

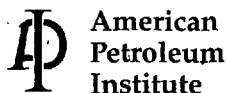
REMEDIATION OF A FRACTURED CLAY TILL USING AIR FLUSHING: FIELD EXPERIMENTS AT SARNIA, ONTARIO

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER DR 225
OCTOBER 1998

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Health and Environmental Sciences Department

API PUBLICATION NUMBER DR 225

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OCTOBER 1998



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EXECUTIVE SUMMARY

Background and Objectives

This report documents a field study of the remediation of a clay soil (a fractured clay till) using air flushing technologies. Unlike numerous other studies conducted at sites where the initial volume and composition of the spill were unknown, this research was conducted using a model "synthetic" gasoline blend of known mass, volume and composition. The gasoline was released into a well-characterized natural soil within a 10m by 10m test cell contained by driven, interlocking sheet pilings. The test site was located in Canada, near Sarnia, Ontario.

Many of the remediation strategies used successfully in permeable soils are thought to be less effective in low-permeability soils (API, 1995). Conventional air flushing technologies, such as soil vapor extraction (SVE) and *in situ* air sparging (IAS), rely on a generally uniform air flow field around the remediation wells and a high degree of air contact with the contaminant to remove significant contaminant mass. However, in low-permeability soils, a released light nonaqueous phase liquid (LNAPL) such as gasoline tends to accumulate in fractures or other secondary pores. Airflow created by remediation wells tends not to be uniform, instead occurring in preferred flow pathways that often short circuit around much of the LNAPL. This research was undertaken to understand whether conventional remediation technologies for soil remediation, SVE and IAS, are effective for removing significant amounts of gasoline from low-permeability soil. An understanding of the limits of these technologies under controlled field conditions provides a basis for evaluating their effectiveness at other sites.

Secondary objectives of this research were to 1) observe the distribution of the gasoline after release to the fractured clay soil, 2) identify new design or operational strategies or pitfalls for air flushing that are important for clay soil remediation, and 3) measure volatile organic compound (VOC) fluxes from the gasoline-contaminated soil during excavation of the test cell.

Scope of Work

This study was conducted over a 3-year period. In September of 1992, 50 liters of a synthetic gasoline were released to the test cell. The gasoline was comprised of pentane, methyl-tert-butyl-ether (MTBE), 2-methylpentane, hexane, benzene, trichloroethylene (TCE), heptane, isooctane, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, 1,2,4-trimethylbenzene, and naphthalene. Samples were collected and analyzed (for gasoline range organics) to establish the three-dimensional distribution of the release. One year after the release, SVE from trenches was conducted for 3 months, followed by a short period of air sparging and a second collection of soils samples. Two years after the release, SVE from vertical wells alone was performed, followed by SVE from both the vertical wells and trenches in various combinations. During this phase of the study, a

horizontal fracture was created below the zone of contamination and was used for dewatering. During all air flushing activities, soil vapor composition and concentration were continuously analyzed. Approximately 3 years after the release, a final set of soil samples was analyzed and volatilization flux experiments were conducted as portions of the test cell were excavated. Microbial studies were also performed at this time.

Key Results

SVE from trenches, followed by combined IAS/SVE, was able to remove ~40% of the spilled mass during the initial 2 months of operation. During the SVE phase, vapor concentrations decreased by approximately one order of magnitude. However, as the result of increasingly aggressive extraction conditions, mass recovery remained fairly constant during the 2 months of extraction/injection. At the conclusion of this phase of the remediation, the SVE system was removing air at a rate of ~22 scfm and the vacuums at the extraction trenches were ~0.5 atm. These conditions represented the capacity of the positive-displacement pump system used for the SVE system; thus, the observed mass recovery rate could not have been sustained. IAS combined with SVE removed significant additional mass after SVE alone had become less effective. However, only a fraction of the mass removed by IAS could be recovered by the SVE system, based on tracer tests. Extraction from vertical wells resulted in a very small amount of mass removal (<2 lb. [1 kg]).

The total percent of compounds of interest removed as vapor by air flushing is as follows: benzene – 24%, toluene – 34%, ethylbenzene – 14%, naphthalene – 0%, and MTBE – 65%.

Following active remediation, a detailed analysis of soil samples taken from trench walls was made using gas chromatography/mass spectrometry (GC/MS). These data indicated that primarily the low-volatility compounds (e.g., naphthalene and 1,2,4-trimethylbenzene) remained in the soil and that almost no benzene or toluene remained.

The compound-specific analyses of the SVE offgas as well as the GC/MS analyses of soil samples at the conclusion of the project provided important insights into the processes at the site. In particular, essentially all of the naphthalene initially released at the site could be accounted for in the final soil analysis. In addition, mass balances were good for a number of compounds, including isooctane, TCE, and to a somewhat lesser extent MTBE. In contrast, overall mass recoveries for the BTEX compounds were on the order of 20%. Based on the mass balance data, it can be concluded that the BTEX compounds showed evidence of *in situ* degradation. This is consistent with the conclusions of the biodegradation capacity study (Appendix B).

Conclusions

1. The characteristics of the clay till soil (i.e., high water content, low permeability and primarily fracture flow) lead to low concentrations of contaminants in the soil (e.g.,

generally less than 1000 mg/kg at this site). Also, the low fracture or effective porosity of the soil means that small spills can contaminate large soil masses (i.e., low residual saturation of 2 L/m³ at this site).

2. Even at modest biodegradation rates (e.g., 1 mg/kg/d), the relatively low contaminant levels in the soil may mean that biodegradation has the potential to account for a significant mass removal even within the "source" zone. This is especially true for the BTEX compounds; however, less volatile PAH compounds are not as biodegradable.
3. Both SVE and IAS were initially able to remove a significant mass of the gasoline, especially if the mass was still present in the fractures. However, as with most active site remediations, the high removal rates were short lived. Changes in the airflow caused by altering the air flushing operating conditions (e.g., switching trenches or switching from trenches to wells) increased mass recovery at the Sarnia test site. This increase is attributed to initiation of airflow in NAPL-filled fractures that were inaccessible during a prior air flushing configuration. Both techniques may also have improved aerobic biodegradation at the site.
4. At the conclusion of the fieldwork, calculations indicated that greater than 90% of the spilled mass had been removed from the soil at the site. For the BTEX compounds, the percent removals were significantly higher (95–99%). Both active (i.e., SVE and SVE/IAS) and passive (i.e., biodegradation) remediation were important to overall success. At the same time, the naphthalene data suggest that it will be difficult to remediate less volatile contaminants such as the polynuclear aromatic hydrocarbons (PAHs) using air flushing in low-permeability soils.
5. Extraction trenches and wells at the Sarnia test site were closely spaced: 20 ft (6.25m) and 6 ft (2m) apart, respectively. However, vapor monitoring during extraction indicated that the airflow distribution within the zone of contamination was not uniform. The inability to induce a uniform air flow with closely spaced extraction points suggests that effective air-contaminant contact will be difficult at non-research sites with less dense extraction point networks.
6. Air short-circuiting to the atmosphere was shown to inhibit thorough LNAPL-air flow contact at the Sarnia test site. Air short-circuiting may be more severe at many sites where the sealing quality of the surface cover is likely to be poorer than at Sarnia, where the engineered cover experienced significant leakage.
7. The recovery of MTBE (65%) by air flushing was greater than expected. MTBE's high solubility means it moved readily into the saturated soil matrix, where diffusion dominated transport. However, due to MTBE's low retardation and high aqueous mobility it appears also to have moved out of the matrix relatively easily, where it became accessible to the SVE/IAS air. At the same time, little of the MTBE remained in the soil at the conclusion of the project (~2.2–5.0% of the initial mass). The reason(s) for less than 100% recovery of the MTBE is not known.

8. Limitations present at many actual spill sites may prevent one from reaching the degree of mass removal or compound degradation observed at the Sarnia test site. The presence of buildings and subsurface obstructions may make it impractical or impossible to fully delineate the LNAPL distribution at some sites. Uncertainty in the LNAPL distribution and problems with access may result in an inadequate or impractical density of trenches or wells to flow air through LNAPL-filled fractures. This may result in diminished mass recovery or degradation when compared to the Sarnia results. The inability to install closely spaced wells or trenches at many storage tank release sites also may limit the ability to beneficially alter the direction of airflow through a site.
9. The vapor flux data indicated good agreement between calculated values and static measurements. Data from the flow-through flux chamber were greater than expected by one to two orders of magnitude. During the period of the test, the barometric pressure was dropping and thus advective flow could have contributed to these higher values.

I. INTRODUCTION

A. Background

Silts, clays, tills, and other "tight" soils are common in many regions of North America. When these soils become contaminated with petroleum hydrocarbons or other non-aqueous phase liquids (NAPLs) they have a number of characteristics which make them difficult to remediate. NAPLs introduced into low-permeability soils prefer to migrate along preferential pathways, typically within fractures. Soluble constituents of the NAPL can then dissolve into the soil matrix between the fractures. The soil matrix frequently has a high water content and as a result, mass transfer back out of the matrix during remediation may be controlled by aqueous phase diffusion. In this case years or decades may be required to remove the contaminants. Aggressive remediation approaches, such as soil heating by steam or electrical resistance, may accelerate mass transfer from the soil matrix, however, they can be costly and for gasoline hydrocarbons may significantly reduce natural attenuation due to biodegradation. At the same time, conventional flushing techniques may not be very effective at accessing mass in the soil matrix. As a consequence, there is currently no widely accepted approach for remediation of gasoline contamination in tight fractured soils.

Air flushing, specifically soil vapor extraction (SVE) and *in situ* air sparging (IAS) of fine grained soil is examined here. SVE is widely used for remediating permeable soils; however, there are a number of unknowns related to its application in fine-grained fractured soils. These include the generation and propagation of adequate flow rates through the fractured media and the air flow paths relative to the location of the contaminants. A number of air flushing approaches have been used in contaminated tight soils, including extraction trenches (as opposed to "conventional" vertical wells), very-high extraction vacuums (i.e., > 0.75 atm), bioventing, and induced hydraulic fractures. Each of these will be discussed below.

IAS has not generally applied to tight soils, however, it does provide the opportunity to access water-filled fractures which are not reached by SVE. Because both IAS and SVE focus on flow through the fractures (as does infiltrating water), they can often quickly reduce contamination in the fractures and as a result, they may reduce the risk posed by leaching in the contaminated soil. Thus, while the time frame for complete remediation of the soil may still be on the order of years, the combination of IAS and SVE may be able to significantly reduce the risk posed by the soils in a much shorter period of time. Furthermore, both IAS and SVE will increase oxygen delivery to the soil and may thus enhance biodegradation.

B. Objectives

The primary objective of this project is to measure the ability of SVE and IAS to remove gasoline from a fractured, low-permeability soil. An understanding of the limits of these technologies under controlled field conditions will provide a basis for evaluating remediation effectiveness at

other sites. Ultimately, the usefulness of air flushing techniques will depend upon their site-specific ability to significantly reduce the risk of future contaminant exposure.

Secondary project objectives relevant to remediating gasoline-contaminated low-permeability soil include: 1) observation of light non-aqueous phase liquid (LNAPL) distribution following its release into the fractured soil, 2) quantification of mass removal by air flushing and biodegradation, 3) identification of design or operational strategies for air flushing techniques and 4) measurement of volatile organic compound fluxes from a trench excavated in contaminated soil.

C. Experimental Approach

The experimental approach used to address the above objectives involved: 1) a controlled release of a synthetic "gasoline" mixture of known composition and mass into an undisturbed, naturally fractured low-permeability soil conducted within a 30 ft by 30 ft (10 m by 10 m) sheet-pile cell; 2) a ten month undisturbed period after the release to allow the spilled gasoline to distribute between the fractures and the soil matrix; and 3) two field seasons of air flushing, including vapor extraction from trenches and vertical wells, air injection into vertical wells, and vapor extraction from a well in contact with a hydraulically induced fracture. Throughout the process, numerous soil samples were collected and analyzed and a compound-specific analysis of the SVE offgas was performed. The goal was to have an accurate mass balance on a compound-by-compound basis at the conclusion of the project. In addition, at the conclusion of the field work, several large-diameter cores were collected for future leaching and volatilization experiments.

D. Overview

This report describes project activities from the initiation of the project through the final soil sampling event following remediation. The body of the report is divided into 14 sections. The first five sections describe the project and the site, and include an overview of *in situ* remediation and conceptual model for LNAPL movement in low-permeability soils. Described in Section VI are the experimental set-up (cell construction and gasoline release) and equipment used (e.g., wells and trenches) along with soil coring and microbial analysis. Air permeability and effective porosity were determined at the field site and the results are presented in Section VII.

