

AN ABSTRACT OF THE THESIS OF

Sarayu Gottipati for the degree of Master of Science in Civil Engineering
presented on January 16, 1996.

Title: Radon-222 as a Tracer for Performance Assessment of NAPL Remediation Technologies in the Saturated Zone: An Experimental Investigation.

Abstract approved:

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Lewis Semprini

Persistence of Non aqueous phase liquids (NAPLs) in the subsurface at residual saturations eventually contributes to undesirable groundwater contamination. Proper characterization of subsurface NAPL, its location, composition and distribution, is essential for the chosen remediation technology to be effective. It is also desirable to assess the performance of remedial actions at NAPL-contaminated sites in order to verify the technoeconomic viability of the selected method. The unique properties of radon-222 gas make it a good indicator for organic phase liquids. It is ubiquitous in the subsurface, chemically inert, radioactive, and most importantly, partitions into NAPLs. This research explores the practicality of using radon to indirectly monitor the progress of NAPL remediation efforts.

The effectiveness of surfactant flushing in remediating NAPL contamination was also studied in the process. Preliminary studies were conducted using micro-columns to evaluate the efficiency of the surfactant selected for the study, triton. These studies show that triton is more effective at higher concentrations in solubilizing residual soltrol and its solubilizing capacity is greatly enhanced after batch equilibration. These observations suggest that surfactant solubilization of NAPLs is rate-limited rather than instantaneous. These studies also indicate the adverse effect of aged NAPL on surfactant solubilizing capacity. Two independent methods, total organic carbon analysis and HDPE strip test,

were also designed for analyzing the aqueous and sand samples and estimating the level of cleanup achieved.

Since triton proved to be effective in micro-column studies, the remediation of the soil columns was performed by flushing triton through the columns in a sequential batch mode. The soil columns employed in the study had been previously packed and used by Hopkins (1994). The influence of the decrease in residual soltrol saturations on breakthrough of radon was observed. The gradual cleanup of columns at various initial residual soltrol saturations (1.0%, 5.0%, and 8.0%) through surfactant flushing was well reflected by radon. The aqueous radon concentrations increased and the retardation of radon lessened as residual soltrol was removed from the columns. The linear equilibrium partitioning model of radon was used to estimate the initial residual NAPL saturation in each column and the subsequent saturations as the remediation proceeded. The saturation estimates were based on retardation factors obtained from maximum aqueous radon concentrations and breakthrough of radon. These estimates correlated fairly well with those based on TOC analyses and HDPE strip tests, supporting radon's capability of detecting and quantifying NAPLs, and monitoring the progress of NAPL remediation.

The results of this study demonstrate the potential of radon as a tracer for evaluating the performance of NAPL remediation techniques. This study also substantiates the ability of surfactants to enhance NAPL recovery from subsurface. However, clogging problems have been encountered, which are believed to be caused by surfactant micelles, while sampling columns. Hence, careful selection of appropriate surfactant, among other criteria, is essential to get maximum benefits of surfactant-enhanced NAPL remediation technology.

Radon-222 as a Tracer for Performance Assessment of NAPL Remediation
Technologies in the Saturated Zone: An Experimental Investigation

by

Sarayu Gottipati

A THESIS

submitted to

Oregon State University

In partial fulfillment of
the requirements for the
degree of

Master of Science

Completed January 16, 1996

Commencement June, 1996

Master of Science thesis of Sarayu Gottipati presented on January 16, 1996

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Acknowledgments

I am extremely grateful to my parents and my relatives for their endless love and continuous support. Their encouragement has always been instrumental in bringing the best out of me and helping me realize my dreams.

I thank my major professor, Dr. Lewis Semprini, for his esteemed guidance, support, and advice. Successful completion of this research work would have been highly impossible without his constant encouragement. I also thank Dr. Jonathan Istok, my minor professor, Dr. Kenneth Williamson and Dr. John Baham, members of my committee, for their support and cooperation.

Special thanks and appreciation are also due to all friends and fellow graduate students for their thoughtful suggestions, help and friendship. I particularly thank Dr. Azizian, Omar Hopkins, Young Kim, George Pon, Vijay Bhaskar, Pugazhendhi, and Jason Cole for assisting me in mending critical equipment problems.

This research was funded by the Department of Energy through the U.S. EPA sponsored Western Region Hazardous Substance Research Center under agreement R-815738. Porex Technologies, Georgia, supplied the HDPE sample strips used in the research. Their contributions are gratefully acknowledged.

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Radon-222 as a Tracer for Performance Assessment of NAPL Remediation Technologies in the Saturated Zone: An Experimental Investigation.

Chapter 1 Introduction

The Problem

Non-Aqueous Phase Liquids (NAPLs) are widely used not only in industry but also in day-to-day life as fuels, organic solvents, cleaners, and degreasers. As a consequence, they make their way into the subsurface during disposals, spills or accidental releases. At their residual saturations, NAPLs get entrapped in the pores of the aquifer matrix. These entrapped NAPLs serve as persistent sources of contamination as they slowly dissolve and reach groundwater (EPA Report, 1990). Although NAPLs are immiscible with water, their water solubilities are several orders of magnitude above their drinking-water standards. This necessitates their cleanup from the subsurface.

The success of remedial technologies in cleaning up NAPL contamination depends largely on accurate estimation of the quantities of NAPLs present and their distribution in the subsurface (Cohen and Mercer, 1993). It is also desirable to monitor the progress of remediation efforts to assess the extent of cleanup achieved and verify the techno-economic viability of the selected remedial strategy. Direct methods of detecting and delineating subsurface NAPLs are presently limited owing to the complex nature of NAPL behavior and transport in the subsurface formations. Characterization of subsurface NAPL contamination by indirect methods such as, geophysical logging and sampling, is expensive. These methods require testing to be done in close proximity of the contamination zones to yield representative and reliable results (EPA, DNAPL Workshop, 1992, Cohen and

Mercer, 1993). Recent research indicates that partitioning tracers can be reliably employed to detect and quantify NAPLs in the subsurface indirectly (Semprini et al., 1993, and Jin et al., 1995).

Radon-222 gas possesses unique properties that make it a good tracer for organic phase liquids. Radon is abundantly available in the subsurface, chemically inert, easy to detect, and most importantly, partitions into nonaqueous phase liquids. Work done by Semprini et al. (1993) in a sandy aquifer site at Borden, Ontario, showed that naturally occurring radon has potential for detecting and quantifying dense NAPLs in the saturated zone. Hopkins (1994) successfully validated radon's use as a NAPL tracer by verifying the linear equilibrium partitioning model of radon. This model predicts decreasing aqueous radon concentrations as the residual NAPL saturation increases. This research explores the practicality of using radon to evaluate the performance of NAPL remediation technologies.

The efficacy of pump-and-treat technique, a commonly used and a highly recommended technology, in NAPL remediation is minimized due to the immiscibility of NAPLs with water. In order to increase the efficiency of the pump-and-treat technique in remediating NAPL contamination, surfactants are being employed of late. Surface active agents aid in considerably increasing the aqueous solubilities of NAPLs by either solubilization or mobilization mechanisms. This results in significantly improved efficiency of contaminant extraction and also reduction in the number of pore volumes and time required for restoration of the aquifer (Shiau et al., 1992). The effectiveness of surfactant-enhanced NAPL remediation technology is evaluated by radon in this study.

Objectives

The overall objective of this research was to evaluate the practicality of radon-222 method for monitoring the progress of NAPL remediation. A two-fold study was conducted towards that end, the components of which were to:

- ◆ Evaluate the effectiveness of surfactant flushing technology in remediating NAPL contaminated soil columns.
- ◆ Validate radon's use as a tracer for monitoring the progress of NAPL cleanup efforts in the saturated zone.

The various tasks undertaken in this research to achieve these particular objectives were to:

- conduct preliminary experiments to test the efficiency of the surfactant chosen for the study, Triton® X-100, in solubilizing soltrol at residual concentrations in soil columns.
- develop independent methods for analyzing aqueous and sand samples from the soil columns for monitoring cleanup - test the practicality of using total organic carbon (TOC) analyses for aqueous samples and high density polyethylene (HDPE) strip tests for sand samples.
- perform micro-column studies to determine the optimal concentrations of surfactant for remediating residual soltrol saturations.
- conduct repeated batch exchange experiments on Borden sand packed columns at 1.0%, 5.0%, and 8.0% residual soltrol saturations with the selected concentrations of aqueous surfactant solutions; the columns have been used in previous studies by Hopkins, 1994.
- quantify the NAPL in the columns before remedial action and, as the remediation process proceeds using the linear equilibrium partitioning model of radon (Hopkins, 1994); verify model predictions that the maximum aqueous radon concentrations in the columns would increase and the

retardation of radon transport would decrease as the columns gradually get cleaned up.

- compare the results based on radon quantification with those from TOC analyses and HDPE strip tests to assess the reliability of the estimations made.
- evaluate the efficiency of triton in remediating soltrol contamination.

Chapter 2

Literature Review

Introduction

The use of radiotracers to assess the effectiveness of the remediation efforts to cleanup contamination due to Non-Aqueous Phase Liquids (NAPLs) is a relatively new concept. Some research has been done on the use of radioisotopes as groundwater tracers (Hoehn, 1992; and Semprini, 1985). A few studies are available on the use of stable partitioning tracers for detecting NAPLs in the subsurface (Tang, 1992; Wilson et al., 1995; Jin et al., 1995). Some work has been done employing radon as an indicator for the detection and quantification of DNAPLs in the saturated zone (Semprini et al., 1993; Hopkins, 1994; Tasker, 1995). This research aims at the possibility of extending the scope of radon's use as a tracer and utilizing it to evaluate the success of NAPL remediation efforts.

Surfactant enhanced NAPL recovery has also been extensively researched over the past few years owing to the seriousness of NAPL contamination problems. Research has involved both laboratory testing of the efficiency of surfactants to aid in remediating NAPL-contaminated aquifers (Pennell et al., 1993; Pennell et al., 1994; Soerens et al., 1992; and Shiau et al., 1992) as well as field demonstrations (Fountain, 1992; and Kimball et al., 1992).

The present study is undertaken to develop a non-intrusive means of performance assessment of NAPL remediation technologies. Radon is chosen as the tracer for its unique properties. As a radioactive tracer, radon offers advantages such as abundance, easy detectability, and chemical inertness. In addition, its ability to partition into organic phase liquids adds to its utility as an indicator to estimate the success of NAPL remediation efforts. We decided to test the effectiveness of most recent development in remediating NAPLs, the surfactant enhanced aquifer remediation (SEAR) technique, using radon as the tracer.

Radon

Radon is a radioactive, odorless, colorless, inert gas having an atomic number of 86. Radium undergoes α -decay to form radon in the naturally occurring uranium and thorium decay series. Radon exists in a gaseous state at all aquifer and surface temperatures (Kruger and Semprini, 1987). At low concentrations, radon is completely soluble in water. Its solubility in water is inversely proportional to temperature.

Radon-222 is ubiquitously found in the subsurface due to the abundance of uranium deposits in the earth's crust and the continuous radioactive decay of uranium and its daughter product, radium-226. Naturally occurring radon thus makes its use as a tracer, economical. Radon, being a noble gas, is chemically inactive. It does not interact with the subsurface fluid components or adhere to the aquifer matrix. Hence, it can be considered as a conservative and non-destructive tracer after accounting for its radioactivity. Interference with other elements or molecules which is common with chemical tracers is eliminated when radon is utilized.

Radioactivity of Radon

It is easy to detect radon and make sensitive measurements with high precision due to its radioactivity. Radon-222 is produced from α -decay of radium-226 and in turn undergoes radioactive decay to form polonium-218 through α -decay. The first order radioactive decay law (Eq. 2.01) governs the rate of production of radon and its subsequent decay rate.

$$\frac{dN}{dt} = -\lambda N \quad (\text{Eq. 2.01})$$

where N Number of radioactive atoms present in the source
 λ Decay constant, a characteristic property of the isotope
t Time during which decay occurs

The solution to the above differential equation yields the general radioactive decay equation (Choppin and Rydberg, 1980) given below.

$$N = N_0 e^{-\lambda t} \quad (\text{Eq. 2.02})$$

where N_0 Number of radioactive atoms present at initial time, t_0

Radon concentrations are reported in radioactivity units of Curies, where 1 Curie is equal to 3.7×10^{10} disintegrations per second (Kruger and Semprini, 1987). Half-life ($t_{1/2}$) is also commonly used to express radioactivity. It is defined as the time required to reduce the amount of radioactive material present to half its original amount and is given by the equation:

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \quad (\text{Eq. 2.03})$$

An equilibrium is achieved between the parent radionuclide and its daughter when no external removal mechanisms other than decay are present as given in Eq. 2.04 (Choppin and Rydberg, 1980):

$$\lambda_{\text{parent}} N_{\text{parent}} = \lambda_{\text{Daughter}} N_{\text{Daughter}} \quad (\text{Eq. 2.04})$$

Since the half-life of radium-226 (1600 years) is very long compared to that of radon-222 (3.83 days), it is reasonable to assume that concentration of radium and therefore, radon's source term is constant over the experimental period. Another equation of importance (Eq. 2.05) gives the build up of radon in a closed system.

$$C = C_{\infty}(1 - e^{-\lambda t}) \quad (\text{Eq. 2.05})$$

where C Radioactive concentration of radon, pCi/L

C_{∞} Radioactive concentration of source, radium, pCi/Kg

With a half-life of 3.83 days, it takes about 20 days for radon to reach approximately 98% of its secular equilibrium concentration.

The disintegration of radium to radon through alpha-particle decay is accompanied by the release of 86 Mev of decay energy. This energy is dissipated by the radon atom during its travel through the aquifer medium either by direct recoil or diffusion or combination of both the processes. The fraction of radon produced in the grains that enters the pore fluid is defined as the emanating power, E_p , and is given by Eq. 2.06 (Kruger and Semprini, 1987).

$$E_p = \left[\frac{R_p}{4} + \left(\frac{D_r}{\lambda} \right)^{1/2} \right] S_A \rho_r \quad (\text{Eq. 2.06})$$

where E_p Emanating power, pCi/pCi
 R_p Recoil path length of radon, m
 D_r Solid phase diffusion coefficient, m^2/s
 S_A Specific surface area, m^2/Kg
 ρ_r Density of the rock, Kg/m^3

Hence, for an aquifer material with specific surface area of $1 \times 10^3 m^2/Kg$, density of $2710 Kg/m^3$, recoil path length of $3 \times 10^{-8} m$, and diffusion coefficient of $8 \times 10^{-24} m^2/s$, the estimated emanating power would be 2.56%. Generally reported values for emanating power varied from less than 1% to 30%. The other parameters that influence emanation of radon into water are hydrothermal conditions such as moisture content, temperature, permeability of the medium and mineralogy.

Radon in Groundwaters

Radon is found in the pore fluids of saturated zone due to its continuous emission by radium-bearing aquifer solids. The concentration of radon in stationary geofluids is dependent on the content of radium in the aquifer material, nature of the aquifer medium, and the emanating power. This is expressed in equation (Eq. 2.07) which gives equilibrium aqueous radon concentration, C_{Rn} , in the saturated zone.

$$C_{Rn} = \frac{C_{Ra} E_p \rho_b}{e} \quad (\text{Eq. 2.07})$$

where C_{Rn} Aqueous radon concentration, pCi/L
 C_{Ra} Radium concentration, pCi/Kg
 E_p Emanating power, atom/atom
 ρ_b Bulk density of aquifer solids, Kg/L
 e Porosity of the aquifer

Some typical concentrations of radon found in groundwaters are in the range of 0.017 - 135 nCi/Kg in liquid dominated aquifers and 8 - 307 nCi/Kg in vapor dominated aquifers (Semprini, 1985). Radon has low solubility in water and preferentially partitions into the vapor phase, if the latter is present. The ratio of radon concentration in the liquid of interest to its concentration in air is termed as the Ostwald coefficient, L.

$$L = \frac{[C_{Rn}]_{Liquid}}{[C_{Rn}]_{Air}} \quad (\text{Eq. 2.08})$$

Table 2.01 Ostwald Coefficients and Estimated Organic-Water Partitioning Coefficients for Radon-222 (adapted from Hopkins, 1994)

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

The ability of radon to partition between two liquid phases is measured by the partition coefficient, K. The partition coefficient is defined as the ratio between the Ostwald coefficients for radon in the liquids concerned, according to Nerst Distribution Law (Denbigh, 1971). It can be inferred from the partition coefficient

values for radon-222 shown in Table 2.01 that radon prefers to concentrate in the organic phase than in the aqueous phase. This particular property of radon makes it a potential candidate for use as NAPL indicator.

A linear equilibrium partitioning model has been proposed and verified for radon distribution between aqueous and nonaqueous phases (Hopkins, 1994). It follows from the fact that the ratio of radon concentration in the NAPL phase, C_N , to that in the water phase, C_w , which is also referred to as the partition coefficient, K , is a constant (Eq. 2.09).

$$K = \frac{C_N}{C_w} \quad (\text{Eq. 2.09})$$

In a saturated system with two immiscible phases, partitioning of radon, emanated by the aquifer solids, between the two phases can be expressed as:

$$C_{Rn} = S_N C_N + S_w C_w \quad (\text{Eq. 2.10})$$

where S Volumetric phase saturation, L/L

C Concentration of radon in the phase, pCi/L

C_{Rn} Equilibrium Aqueous radon concentration, pCi/L

From equations 2.09 and 2.10, we get an expression for the ratio of equilibrium radon to aqueous radon concentration in terms of a known NAPL saturation, S_N , and radon partitioning coefficient for the NAPL, K .

$$\frac{C_{Rn}}{C_w} = 1 + S_N(K - 1) \quad (\text{Eq. 2.11})$$

It is obvious from Equation 2.11 that the presence of residual NAPL results in a decrease in aqueous radon concentrations. This is due to partitioning of a fraction of equilibrium radon into the residual NAPL present. The deficit in aqueous radon concentrations increases with increase in NAPL residual saturations. A NAPL for which radon has high partitioning coefficient also tends to decrease aqueous radon concentrations considerably.

The phenomenon of retardation is exhibited by groundwater constituents due to adsorption or partitioning mechanisms. They move at a slower rate in the

aquifer than the groundwater. Retardation can be expressed either as the ratio of velocities (Fetter, 1993) or as a function of volumetric phase saturations and partitioning coefficient (Semprini et al., 1995). In case of radon, retardation, R , is given by,

$$R = \frac{V_{\text{Groundwater}}}{V_{\text{Radon}}} = 1 + K \left(\frac{S_N}{S_W} \right) \quad (\text{Eq. 2.12})$$

Retardation is profoundly evident in the delay of breakthrough of radon as the residual saturation of NAPL increases in the columns. So when a NAPL-contaminated column is being cleaned up, translation of the radon breakthrough curve is expected as retardation decreases with decreasing residual saturation.

Nonaqueous Phase Liquids

Non-Aqueous Phase Liquids (NAPLs) are synthetic organic compounds with characteristic low aqueous solubilities. NAPLs may be a single toxic compound (for example: trichloroethylene, TCE) or a mixture of harmful hydrophobic organic compounds, HOCs (for example: gasoline, soltrol-220). Although NAPLs are sparingly soluble in water, their water solubilities are several orders of magnitude above their drinking-water standards (see Table 2.02). Therefore, they are ubiquitous undesirable groundwater contaminants.

Depending on the properties and volume of the NAPL released, it is found in different environmental spheres of the earth. As illustrated in Figure 2.01, when released at or near earth's surface, a part of the NAPL will volatilize into the atmosphere; another fraction will be trapped in the pore spaces of the vadose zone and the saturated zone as residual saturation; and, a third portion will migrate further down the saturated zone until it encounters an impermeable layer or reaches groundwater.

Table 2.02 Properties of selected NAPLs (Montgomery, 1994)

	CT carbon tetrachloride	CF chloroform	TCE trichloroethylene	Soltrol- 220
Formula	CCl_4	CHCl_3	$\text{CHCl}=\text{CCl}_2$	$\text{C}_{15}\text{H}_{32}$ ^a
Boiling Point (°C)	76.5	61.7	87.2	-
Aqueous Solubility @ 20°C (mg/L)	800	8000	1100	n/a
Specific Density ¹	1.594	1.489	1.464	0.809 ^b
Log Octanol Water Partition Coefficient	2.73-2.83	1.90-1.97	2.29-3.30	-
U S Drinking Water MCL ² (µg/L)	5	100	5	n/a

¹ at 20 °C; ² Norris et al., 1994; ^a Estimated formula; ^b Hopkins, 1994

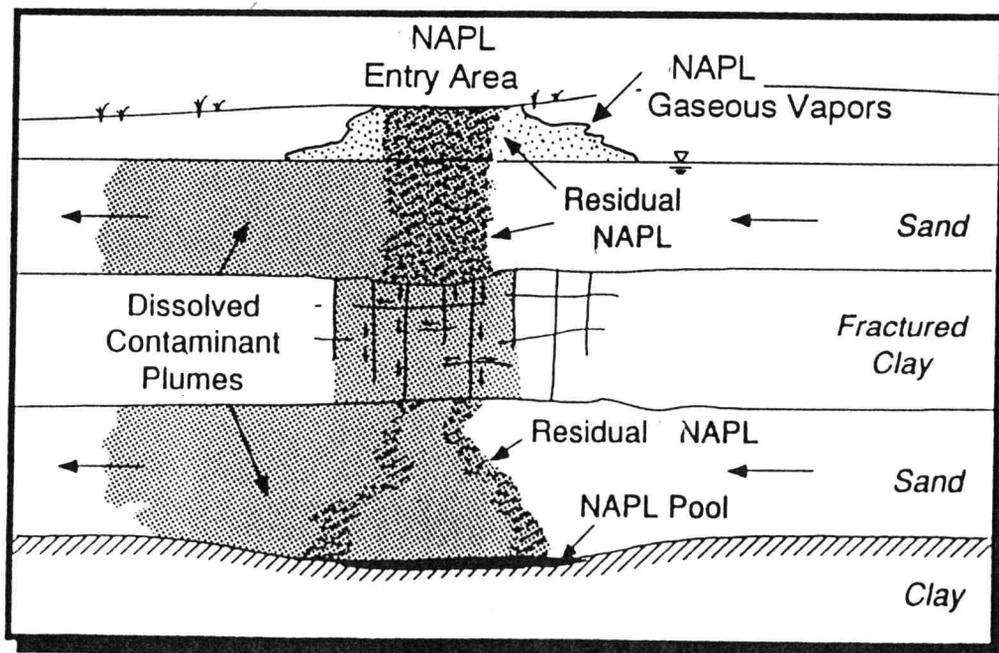


Figure 2.01 Distribution of NAPL Chemicals among Various Phases in the Subsurface (modified from Cohen and Mercer, 1993)

NAPLs can be divided into two types, namely LNAPLs and DNAPLs, based on their characteristics. Light Non-Aqueous Phase Liquids (LNAPLs), such as gasoline, diesel and motor oil, are less dense than water. Hence they float on water and occur as free product near the water table. Dense Non-Aqueous Phase Liquids (DNAPLs), such as carbontetrachloride (CTET), 1,1,1-trichloroethane (1,1,1-TCA) and 1,2-dichloroethane (1,2-DCE), being denser than water sink through to the saturated zone. It is difficult to remove them because the DNAPL loses contiguity with the mineral surface and gets trapped within the pores of the aquifer media.

Halogenated solvents which are DNAPLs are the most frequently detected organic contaminants in the saturated zones at industrial or waste disposal sites. This is because of their extensive production and use, relatively high mobility as a separate phase (high density:viscosity ratio), and significant solubility (Cohen and Mercer, 1993). It is suggested by recent research that the NAPL forms continuous or discontinuous blobs within the pore bodies and water flows around the blobs. They slowly dissolve into the infiltrating pore water and contaminate groundwater eventually. Thus, NAPLs serve as persistent sources of contamination and so, are a major environmental concern.

Properties of NAPLs

It is essential to study the properties of NAPLs as they largely dictate their subsurface behavior and movement. Some properties of DNAPLs (many principles apply to LNAPLs as well) that are of importance in this respect are discussed here.

In case of halogenated solvents which are DNAPLs, the density is directly proportional to their degree of halogenation. The typical range of densities for DNAPLs is between 1.01 and 1.65 (Cohen and Mercer, 1993). The rate of vertical movement of a DNAPL in the subsurface is governed by its density.

Density differences (between water and DNAPL) of different magnitudes, of about 1% (Mackay et al., 1985) to 0.1% (Schmelling, 1992), have been demonstrated to affect the flow of fluid in the subsurface.

Hydraulic conductivity varies inversely with absolute fluid viscosity. Therefore, assuming all other factors to be similar, a NAPL with low viscosity spreads more quickly than a high viscosity NAPL. Viscous fingering fosters deeper NAPL penetration and increased dissolution of NAPL into pore fluid. Viscosity also affects the rate of lateral spreading of DNAPLs when an impermeable layer is encountered. Mobility ratio, which is defined as the ratio of the mobility of the displacing fluid (relative permeability/viscosity for water) to the mobility of the displaced fluid (for NAPL), is another factor that is based on viscosity. A mobility ratio of less than 1 is desirable for the flow and recovery of NAPL (Cohen and Mercer, 1993).

Temperature, presence of cosolvents above certain concentrations, and, dissolved organic matter enhance the solubility of hydrophobic organic compounds in water whereas salinity has the opposite effect. Effective solubility of NAPL components is another important factor that affects NAPL dissolution into water and its consequent depletion from the subsurface. Also of concern is the fact that NAPLs are generally found in groundwater at concentrations much less than their aqueous solubilities. This can be attributed to non-uniform groundwater flow, aging of NAPL and reduction of NAPL-water contact area with time. Hence, dissolution process cannot be solely relied upon to effectively remove substantial quantities of NAPLs economically.

DNAPL migration in the subsurface is also dependent on capillarity, which is caused by the pressure difference between the two immiscible fluids at the interface. In the saturated zone, fine-grained layers act as barriers and restrict the flow of NAPL into the media until a threshold capillary pressure is overcome. DNAPL saturation increases with capillary pressure because higher capillary pressures are required to displace water from incrementally smaller pore openings (Cohen and Mercer, 1993).

The preferential spreading of one fluid over solid surfaces in a two-fluid system is referred to as wettability. This is governed by the interfacial tension (IFT). Adsorption and/or deposition on mineral surfaces of organic matter and surfactants derived from NAPL or water (Honarpour et al., 1986; Thomas, 1982; JBF Scientific Corp., 1981), and aging (Craig, 1971) favor NAPL wetting and hence, migration of NAPLs into low permeability zones.

The transport of DNAPL is primarily governed by the interfacial tensions developed at the interface between immiscible fluids due to unbalanced forces of molecular attraction. As a result of interfacial tension, non-wetting DNAPLs tend to form globules in water and water-saturated media (Cohen and Mercer, 1993). The interfacial tensions can be altered suitably to solubilize or mobilize the DNAPL by modification of temperature and pH, and/or presence of surface-active agents or gas in solution (Schowalter, 1979).

The fraction of the pore volume occupied by discontinuous blobs of NAPL, which cannot be mobilized by altering the capillary pressure or through displacement by another immiscible fluid, is termed as residual saturation. Reported values for residual saturation in saturated media are in the range of 0.10 to 0.50 (Cohen and Mercer, 1993). Removal of NAPL trapped in both vadose and saturated zones as residual saturation is necessary to avoid leaching of the contaminant to ground water by water infiltrating through the zones. As NAPLs are present as immobile globules at residual saturation, it is difficult to collect them to a well and remove them.

