needle perforating its septa to trap T1. The helium carrier gas is attached to the sample vial by a needle

that sparges from the bottom of the sample. Trap T1 removes any liquid phase water. Trap T2 is immersed in a propynol-dry ice bath (between -45°C and -50°C), contains steel wool and removes any water vapor. Trap T3 contains Ascarite II™ which removes the CO_2. Trap T4 contains granular activated carbon (GAC) to which the radon is adsorbed. Initially this trap is immersed in a propynol-dry ice bath for the removal of radon from the gas stream. The remaining gas stream is evacuated through valve V4 and discharged to the atmosphere. After sparging the sample for at least five minutes valves V1 and V3 are closed. The GAC trap (T4) is allowed to heat up to 45°C before valve V4 is closed. This allows other gases that have sorbed onto the carbon to be removed while the radon remains on the GAC. Trap T4 is then heated to over 200°C.

Valve V5 is opened, the aliquot A1 is filled with helium gas, and then valve V5 is closed again. Valve V6 is opened, the aliquot of helium is transferred into the trap T4, and valve V6 is then closed. The peristaltic pump is run until the vacuum gage G3 reads 28-29 inches of mercury. This process is repeated until four aliquots of helium containing radon have been transferred to the scintillation flask.

The scintillation flask was allowed to age for at least four (4) hours before counting to allow radon to achieve equilibrium with its daughter products.

Results

0.0% Residual NAPL Saturation

For the NAPL-less columns, 0.0% saturation, three columns were identically packed and tested for aqueous radon content. The columns are labeled with numbers that refer to the entry in the laboratory notebook and with **-A**, **-B**, or **-C** suffixes that indicate columns with the same Borden sand. Thus for the NAPL-less data two columns were run twice and one column was run once. The data for the NAPL-less columns are presented in Table 4.01 and Figure 4.03. The Weighted Fits were determined by KaleidaGraph (Abelbeck Software, 1990, v1.0) using the weighted fit function with a smoothing factor of 40%.

Table 4.01 Data from Columns with 0.0% Residual NAPL Saturation

Exchange No.	Volume Exchanged	Aqueous Radon (pCi/L)	Contact Time (hrs)	Normalized Aqueous Radon (pCi/L)
3-C	48.2	146		146
	222.8	171		171
	398.0	153	803	153
	576.3	15		15
	754.4	2		2
	934.0	4		4
4-A	49.9	144		144
	227.8	171		171
	405.3	149	933	149
	571.4	21		21
	750.4	10		10
	922.6	6		6
5-B	46.4	134		148
	221.7	175		194
	396.6	145	312	160
	564.7	11		12
	738.6	3		3
	903.5	10		11
6-C	49.1	130		145
	229.1	137		165
	409.0	129	238	155
	588.0	22		26
	764.3	6		7
	934.7	7		9
7-A	49.3	138		156
	203.0	144		163
	298.0	145		164
	397.9	117	288	132
	493.8	35		39
	585.0	12		13
	680.7	7		8
	777.8	12		13
	925.4	8		9

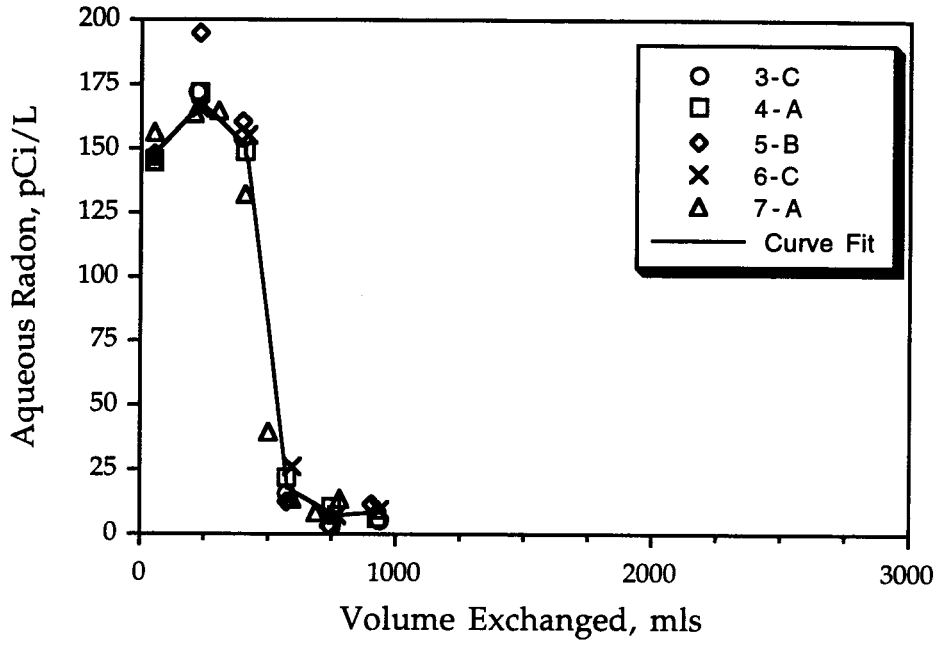

Figure 4.03 Breakthrough of Radon Concentration vs volume of Radon Free Water Exchanged for 0.0% Residual NAPL Saturation

In general the data appear to be extremely reproducible. The average maximum radon concentration for the 0.0% residual saturation, is 173 pCi/liter. The breakthrough point, the point at which the aqueous radon equal to 50% of average maximum concentration, is at 450 ml point. This agrees very well with the expected value from the porosity estimations (breakthrough at the 445 ml point).

The maximum radon concentration as determined in the column is slightly higher than the value expected based on the emanation coefficient. Based on Eq 2.06, a column of 1660 gms with a porosity of 0.42 (e.g. a pore volume of 445 mls), and an emanation coefficient of 0.033 ± 0.008 pCi/gm, the anticipated maximum aqueous radon concentration would be 123 ± 30 pCi/L. In order to achieve a 173 pCi/L aqueous radon concentration with a emanation coefficient the porosity would have to be 0.30, substantially different from the estimated value. The difference might be due to losses of radon through the septa of the 125 ml serum vials during the batch emanation experiment.

The first sample point has a lower average radon concentration, 148 pCi/L, than the subsequent points prior to breakthrough. This is 85% of the average maximum value. This is probably due to either losses through the teflon cap, or to radon sorbing to the teflon. This end effect indicated the zone at the end of the column was not representative of the conditions in the interior of the column and was therefore not considered in the analysis of peak radon concentrations in the subsequent trials with different amounts of residual NAPL saturation.

After the data for the five runs were collected the porosity of the columns was determined. This was done by weighing the entire packed and saturated column. The solids were then removed and the column was weighed empty. The solids were then dried on a steam table. The column was then filled with water and weighed again. The volume of the column, **V**, was determined by taking the difference between the empty weight of the column and water full weight. The weight of the saturated media, **W**, was determined by taking the difference between the full saturated weight and the empty column weight. The entire weight of the saturated media is the sum of the weight of the water and solids. Water has density of 1.0 gm/ml and the Borden solid has a density of 2.71 gm/ml. The porosity, e, can be determined with the following equation,

$$V\left[1.0e + 2.71(1-e)\right] = W \qquad \textbf{Eq 4.01}$$

From the porosity it was possible to estimate the weight of the dry solids and compare it with the actual weight of the dry solids. The data and the results for the three columns is summarized below in Table 4.02.

Table 4.02 Porosity Estimations

	Column A	Column B	Column C
Packed and Saturated Column Weight, gms	3407	3383	3395
Water Full Weight of Column, gms	2362	2360	2353
Empty Weight of Column, gms	1300	1307	1295
Volume, mls	1062	1053	1058
Weight of Saturated Media, gms	2107	2076	2100
Porosity	**0.425**	**0.43**	**0.42**
Estimated Weight of Dry Solids, gms	1655	1627	1663
Actual Weight of Dry Solids, gms	1668	1622	1645

The average porosity for the three trials was 0.42. The results for these trials suggest that packing method produced columns that were nearly identical. Based on the estimated porosity of 0.43 and a volume of 1060 mls the pore volume for the columns was estimated to be 445 mls. This agrees with the estimated pore volume shown by the breakthrough curve of 450 mls. Since the porosity estimation agrees with the breakthrough point, this suggests that the emanation coefficients determined in Chapter 3 are low.

1.0% Residual NAPL Saturation

The data for this residual soltrol saturation was taken from repeated experiments using the same column. The solids from column C were taken, dried, and used as the Borden solids in this experiment. The columns have a pore volume of 445 mls, and in order to achieve a 1% residual saturation 4.4 mls of soltrol mixture were added to the solids. The data for 1.0% residual soltrol saturation are presented in Table 4.03 and Figure 4.04.

Table 4.03 Data from Columns with 1.0% Residual NAPL Saturation

Exchange No.	Volume Exchanged	Aqueous Radon (pCi/L)	Contact Time (hrs)	Normalized Aqueous Radon (pCi/L)
9-C	47.3	85		102
	217.2	105		126
	390.3	107	237	129
	562.9	87		104
	735.5	13		16
	898.4	4		5
12-C	41.6	92		102
	226.6	110		121
	420.1	114	314	126
	603.9	73		81
	792.0	10		11
	968.1	7		8
15-C	42.2	79		88
	228.5	99		109
	420.4	98	309	108
	582.8	80		88
	766.8	13		14
	976.1	7		8

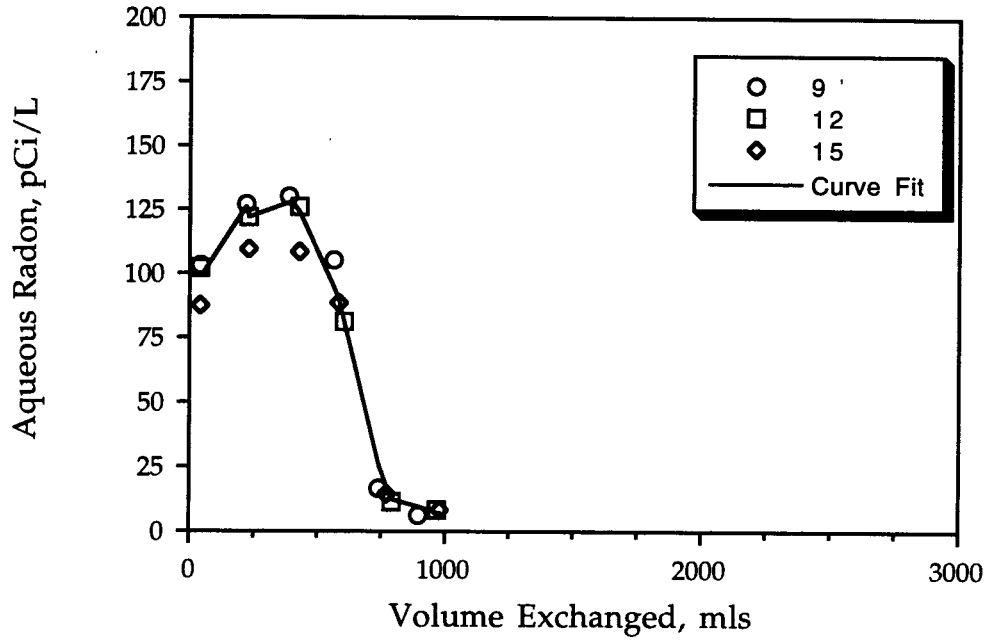

Figure 4.04 Breakthrough of Radon Concentration vs volume of Radon Free Water Exchanged for 1.0% Residual NAPL Saturation

The maximum aqueous radon concentration for the 1.0% residual soltrol saturation was 121 pCi/L. This is 70% of the average maximum radon concentration in the columns with 0% residual saturation. As in the 0.0% residual saturation column there was an end effect in this column. The first sample point averaged 97 pCi/L, or 80% of the average maximum value in these columns. The breakthrough point of the radon free water was at the 650 ml point. It was retarded by a factor 1.44. This set of runs closely mimicked the original 0.0% NAPL concentration columns except for the diminution of the maximum radon concentration and the delay of the breakthrough point.

2.5% Residual NAPL Saturation

The data for this residual soltrol saturation was taken from repeated experiments on the same column. The solids from column A were taken, dried, and used as the Borden solids in this experiment. In order to achieve a 2.5% residual saturation 11.3 mls of soltrol

mixture were added to the solids. The data for 2.5% residual soltrol saturation are presented in Table 4.03 and Figure 4.05.

Table 4.04 Data from Columns with 2.5% Residual NAPL Saturation

Exchange No.	Volume Exchanged	Aqueous Radon (pCi/L)	Contact Time (hrs)	Normalized Aqueous Radon (pCi/L)
10-A	46.4	95		105
	289.4	93		103
	539.0	73	311	81
	801.1	48		53
	1080.9	21		23
	1317.2	9		10
13-A	48.3	88		106
	309.7	76		92
	559.9	66	236	80
	809.4	48		58
	1051.7	20		24
	1302.9	8		10
16-A	45.1	98		114
	335.8	81		94
	580.5	64	264	74
	827.8	37		43
	1053.5	14		16
	1310.2	13		15
19-A	41.5	99		104
	295.9	92		97
	578.8	71	406	75
	827.8	37		39
	1077.7	27		28
	1329.4	2		2

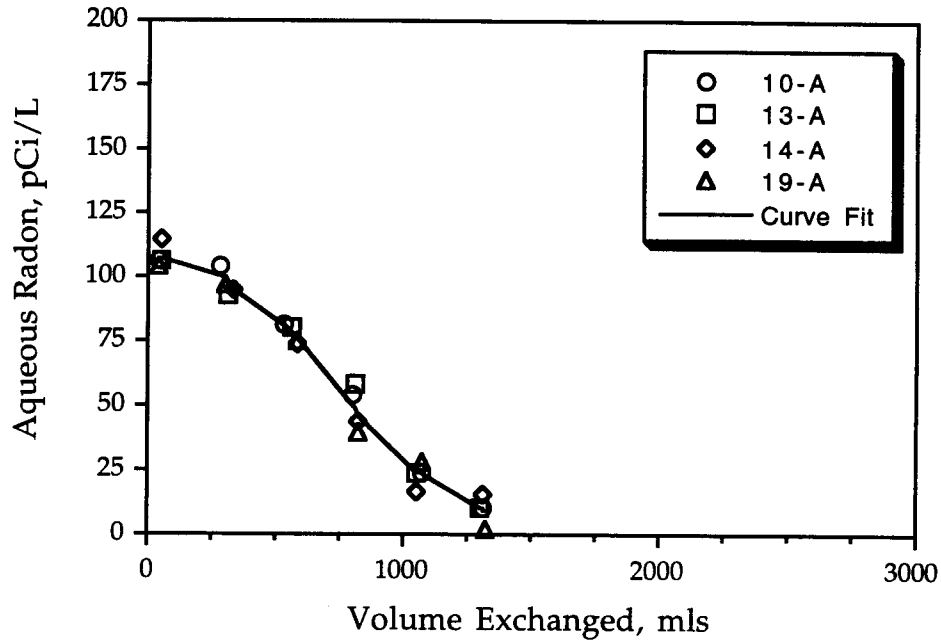

Figure 4.05 Breakthrough of Radon Concentration vs volume of Radon Free Water Exchanged for 2.5% Residual NAPL Saturation

The first sample point averaged 105 pCi/L, or 111% of the 0.0% residual saturation equilibrium radon concentration. The first point was not considered to be entirely representative of the conditions in the rest of the column. In addition to the previously mentioned "end effects" the curve generated by these data were much more dispersed, with no clear breakthrough point. Also, due to difficulty in packing the column, the last lift in the column may not have had the residual saturation of the rest of the column, specifically it may have had a lower NAPL content. When the last lift of sand was added the column was already quite full and there was no space left to allow the sand to mix effectively. The lower NAPL content may have meant that less radon partitioned out of the water into the NAPL and that therefore, there was a higher aqueous radon concentration in the first sample extracted than from the rest of the column. The average maximum aqueous radon concentration was 95 pCi/L, which is 55% of the 0.0% residual saturation equilibrium radon concentration. The breakthrough was estimated to be at the 800 ml point.

