

**Remediation of LNAPL in a Naturally Fractured Clay Till:
Physical and Numerical Modeling**

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This dissertation "Remediation of LNAPL in a Naturally Fractured Clay Till: Physical and Numerical Modeling" by Diane Elizabeth Grady has been examined and approved by the following Examination Committee:

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DEDICATION

This work is dedicated to my mother and father. They may not always understand what I do or why I do it, but their unfailing support and love helped me reach this goal.

ACKNOWLEDGEMENTS

It all started halfway through my third year of Engineering, when Dr. Grahame Farquhar (University of Waterloo) told me he had set-up an interview between Dr. Richard Johnson and myself. After talking with Rick for about 30 minutes, I thought OGI could be a fun place for graduate school. A call to Jane Allan (one of Rick's current students and UW alumni) and I was hooked. Four years later I look back and don't regret my decision to attend OGI. Thanks for the advice Fark.

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ABSTRACT

Remediation of LNAPL in a Naturally Fractured Clay Till: Physical and Numerical Modeling

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Contaminants entering a fractured clay migrate by advective transport in the fractures with subsequent diffusion into the matrix. As the contaminants diffuse into the matrix they become less accessible to most in-situ remediation technologies. A field experiment in a naturally fractured clay was part of a project to evaluate technologies, processes and risks associated with remediation of low-permeability soils.

Fifty liters of a hydrocarbon LNAPL (light non-aqueous phase liquid) mixture was released into the fractured clay below ground surface and remained undisturbed for ~10 months. The fractured clay till was then actively remediated for ~2 months using soil vapor extraction (SVE) from trenches and in-situ air sparging from wells. During this time ~40% of the original mass was removed. Mass removal was limited by high water contents and preferential flow paths through the fractures. Subsequent SVE from vertical

wells removed less than ~2% of the mass spilled. The vertical wells were not as effective at mass removal as horizontal trenches because the latter intercepted a greater number of fractures. To evaluate air flow through the soil, tracer tests were conducted in the contaminated zone during SVE. These tests indicated that preferential flow through the fractures was occurring along with significant surface leakage through a concrete cap.

A one-dimensional multicomponent diffusion model was used to simulate the initial partitioning of LNAPL between the fractures and the matrix. The more soluble compounds were found to move into the matrix, while the less soluble compounds remained largely in the fractures, suggesting that the less soluble compounds are more easily remediated by SVE. The model was then used to simulate contaminant movement into and out of the fracture-matrix interface prior to and during remediation. Simulation of vaporization due to SVE air passing through the fractures indicated that some of the mass which had moved into the matrix prior to remediation was diffusing back into the fracture where it became accessible to the SVE system. The model results showed good agreement with mass balance results from the field, which were calculated from soils analysis, offgas analysis and biodegradation estimates.

CHAPTER 1

INTRODUCTION

BACKGROUND

Low permeability or "tight" soils usually refers to silts, clays or tills whose hydraulic conductivities are less than 10^{-7} m/s. Permeabilities in these materials may be dominated by secondary fractures which result from numerous processes including weathering and desiccation. Open fractures above the water table are generally air-filled while the adjacent matrix (solid) blocks are water saturated due to capillary pressures.

When LNAPL (light non-aqueous phase liquid) is released into these soils it will predominately move through the fractures and bypass the matrix blocks until the capillary fringe is encountered. At that point, the NAPL (non-aqueous phase liquid) will tend to spread laterally in cross-cutting fractures (Walden, 1995). The NAPL phase will generally not migrate into the matrix blocks due to the large entry pressures required to move the NAPL inward. However, some of the NAPL can dissolve into the soil pore water and diffuse into the immobile pore water of the matrix blocks (Figure 1.1). As the NAPL moves through the soil it may also undergo sorption and biodegradation in both the fractures and the matrix. Therefore, with time the fraction of NAPL in the fractures may become significantly reduced.

The dissolved mass that has moved into the soil matrix will, in general, be much

more difficult to remediate than the NAPL in the fractures. The low-permeability of the matrix blocks along with low diffusion fluxes from the matrix translate into long remediation periods for removing contamination from the matrix. For example, simple diffusion calculations indicate that 85% mass recovery will take almost 10 times as long as the contamination has been in the ground prior to remediation. In other words, in a spill which occurred two years prior to remediation (i.e., air or liquid flushing to clear the fractures) it can take 20 years to remove 85% of the mass and 200 years to achieve 95% mass removal (McWhorter, 1995).

The water yields of tight soils are typically small, and therefore are rarely used as water supplies; the risk to human receptors is minimal. However, if a tight soil is underlain by a more permeable aquifer, the more permeable materials may become contaminated by water moving down through the tight soil (Figure 1.2). Infiltrating water will tend to move down through the fractures in the tight soil along pathways similar to those taken by the NAPL. When it comes into contact with NAPL in the fractures, the infiltrating water will quickly become saturated with the components of the NAPL. The contaminated water may then continue to move down to the more permeable materials which underlie the fine-grained soil. In this scenario, the presence of NAPL in the fractures is important in contaminating the infiltrating groundwater (Harrison, et al., 1992).

Research on soil vapor extraction (SVE) of LNAPLs has been conducted at the lab scale for nearly a decade. In most cases the investigations involved an uniformly mixed product within a homogeneous, unsaturated medium (Baehr et al., 1989; McClellan, 1991). More recently, studies have shifted to field-scale projects (McClellan and Gillham, 1992; Armstrong et al., 1994; Thorbjarnarson and Mackay, 1994) which also deal with a relatively homogeneous, unsaturated medium. There are few studies dealing with heterogeneous soils (e.g., Allan, 1995) and even fewer of low permeability soils.

A field pilot study was conducted by Gibson et al. (1993) using SVE in a clay soil. The clay was contaminated with paint thinner (a mixture of volatile aromatic hydrocarbons). Fractures and macropores in the clay are channels that increase the effective permeability of the soil. Gibson's study found air flow was mainly through the

fractures and the effective air permeability depends on the degree of fracturing and can not be estimated as a function of liquid saturation in the soil pores, as it is in higher permeability soils. The maximum air flow was dictated by the soil permeability and SVE blower capacity. A sharp decrease in pressure drawdown with increasing distance from the extraction well was observed. They concluded that vapor extraction caused a notable decrease in paint thinner vapor concentrations and preferentially removed the more volatile hydrocarbon compounds. A general observation on the effectiveness of SVE can be made; however, there has been very little experience in applying SVE to low permeability soils.

The goal of the study described here was to evaluate the feasibility of remediating a fractured fine-grained soil using air flushing (i.e., SVE). Several design criteria were evaluated to determine the most effective conditions for mass removal. The experiments were conducted at a site near Sarnia, Ontario, Canada. The site was selected for a variety of reasons, including: 1) it is possible to create spills at the site; 2) the site is a fractured till, which is recognized as a difficult medium to remediate; and 3) the geology of the site has been well documented.

The ability to create a spill is important because it allows the release of a product of known mass and composition for the purpose of obtaining a mass balance. In addition, the specific site characteristics can be carefully examined and selected prior to the spill. Preparations for the release can be made and the experimental conditions of the spill and the remediation can be optimized. Therefore the Sarnia study site was ideal.

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, McKay et al., 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.

Air flushing technologies, specifically SVE and in situ air sparging (IAS), were chosen for these experiments because they have become widely used for permeable soil. At the same time, these technologies have been applied to fine-grained soils, although few

data are available. SVE is a process that induces air flow through a unsaturated zone by creating pressure gradients. The induced air movement will "strip" volatile and semi-volatile contaminants from the vadose zone, and in some cases, also from the capillary fringe. Two removal mechanisms are possible with SVE: evaporative recovery and biodegradation. The contaminants are evaporated and transported with the induced air. SVE system also supplies oxygen to the soil which in turn enhances biodegradation (Payne, 1995).

Air sparging involves injecting air directly into the saturated subsurface to provide oxygen for bioremediation or to strip or volatilize the contaminants out of the groundwater (Hinchee, 1994). Air sparging strips volatiles in saturated zones and is usually combined with SVE to capture fugitive vapors. IAS also provides oxygen to the subsurface which will promote biological activity to degrade organics. However at present few data are available on how effectively oxygen can be transferred from the air to the water (Johnson, 1994).

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, as well as the role of matrix diffusion in controlling the final distribution of the contaminant. In addition, there is currently considerable debate about the best approach to air flushing in low permeability soil. Vapor extraction strategies for these soils can generally be divided into three categories: 1) SVE systems using a high vacuum (vacuum at extraction point " >0.5 atm"); 2) SVE systems using a medium to low vacuum (vacuum at extraction point " <0.5 atm"); and 3) SVE systems used in combination with air injection.

Each 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. As a result, the air moving through the system usually finds preferential pathways and therefore may bypass much of the soil. High vacuum systems may help remove water from the soil and fractures and thus improve air flow, however this could come at a high operation-and-maintenance cost. In addition, it is often difficult to prevent leaks with high vacuum applications and the induced vacuums tend to drop off quickly with distance from the

extraction point. These difficulties are compounded by the fact that fracture density, and therefore air permeability in fractured soils, often increases dramatically as ground surface is approached. As a result, the possibility of surface leakage increases. In low vacuum systems operation-and-maintenance costs tend to be lower. However, it may not be possible to generate adequate air flow to effect a reasonable remediation without the installation of many extraction points, which may make the cost of installation prohibitive. The combination of SVE and IAS has the potential to remediate both the volatile fraction of the residual NAPL and the dissolved fraction of the organics. However, installation of IAS wells will increase both installation and operation-and-maintenance costs.

SVE performance also will be affected by the design of the extraction points. Vertical wells are by far the most common type. However, the radial nature of the flow means that applied vacuums drop off very quickly with distance from the well. Alternatively, trenches (or horizontal wells) can be used which may avoid the rapid drop in vacuum that occurs radially around vertical wells. Therefore, trenches usually achieve higher flow rates at similar vacuums. However, they may be expensive or technically difficult to install at many sites. 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.

Subsurface remediation activities traditionally have been designed to prevent the formation of fractures since they complicate engineering projects, such as grout injection, deep-well injection and dam construction. However, low fluid flow is a major constraint on the remediation of low permeability soils. One way to avoid this limitation is to create fractures which will increase the effective permeability and change the fluid flow pathways in soils. Hydraulic fracturing is a method of creating sand-filled lenses in subsurface formations. This technique has been used for more than 50 years in the petroleum industry to increase the yields of oil wells. However, oil reservoirs are typically deeper and are composed of different geologic materials than shallow subsurface regions, so application of the fracturing method used in the petroleum industry must be adjusted for unlithified materials.

Murdoch, et al., (1991), have shown that hydraulic fractures can be created at shallow depths in soils. However for a fracture to be useful a propping agent (e.g., sand) must be injected into the fracture to prevent collapse. Usually a coarse grained sand or some other granular material is mixed with a viscous fluid (guar gum gel) and is injected into the induced fracture as a slurry. The gel decomposes after pumping and the fracture remains propped open by the granular material. The induced fractures are typically flat lying in the region around the borehole. At some distance from the borehole the fracture tends to dip gently upward or it may dip uniformly from the borehole to its end (Figure 1.3). These induced fractures should enhance in-situ remediation techniques that require fluid flow. High water content at many sites has a strong adverse affect on recovery rates during SVE (Murdoch, 1995). Therefore, hydraulic control of the soil, through dewatering using a hydraulic fracture, could improve the air flow through the subsurface.

EXPERIMENTAL OBJECTIVES AND TASKS

The primary objectives of the research presented here were to assess the effectiveness of SVE and enhanced SVE for remediating LNAPL spills in a naturally fractured clay. Enhanced SVE includes combining SVE and IAS and using an induced hydraulic fracture to improve air flow through better hydraulic control. Fifteen compounds including gasoline range organics (GROs), methyl-tert-butyl-ether (MTBE) and trichloroethylene (TCE) were chosen as a representative LNAPL mixture since they are common subsurface contaminants and their physical and chemical properties are well known. The experiments were conducted at a field site in a 10 x 10 m experimental cell located in a natural massive clay formation. To meet the objectives of this research three major tasks were completed.

Distribution of the LNAPL

Approximately 50 liters of a gasoline mixture was released into the fractured clay using a constant-head reservoir. The spill was left undisturbed for about ten months to

allow partitioning between the fractures and the clay matrix. Initial distribution of the contaminants between the fractures and the matrix was modeled in order to determine the amount of contaminant that should be accessible to SVE. Soil cores collected prior to remediation were used to establish the areal extent of the spill. Also, to further understand the physical conditions that would influence the SVE system, field measurements of the air permeability and the effective porosity were conducted. These experiments are presented in Chapter 2.

SVE and Enhanced SVE Experiments

Mass removal by SVE using trenches at low vacuum (i.e., "<0.5 atm" vacuum), was examined during the initial field season (1993). In addition, mass recovery using both SVE and IAS was also examined during this season. During the second field season, recovery using vertical wells, at high vacuums (i.e., ">0.5 atm" vacuum), was examined. A hydraulic fracture was induced in the second season to promote better air flow in the subsurface through dewatering. During all SVE configurations both pressure and flow measurements were recorded. Mass balance was calculated through a series of soil core analyses, biodegradation measurements and mass recovery through SVE. These experiments are described in Chapter 3.

Numerical Modeling

The numerical model uses a simple one-dimensional finite difference diffusion equation to simulate diffusion from the fractures into the matrix. The model also simulates reverse diffusion from the matrix to the fractures as the fractures are "cleared-out" during SVE operations. The calculated flux of the contaminate into and out of the matrix compared with the field data provides an indication of the diffusion and sorption mechanisms within the clay matrix. The results of these simulations are discussed in Chapter 4.