As many of the contaminants in residual saturation have greater affinity towards NAPL than water, the dissolution of contaminants in water is very slow (Schmelling, 1992). So the residual NAPL acts as a continuous source of contamination for decades. This stretches out the time and increases volumes of water required to remediate the aquifer. Thus arises the necessity for significantly elevating the aqueous solubility of the NAPL to make remediation efforts markedly efficient.

In addition to the NAPL properties, porous media characteristics also control the fate and transport of NAPLs in the subsurface. Fine-grained layers of the media with low permeabilities act as barriers for penetrating NAPLs and foster lateral spreading of NAPLs. In the saturated zone, DNAPLs preferentially flow through soil and rock fractures, and root holes that offer little resistance to flow. The structure of the soil, heterogeneity, and grain-size distribution affect the amount of NAPL trapped as residual saturation and its manner of distribution. Thus uniform distributions of NAPLs are not likely to occur.

Site Characterization

Prior to designing and implementing remedial measures, NAPL contaminated sites need to be evaluated for the presence and migration potential of NAPLs. This is difficult due to the complex nature of NAPL behavior and transport in the subsurface. Inadequate precautionary measures may lead to unwanted spreading of NAPL contamination and elevated remedial expenses. Site characterization should be reasonably elaborate to cover the following aspects -- estimation of quantities and types of NAPLs released and present in the subsurface, delineation of DNAPL release source areas, determination of subsurface NAPL zone and site stratigraphy, determination of immiscible fluid and fluid-media properties, and determination of the nature, extent, migration rate and fate of contaminants (Cohen and Mercer, 1993).

There are demonstrable and well defined techniques to assess most of the above mentioned parameters. However, direct methods for detecting and delineating subsurface NAPLs are presently limited. Invasive methods, such as, drilling and well installation, are risky as they promote migration of contamination to clean areas. Hence, non-invasive methods are gaining popularity. Surface geophysical surveys, soil gas analysis, and air photo-interpretation are a few indirect techniques for subsurface NAPL characterization but they are expensive and sometimes, have

limited applicability. Recently, research is directed towards evolving cost-effective and non-destructive means for detecting and quantifying subsurface NAPL contamination utilizing radioactive (Semprini et al., 1993; Hopkins, 1994) and stable (Mackay et al., 1995) tracers.

Surfactants

An acronym for SURFace ACTIVE AgeNTS, Surfactants, refers to “materials which exhibit the characteristic of modifying interfacial interactions by way of enhanced adsorption at interfaces” (Myers, 1992). Surfactants have a wide range of application in day-to-day life as motor oils, lubricants, laundry detergents, food additives, and of late, they are being used extensively for oil recovery.

Surfactant molecules consist of two portions in their chemical structure which imparts amphiphilic character to the molecules. The lyophilic or the hydrophobic tail has little attraction to the bulk phase or water. On the other hand, the lyophobic or the hydrophilic portion, which forms the polar head group, has strong affinity to the bulk aqueous phase. It is this amphipathic nature that contributes to the surface activity of the surfactants. Based on the nature of the charge on the polar head group of the molecule, surfactants are broadly classified as Anionic Surfactants (Sodium dodecyl sulfate, SDS), Cationic Surfactants (Benzyl trimethyl-ammonium bromide), Amphoteric or Zwitter-ionic Surfactants (B-N-alkyl amino propionic acid), and Non-ionic Surfactants (Triton X-100).

Removal Mechanisms

Two general mechanisms by which surfactants enhance remediation of NAPLs are solubilization and mobilization (West et al., 1992). Surfactants tend to decrease the interfacial tensions between the NAPL, water, and soil phases which

helps the NAPL to mobilize from the entrapping pores. They also increase the solubilization capacity of the NAPL in water through micelle formation thus, increasing their rate of removal.

The increased solubilities of NAPLs in water in presence of the surfactants is brought about by a unique phenomenon called micelle formation. Micelles are dynamic clusters of surfactant molecules which are formed as a result of the thermodynamic interactions between water and the hydrophobic portions of the surfactant molecules. The concentration of a surfactant in the bulk solution which leads to a change in solution properties and to the formation of micelles is known as Critical Micelle Concentration (CMC) (Myers, 1992). The CMC is dependent on the surfactant structure and composition, temperature, ionic strength and the presence and type of organic additives in the solution (Rosen, 1989).

The non-polar interiors of the micelles incorporate the hydrophobic and non-polar organic contaminants of the contaminated water and thereby, increase the contaminants' aqueous solubilities manifold. In an aqueous system, the tendency of the contaminant to concentrate inside the micelle is directly proportional to its partition coefficient. Hence, the solubilities in water of the NAPLs with large K_{ow} is increased remarkably in the presence of surfactant micelles. For solubilization to take place, it is necessary that surfactant micelles be present and remain stable in the aqueous phase.

The requirement for mobilization is the occurrence of a proper balance of the hydrophilic and hydrophobic interactions at the interface to achieve large reductions in the interfacial tension (IFT) (West et al., 1992). Typical values of IFT for NAPL-water interface, γ_{NW} , are 30 - 50 dynes/cm (Wilson et al., 1990). The higher the IFT, the more the energy (pressure drop per unit of distance between the injection and extraction wells, $\Delta P/L$) required for mobilization of the NAPL blob. Achieving an ultra low IFT of less than 10^{-3} dynes/cm is the main consideration for selecting an appropriate surfactant to attain mobilization (Rosen, 1989).

When a surfactant dissolves in water, the hydrophobic tail increases the overall free energy of the system by disrupting the water structure. This lessens the work required to increase the interfacial area and consequently, to decrease the interfacial tension of the system (Myers, 1992). The rate of NAPL removal through mobilization is far greater than that due to solubilization. But it should be judiciously employed for enhancing removal of NAPLs since there is a great potential for the mobilized NAPL to spread to uncontaminated zones of the aquifer.

Selection Criteria

Besides efficient solubilization and mobilization of the NAPL, there are other factors that need to be kept in mind while selecting surfactants. Surfactants should be readily biodegradable lest they are left behind in the aquifer after the operation has been carried out. They should also be compatible with the contaminated medium and the contaminants. Adsorption of surfactant to the aquifer sediments reduces the active surfactant concentration. The lower the water solubility of the surfactant, the higher the tendency for adsorption. Surfactants should be selected such that adsorption is minimal. Another consideration is the precipitation of surfactants. The susceptibility of the surfactant to precipitation can be decreased by factors that lower the CMC of the system. For example, ionic and nonionic surfactant mixtures have a lower CMC and consequently a higher tolerance for ions that would precipitate the ionic surfactant by itself (West et al., 1992).

Triton[®] X-100, a nonionic surfactant, was chosen for this research due to its ready availability and low foaming characteristics. Also, previous studies show that it is capable of desorbing HOCs from soils and sediments. Moreover, it is relatively stable under high temperature and harsh chemical conditions and less susceptible to precipitation.

Laboratory Studies at Oregon State University

The potential of Radon-222 to detect and quantify DNAPLs in the saturated zone has been studied at Oregon State University (OSU), Corvallis (Hopkins, 1994). The present research work has been built upon those experiments. Hence, it is worthwhile to provide the results from that study.

The laboratory study was two-fold. It involved verification of the proposed linear equilibrium partitioning model for radon in a two-phase system, and testing whether the resulting relationship can be successfully applied to estimate residual NAPL saturations in a complex situation.

In order to verify the partitioning model, five sets of soil column experiments were run. Clean sands from Borden aquifer site, Ontario, were mixed with known amounts of soltrol, the NAPL selected for the experiments. Thus soltrol-contaminated Borden aquifer material served as the aquifer medium in these columns. The aqueous radon concentrations were determined at various residual saturations of soltrol ranging from 0.0 to 8.0 percent. The columns were allowed to reach a radon-222 equilibrium and then flushed with deaired (radon free) synthetic Borden water. The procedure used for exchanging the columns is similar to that described for remediation batch exchange columns under Procedures for Exchanging the Columns (in Chapter 3). For each batch exchange, the effluent pore fluid was collected and the effluent samples were analyzed for radon according to the procedure outlined in Radon Quantification (refer Chapter 3).

Breakthrough curves, plots of aqueous radon concentration versus volume of water exchanged, were obtained from the data. As the initial effluent is radon-equilibrated pore water, the initial samples have high aqueous radon concentrations. The aqueous radon concentrations gradually decrease as the fresh influent starts getting displaced. The volume of water where aqueous radon concentration equals 50% of the maximum value is defined as the breakthrough point of radon. The results of these studies are summarized in Figure 2.02. We see that as the residual saturation increases, the peak aqueous radon concentration decreases and the

breakthrough point is delayed. This is due to partitioning of radon into the organic phase and consequent retardation. The partitioning coefficient for radon between the soltrol mixture and pore water fluids was estimated to be 38.4, which agrees well with estimates for hydrocarbons given in Table 2.01.

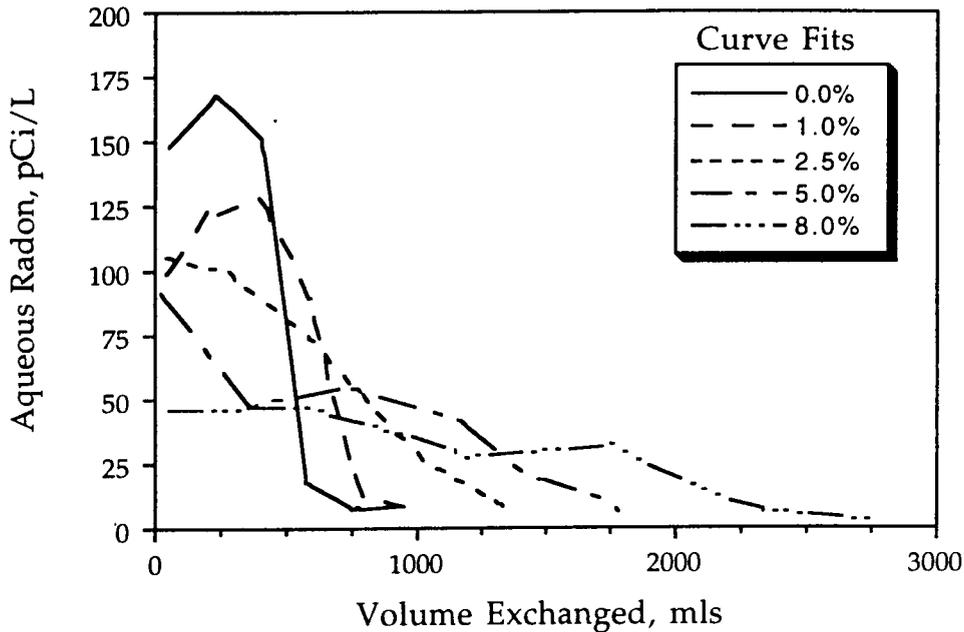


Figure 2.02 Breakthrough Curves for 0.0 to 8.0 Percent Residual Saturation Columns (Hopkins, 1994)

The one-dimensional 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. The experimental column had been packed with clean Borden sand upto 30 cm from the bottom of the column. Soltrol-contaminated Borden sand at an estimated 5% residual saturation followed for a length of 15 cm. The top 55 cm length of the column was packed with soltrol-free Borden sand. The static test involved sampling of the radon-equilibrated pore fluid through the six different ports along the column. The measured aqueous radon concentrations agree well

with the values predicted using the linear partitioning model except for the end effects (Figure 2.03).

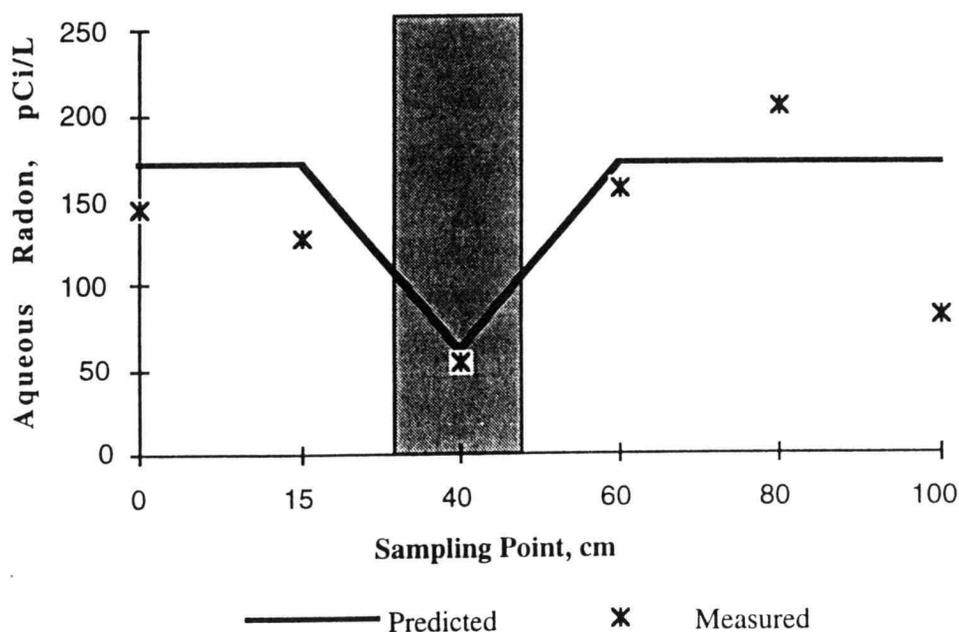


Figure 2.03 Predicted and Measured Aqueous Radon Concentrations from Static Test (Hopkins, 1994)

The concentration of radon was greatly attenuated in the NAPL-zone as expected and the recovery to background levels was fairly quick. The static test results indicate the potential of radon as a tracer for the presence of NAPLs in the saturated zone.

A dynamic test was also run using the same one-dimensional column that was previously used for the static test. The only difference between the tests was that synthetic Borden groundwater was pumped through the column at a constant rate of 148 mls/day to mimic flow conditions in the field. Samples were collected

from the ports when the system was assumed to have reached steady state. As can be seen from Figure 2.04, the observed aqueous radon concentrations deviate from the predicted trend.

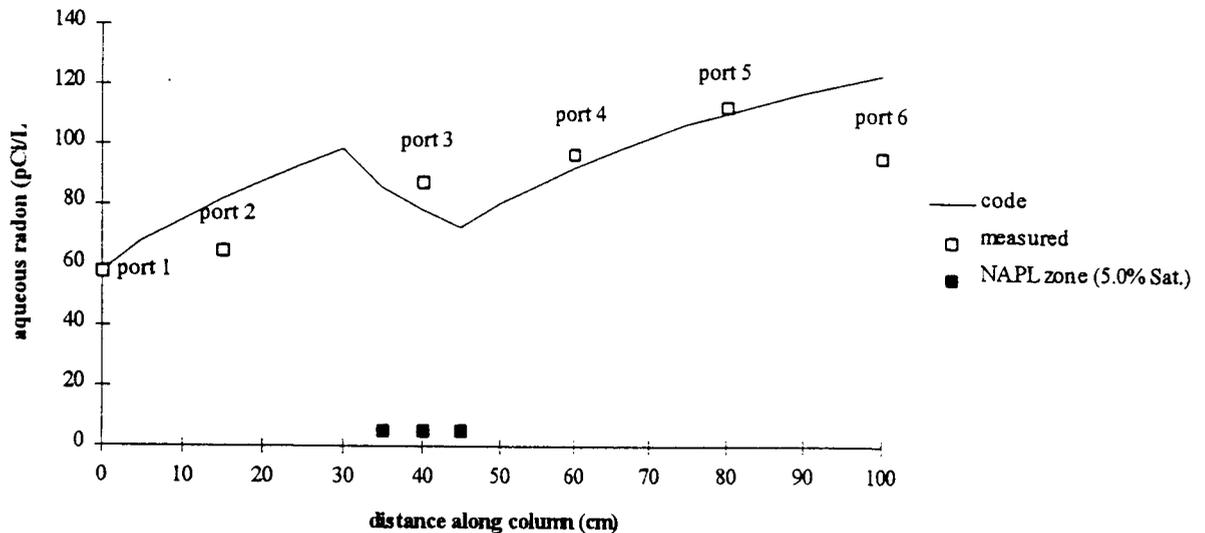


Figure 2.04 Comparison of One-Dimensional Test Results with Modeled Equilibrium Aqueous Radon Concentrations at Sampling Ports (from Tasker, 1995)

It has been hypothesized that the NAPL in the 15 cm zone might have redistributed itself during the mixing observed while resaturating the column in between unsuccessful attempts to sample the column (Hopkins, 1994). The results from the dynamic test are, however, inconclusive and additional work needs to be done to see if radon can be used as a NAPL indicator in flow situations.

Summary

Proper characterization and delineation of subsurface NAPLs is very essential for the success of NAPL remediation efforts. The laboratory studies at OSU indicated that radon-222 has the potential to detect and quantify NAPLs. Hence, radon, as a tracer for NAPLs, provides a non-destructive and economical means of characterizing subsurface NAPL contamination.

The objective of this research is to further explore the practicality of the radon-222 method. Another significant utility of radon as a tracer could be in the evaluation of the effectiveness of NAPL remediation techniques. The possibility of using radon to monitor the progress of NAPL cleanup efforts in the saturated zone is examined in this study.

In order to achieve this objective, soltrol-contaminated batch exchange columns that had been used for the laboratory studies at OSU (described above) were used. As they had been used for previous studies, the conditions and behavior of the columns at various soltrol saturations were well established. The goal was to remediate the columns and quantify the removal of residual soltrol based on radon observations. These estimates would then be compared to estimates based on independent techniques to verify their accuracy.

The study also aims to evaluate the efficiency of surfactant flushing technique for NAPL recovery. We selected triton, a non-ionic surfactant, due to its ready availability and reported efficiency in solubilizing NAPLs. A series of micro-column studies were designed to test the effectiveness of triton before using it for remediating batch exchange columns. Preliminary studies also included development of alternative techniques for estimating the level of cleanup achieved in the soil columns, to compare with radon estimates. TOC analyses was developed for aqueous samples and HDPE strip test assay, for sand samples. The details of the methods used and the results of the studies are presented and discussed in the following chapters.

Chapter 3 Materials and Methods

Materials and Equipment Set-up

The Medium: This research was done as part of an ongoing project. The experiments were, therefore, conducted using columns that had been previously packed and used by Hopkins (1994) for evaluating radon-222's potential for detecting NAPLs. Hence, these columns had residual saturations of NAPL already in place. He also did extensive characterization of the Borden site sands which served as the aquifer medium in this study. He concluded that the primary constituents of the sand are quartz and feldspar. The density was measured to be 2.71 g/cm^3 and the organic carbon content, $0.018\% \pm 0.006\%$. The bulk radon emanation coefficient of the Borden sands was determined to be 0.030 - 0.033 pCi/g of solids.

The Contaminant: Soltrol-220[®] (soltrol) was employed as the NAPL as it is relatively safe, fairly hydrophobic and moderately volatile. Hopkins (1994) altered the spreading characteristics of soltrol by the addition of 0.5% by weight Lubrizol[®] and 0.01% by weight Sudan III dye in order to make it the wetting phase on the aquifer solids. This alteration immobilized the soltrol and enabled the construction of soil columns with known residual saturations of soltrol. The immobilized soltrol, therefore, represented an immobilized NAPL in the saturated zone. The columns used in this study had soltrol mixture at 1.0%, 5.0%, and 8.0% residual saturations.

The Cleanup Agent: Recent research has demonstrated that surfactants are efficient NAPL solubilizers. Triton[®] X-100 (Aldrich Chemical Company, Inc., Wisconsin), a heterogeneous nonionic octylphenoethoxylate surfactant, was selected for remediating soltrol-contaminated columns in this research. In addition to its ready availability and reported effectiveness in solubilizing organic compounds (Kan

et al., 1992), the advantages it offers as a nonionic surfactant were responsible for its selection.

Triton[®] X-100, molecular formula $C_8H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$, weighs 625 grams/mole and has a critical micelle concentration (CMC) of 112.5 mg/L (Edwards et al., 1994). Triton[®] X-100, density 1.07, was used as obtained without any modifications. Triton[®] X-100 (hereafter, triton) was added to distilled water on weight-volume basis to make the various concentrations desired. The procedures for making the various influent solutions used in this research are described in Appendix A.

Construction and Operation of Soil Columns

Micro-Columns:

Preliminary studies were designed to test the effectiveness of triton as a surfactant. Another purpose was to select the optimal surfactant concentrations for remediating the soltrol-contaminated soil columns at various residual saturations. These studies were done on a smaller scale, appropriately named micro-column studies, using glass culture tubes available in the laboratory. Open-top screw caps underlined by PTFE backed silicone septa were used to cap the culture tubes. The diameter of each micro-column was approximately 1.6 cm. The pore volume when packed with Borden sands was approximately 6 mls based on an estimated effective porosity of 0.40.

Micro-column studies were conducted for residual soltrol saturations of 1.0% and 5.0%. Clean Borden sand mixed with required amounts of soltrol served as the aquifer medium in the micro-column studies. As control, a micro-column was packed with clean Borden sand as the aquifer material.

The micro-columns (see Figure 3.01 for an illustration) were constructed as follows: The first step was to pack some glass wool at the bottom of the clean

and dry culture tubes to prevent clogging of the effluent collection needle by aquifer solids during the test. The micro-columns were then filled with synthetic Borden water to maintain saturated conditions in the column during filling (Semprini, personal communication, 1994). Clean or pre-mixed sands were spooned into the micro-columns and allowed to settle through the overflowing groundwater.

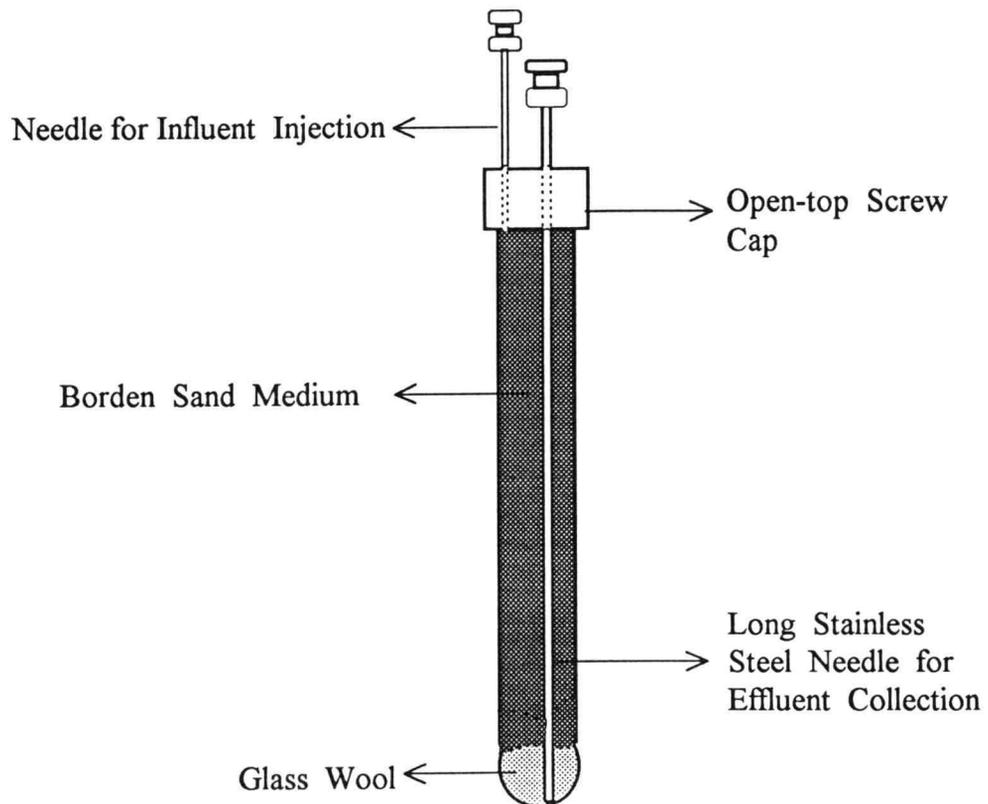


Figure 3.01 Details of Micro-column Design

The sand was periodically tapped and stirred with a glass rod to ensure that no air bubbles were entrapped during the packing. Each culture tube was filled to the neck with Borden sand and closed using a silicone septum (Kimble Corporation, IL) backed open-top screw cap. A long stainless steel needle (22 gauge) with a nichrome wire (28 gauge) in place was then forced through the

silicone septum into the sand and into the glass wool at the bottom of the culture tube. The nichrome wire was removed from the needle. The needle now acts as the effluent collection port.

Remediation Batch Exchange Columns:

Liquid chromatography columns (Kontes, NJ), 4.8 ID x 60 L in cm, equipped with semi-permeable teflon end caps (VWR, WA) and fitted with one ON/OFF valve (Whitey Co., Ohio) on each end were used for the remediation batch exchange experiments. The columns used for this study have been previously packed by Hopkins (1994). The total volume of each column was determined to be 1060 mls and the pore volume was approximately 445 mls based on a porosity of 0.42 estimated by Hopkins. To achieve the following residual saturations, Hopkins added the following soltrol mixtures: 1.0% residual saturation, 4.4 mls of soltrol mixture; 5.0% residual saturation, 22.6 mls of soltrol; and 8.0% residual saturation, 34.7 mls of soltrol. Hopkins packed the columns in lifts of dry sand and soltrol, mixing the column with a combination of end-over-end and rotational movements intermittently. The packed column was then placed in a vertical position, flooded with CO₂, and then saturated by passing about 10 pore volumes of deaired synthetic Borden groundwater through the bottom port (see Appendix C, Hopkins, 1994, for details).

The sands in all the columns had settled down during the time interval between their packing and their use in this research work. In order to reduce the end effects due to the lack of sand at the top of the column, Borden sand at corresponding residual saturations was added to each column in sufficient amounts to repack the column.

Procedures for Exchanging the Columns

Micro-columns:

The experimental procedure consisted of exchanging the pore fluids in the micro-columns with surfactant solutions of appropriate concentrations (see Triton® X-100 Solutions, Appendix A, for preparation instructions). The influent was injected into the micro-columns manually using a 1 cc disposable plastic syringe (monoject® Tuberculin Syringe) fitted with a short needle. Effluent samples were collected with a 1 cc glass-barrel syringe and transferred to 10 cc glass beakers. The average size of each effluent sample was approximately equal to the pore volume of the micro-column or its multiple.

The micro-columns were operated in a batch mode with exchanges of the micro-column fluid occurring between periods of flow interruption (about 1 to 10 days between exchanges). This was done to allow for substantial micelle formation in the micro-column so that more soltrol could be solubilized, and to mimic the operation of larger remediation batch exchange columns.

Micro-column studies were also conducted at higher temperatures. A circulating water bath was employed to heat the micro-columns to a temperature of about 50 °C. The intention was to study the effect of temperature on solubilization capacity of triton, if any, and to achieve faster cleanup of contaminated columns, if possible. The water in the water bath was pre-heated to 70 °C by adjusting the thermostat. The circulating water bath was then run to allow the hot water to pass through the polyethylene tubing wound around the whole length of the micro-column. Insulation was provided by the double layer of bubble wrap wound around the polyethylene tubing. The exchange of the micro-columns was performed after circulating water for at least seven hours.

Remediation Batch Exchange Columns:

The method developed by Hopkins (1994) was used for the remediation batch experiments with some alterations. The experimental procedure consisted of leaving a saturated Borden sand-packed column at a known residual soltrol saturation undisturbed for a period of 10 days or more to allow it to reach a radon-222 equilibrium. The equilibration time served two purposes in these experiments. It allowed for the radon that built-up in the closed system, (given by Eq. 2.05), to partition between the NAPL and the other pore fluid, synthetic Borden groundwater or triton. It also allowed more contact time that helped enhance the formation of surfactant micelles that in turn increased the rate of soltrol solubilization.