5.0% Residual NAPL Saturation

The data for this residual soltrol saturation was taken from repeated experiments on the same column. The solids from column B were taken, dried, and used as the Borden solids in this experiment. In order to achieve a 5.0% residual saturation 22.6 mls of soltrol mixture were added to the solids. The data for 5.0% residual soltrol saturation are presented in Table 4.03 and Figure 4.06.

Table 4.05 Data from Columns with 5.0% Residual NAPL Saturation

Exchange No.	Volume Exchanged	Aqueous Radon (pCi/L)	Contact Time (hrs)	Normalized Aqueous Radon (pCi/L)
8-B	16.3	84		95
	352.8	43		49
	709.2	52	288	59
	1192.4	44		50
	1488.2	19		22
	1732.2	11		12
11-B	46.0	82		90
	422.6	47		52
	770.9	51	317	56
	1482.0	23		25
	1707.5	12		13
14-B	38.5	75		79
	368.2	39		41
	751.0	44	410	46
	1442.1	10		10
	1782.7	4		4

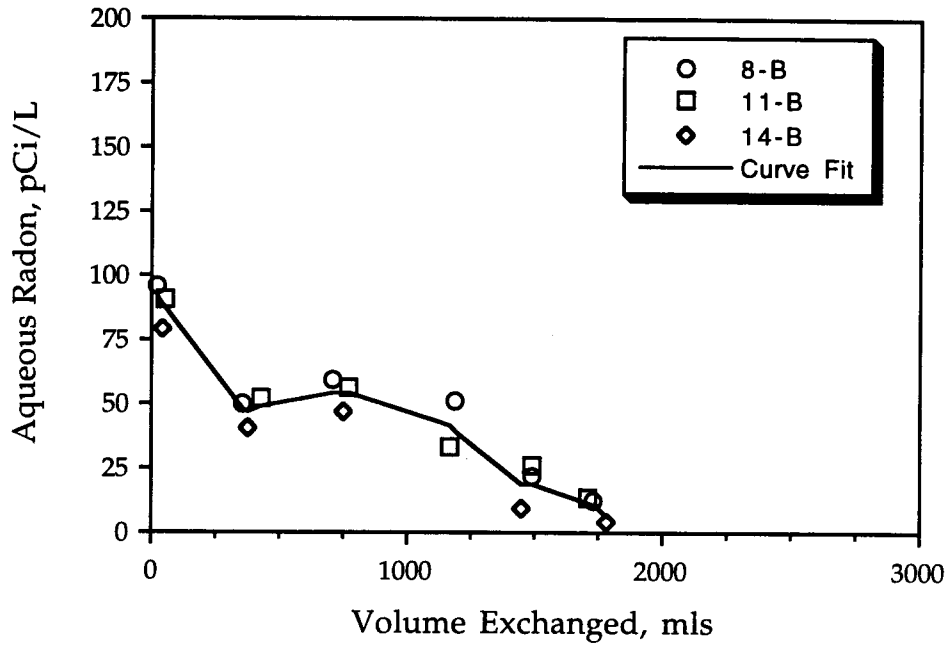

Figure 4.06 Breakthrough of Radon Concentration vs volume of Radon Free Water Exchanged for 5.0% Residual NAPL Saturation

The average maximum aqueous radon concentration was 54 pCi/L, which is 31% of the NAPL-less equilibrium radon concentration. The first sample point averaged 88 pCi/L, or 163% of the NAPL-less equilibrium radon concentration. As in the 2.5% residual saturation column, the end effect was believed to be due to an inhomogeneous distribution of soltrol throughout the column. The breakthrough was estimated to be at the 1430 ml point.

8.0% Residual NAPL Saturation

The data for this residual soltrol saturation was taken from repeated experiments on the same column. For this column new sand, labeled with the suffix **-D**, was taken and packed into the column. It was assumed that under similar packing methods the porosity would not change significantly. 1569 gms of sand were packed into the column. In order to achieve a 8.0% residual saturation 34.7 mls of soltrol mixture were added to the

solids. The data for 8.0% residual soltrol saturation are presented in Table 4.03 and Figure 4.07.

Table 4.06 Data from Columns with 8.0% Residual NAPL Saturation

Exchange No.	Volume Exchanged	Aqueous Radon (pCi/L)	Contact Time (hrs)	Normalized Aqueous Radon (pCi/L)
26-D	48.4	28		30
	637.2	34		37
	1182.4	25	333	27
	1759.8	30		33
	2324.6	5		5
	2739.7	2		2
27-D	49.6	41		45
	583.7	42		47
	1110.9	28	310	31
	1877.9	19		21
	2245.2	8		9
	2674.6	4		4

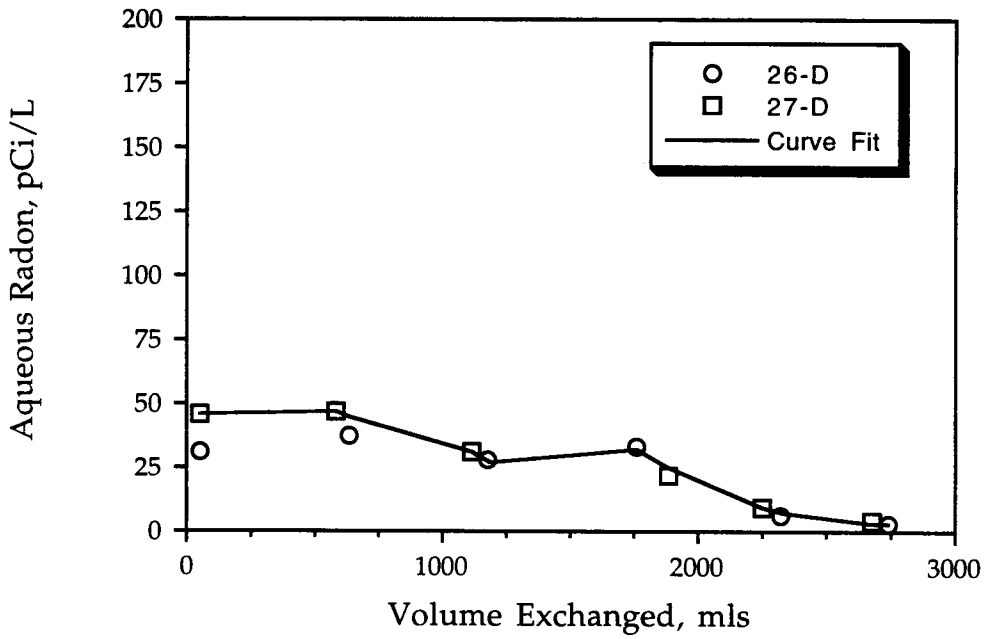

Figure 4.07 Breakthrough of Radon Concentration vs volume of Radon Free Water Exchanged for 8.0% Residual NAPL Saturation

The average maximum aqueous radon concentration was 42 pCi/L, which is 24% of the average maximum radon concentration in the columns with 0% residual saturation. The first sample point averaged 42 pCi/L, or 24% of the average maximum aqueous radon concentration. The end effect was not particularly noticeable in this column. Since this column was packed after the data on 2.5% and the 5.0% columns had been collected greater care was placed on ensuring a uniform soltrol distribution throughout the column. The breakthrough was estimated to be at the 2050 ml point.

Discussion

Organic Phase Liquids as a Retardant for the Transport of Radon

Figure 4.08 shows the best fits for the data sets from each residual NAPL saturation (0.0, 1.0, 2.5, and 8.0 percents). This figure shows that as the residual saturation increases the peak aqueous radon concentration decreases and the breakthrough point is delayed. Integrating the area under each best fit curve produces the total amount of radon extracted from each column. In each case this was found to be approximately 75 pCi. This indicates that the partitioning kinetics of radon between soltrol and water is fairly rapid, relative to the experimental time frame of four hours. The breakthrough curves are subject to more scatter as the residual saturation increases. This is due to lower aqueous radon concentrations which are reflected in lower disintegration events during the counting period. Since the determination of radon concentrations is based on its statistical rate of decay, lower counts mean less certainty.

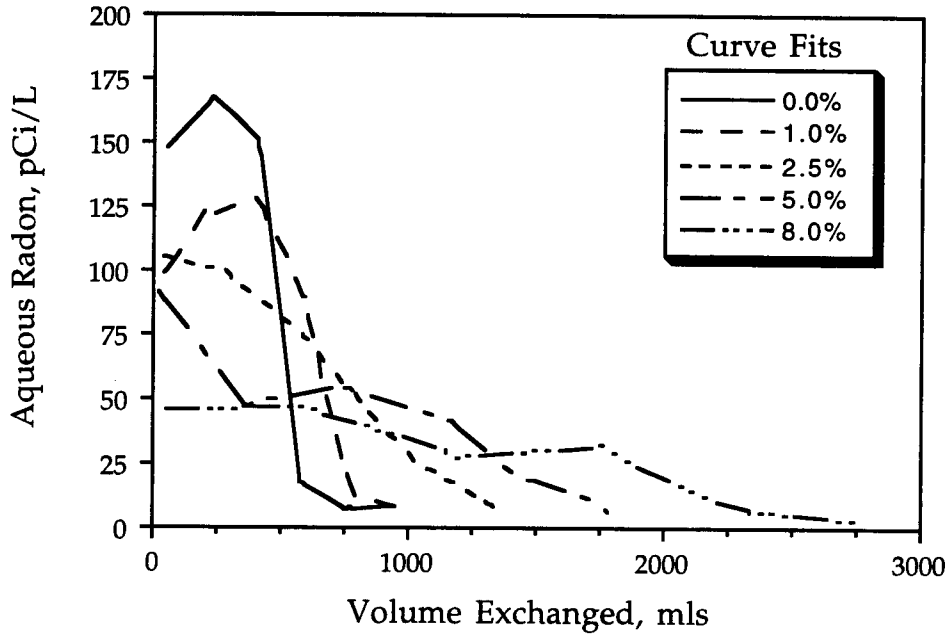

Figure 4.08 Curve Fits for 0.0 to 8.0 percent Residual NAPL Saturation

By examining the point at which breakthrough of de-aired (and de-radonized) water occurs a series of retardation values were estimated for each separate concentration of Soltrol. The retardation factor, R, was calculated by the following equation previously defined in Chapter 2:

$$R = \frac{V_{Rn}}{V_{Groundwater}} \qquad \textbf{Eq. 4.02}$$

From Equation 4.02 was possible to determine the retardation factors for each of the residual NAPL saturations. The estimated percent aqueous radon was determined from the retardation factor defined in Equation 4.03,

$$R = \frac{[Rn]_{Voids}}{[Rn]_{W}} \qquad \textbf{Eq 4.03}$$

where the total concentration of radon in the pore fraction (the numerator in Eq 4.03) is,

$$\left(C_{Ra}E_p\rho_b\right)/e$$

Table 4.07 Estimated Aqueous Rn Concentration Based on Retardation Factor

% NAPL in Column	Breakthrough Point	Retardation Factor	Estimated %Rn aqueous
0.0	450	1.00	1.00
1.0	650	1.44	0.69
2.5	800	1.78	0.56
5.0	1430	3.18	0.31
8.0	2050	4.55	0.22

The estimated aqueous radon concentrations correlate very closely to those determined by direct measurement of exchanged water. Table 4.08 compares the values for the measure reduction of aqueous radon against the estimated reduction based on the retardation of the breakthrough of the radon free water (Eq 4.03).

Table 4.08 Measured Aqueous Rn vs. Estimated Aqueous Rn from Breakthrough Concentrations

% NAPL in Column	Average Measured max. aqueous Rn	Average Measured Rn % of max.	Estimated %Rn aqueous
0.0	173	1.00	1.00
1.0	122	0.71	0.69
2.5	96	0.55	0.56
5.0	58	0.34	0.31
8.0	42	0.24	0.22

From the above data it is possible to estimate the value of the partitioning coefficient, K, from,

$$C_W = \frac{\left(C_{Ra}E_p\rho_b\right)/e}{1 + S_N\left(K - 1\right)} \qquad \textbf{Eq 4.04}$$

the term,

$$\left(C_{Ra}E_p\rho_b\right)/e$$

is constant and can be determined from the data of the 0% NAPL column. In that case S_N = 0 which means that,

$$C_{W(0\%)} = \left(C_{Ra}E_p\rho_b\right)/e \qquad \textbf{4.05}$$

in every other column, 1 through 8 percent, the numerator, C_W, and S_N are known. K can be determined by rearranging Eq 4.04 to,

$$K = \frac{\left[\dfrac{C_{Ra}E_p\rho_b/e}{C_W} - 1\right]}{S_N} - 1 \qquad \textbf{4.06}$$

The estimated coefficient of partitioning, based on average peaks for the data from 1 through 8 percent residual saturation columns is presented in Table 4.09.