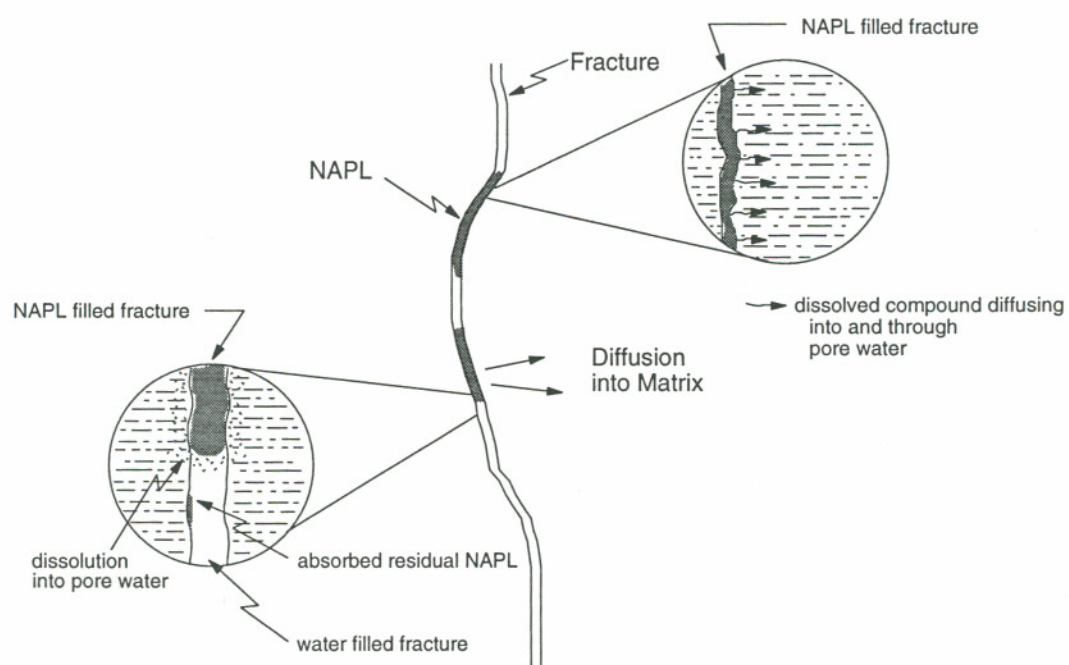


Figure 1.1. Schematic drawing of dissolution and diffusion from a fracture into a clay matrix.

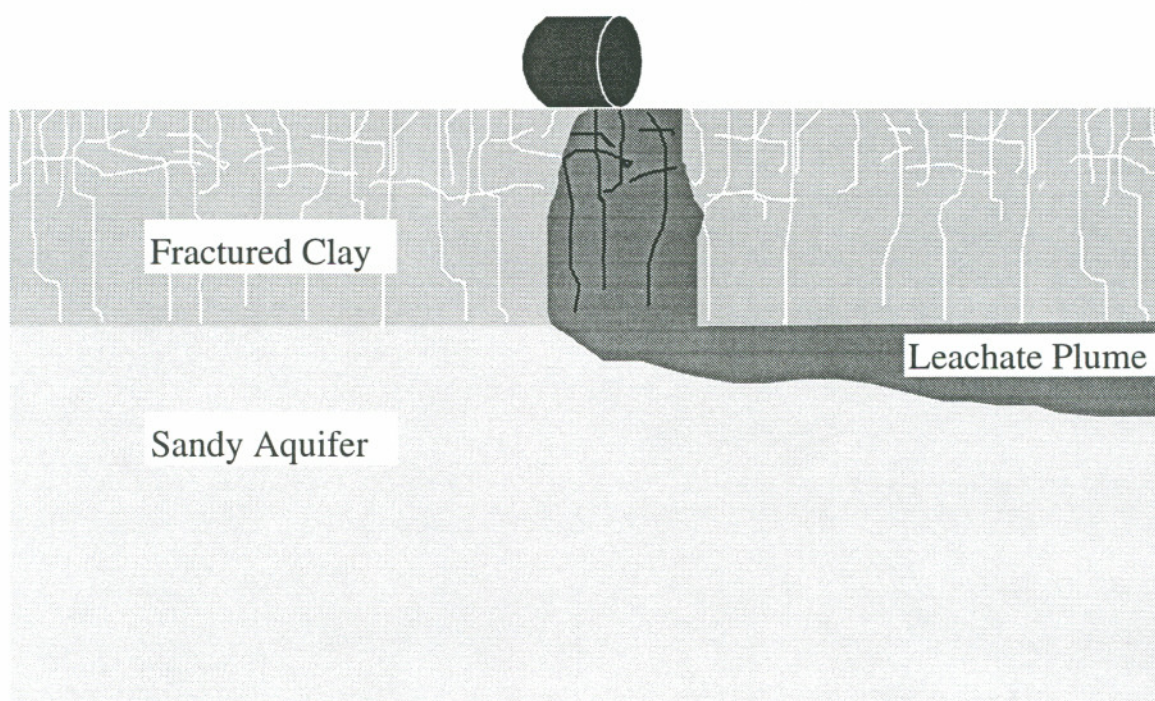


Figure 1.2. Schematic drawing of contamination of a sandy aquifer by an overlying fractured clay.

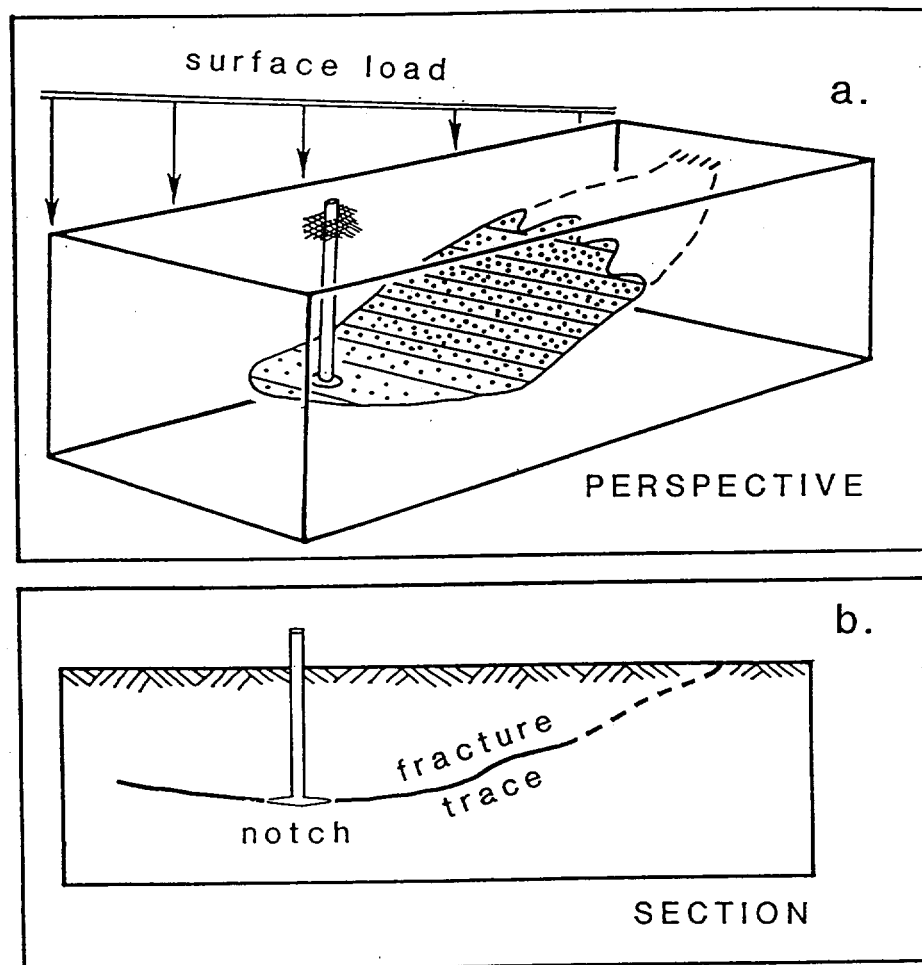


Figure 1.3. Idealized hydraulic fracture created at shallow depths in over consolidated silty clay (from Murdoch, et. al., 1991).

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CHAPTER 2

CHARACTERIZATION OF AN LNAPL SPILL IN A NATURALLY FRACTURED CLAY

INTRODUCTION

Hydrocarbon fuels are often stored in large volumes above and below ground and frequently find their way into the subsurface through spills and leaks affecting unsaturated soil and often migrating to the underlying water (e.g., Beckett and Huntley, 1994; Farr, et al., 1990; and Hunt, et al., 1988). Once in the subsurface fuels can exist in several states including: 1) light non-aqueous phase liquids (LNAPLs), 2) dissolved in water, 3) sorbed to aquifer materials, or 4) volatilized in soil gas. The transport of LNAPLs (e.g., gasoline) in porous media has been examined both in the laboratory and field by a number of researchers (e.g., Eckberg and Sunada, 1984; Hunt, et al., 1988; and Mercer and Cohen, 1990). Although most studies of transport and remediation of LNAPLs have been conducted in homogenous sandy materials, spills typically occur in more complicated geologic media such as fine-grained soils and fractured rock. Research investigating LNAPL releases in these low permeability and fractured media is therefore necessary to better understand the chemical and physical limitations influencing the efficiencies of remediation technologies.

Low permeability soils (silts, clays and tills) contaminated with petroleum

hydrocarbons or other LNAPLs have a number of characteristics which makes them difficult to remediate. The permeabilities of these soils are low and the water contents are generally high. They typically contain fractures or other preferential pathways separated by intact blocks of soil. While the fractures may occupy only a small fraction of the total volume, depending on fracture aperture and frequency, they may represent the primary transport pathways and can increase the otherwise low hydraulic conductivity of these soils by several orders of magnitude. The water contents of the fractures may change substantially due to water table fluctuations, but the blocks of clay between these fractures remain largely saturated. As a result of the high water content of the matrix blocks, LNAPL movement within the soil also will be almost exclusively within the fractures; as a consequence, even a small spill may contaminate a large soil mass. Once the LNAPL is in the fracture, dissolution and diffusion of the NAPL (non-aqueous phase liquid) components into the clay matrix can become important (Figure 2.1). Simple analytical calculations of diffusion rates based on the estimated size of the fractures suggest that some of the NAPL components will largely disappear into the matrix within a matter of months, while others will remain in the fractures for a longer period of time.

Water yields of low permeability soils are typically small and therefore these soils are rarely used as water supplies. However, contaminants can migrate down through these tight soils into an underlying aquifer through vertical fractures that completely penetrate a clay aquitard or migrate laterally in the shallow weathered and fractured zone (McKay, et al., 1993a). As a consequence, tight soils can be a long term source of contamination to drinking water aquifers. Unfortunately, remediation is often difficult due to various physical and chemical limitations associated with fine-grained soils. This chapter presents the results of an LNAPL spill in a naturally fractured clay till. Details of the field site and the gasoline spill are presented along with a description of the installation of monitoring wells used in this project. Also described are field determinations of air permeability, effective porosity, and initial distribution of the spill, along with the expected phase distribution of the spill. These field determinations represent the initial conditions of the site before remediation by air flushing, which will be described in the soil vapor extraction chapter.

SITE DESCRIPTION

The field site for these experiments is located 12 km southeast of Sarnia, Ontario (Figure 2.2) at a hazardous waste treatment and disposal site owned by Laidlaw Environmental Services, Ltd. (formally Tricil, Ltd.). The site is in the St. Clair Clay Plain which covers an area of 5900 km² and extends from Sarnia to the Windsor/Detroit area. It consists of natural water-lain till and glaciolacustrine deposits 40 to 50 m thick (McKay, et al., 1993a). Approximately 25-40% of the till is clay-sized particles, including illite and chlorite, the remainder consisting of silt and sand-sized materials with less than 5% gravel.

The Sarnia site has been well characterized, including descriptions of the fracture network and experimental measurement of diffusion. Diffusion in the fractured clay has been studied by several researchers (Desaulniers, et al., 1981; Crooks and Quigley, 1984; Johnson, et al., 1989; and Myrand, et al., 1992), and the fracture network was characterized by McKay, et al., (1993a and 1993b). The fractures are a result of desiccation and have an effective hydraulic aperture between 10 and 100 μ m, with fracture spacings of a few centimeters at the surface to more than a meter at a depth of 4 m (McKay, et al., 1993a).

The clay deposit has two till zones, the upper zone extends down 6 m and is visibly weathered and fractured with a hydraulic conductivity of 10^{-9} to 10^{-7} m/s, while the lower zone is unweathered and unfractured and has a lower hydraulic conductivity (10^{-11} to 10^{-10} m/s) (Harris, 1994). The groundwater movement in the lower zone is dominated by diffusion, whereas groundwater movement in the upper zone occurs more rapidly due to advective flow in the fractures. The vertical hydraulic gradients in the upper zone are usually unpredictable (McKay, et al., 1993a), because the water table fluctuates from ground surface to a depth of ~2 m. Large fluctuations in the water table occur after most rain events because the clay matrix between the fractures is essentially always saturated due to capillary effects and thus only the fractures are affected by the infiltrating rainwater. Groundwater velocity in the unweathered zone is generally slow (<1 cm/yr) due to the low hydraulic conductivity. However, the hydraulic conductivity

in the weathered zone can be 3 to 4 orders of magnitude higher with lateral groundwater velocities up to 25 m/day (under a horizontal gradient of 0.24), depending on aperture size (McKay, et al., 1993a).

EXPERIMENTAL SET-UP

Cell Construction

The experimental facility is in an open field used in recent years for agriculture. The study area is a 10 by 10 m experimental cell constructed by driving sealable sheetpiles to a depth of ~5 m (Figure 2.3). In 1992 a temporary impermeable surface cover was created within the cell by smoothing the ground surface and covering it with a thin layer of bentonite clay followed by 0.25 mm plastic sheeting and finally by 15 cm of sand. At the end of the 1992 field season a wooden deck was constructed over the experimental cell to exclude rain and snow. After installation of a soil vapor extraction (SVE) system in 1993, the bentonite-plastic cover was removed and replaced with a 10 cm thick concrete cover.

LNAPL Release Description

Fifty liters (40.6 kg) of a synthetic "gasoline" mixture containing gasoline range organics (GRO) and a few compounds of special interest was spilled at the field site in September, 1992 (Table 2.1). The spill mixture included both high solubility (methyl-tert-butyl-ether (MTBE)) and low solubility (isooctane) constituents. Pentane was used to provide a "light end" fraction and naphthalene was added to represent a higher molecular weight gasoline constituent. Trichloroethylene (TCE) was added to provide a semi-volatile component that does not easily biodegrade aerobically but has similar physical characteristics to the other components.