The columns were then exchanged with de-aired, hence radon free, surfactant solution or synthetic Borden water. Figure 3.02 shows a schematic for the batch exchange experimental set-up. The influent reservoir was placed at an elevated position to create a pressure differential. The pressure head caused flow of the influent from the reservoir into the inlet port of the column. The equilibrated pore water was collected as the effluent through the bottom outlet port.

Labeled and pre-weighed 125 ml serum vials with PTFE backed red rubber septa crimped-caps were used as effluent collectors. The sample volume ranged from 90 - 120 mls and was determined gravimetrically from the difference between weights of the vials measured before and after sample collection. The vials were purged with helium to reduce atmospheric radon in the vials and evacuated immediately prior to sample collection. Less vacuum was applied when the influent and the pore fluid contained triton since more resistance to flow was encountered and too high a vacuum resulted in draining of the column. The volume of influent flushed in each exchange varied from column to column, depending on its residual soltrol saturation. Care was taken to exchange sufficient influent solution in order

to obtain an entire breakthrough curve for radon. The vials were stored in an inverted position until they were analyzed for radon to reduce losses of radon.

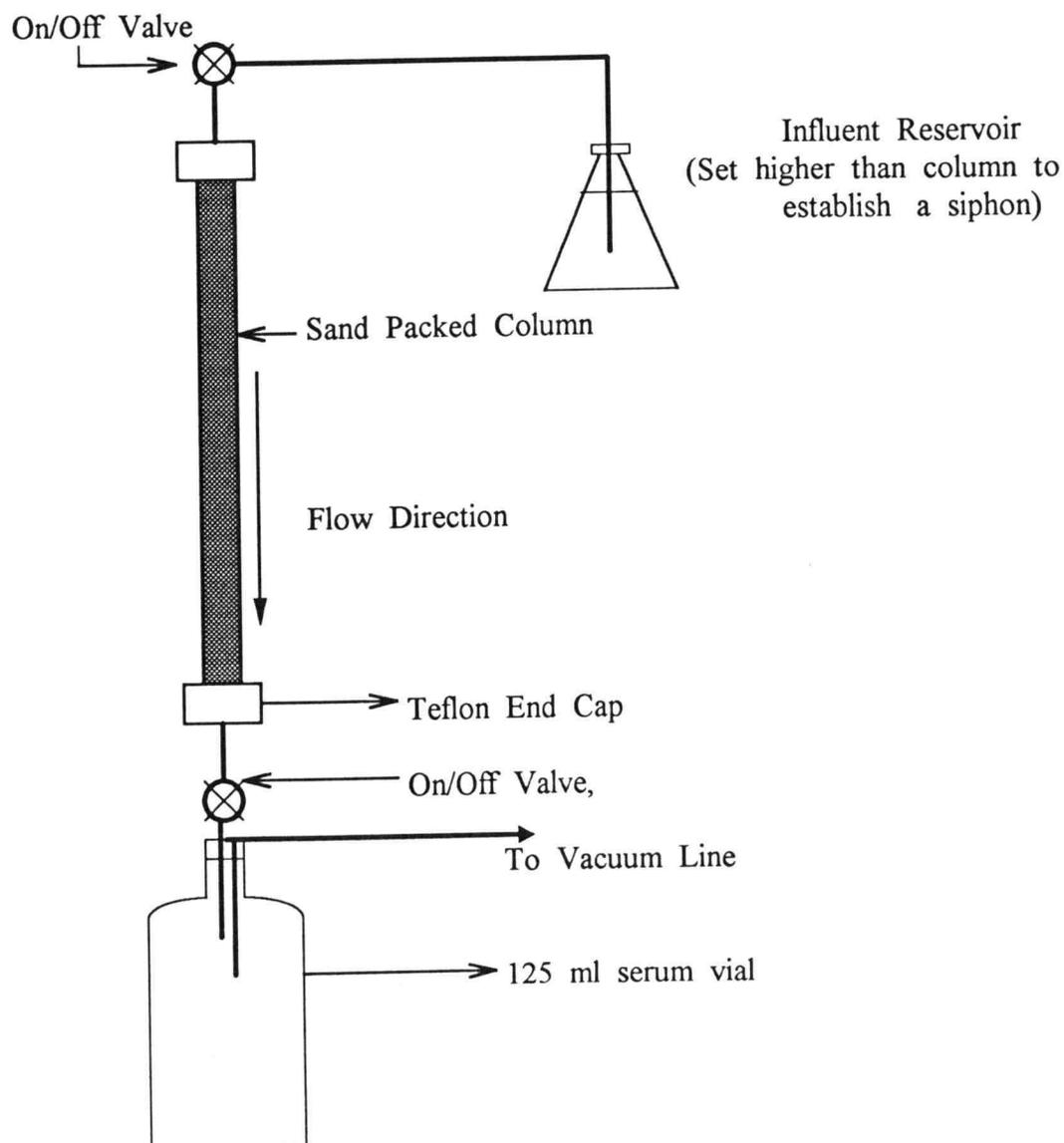


Figure 3.02 Remediation Batch Exchange Experimental Set-up

Remediation batch exchange studies were also conducted at higher temperatures with the intention of hastening the remediation of contaminated columns. A circulating water bath was employed for these studies and the operational procedure was similar to that used for micro-column studies at elevated temperatures. The columns were exchanged after about 12 to 20 hours of water circulation. The columns were not heated for longer time periods since radon emanation is temperature dependent. The method used to exchange the columns was the same as that described above for batch exchange experiments conducted at room temperatures. The vials with hot effluent sample were allowed to cool down to room temperature and then weighed to eliminate inaccurate measurements of sample volume.

Analytical Methods

The aqueous samples from micro-columns studies and remediation batch exchange experiments were analyzed for total organic carbon content. Some aqueous samples obtained from remediation batch exchange experiments were analyzed for radon. After the final batch exchange on each column, the sands from all the columns were tested for residual organic content using the HDPE strip test assay. The rationale for employing these analyses and the experimental procedures are discussed here in brief.

Total Organic Carbon (TOC) Analysis

TOC analysis was used to estimate the extent of soltrol solubilization achieved by each surfactant flushing, in the micro-columns as well as the batch exchange columns. As triton is an organic compound, its TOC content can be effectively used as a measure of the background TOC being added to the

columns. Furthermore, since soltrol is a hydrocarbon mixture, it can also be analyzed for TOC. The difference between the TOC contents of the influent and effluent solutions gives an estimate of the amount of soltrol that has been removed during the exchange of the column. Thus, TOC served as a gross measure of soltrol solubilized during each exchange. The results from the TOC analysis provided a basis for judging the performance of triton qualitatively at low residual saturations and quantitatively at high residual saturations. Another reason for using TOC analysis is that it was easy to perform in our laboratory.

The TOC contents of the influent and effluent samples were analyzed using a DC-190 High-Temperature TOC Analyzer (Rosemount Analytical Inc., Dohrmann Division, Santa Clara, CA) according to the procedures outlined in Appendix B Analysis of Total Organic Carbon in Samples. The TOC analyzer was primarily calibrated with standard Potassium Acid Pthalate (KHP) solution before analyzing the samples (refer Appendix B). It is assumed that soltrol gets oxidized as efficiently as KHP and so, the TOC values of the effluent samples calibrated to that of KHP are reliable and valid.

An attempt was made to obtain a calibration curve for TOC analyses based on known concentrations of aqueous soltrol solutions. The calibration curve was intended to be used as a basis for mass balance calculations. However, it was not possible due to immiscibility of soltrol in water. The hydrophobic soltrol formed discontinuous blobs when mixed with water. The aqueous soltrol solution thus obtained was not homogeneous which led to inaccurate and unreliable TOC measurements. Moreover, the DC-190 TOC analyzer was sensitive and could not handle samples containing blobs of concentrated soltrol.

The TOC of influent triton which served as the background is very high. The effluent samples generally contain triton in relatively higher proportions than soltrol. The difference in TOC values for effluent and influent samples yields an estimate of soltrol solubilized. However, there is an inherent error associated with this estimation as we are subtracting high numbers from higher numbers to obtain low numbers. Triplicates of each sample were analyzed and care was taken to

keep the standard deviation less than 5% in all cases to alleviate this error. Solutions of soltrol based in other organic solvents were not tried for obtaining the calibration curve as the organic solvents would represent high TOC. Thus, the mass balance calculations were based on theoretical TOC values for soltrol (refer Appendix F, Mass Balance Calculations for details).

HDPE Strip Test on Sands

The amount of soltrol remaining on the sand at the end of batch exchange solubilization experiments was determined using the HDPE strip test assay developed by Cary et al. (1991). This analysis was used to estimate the final organic content of the soil samples, thus indicating the extent of cleanup achieved in the micro-columns and the remediation batch exchange columns. HDPE strip test was also performed on sands prior to flushing batch exchange columns with triton in order to obtain an estimate of the initial residual soltrol saturation.

One of the limitations of the HDPE test is that the results are not accurate if detergents are present in the organic liquid or the soil. This is due to the fact that a significant amount of water may be adsorbed with the organic liquid in the polyethylene pores leading to erroneous measurements (Cary et al., 1991). Hence, prior to analyzing the sands, the micro-columns were flushed with distilled water to remove the triton solution as best as possible. The other procedure was to wash the sand before analysis.

The sand was spooned out into labeled weighed beakers. The organic (presumably, soltrol) content of the soil samples was determined according to the assay described in Appendix C HDPE Strip Test for Soil Samples. Two control samples were analyzed with each run of the strip test to calibrate the results. One control sample contained Borden sand with known amount of soltrol and the second consisted of water with known amount of soltrol. The sand control sample was used to eliminate the error due to soil particles trapped by the HDPE strip

during shaking. The efficiency of the strip to recover soltrol was measured by the water control. All the operational parameters such as size of the strips and duration of shaking for the control samples were kept as similar as possible to the test samples to enable standardization of the results. Corrections were applied to the results obtained from test samples to yield final estimations of residual organic content of the sand samples. The procedures for correction and estimation based on HDPE strip test results are described in Appendix G, Estimating Organic Content of Sand Samples.

Radon-222 Quantification

Quantification of radon in the aqueous samples involved two steps: (1) Extracting radon from the aqueous solution as gas into a scintillation flask, and (2) Measuring radon. The procedure developed by Stoker and Kruger (1975) was used for extracting radon from the aqueous batch exchange samples and counting it. The schematic of the extraction apparatus is presented in Figure 3.03.

The extraction procedure involves use of helium to strip radon from the aqueous sample. Traps T1 through T3 are used to remove water, water vapor, and gases other than radon from the gas stream as it flows through the extraction system. Radon from the gas stream adsorbs onto the granular activated carbon in trap T4, which is previously cooled down to $-45\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$ using a isopropanol dry-ice mixture. Trap T4 is then initially warmed to $45\text{ }^{\circ}\text{C}$ to remove noncondensable gases such as N_2 and CH_4 . Next, the GAC trap is heated to around $210\text{ }^{\circ}\text{C}$ in a closed system to desorb all radon from GAC. Finally, four to five successive aliquots of helium are used to transfer radon to an evacuated Lucas-type scintillation flask (SF) by means of a peristaltic pump. The details of the extraction procedure are outlined in Appendix D Extraction of Radon From Aqueous Samples.

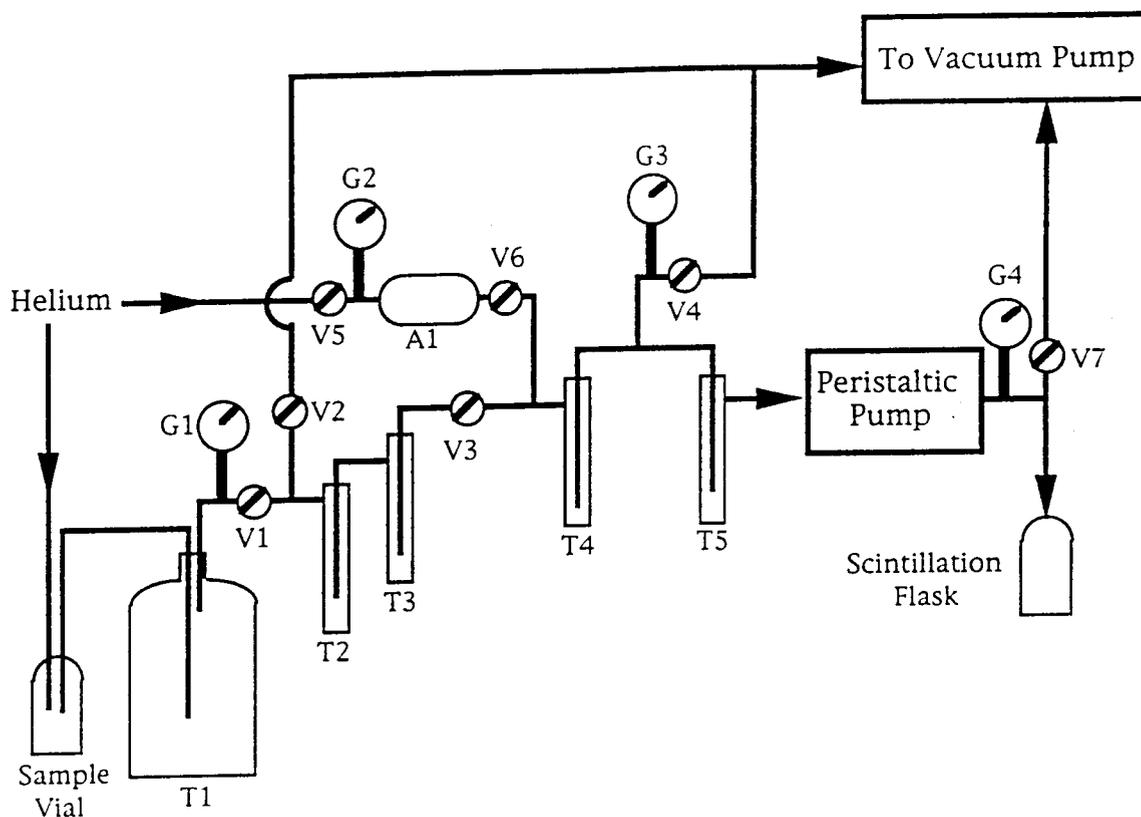


Figure 3.03 Schematic of Radon Extraction and Transfer Set-up (Hopkins, 1994)

The Lucas cells (Lucas, 1964) were allowed to age for at least 4 hours before counting. This time period allowed radon to reach a quasi-equilibrium with its daughter products. A scintillation counter equipped with a photomultiplier tube was used to count the alpha particles produced by the decay of radon and its daughter products, in the ZnS coated Lucas cells. The photoelectrons emitted by the ZnS phosphorescent material upon impact of alpha particles, get multiplied in the photomultiplier tube. The photoelectrons eventually get converted to electrical pulses and are measured by a counter. The voltage supply was adjusted to 970

volts in order to eliminate radiations with energies less than that of alpha particles from being detected by the single-channel analyzer. A counting time of 1800 seconds was chosen for each Lucas cell to obtain a statistically sound measurement.

The concentrations of radon in the aqueous samples were calculated from the above made measurements using a spreadsheet. The details are underlined in Appendix E Calculating Aqueous Radon Concentration.

Chapter 4 Micro-Column Studies

Introduction

Micro-columns at 1.0% and 5.0% residual soltrol saturations were constructed according to procedures described under Construction and Operation of Soil Columns in Chapter 3. Micro-column studies were also done with the sand sampled from remediation batch exchange columns at 5.0% residual soltrol saturations to study the effects of aging NAPL on surfactant solubilization capacity. The procedure for constructing these micro-columns remained much the same. The only exception was that sand from the batch exchange columns were used instead of fresh soltrol-mixed sand or clean sand. The effect of temperature on surfactant solubilization of soltrol was another factor that was studied. The details of the different micro-columns used in this study are tabulated in Table 4.01.

Table 4.01 Various Physical Parameters of Micro-columns Used in the Study

Micro-column ID	Volume cc	Estimated porosity	Residual NAPL (%)	Surfactant conc., %w:v	Temperature conditions	Soil origin
BT0	15.69	0.41	0	0.5	Room	Clean
BT1	15.70	0.40	1.0	0.5	Room	Fresh-mix
BT2	15.65	0.42	1.0	0.1	Room	Fresh-mix
BT51	15.81	0.41	5.0	0.5	Room	Fresh-mix
BT53	15.65	0.40	5.0	2.5	High	Fresh-mix
BT54	15.59	0.38	5.0	2.5	High	Column 8

Two different kinds of analyses were performed in these studies. The aqueous samples from batch exchange of the micro-columns were analyzed for TOC content. The sands from these micro-columns were tested for their final residual organic contents using the HDPE strip test assay. The results from these analyses are presented and discussed based on the residual soltrol saturations of the micro-columns.

Results and Discussion

TOC Analysis

Control Micro-column, BT0:

Micro-column BT0 was packed with clean Borden sands. As it was free of residual soltrol, it served as an experimental control. The details of micro-column BT0 are provided in Table 4.01. Approximately seven pore volumes of 0.5% triton (w/v) solution were flushed through micro-column BT0 at room temperature. The influent and effluent samples were analyzed for TOC content after being diluted in 1:100 ratio. The results from the TOC analysis are presented in Table H.1 (see Appendix H Sample Data Tables) and in Figure 4.01, hereafter referred to as batch exchange curve.

The volume of influent solution exchanged (the midpoint of each sample volume) is plotted versus the difference in the TOC of the effluent and that of the influent. Given the low organic carbon content of the Borden sand, it can be assumed that the difference in TOCs is attributable to the soltrol, the only other organic compound than triton in the system.

The initial effluent samples had a very low TOC (one value of -1400 ppm was omitted in Figure 4.01 for clarity purposes) compared to the influent resulting in negative values. It can be reasoned that the resident pore water in the column

lacking triton is displaced during the first few pore volumes which dilutes the effluent sample.

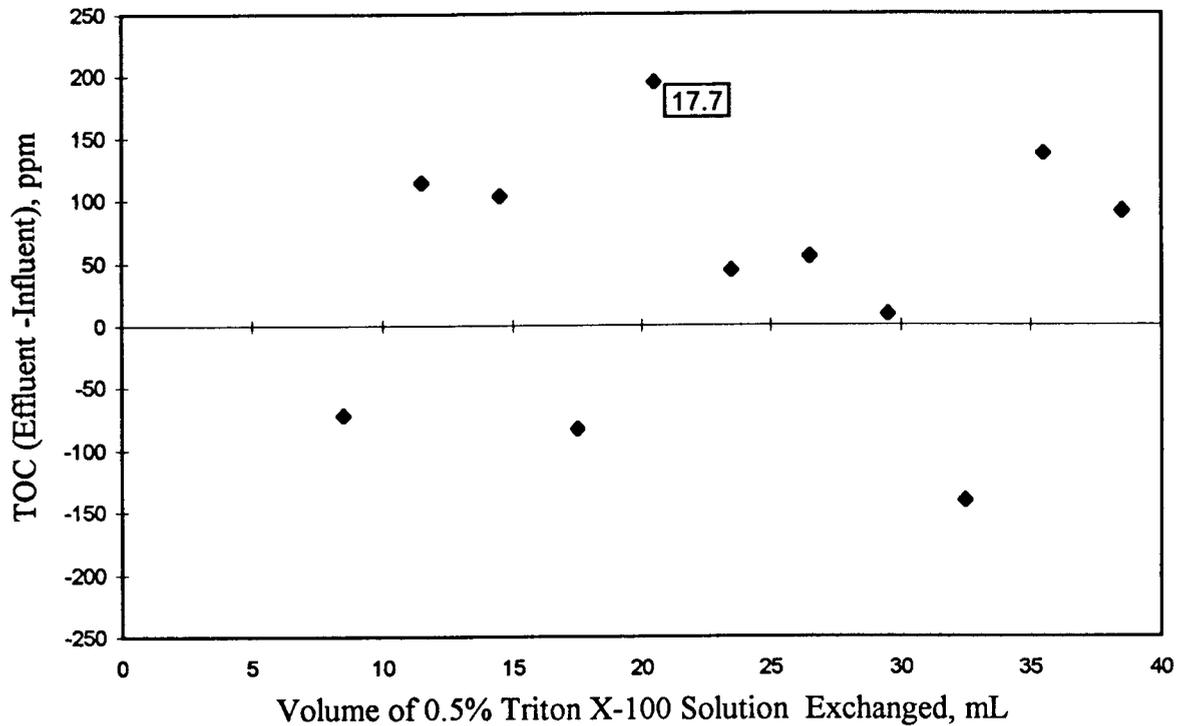


Figure 4.01 Batch Exchange Curve for Control Micro-column BT0. Boxed number in the plot represents duration of batch equilibration period in hours.

The other data points (in Figure 4.01) are relatively dispersed around the X-axis. The negative values for some intermediate sample points suggest that the displacement of pore water by triton solution during flushing may not have been uniform. The deviation of many differential TOC values from zero, which is not expected for a control column, supports the contention that the results from TOC analysis are more of qualitative significance, than quantitative at low residual saturations.

1.0% Residual NAPL Saturation Micro-columns:

Two micro-columns, BT1 and BT2, at 1.0% residual soltrol saturations were used for evaluating the effectiveness of triton as a surfactant for soltrol removal. Micro-columns BT1 and BT2 were flushed with 0.5% and 0.1% (w/v) aqueous triton solutions respectively. The results of the TOC analyses of the influent and effluent samples from BT1 are presented as batch exchange curve in Figure 4.02 and those from BT2 are presented in Figure 4.03.

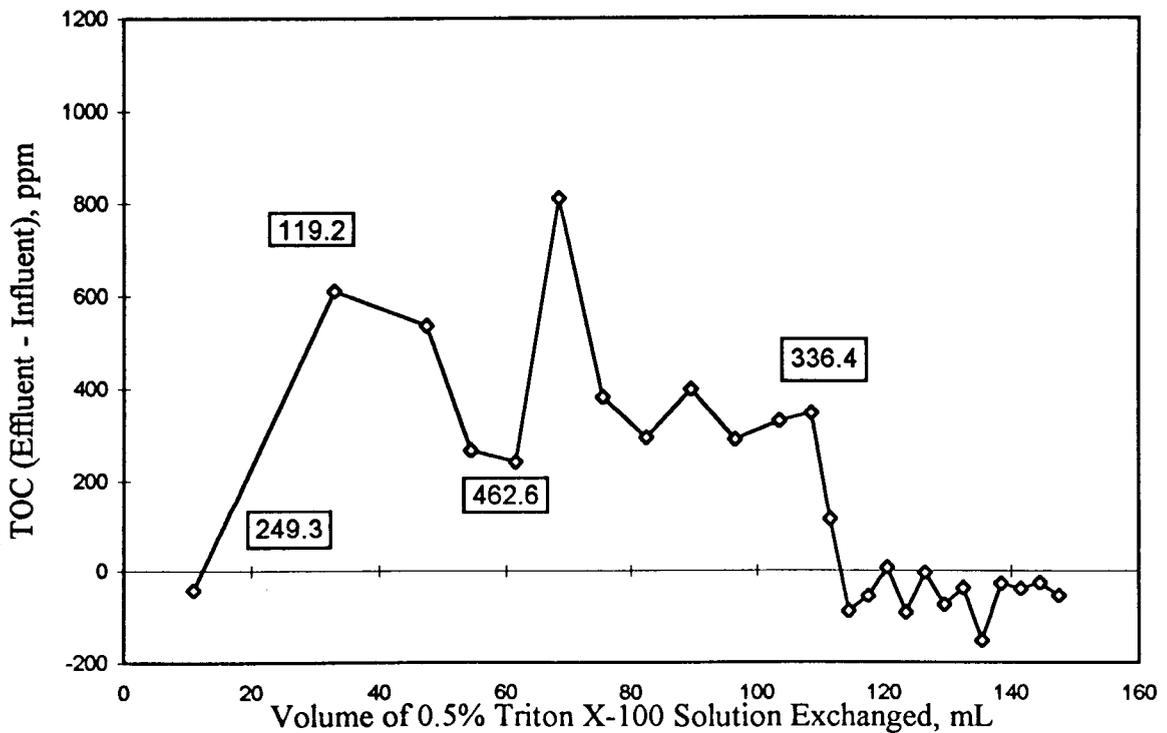


Figure 4.02 Batch Exchange Curve for Micro-column BT1 at 1.0% Residual Soltrol Saturation Using 0.5% Triton. Boxed numbers in the plot represent durations of batch equilibration periods in hours

The first sample point has a negative differential TOC value in both cases. This can be attributed to the dilution of the initial effluent samples with pore water. Approximately 40 mls of 0.5% triton solution were exchanged in each of the four exchanges for micro-column BT1. Figure 4.02 shows that approximately 120 mls (19 pore volumes) of 0.5% triton solution were required for solubilizing most of the residual soltrol present in micro-column BT1. Mass balance calculations (see Appendix F for procedure) indicate that nearly 93% of initial residual soltrol in micro-column BT1 was removed by surfactant flushing. More soltrol was solubilized during the initial exchanges compared to the later exchanges as indicated by the decrease in differential TOC values from 800 ppm to 400 ppm.

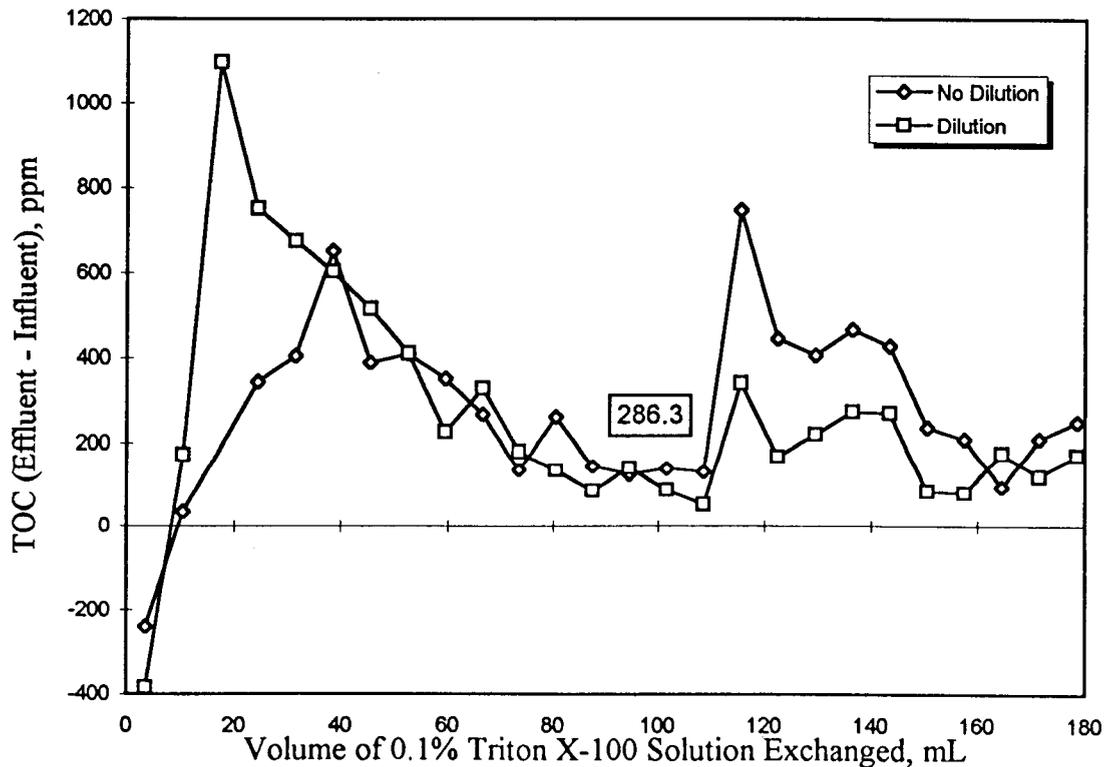


Figure 4.03 Batch Exchange Curve for Micro-column BT2 at 1.0% Residual Soltrol Saturation Using 0.1% Triton. Boxed number in the plot represents duration of batch equilibration period in hours

In comparison, the cleanup of micro-column BT2 with 0.1% triton solution required about 185 mls (28 pore volumes) in two exchanges. Mass balances showed approximately 100% removal of the initial soltrol for both diluted and non-diluted sample analyses. It is interesting to note (in Figure 4.03) that although the areas under both the curves seem to be almost equal, the trends of the curves differ during the first 100 mls. During the second exchange, the pattern of the curves is the same but the differential TOC estimations made by diluting samples measure lower than those made without diluting. The deviations observed could be either due to experimental error associated with making dilutions or the sensitivity of the TOC analyzer to high concentrations.