Remediation activities and results are described in Sections VIII to XI. These activities included SVE from two trenches (Section VIII), SVE from vertical wells (Section IX), SVE and IAS (Section X) and hydraulic fracturing (Section XI). Mass balance analysis and volatilization flux experiments are presented in Sections XII and XIII, respectively. The final section (XIV) presents a summary of the project and conclusions based on this study. A chronological list of important events during this project is contained in Table I.

Table I. Chronology of events at the Sarnia site.

DATE	EVENT
Sep., 1992	gasoline release
Jun.-Aug., 1993	collect 2-inch diameter soil cores install vapor monitoring and air sparge wells install extraction trenches
Aug., 1993	initiate SVE from west trench
Sep., 1993	switch to extraction from east trench
Oct., 1993	IAS with extraction from both trenches
Oct.-Nov., 1993	collect 2-inch diameter soil cores close site for season
Jul., 1994	collect 4-inch diameter soil cores install vertical 2-inch diameter vapor extraction wells SVE from both trenches (same conditions as end of 1993 season)
Aug., 1994	create hydraulic fracture in experimental cell switch to extraction from vertical 2-inch vapor extraction wells
Aug.-Nov., 1994	switch extraction between vertical extraction wells and extraction trenches
Sep., 1994	initiate dewatering from hydrofracture well
Nov., 1994	flow tests on SVE pumps and extraction wells/trenches close site for season
Aug., 1995	excavate trenches in experimental cell collect trench wall soil samples perform volatilization flux experiments Oak Ridge National Laboratory (ORNL) collection of microbial samples
Sep., 1995	close site

II. OVERVIEW OF *IN SITU* REMEDIATION OF LOW-PERMEABILITY SOIL

There are few reported studies where low-permeability soils have been cleaned *in situ*. A field pilot study was conducted by Gibson *et al.* (1993) using SVE in a clay till soil. The clay was contaminated with paint thinner, consisting of a mixture of volatile aromatic hydrocarbons. They found air flow was mainly through the fractures and macropores and the air permeability depended on the degree of fracturing. The study concluded that air permeability could not be estimated as a function of liquid saturation in the soil pores, as is the practice in higher permeability soils. A rapid decrease in pressure drawdown with increasing distance from the extraction well was also observed. Their conclusions included: 1) the clay soil developed fractures in the presence of the paint thinner; 2) a vapor extraction well was able to extract air at 11 scfm with a radius of influence of ~ 20 ft; and 3) the mass amount of contaminant removed was 19% of the estimated pre-remediation amount.

Siegrist *et al.* (1995) used *in situ* soil mixing to remove contaminants, including NAPLs, in geologically complex soils which included low-permeability materials. The technique involves the use of large-diameter augers to mix columns of soil in order to modify geologic properties (e.g., homogenize the soil), add chemical agents or introduce other treatment processes to the soil. Because the technique is quite aggressive, Siegrist *et al.* (1995) recommend that it be used primarily on large source areas.

A number of projects are currently underway using induced fractures to enhance mass removal. For example, Murdoch *et al.*, (Personal communication, 1996) have examined hydraulically induced fractures coupled with steam injection to remove volatile contaminants from low-permeability soils. Multiple "stacked" horizontal fractures (e.g., 1-foot spacings) can be used to divide massive fine-grained soils into regions that are more directly accessible for treatment. However, application to some soils is limited because of the difficulty in propagating fractures. This is particularly true at shallow depths.

Steam injection can be used without fractures to heat stratified systems or low-permeability soils where some fracture network already exists (Udell *et al.*, 1995). Other sources of heat (e.g., electrical resistance and radio frequency) are potentially well-suited to low-permeability media because those media often have good electrical or thermal properties. However, these techniques may inhibit natural attenuation due to biodegradation.

Soil mixing, fracturing and steam injection require a significant amount of technical expertise and specialized equipment and may have a significant impact on the soil. Air flushing, on the other hand, may be less costly and more straightforward to implement, and is widely accepted as a remediation technology (Walden, 1995). However, it has not been widely used for low-permeability soils. Therefore, it is important to evaluate the extent to which SVE/IAS can be extended to low-permeability media.

III. DESCRIPTION OF THE SARNIA FIELD SITE

A. Overview

The experiments described here were conducted at a site near Sarnia, Ontario, Canada. The site was selected for a variety of reasons, including: 1) it is possible to release hydrocarbons into the subsurface to create spills at the site; 2) the site is a fractured clay till, which is recognized as a difficult matrix to remediate; and 3) the geology of the site is well understood.

The ability to create a spill is important because it allows the release of NAPL of a known mass and composition and therefore permits mass balances to be made during the remediation process. In addition, prior to the spill, preparations for the release can be made (i.e., spill location and depth), and the experimental conditions of the spill and the remediation can be optimized (i.e., installation and evaluation of monitoring equipment prior to release). Finally, the specific site characteristics can be carefully examined and selected prior to the spill. In the latter context, the Sarnia study site is ideally suited.

Contaminant transport in the Sarnia till has been studied for the last 15 years by a number of researchers (Crooks and Quigley, 1984; Desaulniers *et al.*, 1981; Johnson *et al.*, 1989; D'Astous *et al.*, 1989; McKay *et al.*, 1993a, 1993b; Myrand *et al.*, 1992; Ruland *et al.*, 1991). In addition, the structure of fractures at the site has been examined in detail (McKay, 1991). As a result, more is known about the movement of both inorganic and organic contaminants in this till than in any other tight soil.

B. Site Geology

The study site is located about 10 kilometers southeast of Sarnia, Ontario (Figure 1). It lies in the Lake St. Clair Clay Plain, a large region of glacial till which was the site of an ice age lake (Goodall and Quigley, 1977). McKay *et al.* (1993a) describe the lithology as a clay-rich till (25–40% clay with silt, sand and a few pebbles). In the vicinity of the site the till is about 150 ft (50 m) thick, and is underlain by marine shale. The till can be divided into two vertical zones based on weathering and permeability. The upper zone, extending from ground surface to a depth of ~16 ft (5 m) is oxidized and contains a network of fractures. The hydraulic conductivity measurements in the upper layer range from 10^{-10} m/s to $\sim 10^{-6}$ m/s (McKay *et al.*, 1993a) with values from the most reliable measurements falling in the 10^{-7} to 10^{-8} m/s range. The lower zone is unweathered and its hydraulic conductivity is quite low (e.g., 10^{-10} m/s)(*ibid*).

Contaminant transport in the lower zone is primarily by diffusion. Desaulniers *et al.* (1981) demonstrated that the chloride concentration decreased with distance from the underlying marine shale to near ground surface. This was simulated using a diffusion model and an ~14,000 year diffusion time. In the upper zone, water movement is much more rapid due to the fractures. McKay *et al.* (1993a,b) characterized the fractures as being primarily vertical and resulting from desiccation. The effective hydraulic apertures ranged from 10 to 100 μm and the fracture spacings

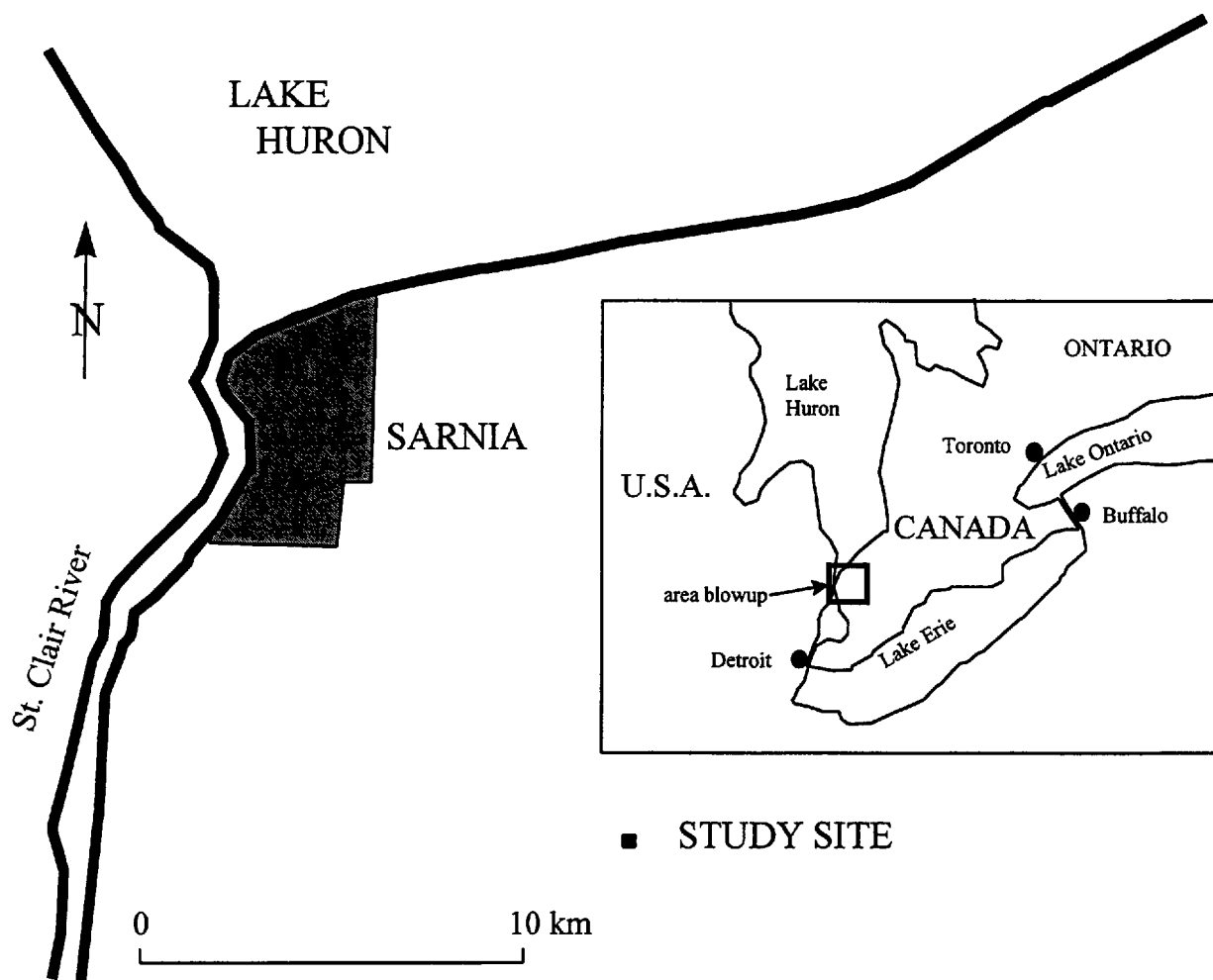


Figure 1. Location of the study site relative to Sarnia, Ontario.

increased from a few centimeters at the surface to 3 ft (1 m) or more at a depth of 13 ft (4 m). Soil characteristics are summarized in Table II.

The water table at the site generally fluctuates from near ground surface to a depth of ~6.5 ft (2 m). During the 1993 study period the water table fluctuated from ground surface to a depth of only about 3.2 ft (1 m). The clay matrix between the fractures is probably completely saturated due to capillary effects (McWhorter, 1995). In addition, many of the fractures themselves are likely to be filled with water, again due to capillary effects. As a consequence, relatively small volumes of water added to the system can cause significant increases in the water level.

Table II. Summary of soil characteristics.

Parameter	Value
Textural analysis ^a	~25-40% clay with silt, sand and pebbles
Matrix permeability ^a	$\sim 10^{-17} \text{m}^2$
Fractured permeability ^b	$\sim 10^{-14} \text{m}^2$
Total porosity ^a	~40%
Fracture porosity ^b	~0.1-1%
Depth to groundwater ^b	~0-2 m

^a McKay *et al.*, 1993a^b this report

IV. CONCEPTUAL MODEL FOR LNAPL DISTRIBUTION IN A LOW-PERMEABILITY SOIL AND POTENTIAL IMPACT ON GROUNDWATER

A. LNAPL Distribution

When “tight” soils become contaminated with petroleum hydrocarbons (e.g., gasoline) or other NAPLs, they have a number of characteristics which make them difficult to remediate. These soils typically contain fractures or other preferential flow pathways that transect the fine-grained matrix. While the fractures may occupy only a small fraction (effective porosity between 0.001-1%, Freeze and Cherry, 1979) of the total soil volume, depending on fracture aperture and frequency, they can increase the otherwise low fluid conductivity of these soils by several orders of magnitude. This means that even a small spill will result in a large volume of contaminated soil. For the case of 20 μm fractures separated by 2 cm of matrix, the effective porosity (i.e., the volume of the fractures divided by the total volume of the soil) is only 0.001 or 0.1%. As a consequence, an ~1000 gal (4000 L) gasoline release could affect >5000 yd^3 (~4000 m^3) of a fractured soil compared to ~12–20 yd^3 (10–16 m^3) of a sandy soil (see Example Calculation #1).