The chemicals were injected 60 cm below ground surface using a constant head reservoir placed 2 m above the release point (Figure 2.4). The spill mixture was left

undisturbed in the ground for approximately ten months to allow for dissolution and partitioning of the gasoline compounds between the matrix and the fractures. During the 10 month period it was expected that some of the more soluble components would diffuse out of the fractures into the clay matrix, while the less soluble components would remain in the fractures.

Well Construction

In 1992, three wells used for pneumatic pumping and effective porosity tracer experiments (P1, P2, and P3) were hand augured to a depth of 0.6 to 0.7 m (see Figure 2.5 for locations). D'Astous, et al., (1989), demonstrated that auguring tended to form a smear zone, thereby closing many of the fractures. To prevent this the smear zone caused by the auguring process was removed by carefully scraping the well walls to expose fractures and other features. The final diameter of each well was ~25 cm. A capped section of 2.5 cm slotted PVC pipe was then installed in the hole. The well slots extended to within ~15 cm of ground surface (Figure 2.6). The hole was backfilled with quartz sand to within 10 cm of ground surface. Above the sand pack the hole was carefully sealed with bentonite. Once the pumping and tracer experiments were completed, the wells were removed and the well holes sealed before placing the bentonite-plastic surface cover.

Monitoring wells previously installed inside and outside the cell were used to record water levels. Water level data stored on a data logger (Terra, Ltd.) indicated that the water table prior to the 1993 field season had fluctuated between ground surface and ~2 m below ground surface.

At the beginning of the 1993 field season, 5 cm-diameter cores were collected to depths of 1 and 1.5 meters (3 and 5 ft) to characterize the distribution of the gasoline within the cell (see Figure 2.7 for locations and Figure 2.8 for well construction). These holes created by the coring were used to install vapor monitoring wells (V-wells) and air sparging wells (AS-wells) once the smear zone had been carefully removed. Five vapor monitoring wells were installed in the 1-m core holes, while seven air sparging well were

installed in the 1.5-m core holes. Each well consisted of a 2.5 cm O.D. stainless steel tube with a section of geotextile sock wired to the bottom. Approximately 15 cm of quartz sand was placed in the bottom of the hole and the tube inserted. Another ~15 cm of sand was added once the tube was in place. This design eliminates the need for conventional slotted well screen, since the pressure is distributed throughout the sand pack. The remainder of the hole was filled with bentonite to ground level.

When the concrete cover was poured, sections of 2-inch PVC pipes were placed through out the cell (designated as C-wells, see Figure 2.7 for locations). These were placed to provide an easier method of installing future wells through the concrete cover. At one of these core holes (C-15) eight thermocouples were installed at 30 cm intervals from 0.1 to 2.2 m below ground surface. The thermocouples were connected to the Terra data logger. In addition, four pressure-monitoring points were installed (C-2, C-9, C-14 and C-20) roughly 60 cm below ground surface. Pressure measurements were taken periodically with a magnehelic gauge to indicate the vacuum generated by the SVE system across the cell.

Soil Core Collection and Analysis

Prior to remediation activities soil samples were collected (well locations V-1 to V-7 and AS-1 to AS-5, see Figure 2.7). These samples were collected at 30 cm (1 foot) intervals using a jackhammer to drive 30 cm long by 5 cm O.D. stainless steel tubes into the soil. The cores were sampled immediately upon removal from the ground by first removing the bottom few centimeters of soil and then collecting a sample directly into 40-mL glass vials partially filled with methanol. The samples were then sealed and stored in the dark at 4°C until they were transported by hand to the analytical laboratory (Kemron Environmental Services, Ltd., Marietta, Ohio). Methanol extracts from the soil samples were analyzed by gas chromatography and the results were reported as gasoline range organics (GROs).

RESULTS AND DISCUSSION

Air Permeability

Three wells (P1, P2, and P3; see Figure 2.5 for locations) described above were used to determine air permeability. Individual pumping tests were conducted at each well. To conduct each test, the pumping flow rate was adjusted until the pressure at the test well was 0.500 atm below atmospheric. The flow was then measured by a rotameter, and the actual flow was calculated by adjusting for the reduced pressure at the wellhead. Once steady state conditions had been achieved, pressure drawdown was measured at the other two wells.

As seen in Table 2.2, the pneumatic pumping test flows at the test well were generally in the range of 2 scfm. Pressures at the other two wells were on the order of "0.003 atm" compared to "0.500 atm" vacuum at the test well. The effective permeability of air through the fractured clay was calculated using an in-situ air permeability test protocol developed for the U.S. Air Force (Hinchee, et al., 1992). The protocol recommends the following equation for estimating air permeability:

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

where: k_a = air permeability (m^2)

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_l = 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 from Equation 1 ranged from 10^{-15} to 10^{-16} m^2 , with an average value of $\sim 5 \times 10^{-16} \text{ m}^2$. Another method for calculating the air permeability (k_a) uses the "cubic law" (Freeze and Cherry, 1979),

$$k_a = \frac{b^3}{12 * B} \quad (2)$$

where b is the fracture aperture and B is the spacing between fractures. Table 2.3 shows the range of air permeability values calculated using a range of fracture aperture and spacing values. The value of k_a for 10 μ m fractures on 10 cm spacings, $8.3 \times 10^{-16} \text{ m}^2$, is close to the value of air permeability estimated from equation 1 ($5 \times 10^{-16} \text{ m}^2$).

Reported values of permeability in glacial tills range between 10^{-18} and 10^{-14} m^2 (Freeze and Cherry, 1979). The permeability values determined at the Sarnia site fall within this range, suggesting that these values may be representative of other glacial tills. The hydraulic conductivity of the till was calculated using,

$$K = \frac{k \rho g}{\mu} \quad (3)$$

where: K = hydraulic conductivity, m/s

k = permeability, m^2

ρ = density of water, 10^3 kg/m^3

g = gravity, 9.81 m/s^2

μ = viscosity of water, 10^{-3} kg/m-s .

Using Equation 3, a hydraulic conductivity of $5 \times 10^{-9} \text{ m/s}$ was calculated, which is on the same order of magnitude as field measurements (10^{-9} to 10^{-8} m/s , (Harris, 1994)). Therefore, it is anticipated that remediation technologies that use water flushing or air flushing will be less effective in these tight soils than in sandy or silty soils which have higher permeabilities.

Effective Porosity

The wells used for the pneumatic tests (P1, P2, and P3) were also used to determine the effective porosity (see Figure 2.5 for locations). In these tests a tracer was introduced at one well while air was extracted from another. The volume of air required

to move the tracer to the extraction well was used to calculate effective porosity. Sulfurhexafluoride (SF_6) was used as the tracer gas since it is transported and dispersed like other atmospheric gases, and it is non-toxic and chemically inert. The extracted air was pumped directly to a GC for analysis. The flow rate at the pumped well ranged from 1.5 to 2 Lpm. Four pumping tracer experiments were conducted: 1) from well P2 to well P1; 2) from well P3 to well P1; 3) from well P1 to well P3; and 4) from well P3 to well P2.

The effective air porosity of the fractured clay was estimated using a volumetric calculation. First, the volume of soil contained within a cylinder whose center is at the extraction well and whose perimeter is at the injection well was calculated (Figure 2.9). Second, the extraction volume necessary for tracer breakthrough was determined from the experimental data. Making the assumption that the tracer velocity was uniform over the depth of the cylinder, the effective porosity is simply the ratio of the extraction volume to the cylinder volume.

Figure 2.10 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 inflection point on the breakthrough curve, which occurs at 50% of the maximum concentration, is used to determine the breakthrough volume. However, because of the large reservoir of SF_6 which remains in the injection well, the inflection points are often difficult to determine and therefore were not used. The units on the vertical axis relate to concentration, but since the extracted air volume (i.e., the horizontal axis) was the only measurement used in the calculations arbitrary unit for the y-axis were used. Table 2.4 gives the cylinder radii, cylinder volumes, extraction volumes and effective air porosities for the four tracer tests. The effective porosity values range from 0.001 to 0.006. These values are within an order of magnitude suggesting an effective air porosity of <0.01 , which is a reasonable value given the heterogeneous and anisotropic fractured clay.

Another estimate of effective porosity can be made using fracture spacing and fracture apertures. The zone of concern in this study was within the top 2 m of the

surface (based on water table data), therefore a range of 10 to 20 cm for fracture spacings and 20 to 40 μm for aperture size are reasonable (McKay, et al., 1993a). The effective porosity can then be estimated by dividing aperture size by fracture spacing. This results in an effective porosity in the range of 0.001 to 0.004. These values are similar to the values determined from the pumping tests, 0.001 to 0.006. Values of fracture porosities (effective porosities) determined at the Sarnia site (McKay, et al., 1993a) indicate that porosities decrease exponentially with depth. McKay measured values of $\sim 10^{-3}$ at a depth of 1.6 m and $\sim 10^{-5}$ at 4.8 m. Therefore, an estimated effective porosity between 10^{-3} and 6×10^{-3} at a depth of ~ 1 m is within the expected range.

Water Level and Soil Temperature

Water level and soil temperature were continuously monitored prior to the soil vapor extraction experiments. Figure 2.11 shows water depth data from the time of the spill in 1992 until the end of the first seasons remediation activities. Precipitation was not measured at the site prior to remediation. The data indicate that the water table fluctuated between ground surface to ~ 0.8 m below ground surface.

Figure 2.12 shows soil temperature data during the 1993 remediation period as a function of depth. The data indicates the influence of atmospheric temperatures on the top of the soil profile which varied from approximately 24°C in August to 14°C in October. In contrast the lower soil profile temperatures varied only by about 2°C , indicating little atmospheric temperature effects below 2 m depth.

Initial Distribution of the Spill

In July 1993 (i.e., ~ 300 days after release) soil samples were taken at 30 cm vertical intervals at 12 locations to determine the distribution of the hydrocarbons within the soils (core hole locations marked by V and AS wells, Figure 2.7). Based on analysis of the soil cores, the spill extended in a slightly elliptical pattern over a 5 by 6 m area and vertically approximately 1.2 m, suggesting that hydrocarbons were contained within

approximately 25 m³ of soil. Figures 2.13 to 2.16 show the soil concentration contours at the sample intervals. Given the total gasoline spill of 50 L, the average residual gasoline saturation was on the order of 2 L/m³. This residual saturation is significantly smaller than most reported values (e.g., Cohen and Mercer, 1992). This is also consistent with the measured low effective porosity values between 0.001 and 0.006 measured at the site. Given this small residual saturation and low effective porosity, it is clear that even small spills can occupy relatively large soil volumes. For example, a 500 L release in a till with an effective porosity of 0.001, could result in 500 m³ of soil being contaminated or a residual saturation of 1 L/m³.

Based on these soil concentration data and integrating over the volume of the zone of contaminated soil, approximately 13.1 kg or 32% of the mass spilled could be accounted for. Given the density of the sampling grid, it is unlikely that significant quantities of hydrocarbons migrated out of the sample region. However, it is possible that under-estimation of the mass resulted from several potential sources of error in the sampling process. One possible source of error may be because the fractures are primarily vertical, as was the coring process. Therefore, the small (5 cm diameter) cores may not have sampled a representative number of fractures. Given what is known about air and water flow in the till, it is also likely that the mass was not uniformly distributed within the till. Finally, compaction during could also have forced NAPL out of the fractures during the coring process. Another possibility for the "missing" mass is biodegradation, this was investigated and the results are presented in Chapter 3.

Phase Distribution of the Spill

Gasoline released into the subsurface will initially move through the fractures. It can dissolve in the water and move into the soil matrix where it will be more difficult to remediate. Therefore, it is important to know the fraction of gasoline remaining as NAPL in the fractures since this is the mass most readily accessible to a SVE air flow system. Assuming equilibrium partitioning between the NAPL, soil, and water phases, the percent of each gasoline component remaining in the fractures can be estimated based on the

mixture solubility of each component and the characteristics of the soil.

A multi-component, one-dimensional, explicit finite difference numerical diffusion model was used to track the movement of the gasoline from the fractures into the matrix. The following diffusion equation was used,

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} \quad (4)$$

where: $\delta C/\delta t$ = change in concentration with time ($M/L^3/T$)

D = apparent diffusion coefficient (L^2/T)

$\delta^2 C/\delta x^2$ = change in concentration gradient ($M/L^3/L^2$).

The model simultaneously tracks the 15 components in the spill and accounts for dissolution out of the fracture, diffusion in the matrix, and sorption to the soil. To account for dissolution of the NAPL out of the fractures, solubilities based on the mole fractions of each component were used and updated every time step as the mole fractions changed. Partitioning between the water and soil is assumed to be an equilibrium process that follows a linear Freundlich isotherm. Diffusion coefficients were calculated from molecular weights and densities of the individual components, (Johnson, et al., 1989; Wilke and Chang, 1955),

$$\frac{D_1}{D_2} = \left(\frac{MW_2 \rho_1}{MW_1 \rho_2} \right)^{0.6} \quad (5)$$

where: D = free-solution diffusion coefficients of compound 1 and 2

MW = molecular weights of compound 1 and 2

ρ = densities of the compound 1 and 2 at their boiling points.

Individual component diffusion coefficients were calculated using an observed benzene diffusion coefficient 2×10^{-7} cm²/sec, as determined at the Sarnia site by Johnson, et al., (1989). The base case for these simulations used the parameters listed in Table 2.5.

Chapter 4 contains a detailed description of the numerical model.

Figure 2.17 shows the percent of each component in the fractures that was calculated to be in the NAPL phase at the onset of remediation (~10 months or 300 days). Water at the fracture/matrix interface was assumed to be saturated with each compound in the mixture. The model indicates that the more soluble components (MTBE, TCE, benzene and toluene) disappear fairly quickly into the soil matrix with <25% remaining in the fractures. Compounds that are less soluble (heptane and isooctane) persist in the fractures for longer periods. The percent of initial mass remaining in the fractures as a function of time for several spill components are shown in Figures 2.18 and 2.19.