Substantial increase in the effluent concentration of soltrol is observed after batch equilibration (Figures 4.02 and 4.03). This observation is consistent with that of Pennell et al. (1993) and is indicative of rate-limited rather than instantaneous solubilization of soltrol. The initial effluent with elevated concentrations of soltrol represents the pore volume residing with in the column during the batch equilibration period. The soltrol concentrations in the samples decrease following the elution of the resident pore fluid.

Based on the number of pore volumes that were required for cleaning up BT1 and BT2, it can be concluded that 0.5% triton solution is more effective in solubilizing soltrol at 1.0% residual saturation than 0.1% triton solution. However, this conclusion is based on the assumption that the sensitivity of TOC measurements is same for both triton concentrations.

5.0% Residual NAPL Saturation Micro-columns:

Preliminary studies were conducted on three micro-columns, BT51, BT53, and BT54, to study the effect of various factors on solubilization of soltrol at 5.0% residual saturation. The factors studied were concentration of the influent triton solution, temperature, and aging of NAPL.

Micro-column BT51 was packed with sand freshly mixed with soltrol to achieve 5.0% residual soltrol saturation. The influent was 0.5% (weight/volume) triton solution. The exchange was conducted at room temperature. The results of TOC analyses on the influent and effluent samples from batch exchange of micro-column BT51 are presented in Figure 4.04.

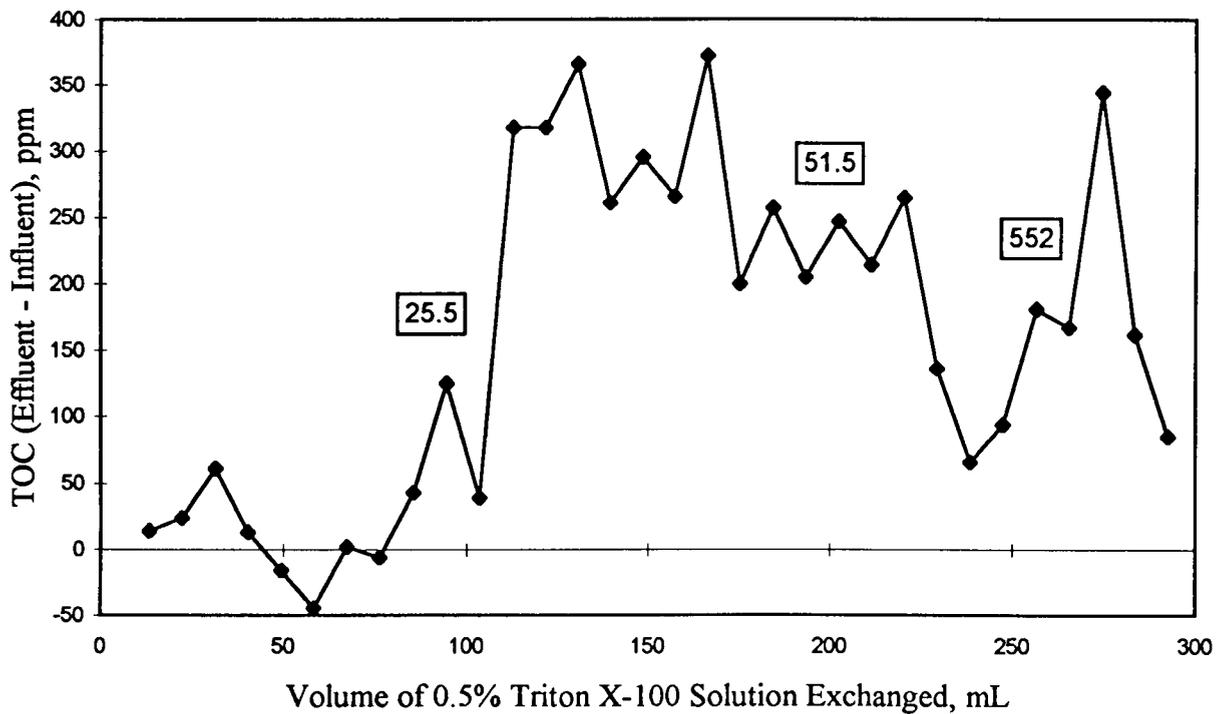


Figure 4.04 Batch Exchange Curve for Micro-column BT51 at 5.0% Residual Soltrol Saturation. Boxed numbers in the plot represent durations of batch equilibration periods in hours

Micro-column BT51 behaved in a manner similar to micro-column BT1 at 1.0% residual saturation in some respects. Significant amounts of soltrol were

solubilized by the surfactant solution following periods of batch equilibration in case of micro-column BT51 also. However, it is interesting to note from figures 4.02 and 4.04 that the maximum differential TOC is higher for micro-column BT1 (about 800 ppm C) than for micro-column BT51 (about 350 ppm C), even though BT51 has higher residual soltrol saturation. Longer periods of batch equilibration in micro-column BT1, which means more contact time between surfactant micelles and residual soltrol, may be the reason for the observed higher solubilization rate.

Approximately 300 mls (47 pore volumes) of 0.5% surfactant solution were flushed through micro-column BT51 at 5.0% residual soltrol saturation. This accomplished only about 21% removal of initial residual soltrol based on mass balance calculations. On the other hand, only about 19 pore volumes of 0.5% triton solution achieved almost 93% residual soltrol removal in BT1 at 1.0% residual soltrol saturation. This result indicated that 0.5% triton solution was not as effective in solubilizing soltrol at 5.0% residual saturation as it was with 1.0% residual soltrol saturation. Hence, the consecutive micro-column studies performed at 5.0% residual soltrol saturation employed triton solutions at higher concentrations.

As will be discussed later in Chapter 5, it was observed that batch exchange macro-column 6 at 1.0% residual soltrol saturation behaved differently from its micro-column counterpart. Macro-column 6 had the soltrol residing on it for approximately 15 months. As will be discussed in Chapter 5, the amount of soltrol solubilized by 0.1% triton solution in column 6 was very less compared to that observed in micro-column BT2. It was suspected that aging of soltrol in column 6 might be the reason for the observed deviation in behavior. So, the effect of aging on soltrol solubilization capacity of triton was also studied in this micro-column study.

Micro-column BT53 was constructed to estimate the efficiency of 2.5% (w/v) triton solution in cleaning up column at 5.0% residual soltrol saturation. Micro-column BT53 was packed with freshly mixed sand. The exchange was conducted at a higher temperature (about 50 °C) to hasten cleanup of the column.

Micro-column BT54, constructed to study the effect of aging NAPL, is similar in construction and operation to micro-column BT53. The only difference is that the aquifer medium in BT54 is the sand sampled from batch exchange column 8 which is at an estimated 5.0% initial residual soltrol saturation. This residual saturation had resided on column 8 for a period of approximately 18 months. The results of TOC analyses on effluents from micro-columns BT53 and BT54 are presented in the same plot (Figure 4.05) for comparison purposes. The initial negative differential TOC values have not been included for both the curves to give a clear picture of other significant data.

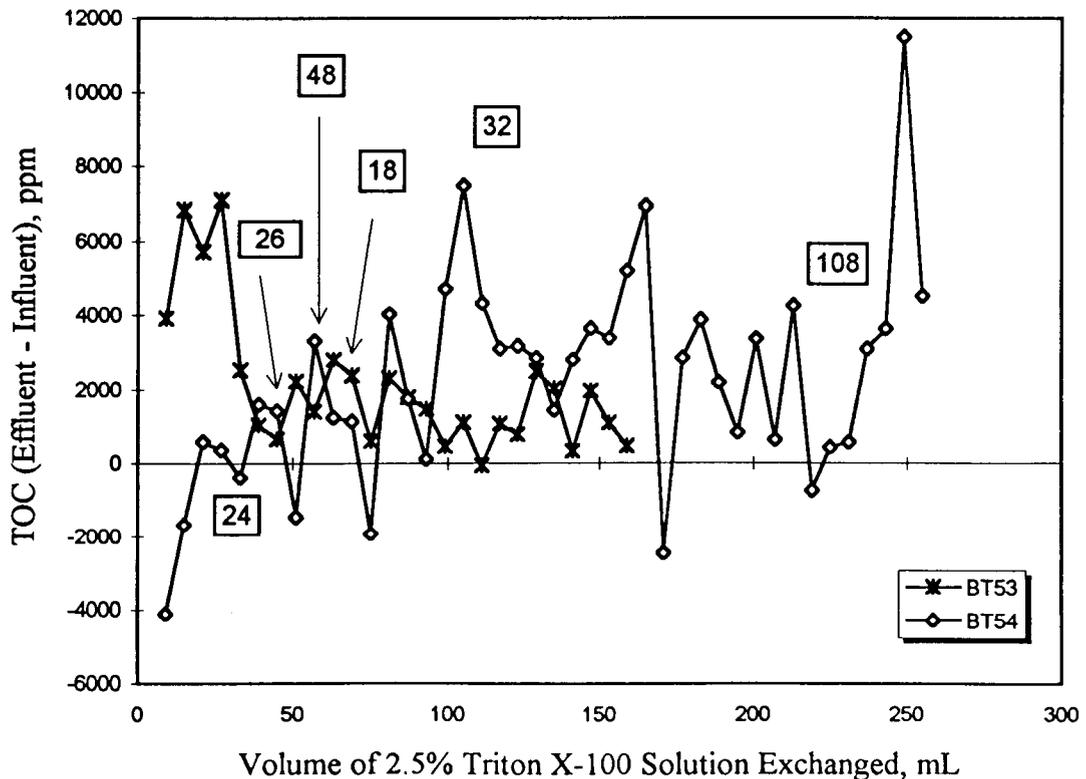


Figure 4.05 Comparison of Batch Exchange Curves for Micro-columns BT53 and BT54. Boxed numbers in the plot represent durations of batch equilibration periods in hours for micro-column BT54 with aged soltrol. Both exchanges were conducted at 50 °C.

Figure 4.05 shows that micro-column BT53 required approximately 158 mls (25 pore volumes) of 2.5% triton solution to achieve about 100% removal of soltrol on mass basis. On the other hand, micro-column BT54 was flushed with about 258 mls (44 pore volumes) of 2.5% triton solution. We observe from Figure 4.05 that the differential TOC values fluctuate but do not converge to zero. This indicates that soltrol may still be present in the column although mass balance calculations indicate 224% removal of initial soltrol from the column.

The initial amount of soltrol in BT54 was estimated based on the total volume of soltrol used for packing column 8. This initial estimate of soltrol content, based on the assumption of homogeneous conditions, for the sand sampled from column 8 may not be accurate. This inaccuracy could have resulted in the unreliable estimate for soltrol removal based on mass balance calculations. However, the estimate for initial residual saturation of the sand sampled from column 8 based on HDPE strip test assay is 4.0%. This estimation rules out the possibility of the presence of higher amounts of soltrol in the sand sample due to non-uniform distribution of soltrol in the column. The reasons for the discrepancy are unexplainable.

It is worth noting is that major solubilization of soltrol occurred during the first four pore volumes in micro-column BT53 and the subsequent flushings removed lesser amounts of soltrol. The solubilization of soltrol in micro-column BT54 does not follow the trend observed in micro-column BT53. There is no proportionality between the amounts of soltrol solubilized in BT54 and the periods of batch equilibration either. It was also observed that each time the exchange was resumed after batch equilibration, the first effluent sample had lower TOC than the influent. The reasons for these observations in column BT54 are unknown. But they indicate the complex nature and behavior of aged NAPL columns during surfactant flushing.

It can be inferred from these observations, that aging of NAPL does affect the solubilization capacity of surfactant solutions. The longer the contact time between the NAPL and aquifer solids, the stronger the sorption of NAPL to the

solids. Also, aging makes NAPL a wetting fluid which then spreads into low permeability zones of the aquifer medium (Craig, 1971). Consequently, it becomes difficult for the surfactant micelles to desorb NAPL from the aquifer matrix and solubilize it. This is evident from the differences observed in the efficiency of triton solution in solubilizing fresh and aged soltrol. Thus, aged NAPL requires larger volumes of surfactant solution than fresh NAPL.

Temperature played an important role in maximizing soltrol solubilization in both micro-columns, BT53 and BT54. The amount of soltrol removed by flushing columns with triton solution at high temperatures (Figure 4.05) was nearly ten times that removed in experiments conducted at room temperatures (Figure 4.04). It should be mentioned that the experiments performed at higher temperatures also used higher triton concentrations. Hence, the increase in soltrol solubilization at higher temperatures may not be solely due to temperature effect. Based on this observation, the remediation batch exchange experiments on column 8 were performed at high temperatures and high triton concentrations to achieve more rapid cleanup.

HDPE Strip Test

The HDPE strip test assay provided a means of verifying the reliability of cleanup level estimates made based on the results from TOC analyses. The final residual soltrol saturations of sand in the micro-columns were determined using this assay. Prior to analysis, the sands were washed with distilled water to remove any triton present. The experimental method is outlined in [Appendix C](#) and the procedure used for calculations is described in [Appendix G](#). The results from these tests are tabulated in Table 4.02.

Table 4.02 Estimated Final Residual Saturations in Micro-columns Using HDPE Strip Test

Micro-column	Initial Residual Saturation, %	Estimated Final Soltrol Volume, cc	Estimated Final Residual Saturation, %	% Soltrol Removed
BT0	0	-0.0002	-0.0033	-
BT1	1.0	0.0027	0.0428	95.72
BT2	1.0	0.1419	0.0226	97.74
BT51	5.0	0.2182	3.3520	32.96
BT53	5.0	0.0017	0.0269	99.46
BT54	5.0	0.0014	0.0234	99.53

In case of control column BT0, the final weight of the HDPE strip measured a little less than its initial weight. The minor error may be due to the insensitivity of the balance. This lead to the unreasonable estimate of residual saturation for BT0 (Table 4.02). The cleanup level estimates achieved in the micro-columns, indicated by percent soltrol removed, are compared with the estimates based on TOC analysis in Table 4.03.

Table 4.03 Comparison of Cleanup Level Estimates for Micro-columns

Micro-Column	Based on HDPE Strip Test	Based on TOC Analysis
BT1	95.72	93
BT2	97.74	100
BT51	32.96	21
BT53	99.46	100
BT54	99.53	224

The estimates from the independent methods are in reasonable agreement except for micro-column BT54. The HDPE strip test indicates that the column is almost free of residual soltrol after flushing with 218 mls of 2.5% triton solution. The integrity of the estimate based on TOC analysis is doubtful as it indicates recovery of more soltrol than was initially in BT54. One possible explanation could be that the fraction of sample used for TOC analysis contained micelles and was not representative of the effluent itself. Extrapolation of the high TOC values thus obtained, to determine the amount of soltrol solubilized in the effluent samples, may have lead to the erroneous estimate of 224% soltrol recovery in BT54.

Summary

The results from micro-column studies and their implications can be summarized as follows:

- ◆ Surfactant solutions at higher concentrations were more effective in solubilizing residual soltrol than surfactant solutions at lower concentrations. The efficiency of higher surfactant concentrations may be attributed to formation of micelles in larger numbers. More surfactant micelles means incorporation of more soltrol, which results in higher soltrol recovery rates.
- ◆ The amount of soltrol solubilized increased for exchanges done after long batch equilibration periods. This observation is noteworthy as it provides a way of enhancing solubilization capacity of surfactants when employed for remediating NAPL-contaminated sites.
- ◆ Aged NAPL affected the solubilization capacity of surfactant solutions considerably. Thus, surfactant solution at a particular concentration may not be effective in remediating aged NAPLs even though it efficiently solubilizes fresh NAPLs.

- ◆ The soltrol solubilizing capacity of triton was found to increase manifold at elevated temperatures in these studies. The increased recovery of soltrol is probably due to decreasing adsorption, decreasing interfacial tension, and increasing solubilities with increasing temperature coupled with high surfactant concentrations.
- ◆ The HDPE strip test results are in reasonable agreement with estimations of soltrol recovery based on results from TOC analyses.

Chapter 5

Remediation Batch Exchange Studies

Introduction

The potential of Radon-222 as a tracer to monitor the progress of NAPL remediation efforts was studied through a series of remediation batch exchange experiments. Three sets of column experiments were conducted to examine the presence of soltrol at various residual amounts (columns initially at 1.0%, 5.0% and 8.0%) on radon transport and breakthrough. Solubilization of soltrol in the columns was achieved by flushing aqueous triton solutions in a sequential batch mode. The influence of reduced residual soltrol saturations on breakthrough of radon was studied. Some batch exchange experiments were conducted at room temperatures and some, at higher temperatures of about 50 °C. The exchanges were labeled with the column number suffixed by a hyphenated alphabet in chronological order to denote consecutive exchanges on the same column.

Prior to flushing the columns with triton and remediating them, some sand was removed from the bottom of the columns for use in micro-column studies and evaluation of initial residual soltrol saturation using HDPE strip test. The columns were repacked with sand containing equivalent amounts of soltrol. The estimated physical parameters for the batch exchange columns are tabulated in Table 5.01.

Table 5.01 Details of Remediation Batch Exchange Columns

Column No.	Volume, cc	Estimated Porosity, e	Pore Volume, cc	Initial Soltrol Saturation, %	Initial Weight of Soltrol, gm
6	1058	0.42	444	1.0	3.5949
8	1053	0.43	453	5.0	19.1818
7	1062	0.425	451	8.0	30.7731

Breakthrough curves obtained from remediation batch exchange experimental data can be used to evaluate the ability of radon as an indicator to assess the effectiveness of NAPL remediation efforts. The plot of aqueous radon concentration versus volume of influent solution exchanged is referred to as breakthrough curve for radon in this study. The breakthrough point, an important feature of breakthrough curves, is defined as the estimated volume of influent where aqueous radon concentration equals 50% of the maximum value. The maximum aqueous radon concentration was determined by visual inspection of the breakthrough curve and the data points affected by end conditions of the column, if any, were neglected.

In addition to radon measurements, the aqueous samples from batch exchange studies were analyzed for their TOC content. HDPE strip tests were performed on the sands from batch exchange columns to evaluate their initial and final residual organic contents. The results of these analyses for the three batch exchange columns and the control column are presented and discussed separately.

Results and Discussion

Control Column C

A background breakthrough curve for radon is essential to know whether a soil column has been completely cleaned up. The data for a 0.0% residual saturation column, column C, from a previous study (Hopkins, 1994) served as control data for radon quantification experiments. Column C did not exist at the start of this study. So, data collected by Hopkins (1994) is used. Since both the studies were conducted using identical procedures and under similar conditions, it is justifiable to use the data collected for column C as experimental control in this study. The data collected by Hopkins (1994) from the batch exchange of column

C with de-aired synthetic Borden groundwater are presented in the breakthrough curve shown in Figure 5.01.

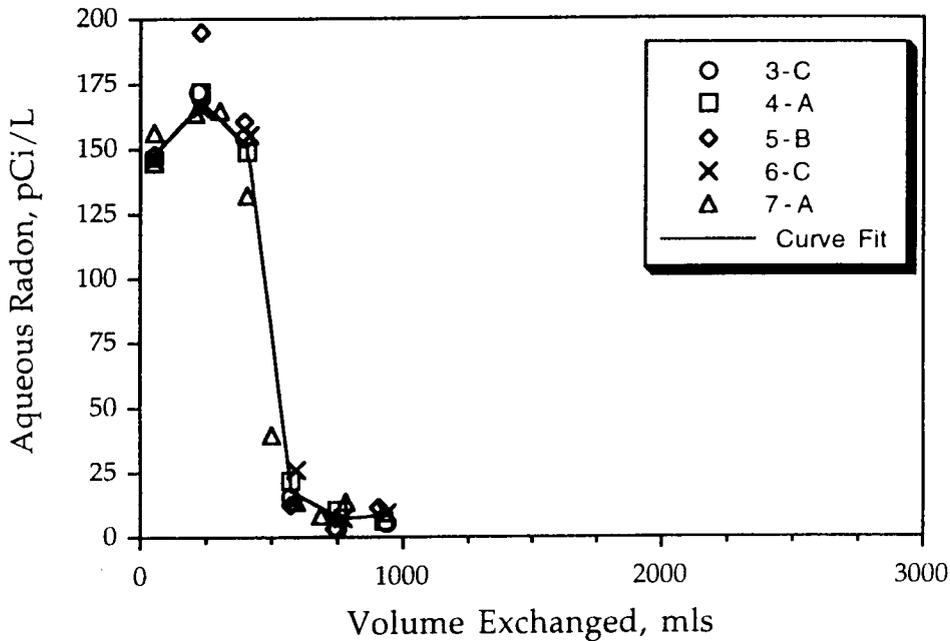


Figure 5.01 Breakthrough Curve for 0.0% Residual Saturation Column C - The Experimental Control (from Hopkins, 1994)

The initial effluent from the column is the radon-equilibrated pore water having high aqueous radon concentrations. The dissolved radon concentrations in the aqueous samples gradually decrease as the fresh influent displaces the pore water. The average maximum radon concentration for Column C is 173 pCi/L and the 50% breakthrough point is estimated to be 450 ml. This estimation may not be precise due to lack of data points in the 400 - 550 ml region. The first sample point has a lower average aqueous radon concentration probably due to end effects where radon is lost via sorption through the teflon end cap. The estimated

pore volume of 450 mls from the breakthrough curve agrees well with the pore volume estimated (445 mls) based on porosity ($e = 0.43$) measurements by Hopkins (1994). This indicates the absence of retardation of radon in NAPL-free columns.

1.0% Residual NAPL Saturation Column 6

Batch exchange column 6 was initially at an estimated residual soltrol saturation of 1.0%. The details of the column are presented in Table 5.01. Column 6 was the first column on which surfactant flushing technique was tried. Different concentrations (w/v basis) of triton solution were used as influent solutions for these experiments performed in a sequential batch mode. The concentration of the influent surfactant solution was increased for successive exchanges with the intention of increasing the removal rate of soltrol from the column. Approximately 1000 mls of the influent solution were flushed through the column for each exchange. The results of various analyses performed on aqueous and sand samples from column 6 are presented here and briefly discussed.

Radon Quantification:

The data were collected by repeated experiments on column 6. Prior to flushing the column with triton solution, the column was exchanged with de-aired synthetic Borden groundwater to obtain the initial breakthrough curve. Data obtained from four exchanges (6-C through 6-F), done with 0.1% triton solution as influent, have been excluded. A problem with the analytical method of quantifying radon has been discovered later. So, the data collected during that time are of suspect and are not representative of the conditions in the column. The

results from the remediation batch exchange experiments conducted on column 6 are presented in Figure 5.02.

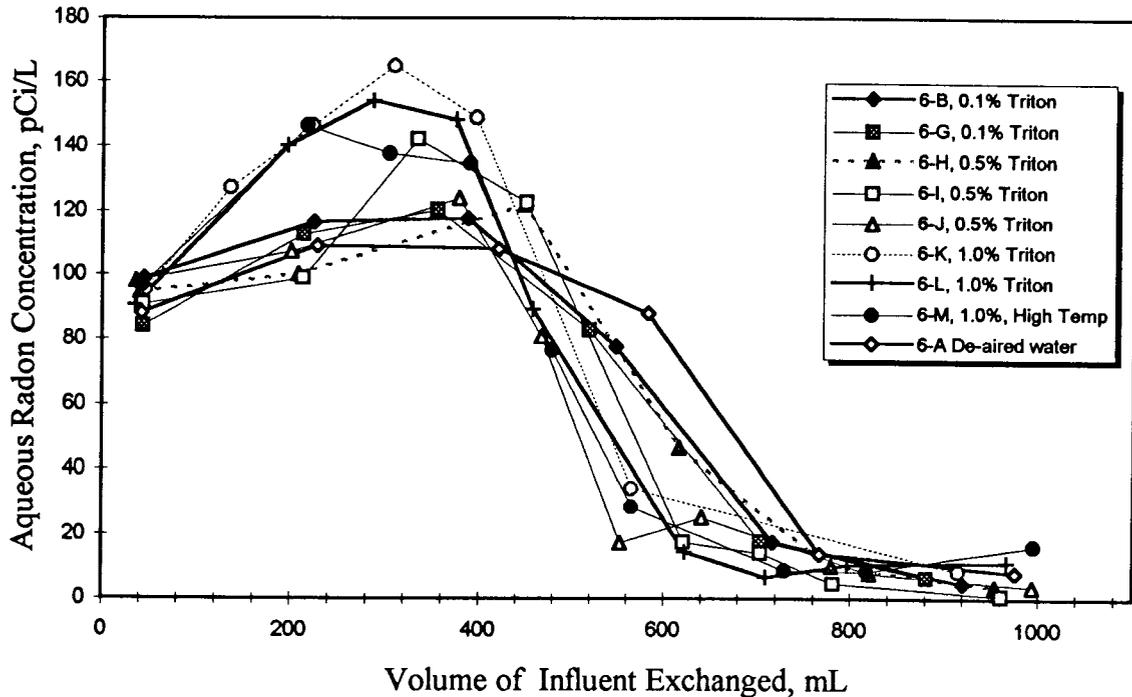


Figure 5.02 Breakthrough of Aqueous Radon Concentrations in Column 6 Initially at 1.0% Residual Soltrol Saturation

The initial batch exchange (6-A) with de-aired synthetic groundwater gives a maximum aqueous radon concentration of 110 pCi/L and a 50% breakthrough point of 670 ml. As can be seen from Figure 5.02, the maximum aqueous radon concentration increased and the breakthrough point decreased gradually with subsequent exchanges of the column with triton solutions. It is interesting to note that the shape of the breakthrough curves remains almost the same. The estimated maximum aqueous radon concentrations and the breakthrough points for the exchanges are tabulated in Table 5.02.

Table 5.02 Estimated Parameters Based on Breakthrough Curves for Column 6

Exchange No	Influent	Maximum Aqueous Radon Concentration (pCi/L)	Breakthrough Point, mL
6-A	De-aired water	110	670
6-B	0.1% triton	118	600
6-G*	0.1% triton	124	588
6-H	0.5% triton	122	582
6-I	0.5% triton	142	536
6-J	0.5% triton	124	496
6-K	1.0% triton	164	485
6-L	1.0% triton	154	485
6-M	1.0% triton	152	480

* Data from exchanges 6-C to 6-F suspected and so, not included in estimations

For some exchanges, it was observed that the translation of the breakthrough curves wasn't substantial. This indicated ineffective soltrol solubilization by the influent triton solutions. 0.1% triton solution appeared to be very effective in solubilizing soltrol during the first exchange but it became less effective later. For example, with six exchanges of 0.1% triton solution (exchanges 6-B through 6-G), the maximum aqueous radon concentration increased only by about 14 pCi/L. The breakthrough point also decreased from 600 ml to only 588 ml. In addition, 0.1% triton solution was not found as effective based on the number of pore volumes exchanged through column 6 when compared to its performance on its micro-column counterpart, BT1. The concentration of the influent triton solution was therefore increased in order to hasten cleanup.