Because of the small fracture porosity (and corresponding small storage capacity) of the fractured tight soil, large seasonal fluctuations of the water table are common. As a result of water level fluctuations, the NAPL can become smeared in the fractures over significant vertical distances. As with porous media, the movement of NAPL and water in the fractured media causes small droplets or ganglia to become “snapped off” from the main body of NAPL, and as a result to become immobilized as residual NAPL (Wilson *et al.*, 1990). This residual NAPL in the fractures can act as a long-term source of soluble contaminants to groundwater. Also, even if the water content of the fractures changes in response to water table fluctuations, the blocks of soil between these fractures may remain essentially water-saturated. As a result of the high water content of the matrix blocks, NAPL movement within the soil occurs almost exclusively within the fractures (McKay *et al.*, 1991; McWhorter, 1995).

Depending upon its composition, some of the NAPL initially present in the fractures will dissolve into the pore water and diffuse into the soil matrix between the fractures (Figure 2). The dissolved hydrocarbons from the NAPL mixture may also partition to the soil grains. As a consequence, after some period of time the volume of NAPL in the fractures may become significantly reduced (Parker *et al.*, 1994). Example Calculation #2 shows that most of the mass of a moderately soluble, single-component NAPL can dissolve and move into the matrix. The dissolved mass that has moved into a saturated soil matrix will, in general, be much more difficult to remove from the system than the NAPL present in the fractures because the flux of contaminant from the matrix will be limited by desorption and aqueous-phase diffusion. As a consequence, the time frame for remediation of the soil matrix may be quite long. For example, simple diffusion calculations indicate that to achieve 85% mass recovery from the soil matrix will take almost 10 times as long as the contamination has been in the ground prior to

Example Calculation #1. Total fracture porosity and soil volume contaminated.

Fractured soil:

20 μm fracture separated by 2 cm of matrixTotal fracture porosity: $2 \times 10^{-5} / 2 \times 10^{-2} = 0.001$ (0.1%)

Volume released: 4000 L (~1000 gal)

Soil volume contaminated: $4000 \text{ L} / 0.001 = 4000 \text{ m}^3$ (>5000 yd^3)

Sandy soil:

Total porosity: 25-40%

Volume released: 4000 L (~1000 gal)

Soil volume contaminated: $4000 \text{ L} / 0.25 = 16 \text{ m}^3$ (>20 yd^3)
 $4000 \text{ L} / 0.40 = 10 \text{ m}^3$ (>12 yd^3)

This calculation assumes that 100% of the porosity is occupied by NAPL. Under field conditions, NAPL saturation rarely approaches 100% of the pore space.

remediation. In other words, for a spill which occurred 2 years prior to remediation, 20 years can be required to remove 85% of the mass and 200 years to achieve 95% mass removal (McWhorter, 1995).

In order to track the movement of the “synthetic” gasoline out of the fractures and into the matrix a multi-component numerical diffusion model was developed (Grady, 1997). A one-dimensional finite difference approach was used. The model simultaneously tracks up to 15 components and accounts for dissolution using solubilities based on the mole fractions of each component in the NAPL (solubilities are updated every time step), diffusion in the soil matrix blocks, and sorption to the soil. Partitioning between the water and soil is assumed to be an equilibrium process and to follow a linear Freundlich isotherm. Diffusion coefficients were calculated from molecular weights and densities of the individual components. Biodegradation was not accounted for. The base case parameters for these simulations are listed in Table III.

Simulations from the time of the release until the onset of remediation for the Sarnia site (~10 months) are shown in Figure 3. The more soluble components (methyl-tert-butyl-ether [MTBE], trichloroethylene [TCE], benzene) disappear relatively quickly into the soil matrix. Compounds like naphthalene and isooctane persist for longer periods and in some cases indefinitely.

B. Microbiological Activity

It is now recognized that petroleum hydrocarbons, particularly the BTEX (benzene, toluene, ethylbenzene and xylenes) compounds, are degraded by both aerobic and anaerobic bacteria in the subsurface. It is likely in low-permeability soils that conditions exist where a number of degradation pathways may exist. At the Sarnia site the contaminated soil was near to ground surface and so the distance over which oxygen had to travel to reach the contaminated soil was fairly short (e.g., 1 m). In this context the air-filled fractures within the soil would provide the pathway for oxygen transport. However, the bulk water content of the soil matrix was high, so diffusion of oxygen within the soil matrix would be quite slow, and it would be expected that anaerobic conditions would quickly develop within the intact soil blocks. Under those conditions, anaerobic reactions using a series of electron acceptors is possible. Based on geochemical analyses of soil from the site (Section XII.B) it appears that conditions would support both sulfate and nitrate reducing organisms.

As discussed in Section IV.A., the fractured nature of the clay till leads to low residual saturations of hydrocarbons (e.g., 2 L/m³ for the Sarnia soil compared to 10–20 L/m³ for silty-sand soils, Cohen and Mercer, 1993). Under low residual saturation conditions, even modest biodegradation rates (e.g., 1 mg/kg/day) could remove a significant fraction of the mass within a relatively short period of time (e.g., 1 year). Therefore, it would appear that both aerobic and anaerobic biodegradation could play important roles in the remediation of low-permeability soils such as those at the Sarnia site.

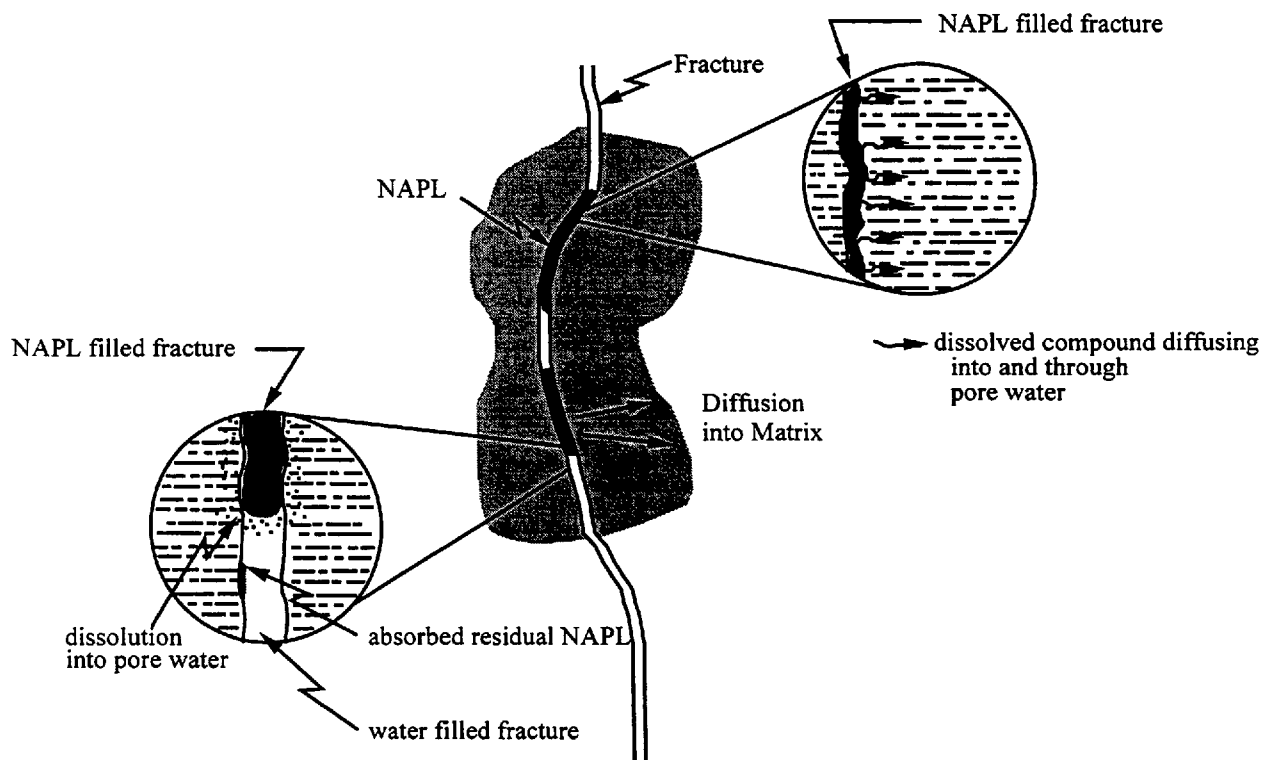


Figure 2. Schematic drawing of dissolution and diffusion of hydrocarbons in a fractured porous medium.

Example Calculation #2. Estimated single-component NAPL dissolution into soil matrix.

Consider a fractured clay with 20 μm wide vertical fractures separated by 2 cm of water saturated soil matrix.

The fractures are 10% filled with NAPL at residual saturation (density of 1 g/mL).

The single-component NAPL has a solubility of 1000 mg/L.

Mass of NAPL in the fractures:

Volume in NAPL/ m^3 of soil:	0.1 L/ m^3
Mass of NAPL in 1 m^3 of fractures:	1 g/mL * 100 mL / m^3 = 100 g

Capacity of the matrix:

Total porosity of soil:	~40%
Volume of water/ m^3 of soil:	0.40 * 1 m^3 = 400 L
Capacity of the matrix (without sorption):	solubility * volume of water 1000 mg/L * 400 L = 400 g

The capacity of the matrix (400 g) exceeds the mass of NAPL in the fractures (100 g), thus all of the NAPL could dissolve into the matrix.

Table III. Base case parameters for the numerical diffusion model.

Parameter	Value
porosity	37% ^a
bulk density	1.5 g/ m^3 ^a
soil organic content	0.011 ^a
fracture spacing	2 cm ^b
fracture aperture	20 μm ^b

^a Johnson *et al.*, 1989

^b McKay *et al.*, 1993a

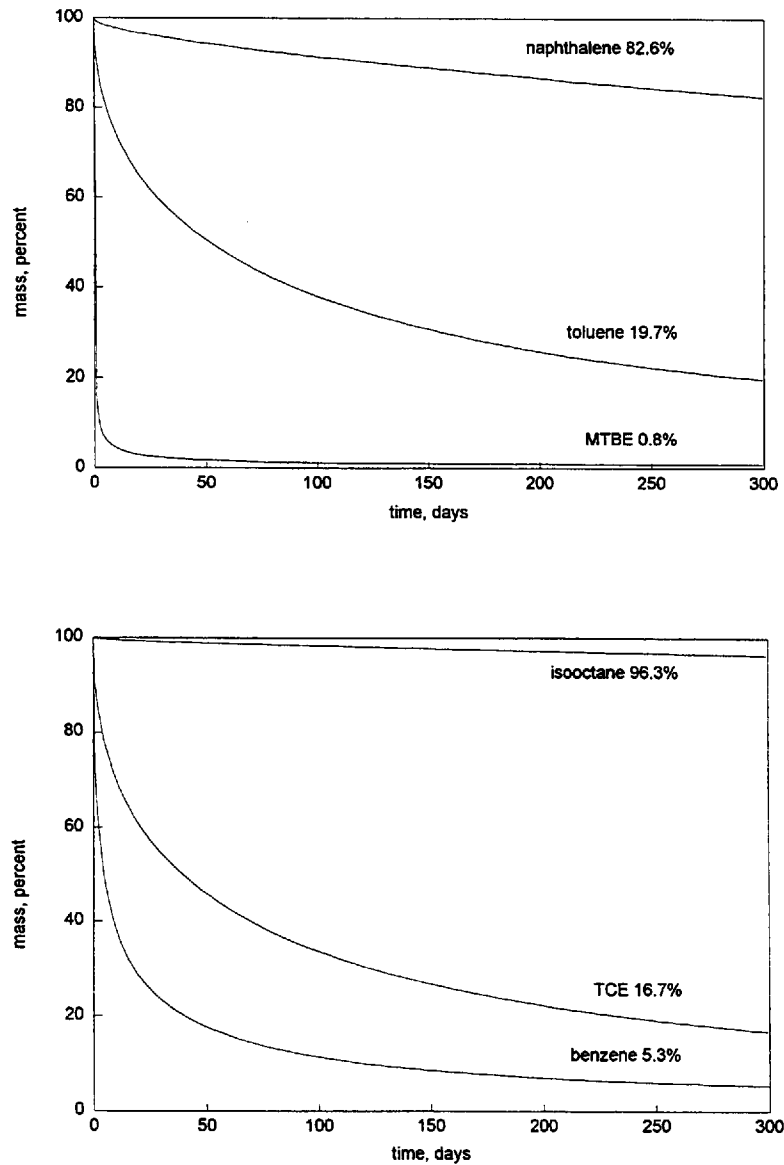


Figure 3. Estimated percent initial mass remaining in the fractures as a function of time (gasoline release, day 0, to start of remediation, day 300) for the base case numerical diffusion model.