Table 4.09 Estimated Coefficient of Partitioning, K

Data Set	Average Peak Aqueous Rn	Estimated K
1.0%	129	33.1
	126	36.3
	109	57.7
2.5%	103	26.2
	92	34.2
	94	32.6
	97	30.3
5.0%	59	37.6
	56	40.8
	46	54.2
8.0%	37	44.9
	47	32.5
Average		38 ± 9.5

The partitioning value for radon between the soltrol mixture and pore water fluids is K = 38.4. This agrees closely to the partitioning values for other hydrocarbons from Table 2.03: Toluene (K = 46), Benzene (K = 45), Hexane (K = 58), and Di-ethyl-ether (K = 53). Figure 4.09 shows the predicted aqueous radon concentration based on the linear equilibrium model (Eq 2.12) and using the average partitioning coefficient of all the batch exchanges. The measured peak values aqueous radon concentrations are also plotted for comparison.

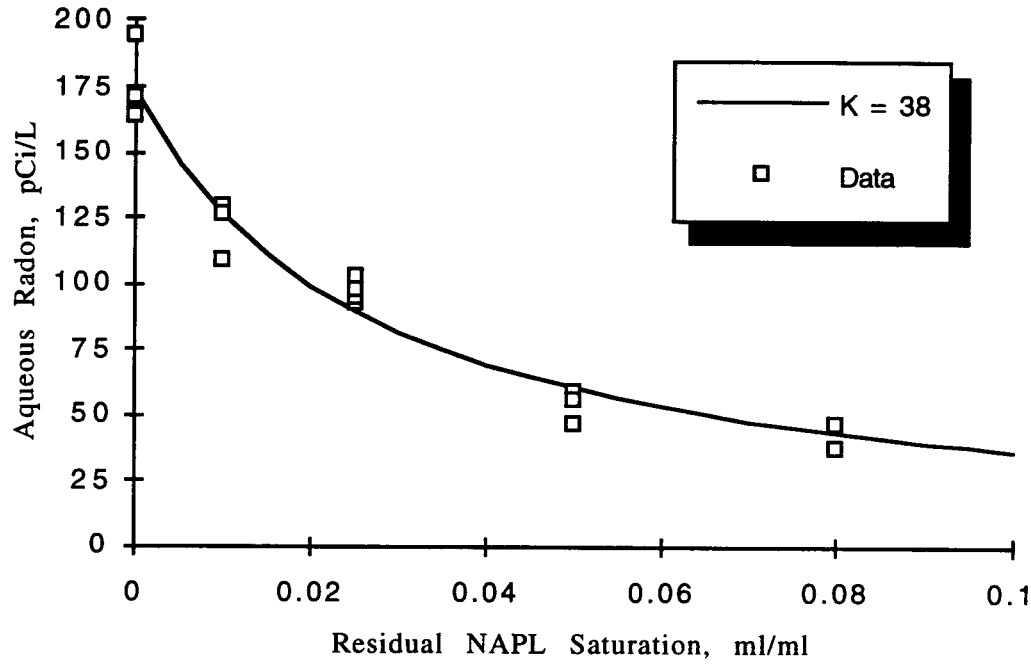

Figure 4.09 Estimated Partition Coefficient and Data

Figure 4.10 shows the correlation between the estimated aqueous radon concentration, based on the linear equilibrium partitioning model and the averaged value for the partitioning coefficient, and the actual measured partitioning coefficient for each batch exchange. A regression was run and the R^2 was found to be 0.927 showing a high degree of correlation between the model and the experimental results.

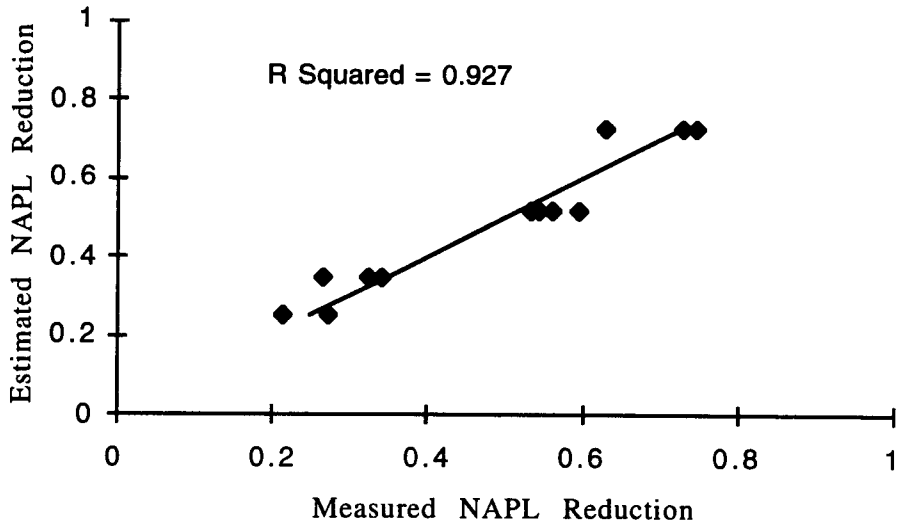

Figure 4.10 Correlation Between Estimated and Measured Reduction in Aqueous Radon

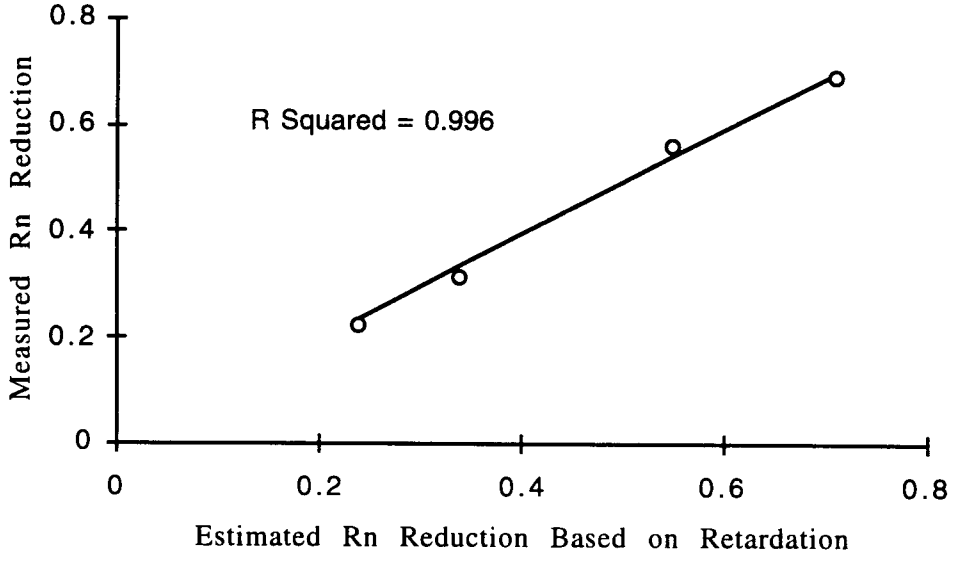

Figure 4.11 Correlation Between Measured and Retardation Based Estimates of Aqueous Radon Reduction

Figure 4.11 shows the correlation between the estimated value of the aqueous radon concentration based on the breakthrough retardation and the measured value of the aqueous radon concentration. The high correlation, R^2 of 0.996, between the estimated and measured aqueous radon values proves the validity of the partitioning model based on retardation.

Emanating Power of Borden Sands

The emanation constant as determined in Chapter 3 of 0.033 pCi/gm seems low when compared to the value of 0.047 pCi/gm as determined by the peak average value for aqueous radon in the 0.0% residual saturation columns. As was clearly seen in the 0.0% and 1.0% residual saturation columns end effects, possibly diffusional losses through the rubber septum, can play a role in reducing the radon concentration. In the batch emanation studies (Chapter 3) radon may have diffused out through the septa of the 125 ml serum vial and therefore reduced the amount of radon measured. If the relative amount of radon lost due to end effects is the same in both the vial and the column, 15% reduction, then the emanation value from the vial should have been approximately 0.039 pCi/L. Previously, the emanation coefficient was estimated to be 0.025 ± 0.005 pCi/g (Semprini et al., 1993b).

Conclusions

The results from this chapter showed that there is a strong correlation between the aqueous radon concentration and the residual soltrol fraction. The linear equilibrium partitioning model accurately describes this relationship for these low concentrations of radon. Since radon will always be a trace compound, the linear partitioning model should be applicable under most conditions. Integrating the areas under the best fit curves for each residual saturation shows that in each case approximately 75 pCi of radon were recovered. This indicates that there is no appreciable difference in the emanation rates for radon from the Borden sands when the pore volume is packed with up to 8 percent soltrol and that the mass transfer of radon from the soltrol to the pore fluid is rapid relative to the time frame of the experiment. The estimated aqueous radon

concentrations, based on retardation and the partitioning of radon between the two fluids (Eq 4.03), very closely approximated the measured aqueous radon concentrations. This shows that the retardation of radon is a function of its partitioning between the NAPL phase and the aqueous phase.

Chapter 5
One-Dimensional Model

A one dimensional physical flow model of a spill in an aquifer was designed to test the hypothesis that radon could be used to detect NAPLs in the saturated zone. This experiment used the Borden sands and a soltrol based mixture as a NAPL both of which were previously characterized in Chapter 3. The partitioning data (K = 38) from Chapter 4 was used in designing this experiment.

Methods

A schematic of the experimental set up is shown in Figure 5.01.

The contact chamber allowed radon to build up in the synthetic groundwater prior to entering the experimental column. The volume of the contact chamber was 1.05 liters. A porosity of 0.42 was assumed. Thus the pore volume of the contact chamber was 440 mls. The contact chamber was packed with NAPL-less sand.

The main experimental column is 4.8 cm ID x 100 cm long. Its volume is 1.81 liters. The pore volume is 760 mls based on a porosity of 0.42. Four glass ports were fused along the side of the column, at 15, 40, 60, and 80 cm. The ports had a 6 mm ID. Each port was sealed with PTFE backed red-rubber septa. 12 to 15" of 1/8" OD stainless steel sampling tubing perforated each septa and was used to collect samples from the center line of the column. Each of the stainless steel tubes was fitted with a Swagelok plug to seal the port. The first 30 cm of the column were packed with NAPL-less sand. The NAPL zone is 15 cm long. The sand and the soltrol mixture were mixed outside the column and added to the column via a large bore funnel and tubing. This allowed for the sand-soltrol mixture to be added in the section desired without have the soltrol come in contact with the walls of the rest of the column. 507 gms of sand were mixed with 6.2 mls of soltrol mixture to produce an estimated 5.0% residual saturation when packed in the column. 5 percent residual saturation was chosen in order to produce an substantial reduction in the aqueous radon concentration. Of the material mixed 453.5 gms were utilized, thus 5.5 mls of soltrol was transferred into the column. 441.4 gms of material

were estimated to fill a 4.8 cm ID x 15 cm long section of the column at 0.42 porosity. The rest of the column, 55 cm, was packed with NAPL-less sand.

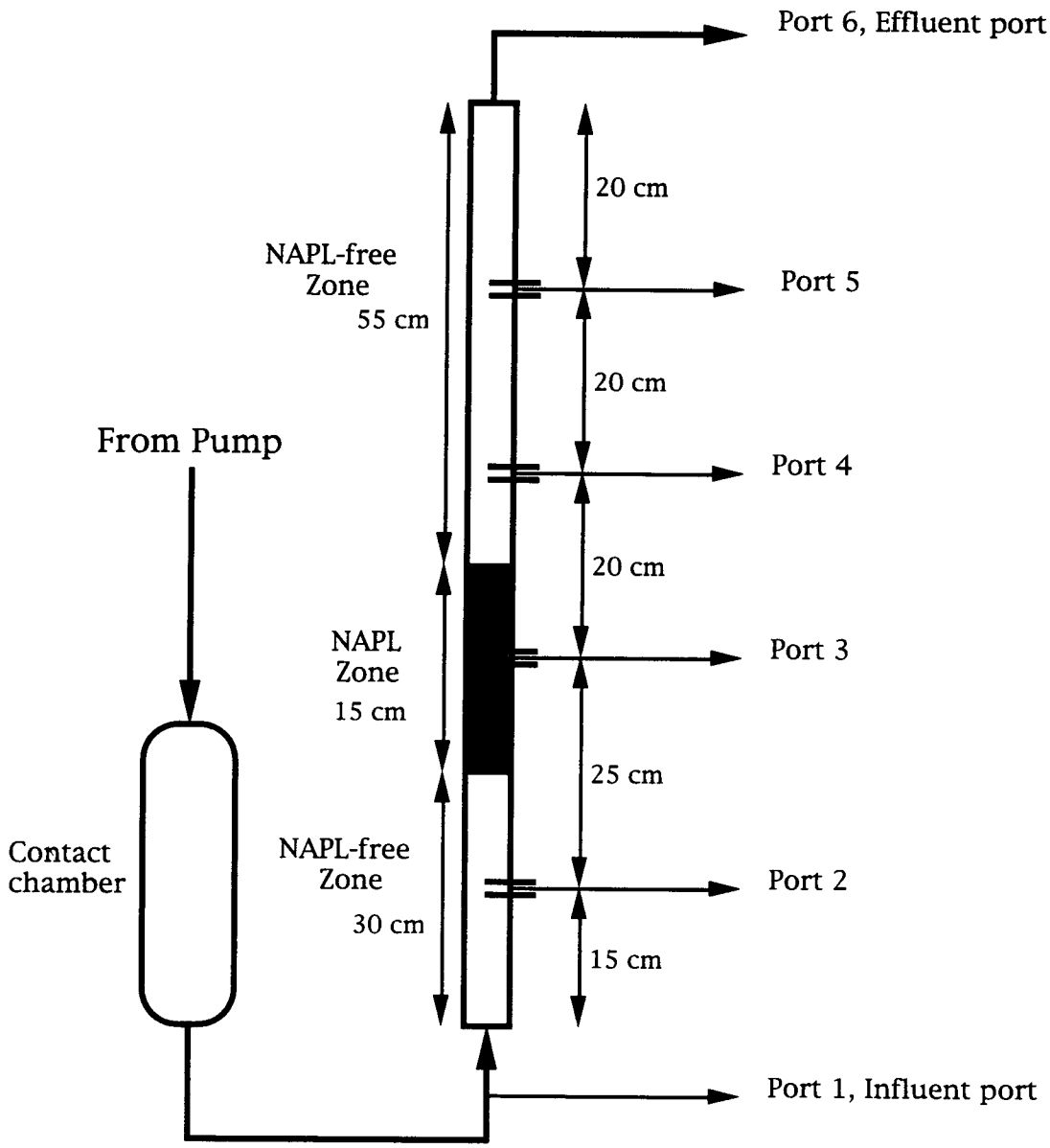

Figure 5.01 Schematic of the Experimental Set Up

The two columns were connected with the shortest practical length of 1/4" tygon and 1/8" OD copper tubing, approximately 15 cm. The influent port (P1) was a Swagelok

union "T" fitting and was connected with a 5 cm length of 1/8" OD copper tubing. As on the interior ports, the port had a Swagelok plug when it was not it use.