As more and more soltrol is removed from the column by triton, the radon concentration increases in the aqueous phase. The retardation of radon is also

lessened as the remediation progresses because there is less soltrol present for radon to partition into. Thus, the maximum aqueous radon concentrations reflect local residual NAPL saturation in the column while the breakthrough points indicate the overall condition of saturation. The breakthrough points for exchanges 6-J through 6-M are almost the same demonstrating the absence of retardation. It may be inferred from this observation that column 6 has fairly less residual soltrol left after the final exchange. The maximum aqueous radon concentrations are higher for later exchanges. This may indicate removal of soltrol, which has redistributed and accumulated at the bottom of column 6, during the later exchanges.

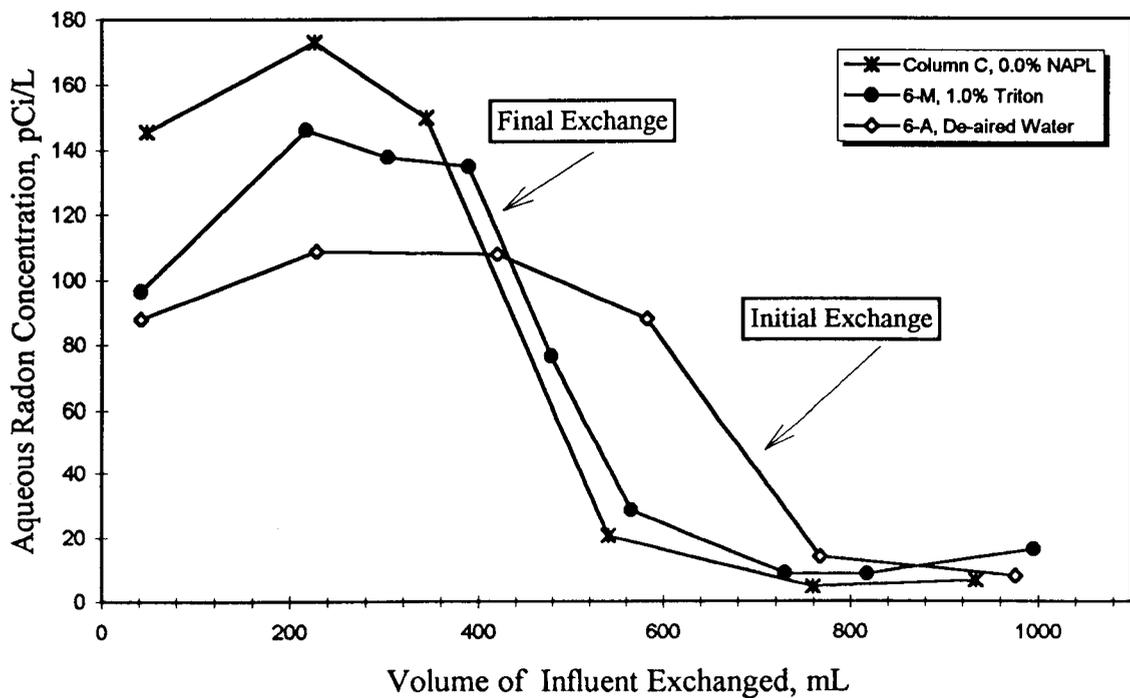


Figure 5.03 Illustration of Radon's Potential as a Tracer for Remediation Performance Assessment in Column 6 at 1.0% Residual Soltrol Saturation

The potential of radon in indicating the progress of NAPL remediation efforts is well illustrated by the breakthrough curves. We see from Figure 5.03 that the initial breakthrough curve for radon (6-A) translates gradually towards the breakthrough curve for control column C at 0.0% residual saturation as remediation of the column progresses.

The final breakthrough curve (6-M) for radon falls more or less on the breakthrough curve for control column C except for the first few sample points. The deficit in aqueous radon concentrations for the initial samples may be due to the presence of soltrol at the bottom of column 6. The residual soltrol may have been redistributed during surfactant flushing, pushed down and accumulated at the bottom part. Hence, the final breakthrough curve for radon indicates that the cleanup of column 6 is not complete. This hypothesis is also supported by the results from TOC analyses and HDPE strip tests, discussed later.

When triton was added to be influent solution, draining of the column was observed sometimes during sampling. It may have been due to clogging of pores by the surfactant micelles formed. The clogging could have lead to channeling in the column. The inaccessibility of mobile influent solution to some areas of column 6 may be one possible reason for the observed minor delay in breakthrough of radon for the final exchange.

TOC Analysis:

The aqueous effluent samples from the remediation batch exchange experiments on column 6 were analyzed for their TOC concentrations in order to obtain an estimate of soltrol solubilization occurring during each exchange. The differences between the TOCs of the effluent samples and that of corresponding influent samples are plotted against the total volume of triton solution exchanged (mL) through the column. This batch exchange curve for column 6 is presented in Figure 5.04. Two data points from the last exchange (around 12000 ml point)

with high negative differential TOC values, about -900 ppm C, have been omitted from the plot to better present the other significant data.

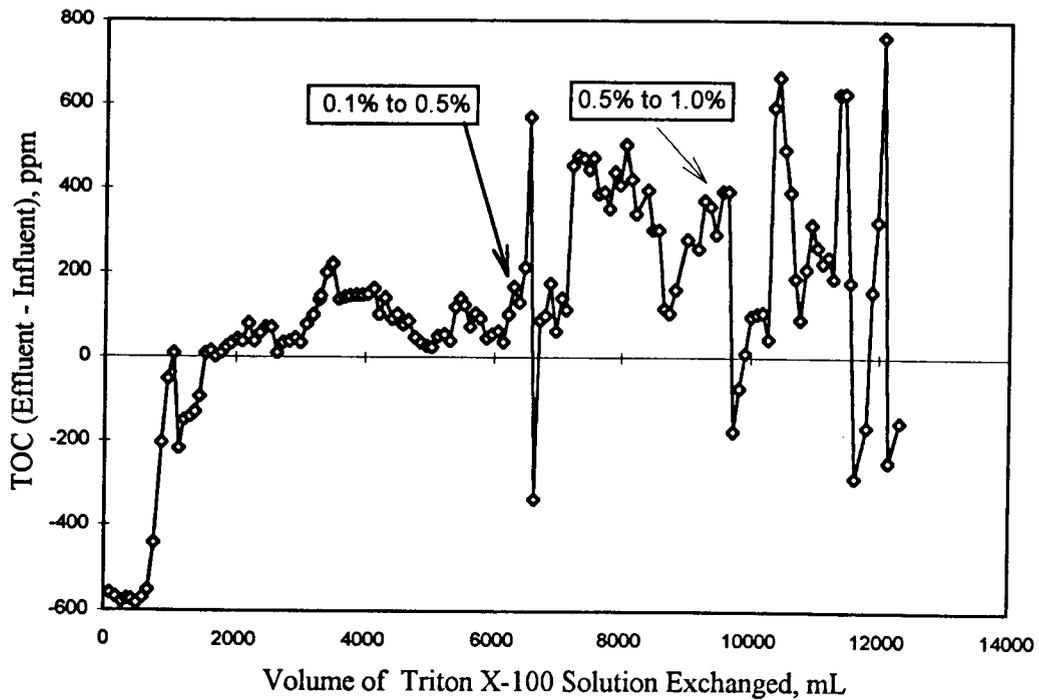


Figure 5.04 Results of TOC Analyses of Effluent from Batch Exchange of Column 6 initially at 1.0% Residual Soltrol Saturation

The negative or low differential TOC values for some of the initial effluent samples are due to the fact that the influent solution gets diluted by the original pore fluid in the column that lacks triton. Figure 5.04 shows that the differential TOC values increase with increase in the concentration of influent triton solution.

This indicates that the amount of soltrol solubilized increases as the concentration of the surfactant solution increases. The amount of soltrol solubilized also increased substantially after batch equilibration, even at the same concentration of influent surfactant solution. For example: this increase is observed around 3000 ml and 5000 ml points when the influent was 0.1% triton solution; around 7000 ml and 9000 ml with 0.5% triton as influent; and also at about 11,000 ml of cumulative triton volume.

A total of approximately 12,200 mls of surfactant solution at various concentrations (w/v basis) were flushed through column 6. This amounts to about 28 pore volumes based on the initial estimated porosity of 0.42. Based on the mass balance calculations on soltrol in terms of its total organic carbon content, about 62% of initial soltrol was estimated to be removed from the column during surfactant flushing. This estimate is not completely accurate as negative values in the data were not included in the calculations. But it can be inferred from these results that the cleanup of column 6 is not complete. The final estimated residual soltrol saturation of column 6 based on the breakthrough point of the radon breakthrough curve is 0.18% and that based on maximum aqueous radon concentration is 0.48%. Thus, radon quantification results indicate between 82% and 52% removal of initial residual soltrol from column 6. This inference reasonably agrees with that based on TOC results.

HDPE Strip Test:

The sand from column 6 was analyzed for final organic content using the HDPE strip test assay developed by Cary et al. (1991). The residual soltrol saturation of the column at the end of remediation experiments was estimated for comparison with estimates based on radon and TOC observations. Duplicates of sand samples collected from the top and bottom of the column were analyzed separately to verify if the column had been uniformly cleaned up. The results of

the analyses and the estimated final residual soltrol saturations of the sand samples are presented in Table 5.03.

Table 5.03 Final Residual Saturation Estimates and Soltrol Removal Rates for Column 6 Based on HDPE Strip Test Results

Sample ID	Sample Location	Weight of Sand Sample, gm	Volume of Soltrol Recovered, cc	Estimated Final Residual Saturation, %	% Soltrol Removed from Column 6
C39S1	Bottom	75.2	0.2160	0.684	31.6
C39S2	Bottom	51.97	0.1707	0.782	21.8
C39S3	Top	49.24	0.0460	0.223	77.7
C39S4	Top	40.47	0.0270	0.159	84.1

The HDPE strip test estimates that there is some residual soltrol left in column 6 at the end of remediation experiments. This suggests that the column is not completely cleaned up, which is consistent with the conclusions based on radon and TOC observations. From Table 5.03, it is evident that there is more residual soltrol present at the bottom of the column than at the top. This observation likely explains the deficit in aqueous radon concentrations observed in the first few samples during the last exchanges of column 6. Radon partitions into the soltrol present at the bottom of the column and thus radon concentrations in water sampled initially are lower.

Using the partitioning model of radon based on aqueous radon deficit measured for the first effluent sample of the last exchange of column 6, 6-M, the retardation factor is calculated as 1.507 which represents a residual saturation of 1.35%. Thus, radon observations indicate that there is more soltrol at the bottom than that suggested by the strip test. This estimate also suggests that the residual

soltrol saturation of the bottom column is greater than the initial 1.0%. It may be inferred from this observation that soltrol which was mobilized from the top of the column accumulated at the bottom during surfactant flushing.

The estimated residual saturation values of 0.223% and 0.159% represent removal efficiencies of about 78% and 84% respectively. These removal rates are in good agreement with the estimates based on radon (52% and 82%) and TOC (62%) results for the column. Thus, the agreement of HDPE strip test estimates with those based on radon supports the use of radon as a tracer to monitor the progress of NAPL remediation efforts.

5.0% Residual NAPL Saturation Column 8

Column 8 initially had an estimated residual soltrol saturation of 5.0%. Based on the results of micro-column studies, an aqueous triton concentration of 2.5% (w/v) was selected as influent solution for remediating this column.

The column was first exchanged with 1800 mls of de-aired Borden synthetic groundwater to obtain the initial breakthrough curve. Next, 2.5% triton solution was flushed through the column. The subsequent three exchanges, exchanges 8-B through 8-D, were conducted at elevated temperatures of about 50° C by means of a circulating water bath. The column was heated only for about 22 hours prior to and including the exchange time as to not affect the emanation properties of radon considerably.

The volumes of influent (2.5% triton solution) exchanged varied between 1300 mls to 1800 mls for each exchange. The exchanges were cut short when clogging problems were encountered. This was done to not change the saturated conditions in column 8 drastically since clogging often caused air to enter the column. In the later stages, the column did become desaturated. In order to completely resaturate the column, about 4 liters of de-aired synthetic Borden

groundwater were flushed through the column. The column was then equilibrated to obtain the final breakthrough curve. The last exchange, 8-E, was performed at room temperature with approximately 1850 mls of de-aired synthetic groundwater.

Radon Quantification:

The data were collected from five batch exchange experiments performed on column 8. The results from these exchanges are presented as breakthrough curves for radon shown in Figure 5.05.

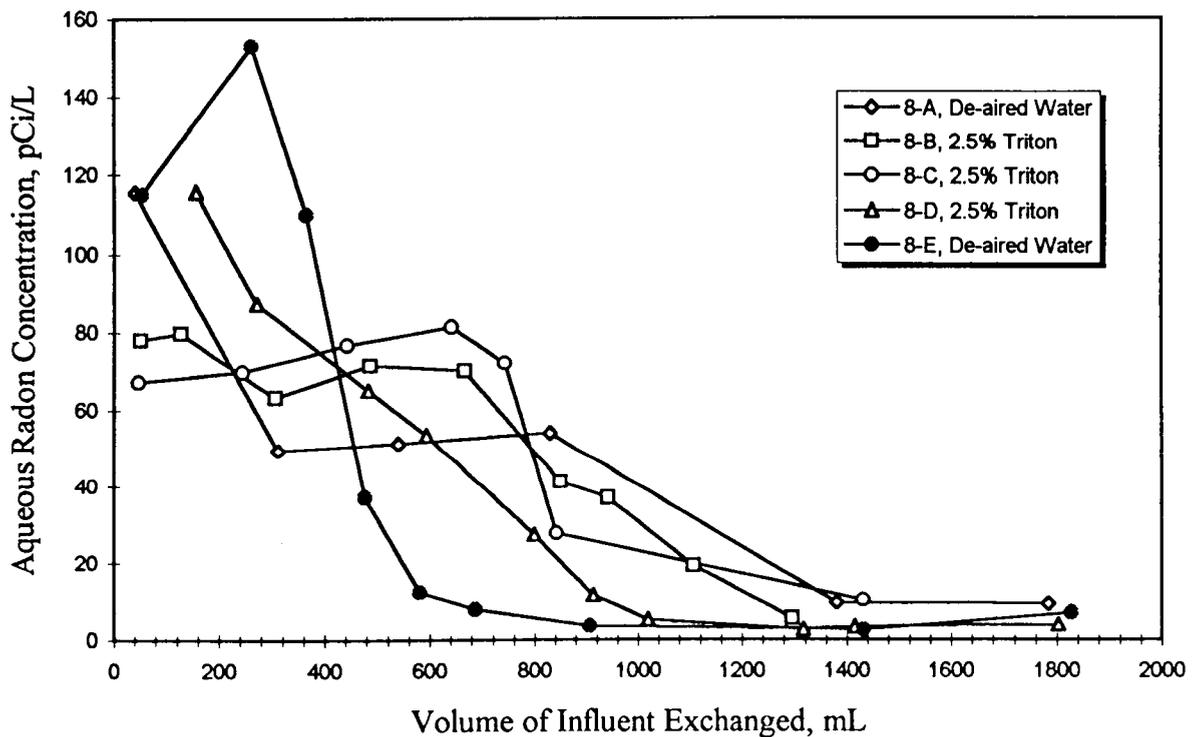


Figure 5.05 Breakthrough of Aqueous Radon Concentrations in Column 8 Initially at 5.0% Residual Soltrol Saturation

By inspecting the breakthrough curve for radon in exchange 8-A, the maximum aqueous radon concentration is estimated as 54 pCi/L and the 50% breakthrough point is 1200 mls. The initial sample point at 50 ml is believed to be affected by end effects due to lower residual saturation existing at the end of the column. After the first exchange, some sand was sampled out from bottom part of column 8 for other tests. The bottom part of the column was repacked with fresh soltrol-mixed sand. Hence, it is not believed to possess the same characteristics as the rest of the column. Therefore, the initial sample point has not been considered in estimation of these parameters for all the breakthrough curves.

A gradual increase in aqueous radon concentrations and decrease in retardation of radon is observed for subsequent exchanges on the column (Figure 5.05). The shape of the breakthrough curves for radon, neglecting the first few sample points, remains almost the same in all the exchanges. The breakthrough curve for exchange 8-D is an exception though. When column 8 was being sampled during this exchange done at high temperature, air has entered the column and disturbed the saturated conditions in the column. The presence of air pockets in the column affected the partitioning characteristics of radon. This resulted in the breakthrough curve obtained for exchange 8-D.

The subsequent exchange, 8-E, was performed after resaturating the column. The shape of the breakthrough curve obtained from this exchange is similar to the shapes of the initial curves, and shows a significant increase in maximum radon concentration and decrease in retardation. The result supports the hypothesis that air-entry significantly affected the earlier breakthrough curve (8-D). Table 5.04 shows the estimated maximum aqueous radon concentrations and the breakthrough points for exchanges on this column.

Table 5.04 Estimated Parameters Based on Breakthrough Curves for Column 8

Exchange No.	Influent	Maximum Aqueous Radon Concentration, pCi/L	Breakthrough Point, mL
8-A	De-aired water	56	1160
8-B	2.5% triton	72	950
8-C	2.5% triton	82	785
8-E*	De-aired water	154	410

* Data from exchange 8-D omitted as it isn't reliable for estimating parameters.

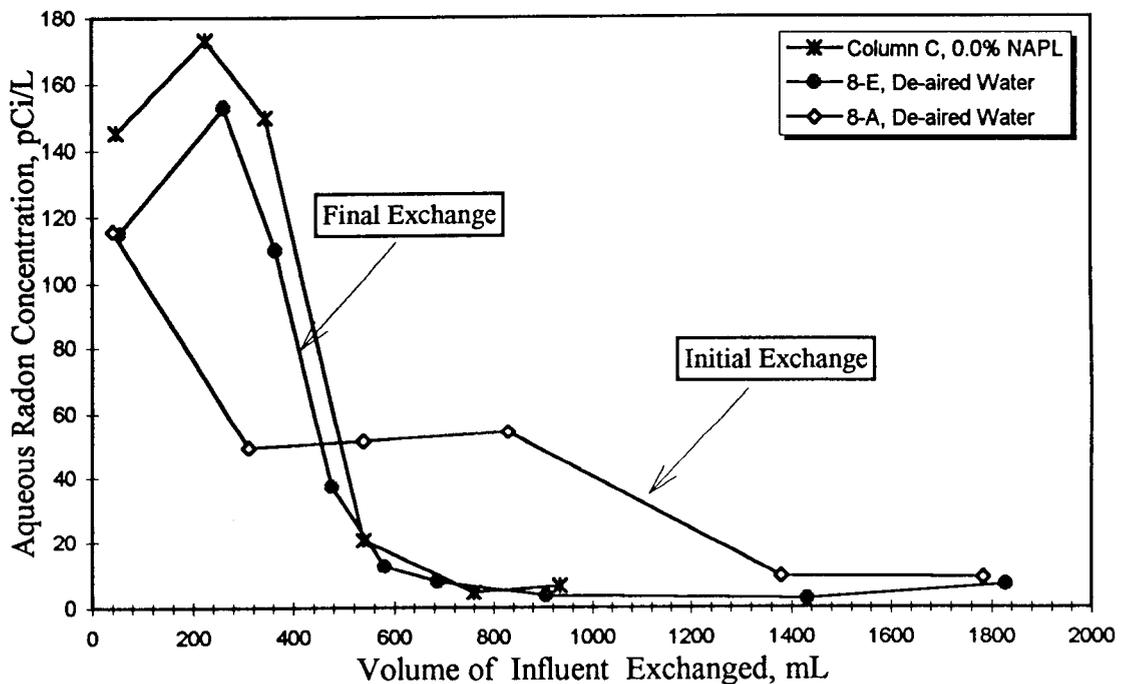


Figure 5.06 Illustration of Radon's Potential as a Tracer for Remediation Performance Assessment in Column 8 at 5.0% Residual Soltrol Saturation

For subsequent exchanges of the column with surfactant solution, the maximum aqueous radon concentration gradually increases and the breakthrough point value decreases. This indicates that the residual soltrol saturation in column 8 is decreasing. The maximum aqueous radon concentration increased from 82 pCi/L to 154 pCi/L and the breakthrough point decreased from 785 ml to 410 ml over the last three exchanges (see Table 5.04). It appears from the shift in the parameters that substantial soltrol was solubilized in exchange 8-D.

Figure 5.06 shows the translation of the initial breakthrough curve for radon (8-A) towards the control breakthrough curve due to surfactant flushing of column 8. This translation demonstrates the ability of radon to reflect changes in residual NAPL saturations during remediation processes. The maximum aqueous radon concentration for the breakthrough curve obtained from the final exchange, 152 pCi/L, agrees well with that for the control curve. The breakthrough points, 410 mls and 450 mls for exchange 8-E and the control respectively, are in reasonable agreement too.

The minor discrepancy is probably due to changes in porosity of the column during the exchanges. Thus, column 8 appears to be fairly soltrol-free after the final exchange. The low aqueous radon concentration for the initial sample of the final exchange may indicate presence of some soltrol at the bottom of the column due to soltrol redistribution during remediation or end effect.

TOC Analysis:

The influent and the effluent aqueous samples collected from remediation batch exchange experiments on column 8 were analyzed for TOC. The results are presented in Figure 5.07. As was observed in the other TOC studies, there was an increase in soltrol solubilization following periods of batch equilibration (marked by boxed numbers in Figure 5.07).

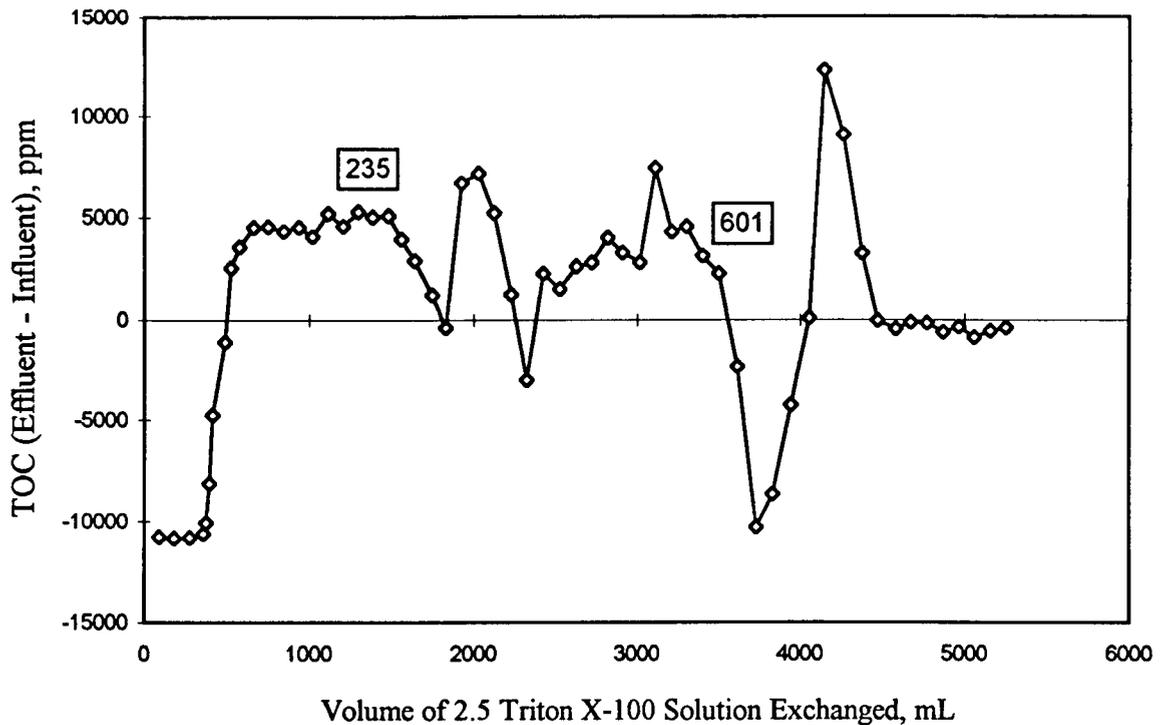


Figure 5.07 Results of TOC Analysis of Effluent from Batch Exchange of Column 8 initially at 5.0% Residual Soltrol Saturation. Boxed numbers in the plot represent durations of batch equilibration periods in hours.

Interestingly, column 8 behaves similar to micro-column BT54 that was packed with sand from the column. Each time the exchange was resumed after batch equilibration, the first few effluent samples had lower TOC than the influent solution. Thus, the net result is that some of the samples have negative differential TOC values as can be seen from Figure 5.07. Mass balance calculations on soltrol indicate that about 5300 mls of 2.5% triton solution aided in removing 85% of initial soltrol from column 8. In comparison, estimations based on the breakthrough point of radon indicate that the column is 100% cleaned up. The final residual saturation estimate calculated using maximum aqueous radon concentration indicates that 93% of initial soltrol is removed from the column. The independent estimates agree with each other reasonably well.

HDPE Strip Test:

HDPE strip test assay was used to estimate the initial and final residual soltrol saturations of column 8. Prior to flushing the column with triton and remediating it, sand was sampled from the bottom of the column and tested for its organic content. This was done to verify if there had been any significant changes in the characteristics of the column since the time of its construction. The initial residual saturation of column 8 based on the results of the HDPE strip test assay was estimated to be 4.0%. This estimate is lower than the expected residual saturation of 5.0%, but is in close agreement. Since the soltrol must have sorbed to the solids very strongly, it may have been difficult for complete extraction of soltrol by the strip, which resulted in the lower estimate observed. It may also have been possible that soltrol was actually present in lower quantities than required at the bottom of the column due to non uniform mixing while packing.

The final residual soltrol saturation of column 8 was estimated based on the results of HDPE strip test on three samples taken at various lengths of the column. The estimates thus obtained and the corresponding levels of cleanup achieved in the column are tabulated in Table 5.05.

Table 5.05 Final Residual Saturation Estimates and Soltrol Removal Rates for Column 8 Based on HDPE Strip Test Results

Sample Id	Sample Location	Volume of Soltrol Recovered, cc	Estimated Residual Saturation, %	% Soltrol Removed
C8S1	Bottom	1.0739	0.2371	95.26
C8S2	Bottom	1.5510	0.3424	93.15
C8S3	Top	0.4692	0.1036	97.93

The estimated final residual saturations for all the samples are far less than the initial 5.0% which indicate that the column has been remediated fairly well. The clean up levels determined from the saturation estimates suggest nearly 95% of the initial soltrol was removed by 2.5% triton solution. Radon observations, which indicated 93%-100% clean up of column 8, agree well with this inference. A soltrol removal rate of 85% estimated for the column based on TOC analyses is also reasonably consistent with the strip test estimate.

The samples taken from the bottom of the column also show about 94% soltrol removal (Table 5.05). The deficits in the maximum and initial aqueous radon concentrations for the final exchange compared to that of the control column (in Figure 5.06) are probably due to soltrol present in residual amounts (0.24% and 0.34%) at the bottom of the column. The residual saturation estimate for column 8 based on the partitioning model of radon using deficit in aqueous radon for the initial effluent sample of exchange 8-E, 0.71%, is in good agreement with the strip test estimate. This agreement supports the previous observation that soltrol may have redistributed to the bottom of the column during surfactant flushing.