C. Water Flow

Since the water yields of tight soils are typically small, they are rarely used as water supplies, and as such the risk to human receptors is minimal. However, if the tight soil is underlain by more permeable aquifer materials, then the more permeable materials may become contaminated due to water leaching down through the tight soil (Figure 4). Infiltrating water will tend to move down through the fractures in the fine-grained soil along pathways similar to those used by the NAPL. When it comes into contact with NAPL in the fractures, the infiltrating water will quickly become saturated with regard to the components of the NAPL. The contaminated water may then continue to move down to the more permeable materials which underlay the fine-grained soil depending on the hydraulic heads in the confined and unconfined aquifer. In this scenario, the presence of NAPL in the fractures can play an important role in contaminating the infiltrating groundwater (Harrison *et al.*, 1992). If the NAPL is removed from the fractures, then infiltrating water will only become contaminated by mass diffusing out of the matrix. Matrix diffusion is a relatively slow process, and as a consequence the infiltrating water may have concentrations far below saturation values. In this case, removal of the NAPL from the fractures and the resulting drop in leachate concentrations could result in a significant reduction in risk, while removing only a fraction of the contaminant mass in the system.

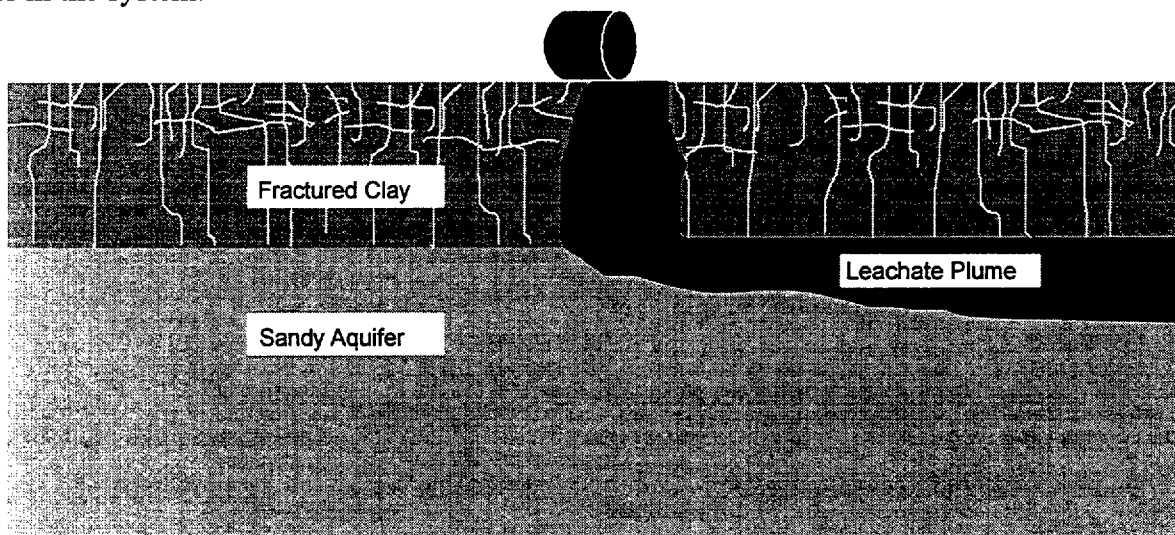


Figure 4. Schematic drawing of contamination of a sandy aquifer by an overlying fractured clay.

D. Air Flow

Air flow, like water flow will be controlled by the secondary (i.e., fracture) porosity of the low-permeability soil. In addition, air flow will also be strongly affected by the liquid content of the fractures. Two other factors strongly affect the use of air flushing techniques for remediating soil at the Sarnia site. First, the primary orientation of the fractures is vertical and the frequency of the fractures drops off dramatically with depth. As a consequence, it is very difficult to induce air flow through the contaminated zone over lateral distances and/or at depth (i.e., air flow tends to “short circuit” to ground surface). The field data indicate that even the presence of a competent concrete cap at ground surface does not significantly improve the lateral flow of air at depth.

V. APPLICATION OF AIR FLUSHING TECHNOLOGIES IN LOW-PERMEABILITY SOILS

Air flushing technologies, specifically SVE and IAS, were chosen for these experiments because they have become widely used for remediating permeable soils in recent years. These technologies have also been applied to fine-grained soils, although few data are available in the literature. There are a number of unknowns relating to SVE and IAS performance in fine-grained fractured soils. These include the role of fractures in NAPL, air and water transport, and the role of matrix diffusion in controlling the final distribution of the mass as well as the importance of biodegradation.

There is currently considerable debate about the best approach to air flushing in low-permeability soil. Air flushing strategies for these soils can generally be divided into three categories: 1) vapor extraction systems using a high vacuum (vacuum at extraction point > 0.5 atm); 2) SVE systems using a medium vacuum (vacuum at extraction point < 0.5 atm), often with a large number of extraction wells; and 3) SVE systems used in combination with air injection. Each one of these categories has a number of practical difficulties and benefits. The high water content of most fine-grained soils tends to inhibit air flow. Air moving through these soils tends to find preferential pathways, and as a consequence may bypass large portions of the soil. High vacuum systems may help remove water from the soil and fractures and thus improve air flow, however this may come at a high operation and maintenance cost. In addition, it is often difficult to prevent surface leaks with high-vacuum applications, and vacuums tend to drop off quickly with distance from the extraction point. This is compounded by the fact that fracture density and aperture, and therefore air permeability in fractured soils, often increase dramatically with decreasing depth. In low vacuum systems, on the other hand, it may not be possible to generate adequate air flow to effect a reasonable remediation without the installation of a large number of extraction points, which may make the cost of installation prohibitive.

SVE performance will also be affected by the design of the extraction points. Vertical wells are by far the most common type of extraction points used. However, the radial nature of the flow means that applied vacuums will drop off quickly with distance from the well. Alternately, horizontal wells or trenches can be used. The latter may avoid the rapid drop in vacuum that occurs radially around vertical wells. As a consequence, higher flow rates at similar vacuums can usually be achieved using trenches. However, they may be expensive or technically difficult to install at many sites. In addition, preferential pathways may form at discrete points along the horizontal run of the trench, and much of the flow may be diverted through a relatively small fraction of the soil. In the experiments described below, a system was constructed consisting of two extraction trenches with a network of vertical wells between them. A number of flow conditions were tested to determine the strengths and weaknesses of each vapor extraction strategy.

Air injection (e.g., IAS) coupled with SVE has the potential to improve air flow over SVE alone. Air injection is likely to increase mass removal due to the addition of air pathways to the flow system. In addition, SVE and IAS supply oxygen to the subsurface which in turn may enhance biodegradation. However, it may be difficult to capture all of the injected air, and as a consequence off-site migration of the vapors may be possible. Nevertheless, the use of well-designed air injection systems in conjunction with SVE may provide a useful tool for remediating low-permeability soils.

VI. EXPERIMENTAL SETUP AND TECHNIQUES

A. Cell Construction

The experimental cell at the Sarnia site was constructed by driving sealable sheet pile to a depth of ~16 ft (5 m) in a square roughly 30 ft (10 m) on a side. A plan view of the cell is shown in Figure 5. To prevent rain and snow from entering the cell, a wooden deck was constructed over the cell. The deck was covered with UV-resistant plastic sheet to eliminate leaks. In order to create an impermeable surface cover, the ground within the cell was smoothed, covered with a thin (<1 cm) layer of bentonite clay followed by 0.25 mm plastic sheet and finally by ~6 inches (15 cm) of sand. Prior to remediation at the site the sand was replaced with 4–6 inches (10–15 cm) of concrete.

B. Controlled Gasoline Release

In September 1992, approximately 13.2 gal (50 L or 40.6 kg) of a synthetic mix of gasoline-range hydrocarbons were released into the cell from a constant head reservoir (Figure 6). The point of release was ~2 ft (0.6 m) below ground surface in a shallow borehole filled with sand and bentonite. (The total pore volume of the sand pack was ~0.4 gal [1.6 L], so nearly all of the release should have moved out of the borehole.) The release rate was controlled by a constant-head reservoir, and the total time for the release was approximately 90 minutes.

The composition of the mixture is listed in Table IV. Some relevant physical properties of the components are also listed in Table IV. The hydrocarbon mixture was allowed to remain undisturbed in the ground for ~10 months to allow partitioning of the “gasoline” between the fractures and the soil matrix.

C. Vapor Extraction/Air Sparging System

1. Vapor Monitoring and Air Sparging Well Design

In June and early July 1993, the deck over the cell was modified so that it could be rolled off of the cell to allow work inside the cell. In July 1993, a number of 5 cm-diameter cores were collected to depths of 3 and 5 feet (~1 and 1.5 m) to characterize the distribution of the gasoline within the cell. The holes created by the coring were used to install vapor monitoring wells and IAS wells. These wells consisted of 1 inch (2.5 cm) O.D. stainless steel tubes with a section of geotextile sock wired to the end (Figure 7).

Approximately 6 inches (15 cm) of coarse sand was placed in the bottom of each hole and the tube was inserted into the sand. The rest of the hole was filled with powdered bentonite to ground surface. This design eliminates the need for conventional slotted well screen. The locations of the vapor monitoring and sparge wells are shown in Figure 8.

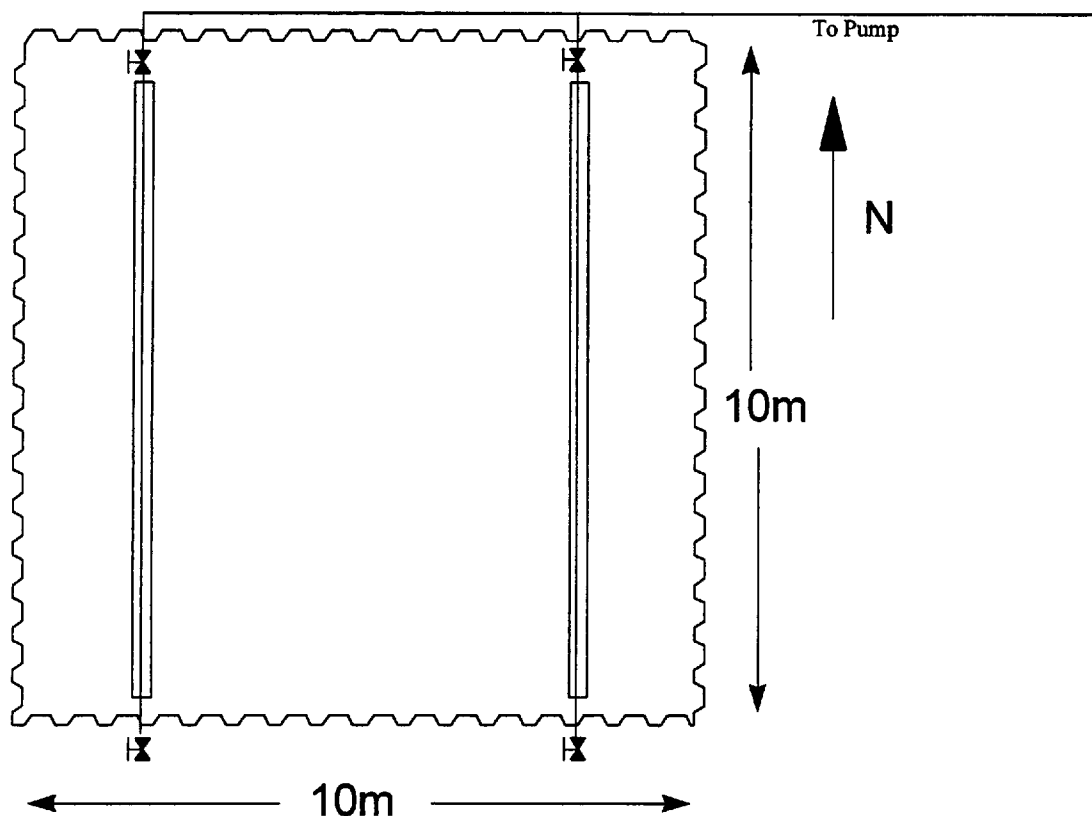


Figure 5. Schematic plan view of the cell and the extraction trenches.