Even though many assumptions are inherent in these calculations, it is evident that a lower percentage (mass-based) of less-soluble compounds moved into the matrix than more soluble compounds. It is important to recognize that as the residual saturation decreases (i.e., fractures become farther apart or the initial mass of NAPL in the fractures is less) the percent of mass remaining as NAPL also decreases. Even though the NAPL may move into the matrix relatively quickly, the reverse diffusion of mass from the matrix into the fracture will be substantially slower due to the smaller concentration gradient in the matrix. Therefore, the matrix can act as a long term source of contamination to an underlying aquifer, as the contaminant diffuses back into the fractures and is leached downward. Also, the amount of time between the spill and the start of remediation will affect the amount of NAPL remaining in the fractures. Figure 2.20 indicates that 1000 days after the spill (with no remediation), >80% of the BTEX mass had moved into the matrix, while the least-soluble compounds isooctane (90%) and heptane (84%) remained largely in the fractures. This implies that if delayed, remediation of the BTEX compounds via the fractures will become less effective with time. A discussion of the role of sorption and the diffusive flux into and out of the matrix is presented in Chapter 4. Also contained in Chapter 4 are the effects of remediation on the movement of contaminant into and out of the matrix.

CONCLUSIONS

In September 1992, fifty liters (40.6 kg) of a synthetic gasoline mixture were released 0.6 m into a clay till. The naturally deposited clay till is characterized by fracture apertures of 10 to 100 μm at fracture spacings of a few centimeters in the upper till zone (McKay, et al., 1993a), which contains the spill. The experimental cell used for this project consists of a 10 x 10 m sealable sheetpile wall with various wells and monitoring points throughout the cell.

Air permeabilities determined using pneumatic pumping field tests and the cubic law agreed well and gave values of approximately 10^{-16} m^2 . These values are many orders of magnitude greater than the permeability of the unfractured clay matrix, indicating that the air movement (also water and NAPL movement) will occur in the fractures. Based on pumping tracer tests the effective air porosity of the clay was determined to be <0.01 , which is on the same order of magnitude as the effective porosity calculated using fracture spacing and fracture aperture size.

Using the estimated range of effective porosity it was determined that 12.5 to 50 m^3 of soil could be contaminated by the 50 L spill. Coring prior to remediation indicated that the spill contaminated a 5 by 6 m elliptical area of soil to a maximum depth of 1.2 m, which is equivalent to 25 m^3 of soil being contaminated. This translates into an average residual gasoline saturation of 2 L/m^3 . The low residual saturation is due to the small effective porosity of the till (i.e., <0.01). The small effective porosity caused the initial release of gasoline to spread laterally. In addition, because of the low effective porosity of the till, relatively small amounts of water cause large water level changes. As a result, during the ten months between the release and the initiation of SVE, the NAPL probably was smeared vertically.

The soil core data accounted for $\sim 32\%$ of the spilled mass. Some portion of the missing mass may be due to sampling difficulties and some may be due to biodegradation. A complete mass balance analysis is presented in Chapter 3.

The diffusion model indicates that the more soluble compounds could have largely moved from the fractures into the matrix ($>75\%$), while the less soluble compounds

would largely remain in the fractures. As a consequence, mass removal by fluid flushing in the fractures may be limited by diffusion from the matrix. This will be examined in the following chapters.

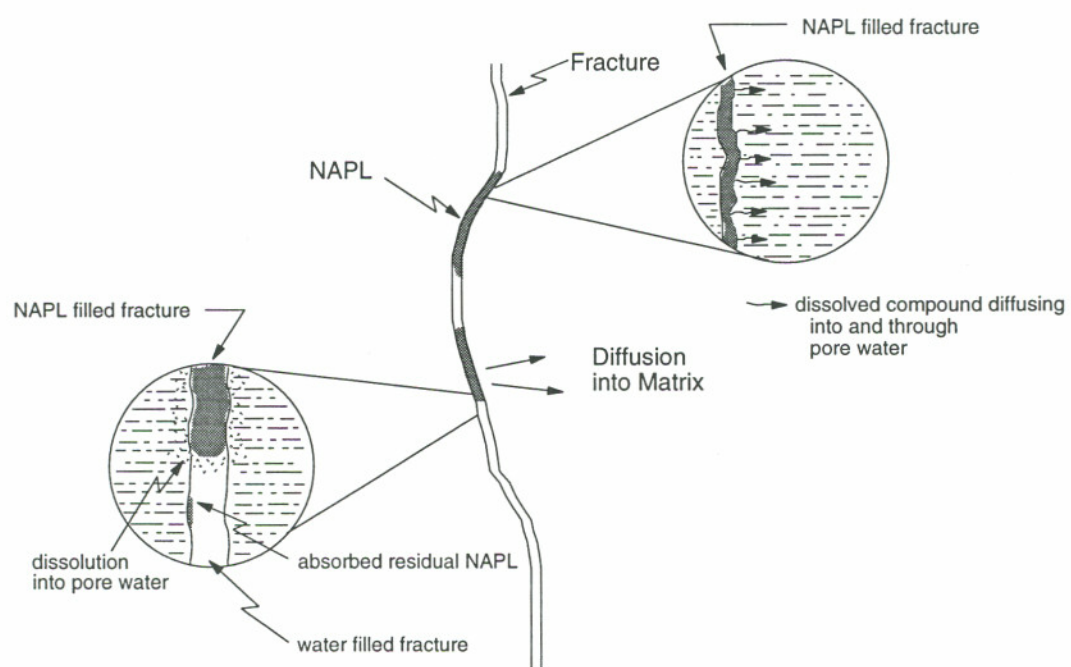


Figure 2.1. Schematic drawing of dissolution and diffusion from a fracture into a clay matrix.

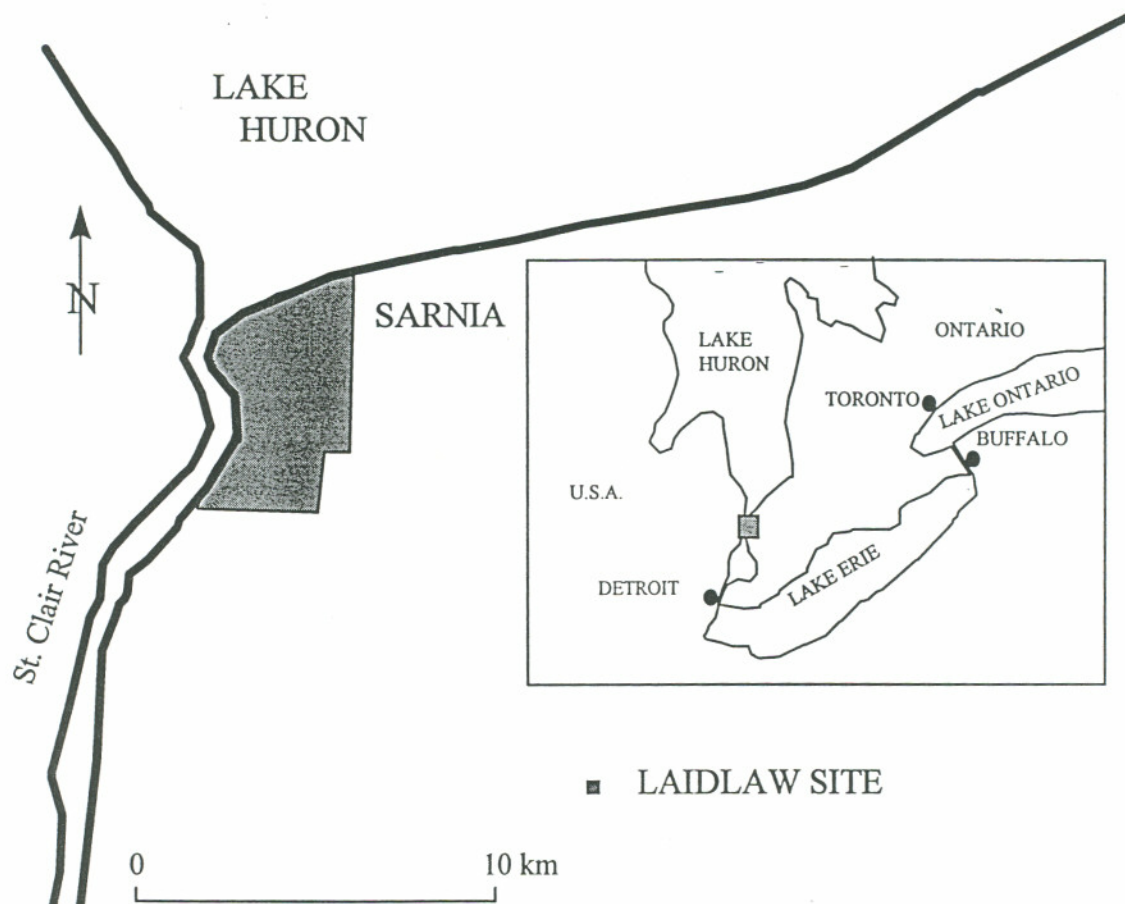


Figure 2.2. Location of the study site.

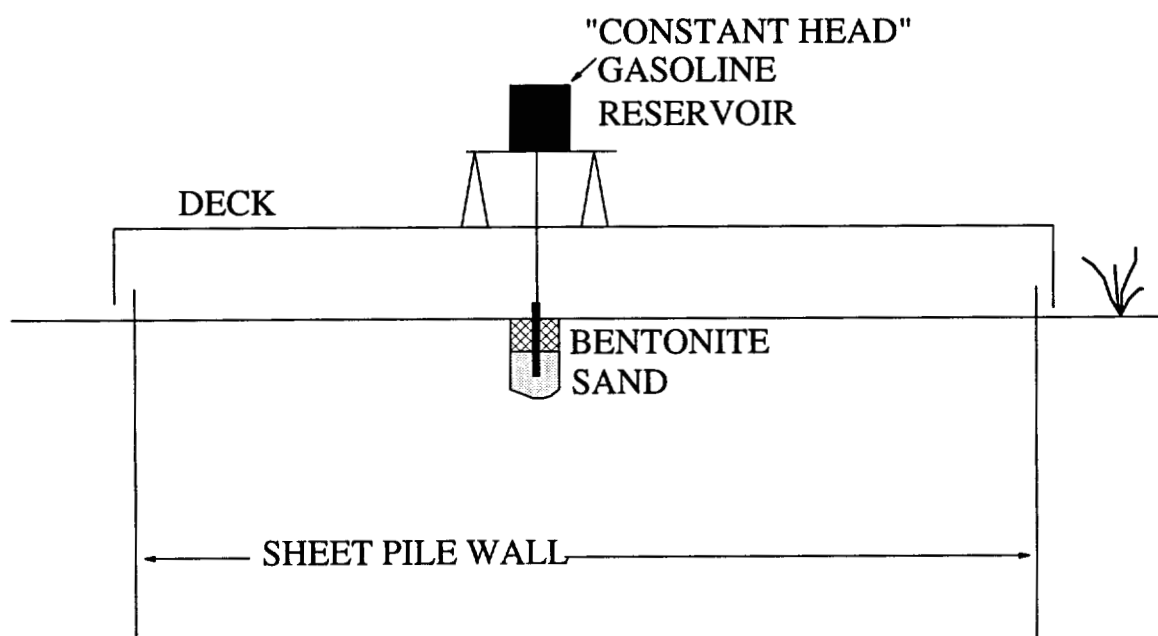


Figure 2.4. Schematic section view of the release of gasoline into the experimental cell.

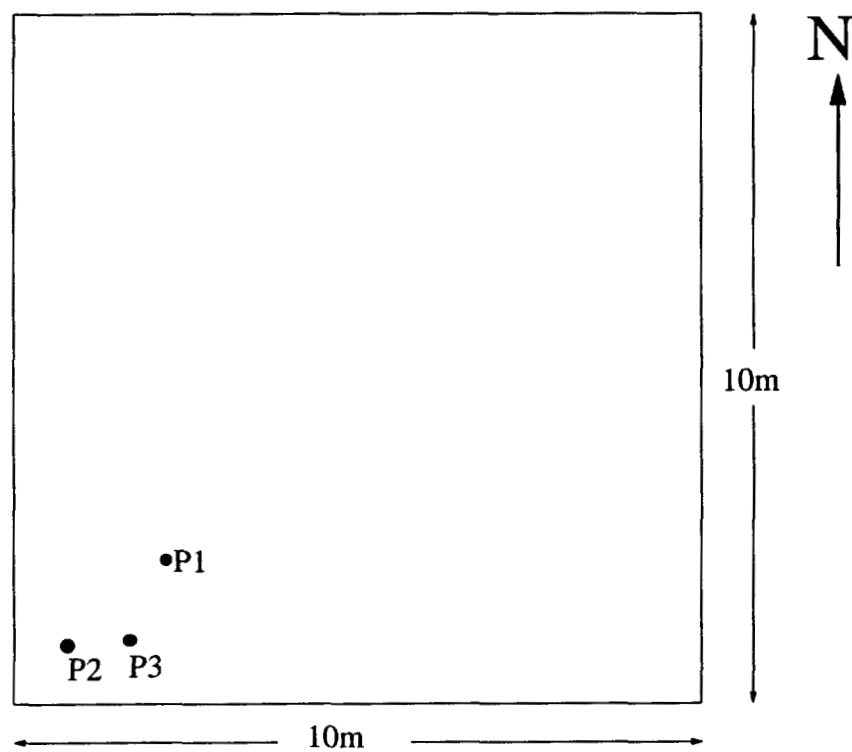


Figure 2.5. Plan view of the test cell showing the location of the pumping wells.