The effluent port (P6) was a Swagelok On/Off valve and was attached to the column by a 6 cm length of 1/8" OD copper tubing.

The columns were then flooded with CO_2. De-aired water was then pushed through the column until all the bubbles had dissolved.

Static Test

Initially the column was allowed to sit for 29 days and then a sample was taken from each port to determine radon concentrations under static conditions. The samples were collected in a gas tight syringe fitted with a micro-valve and Luer to Swagelok adapter. The plugs were removed and the syringe attached. The ports were sampled beginning a P1 and working towards P6. This was done because each sample drew in water from downstream. Thus a synthetic groundwater reservoir had to be attached to the influent point (prior to the contact chamber) in order to replace water withdrawn. The results are summarized in Table 5.01 and Figure 5.02.

Table 5.01 Predicted and Measured Radon Concentration in a Stationary Column

Distance along Column	Port No.	Estimated Aqueous Radon, pCi/L	Measured Aqueous Radon, pCi/L
0	1	171	145
15	2	171	128
40	3	60	55
60	4	171	157
80	5	171	204
100	6	171	81

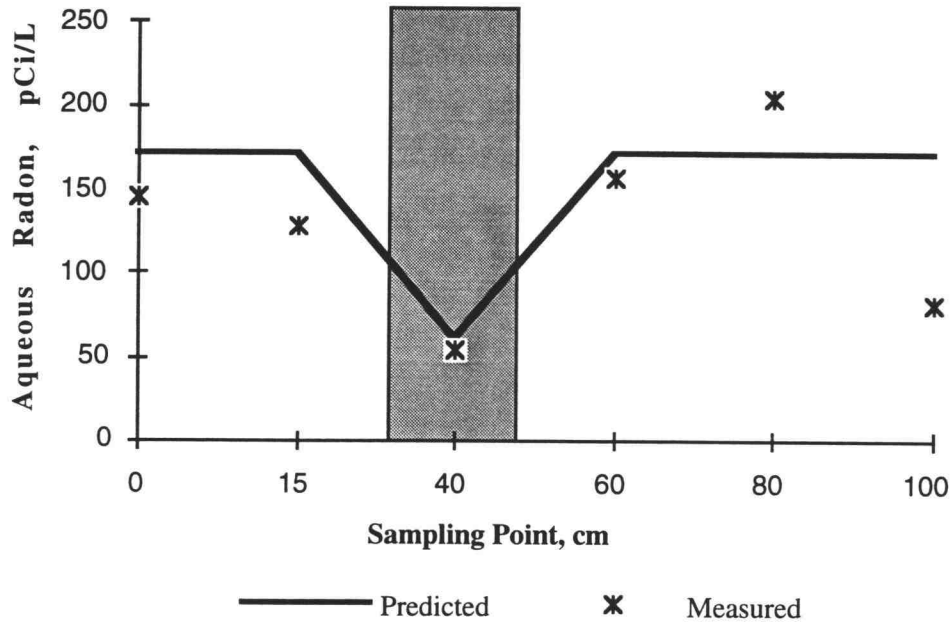

Figure 5.02 Predicted and Measured Radon Concentration in a Stationary Column

The measured aqueous radon concentrations follow the trend of the predicted values. The value that appears to deviate significantly is the aqueous radon concentration at the effluent port (P6 at 100 cm). This low value is due in part to the settling that occurred in the column after saturation. The settling left a volume, approximately 70 mls, at the top column (about 4 cm in length) that was not filled with Borden sand. This free water above the sand would be expected to have a lower radon concentration. As has been noted previously end effects can also have a significant effect in reducing radon concentrations. The value for the influent port, 145 pCi/L is approximately equal to the average aqueous radon concentration of the first point of the NAPL-less columns, 148 pCi/L. The initial value measured for Port 5 was 335 pCi/L. This value was found to be exceptionally high and the sample was recounted. The initial value was rejected for inclusion due to its substantial variance from the predicted value. The results presented in Chapter 4 indicate that the results should be both fairly close to the predicted value and fairly reproducible.

Dynamic Test

The combined pore volume of the two columns was 1200 mls. A target flow rate of 150-175 mls/day was determined to be ideal. At this rate a pore volume of fluid would pass through the column in about a week at which point the system could be assumed to be at or near steady state. It also allowed for a sufficient amount of radon to build up so as to be detectable. A Fluid Metering Inc. pump was used to meter the flow. The final flow rate was 148 mls/day, Figure 5.03 shows the anticipated aqueous radon concentrations in the column based on build up (Eq 2.04) and partitioning (Eq 2.12) in the NAPL zone.

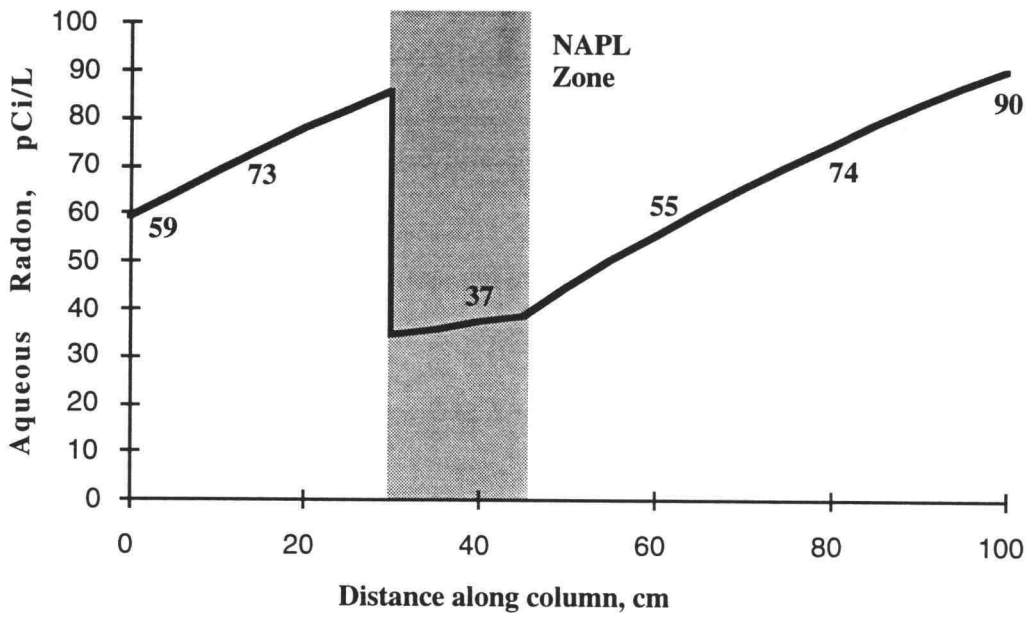

Figure 5.03 Estimated Equilibrium Aqueous Radon Concentration at the Sampling Ports

Between the running of the static test and the dynamic test, there were several unsuccessful attempts at running the dynamic test. During the course of running these unsuccessful attempts air was entrained in the column. In order to ensure total saturation of the column several pore volumes of CO_2 were passed through the column. During this process some slight mixing was observed. The mixing was generally of vertical type (the media moved up and down). Overall the mixing appeared not to be substantial. The column was resaturated and it was noted that some additional settling

had occurred (beyond what had been noted for the static test), approximately another 4 cm.

The sampling procedure was altered slightly for the dynamic test. Instead of testing along the center line of the column the sample were taken from the column wall near the sampling ports. This was done because of problems encountered by sand clogging the sampling needles. Therefore, the septa were removed, a small amount of glass wool was packed in the port to provide a filter, the septa were replaced, and the sampling needle was inserted such that it did not pass beyond the glass wool filter. In addition the plugs were removed and replaced with Swagelok On/Off valves. During sampling the pump was adjusted to its maximum rate (2 mls/min). Similar to the static test, the column was sampled by closing all the ports except for one and the water was pumped into a gas tight syringe fitted with a micro-valve and Luer fitting to Swagelok adapter.

The data for the dynamic test are presented in Table 5.02.

Table 5.02 Aqueous Radon Concentrations from the One-Dimensional Dynamic Test

Port No.	Distance from Influent Port, cm	Aqueous Radon pCi/L
P1	0	58
P2	15	65
P3	40	88
P4	60	97
P5	80	113
P6	100	96

The data do not follow the aqueous radon concentrations predicted in Figure 5.03. The trend indicated by the data indicate a gradual build up of radon, except at Port 6. This indicates that the NAPL is not confined to the 15 cm section in which it was originally placed but appears to have redistributed itself throughout the column.

During the static test the estimated volume occupied by the Borden sand was 1.73 liters and the assumed porosity was 0.42. The solids therefore have a volume of 1.00 liters. The additional settling caused a reduction of approximately 70 mls, thus the volume occupied by the Borden sand was 1.66 liters. The volume of the solids remains the same therefore the pore volume for the static test was 660 mls, or a porosity of 0.39.

If the 5.5 mls of soltrol added to the column were distributed throughout the column the residual NAPL saturation would be 0.83% (5.5 mls soltrol/660 mls pore volume). From the equation presented in Chapter 2,

$$C_W = \frac{\left(C_{Ra} E_p \rho_b\right)/e}{1 + S_N\left(K - 1\right)} \qquad \textbf{Eq 5.01}$$

the average reduction in aqueous radon concentration is 76%.

The reduced porosity would increase the apparent aqueous radon concentration while the residual NAPL saturation would reduce it. Figure 5.04 shows the predicted value of aqueous radon concentration and the data collected.

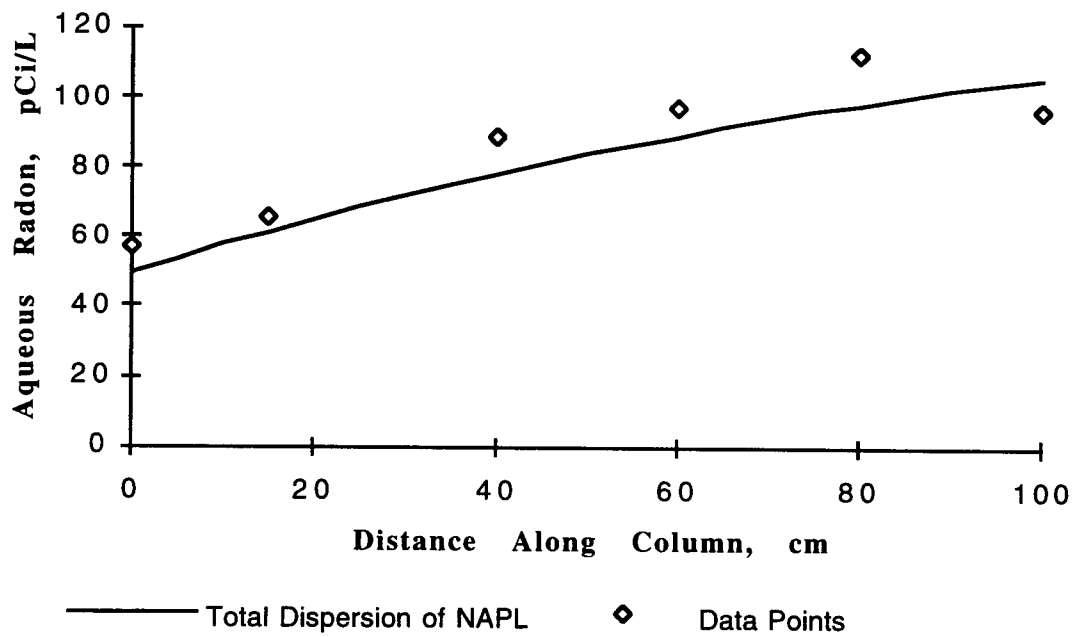

Figure 5.04 Data from the One-Dimensional Dynamic Test and the predicted Aqueous Radon Concentrations based on e = 0.39.

As can be seen from Figure 5.04 the shape of the curve closely approximates the data. The data are above the predicted value with the exception of the value for Port 6. Port 6 shows a reduction in aqueous radon concentrations for the same reasons it did during the

static test. Based on the data I predict that the porosity is less than 0.39. Figure 5.05 shows the effect of a porosity of 0.35 .

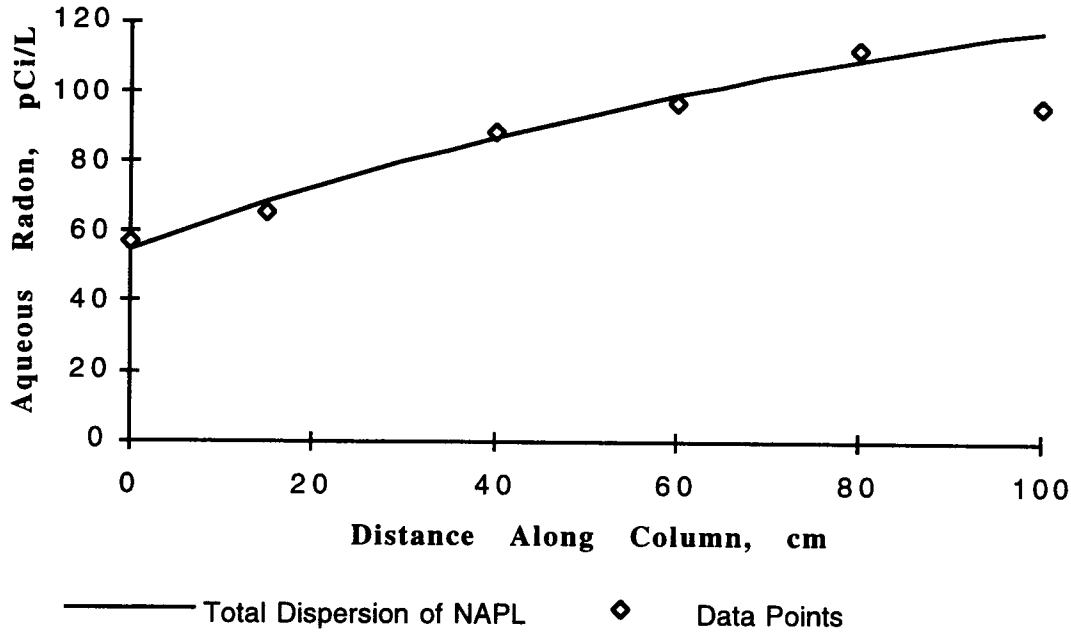

Figure 5.05 Data from the One-Dimensional Dynamic Test and the predicted Aqueous Radon Concentrations based on e = 0.35.