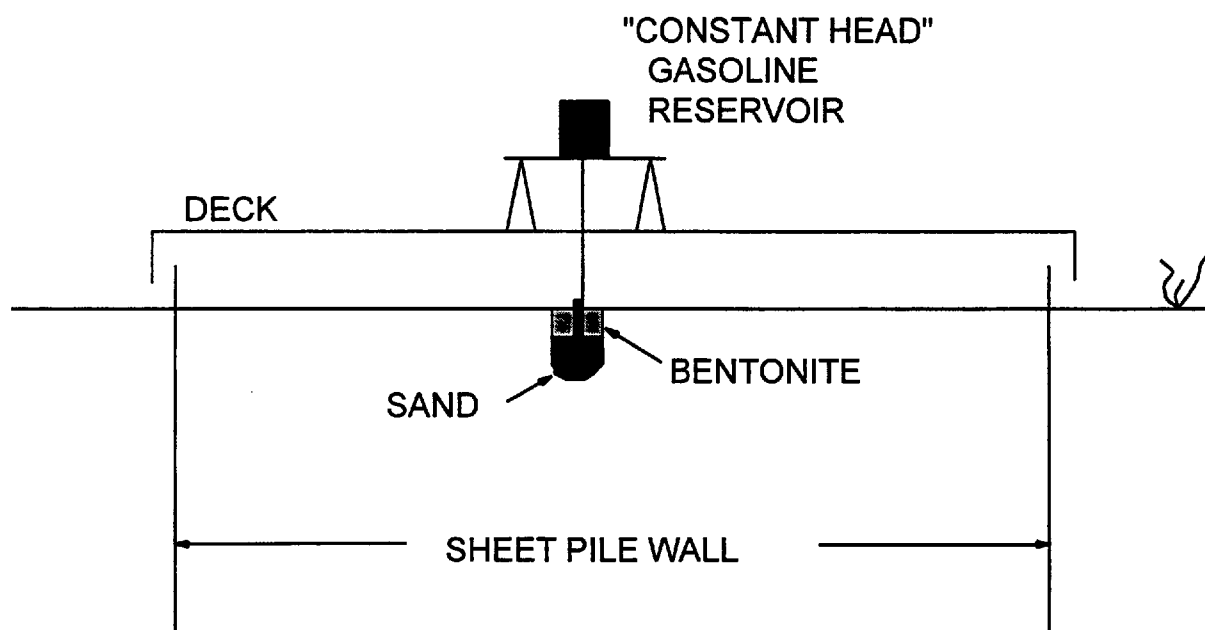


Figure 6. Schematic section view of the release of gasoline into the experimental cell.

Table IV. Composition and physical properties of the spilled hydrocarbons.

Compound	Mass spilled (kg)	Mole fraction	Mix vapor pressure (atm)	Mix equilibrium solubility (mg/L)
pentane	2.48	8.5E-2	4.84E-02	3.4E0
methyl-tert-butyl-ether	1.50	4.2E-2	1.09E-02	2.0E3
2-methylpentane	1.30	3.7E-2	7.83E-03	5.2E-1
hexane	2.64	7.6e-2	1.21E-02	1.0E0
benzene	1.76	5.6E-2	5.56E-03	9.9E1
trichloroethylene	2.96	5.6E-2	4.18E-03	6.1E1
heptane	1.36	3.4E-2	1.54E-03	1.0E-1
isooctane	4.14	9.0E-2	4.57E-03	2.0E-1
toluene	5.22	1.4E-1	4.90E-03	7.2E1
ethylbenzene	1.74	4.1E-2	3.04E-04	7.3E0
p-xylene	3.52	8.2E-2	7.04E-04	1.6E1
m-xylene	3.48	8.1E-2	5.34E-04	1.3E1
o-xylene	3.56	8.3E-2	6.63E-04	1.5E1
1,2,4-trimethylbenzene	2.70	5.6E-2	1.05E-04	3.2E0
naphthalene	2.28	4.4E-2	6.15E-06	1.5E0
totals	40.64	1.0E0		2.3E3

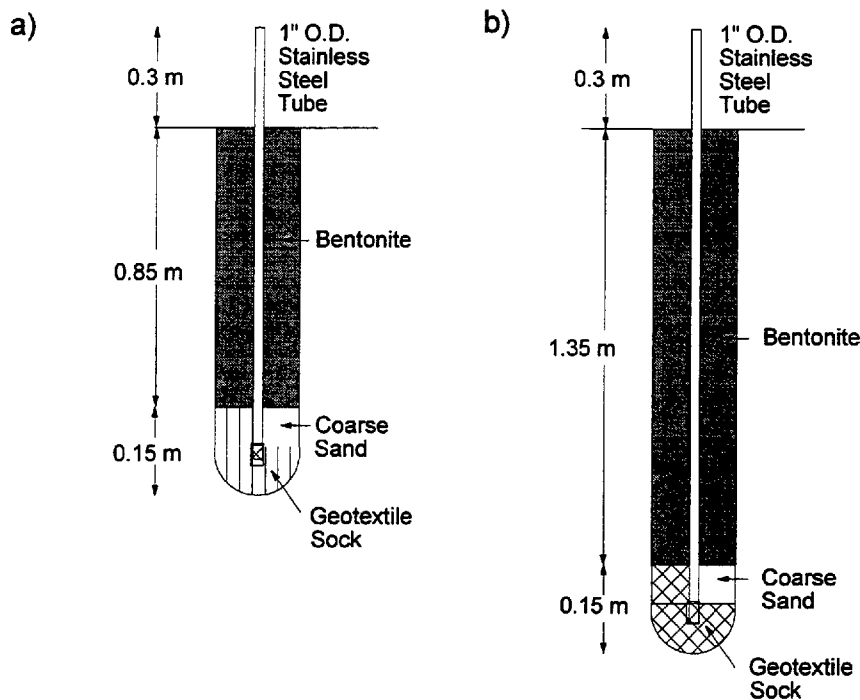


Figure 7. Schematic "as built" diagrams for the a) vapor monitoring and b) sparge points.

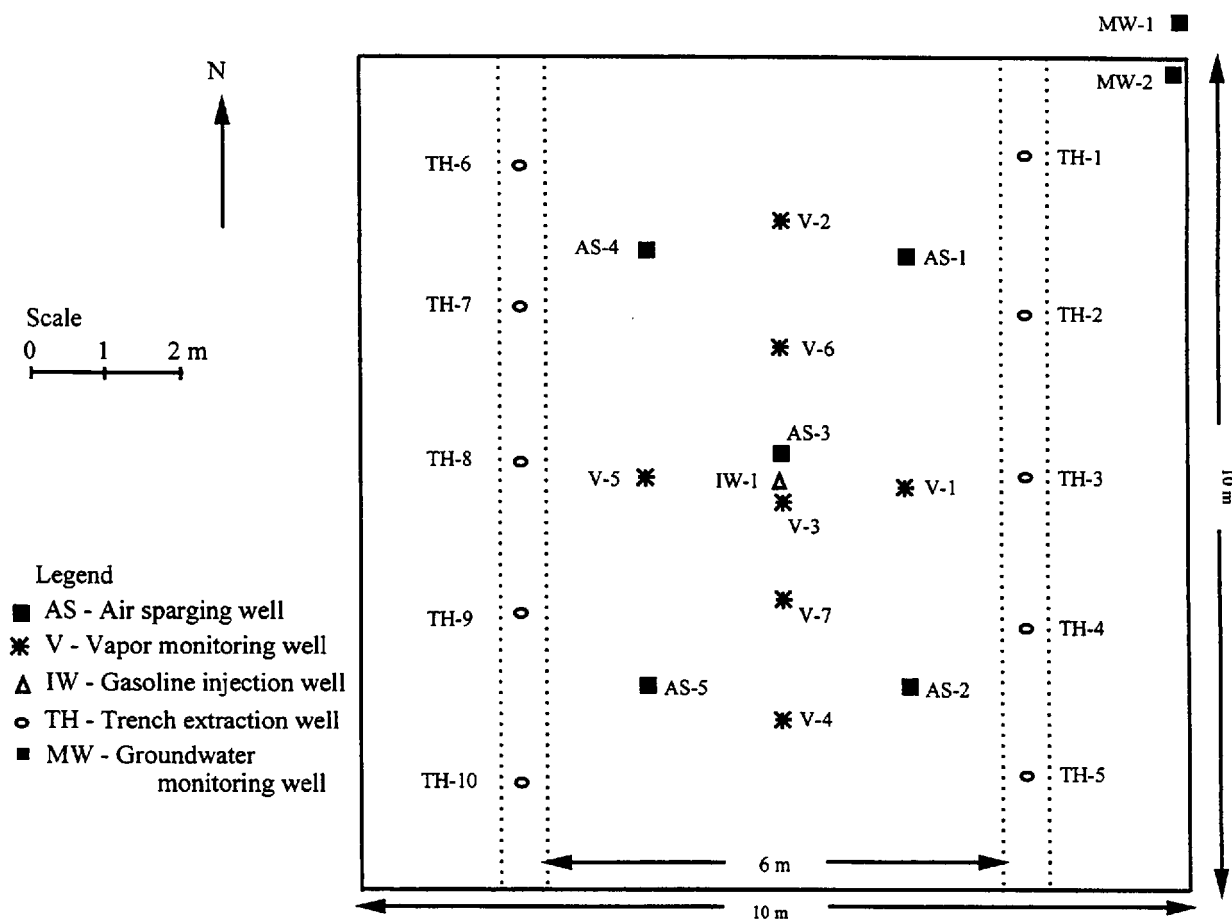


Figure 8. Plan view of the cell showing the locations of the vapor monitoring and sparge wells.

2. Trench Design

Two vapor extraction trenches were constructed in the cell. They were ~4 ft (1.2 m) deep, 6 in (0.15 m) wide and separated by ~20 ft (6 m) (Figure 9). Approximately 1 ft (0.3 m) of fine to medium sand was placed in the bottom of the trenches. Approximately 2 ft (0.6 m) of powdered bentonite was placed on top of the sand and the remainder of the trench was filled with concrete. (Soil samples collected from the trench during excavation were analyzed and shown to be free of hydrocarbons.) Five vertical wells constructed of 2-inch PVC were installed in each trench. Each well had ~8 inches (0.2 m) of slotted screen and a cap at the bottom. The five wells were connected together with a 2-inch PVC manifold which ran to the extraction pump. The vacuum in each trench could be controlled by a ball valve at the pump end of the trench and a ball valve that could be opened to the atmosphere at the other (Figure 5). In addition to the extraction wells, two 1-inch PVC dewatering wells were installed in each trench. Following installation of the trenches, the existing plastic and sand/bentonite surface of the cell was replaced with 4 to 6 inches (10–15 cm) of concrete.

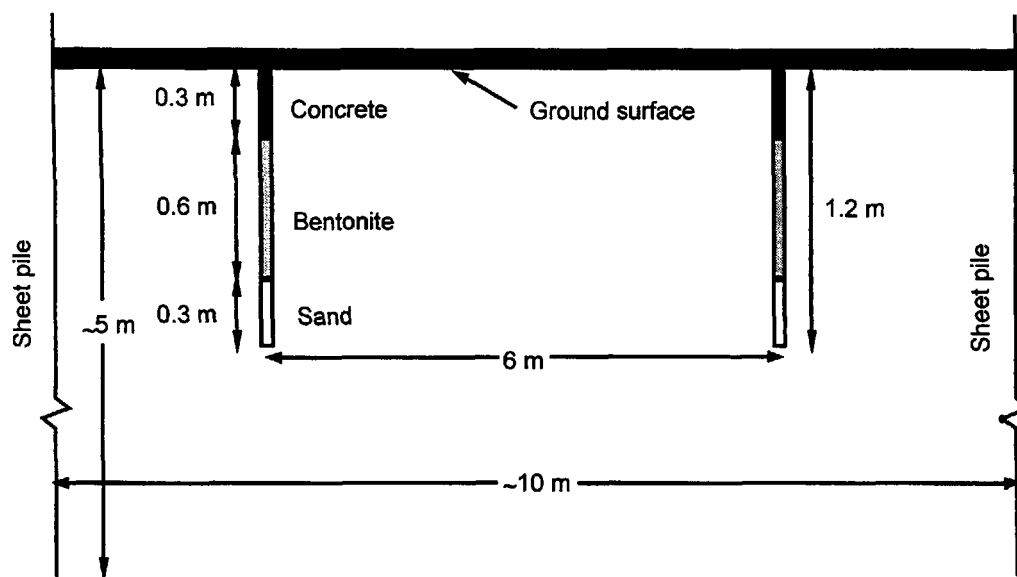
3. Vertical Vapor Extraction Well Design

In July 1994, five SVE vertical vapor extraction wells (W-wells) were installed in the experimental cell (Figure 10). These wells were constructed from 2-inch PVC standpipes with a sand pack over the depth of 3–4 ft (0.9 to 1.2 m). A capped 8 inch (15 cm) section of slotted screen at the bottom of each standpipe distributed the applied vacuum through the sand pack. The remainder of the hole was backfilled with bentonite to ground surface and topped with a concrete seal.