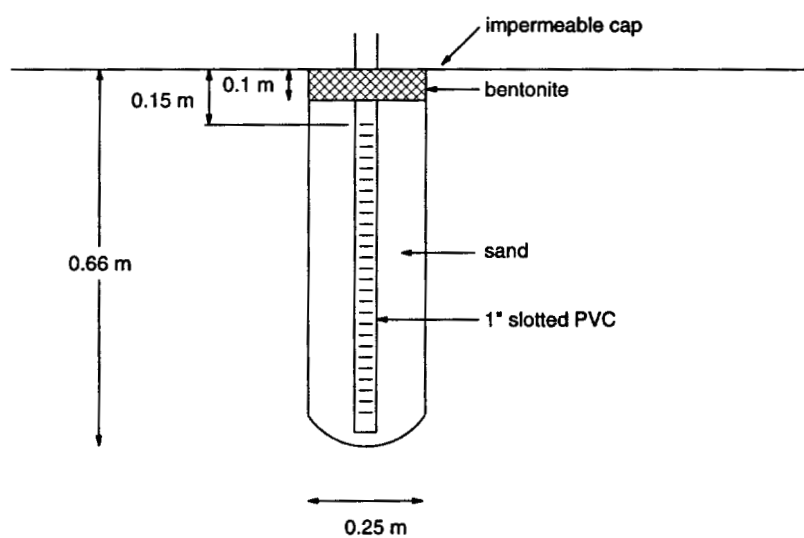


Figure 2.6. Schematic drawing showing the design of the air flow test wells (P1, P2 and P3).

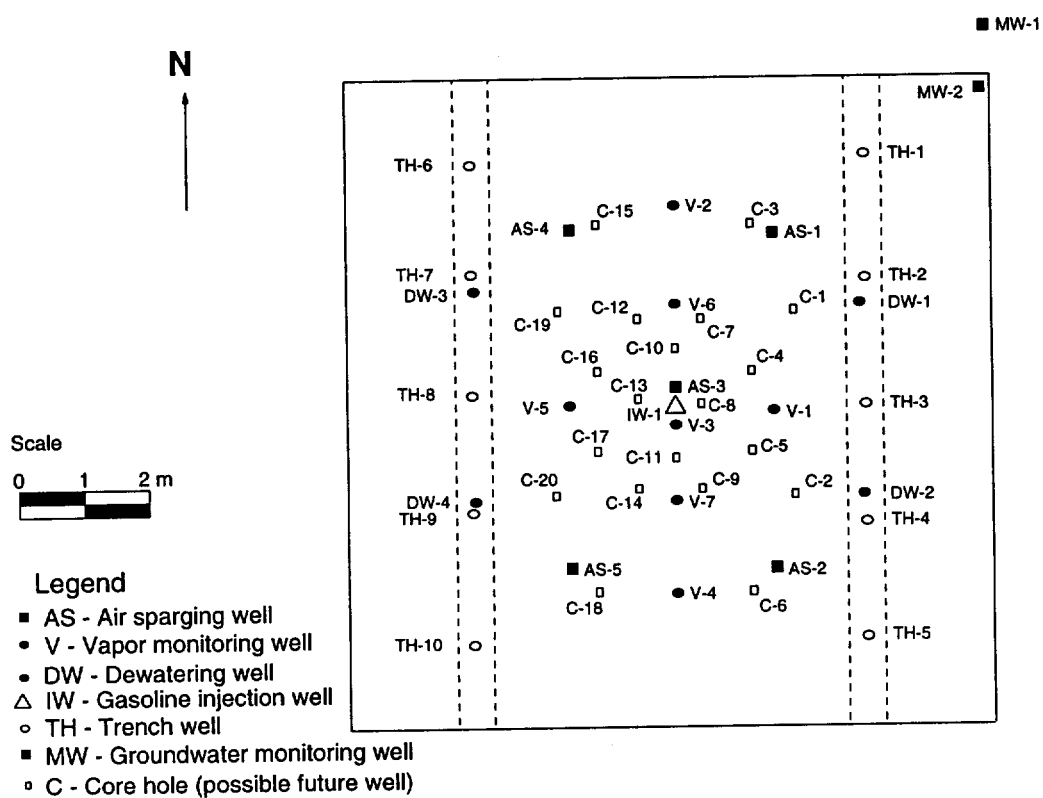


Figure 2.7. Plan view of the cell showing the locations of the soil cores and wells.

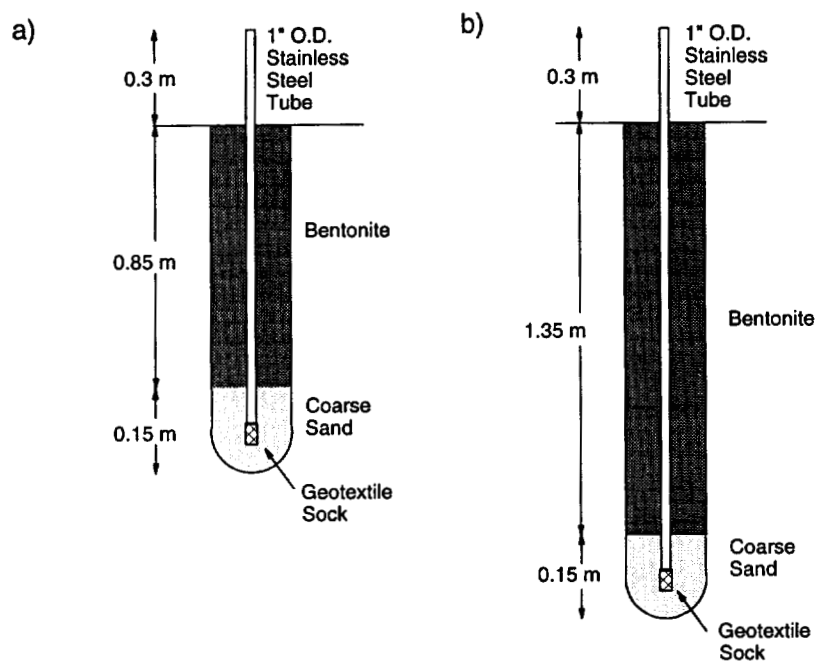


Figure 2.8. Schematic "as built" diagrams for the vapor monitoring and sparge points.

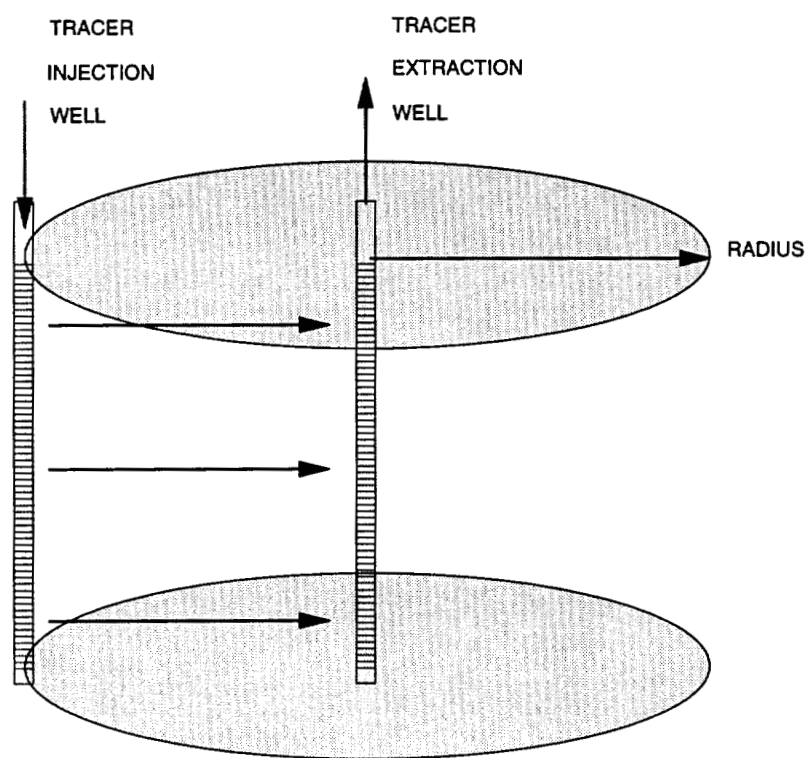


Figure 2.9. Conceptual drawing of the cylinder used for calculating effective porosity from the pumping tracer tests.

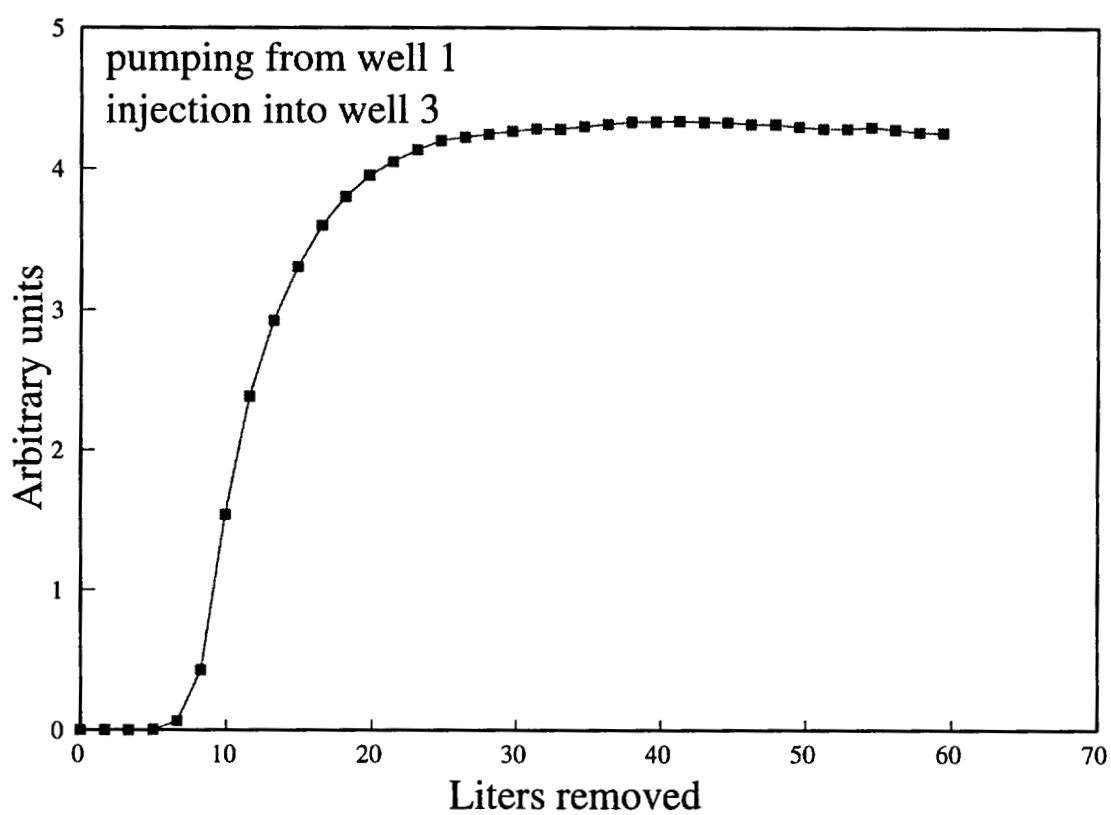


Figure 2.10. Tracer recovery as a function of volume for the test P3 to P1.

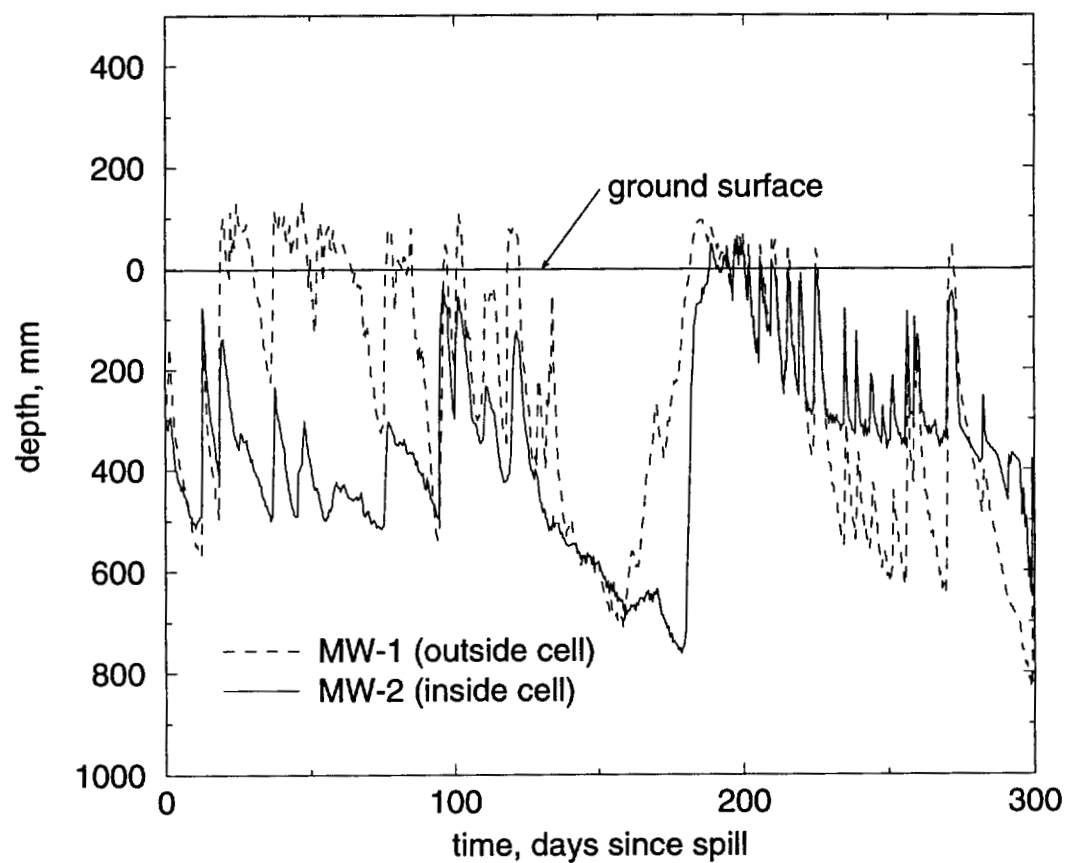


Figure 2.11. Water table depths measured inside and outside the cell for the time of release to the initiation of remediation (~10 months).