8.0% Residual NAPL Saturation Column 7

Remediation batch exchange experiments were conducted on column 7, initially at an estimated 8.0% residual soltrol saturation. For these experiments, triton concentration of 2.5% (w/v) was selected as the influent solution based on its effective performance in remediating column 8 at 5.0% residual soltrol saturation.

To obtain the initial breakthrough curve, the column was first exchanged with nearly 2600 mls of de-aired synthetic Borden groundwater (7-A). Approximately 2700 mls of 2.5% triton solution were then exchanged through column 7 to solubilize residual soltrol during exchange 7-B. Exchanges 7-B

through 7-D were done at elevated temperatures after the column had been heated up to about 50 °C by means of a circulating hot water bath, in a manner similar to column 8. The column was heated only for about 16 hours prior to the exchange to not affect the emanation properties of radon considerably. A positive displacement pump was used for 7-B to displace the pore fluid in the column since pulling vacuum on the collection vials created problems. Exchange 7-C was also conducted using a pump but the flow rate of the influent for this exchange, 2.5% triton solution, has been adjusted such that the exchange time is comparable to other exchanges.

Approximately 1060 mls of 2.5% triton solution were flushed through the column at 50 °C during exchange 7-D to solubilize more soltrol. Later, about 2 liters of de-aired synthetic Borden groundwater were exchanged not only to displace triton solution from the column but also to fully resaturate the column. The final exchange, 7-E, was done at room temperature with approximately 1680 mls of de-aired groundwater to obtain the final breakthrough curve.

Radon Quantification:

The data were collected from three batch exchange experiments on column 7. The results from exchange 7-B have not been presented here as the exchange took place over a longer time frame (nearly 24 hours) than the other exchanges (average 3 hours). The samples from exchange 7-D were collected in unsealed vials and could not be analyzed for radon and so, the results are not included either. Figure 5.08 presents the results from the exchanges on column 7.

Initially, the maximum aqueous radon concentrations were about 30 pCi/L (neglecting end effects) and the 50% breakthrough point was estimated to be 2125 ml for 7-A. The breakthrough curve for exchange 7-C has similar shape as that for 7-A and shows that the maximum concentration did not increase as would be expected if soltrol were removed. Prior to exchange 7-C, fresh soltrol-mixed

Borden sand was packed at the bottom of the column to replace the sand removed for HDPE strip test. The attenuation of aqueous radon concentrations for the first few sample points may have been caused by the freshly packed sand. As these points are not believed to represent the conditions in the column, they are not considered in estimating the parameters.

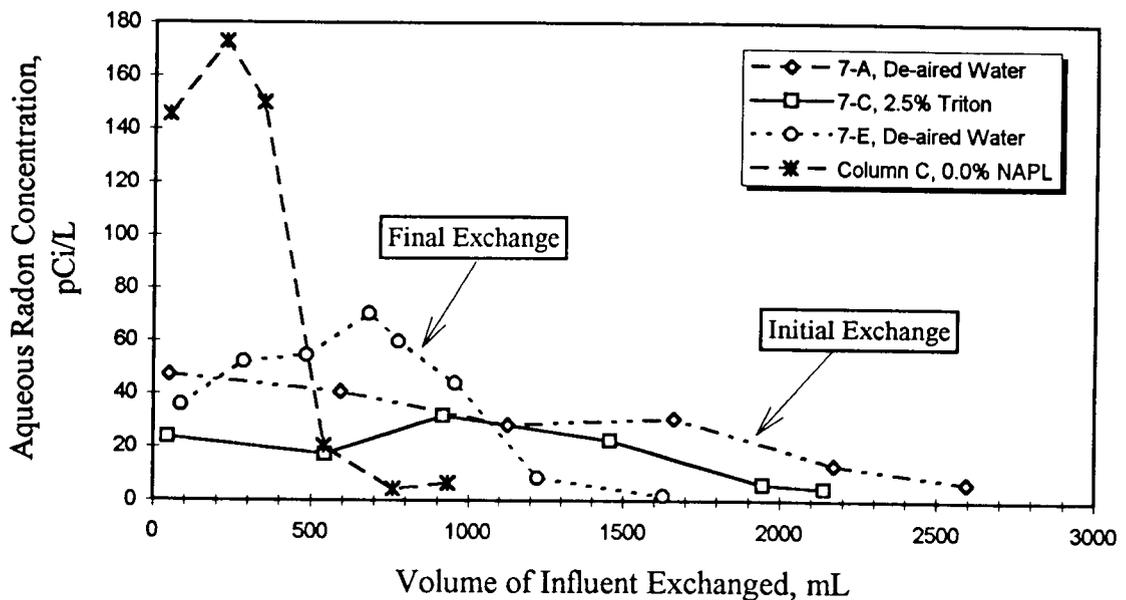


Figure 5.08 Breakthrough of Aqueous Radon Concentrations in Column 7 initially at 8.0% residual soltrol saturation and in Control Column C

The estimated breakthrough point shifted to 1688 ml indicating that soltrol had been removed from the column between exchanges 7-A and 7-C. The maximum aqueous radon concentration (70 pCi/L) for exchange 7-E is higher than that for the previous exchanges. The increase in maximum aqueous radon concentration is also accompanied by decrease in breakthrough point to 1017 mls.

The translation of the breakthrough curves for radon in column 7 towards that for the control column indicates that the residual soltrol saturation of the column has gradually reduced. The breakthrough point of the final exchange (7-E) is delayed when compared to that of the control curve. This observation indicates that column 7 still has a considerable amount of residual soltrol after the final exchange which acts to retard radon transport. A decision was made to leave soltrol on this column for future studies that are being planned.

TOC Analysis:

TOC analyses were performed on all the samples from batch exchange of column 7, even on samples collected from 7-D which were not analyzed for radon. The batch exchange curve is presented in Figure 5.09.

An increase in soltrol solubilization was observed following periods of batch equilibration. The increase was about ten times greater than that observed in column 8 at 5.0% residual soltrol saturation. This observation indicates that higher degree of solubilization is achieved when NAPL is present at higher residual saturations than at lower saturations and that NAPL solubilization is mass-transfer limited. Each time the exchange was resumed after batch equilibration, the first few effluent samples had lower TOC than the influent solution, resulting in negative differential TOC values.

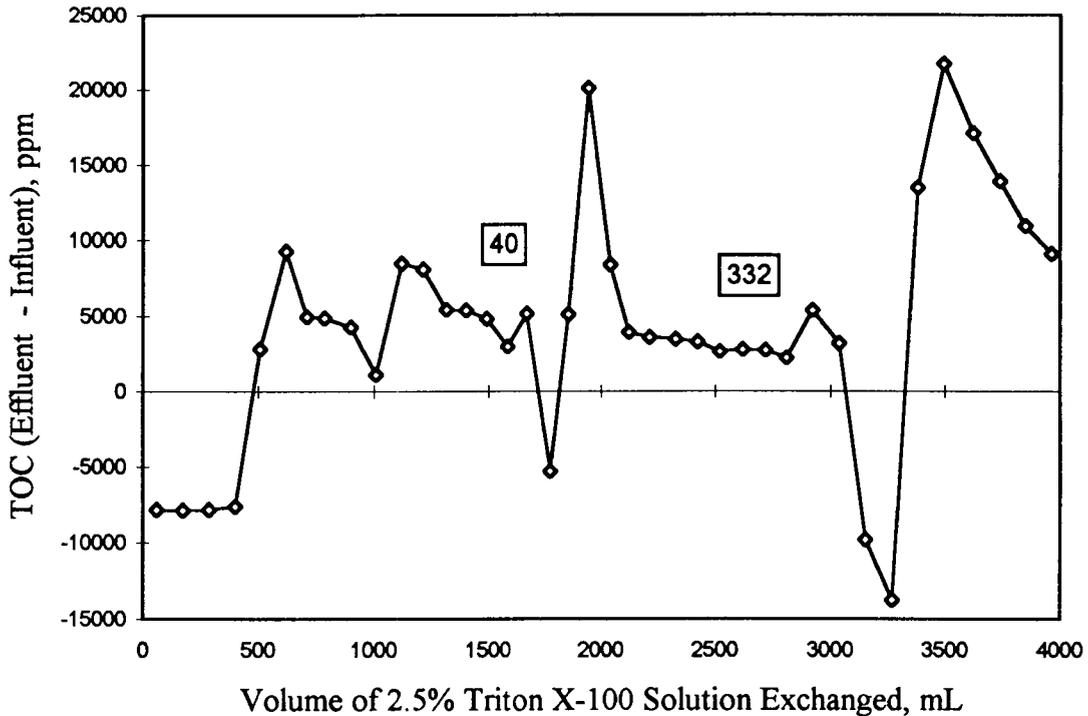


Figure 5.09 Results of TOC Analysis of Effluent from Batch Exchange of Column 7 initially at 8.0% Residual Soltrol Saturation. Boxed numbers in the plot represent durations of batch equilibration periods in hours

Mass balance calculations indicate that about 4000 mls of 2.5% triton solution were required to remove approximately 75% of the initial soltrol from column 7. The residual soltrol saturation of column 7 after the final exchange was estimated as 3.01% and 3.88% based on the linear partitioning model of radon. This is equivalent to approximately 62% and 52% removal of initial soltrol from the column through surfactant flushing, which is in reasonable agreement with the estimate based on TOC results.

HDPE Strip Test:

The initial and final residual soltrol saturations of column 7 were estimated by means of HDPE strip test assay. The sand sampled from the bottom portion of column 7 before flushing the column with triton was used to estimate its initial residual soltrol saturation. Two sand samples, each weighing about 45 grams, were analyzed for their organic content. Both the samples estimated the initial residual saturation of column 7 to be approximately 5.5%. This estimate is lower than the expected residual saturation of 8.0%. Interestingly, the HDPE strip test yielded a low initial residual saturation estimate for column 8 also. The low estimate may probably due to incomplete extraction of soltrol by the saturated strip or presence of low amounts of soltrol at the bottom of the column as a consequence of non uniform mixing and difficulty in packing.

The estimates for the final residual soltrol saturation of column 7 were determined from the organic content of four sand samples. The samples, two each from the top and bottom portions of the column, were analyzed using HDPE strip test assay after performing final batch exchange on column 7 (Exchange 7-E). Table 5.06 presents the estimated final residual soltrol saturations and the corresponding clean-up levels for the column.

Table 5.06 Final Residual Saturation Estimates and Soltrol Removal Rates for Column 7 Based on HDPE Strip Test Results

Sample Id	Sample Location	Volume of Soltrol Recovered, cc	Estimated Residual Saturation, %	% Soltrol Recovered
C7S1	Bottom	4.6495	1.0309	87.11
C7S2	Bottom	5.2547	1.1651	85.43
C7S3	Top	4.7952	1.0632	86.71
C7S4	Top	3.5377	0.7844	90.19

The estimated final residual saturations and the soltrol removal rates in Table 5.06 indicate that about 87% cleanup is achieved in column 7 by surfactant flushing. The estimated level of cleanup is higher than the estimate based on radon observations (62%) and that based on TOC analyses (75%). The soltrol removal rate estimates based on strip test results were higher than those obtained from radon and TOC analyses in case of columns 6 and 8 also. This may suggest that the HDPE strip is not quite efficient in extracting all the soltrol present in the sand sample. The possible reasons for the inefficiency could be that soltrol is present in very low quantities and strongly sorbed to the solids. The estimated residual soltrol saturations for all samples taken from column 7 are almost the same suggesting uniform clean-up of the column by the surfactant solution.

The strip test estimates that about 1.1% residual soltrol is present at the bottom of column 7 after the final exchange. However, the deficit in aqueous radon concentration for the first effluent sample of final exchange relates to a residual soltrol saturation of 8.1% based on the partitioning model. Although the estimates do not agree, they suggest the accumulation of soltrol in the bottom of the column during remediation.

Summary

The soltrol-contaminated batch exchange columns have been completely or partially remediated. Triton solution was effective in solubilizing soltrol at various residual saturations. The degree of soltrol solubilization by triton was found to be greater at high residual saturations than at low residual saturations. Radon successfully indicated the changes in residual soltrol saturations of the columns as the remediation progressed. There was good agreement between inferences about the degree of cleanup achieved in the columns based on radon quantification and the other independent methods, TOC and strip test analyses.

Chapter 6 Discussion of Results

Radon for Remediation Performance Assessment

We have seen in Chapter 5 that the translation of breakthrough curves of radon effectively indicates the progress of NAPL remediation efforts. The parameters estimated from the breakthrough curves namely, the maximum aqueous radon concentration and the 50% breakthrough point, can be used to evaluate the extent of cleanup achieved through remedial actions. The maximum aqueous radon concentration estimates the residual NAPL saturation at the sampling location while the breakthrough point yields the NAPL saturation estimate for the sampling area. The linear equilibrium partitioning model for radon can be used to make these estimations.

In a saturated system with two immiscible phases, partitioning of radon between the two phases can be expressed as:

$$S_N C_N + S_w C_w = \frac{C_{Ra} E_p \rho_b}{e} \quad (\text{Eq. 6.01})$$

- where S Volumetric phase saturation, L/L
 C Concentration of radon in the phase, pCi/L
 ρ_b Bulk density of aquifer solids, Kg/L
 e Porosity of the aquifer
 C_{Ra} Radium concentration, pCi/Kg
 E_p Emanation power of aquifer solids, pCi/pCi

If we assume that the linear equilibrium partitioning model of radon is valid, then,

$$C_N = K C_w \quad (\text{Eq. 6.02})$$

Substituting equation 6.02 in equation 6.01 and rearranging, we arrive at the relationship for residual NAPL saturation expressed in Equation 6.03.

$$S_N = \left[\frac{C_{Ra} E_p \rho_b / e - 1}{\frac{C_w}{K - 1}} \right] \quad (\text{Eq. 6.03})$$

The term, $\left[C_{Ra} E_p \rho_b / e \right]$, represents the concentration of radon in the pore fraction which is a constant. It is equal to the maximum aqueous radon concentration for a 0.0% NAPL saturation column. The term, C_w , is the aqueous radon concentration when NAPL is present. Thus, equation 6.03 can be also used for measuring aqueous radon concentrations compared to background in the following rearranged form:

$$\frac{C_{Ra} E_p \rho_b / e}{C_w} = 1 + S_N (K - 1) \quad (\text{Eq. 6.04})$$

The left hand side term in equation 6.04 is also equal to retardation factor by definition of retardation. The residual soltrol saturations of the batch exchange columns were estimated using equation 6.04. A partitioning coefficient of 38.4, estimated by Hopkins (1994), was used for soltrol in these calculations. The retardation factors were estimated by examining the breakthrough of radon and maximum aqueous radon concentrations.

The maximum aqueous radon concentration for the final exchange of each column was estimated by inspecting the respective breakthrough curve. The ratio of maximum aqueous radon concentration for the control column, 173 pCi/L, to that of the column gives the retardation factor for that column. The final residual saturation estimates calculated based on these retardation factors for the columns using Equation 6.04 are presented in Table 6.01 along with the estimates based on TOC and strip test results.

Table 6.01 Comparison of Residual Soltrol Saturation Estimates Based on Aqueous Radon, Strip Test and TOC Observations for Batch Exchange Columns

Column -Initial RS	Maximum Aqueous Radon, pCi/L	Retardation Factor	FRS [*] , % Based on Radon	FRS [*] , % Based on TOC	FRS [*] , % Based on Strip Test
C-0.0%	173	1.00	0	-	-
6-1.0%	146.2	1.18	0.49	0.38	0.46
8-5.0%	152.9	1.13	0.35	1.64	0.23
7-8.0%	70.5	2.45	3.88	1.95	1.01

* FRS denotes Final Residual Saturation

The estimates based on strip test reported here are the averages of all samples tested for each column. Table 6.01 shows that the residual saturation estimates based on the three methods agree well for column 6 and reasonably well for column 8. The estimate for column 7 based on aqueous radon measurement is higher than the estimates from other two tests. The disagreement between the estimates is possibly due to the influence of redistributed soltrol on the maximum aqueous radon concentrations. The retardation factors calculated from the breakthrough of radon may be more representative of the conditions in the columns.

The breakthrough point, volume of influent solution where aqueous radon concentrations equaled 50% of maximum aqueous radon, was determined for each breakthrough curve. The initial data points for which aqueous radon concentrations were affected by redistribution of soltrol in the columns were neglected in these calculations. The breakthrough point thus determined for each curve was divided by the breakthrough of radon in control column C, 450 mls, to obtain the retardation factor for the corresponding exchange. As NAPL is not present in

column C, breakthrough of radon in the column is not supposed to be delayed. Thus, the retardation of radon due to residual NAPL in other columns is measured with respect to the breakthrough of radon in NAPL-less column C. The residual soltrol saturations of the three batch exchange columns estimated for each surfactant flushing based on the model and the TOC analyses are tabulated in Table 6.02.

Table 6.02 Comparison of Residual Soltrol Saturation Estimates Based on Breakthrough of Radon and TOC Analyses for Batch Exchange Columns

Exchange No.	Breakthrough Point, mL	Retardation Factor	Residual Saturation %, Radon	Residual Saturation %, TOC
Column C	450	1	0	-
6-B	600	1.33	0.91	0.99
6-G	588	1.31	0.83	0.88
6-H	582	1.29	0.79	0.83
6-I	536	1.19	0.52	0.68
6-J	496	1.10	0.28	0.62
6-K	485	1.08	0.21	0.56
6-L	485	1.08	0.21	0.45
6-M	480	1.07	0.18	0.38
8-A	1160	2.58	4.26	5.00
8-B	950	2.11	3.00	3.40
8-C	785	1.74	2.01	1.64
8-E	410	0.91	-0.002	0.75
7-A	1900	4.22	7.72	7.58
7-C	1680	3.73	6.55	4.49
7-E	1017	2.26	3.02	1.95

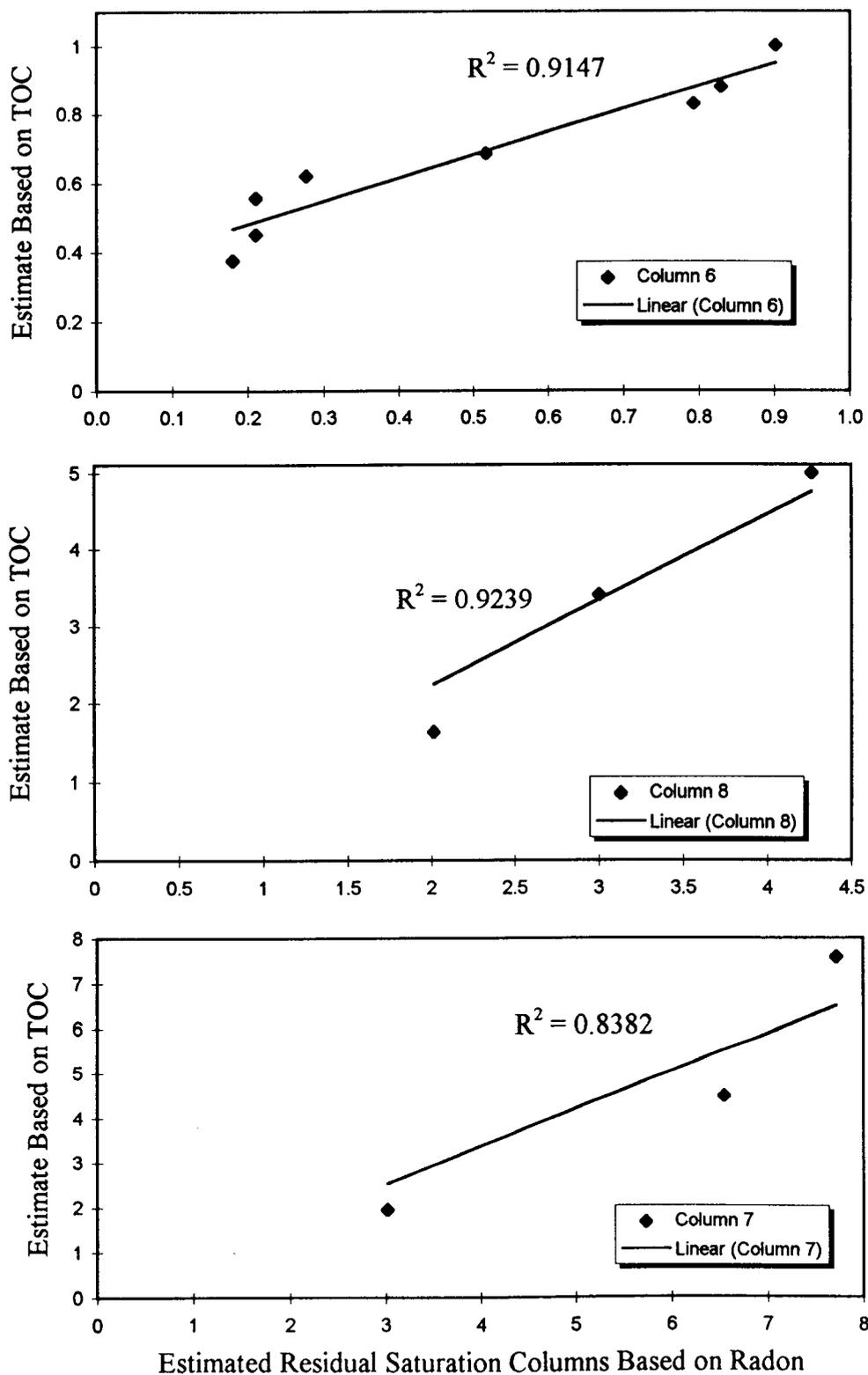


Figure 6.01 Correlation between Radon and TOC Based Estimates of Residual Soltrol Saturations in Batch Exchange Columns 6, 8, and 7

Figure 6.01 shows correlations between the estimated residual soltrol saturations of the three batch exchange columns based on radon and TOC data from the corresponding columns. We observe that the data points are more scattered around the regressed line at lower residual saturations (0% to 0.5%) than at higher residual saturations (0.5% to 1.0%) for column 6. This deviation suggests that there may be inaccuracy associated with TOC method at low residual saturations.

Column 6 (initially at 1.0% residual saturation) has an intercept around 0.3. On the other hand, the linear model with zero intercept fits better for columns 7 and 8 at higher initial residual saturations (refer Figure 6.01). This observation also supports the hypothesis that TOC measurements are less accurate and unreliable at low residual saturations. The regression parameters, R-squared values, which measure dispersion of the estimates for the batch exchange columns are summarized in Table 6.03.

Table 6.03 Regression Parameters for Remediation Batch Exchange Columns

Column Number	Residual Soltrol Saturation, %	R-squared Value
6	1.0	0.9147
8	5.0	0.9239
7	8.0	0.8352

A high degree of correlation between the estimates, indicated by R-squared values, is observed in all the three cases. The agreement between the two methods demonstrates the ability of radon to quantify residual NAPL saturations at various stages of remediation accurately and thereby, evaluate the performance of NAPL remediation methods. The agreement between the estimates also validates the use

the linear equilibrium partitioning model of radon based on retardation factors in estimating the residual NAPL saturations.

Efficiency of Triton in Remediating Soltrol Contamination

The residual soltrol saturations estimated, as described above, for column 6 (initially at 1.0% residual soltrol saturation) based on radon and TOC results are plotted against the cumulative mass of triton exchanged through the column (Figures 6.02 and 6.03). This was done to estimate the effectiveness of triton in solubilizing soltrol, and hence, in remediating NAPLs.

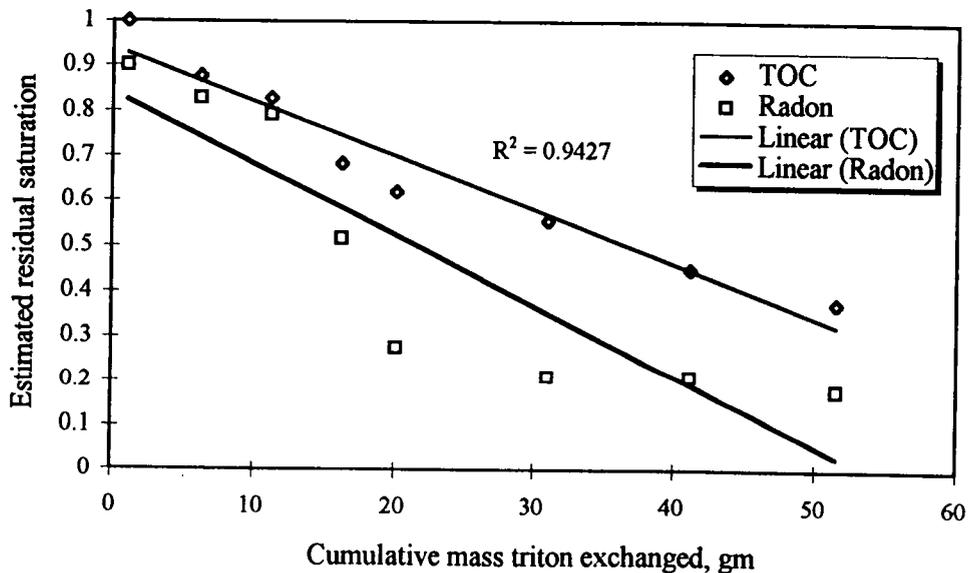


Figure 6.02 Linear Correlation between Estimated Residual Saturations of Column 6 (Initially at 1.0% Residual Saturation) and Cumulative Mass of Triton Exchanged

Figure 6.02 shows the linear regression on the estimated residual saturations and the cumulative mass of triton exchanged. The linear model fits the data points well for TOC based estimates but not the radon based estimates. The correlations in Figure 6.01 suggest that TOC method is less accurate at low residual saturations. The differences between the radon and TOC estimates observed in Figure 6.02 could possibly be due to decreasing sensitivity of the TOC method with decrease in residual saturation of column 6.

A polynomial regression of second order fits the data better for both TOC and radon based estimates (Figure 6.03). The correlation indicates that the residual saturation of the column decreases less during the later exchanges even though triton is flushed through the column. This indicates that not much soltrol is removed from the column during those exchanges. It may be inferred from this observation that triton works more effectively at higher residual NAPL saturations

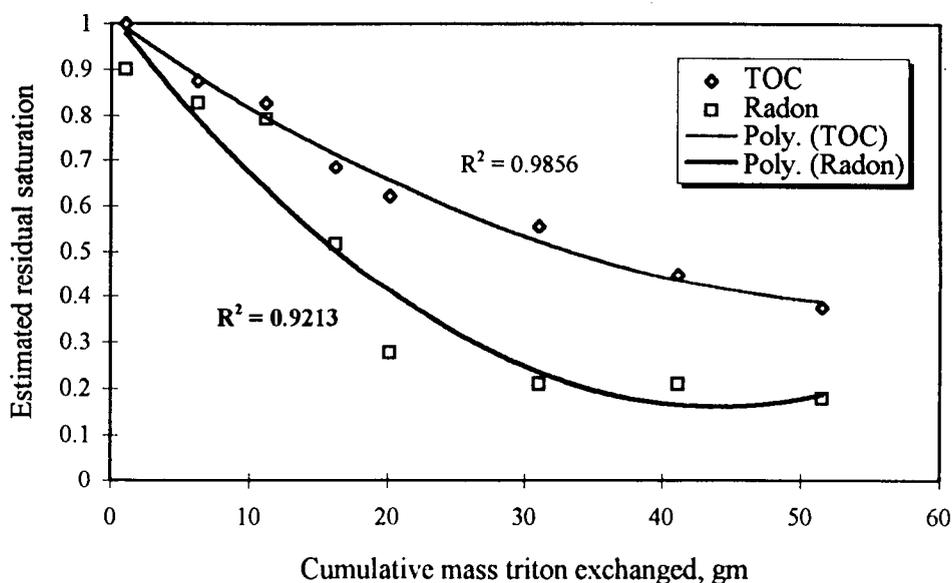


Figure 6.03 Non-Linear Correlation between Estimated Residual Saturations of Column 6 (Initially at 1.0% Residual Saturation) and Cumulative Mass of Triton Exchanged

than at lower residual saturations. One possible reason for the inefficiency of triton is the mass transfer limitations associated with very low residual saturations. The total interfacial area between NAPL and aqueous surfactant phases decreases with reduction in residual saturation. This leads to reduced mass transfer across larger globules and consequent decrease in solubilization capacity of the surfactant. This hypothesis is supported by observations of Miller et al. (1990) that mass transfer coefficients depend on volumetric fraction of NAPL present in the system.