4. Pumping Equipment

The extraction pump used during the 1993 field season was a Roots positive-displacement blower (PD, Air Components Engineering, Grand Rapids, MI) capable of sustained vacuum up to ~15 inches of mercury (0.5 atm or 200 inches of water) and a maximum flow of about 30 standard cubic feet per minute (scfm). Throughout the course of the experiments, air was extracted from the trenches at a variety of flow rates ranging from 1 to 25 scfm. The latter corresponded to about half an atmosphere of vacuum, and represented the maximum capacity of the blower. During the 1994 field season the PD blower was used on the extraction trenches, while a liquid ring (LR) pump was used on the vertical vapor extraction wells. The LR pump operated at ~27 inches of mercury (0.9 atm or 365 inches of water) vacuum and a flow rate of ~30 scfm. Air sparging wells located within the hydrocarbon plume were individually activated using an oil-less compressor capable of injecting air at a rate of ~1 scfm.

a) Cell Cross-section Perpendicular to Trenches



b) Trench Cross-section

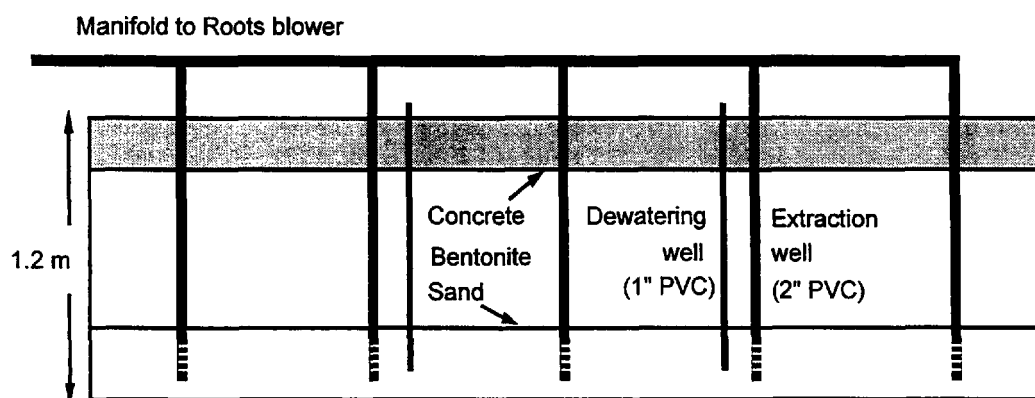


Figure 9. Schematic "as built" diagrams of the SVE extraction trenches.

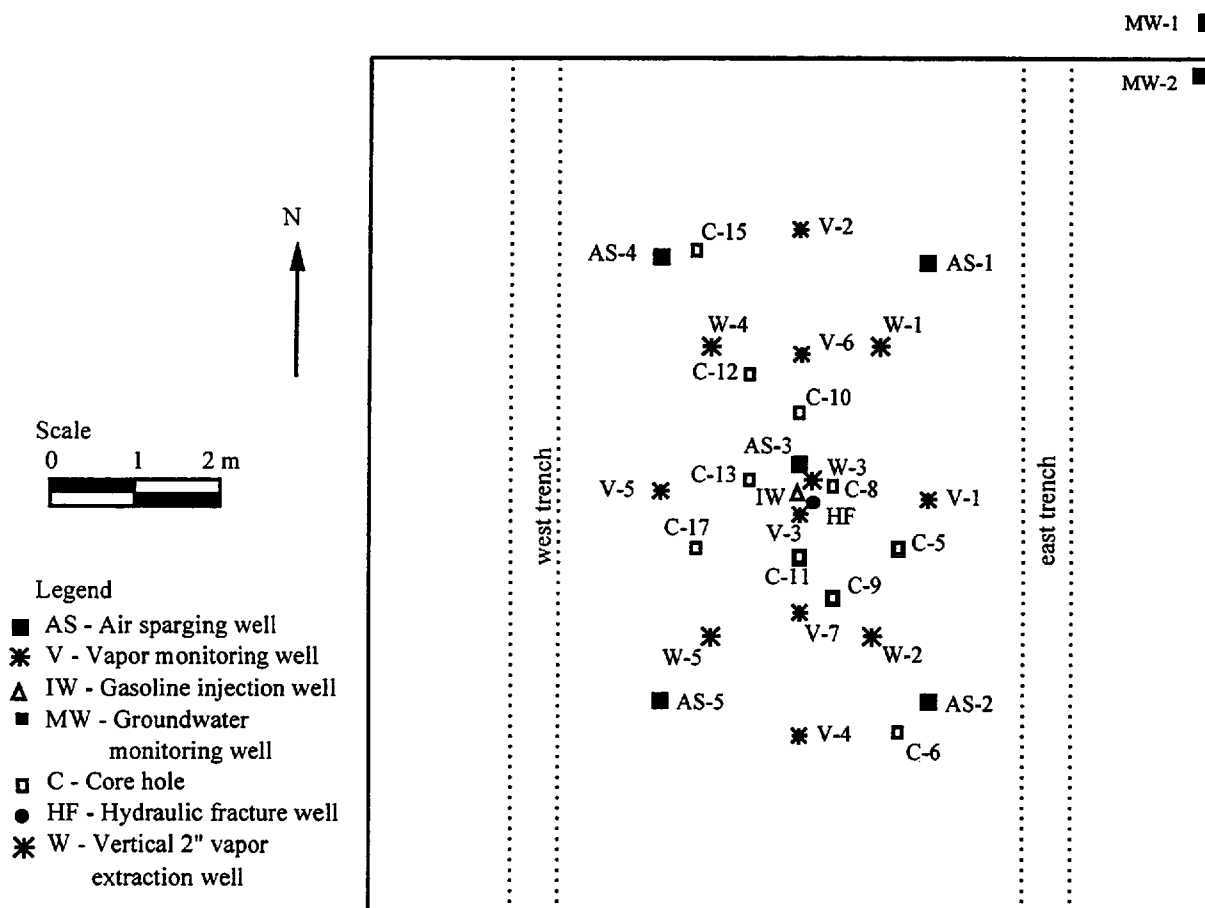


Figure 10. Plan view of the cell showing the locations of the extraction trenches and vertical extraction wells.

D. Soil Vapor Monitoring and Analysis

The analytical system for determining hydrocarbon concentrations in the SVE system offgas is shown schematically in Figure 11. Vapors drawn from the cell by the SVE system were pumped from the manifold to a gas chromatograph (GC, Hewlett Packard Model 5890 with a flame ionization detector) using a diaphragm pump. The components of the gasoline vapors were separated on the GC using a 100 m long Petrocol® column (Supelco Inc.). The temperature program for the separation was -50 to 200°C. Chromatograms were collected on a data system (Nelson Analytical, Cupertino, CA) and stored on a computer. The system was automated for 24-hour-a-day operation.

Calibration of the GC system was accomplished using both external and internal standards. Three types of external standards were used. The first external standard was a commercially prepared mixture in pressurized cans (Liquid Carbonics, Chicago, IL). It contains a number of the components of the spill mixture, but not all of them. The second type of external standard was prepared on-site by injecting a known mass of the spill mixture into 0.8-L stainless steel canisters. The canisters were then pressurized to a known pressure to produce a standard of known vapor concentration. The third type of external standard was produced in the manifold of the SVE system by adding the spill mixture at a known rate to the air stream using a syringe pump. The rates of addition with the syringe pump were designed to produce vapor concentrations of each component which bracketed the concentrations found in the extracted air. (During this process the end of the manifold was open to the atmosphere [Figure 5], so no air was being drawn from the extraction trench.) The combination of these three standards insured that the concentrations measured in the off gas of the SVE system accurately reflected the actual concentrations coming out of the extraction trenches. Good agreement among all three approaches was achieved. During routine analysis, two internal standards (n-octane and isobutylbenzene) were added at a constant rate via syringe pump at the extraction manifold. The purpose of the internal standards was to insure that the analytical system was working properly during each run.

E. Soil Coring and Analysis

Over the course of the project, soil samples were collected several different ways. Most samples were collected by driving short sections of stainless-steel tube (2 or 4 inch O.D. by 1 foot long) down a hole created by previous tube sections. Sample depths ranged from ~1 to 5 feet (0.3 to 1.5 m) below ground surface. Each core section was sampled by removing ~20 mL of the soil and placing it into a 40 mL vial containing 20 mL of methanol. During the final sampling (July 1995) samples were collected from the walls of large trenches that had been excavated at the site. Soil samples collected in 1993–1994 were shipped to a commercial laboratory for gasoline range organic (GRO) analyses (modified EPA method 8015). The soil samples collected in July 1995 were shipped to OGI for GC/MS analysis. In addition, some replicate samples were sent to the commercial lab for GRO analyses.

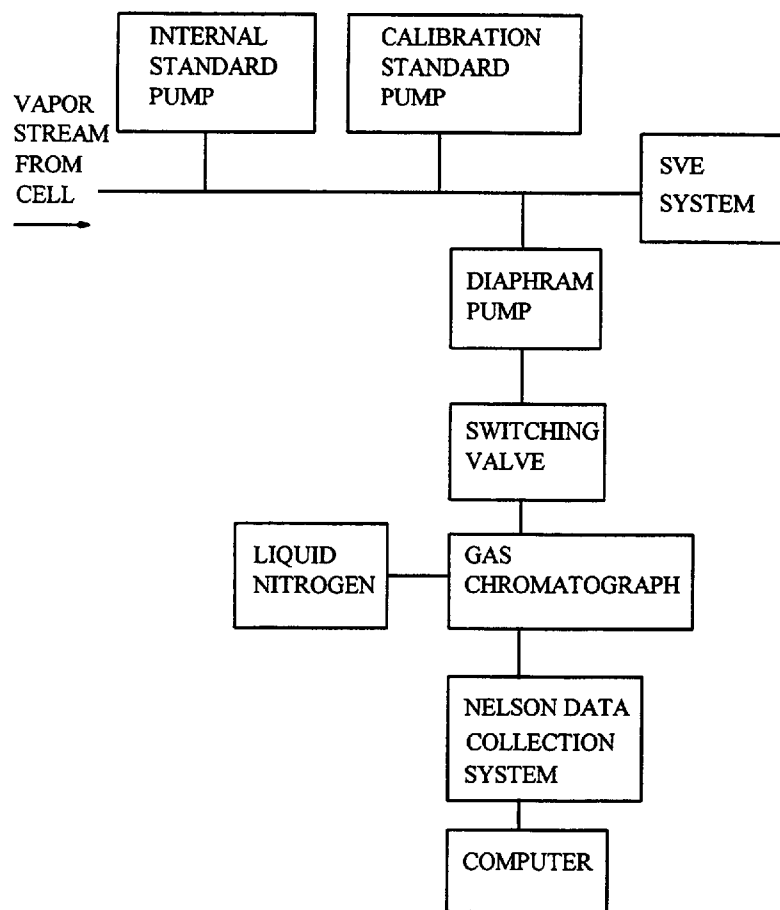


Figure 11. Block drawing of the analysis system.

F. Hydraulic Fracturing

During the 1994 field season six hydraulically induced fractures (hydrofractures) were created in the vicinity of the experimental cell by a team from the University of Cincinnati. In addition, a hydrofracture was induced in the center of the experimental cell. Details of the hydraulic fracturing activities and resulting fractures are contained in Appendix A. The fracture within the experimental cell was designated as HF-1 for this project. The depth of the injection point was 8 ft (2.5 m) below ground surface. Figure 12 shows a cross-section of the cell with the approximate location of the hydrofracture in relation to other features in the cell. Four cubic feet (110 L) of sand mixed with a guar gum gel was injected into the subsurface which created a symmetric 23 ft (7 m) diameter fracture. Uplift of the concrete surface was measured using an array of survey stations which indicated that the average fracture aperture was ~ 0.04 to 0.06 in (1 to 1.5 mm). The hydraulic fracture extended beneath both extraction trenches but did not intercept either trench, thereby avoiding short circuiting of extraction or injection air between the trenches and the hydrofracture.