Discussion

The static test shows that initially in the one dimensional column the data gathered in Chapter 4 can be used to predict residual NAPL saturation. However, the results from the dynamic test are inconclusive in showing that radon can be used to detect NAPLs in flow situations. Given the history of the column, additional work needs to be done to establish if this is because the conditions in the column changed or for other reasons. A second static test should be run. If the aqueous radon concentrations are nearly constant in the column this would reinforce the hypothesis that the NAPL had dispersed throughout the column.

Chapter 6
Summary

A strong correlation between aqueous radon concentrations and residual soltrol saturations exists. Aqueous radon decreased as the residual soltrol fraction increased. The proposed linear partitioning model accurately describes this relationship. The results indicate that radon-222 might be used to monitor and detect residual NAPL saturations in groundwaters.

Engineering Applications

The results from this work show that aqueous radon-222 might be successfully used to detect and quantify the presence of DNAPLs in the saturated zone. This method has great sensitivity for compounds with high partition coefficients, allowing for detection at very low levels. Detection can be by either;

- Measuring aqueous radon deficits, or by
- Measuring radon retardation.

Monitoring the progress of a remediation scheme probably is the best use of this technique. Establish a natural background level of aqueous radon concentration by sampling from a zone of similar geological conditions known to be uncontaminated. With a known DNAPL compound present, measuring the aqueous radon concentration, and therefore the radon deficit, yields an estimated residual DNAPL saturation. The progress of a remediation plan may be monitored by testing for aqueous radon over time, providing a low cost and non-intrusive means for quantifying the change in the residual saturation as the spill is remediated.

The aqueous radon deficit method is flexible since the sample size can be adjusted to compensate for soils with low emanation coefficients or high residual saturations. This also provides another sampling scheme: by sampling increasing volumes at the same sampling port, the residual saturations for increasing volumes centered at the sample port can be estimated. This method can also be used to determine where a plume is not-- if there no deficit then there is probably no residual DNAPL.

Measuring the retardation of radon is also a useful method. Injection of a mass of radon free water (or water with a high aqueous radon concentration) in conjunction with a conservative tracer will yield the retardation and therefore quantify the amount of DNAPL present. This method can be used either with two adjacent wells (for horizontal determination) or in a single recirculating well (for vertical determination).

Important considerations in the use of radon to detect and monitor NAPLs in groundwaters are: one, organic carbon content of the aquifer material; two, spatial inhomogenieties in the aquifer properties; three, groundwater flow rates; four, trapped air in the aquifer; and five emanation coefficients of aquifer materials. Organic materials in the aquifer may impact on the partitioning of radon by providing competing partitioning sites. Inhomogenieties in the aquifer porosity and radium concentrations may have significant effects on local radon concentrations. These variations may add significantly to the background error and decrease the sensitivity of the method. If the aquifer is known to be homogeneous than the variations in aqueous radon concentration can be used to map the spatial variations in DNAPL distribution. Groundwater flow rates play a significant role in the distance beyond the DNAPL plume in which radon depletion may be detected. The rate of groundwater movement in sandy aquifers, on the order of 10 cm/day, is such that radon builds up to near equilibrium concentrations after a week or ten days. During that time the groundwater has moved approximately a meter from the zone of residual saturation. However, this also means that the boundaries of a spill can be determined with a high degree of accuracy and therefore allowing remediation efforts to be concentrated in that area. Higher emanation coefficients imply higher radon concentrations in the pore volume and a higher degree of accuracy in estimating residual NAPL fractions.

Results from this work indicate that the detection of DNAPLs is not likely unless sampling is from the interior of the residual saturation plume. Frequently, zones of probable contamination can be determined; e.g., near areas of use, storage, or disposal of DNAPLs. This knowledge coupled with an inexpensive means of establishing test points (e.g., multi-layer sampling in a drop cone penetrometer bore hole) provides a way of establishing a network of sampling locations.

Directions for Future Work

More work is required before this can become a useful tool in detection and monitoring of DNAPL spills. More complex systems need to be tested and modeled before this will become a useful technique in the field.

- Examine the possibility of determining the water-NAPL partitioning constant for radon by direct measurement of the air-NAPL partition coefficient and the Nerst Distribution Law. This would speed up the process of determining the partition coefficients.

- Remediate the batch exchange columns (possibly by flooding with methanol) and test by the radon method and then retested by an independent method for NAPL content. Run blind tests to ensure that residual NAPL concentrations can be estimated. Develop a method, independent of the radon method--possibly colorometric, to test for residual NAPL saturation.

- Model field conditions with a one dimensional column and develop techniques to work with more complicated systems. This work is now underway.

- Research and develop methods to detect low levels of aqueous radon with more conventional laboratory equipment, e.g., the liquid scintillation counter. This would make the technique more accessible to practitioners.

- Assuming success with the one dimensional column, create and test a more complicated 2 or 3 dimensional physical model. Concurrently, development a computer simulation, based on previous work, to predict aqueous radon concentrations. This allows for a fuller understanding of the use of this method in the field.

- Evaluate the effect of multi-compound plumes on radon partitioning, including the effect of organic carbon in the aquifer. Since many spills sites contain multiple compounds or have high organic carbon contents an understanding of how radon partitions between multiple sites is useful.

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Appendices

Appendix A
Emanation Experiments

A series of radon emanation experiments is being conducted in order to determine the emanating power, E_p, of radon from the Borden aquifer solids. The Borden solids, a fine to medium sand, where characterized by a sieve analysis. The experimental process can be summarized as follows:

- Approximately 100 grams of composite aquifer material where placed in 125 ml serum vials.
- A synthetic Borden ground water was added to fill the vials.
- Each serum vial was sparged for a minimum of three minutes with Helium to remove other dissolved gases.
- Each vial was then topped of with synthetic Borden ground water and sealed with a PTFE backed red-rubber septum.
- Vials were stored in an inverted position for a period of approximately thirty days. This was to ensure that the more mobile gaseous radon phase was not in contact with the septa and therefore less likely to escape from the sealed vial.
- The samples were tested for radon as per Appendix D (Extraction, Transfer, and Counting of a Radon Sample).

The emanating power of ranges of particle sizes was determined by using material retained on the sieves during the grain size analysis.

Equipment:

- 125 ml serum vials, Kimble Corporation (Kimble No. 61000G-125)
- Aluminum/PTFE Rubber closures, Kimble Corporation (Kimble No. 73823-20)

Appendix B

Preparation of Synthetic Borden Ground Water

A water sample can be prepared to mimic the ground water found at the Borden aquifer site in Ontario, Canada. Synthetic groundwater has been used in several previous studies, most notably by William Ball in his dissertation and also by Michael McDonald. Ball's synthetic ground water mimics its natural counterpart except the nitrogen was not added in order to inhibit the growth of microbiological organisms. Ball compares his synthetic to a Borden natural groundwater:

Table B.1 Ball's Synthetic Borden Groundwater

	Concentration (μM)	
Constituent	**Ball**	**In-Situ**
Potassium	16	3-30
Sodium	65	40-90
Magnesium	192	100-250
Nitrate	0	<10
Sulfate	200	100-300
Chloride	65	30-90
Calcium Carbonate	saturation	saturation
pH	8.2-8.4	7.3
TOC	.05	10
Ionic Strength	.0024	not reported

The following recipe was developed by Michael McDonald and used in this research:

Ingredients:

15	**liters of DD/DI water**
17.9	**mg KCl**
57.1	**mg NaCl**
346.8	**mg $MgSO_4$**
2000	**mg $CaCO_3$ (to excess)**

Mix ingredients and stir under a continuous purge of filtered laboratory air for a period of four days.

This compares with the in-situ groundwater as follows:

Table B.2 Synthetic Groundwater Used

	Concentration (μM)	
Constituent	**In-Situ**	**McDonald**
Potassium	3-30	16
Sodium	40-90	65
Magnesium	100-250	192
Nitrate	< 10	0
Sulfate	100-300	192
Chloride	30-90	81
Calcium Carbonate	saturation	saturation
pH	7.3	N/A
TOC	10	N/A
Ionic Strength	n/a	N/A

Chemical Supplies:

- KCl Mallinckrodt AR of Paris Kentucky (Mallinckrodt No. 6858-03, Lot No. 6858 KLMA)
- NaCl Mallinckrodt AR (Mallinckrodt No. 7581-05, Lot No. 7581 KEME)
- $MgSO_4$ MCB Reagents a division of EM Science, Gibbstown, NJ (MCB No. MX0075-1, Lot No. 120.39)
- $CaCO_3$ Mallinckrodt AR (Mallinckrodt No. 4072-03, Lot No. 4072 KLHD)

Appendix C
Batch Exchange Experiments

The batch exchange experiments were designed to demonstrate the effect that various nonmobile NAPL concentrations have on aqueous radon in a fully saturated media.

The Principle:

This experiment allows a column packed with the Borden sand, synthetic Borden groundwater, and a known saturation of NAPL (Soltrol with 0.5% Lubrizol and 0.01% Sudan III dye) to reach a radon-222 equilibrium or close to it (approximately a week or ten days) and then to flush the column with deaired (radon free) synthetic groundwater. Initially all the water exiting the column would be the original water in the column which would be relatively high in dissolved radon in comparison with the displacing water. Eventually the displacing water will begin exit the column and this should show up as a diminution (reduction) in the amount of radon exiting the column. Each column has a volume of 1060 mls and when completely packed with the Borden material (porosity of e = 0.42) has an estimated void space of approximately 445 mls. Six samples of approximately 100 mls with wasted (but measured for volume) water in between each samples.

Equipment Required:

- Liquid Chromatography Column (4.8ID x 60L in cm), Kontes, Vineland, NJ, Kontes No. 420830-6020
- Column support and two large clamps
- 125 ml serum vials (Kimble No. 61000G-125) with red rubber PTFE backed septa (Kimble Article No. 73823-20)
- Vacuum pump (Cenco Hyvac 2, Cenco Scientific Co., Chicago, Catalog No. 91305) and a trap with liter volume
- 1/8 OD copper tubing and 2 ON/OFF valves (Swagelok, Highland Heights, OH, 40 Series Valve B-41).

- 2 short medium gage needles (PrecisionGlide Needle, Benton Dickinson & Co., Rutherford, NJ)
- Large Erlenmeyer flask
- Helium (He) source and appropriate two stage regulator
- Appropriate tygon tubing for connecting the various parts
- Carbon dioxide (CO_2) source and appropriate gear--optional
    - 20-25 liter jug
    - rubber stopper perforated with two glass tubes

The Experimental Procedure:

Setting Up

- Clean and dry Chromatography columns.
    - For new columns or those only filled with inorganic material, it is only necessary to wash, rinse, and dry normally (soap and distilled water).
    - Columns previously containing organic material require additional cleaning.
        - Clean several times alternating with methanol and acetone .
        - Then wash, rinse and dry normally.
    - Where possible run the experiments from low to high concentrations of NAPL.

Packing the Columns

- For clean Borden sand (no NAPL)
    - Fill about 2/3 full and then tap gently until sand settles.
    - Continue until column is filled with the maximum amount of sand.
    - Some settling will occur when the column is saturated.
- For sand with NAPLs
    - Fill about 1/8 full with sand and add 1/7 of the NAPL then mix with a combination of end-over-end and rotational movement.
        - Repeat seven times.
    - Add last 1/8 of sand and mix as best as possible to ensure an even distribution of NAPL throughout the packed column.

- Attach the plug, ensuring that there is no sand along the seal.

Saturating the Columns

- For Low Concentration Columns; 0.0, 1.0, and 2.5% residual saturation.
  - Attach lines as shown in Figure C.1 such that a vacuum can be pulled from the top and water siphoned into the bottom. Be sure to use both traps in the vacuum line. The first trap, in addition trapping the bulk of the water, serves as a vacuum reservoir. The second iced trap removes water vapor and protects the pump.

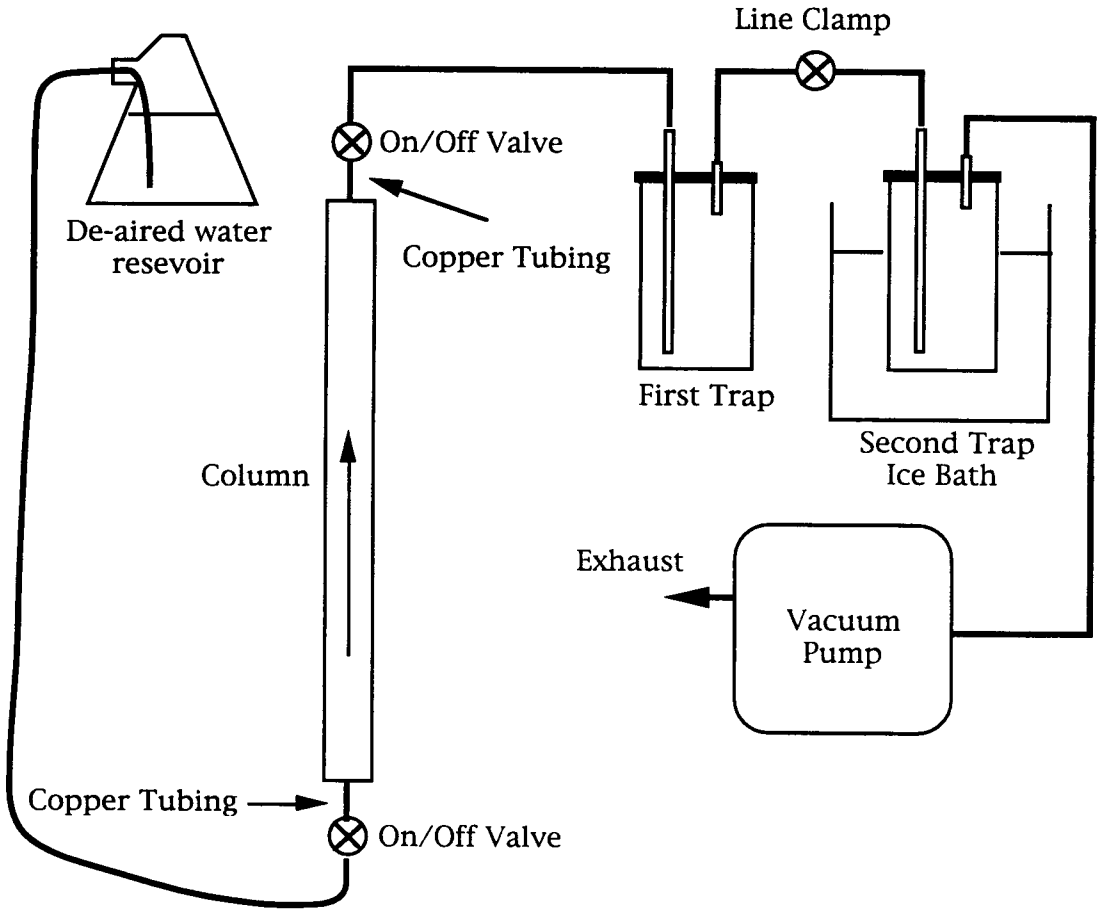

Figure C.1 Saturating a Column

- Set up water siphon and fill lines up to the on/off valve. Try to minimize the amount of water beyond the valve (towards the column) as this will volatilize under a vacuum and make it difficult to achieve a good vacuum in the column.
    - Seal the column. At this point the valve on the bottom (leading to the synthetic groundwater reservoir) should be closed and the one on the top should be open.
    - Turn on vacuum pump and check system for leaks. If there are no leaks allow to run for a while, about 5 minutes, to "boil" off any water remaining above the valve at the bottom of the column.
    - Ensure that a good vacuum exists throughout the column.
    - Pinch the hose connecting the first and second traps (leave the vacuum pump running).
    - Open the valve on the bottom of the column and allow the water to flow upwards into the column until water begins to trickle into the first trap.
    - Shut off the valve at the top of the column.
    - Shut off the valve at the bottom of the column.
- Ensure that there are no bubbles in the media and then shut off equipment (remembering to bleed the vacuum line).