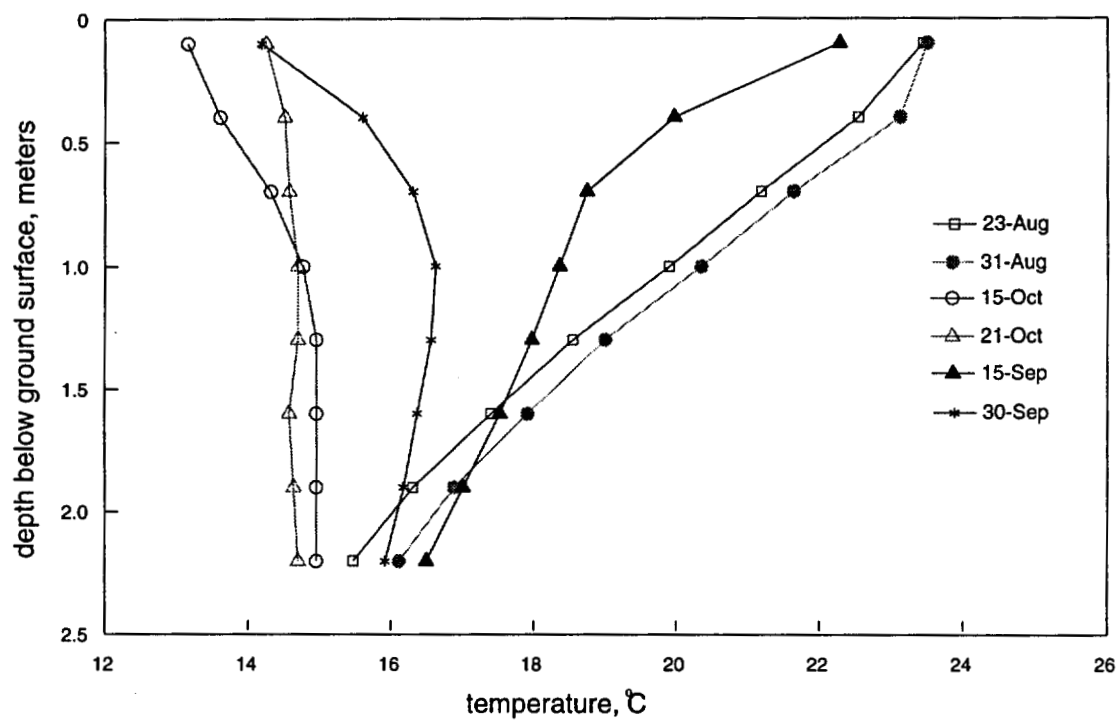


Figure 2.12 Soil temperature profiles during the period of active remediation (Aug-Oct, 1993).

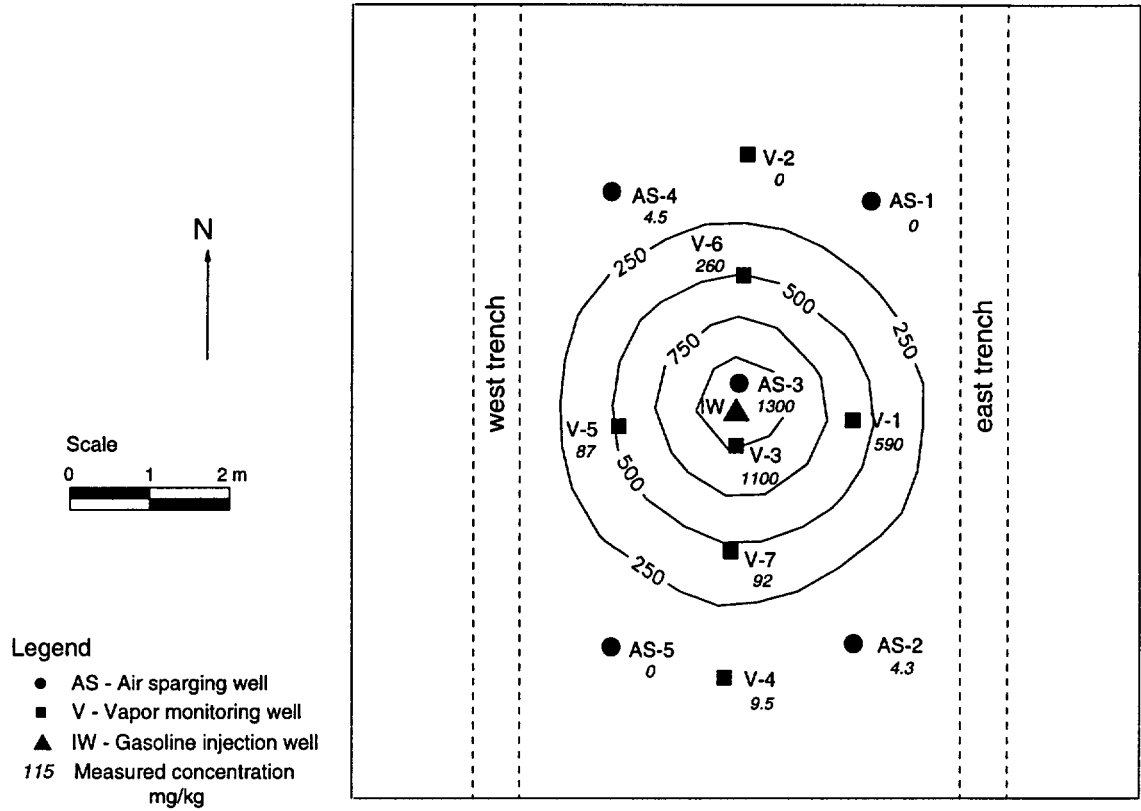


Figure 2.13. Pre-remediation hydrocarbon concentrations (mg/kg) at the 30 cm depth.

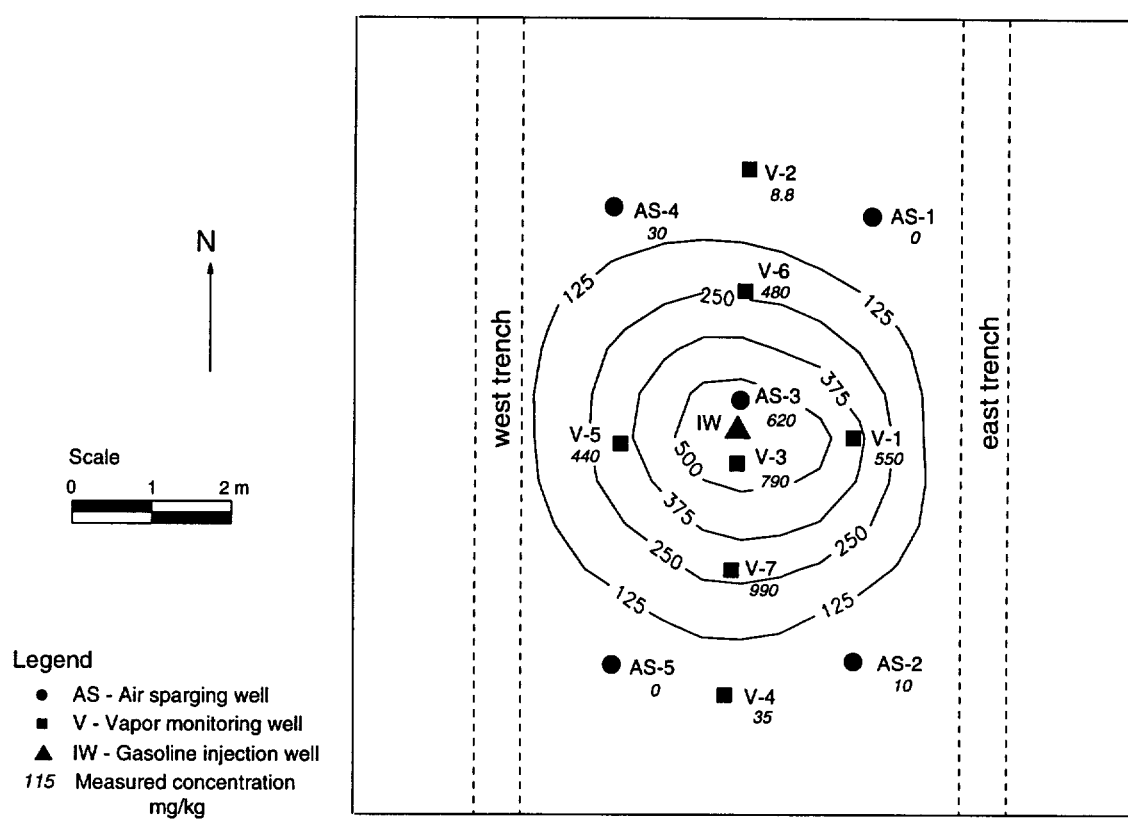


Figure 2.14. Pre-remediation hydrocarbon concentrations (mg/kg) at the 60 cm depth.

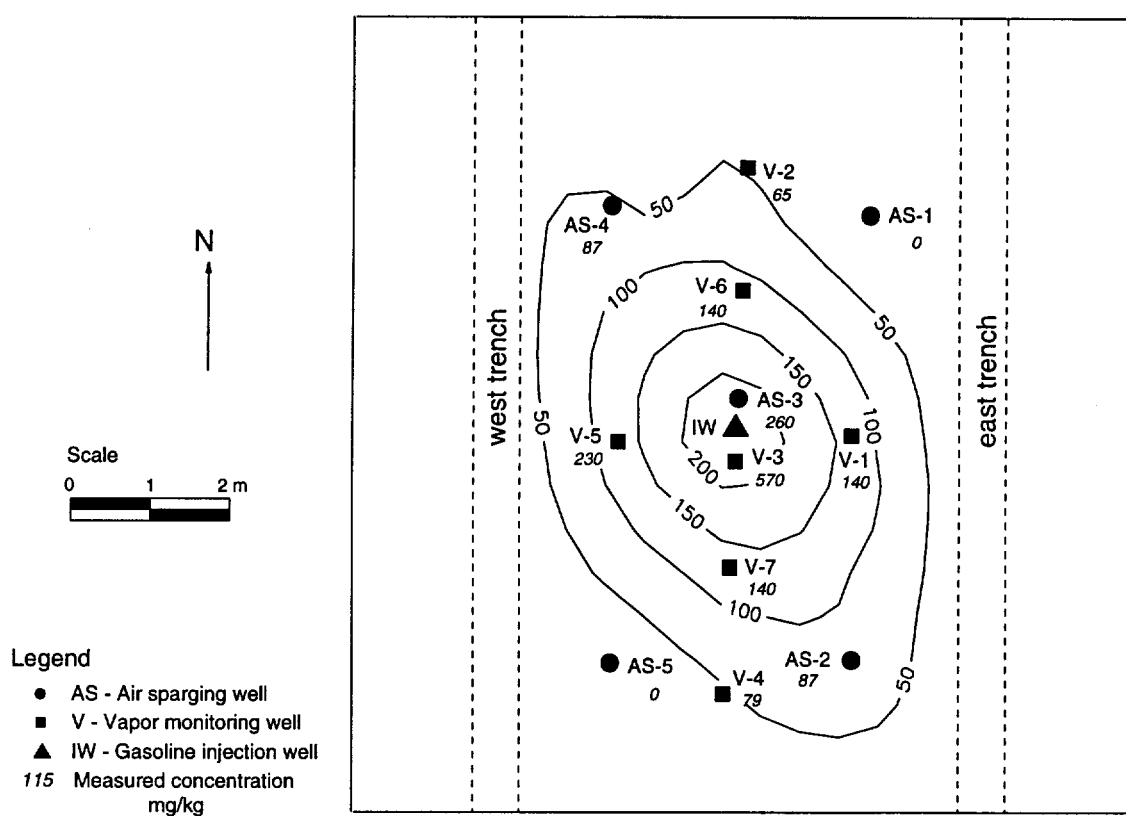


Figure 2.15. Pre-remediation hydrocarbon concentrations (mg/kg) at the 90 cm depth.

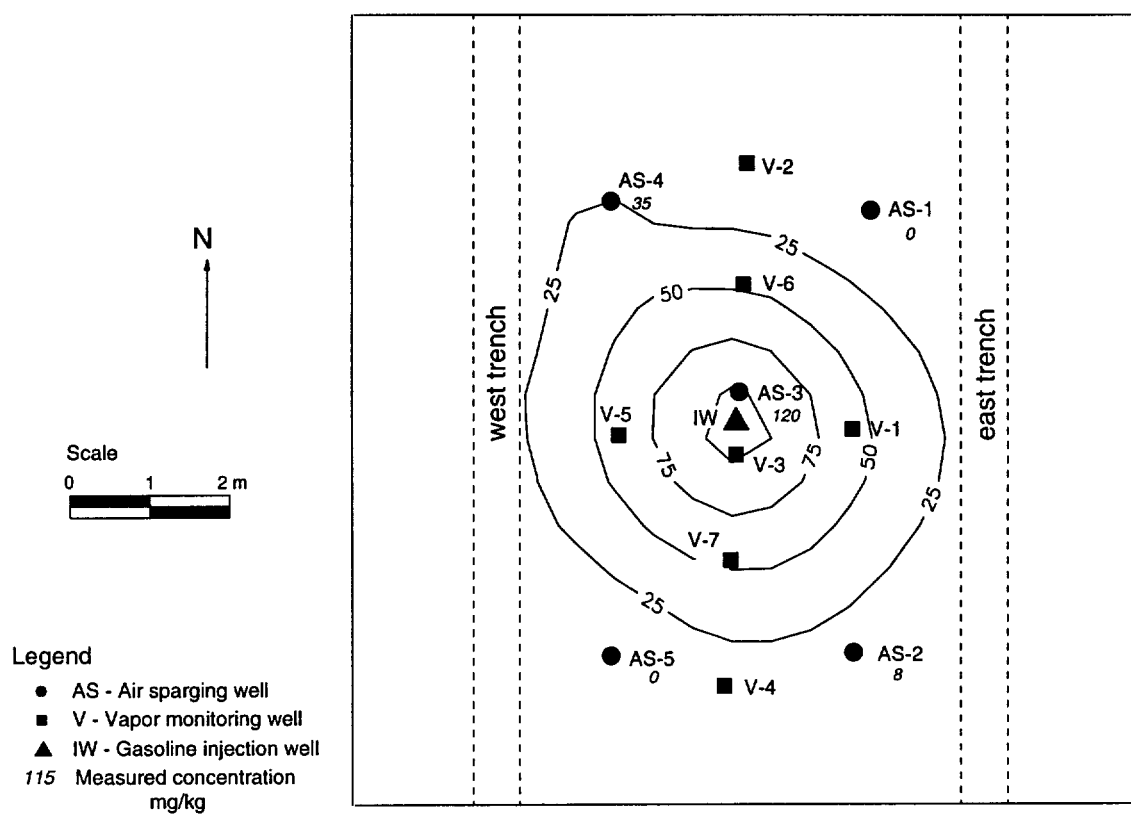


Figure 2.16. Pre-remediation hydrocarbon concentrations (mg/kg) at the 120 cm depth.