G. Microbiological Sampling and Analysis

At the conclusion of the 1995 field season, a team from Oak Ridge National Laboratory (ORNL) collected samples for microbiological analysis. The purpose of the sampling was to determine the microbial population, microbial activity, and NAPL degradation capabilities of the microbes. Most probable number (MPN) and colony forming units (CFU) methods were used to enumerate the biomass, and phospholipid fatty acid methyl ester analysis (PFLA) was used to assess microbial community structure and nutritional status. Core samples were collected from high (1000 mg/kg), and low (200 mg/kg) level contaminated areas within the experimental cell along with uncontaminated cores. At each sample location, cores were collected at ~0.3, 1.6 and 3.3 ft (0.1, 0.5 and 1.0 m) depths. For each sample an aseptic 2-inch (5 cm) diameter by 1 ft (30 cm) long core stainless steel core barrel was driven horizontally into the wall of large trenches excavated in the cell (Figure 13). Each tube section contained ~8 in (20 cm) of core which was extruded and cut into subsamples (~25 to 75 g) using pre-sterilized utensils. Details of the microbiological activities are presented in Appendix B.

H. Water Levels Following the Gasoline Release

Water levels were continuously monitored prior to the SVE experiments. Figure 14 shows water depth data from the time of the spill in September, 1992 until the initiation of SVE. Precipitation was not measured at the site prior to remediation. The data indicate that the water table fluctuated between ground surface to ~2.6 ft (0.8 m) below ground surface.

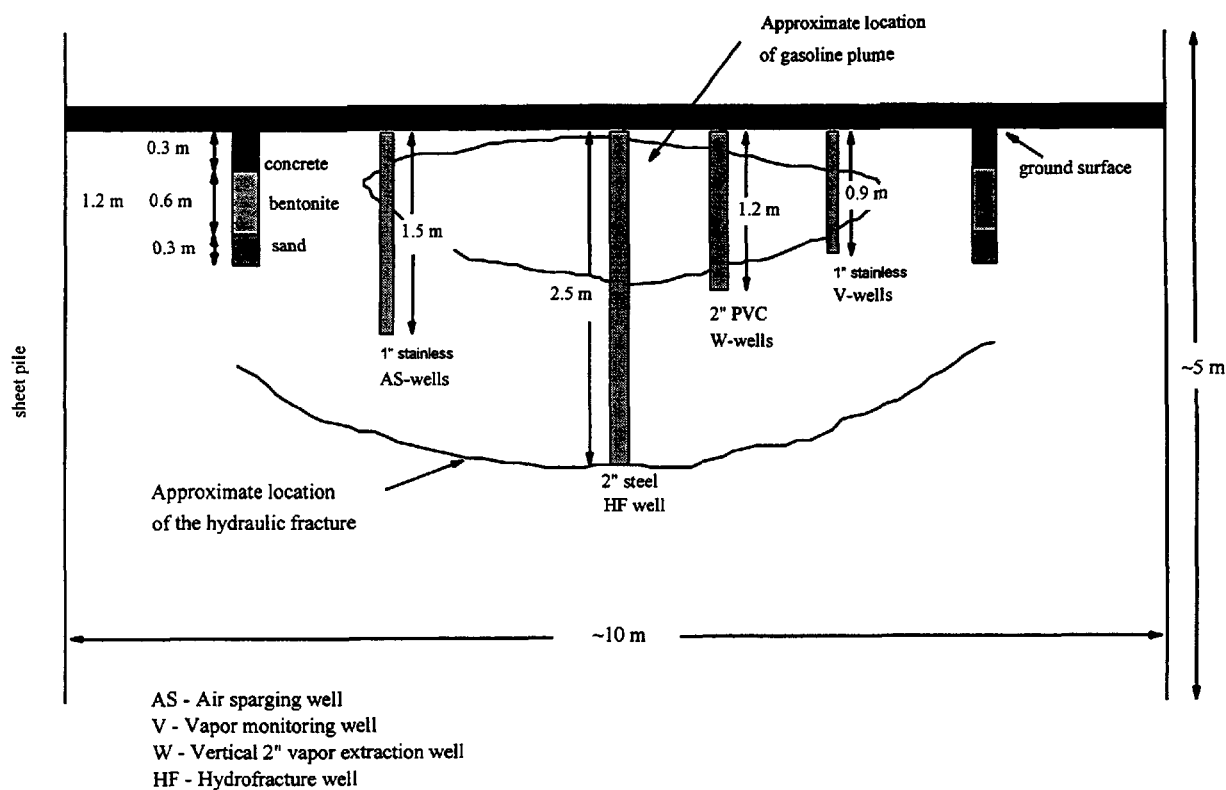


Figure 12. Cross-section view of the experimental cell showing the locations of the trenches, wells, hydrofracture and the hydrocarbon plume.

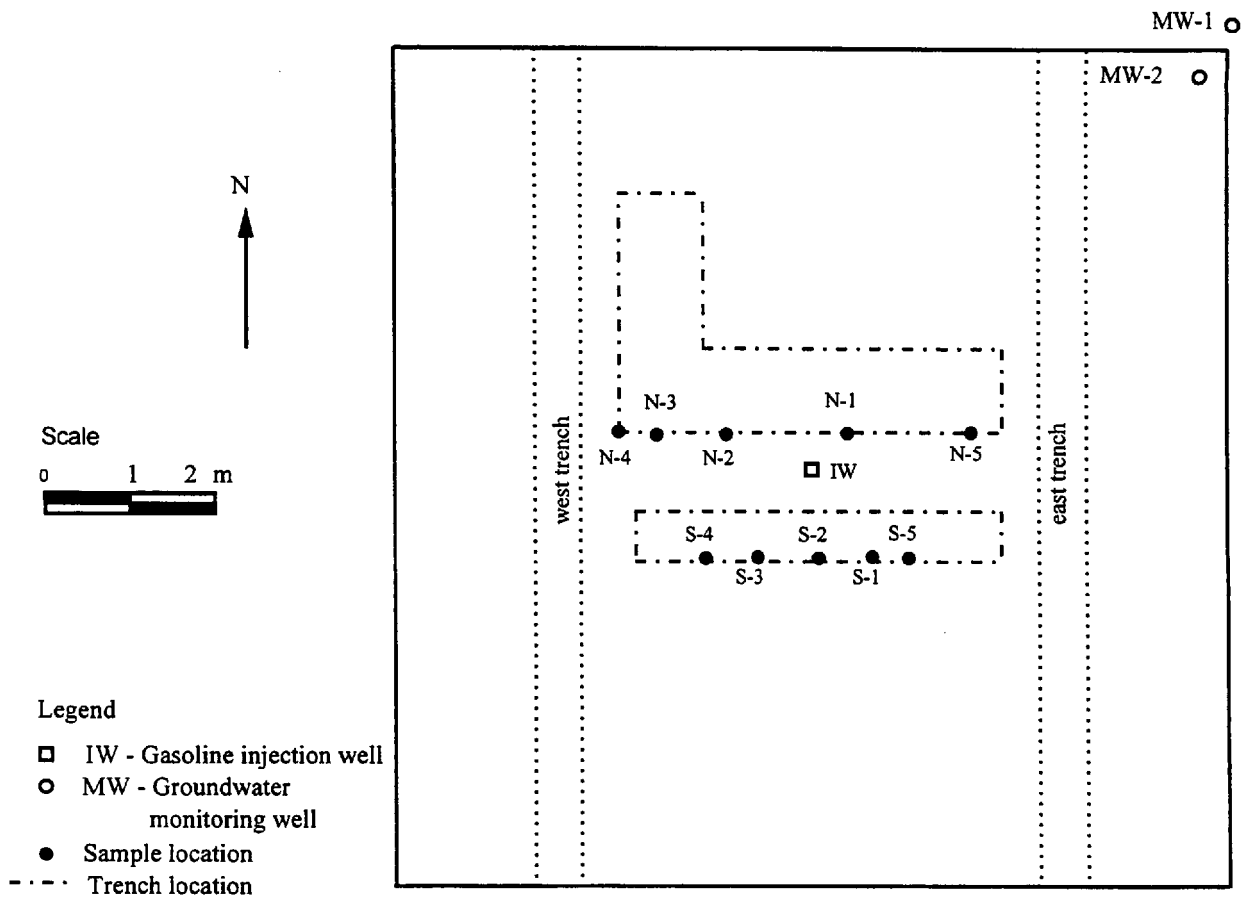


Figure 13. Plan view of the test cell showing the locations of the sampling trenches and the specific sample locations.

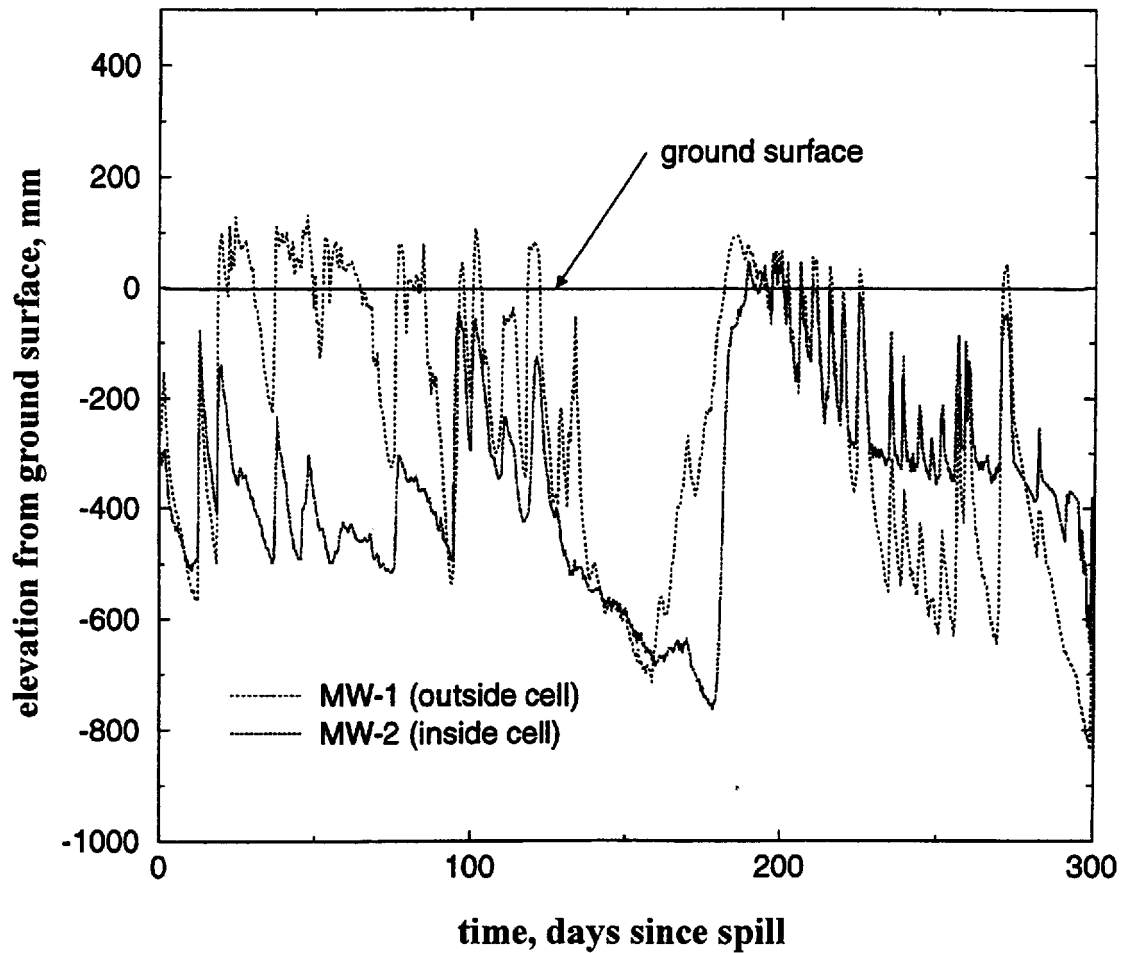


Figure 14. Water table depths measured inside and outside the test cell for the time of release to the initiation of remediation (~10 months).

VII. DETERMINATION OF AIR PERMEABILITY AND EFFECTIVE POROSITY

In order to assess the impact of the fractures and water on air flow, air permeability and effective porosity, measurements were made using three wells within the experimental test cell (Figure 15). Pneumatic tests were conducted by pumping air from one of the wells and measuring the reduction in pressure at all three wells. As discussed below, those data were used to graphically estimate the radius of influence of the extraction well and from that the air permeability was calculated.