- For Columns with high residual NAPL saturations; 5.0 and 8.0 percent.
    - Set up equipment as shown in Figure C.2

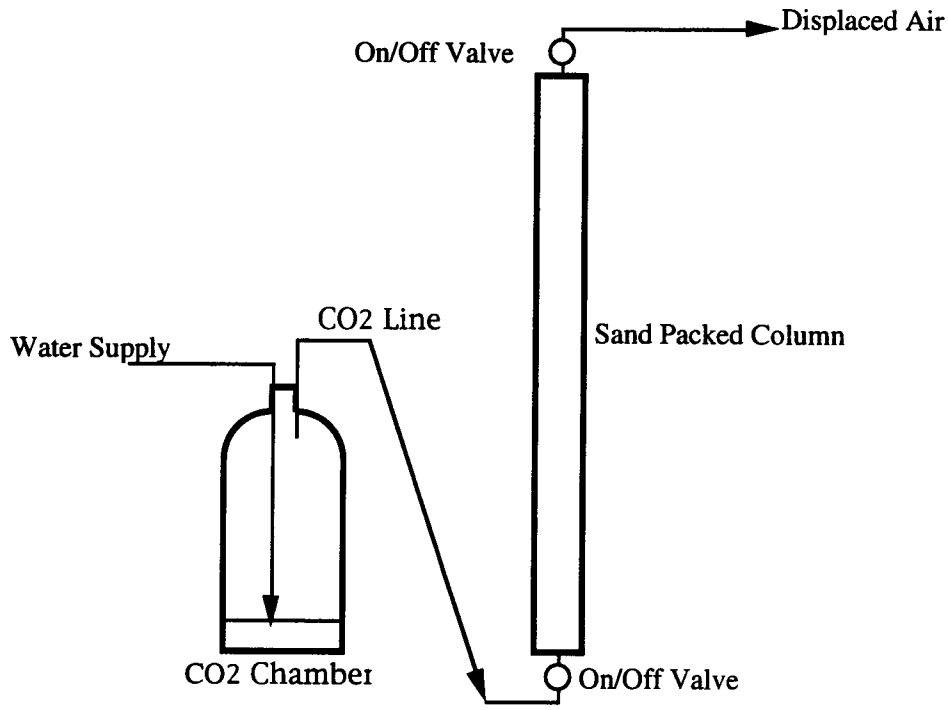

Figure C.2 Flooding Column with CO_2

- Fill a large (20+ liter) jug with CO_2, displace several volumes to ensure a high percentage of CO_2.
- Plug the jug with a rubber stopper with two tube passing through it.
- Attach one tube to the column by way of tygon tubing.
- Attach the second tube to a water source.
- Open both on/off valves on the sand packed column.
- Turn on the water source at a rate of 0.5 to 1.0 liters per minute.
- When the CO_2 chamber is nearly filled with water shut off both on/off valves and the water source.
- De-air 4-5 liters of synthetic Borden groundwater.
- Position the de-aired synthetic groundwater at least 3 feet above the top of the packed column.
- Using tygon tubing siphon water out of the reservoir and to the bottom of the packed column, below the on/off valve.
- Open the on/off valve and allow as many pore volumes (may be as many as 10) of de-aired groundwater to pass through the column as required to desolve all the CO_2.

De-airing the synthetic Borden groundwater.

- Set up the equipment as shown in Figure C.3

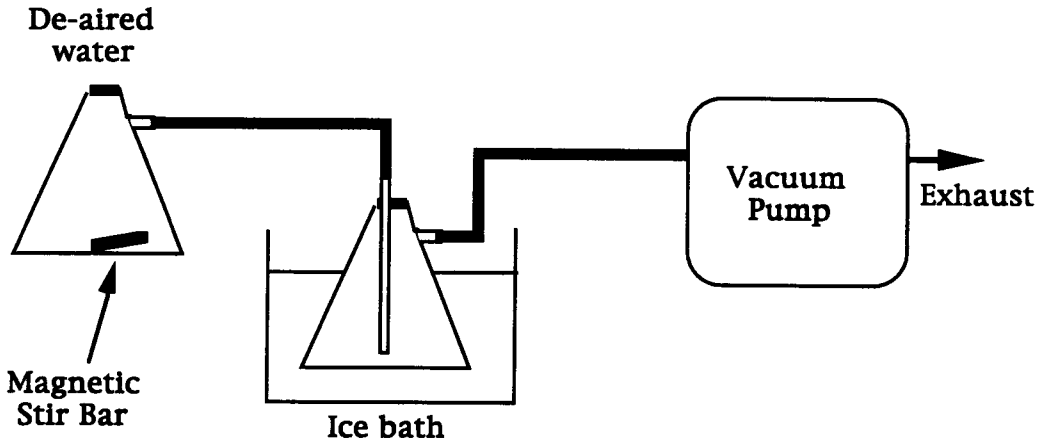

Figure C.3 De-airing Schematic

- Place the water several liters in a large Erlenmeyer flask (sealable) with a large magnetic stir bar.
- Attach the single opening to the flask to a vacuum pump (be sure that there is an iced vacuum trap in the line).
- Run pump and stir bar for about 10 minutes.

Running the exchange.

- Set up the equipment as shown in the Figure C.4

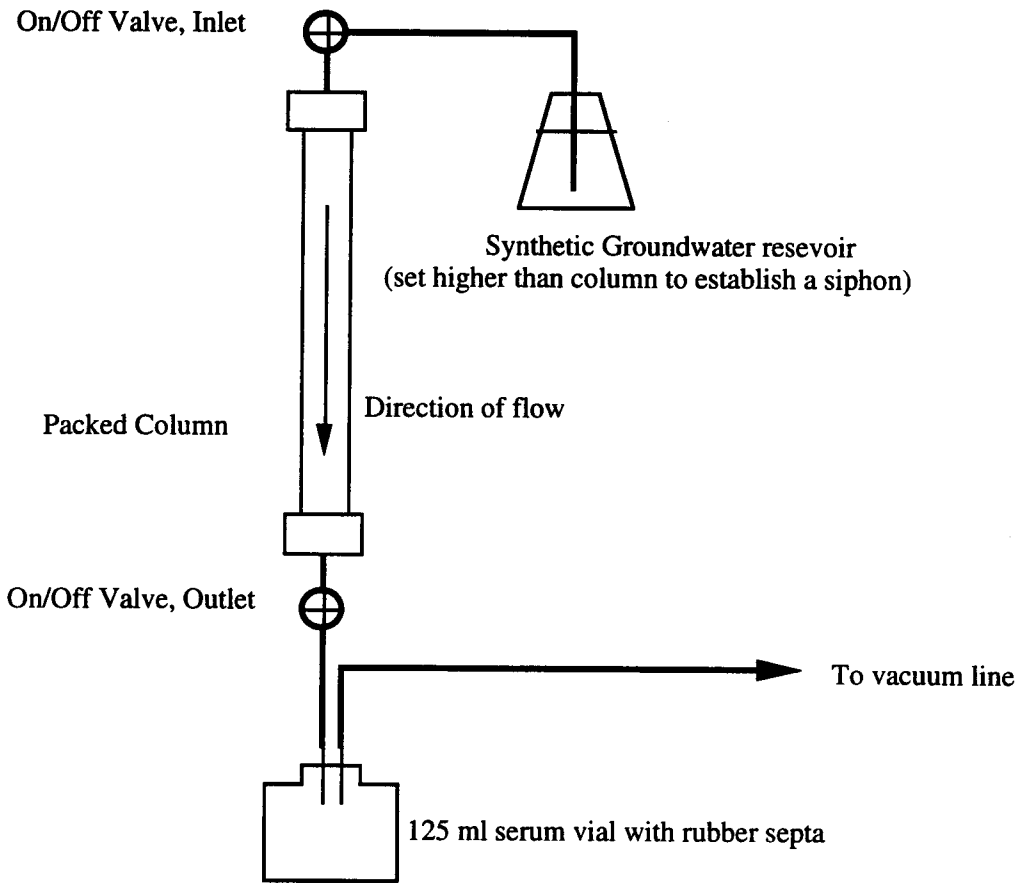

Figure C.4 Exchange Schematic

- De-air the synthetic groundwater.
- Siphon the deaired water into a tube and attach to the valve at the top of the column in such a way as to minimize the amount of air trapped in the line--allow it to flow slowly as it is attached to 1/8" OD tubing exiting the top of the valve.
- Tare all the 125 mls serum vials (with caps and labels) to be used.
- Purge 125 mls vials with Helium.
- Attached 125 mls vials to bottom of column with needle and perforate septa with the second needle from the vacuum line.
- Evacuate for several minutes the 125 mls vials and exit line up to on/off valve.
- Remove the vacuum line--pull the needle out of the septum.
- Open on/off valve at the top of the column (inlet point for the synthetic groundwater).

- Open on/off valve at the bottom of the column and fill the 125 mls vial with approximately 100 mls of water.
- Close on/off valve and remove vial.
- Reweigh to determine the actual amount of water transferred into the vial.
- Sample appropriately as dictated by the amount of NAPL and the partitioning coefficient. Not every 100 mls needs to be sampled but at least the first and last and at a minimum, 4 other 100 ml blocks should be tested for radon content.
- Store vials with aqueous radon sample upside down and lightly coat the stopper with a silicone based stopcock grease if the extraction does not occur promptly.

Appendix D

Extraction, Transfer, and Counting of a Radon Sample

This protocol is based on a procedure developed by Stoker and Kruger (1975). Several steps are required to prepare a sample for counting. In general the procedure can be summarized by the following steps,

- Strip radon from the aqueous sample.
- Separate from other gases and concentrate on GAC.
- Transfer to scintillation (counting) flask by heating GAC and flushing with helium.
- Age sample for at least four hours.
- Count sample.

The equipment required is listed below:

Equipment:

7	High Vacuum Stopcocks (Ace Glass, Vineland, NJ, Ace No. 8206-05)
4	Vacuum gages (VWR, San Francisco, VWR No. 31757-128)
4	Vacuum Traps (Ace Glass, Ace No. 8753-06)
1	Trap with heating element
1	Needle-valve (Ace Glass, Ace No. 8768)
1	He aliquot
1	Peristaltic pump (Sigmamotor, Middleport, NY, Model T6S)
1	Vacuum pump
1	Scintillation flask
2	1000 ml Dewar Flasks (VWR, Catalog No. 63397-000)
20g	Gas adsorption grade charcoal, 7-14 mesh in size, of coconut shells (Fisher Scientific, Fairlawn, NJ, Fisher No. 05-690A)
	Dry ice
	Regular (Water) Ice Cubes
	Propynol
	He source with appropriate two stage regulator
	Vacuum pump trap

Vacuum release valve (to prevent pump oil siphoning)
Thick walled (vacuum) tubing, as required
Sample vial with silica septum
2 Needles, one long (to reach the bottom of sample vial), one short

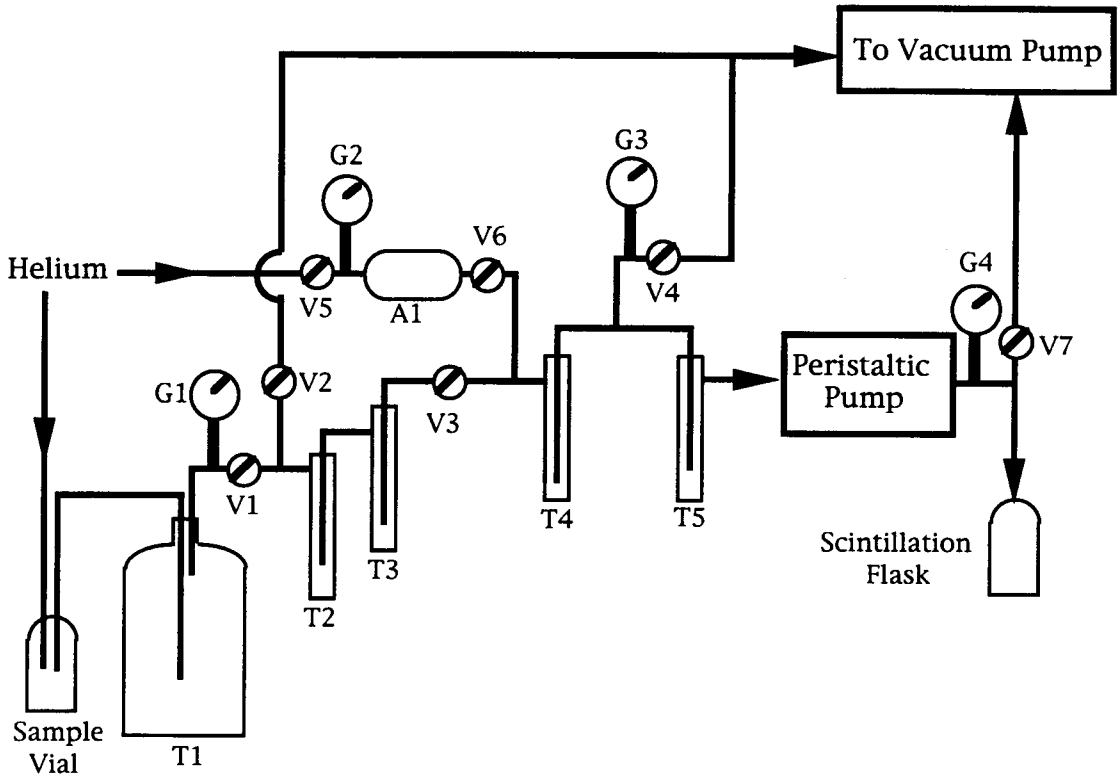

Figure D.1 Radon Extraction and Transfer Equipment

The sealed serum vial with radon containing liquid is sparged with Helium gas in order to remove the radon gas. The Helium and Radon gases then enter into the vacuum line system. Trap **T1** removes any particulate matter, especially the liquid phase water that is extracted during the sparging process. The second trap, **T2**, which is immersed in a dry ice and propynol bath (at -45°C to -50°C) removes water in the system by condensation. The removal of water is necessary so as not to rapidly use up the Ascarite™ (NaOH) on the next trap, **T3**, which removes the CO_2 by absorbing it onto Ascarite™. The third trap, **T4**, is chilled in a dry ice bath and adsorbs the radon on to the granular activated carbon (GAC). The flow rate is maintained by adjusting the second stage regulator on the Helium tank. This ensures that radon adsorbs onto the carbon and

is not forced by the GAC and vented. Heating the charcoal to 200°C to 220°C desorbs the radon gas. The last trap, **T5**, removes any remaining water. Four aliquots of helium ensures that the radon is transferred into the scintillation flask.