Summary

The results of the remediation batch exchange experiments performed on three columns at various residual soltrol saturations support the utility of radon as tracer for monitoring the progress of NAPL remediation efforts. The breakthrough curves for radon successfully reflected the decrease in residual soltrol saturations of columns as the columns were gradually cleaned up. An increase in maximum aqueous radon concentrations accompanied by a decrease in breakthrough points was observed as remediation of the columns progressed. The shapes of breakthrough curves obtained from successive exchanges of the same column were similar. This similarity indicates that the cleanup was uniform and preferential flow paths were not created. Also, the pore volumes have been restored for columns 6 and 8 which were almost soltrol-free at the end of final exchange.

The residual soltrol saturation estimates made based on the linear equilibrium partitioning and retardation model of radon agreed well with those based on TOC and HDPE strip test analyses. Thus, the results from this study validate radon's use in estimating the level of clean-up achieved during NAPL remediation process as well. The progress of NAPL remediation efforts can be monitored in the field using the partitioning model based on the changes in maximum aqueous radon concentrations. Radon concentrations are easier to

measure in the field compared to breakthrough of radon which requires multiple testing and large volumes to be sampled.

Hopkins (1994) demonstrated the use of partitioning model of radon based on changes in maximum aqueous radon concentrations as well as breakthrough of radon. He showed that the maximum aqueous radon concentrations were higher and the breakthrough was less retarded in columns at lower residual soltrol saturations compared to the columns at higher residual soltrol saturations. In this research, done employing some of the columns used in his study, the phenomena of increasing maximum aqueous radon concentrations and decreasing retardation were observed in the same column, as the residual saturation of the column reduced with surfactant flushing. This observation supports the ability of radon to not only detect and quantify NAPLs but also accurately reflect the changes in NAPL saturations during remediation of a NAPL-contaminated site.

The surfactant used in the study, triton, proved to be effective in remediating soltrol contaminated columns. However, problems were encountered during sampling processes due to clogging of pores of the aquifer medium in the columns. This clogging is believed to have been caused by blockage of pore throats by the surfactant micelles formed or dispersion of fine materials. There is evidence in literature that supports this hypothesis. Plugging of sampling wells had been observed in field situations where surfactants were used for cleaning up contamination due to NAPLs (Kimball and Bates, 1992; Nash et al., 1987). Hence, the possibility of facing such problems should be considered before employing surfactants to enhance remediation of NAPL-contaminated sites. Selecting a surfactant that is compatible with the target NAPLs is one possible way to overcome this problem.

Chapter 7 Summary

The results indicate that radon-222 can be successfully employed as a tracer for performance assessment of NAPL remediation technologies. The changes in aqueous radon concentrations and radon transport demonstrated radon's ability to partition quickly between water and soltrol during the experimental time frame. As a consequence, radon indicated the changes in residual NAPL saturations instantaneously. This study also supports the use of linear equilibrium partitioning model of radon based on retardation to quantify the residual NAPL saturations at various stages of remediation and estimate the extent of clean-up achieved. The major findings of this study are:

- ◆ Radon successfully demonstrated the progress of remediation in soltrol-contaminated soil columns. The aqueous radon concentrations increased and the retardation of radon decreased as more soltrol was solubilized with each surfactant flushing of the columns.
- ◆ The linear equilibrium partitioning model of radon based on breakthrough of radon estimated the residual NAPL saturations reasonably well. The estimations were in good agreement with those made based on independent studies.
- ◆ Triton was efficient in solubilizing soltrol and remediating the columns. The solubilization appeared to be rate-limited rather than instantaneous.
- ◆ Aged soltrol in the columns adversely affected the solubilization capacity of triton.

Scope for Radon as Tracer

The ability of radon to partition into NAPLs makes it a good candidate for detecting and quantifying NAPLs. The results from this research suggest that radon can be reliably used to assess the performance of NAPL remediation schemes in the saturated zone. Thus, radon offers a cost-effective and non-intrusive means of not only characterizing NAPL contamination but also monitoring the progress of NAPL remediation efforts.

The effectiveness of the selected remedial scheme can also be evaluated using the linear equilibrium partitioning model of radon. This model facilitates prediction of residual NAPL saturations which indicate the level of clean-up achieved and therefore, the efficiency of the remedial technology. Estimation of residual saturation can be made based on retardation factors if the characteristics of the contaminating NAPL and the aquifer are known. The retardation factors may be calculated by measuring either the deficit in maximum aqueous radon concentration or the breakthrough of radon. The deficit in aqueous radon concentrations estimates residual NAPL saturations at the sampling points where as the breakthrough of radon estimates residual saturations of the integrated areas.

A background breakthrough curve for radon may be obtained by sampling an uncontaminated zone having similar geological characteristics as the contaminated site. The initial breakthrough curve for radon is then obtained by sampling the contaminated zone. Injection of clean water into monitoring wells and analysis of extracted aqueous samples for radon is required to obtain the breakthrough curves. Then, successive breakthrough curves for radon are obtained from the contaminated zone at various stages of remediation. The performance of the remedial technology chosen for NAPL remediation can be assessed by comparing the breakthrough curves. The translation of the initial breakthrough curve towards the background breakthrough curve illustrates the cleanup of the contaminated site.

However, there are a few disadvantages to this method. Once the aquifer is sampled, radon requires time to build back to equilibrium levels in the groundwater. Hence, immediate sampling of the contaminated zone is not possible and consequently, monitoring the progress of the remediation technologies can't be done during periods of radon re-equilibration. In addition, it requires multiple testing to be done. The advantage of estimating residual NAPL saturations using breakthrough of radon is that large areas of the site can be evaluated.

Evaluation of a remediation technology by aqueous radon deficit method is easier and flexible. The sample volumes can be adjusted depending on the characteristics of the site. Increase in aqueous radon concentrations at a sampling well indicates decrease in the residual NAPL saturations and thereby, suggests the progress of remediation. Absence of deficit in aqueous radon concentrations from background indicates complete recovery of NAPL from a previously contaminated location. The estimates of residual NAPL saturations based on deficit method are representative of local conditions rather than those in sampling area.

The reliability and accuracy of the residual saturation estimates and thus, remediation performance assessment by radon depends on many factors. An aquifer matrix with high organic carbon content may act as a sink for radon and contribute to the deficit in aqueous radon concentrations observed. Hence, the organic carbon content of the medium should be considered when estimating residual saturations. The emanation characteristics of the aquifer material also affect the sensitivity of the estimations. The higher the emanation coefficients, the more accurate the measurements of radon concentrations which yield reliable saturation estimates.

Adequate knowledge of the site characteristics, such as porosity and heterogeneities present, is also important since they influence the radon emanation characteristics. High porosity implies less aquifer solids which results in low radon concentrations due to reduced source material. Extrapolation of estimates leads to erroneous conclusions if heterogeneities in aquifer characteristics are present. Extensive characterization of contamination at the site, the NAPLs present and the

radon partitioning coefficients for these NAPLs, is also required to obtain reliable estimates of residual saturations using this method.

Scope for Surfactant-Enhanced Remediation of NAPLs

Triton, the surfactant, used in the study was very effective in solubilizing soltrol and cleaning the NAPL contaminated columns. Thus, the results support the use of surfactants in remediating NAPL-contaminated sites. The efficacy of pump-and-treat technology, commonly used for remediating NAPLs, can be enhanced by employing surfactant solution as the injecting fluid.

The micellar solubilization of soltrol by triton appeared to be rate-limited rather than instantaneous, indicated by greater soltrol removal following periods of batch equilibration. This phenomenon can be capitalized upon to maximize the NAPL solubilizing capacity of surfactants which minimizes the volume of surfactant solution required for NAPL recovery and the expenses involved. Flushing of the contaminated aquifer with surfactant solution can be scheduled so that optimal solubilization of NAPLs is achieved.

Care should be taken to select appropriate surfactants that are compatible with target NAPLs to get maximum benefits of surfactant-enhanced NAPL recovery. Inappropriate surfactant selection may lead to surfactant losses due to precipitation, clogging of aquifer pores due to gel formation, and consequent failure of the technology to remediate NAPL-contamination.

Directions for Future Research

Further research needs to be done to confirm radon's potential in evaluating performance of NAPL remediation techniques prior to field application of the method. The following studies are suggested to better understand radon's NAPL

partitioning capability in complex systems and optimize the utility of radon-222 method in remediation performance assessment.

- ◆ Evaluate the potential of radon to monitor progress of NAPL remediation in a continuous flow situation in laboratory studies. A one-dimensional physical model that mimics real field conditions may be remediated and the response of radon studied for this purpose. The residual saturation estimates based on radon may be compared to estimates made by an independent method to verify radon's ability as a tracer.
- ◆ Model the results from one-dimensional physical model studies to obtain correlations, if possible, that can be used to predict the behavior of radon in the complicated systems of remediation.
- ◆ Examine the possibility of using radon as a tracer for remediation performance assessment in more complex situations if the one-dimensional physical model studies succeed. Two-dimensional and three-dimensional physical models better represent the conditions observed at contaminated sites.
- ◆ Develop techniques for direct measurement of aqueous radon concentrations which would enable quick and easy estimation of residual NAPL saturations. The possibility of using a liquid scintillation counter for quantifying radon concentrations is now being researched.
- ◆ Research analytical methods that could be employed to make reliable estimates of the NAPL removed with each exchange for comparison with residual NAPL saturation estimates based on radon. For example: High performance liquid chromatography may be more accurate in separating and quantifying the organic compounds in the effluents from batch exchange experiments than TOC analysis.
- ◆ Develop methods for field implementation of the technique for use during remediation of an actual site.

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APPENDICES

Appendix A

Preparation of Influent

Synthetic Borden Groundwater

The recipe developed by Michael McDonald closely mimics the in-situ groundwater at Borden aquifer site, Canada. Hence, synthetic Borden groundwater used in this research was prepared using his recipe. No modifications were made.

Steps Involved

- ◆ Take 15 Liters of deionized, distilled water. DD/DI water that had passed through a Nanopure[®] purification system (Barnstead[®] II) was used in this research.
- ◆ Weigh 17.9 mg of KCl, 57.1 mg of NaCl, 346.8 mg of MgSO₄, and 2000 mg of CaCO₃ (in excess) and add them to the distilled water.
- ◆ Mix ingredients thoroughly until they are dissolved. A Lab-line[®] multi-magnestir was used for this purpose in the present study.
- ◆ Stir under a continuous purge of filtered laboratory air for a period of four days.
- ◆ Synthetic water thus prepared should be stored away from light to alleviate sliming.

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)
- MgSO₄ MCB Reagents, a division of EM Science, Gibbstown, NJ (MCB No. MX0075-1, Lot No. 120.39)
- CaCO₃ Mallinckrodt AR (Mallinckrodt No. 4072-03, Lot No. 4072 KLHD)

Triton[®] X-100 Solutions

Various concentrations (0.1% to 2.5% weight/volume) of aqueous Triton[®] X-100 (also, triton) solutions were used for the study. Here, a 2.5% triton solution implies that 2.5 gms of triton was added for every 100 mls of distilled water in the stock solution.

Procedure

- ◆ Weigh the amount of triton required to make a surfactant solution of desired concentration to the nearest 0.01 gm in a beaker. The formula used for calculating the weight of triton (W) required is (Eq. A.1),

$$W = \frac{\%S \times V_s}{100} \quad (\text{Eq. A.1})$$

where %S Concentration of triton solution (weight/volume basis)

V_s Total volume of stock solution intended, mL

- ◆ Transfer triton into a volumetric flask of appropriate volume. Use streams of distilled water from a wash bottle to flush out all the surfactant from the beaker into the flask.
- ◆ Add distilled water to the volumetric flask in fractions of the total volume and mix the contents thoroughly by rotational movements after each addition.
- ◆ Leave the flask undisturbed for a few hours to allow dissipation of the foam that was formed during mixing.

- ◆ When all the triton gets dissolved, make up the solution in the flask to the mark by adding distilled water; cap it and mix end-over-end a few times to obtain a solution of uniform composition.

Chemical Supplies

- Triton[®] X-100 Aldrich Chemical Company, Inc., Milwaukee, Wisconsin
(Catalog No. 23,472-9, Lot No. 00419JG)

De-airing Synthetic Borden Groundwater

The synthetic Borden groundwater needs to be de-aired so as to make it radon-free for batch exchange experiments, or when it is used to resaturate batch exchange soil columns. The de-airing schematic is shown in Figure A.1 and the de-airing process follows.

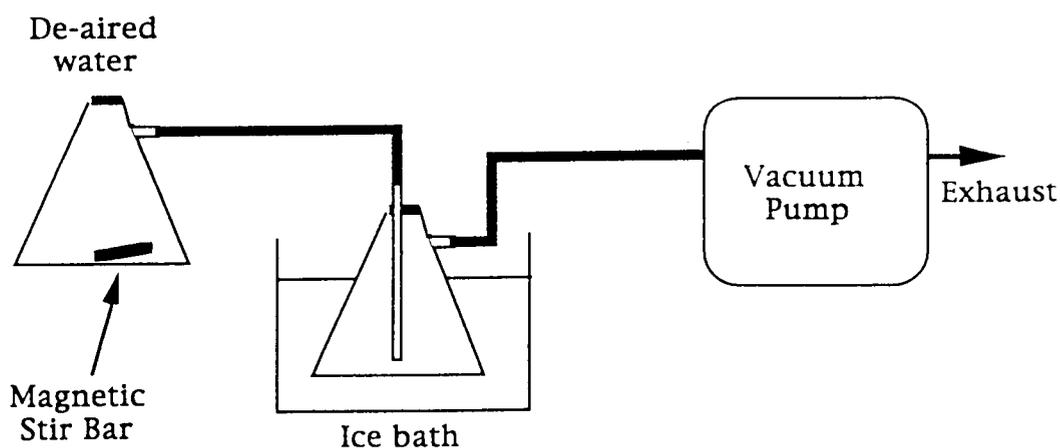


Figure A.1 De-airing Schematic (Hopkins, 1994)

- ◆ Several liters of to-be-deaired water are taken in a sealable Erlenmeyer flask with a single side-opening.
- ◆ A large magnetic stir bar is dropped into the flask and the flask is placed on a magnetic stirrer plate.
- ◆ The single side-opening of the flask is connected to a vacuum pump. An iced vacuum trap should be present in the vacuum line (See Figure A.1).
- ◆ The pump and the stir plate are run for about 20 minutes to accomplish complete de-airing of the solution.

Equipment Required

- 3 L capacity Erlenmeyer flask with stop-cock cap and a side opening
- Vacuum pump, Cenco Hyvac 2, Cenco Scientific Co., Chicago (Catalog No. 91305) and a trap with 1 liter volume
- Magnetic stir plate, VWR[®] DYLASTIR[®], and a magnetic stir bar
- Rubber tubing for connections

Appendix B

Analysis Of Total Organic Carbon in Samples

Total Organic Carbon (TOC) analyses were performed to evaluate the extent of NAPL solubilization achieved by each surfactant flushing. For each exchange, the difference between the TOC contents of the influent and effluent solutions gives a rough estimate of the amount of soltrol that had been removed with each sample in that exchange. TOC analyses results were more of qualitative importance than of quantitative significance in this study owing to the large difference in TOC values for triton and soltrol, and low percentages of NAPL in the effluent solutions compared to triton. Samples from micro-column studies as well as batch exchange experiments were analyzed for TOC using a DC-190 High-Temperature TOC Analyzer fitted with a Non-Dispersive Infra Red (NDIR) detector.

Principle of Operation of the TOC Analyzer

The DC-190 system measures the TOC content of a sample based on the difference between its total carbon (TC) and inorganic carbon (IC) contents. Samples are manually or automatically injected into the combustion tube packed with supported platinum catalyst via an air-actuated port. The combustion tube is continuously heated by a furnace maintained at 680 °C. The sample undergoes catalytic oxidation and the CO₂ gas along with the steam thus formed is swept by the carrier gas, usually oxygen, through a condenser and into a gas/liquid separator. The final water which is left in the gas stream is removed by the dehumidifier. The dried CO₂ containing gas then passes through a halogen scrubber and on to a CO₂ specific NDIR detector for peak quantification and TC content of the sample. Gas concentrations are measured by the NDIR based on the

principle that each type of gas component shows a unique absorption spectrum in the infra red region. In order to quantify the IC content, samples are manually or automatically introduced into the IC reactor via an air-actuated port. The IC reactor contains acidic water solution at room temperature. The carrier gas flowing through the reactor purges out all the inorganic carbon in the sample in the form of CO_2 . The gas then passes on through the dehumidifier to get dried and then continues on to the NDIR detector for quantification. Figure B.1 illustrates the flow of sample through the DC-190 system.

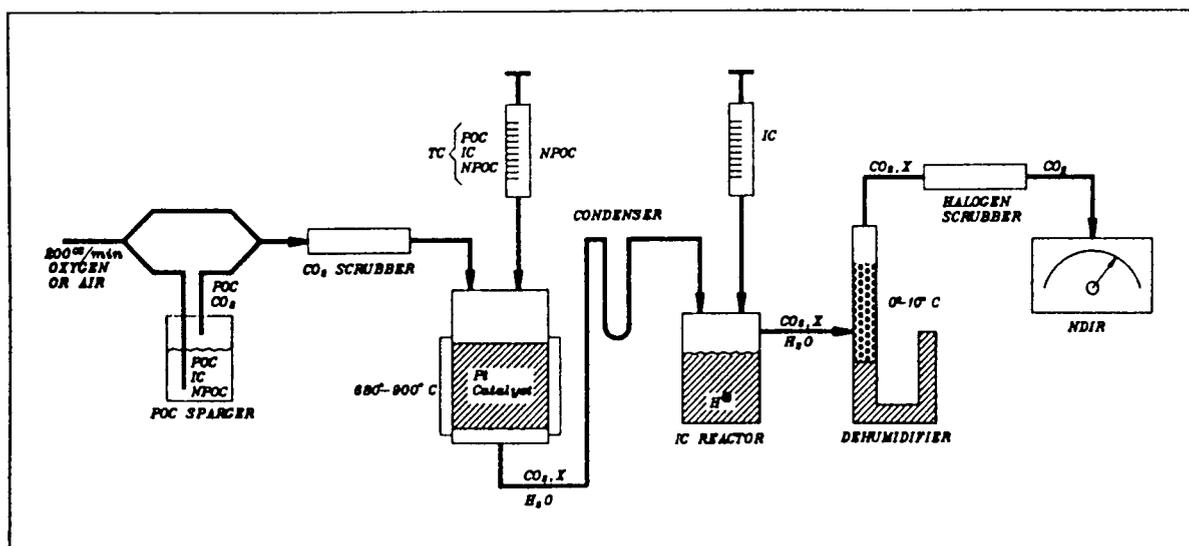


Figure B.1 Flow Diagram of DC-190 System (Adapted from DC-190 Operation Manual)

Equipment and Chemicals Required

- DC-190 High - Temperature TOC analyzer with automatic sampler, Rosemount Analytical Inc., Dohrmann Division, Santa Clara, CA (Part No. 915-262)
- 100 μ L syringe
- 8 ml autosampler vials (as needed)
- 100 ml volumetric flasks (as required)
- Amber borosilicate bottles with Teflon[®]-lined caps
- Aluminum foil
- Phosphoric acid, H₃PO₄ (Concentrated and, 20%)
- Oxygen cylinder, grade 4.4 @ 30 psig
- Potassium Acid Phthalate standard solutions (concentrations as required)
- Deionized/Distilled water

Experimental Procedure

Preparation of Standard Potassium Acid Phthalate Solutions

Potassium Acid Phthalate (KHP) solutions were used as standards to calibrate the TOC analyzer prior to its use. The concentration of the standard solution was selected based on the range of concentrations that were intended to be measured. 100 ml of KHP standard solution is prepared as follows:

- ◆ Weigh required amount of KHP into a 100 ml volumetric flask. The formula to be used to determine the weight of KHP required is given in Equation B.1.

$$W = \frac{mw \times \%C}{N \times 12.01} \quad (\text{Eq. B.1})$$

where

mw molecular weight of KHP, $C_8H_5KO_4$, 204.22 gms

%C concentration of standard in % carbon. For example: 1% for
10000 mg/L

N number of C atoms per molecule, 8

- ◆ Add about 75 ml deionized/distilled water to the volumetric flask and dissolve the compound.
- ◆ Add about 0.1 ml of reagent grade concentrated phosphoric acid to adjust pH below 3.
- ◆ Fill to mark with deionized/distilled water.
- ◆ Transfer to an amber borosilicate bottle with Teflon-lined cap.
- ◆ Store in a refrigerator at 4 °C and keep away from light. Replace after a month for best results.

Preparation of samples

The influent and effluent samples from the experiments were analyzed for TOC without any modifications in case of lower surfactant concentrations (0.1% and 0.5%). As the TOC machine was not able to handle higher concentrations (1% and above) of triton solution, 1:100 dilutions of the influent and effluent samples were used for the TOC analysis. 1 ml of the sample was pipetted into a 100 ml volumetric flask and made up to the mark using distilled water. The flask was capped and thoroughly shaken to obtain uniform mixture.

Procedures for TOC Analysis (Manual Injection)

- ◆ Open gas tank and regulate oxygen gas flow to 30 psig.
- ◆ Check that the side acid bottle is atleast 1/3 full. If it is not, fill it with 20% H_3PO_4 .
- ◆ Check that the IC chamber is half-full by opening the front door of the machine. If it is not, prime acid by pressing the buttons in the following order: Main - 2 - 5 - 1 - 1. This will result in 20 pulses of the acid.
- ◆ Press Main - 1 and check that the system parameters are:
 - Flow rate: 180 - 220 cc/min
 - Dryer temperature: 4 - 5 °C
 - Furnace temperature: 670 - 690 °C
 - Furnace setpoint: 680 °C
- ◆ Select analysis mode as “TOC” and inlet mode as “Syringe”.
- ◆ Rinse the 100 μ l syringe with deionized water several times, then with the standard solution.
- ◆ Press “Calibrate” and begin calibration of the machine by setting Calibration Factor to 1 and System Blank to 0.
- ◆ Enter the standard concentration being used for the run and the volume.
- ◆ Press “Start” to analyze.
- ◆ Ensure that there is no air in the sample taken in the syringe. Open the TC port (indicated by the flashing light), quickly inject sample into the port and close port. Repeat with the IC port.
- ◆ Run four trials to get a good average.
- ◆ Update the calibration factor using “calibrate” button.
- ◆ Rinse the syringe with deionized water thoroughly and next, with the sample solution. Perform rinsing with deionized water and the sample whenever the sample is changed.
- ◆ Prepare a 100 μ l sample ensuring there is no air in the syringe.

- ◆ Press “Start” to analyze and enter the ID number for the sample. As done for calibration, analyze the sample for TC and IC.
- ◆ Run at least four trials for a good average.
- ◆ Repeat until all the samples are analyzed. Be sure not to contaminate samples. Rinse syringe thoroughly in between samples.
- ◆ Obtain the printout containing analyzed data from the printer.
- ◆ Turn off the carrier gas button and close the oxygen tank.
- ◆ Be sure to leave the furnace on.

Procedures for TOC Analysis (Autosampler)

- ◆ Transfer about 6 mls of influent and effluent sample solutions or diluted samples into clean and dry autosampler vials. Close the mouth of the vials with aluminum foil and label them.
- ◆ Place vials in the autosampler tray starting from position 1. Place pegs in the appropriate circle to set vials for calibration.
- ◆ Fill rinse bottle with acidified rinse water.
- ◆ Start as for the manual injection and initialize all calibration parameters.
- ◆ Press “TOC” and “ASM” to set analysis and inlet modes. The latter option gives choices for setting number of trials, sample volume, rinse and stir times for each vial.
- ◆ Move sparge arm to its position.
- ◆ Check if the printer is on and that there is enough paper.
- ◆ Press start to begin TOC analysis in ASM mode. Watch and be sure that the arm functions properly. The samples are analyzed in the order they are placed in the tray.
- ◆ Date prints when all the samples are analyzed. The carrier gas flow will automatically turn off if that option is chosen.

Chemical Supplies

- Phosphoric Acid, H_3PO_4 , (85%), Mallinckrodt AR[®], Paris, Kentucky (Lot No.: 2796KJHJ)
- Potassium Acid Phthalate, KHP, Mallinckrodt AR[®], Paris, Kentucky (Lot No.: 6704KJJB)

Appendix C

HDPE Strip Test for Soil Samples

Principle

The organic liquid content of the soil samples from various columns used in this research was quantified using the assay developed by Cary et al. (1991). The underlying principle is that the hydrophobic high density polyethylene (HDPE) will adsorb the organic liquid displaced from the predominantly polar soil sample by water. The results from HDPE tests provided a means of verifying the conclusions made from other analyses namely, the TOC analysis and the Radon analysis.

Equipment and Materials

- G10 Gyrotory Shaker, NewBrunswick Scientific Co., Inc., N.J.
- Weigh Balance (AG104), Mettler-Toledo
- 10 to 20 μm High Density Polyethylene strips, Porex[®] Technologies Corp., Fairburn, GA (Item No. X-4765A)
- Sand samples from soil columns or micro-columns, and controls
- Kimwipes[®] Ex-L, Kimberly-Clark Corporation, Roswell, GA (Code 34155)
- Soltrol[®]-220
- Porcelain dishes
- Aluminum weigh dishes (57 mm size), Fisherbrand, Fisher Scientific (Catalog No. 08-732, Item No. 019)
- 100 ml glass bottles with screw-top caps
- Distilled water

Experimental Procedure

- ◆ Cut strips of required size from the sheet of 10 to 20 μm porous polyethylene. The size of the strip depends on the amount of organic liquid that needs to be extracted. For efficient extraction, Cary et al. (1991) suggest using at least 1 gm of dry porous polyethylene for each 0.5 ml of organic liquid in the sample.
- ◆ Place them in a labeled aluminum dish and oven dry them. Weigh them after they cool down to room temperature.
- ◆ Pretreat polyethylene strips with a thin layer of Soltrol-220 to ensure maximum hydrophobicity. Wrap each dry polyethylene strip in a soltrol-wet Kimwipe. Leave them undisturbed overnight and let them equilibrate.
- ◆ Weigh them with their corresponding aluminum dishes to get the amount of oil sorbed during pretreatment.
- ◆ Add a known amount of soltrol to clean Borden sands taken in a porcelain dish, mix well and let it equilibrate overnight. The sand sample thus prepared serves as the control sample.
- ◆ Weigh 20 to 50 gm of the soil sample into a labeled pre-weighed 100 ml glass bottle equipped with screw-top cap.
- ◆ Add the pretreated HDPE strip to the bottle. Add 15 to 20 ml of water to displace organic liquid from the hydrophilic pores in the sample. Cap the bottle.
- ◆ Place the bottles thus prepared on a gyrotory shaker for 3 to 4 hours.
- ◆ After gently shaking, remove the strip from the bottle. Use a stream of water from a wash bottle to remove any adhered soil particles.
- ◆ Brush off water droplets with Kimwipes and weigh the strip with the aluminum dish. Determine the amount of mass adsorbed.
- ◆ Correct the values thus obtained for incomplete extraction due to the presence of hydrophobic surfaces in the porous medium. The correction value is

obtained by comparing extraction results on control samples of the porous medium to those from samples with just water and a known amount of soltrol. Hence, one sample containing water and known amount of soltrol without the soil medium is run.