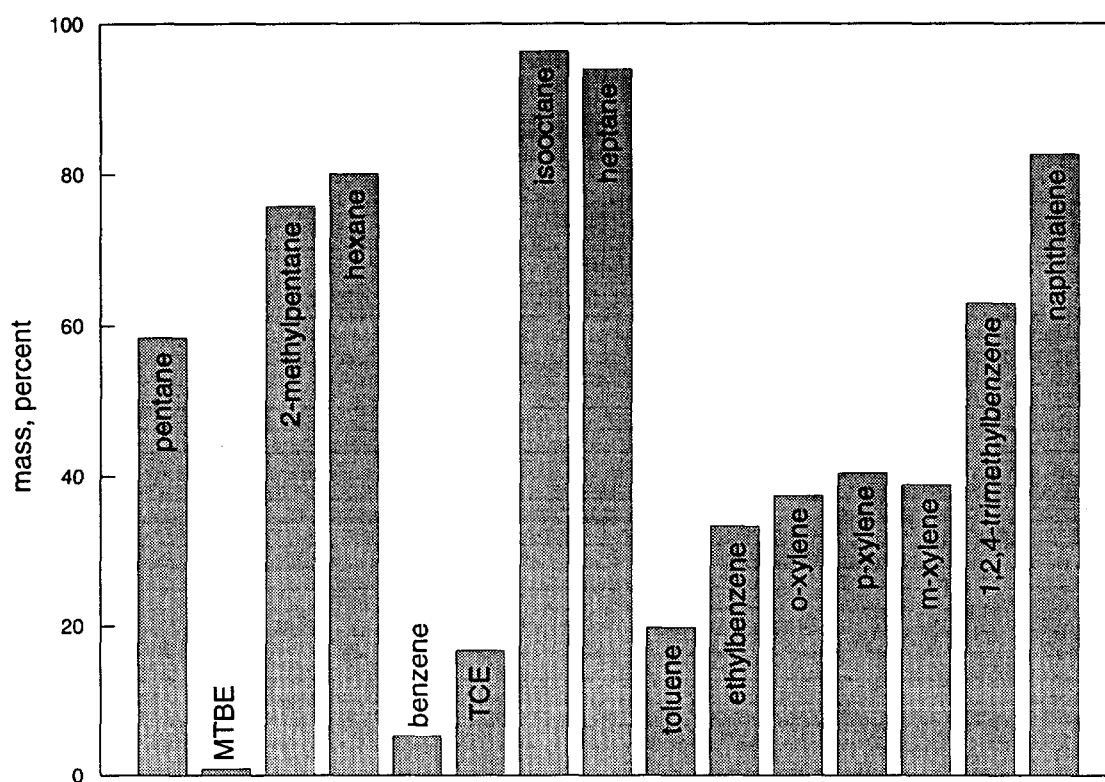


Figure 2.17. Estimated percent of initial mass remaining in the fractures 300 days after the spill and prior to remediation for the base case numerical diffusion model.

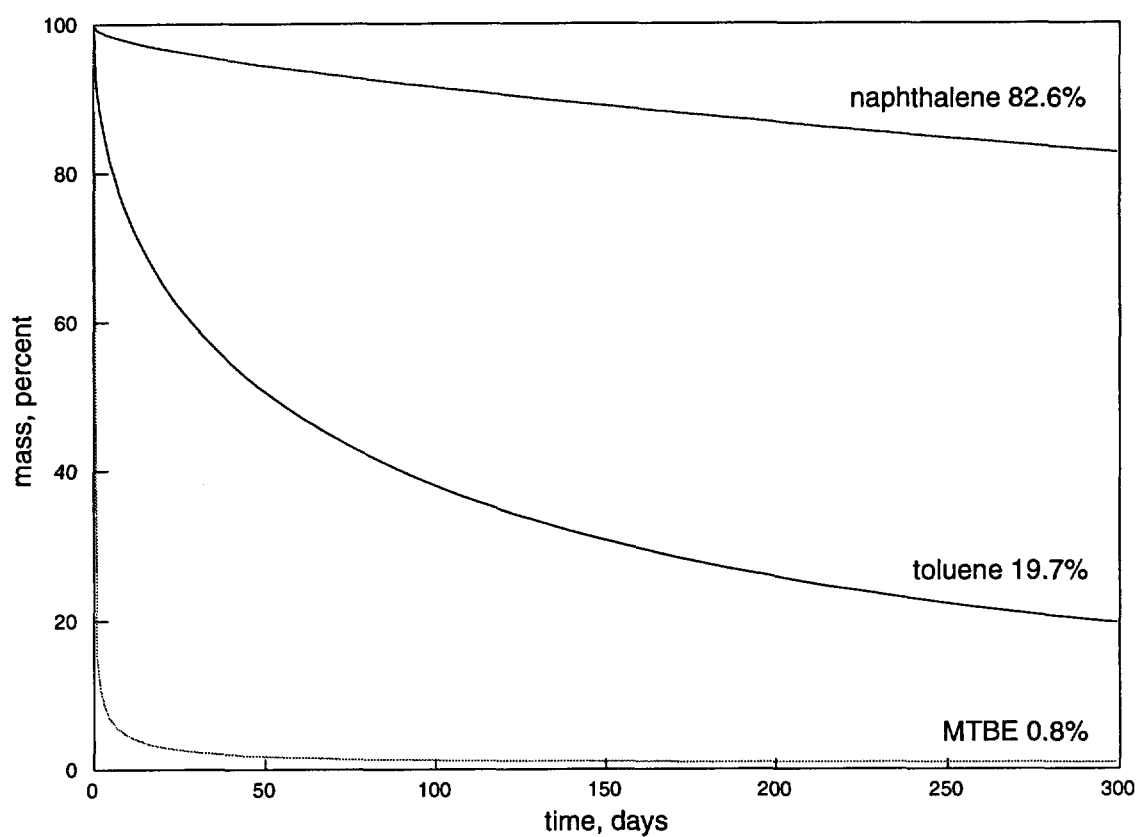


Figure 2.18. Estimated percent of initial mass remaining in the fractures as a function of time for the base case numerical diffusion model (MTBE, toluene and naphthalene).

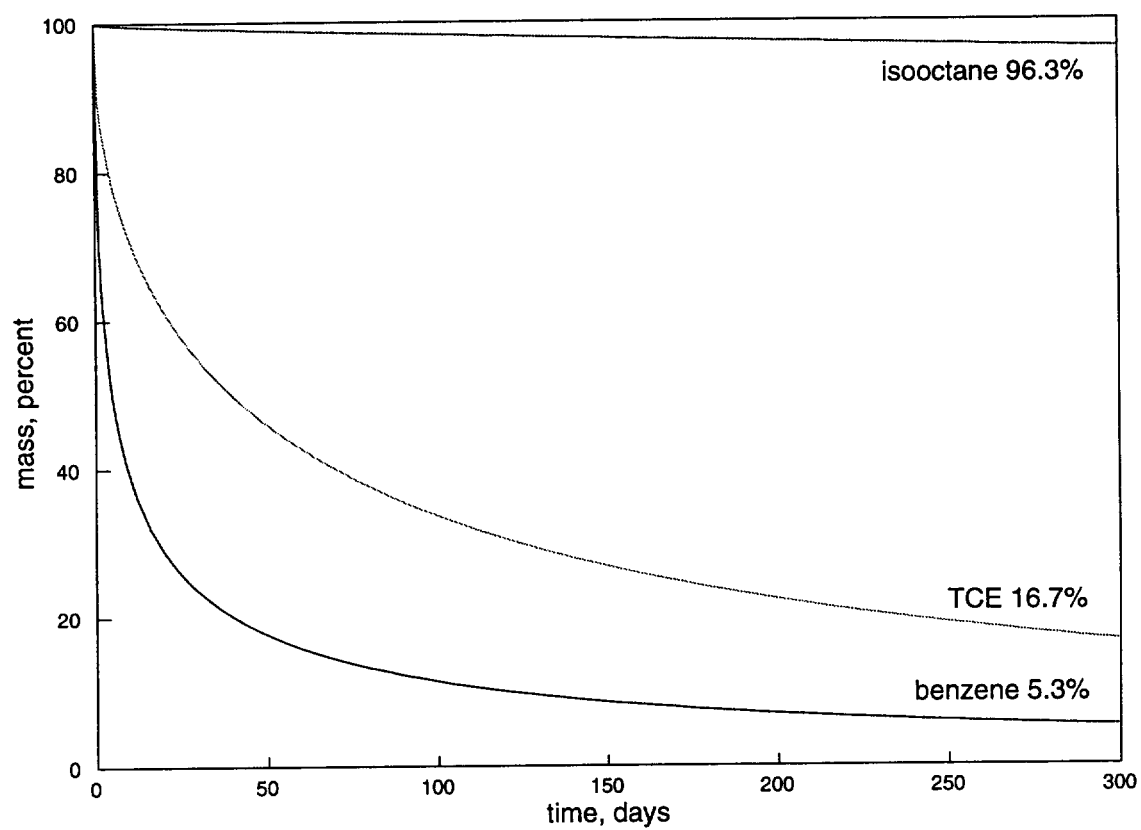


Figure 2.19. Estimated percent of initial mass remaining in the fractures as a function of time for the base case numerical diffusion model (isooctane, TCE and benzene).

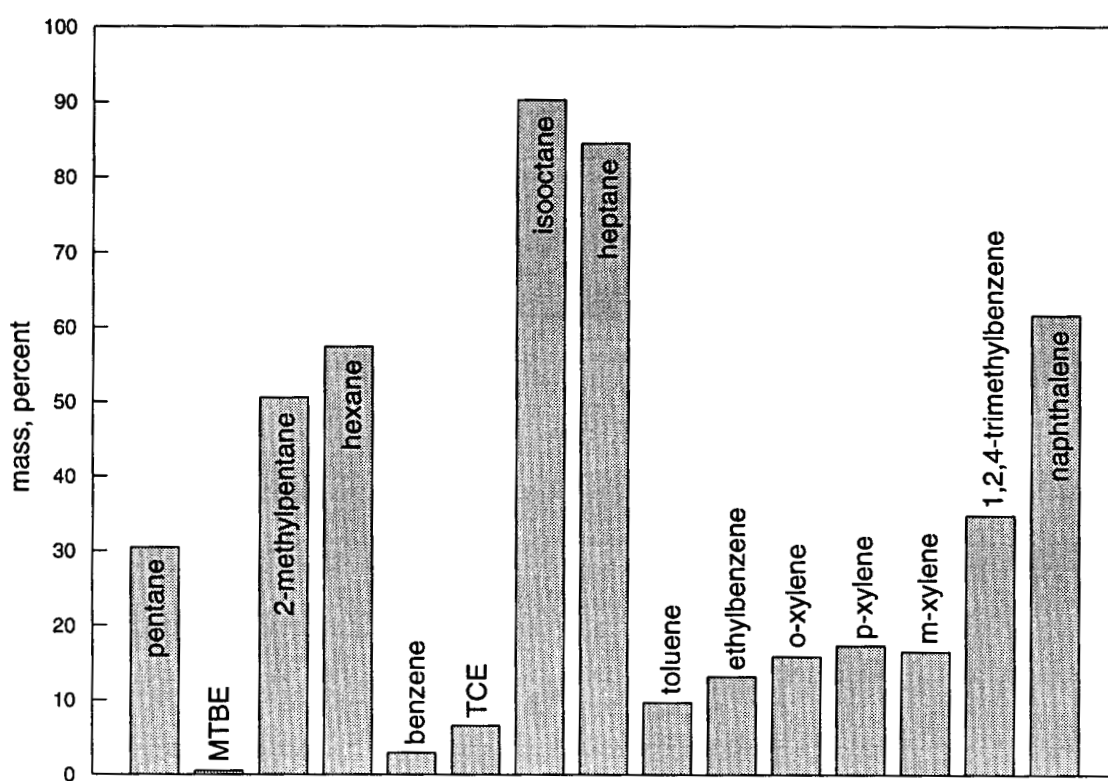


Figure 2.20. Estimated percent of initial mass remaining in the fractures 1000 days after the spill with no remediation for the base case numerical diffusion model.

Table 2.1. Composition and physical properties of the spilled hydrocarbons.

	Mass spilled (kg)	Mole fraction	Mix vapor pressure (atm)	Mix solubility (mg/l)
pentane	2.48	0.0849	4.84e-02	3.398
MTBE	1.50	0.0420	1.09e-02	2017.8
2-methylpentane	1.30	0.0373	7.83e-03	0.522
hexane	2.64	0.0757	1.21e-02	0.984
benzene	1.76	0.0556	5.56e-03	99.05
tce	2.96	0.0557	4.18e-03	61.30
heptane	1.36	0.0335	1.54e-03	0.101
isooctane	4.14	0.0896	4.57e-03	0.197
toluene	5.22	0.1399	4.90e-03	72.07
ethylbenzene	1.74	0.0405	3.04e-04	7.287
p-xylene	3.52	0.0819	7.04e-04	16.22
m-xylene	3.48	0.0810	5.34e-04	13.12
o-xylene	3.56	0.0828	6.63e-04	14.50
1,2,4-trimethylbenzene	2.70	0.0555	1.05e-04	3.163
naphthalene	2.28	0.0439	6.15e-06	1.450
totals	40.64	1	0.102	2311.2

Table 2.2. Pneumatic pumping test measured flows and pressures.