The three vacuum line connections are connected to a vacuum pump through a vacuum trap which rests in an ice bath and which prevents particulates from entering the pump and also prevents the pump oil from being siphoned out of the pump and into extraction apparatus. Opening the pressure release valve at the conclusion of the experiment (or any time after running the vacuum pump) prevents the vacuum pump oil from being siphoned.

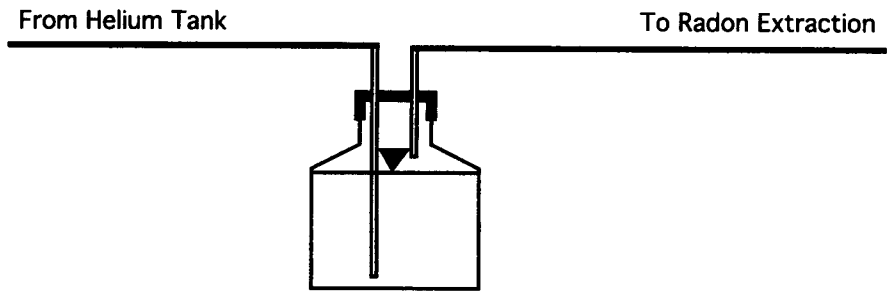

Figure D.2 Details of Sparging Apparatus

<u>Procedure for Extracting and Transferring Radon:</u>

- Ice down (regular ice) vacuum pump trap.
- Cool water vapor trap, **T2**, and the charcoal trap, **T4**, to -45°C to -50°C with dry ice and isopropyl alcohol mixture (should look like bubbles coming up through honey).
- Evacuate scintillation flask, by opening **V7**.
- Open stopcocks **V1**, **V2**, **V3**, **V4**, and **V6**; all others are closed, this ensures that a vacuum has been obtained in the system.
- Close stopcock **V2** and open **V6**.
- Purge Helium from sample.
    - Insert the short needle (that lead to **T1**) through the septa as shallow as possible.
    - Inserting long needle (from the helium tank) to the bottom of the sample.

- Turn on helium source by adjusting the second stage, just enough pressure to bubble gas through the sample.

- After the sample has been sparged for at least five minutes, close stopcocks **V1** and **V3**.
- Remove dry ice bath, continue to evacuate carrier gas, and allow system to warm to 45°C.
- Close stopcock **V4**.
- Heat charcoal trap, **T4**, to 200°C to 220°C, approximately when voltage regulator is at 30 volts.
- Transfer radon to the scintillation flask.
  - Open **V5** and close again, aliquot **A1** should now be filled with helium gas.
  - Open **V6**, wait for pressure to equilibrate, and close.
  - Run peristaltic pump till pressure in trap (gage **G3**) is reduced to a vacuum of 27.5 to 29 inches Hg (about 120 seconds).
  - Repeat this procedure until four (4) aliquots of helium have been sequentially transferred to the scintillation flask.
- Remove the scintillation flask, and allow to age for at least four (4) hours. This allows radon to come to a quasi-equilibrium with its daughter products as shown in Figure D.3.

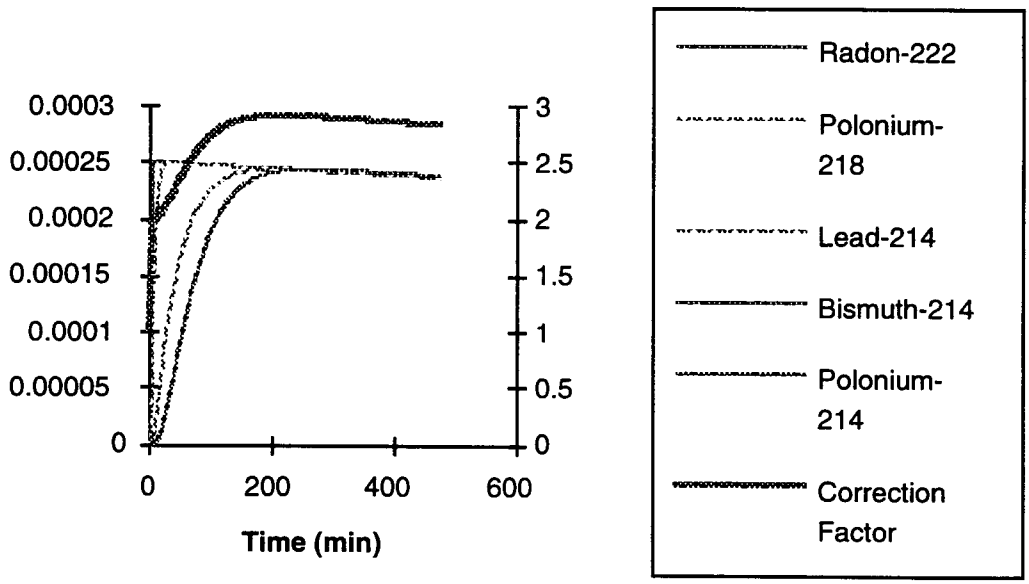

Figure D.3 Build Up of Radon Daughter Products to Quasi-equilibrium Levels

- Shut down vacuum and peristaltic pumps and open the vacuum relief valve.

Note:

- Replace Helium tank when there is less than 50 ft^3 (or 500 psi) remaining. This is done in order to reduce background counts from the radium in the steel tanks.

Procedure for Counting Radon Samples:

The scintillation flask is coated with ZnS along the cylindrical surface and has a tin oxide coated (to prevent preferential migration of Radon daughter ions) quartz window on the bottom. The scintillation flask is placed in the photomultiplier housing after being filled with Radon and Helium gas from the Procedure for the Extraction of Radon Gas. The Radon gas and its daughter products undergo alpha decay (disintegration by emission of a Helium nucleus) which when this particle impacts the ZnS emits a pulse of light, a photon. These photons enter the photomultiplier, are multiplied to readable levels, and are filtered (to eliminate as much "noise" from the system--not only electrical and thermal but also photons generated from beta and gamma decay) and is eventually converted into an electrical pulse which is measured on the counter.

The variable power supply is adjusted in order to minimize interference from the electronic and thermal noise in the system and to maximize the counting efficiency. The voltage needs to be sufficiently high to generate a readable pulse at the detector but not so high that thermal, heat, or beta disintegrations ("noise") also become detectable.

Equipment:

Scintillation Flask
Variable High Voltage Power Supply (EG&G ORTEC, Model No. 556H)
Photomultiplier Tube
Counting Unit/e.g.. HP5201L Scaler-Timer

Setup Schematic:

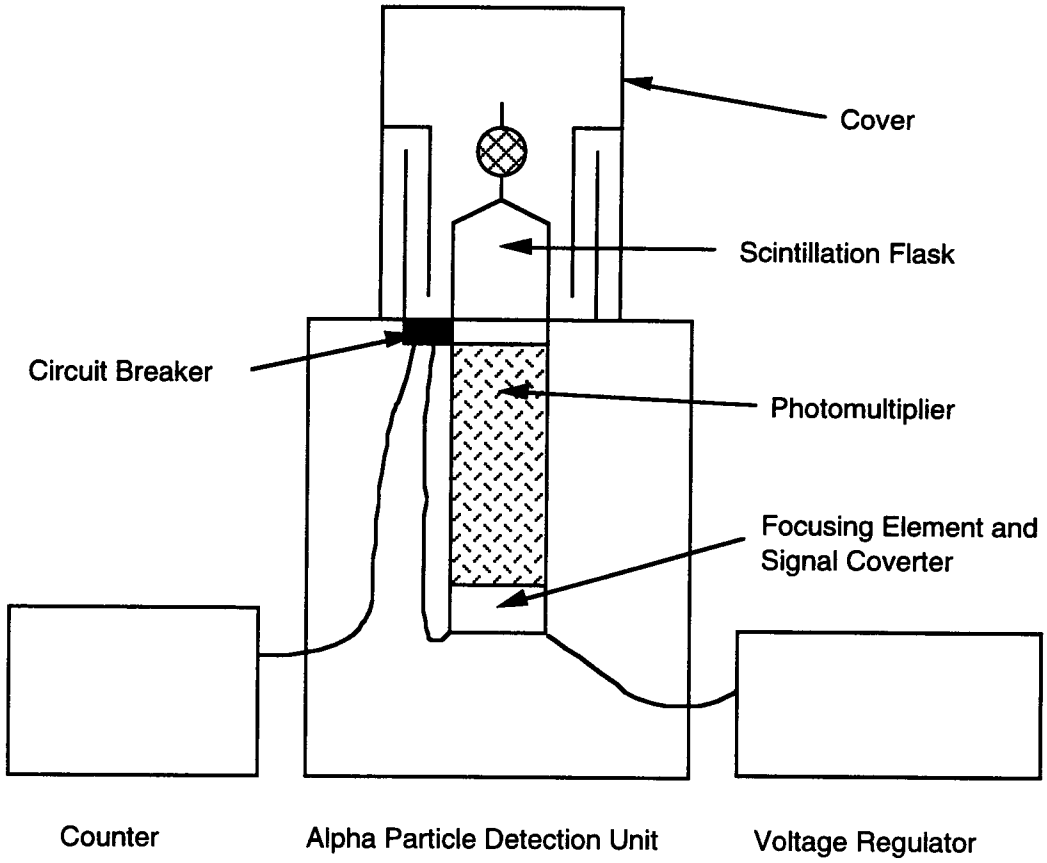

Figure D.4 Counting Apparatus

- Ensure that the voltage regulator is turned down to 70 volts or is off.
- Ensure that the counter has been stopped and reset and that the timer is adjusted to 1800 seconds.
- Open the top of the photomultiplier tube, place the scintillation flask in place, and replace the top.
- Turn the voltage supply up to 970 volts.
- Push the Start button to begin counting.

- Make sure the voltage is down to 70 (or turned off) and the counter is stopped before opening the top of the photomultiplier tube.
- Calculations and a sample spreadsheet are presented in Appendix E (Rn pCi Calculations)

Appendix E
Calculating Radon Concentration

A spreadsheet was set up to calculate the aqueous radon concentrations. This document explains how it functioned, a sample spreadsheet follows the explanation. Radon concentrations were calculated with the following procedure:

Data Required:

Tare Weight of Sample Containers
Final Weight of Sample and Containers
Date and Time of Column Packing
Date and Time of Sample Extraction
Date and Time of Sample Transfer to a Scintillation Flask
Date and Time of Counting
Total Counts in a thirty minute period

Sample Size:

The sample size was determined by the difference between the final weight and the tare weight--in all cases approximately 100 mls of solution were extracted.

Sampling Point:

The estimated sample point was assumed to occur at the midpoint of a sample. Thus a sample point was set at the sum of all previous samples plus one-half of the current sample.

Packing, Extraction, Transfer, and Counting Times:

Since each of these procedure took from 30 to 60 minutes to complete the time was set at the midpoint between start and finish of each process. All times between processes were determined in hours.

Standardizing the Batch Exchange Curves:

All the curves were standardized to an infinite equilibration time in the soil. This ensured that exchanges that occurred after different contact times with the

soil media could be compared with each other. In no case was an exchange run before the equilibration factor was 85%, about 9 days--this ensured that the correction was relatively small compared to the final value.

The Calculations:

A description of the calculation procedure by spreadsheet columns follows:

Sample ID (Column A): This is the sample marker in the form C#S#. The C# refers to the column number and S# refers to the sample number in order of extraction. There are WASTE markers which indicate that water was exchanged but not collected for counting.

Scintillation Flask ID (Column B): This is the scintillation flask into which the radon gas sample is transferred into for the purpose of counting.

Background dpm (Column C): This is the background counting rate for the scintillation flask indicated. The background count increases the apparent counting rate of the sample--see corrected dpm.

Extraction Sample Size (Column D): This is data that is transcribed from the laboratory notebook. This is the amount of water extracted in milliliters (mls).

Estimated Sample Point (Column E): Is the presumed point at which sampling occurs. The estimated sample point was assumed to occur at the midpoint of a sample. Thus a sample point was set at the sum of all previous samples plus one-half of the current sample. The following is an example of a cell formula used:

=SUM(D11:D15)+D16/2

Total Counts (Column F): This is data transcribed from the laboratory notebook. It represents the total number of disintegrations detected in a thirty minute period.

dpm counted (Column G): This is the counting rate in counts per minute. The following is an example of a cell formula used:

=F16/30

corrected dpm (Column H): This is the dpm counted minus the background rate from the scintillation flasks. The following is an example of a cell formula used:

=G16-C16

decay factor (Column I): Due to the radioactive nature of radon some of it will decay over time. This column calculates the amount of radon decayed between the batch exchange and the counting procedure. The following is an example of a cell formula used:

=EXP(-0.0075226*(J16+K16))

Where -0.0075226 hrs^{-1} is the radon decay constant, λ.