As seen in Table V, the pneumatic pumping test flows were generally in the range of 2 scfm. The vacuum at the extraction well was maintained at 0.5 atm. Vacuums at the other two wells were 1 inch of water (0.003 atm). The radius of influence for these tests was estimated to be 10 ft (3 m). The air permeability of the fractured clay was calculated using the *in-situ* air permeability test protocol developed by the U.S. Air Force (Hinchee *et al.*, 1992). The protocol recommends the following equation for estimating air permeability:

$$k_a = \frac{Q \mu \ln(R_w / R_I)}{H \pi P_w [1 - (P_{atm} / P_w)^2]} \quad (1)$$

where: Q = volumetric flow rate from the venting well (m^3/s)

μ = viscosity of air (10^{-5} kg/m-s)

R_w = radius of the venting well (m)

R_I = radius of venting influence at steady-state (m)

H = depth of screen (m)

P_w = absolute pressure at the venting well (Pa)

P_{atm} = ambient pressure ($1.01 \times 10^5 \text{ Pa}$)

Air permeabilities calculated for the test site using equation 1 range from $\sim 10^{-15}$ to 10^{-16} m^2 , with an average value of $\sim 5 \times 10^{-16} \text{ m}^2$.

The data contained in Table V, along with the general fracture orientation at the Sarnia site (McKay *et al.*, 1993a) are shown in Figure 16. Generally, the highest vacuums were generated at wells oriented in the same plane as a set of fractures. For example, pumping to or from P1 and P2 (Test 1 and Test 2, respectively) results in the highest (0.002 atm) vacuum through the clay till, and P1 and P2 are oriented along the general direction of a set of fractures. On the other hand, the smallest vacuum results from pumping to or from P1 and P3 (Test 1 and Test 3, respectively) which are not aligned with a fracture set. Also, the hydrocarbon source zone is slightly elliptical in the direction of the northwest-southeast fracture set (see Appendix A). This may suggest that northwest-southeast is the major fracture direction while the northeast-southwest fractures are secondary fractures. Major and minor fracture directions have not been verified, however, McKay *et al.*, (1993a) suggest a slight fracture domination in the northwest-southeast direction. Based on the above discussion, if a trench is to be used in an SVE system, it

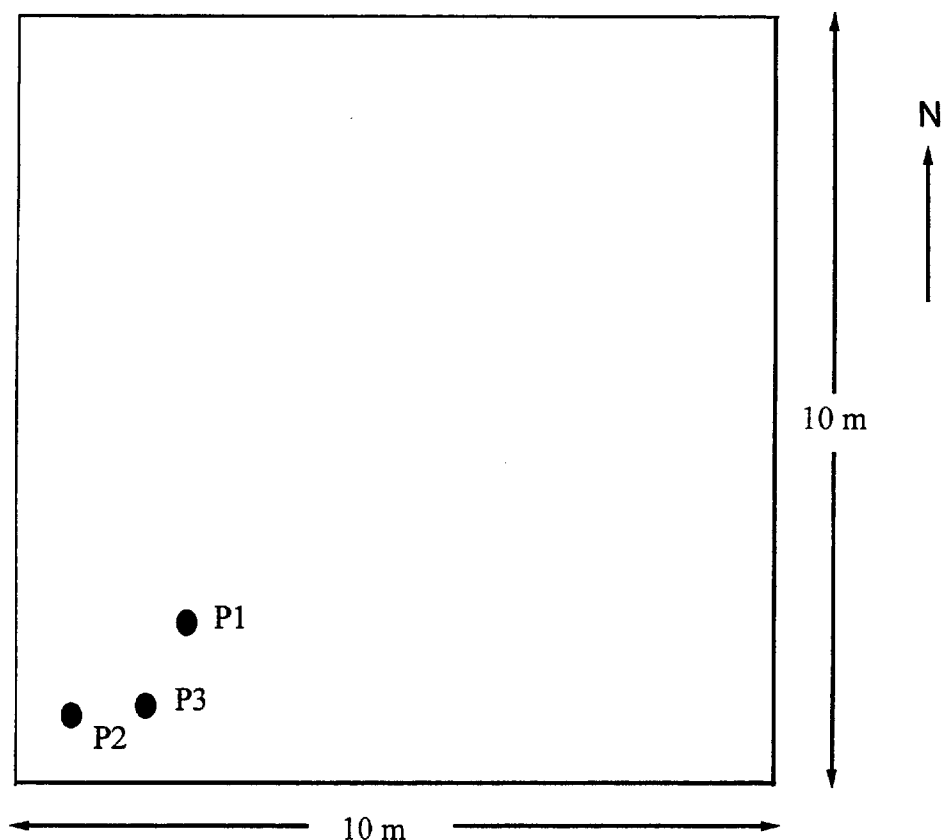


Figure 15. Plan view of cell showing the locations of the wells used for effective porosity and air permeability tests.

Table V. Pneumatic pumping test measured flows and pressures.

	P1	P2	P3
Test 1	2.0 scfm	0.33" water	0.92" water
Test 2	0.3" water	1.9 scfm	1.1" water
Test 3	0.86" water	1.1" water	2.0 scfm

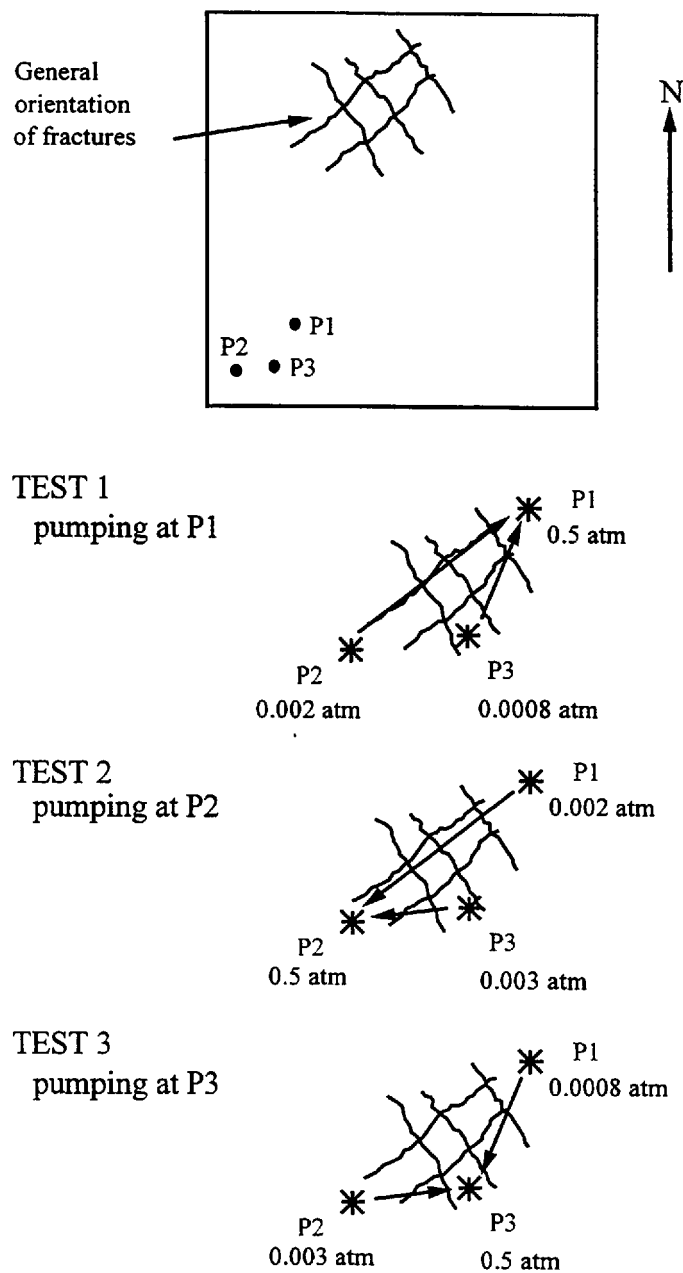


Figure 16. Schematic drawing of the results of the pneumatic pumping tests, including the general orientation of the fracture network.

should intercept as many fractures as possible to maximize the influence of the extraction system. In the case of the Sarnia site, the orientation of the trenches was dictated by the orientation of the existing sheetpile walls.

In order to verify the field measurements of air permeability, an independent method (the “cubic law”) for calculating the air permeability, k_a , was used.

$$k_a = \frac{b^3}{B12} \quad (2)$$

In this equation, b is the fracture aperture and $b^3/12$ represents the planar porosity and is analogous to the volume of the voids. The spacing between fractures, B , accounts for the total volume of the soil. Equation 2 is based on the assumption that flow through a fracture is similar to laminar flow between two smooth parallel plates (Snow, 1968, 1969) and it is assumed here that the fracture aperture is completely air filled (i.e., the relative permeability for air is one). Table VI shows the range of air permeability values (m^2) calculated using a range of fracture aperture and spacing values. The fracture aperture and spacing values used in the table are based on values determined for the Sarnia site by McKay *et al.* (1993a). They measured fracture apertures of $<43 \mu m$ at spacings of 2–100 cm in the top 16 ft (5 m) of the clay till. Fracture spacings larger than 20 cm were not used here since the data of McKay *et al.* (1993a) showed that the fracture spacings decreased as ground surface was approached and since the hydrocarbon plume was located in the top 6.5 ft (2 m) of the soil.

The value of k_a for 10 μm fractures with 10 to 20 cm spacings, ($8.3 \times 10^{-16} m^2$ and $4.2 \times 10^{-16} m^2$, respectively) are on the same order of magnitude as the value of air permeability estimated from the U.S. Air Force protocol analysis of the pumping tests, $5 \times 10^{-16} m^2$. In McKay *et al.* (1993a), 63 field tests using seepage collector trenches indicated a hydraulic conductivity of $8.9 \times 10^{-16} m/s$ (geometric mean), which translates into a permeability of $9.1 \times 10^{-16} m^2$. Again, this is the same order of magnitude as the air permeability determined for the field site.

The effective air-filled fracture porosity of the clay was estimated using a pumping tracer test and a simple volumetric calculation. First, the volume of soil contained within a cylinder whose center was at the extraction well and whose perimeter was at the tracer injection well was calculated (Figure 17). Second, a tracer test was conducted to measure the volume of air that needed to be removed from the extraction well to cause tracer breakthrough. The tracer used for these tests was sulfurhexafluoride (SF_6) and approximately 1 mL was added via a syringe to the injection well. Even though fracture apertures decreased with depth and therefore velocity varied with depth, it was assumed that the tracer velocity was uniform over the depth of the 1-m cylinder. Using the uniform velocity assumption, the fracture porosity was calculated as the ratio of the extraction volume to the cylinder volume. Figure 18 shows the results of a typical breakthrough curve for one of the four pumping tracer experiments. For the analysis presented here it was assumed that the breakthrough volume was given by the initial arrival of the tracer at the injection well. Typically the maximum concentration point, is used to determine the breakthrough volume. However, because of the large reservoir of SF_6 which remains in the injection well, the test does not represent an “instantaneous” injection and therefore the initial

arrival time was used. Table VII gives the cylinder radii, cylinder volumes, extraction volumes and air-filled fracture porosities for the four tracer tests.

The effective air-filled fracture porosity values range from 0.001 to 0.006. Another estimate of effective air-filled fracture porosity can be made using fracture spacing and fracture apertures. The zone of concern in this study (i.e., the vadose zone) is within the top 6.5 ft (2 m) of the surface, therefore ~20 cm for fracture spacings and 20 to 40 μm for aperture are appropriate (McKay *et al.*, 1993a,b) and reasonable. The effective air-filled fracture porosity based on these values is 0.0001 to 0.002. These values are somewhat similar to the values determined from the pumping tracer tests, 0.001 to 0.006.

Table VI. Air permeabilities calculated from fracture aperture and spacing values.

b (μm) ^a B (cm) ^b	10	20	40
1	$8.3 \times 10^{-15} \text{ m}^2$	$6.7 \times 10^{-14} \text{ m}^2$	$5.3 \times 10^{-13} \text{ m}^2$
10	$8.3 \times 10^{-16} \text{ m}^2$	$6.7 \times 10^{-15} \text{ m}^2$	$5.3 \times 10^{-14} \text{ m}^2$
20	$4.2 \times 10^{-16} \text{ m}^2$	$3.3 \times 10^{-15} \text{ m}^2$	$2.7 \times 10^{-14} \text{ m}^2$

^a fracture aperture (McKay *et al.*, 1993a, b)

^b spacing between fractures (McKay *et al.*, 1993a, b)

Table VII. Effective porosity tracer test calculated values.

Test	Cylinder Radius (m)	Cylinder Volume (L)	Breakthrough Volume (L)	Fracture Porosity
P2 to P1	1.88	11,104	70	0.006
P3 to P1	1.28	5,147	7	0.001
P1 to P3	1.28	5,147	12	0.002
P3 to P2	0.89	2,489	10	0.004