- ◆ Oven-dry the strip from the control sample after extraction in the aluminum dish and weigh it. The difference between the final weight and the initial oven dry weight of the strip gives the mass of trapped soil particles. This correction factor should be also applied to all the samples.

Appendix D

Extraction of Radon From Aqueous Samples

The radon gas in aqueous samples obtained from remediation batch experiments needs to be extracted and transferred to a Lucas-type scintillation flask before it can be counted. The extraction apparatus used for this purpose, developed by Stoker and Kruger (1975), is shown schematically in Figure D.1.

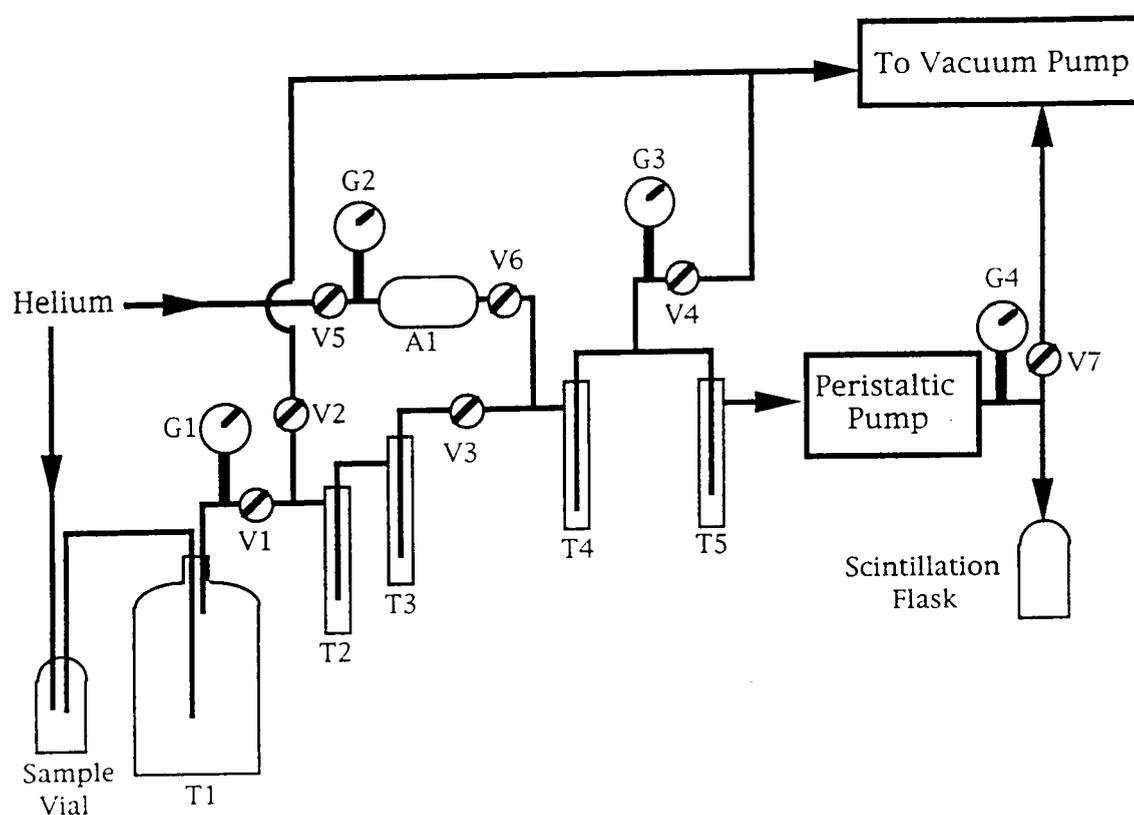


Figure D.1 Schematic of Radon Extraction and Transfer Set-up (Hopkins, 1994)

Procedure

- ◆ Fill the vacuum trap bath (not shown in Figure D.1) with regular ice.
- ◆ Switch on the vacuum pump and close the vacuum relief valve.
- ◆ Check the extraction set up for leaks.
 - Open valves V1 through V4, and valve V6.
 - Close the valves when gauges G1 through G3 show 30 inches of Hg.
 - Wait for half an hour to see if the system is air-tight. If any of the gauges lose vacuum in the meantime, check the connections in that section and repeat the leak test.
- ◆ Immerse traps T2 (which contains steel wool) and T4 (which contains granular activated carbon (GAC)) in separate isopropanol_dry-ice baths and cool them down to $-45\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$.
- ◆ Evacuate Lucas-type scintillation flask by opening V7.
- ◆ Open only valves V1, V2, V3, V4, and V6 and evacuate the apparatus.
- ◆ Close valves V2 and V6 to allow the gas stream to flow through traps T1 to T4 before being exhausted into the atmosphere.
- ◆ Strip radon from the aqueous sample by bubbling helium.
 - Insert a short needle at one end of a tygon tubing into the sample vial. The other end is connected to the water trap, T1.
 - Insert a long needle into the bottom of the vial through the rubber septum. The long needle is connected to a helium tank by means of tygon tubing.
 - Adjust pressure on the helium tank so that helium bubbles through the sample. Sparge helium for at least 10 minutes.
 - Trap T1 removes water, trap T2 removes water vapor, and trap T3 (that contains Ascarite II[®]) removes CO₂ from the gas stream as it passes through the system.

- ◆ Close valves V1 and V3. The radon gas is now adsorbed on to the GAC in trap T4.
- ◆ Remove the dry-ice baths and turn on the thermostat.
- ◆ Allow the charcoal trap, T4, to warm up to 45 °C. Gases, other than radon, that have sorbed to GAC are exhausted into the atmosphere. Close valve V4.
- ◆ Heat trap T4 to around 210 °C by adjusting the thermostat to 30.
- ◆ Transfer radon from GAC trap to scintillation flask.
 - Fill aliquot A1 with helium gas by opening and closing valve V5.
 - Open valve V6 and flush GAC trap with helium. Allow pressure in gauge G3 to equilibrate before closing V6.
 - Run peristaltic pump till pressure in gauge G3 is reduced to a vacuum of 28 to 29 inches of Hg.
 - Flush four to five aliquots of helium to ensure complete transfer of radon.
 - Shut down peristaltic pump and switch off the thermostat.
- ◆ Remove Lucas cell and allow to age for 4 hours before counting.
- ◆ Repeat this procedure to extract radon from all the samples.
- ◆ When all the samples are extracted, open vacuum relief valve and shut down vacuum pump.

Equipment

- Vacuum pump, Cenco Hyvac 2, Cenco Scientific Co., Chicago (Catalog No. 91305) and a trap with 1 liter volume
- Peristaltic pump, Sigmamotor, Middleport, NY (Model T6S)
- He tank with appropriate two-stage regulator
- 7 High vacuum stopcocks, Ace Glass, Vineland, NJ (Ace No. 8206-05)

- 4 Vacuum gauges, VWR, San Francisco (VWR No. 31757-128)
- 4 Vacuum traps, Ace Glass, Vineland, NJ (Ace No. 8753-06)
- 1 Trap with heating element
- 1 He aliquot
- 1 Precison Glide® needle, 20G1 gauge, Becton Dickinson & Co, NJ (Article No. W12534)
- 1 long stainless steel needle, 22 gauge, Hamilton Co., Reno, Nevada (Stock No. 28676, Article No. N722NDL)
- Lucas-type scintillation flasks (as needed)

Chemicals

- 20 g Gas adsorption grade charcoal, 7-14 mesh in size, Fisher Scientific, Fairlawn, NJ (Fisher No. 05-690A)
- 20 g Ascarite II, approximately 20 - 30 mesh in size, Thomas Scientific®, Swedesboro, NJ (Catalog No. C049-U90, Lot No. 6148)
- 20 g Drierite, 8 mesh in size, W.A. Hammond Drierite Company, Ohio (Stock No. 23001)
- Dry ice
- 2-propanol, J.T. Baker Chemical Co., NJ (Stock No. 3-9334, Lot No. 130116)
- Regular ice cubes

Appendix E

Calculating Aqueous Radon Concentration

Purpose

Concentrations of radon in the aqueous samples from remediation batch exchange experiments were calculated using an excel spreadsheet. A template set up by Hopkins (1994) was used for this purpose with little modification. The various formulae used and the correction factors applied to arrive at the concentrations are explained in this section. A sample spreadsheet (Table E.1) is attached for reference.

Calculations

Sample ID (Column A): The sample label, C#S#, is entered in this column. The C# refers to the column number and S# refers to the sample number. The WASTE labels indicate that water that has been exchanged was not used for measuring radon concentrations.

Scintillation Flask ID (Column B): The number of the scintillation flask which was used to collect radon gas from the sample is entered in this column.

Background dpm (Column C): The background counting rate of the scintillation flask in disintegrations per minute is entered in this column.

Extraction Sample Size (Column D): The volume of water exchanged for the sample in milliliters is transcribed from the laboratory notebook into this column.

It is determined gravimetrically by the difference in weights of the sample vials before and after collection of the samples.

Estimated Sample Point (Column E): The estimated sample point was assumed to occur at the midpoint of each sample volume. Thus the sample point for each sample is set at the sum of all the preceding sample sizes and half the sample size of the current sample. An example of a cell formula used is:

$$=SUM(\$D\$14:D21)+D22/2$$

Total Counts (Column F): The total number of disintegrations during a thirty-minute period detected for the sample by the scintillation counter are entered in this column. This value is noted directly from the laboratory notebook.

dpm Counted (Column G): This value denotes the disintegrations per minute counted for the sample. The cell formula used for calculating is:

$$=F22/30$$

Corrected dpm (Column H): This value is obtained by subtracting the background dpm from the dpm counted for the sample. An example of the cell formula used is:

$$=G22-C22$$

Decay Factor (Column I): The amount of radon decayed during the time period between sample collection and counting is expressed by this factor and is calculated using the formula, for example:

$$=EXP(-0.0075226*(J22+K22))$$

where $-0.0075226 \text{ hrs}^{-1}$ is the value for decay constant (λ) of radon.

Time till Extraction (Column J): The time, in hours, that has elapsed since sample collection until transfer of radon to the scintillation flask is calculated separately

and entered in this column. As the sampling, extraction and counting procedures took 30 to 60 minutes for completion, the time for each procedure was set half-way between the start and finish of each process.

Time between Extraction and Counting (Column K): This time, in hours, between the extraction and counting procedures is calculated separately and recorded into the spreadsheet.

Buildup Correction (Column L): In order to account for the radioactivity of the daughter products of radon, the radon counted for each sample is adjusted by a buildup factor given by:

$$=2.90708*(EXP(-0.0075226*(K22-4)))$$

Radon (pCi) (Column M): The actual amount of radon in the sample is calculated by the following sample formula:

$$=H22/(0.725*2.22*I22*L22)$$

where 0.725 estimated efficiency of the extraction and transfer apparatus

2.22 conversion factor for disintegrations to picocuries

Groundwater Equilibration Time (Column N): The time period during which the column was left undisturbed before sampling was calculated separately and entered in this column.

Equilibration Correction (Column O): The correction factor to be applied to the amount of radon calculated in order to give the percent of equilibrium concentration achieved during the contact time with the solids is calculated in this column. An example of a cell formula used follows:

$$=1-EXP(-0.0075226*N22)$$

Adjusted Radon (pCi) (Column P): The equilibrium correction factor is applied to the radon counted in this column. The anticipated equilibrium radon is calculated as:

$$=M22/O22$$

Radon Concentration pCi/liter (Column Q): The aqueous radon concentration of the sample is determined by dividing the adjusted radon by the sample size. The following is a sample cell formula used:

$$=P22/D22$$

Table E.1 Sample Spreadsheet for Calculating Aqueous Radon Concentrations

Remediation Batch Exchange Experiments

Column # 36 was last exchanged on August 16, 95 until 14:40
 This column was initially at an estimated 1% residual saturation. Initially, 4.4 mls of Soltrol mixture were added.
 Exchange took place on 6 September, 1995 between 10:28 and 12:32
 Influent is 1.0% Triton X-100 Solution. Fresh batch prepared from 2.5% Triton X-100 solution.
 Sample was collected at the bottom of the column. Pressure head difference and a little vacuum on the vials enabled sampling

Sample ID	Scintillation Flask ID	Background dpm	Extraction Sample Size	Estimated Sample Point	Total Counts	dpm Counted	Corrected dpm	Decay Factor	Time till Extraction	Time between Extraction and Counting	Buildup Correction	Radon (pCi)	Groundwater Equilibration Time	Equilibration Correction	Adjusted Radon (pCi)	Radon Conc. pCi/liter
C36S1	7	1.0	71.1	35.5	806	26.9	25.9	0.8963	8.13	6.43	2.8544	6.282	500.88	0.977	6.431	90.508
WASTE			80.8													
C36S3	6	1.6	89.4	196.5	1568	52.3	50.7	0.9023	7.05	6.62	2.8503	12.240	500.88	0.977	12.530	140.123
C36S4	7	1.1	90.4	286.4	1163	38.8	37.7	0.6252	51.27	11.17	2.7544	13.590	500.88	0.977	13.912	153.872
C36S5	5	1.7	86.3	374.8	1607	53.6	51.9	0.9077	6.02	6.85	2.8454	12.477	500.88	0.977	12.772	148.009
C36S6	4	1.6	79.9	457.9	922	30.7	29.1	0.9131	5.10	6.98	2.8426	6.973	500.88	0.977	7.138	89.307
WASTE			83.1													
C36S8	3	1.0	84.4	623.1	131	4.4	3.4	0.6320	49.62	11.37	2.7503	1.203	500.88	0.977	1.232	14.591
C36S9	3	1.3	88.1	709.4	112	3.7	2.4	0.9204	3.82	7.20	2.8379	0.579	500.88	0.977	0.592	6.725
C36S10	2	1.4	87.2	797.1	117	3.9	2.5	0.6365	47.88	12.18	2.7336	0.893	500.88	0.977	0.914	10.477
WASTE			84.1													
C36S12	2	1.3	84.0	966.7	157	5.2	3.9	0.9280	2.60	7.33	2.8352	0.929	500.88	0.977	0.951	11.324

* Samples with aqueous radon concentration values in bold were extracted later on 8 Sept. '95.

Chronological Sampling Data

Sample ID	Time and Date of Sampling		Time and Date of Extraction		Time and Date of Counting	
C36S1	10:36	6-Sep	18:44	6-Sep	1:10	7-Sep
C36S3	10:58	6-Sep	18:01	6-Sep	0:38	7-Sep
C36S5	11:13	6-Sep	17:14	6-Sep	0:05	7-Sep
C36S6	11:27	6-Sep	16:33	6-Sep	23:32	6-Sep
C36S9	11:59	6-Sep	15:48	6-Sep	23:00	6-Sep
C36S12	12:29	6-Sep	15:05	6-Sep	22:25	6-Sep
C36S4	11:06	6-Sep	14:22	8-Sep	1:32	9-Sep
C36S8	11:53	6-Sep	13:30	8-Sep	0:52	9-Sep
C36S10	12:07	6-Sep	12:00	8-Sep	0:11	9-Sep

Appendix F

Performing Mass Balance on Soltrol

This section explains the manner in which mass balance calculations were performed on soltrol. As the exact molecular formula for Soltrol-220 isn't available, soltrol is assumed to be a mixture of branched alkanes with 13 to 17 carbon atoms (Martin Schroth, personal communication, 1995). And the molecular formula is taken as $C_{15}H_{32}$. Hence,

$$\text{Molecular weight of soltrol} = (15 \times 12.011 + 32 \times 1.008) = 212.42 \text{ grams}$$

Since each molecule of soltrol has 15 carbon atoms, theoretically,

$$\text{Total Organic Carbon (TOC) of soltrol} = 15 \times 12.011 = 180.17 \text{ grams C}$$

$$\text{Therefore, TOC per gram of soltrol} = \frac{180.17}{212.42} = \mathbf{0.85}$$

Total Initial TOC of Soltrol in a Column

The initial TOC of soltrol in the columns is estimated from the amount of soltrol present in the columns before commencing remediation experiments. The calculation of the amount of soltrol present in micro-columns is pretty straight forward. The volume of soltrol used for constructing each micro-column is multiplied by the density of soltrol to give the weight of soltrol present in that micro-column. This weight when multiplied by factor 0.85 yields the TOC of soltrol, in gram C, in the column.

In case of batch exchange columns, the actual amount of soltrol present is calculated taking into account the soltrol removed along with some sand from columns and the soltrol added to the columns while replacing that sand with fresh soltrol-mixed sand. In making these adjustments, it is assumed that the sands are

uniformly mixed with soltrol. The procedure used for calculating the initial TOC of soltrol in the columns is presented here. Batch exchange column 7 at an estimated initial 8.0% residual soltrol saturation is selected for that purpose.

For Column 7: The volume of column 7 is determined to be 1062 mls. The pore volume of the column is 451 mls based on an estimated porosity of 0.425. Therefore, to achieve 8.0% residual saturation, volume of soltrol initially added is (= 451 x 0.08) 36.2 mls. This amounts to 29.29 gms of soltrol since the density of soltrol is 0.809 g/cc.

About 159.49 gms of sand was removed from the column for other tests. Assuming that 36.2 mls of soltrol was uniformly mixed with 1655 gms of sand used for column 7, the amount of soltrol removed is calculated as follows:

$$= \frac{29.29}{1655} \times 159.49 = 2.82 \text{ gms}$$

The amount of soltrol added to the column with fresh batch of sand replacing the removed sand is 5.33 mls or 4.31 gms. Hence,

Final estimated weight of soltrol in column 7 = 29.29 - 2.82 + 4.31 = 30.77 gms

Therefore,

Initial TOC of soltrol in column 7 = (30.77 x 0.85) x 1000 = **26128.10 mg C**

Estimating Total TOC of Soltrol Extracted

The amount of soltrol extracted with each exchange was calculated using a spreadsheet. An example spreadsheet is presented in Table F-1. For each sample exchanged, the difference between the TOC of effluent solution and that of influent solution is multiplied by the volume of the sample to yield TOC of soltrol extracted. The values of TOC for all the samples are summed to obtain the mass of soltrol removed from the column in mg C. Then,

$$\text{Percent Removal} = \frac{\text{Total mass of soltrol removed from column, mg C}}{\text{Initial mass of soltrol in column, mg C}} \times 100$$

Table F.1 Sample Spreadsheet for Performing Mass Balance on Soltrol

Total TOC of Soltrol Extracted [After Exchange # 8-C]:

Date Exchanged	Sample ID	Exchanged Vol., mls	Influent TOC ppm C	Effluent TOC ppm C	Difference ppm C	TOC of Soltrol mg C
11-Oct-95	C10S1	59.79	7945.0	86.9	<i>-7858.1</i>	<i>-469.84</i>
11-Oct-95	C10S2	114.48	7945.0	70.7	<i>-7874.3</i>	<i>-901.45</i>
11-Oct-95	C10S3	112.86	7945.0	77.5	<i>-7867.5</i>	<i>-887.93</i>
11-Oct-95	C10S4	112.11	7945.0	304.6	<i>-7640.4</i>	<i>-856.57</i>
11-Oct-95	C10S5	108.45	7945.0	10780.0	2835.0	307.46
11-Oct-95	C10S6	114.32	7945.0	17230.0	9285.0	1061.46
25-Oct-95	C16S1	90.11	15770.0	20720.0	4950.0	446.04
25-Oct-95	C16S2	76.25	15770.0	20660.0	4890.0	372.86
25-Oct-95	C16S3	112.55	15770.0	20040.0	4270.0	480.59
25-Oct-95	C16S4	108.04	15770.0	16880.0	1110.0	119.92
25-Oct-95	C16S5	111.69	15770.0	24250.0	8480.0	947.13
25-Oct-95	C16S6	93.15	15770.0	23840.0	8070.0	751.72
25-Oct-95	C16S7	101.66	15770.0	21190.0	5420.0	551.00
25-Oct-95	C16S8	86.16	15770.0	21170.0	5400.0	465.26
25-Oct-95	C16S9	89.19	15770.0	20580.0	4810.0	429.00
25-Oct-95	C16S10	96.04	15770.0	18770.0	3000.0	288.12
25-Oct-95	C16S11	85.19	15770.0	20920.0	5150.0	438.73
25-Oct-95	C16S12	103.74	15770.0	10430.0	<i>-5340.0</i>	<i>-553.97</i>
25-Oct-95	C16S13	78.83	15770.0	20910.0	5140.0	405.19
25-Oct-95	C16S14	90.06	15770.0	35830.0	20060.0	1806.60
25-Oct-95	C16S15	94.31	15770.0	24140.0	8370.0	789.37
25-Oct-95	C16S16	82.31	15770.0	19720.0	3950.0	325.12
25-Oct-95	C16S17	91.31	15770.0	19370.0	3600.0	328.72
25-Oct-95	C16S18	113.41	15770.0	19220.0	3450.0	391.26
25-Oct-95	C16S19	96.89	15770.0	19060.0	3290.0	318.77
25-Oct-95	C16S20	96.03	15770.0	18420.0	2650.0	254.48
25-Oct-95	C16S21	99.78	15770.0	18540.0	2770.0	276.39
25-Oct-95	C16S22	97.65	15770.0	18520.0	2750.0	268.54
25-Oct-95	C16S23	92.69	15770.0	18000.0	2230.0	206.70
3-Nov-95	C19S1	114.05	16050.0	21450.0	5400.0	615.87
3-Nov-95	C19S2	113.97	16050.0	19260.0	3210.0	365.84
3-Nov-95	C19S3	117.80	16050.0	6242.0	<i>-9808.0</i>	<i>-1155.38</i>
3-Nov-95	C19S4	114.84	16050.0	2294.0	<i>-13756.0</i>	<i>-1579.74</i>
3-Nov-95	C19S5	111.84	16050.0	29550.0	13500.0	1509.84
3-Nov-95	C19S6	114.40	16050.0	37750.0	21700.0	2482.48
3-Nov-95	C19S7	128.04	16050.0	33110.0	17060.0	2184.36
3-Nov-95	C19S8	116.32	16050.0	29970.0	13920.0	1619.17
3-Nov-95	C19S9	109.24	16050.0	26990.0	10940.0	1195.09
3-Nov-95	C19S10	113.80	16050.0	25140.0	9090.0	1034.44
Total		3963.35				19748.45

Note: The first few negative values in italics are not considered in calculations

Mass of soltrol removed = 19748.45 mg C

% removal = $100 * (19748.45) / 26128.104 = 75.58$

Appendix G

Estimating Organic Content of Sand Samples

The procedure for estimating residual saturations of the sands sampled from various columns used in this study is described in this section. These estimates were made by determining the organic content of the sand samples by performing HDPE strip tests.

Data Required

- Tare weights of labeled aluminum dishes
- Weights of strips with aluminum dishes
- Weights of pretreated strips with aluminum dishes
- Tare weights of labeled and capped bottles
- Weights of sand samples with bottles
- Final weights of strips with aluminum dishes
- Weight of control-sand sample strip with aluminum dish after oven-drying

Calculations

Weight of Strip: The initial weight of strip is found by subtracting the tare weight of labeled aluminum dish from the weight of strip taken with labeled aluminum dish. This value is used to determine the amount of soltrol adsorbed to the strip during pretreatment.

Initial amount of Soltrol Adsorbed: The difference between the weights of the pretreated strip (with aluminum dish) and the strip (with aluminum dish) gives the

weight of soltrol adsorbed to the strip during pretreatment. This value when divided by the weight of strip yields the initial amount of soltrol adsorbed to the strip in units of gram soltrol per gram strip.

Weight of Sand in Sample: The weight of sand in the sample is determined by the difference between the weight of sand sample with bottle and the tare weight of the bottle.

Final Amount of Soltrol Adsorbed to Strip: This is the actual amount of soltrol removed by the strip from the sand sample during mixing. It is determined from the difference between the final weight of strip (with aluminum dish) and weight of pretreated strip (with aluminum dish).

Recovery Efficiency of the Test: The efficiency of the strip in recovering organic content from the sand sample for the run is determined based on the fraction recovered by the strip in control-water sample. A known volume of soltrol is initially added to water in this sample which doesn't contain sand. The volume of soltrol recovered is calculated from the weight of soltrol adsorbed to the water-control strip based on the density of soltrol. Then,

$$\text{Recovery Efficiency} = \frac{\text{Volume of Soltrol Recovered}}{\text{Initial Volume of Soltrol Added}} \times 100 \quad (\text{Eq. G.1})$$

Corrections

The final amount of soltrol adsorbed to the strip is corrected for the mass of sand particles attached to the strip during shaking. The weight of the trapped mass particles is determined by subtracting the pretreated weight (with aluminum dish) from the oven-dry weight (with aluminum dish) of the strip in control-sand sample. The weight thus obtained is subtracted from the final amount of soltrol

adsorbed to the strips in the sand samples to yield the actual amount of soltrol adsorbed to the strip.

The volume of soltrol recovered from the sand sample is obtained by dividing the actual amount of soltrol adsorbed to the strip in the sample with density of soltrol. A correction is applied to this value to account for recovery inefficiency. The volume of soltrol recovered is divided by the recovery efficiency to obtain the corrected volume of soltrol in the sand sample and, thus the organic content of the sand sample.

Estimating Residual Saturation of Columns

The total volume of soltrol in the column is estimated based on the volumes of soltrol recovered from the sands sampled from the column. The column is assumed to be homogenous with respect to soltrol saturation in making this estimate. The initial residual saturation of the columns is estimated by Equation G.2.

$$\text{Residual Saturation} = \frac{\text{Estimated total volume of soltrol}}{\text{Estimated pore volume}} \times 100 \quad (\text{Eq. G.2})$$

The estimates for final residual soltrol saturations of sands from batch exchange columns were made individually for each sand sample. These estimates were not extrapolated for estimating the residual soltrol saturation of the column. This was done to verify if the remediation of the batch exchange columns by surfactant flushing was uniform.

Appendix H Sample Data Tables

Table H.1 Data from TOC Analyses for Control Column, Micro-column BT0

Date Exchanged	Sample Point, mL	TOC of Influent ppm C	TOC of Effluent ppm C	Difference in TOCs, ppm C
2-Feb-95	3.5	1915	450	-1465
2-Feb-95	8.5	1915	1843	-72
2-Feb-95	11.5	1915	2029	114
2-Feb-95	14.5	1915	2018	103
2-Feb-95	17.5	1915	1832	-83
2-Feb-95	20.5	1915	2110	195
10-Feb-95	23.5	1662	1706	44
10-Feb-95	26.5	1662	1717	55
10-Feb-95	29.5	1662	1671	9
10-Feb-95	32.5	1662	1521	-141
10-Feb-95	35.5	1662	1799	137
10-Feb-95	38.5	1662	1753	91

Table H.2 Data from Exchange 7-B for Column 7 Initially at 8.0% Residual Soltrol Saturation. Exchange took place over approximately 24 hours.

Sample ID	Volume Exchanged mL	Contact Time hrs	Normalized Radon Concentration pCi/L
C7S1	42.0	9960	16.607
C7S2	545.0		27.627
C7S3	1091.7		21.618
C7S4	1620.6		21.107
C7S5	2111.5		16.092
C7S6	2650.4		12.706