Time till extraction (Column J): This is the time, in hours, between the batch exchange and the transfer of radon to the scintillation flask. This number determined by hand and recorded directly into the spreadsheet.

Time between extraction and counting (Column K): This is the time, in hours, between the transfer of radon to the scintillation flask and the counting procedure. At least four hours were allowed to pass to ensure that the build up factor (see buildup correction) had reached its maximum and had begun to decline. This number determined by hand and recorded directly into the spreadsheet.

Buildup correction (Column L): Once in the scintillation flask the radon decays into Polonium-218 which in turn enters a decay process until Lead-210 is reached at which point the decay sequence ends. Throughout this process each radioactive particle is ejecting particles from the nucleus as it decays, some of which are alpha particles (helium nuclei) which will also be detected on the counter. Thus an adjustment needs to be made such that the radon count can be determined from the count of radon and all its daughter products. After the peak has been reached the following cell formula expresses this factor:

=2.90708*EXP(-0.0075226*(K16-4))

Radon (pCi) (Column M): In this column the actual amount of radon in the sample is calculated. The cell formula shows how this is determined:

=H16/(0.725*2.22*I16*L16)

Where: **H16** is the counting rate in disintegrations per minute, **0.725** is the estimated efficiency of the extraction and transfer apparatus, **2.22** is the number of disintegrations per picoCurie (pCi or 1 x 10^{-12} Curie), **I16** is the scintillation buildup factor, and **L16** is the decay factor.

The efficiency was determined at Stanford University by Mike McDonald by using a radium standard. Since no such standard was available during this research, the Borden sand solids were used to establish that the efficiency was similar to that established at Stanford. This was done by estimating the emanation coefficient of the Borden sands (0.033 pCi/gm) and comparing to the value determined at Stanford (0.025 pCi/gm).

Groundwater equilibrium time (Column N): This is the amount of time between the packing of the column and the batch exchange in hours. This number is determined by hand and recorded directly into the spreadsheet.

Equilibrium Correction (Column O): In this column the percent of the equilibrium concentration that has been achieved during the contact time with the solids. The following is an example of a cell formula used:

=1-exp(-0.0075226*N16)

Adjusted Radon (pCi) (Column P): In this column the anticipated equilibrium amount of radon is calculated. This is determined by dividing the amount of radon found the percent achieved. The following is an example of a cell formula used:

=M16/O16

Radon Concentration pCi/liter (Column Q): In this column the anticipated concentration of radon per liter is determined. This is found by dividing the adjusted radon amount by the sample size. The following is an example of a cell formula used:

=P16/D16

Table E.1 Sample Sp

Batch Exchange Expe
Plain Sand and Synth

Column #6 was pack

Sample ID	Scintill. Flasl	Equilibration Correction	Adj Radon (pCi)	Radon Concentration pCi/litre
C6S1 WASTE	2	0.833	14.234	144.950
C6S2 WASTE	3	0.833	16.626	165.428
C6S3 WASTE	4	0.833	15.703	155.475
C6S4 WASTE	5	0.833	2.524	26.132
C6S5 WASTE	6	0.833	0.794	7.452
C6S6	7	0.833	0.845	8.860

Chronological Samplin

Sample Number
C6S1
C6S2
C6S3
C6S4
C6S5
C6S6

Appendix F

Calculation of the Source Term for the Borden Sands

Since,

$$1\mu\text{Ci} = 2.22 \text{ x } 10^6 \text{ dpm}$$
$$1\text{pCi} = 2.22 \text{ dpm}$$

Therefore a maximum concentration of Rn-222 of 173 pCi/L translates to 384.1 dpm or 6.40 dps.

Since,

$$\text{dps} = -\frac{\text{dN}}{\text{dt}} = \lambda \text{N}$$

and,

$$\frac{C}{C_0} = e^{-\lambda t} \Rightarrow \quad t_{1/2} = \frac{\ln 2}{\lambda}$$

since the half life of Rn-222 is 3.83 days or 3.31E+5 seconds

$$\lambda = \frac{\ln 2}{t_{1/2}} = 2.09 \ x \ 10^{-6} \ s^{-1}$$

the amount of Rn-222 atoms is shown by

$$\text{dps} = \left(2.09 \text{ x } 10^{-6}\right) \bullet \text{N}_{\text{Rn-222}}$$
$$6.40 \text{ dps}/2.09 \text{ x } 10^{-6} = \text{N}_{\text{Rn-222}} = 3.06 x 10^6$$

The column porosity is estimated to be 42% and the specific gravity of sand is 2.71. Therefore one liter of water represents the pore volume of 2.38 liters of sand solids or 6452.4 gms of sand.

This gives 473.5 Rn-222 atoms per gram of solids.

At equilibrium conditions,

$$\lambda_{\text{Ra-226}} \bullet \text{N}_{\text{Ra-226}} = \lambda_{\text{Rn-222}} \bullet \text{N}_{\text{Rn-222}}$$

The half-life or Radium (Ra-226) is 1600 years or 5.05E+10 seconds which gives us a λ=1.37E-11 s^{-1}. Thus $N_{Ra\text{-}226}$ = 7.22E+7 atoms of Radium-226 per gram of solid.

From,

$$dps = -\frac{dN}{dt} = \lambda N$$

we get a **dps = 9.90E-4 for Ra-226**, and since 2.22 dpm = 0.037 dps = 1 pCi (10^{-12} Curies) we can

$$\frac{9.90 \times 10^{-4}\ \text{dps}}{0.037\ \text{dps}/1\ \text{pCi}}$$

to get source term,

$$E = \frac{0.027\ \text{pCi}}{\text{g}}$$

This agrees reasonably with the emanation constant determined at the beginning of the research.

$$E = \frac{0.033\ \text{pCi}}{\text{g}}$$

Picking a representative maximum radon concentration say 173 pCi/L and a reasonable cut off point (the breakthrough point) for that high concentration, say after 450 milliliters we can determine that the activity in the column was 173 pCi/L times 0.450 liters or 77.85 pCi in the column. The typical mass of sand in the column was 1660 grams of solids. By dividing the activity by the mass we can determine our emanation coefficient,

$$E = \frac{0.047\ \text{pCi}}{\text{g}}$$

The first two methods yield an approximately identical values for the emanation coefficient. The third method is less reliable and yields a value that is significantly higher. The reason that this method is less accurate is that the area under the radon concentration curve is being integrated and there are only a few points from which to

estimate the shape of the curve. These three techniques yield fairly consistent source terms for Borden aquifer material.

Appendix G
One-Dimensional Column Protocol

The one-dimensional column experiments was designed to that aqueous radon can be used to detect and quantify residual NAPL saturation in a fully saturated media.

The Principle

Radon free water flow through a saturated media for approximately 4 days to build up aqueous radon concentration. It then passes through a short zone of 5.0% residual soltrol (K = 38) saturation where the aqueous radon concentration is reduced. Finally, it passes through a zone of uncontaminated sand where the aqueous radon concentration builds up towards equilibrium levels.

Equipment Required

- Liquid Chromatography Column (4.8ID x 100L, cm), Kontes, Vineland, NJ.
- Liquid Chromatography Column (1.05 liters)
- Gas Tight Syringe, SGE
- Microvalve,
- (6) Swagelok On/Off Valves
- (4) Swagelok 1/16" to 1/8" adapters
- 1/8" Union "T" brass Swagelok fitting
- 125 ml serum vials (Kimble No. 61000G-125) with red rubber PTFE backed septa (Kimble No. 73823-20)
- Metering Pump, FMI
- 1/16" OD stainless steel tubing
- 1/8" OD copper tubing
- Vacuum pump (Cenco Hyvac 2, Cenco Scientific Co., Chicago, Catalog No. 91305)
- Tygon Tubing, ID as appropriate

The Experimental Procedure

Setting Up

- Fuse four sample ports onto the 100 cm column at 15, 40, 60, and 80 centimeters along the column.
    - Each port should be approximately 2.5 cm long and have a 6 mm ID.
    - Each port filled with a small amount of glass wool to serve as a filter pack.
    - A red rubber PTFE backed septa is used to seal each port.
    - (4) Short sections of the 1/16" stainless steel tubing are cut and attached to the adapters which are in turn attached to the On/Off valves.

Packing the Column

- Set up the columns as shown in Figure G.1
    - Attach the column by means of the shortest practical length of copper and tygon tubing.
        - Attach Union "T" close to the 100 cm column.
        - Attach an On/Off valve to the Union "T."
    - Insert 1/16" OD stainless steel tubing and attachments through the sample port septa.
- Fill the contact chamber (the 1.05 liter column) with as much dry sand as possible.
- Fill the 100 cm column with 30 cm of sand.
    - Tap the column to ensure as much settling as possible.
- Prepare enough sand with 5% residual soltrol saturation to fill a 15 cm long section.
    - Assume a porosity of 0.42.
- Use a large ID tygon tube to transfer the sand and soltrol mixture into the column without having the mixture come in contact with the walls of the column above the contaminated zone.
    - Tap lightly on the sand with the tube to compact slightly.
- Add sand to the top of the column.
    - Tap the column to ensure as much settling as possible.

Saturating the Column

- Flood the column with several pore volumes of CO_2.
    - Maintain the direction of flow down through the contact chamber and up through the 100 cm column.

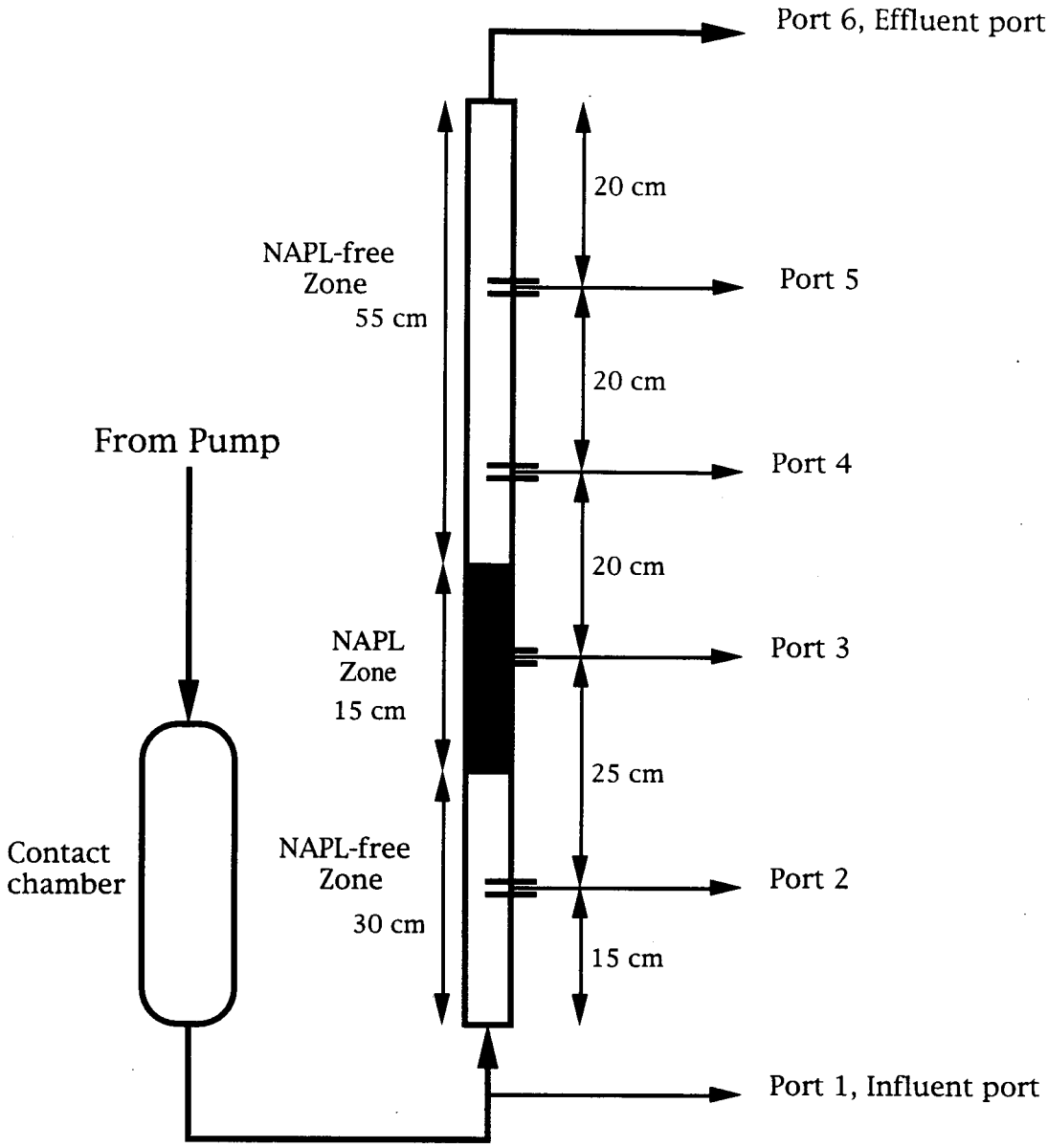

Figure G.1 Schematic of the Experimental Set Up

- Pump De-aired water through the column until the bubbles have desolved, as many as ten pore volumes.
    - Maintain the direction of flow down through the contact chamber and up through the 100 cm column.

<u>Running the Experiment</u>

- Establish an appropriate flow rate, but less than 150 mls/day.
    - Allow to run until at least one pore volume has been exchanged.

Sampling

- Close all the On/Off valves
- Shut of the metering pump.
- Set pump to maximum flow rate, 2 mls/ min.
- Attach the gas tight syringe to the On/Off valves by using the Swagelok-to-Luer adapter and the microvalve.
    - Open the microvalve.
- Turn on the pump.
    - Open the On/Off valve at the port being sampled.
- Collect a 50 - 80 mls sample.
    - Close the microvalve.
    - Close the On/Off valve.
    - Shut off the pump.
- Remove the syringe by taking off the Luer-to-Swagelok adapter.
    - The microvalve stays closed and with the syringe.
- Attach a medium gage needle to the Luer fitting.
    - Insert the needle into an evacuated 125 ml serum vial.
    - Open the microvalve and allow the sample to enter the vial.
- Remove the vial and store in an inverted position until ready to extract the aqueous radon sample.