	Well 1	Well 2	Well 3
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

Table 2.3. Air permeabilities calculated from fracture aperture and spacing values.

B(cm)	b(cm)	0.001	0.002
1		$8.3 \times 10^{-15} \text{ m}^2$	$6.7 \times 10^{-14} \text{ m}^2$
10		$8.3 \times 10^{-16} \text{ m}^2$	$6.7 \times 10^{-15} \text{ m}^2$

Table 2.4. Effective porosity tracer test calculated values.

Test	Cylinder Radius (m)	Cylinder Volume (L)	Breakthrough Volume (L)	Effective Porosity
2 to 1	1.88	11,104	70	0.006
3 to 1	1.28	5,147	7	0.001
1 to 3	1.28	5,147	12	0.002
3 to 2	0.89	2,489	10	0.004

Table 2.5. Base case parameters for the numerical diffusion model.

Parameter	Value
porosity	0.37 ^a
bulk density	1.5 g/cm 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

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CHAPTER 3

SOIL VAPOR EXTRACTION OF LNAPL FROM A NATURALLY FRACTURED CLAY

INTRODUCTION

When silts, clays, tills and other "tight soils" become contaminated with petroleum hydrocarbons (e.g., gasoline) or other non-aqueous phase liquids (NAPLs) they have a number of characteristics that make them difficult to remediate. The water contents of these soils are generally high, and the air and water permeabilities are low (see Chapter 2). These soils, especially near ground surface, typically contain numerous cracks, fractures or other preferential pathways. These pathways are separated by blocks of intact soil. Usually the fractures represent only a small percentage of the total volume of the soil but at the same time, they represent the dominant pathway (Mckay, 1991; McWhorter, 1995) of fluid flow in the medium.

Low-viscosity NAPLs, such as gasoline, when introduced into a fractured media can often move relatively easily through the fractures. Some of the NAPL will dissolve into the soil water and be carried by diffusion into the matrix blocks or the NAPL may partition to the soil grains (Figure 2.1) and as a consequence, the volume of NAPL in the fractures may become significantly reduced over time (Parker, et al., 1994). In general, the NAPL present in the fractures will be easier to remove than the dissolved mass in the

soil matrix since aqueous-diffusion will limit the flux of contaminants from the matrix. As a consequence, the time frame for remediation of the soil matrix may be quite long.

A variety of approaches can be used for remediating contaminated tight soils, including air flushing, water flushing and heating. Each technique has both practical difficulties and benefits. The high water content and preferential flow paths of most fine-grained soils tends to inhibit flushing technologies since flow through the system tends to be only in the preferential pathways and, consequently, may bypass large portions of the soil. Heating the soil may cause desiccation fracturing and thereby form additional preferential pathways which would be initially uncontaminated. These desiccation fractures may then act as additional contaminant pathways and subsequently increase the extent of the spill zone.

Air flushing, specifically soil vapor extraction (SVE) and in situ air sparging (IAS) will be examined here. Air flushing is advantageous in that SVE/IAS components are typically off-the-shelf items and both technologies have become widely used for permeable soils. However, as mentioned above, there are many practical difficulties related to the application of SVE/IAS in fine-grained fractured soils. These include the generation and propagation of adequate flow through the fractured media and the location of air flow paths relative to the contaminants. The objective of this field study was to assess the effectiveness of SVE and combined SVE/IAS for reducing the risk to groundwater contamination associated with an LNAPL spill in fractured clay.

Air injection/IAS coupled with SVE has the potential to improve air flow over SVE alone. However, it may be difficult to capture all of the injected air so off-site migration of the vapors may be possible. This is likely to be compounded by the injected air finding preferential vertical flow paths to the surface and therefore vapor may not be captured by the SVE system. However, air injection is likely to increase mass removal due to the addition of these pathways to the flow system. Therefore, the use of well-designed air injection systems in conjunction with SVE may provide a useful tool for remediating low-permeability soils.

Air flow through fractured soils may be improved by controlling the water content in the fractures. One approach to this is to dewater the fractures using high vacuum

extraction, another is to add horizontal fractures that intersect the vertical fractures and enhance water flow. Inducing hydraulic fractures should increase the rate of delivery and recovery of fluids and vapors at shallower depths, just as it increases yields in oil wells. By increasing the rate of recovery, the effectiveness of site remediations involving fluid flow (e.g., vapor extraction, soil flushing, bioventing, steam stripping and pump and treat) should improve. Application of induced hydraulic fracturing is of particular interest in low permeability soils where conductivity is low and vapor extraction is less effective. Hydraulic fracturing has many potential advantages which include increasing the radius of influence of extraction wells, thereby reducing the number of required wells and increasing the rate of recovery. The net benefit of these effects is to shorten the time for remediation.

This chapter presents the remediation results of an LNAPL spill in a naturally fractured clay till. SVE using trenches and vertical wells is described. Air sparging was used to enhance SVE from the trenches. To improve water control and therefore air flow within the experimental cell, a hydraulic fracture was induced in the subsurface and a high vacuum extraction pump was attached to the SVE system. Along with mass removal data, pressure and flow measurements during the various remediation scenarios are presented. Details of the field site and gasoline spill, along with installation of monitoring wells have been presented previously (see Chapter 2).

EXPERIMENTAL SET-UP

Site Description

The field site for these experiments is located ~12 km southeast of Sarnia, Ontario (Figure 2.2) at a hazardous waste storage and treatment site owned by Laidlaw Environmental Services, Ltd., (formally Tricil, Ltd.). Chapter 2 contains a detailed description of the naturally fracture clay till. Briefly, the till is composed of ~20 to 40% clay sized particles and has two till zones. The upper zone extends down ~6 m and is weathered and fractured, while the lower zone (~30 to 40 m thick) is unweathered. The

hydraulic conductivity of the upper zone is $\sim 10^{-7}$ m/s compared with $\sim 10^{-10}$ m/s in the lower zone (Harris, 1994).

An experimental cell was constructed by driving sealable sheet piles to a depth of ~ 5 m in a square roughly 10 m on a side. In September 1992, approximately 50 L (40 kg) of a synthetic mix of gasoline-range hydrocarbons was released below ground surface into the cell from a constant-head reservoir. The composition of the mixture and some relevant physical properties of the components are listed in Table 2.1. 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 matrix.

Horizontal Trenches

Two vapor extraction trenches were constructed in the cell approximately 6 m apart. The analysis of soil cores and samples collected from the trenches during excavation showed the trenches to be outside any hydrocarbon contamination. The trenches are 1.3 m deep, 0.15 m wide and extend the length of the cell (Figure 3.1 and 3.2). Smearing along the trench walls was carefully removed. Approximately 15 cm of sand was placed in the bottom and five equally-spaced vertical 2-inch PVC wells were installed in each trench, then another 15 cm of sand was added to each trench. Finally, 60 cm of bentonite was placed with concrete filling the remainder of the trenches. The two sets of five vertical wells each had ~ 20 cm of slotted screen and a cap at the bottom. Each set was connected together above ground with a 2-inch PVC manifold which ran to the extraction system. Ball valves were installed upstream and downstream of the trenches to allow either trench to be actively pumped or used as a passive air inlet (Figure 2.3). After installation of the SVE trench system, a 10 cm thick concrete cap was placed over the entire cell.

Soil Coring and Analysis Description

Over the course of the project soil samples were collected by several methods.

Most samples were collected by driving short sections of stainless-steel tube (2-4 inch O.D. by 1 foot long) down a hole created by previous tube sections. Sample depths ranged from ~0.3 to 1.5 m below ground surface (see Figure 3.1 for locations). 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. Soil samples collected in 1993-4 were shipped to a commercial laboratory (Kemron Environmental Services, OH) for GRO (gasoline range organics) analyses (Modified 8015).

In 1995 soil samples were collected from trenches excavated within the cell (see Figure 3.3 for locations) at ~15 cm intervals (Figure 3.4). The samples were analyzed at the Oregon Graduate Institute (OGI) by high-resolution capillary GC/MS (gas chromatograph/mass spectrometer) using a 100-m long Petrocol column (Supelco, PA) and a Hewlett-Packard 5971 Mass Selective detector. The samples were shipped to OGI overnight and kept cold and in the dark until analyzed. Prior to analysis 100 µg of naphthalene- d_8 was added as an internal standard to each sample. The soil and methanol in the samples were then mixed by tumbling end-over-end for 24 hours. The methanol extract was separated from the soil by centrifugation. Approximately 2µg of methanol was removed from the vial and injected into a split/splitless injector on the gas chromatograph. In addition, several replicate samples were sent to the commercial lab for GRO analyses.

Vertical Wells

Field activities began in 1993 by collecting 5 cm-diameter cores to depths of 1 and 1.5 m (3 and 5 ft) to characterize the distribution of the gasoline within the cell. The holes created by the coring were used to install vapor monitoring (V) wells and IAS (AS) 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. Approximately 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 and sparge wells are shown

in Figure 3.1.

In 1994 five SVE vertical wells (W-wells) were installed in the experimental cell (see Figure 3.1 for locations). These wells were constructed from 2-inch PVC standpipes with a sand pack over the depth of ~0.9 to 1.2 m. A capped 0.15 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 cement seal.

SVE Pumps

The extraction pump used in 1993 was a Roots (positive displacement) blower (Air Components Engineering, Grand Rapids, MI) capable of sustained vacuum up to 0.5 atmospheres (15 inches of mercury or ~200 inches of water) and a maximum flow of about 30 scfm. During the course of the experiments, flows from the trenches ranged from 1 to 25 scfm. The latter corresponded to approximately half an atmosphere of vacuum and represented the maximum capacity of the blower. In 1994 a liquid ring pump with a 30 scfm capacity at ~1 atm was used. During both 1993 and 1994, air sparging wells located within the spill zone were individually activated using an oil-less compressor capable of injecting air at a rate of ~1 scfm.

Analytical Monitoring Equipment

Effluent from the SVE system is carried through a PVC manifold to the extraction pump (RootsTM, Air Components Engineering, Grand Rapids, MI) (Figure 3.5). Between the trenches and the extraction pump an airstream was removed from the manifold by a metal bellow diaphragm pump. Copper tubing extended from the PVC manifold through the diaphragm pump directly to a gas chromatograph (HP 5890 GC, Hewlett-Packard Co., Avondale, PA) located in the site trailer. Samples were drawn automatically from the copper tubing using an eight-port gas sampling valve (Valco Instruments Co., Inc., Houston, TX). In the active or sampling mode, effluent from the SVE system was

pumped into a stainless steel sample loop. Three sample loop sizes (0.21, 0.42 and 0.83 ml) were used depending on the sample concentration. The 8-port valve was activated by a Nelson Analytical 3000 Series Chromatography Data acquisition system (Nelson Analytical Inc., Cupertino, CA) to take samples at either two or four hour intervals. The sample in the sample loop was then flushed via a carrier gas (He) to the gas chromatograph (GC) equipped with a flame ionization detector. The gasoline vapor components were separated in the GC using a 100 m long, 0.25 mm diameter Petrocol column (Supelco, Inc., Supelco Park, Bellefonte, PA).

The GC continuously monitored effluent air to record mass removal rates over time whenever the SVE system was in operation. Samples were analyzed 24 hours a day at two or four hour intervals. Two hour samples were taken when the SVE system was turned on, either initially or after a shutdown, and when the trench configuration or the flow rate was changed. Once the extraction concentrations had stabilized, four hour sample intervals were used.

In order to ensure accuracy and reliability of the system, four types of standards were employed. Using the spill mixture, gas phase standards were prepared in 0.8 L stainless steel canisters equipped with stainless steel below valves (Whitey Co., Highland Heights, OH). The canisters were initially cleaned by heating them while alternately evacuating and pressurizing to 10 atmospheres with nitrogen gas. A known quantity by volume of the spill mixture was injected into a canister with a gas tight syringe. The canister was then pressurized with nitrogen to obtain the desired mixture concentration. Serial dilutions were made in additional canisters by taking aliquots from the original canister and pressurizing to pre-determined levels. Periodic injections into the GC from these canisters provided a gas phase calibration standard. Direct injection of the spill mixture into the SVE manifold via a syringe pump (KD Scientific, Model 100) also provided periodic calibration standards. When using the syringe pump the SVE system was extracting from the manifold, which was open to the atmosphere so that no mass was removed from the experimental cell.

An independent hydrocarbon standard (Liquid Carbonics) in stainless steel canisters was also used to verify daily reproducibility and accuracy of the GC analytical

system. Internal standards (n-octane and isobutylbenzene) were continuously added at the SVE manifold to ensure that the analytical equipment was working properly.

Hydraulic Fracturing

During the 1994 field season six 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 2.5 m below ground surface. Figure 3.6 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 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 ~1 to 1.5 mm. The hydraulic fracture extended to both trenches and did not intercept either trench, thereby avoiding short circuiting of extraction or injection air between the trenches and the fracture.

Microbiological Sampling

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) were used to enumerate the biomass and phospholipid fatty acid methyl ester analysis (PLFA) was used to assess microbial community structure and nutritional status. Core samples were collected from high (1000 ppm), and low (200 ppm) level contaminated areas within the cell along with uncontaminated cores. At each sample location cores were collected at 0.1, 0.5 and 1.0 m depths. To collect the samples

an aseptic 5 cm diameter core barrel was driven horizontally in 30 cm stainless steel tube sections into the soil through the wall of the large trenches excavated in the cell (see Figure 3.3). Each tube section contained ~20 cm of core which was extruded and cut into subsamples (~25 to 75 g) using pre-sterilized utensils. Details of the activities are presented in Appendix B.

RESULTS AND DISCUSSION

Soil Vapor Extraction from the Trenches

Pressure and Flow Measurements

During the 1993 field season air was extracted from one or both trenches at between 1 and 25 scfm. The pressure distribution within the cell was measured under a variety of conditions using magnehelic gauges. Figure 3.7 shows the vacuum distribution for the case where air is being extracted from both trenches at a combined flow of ~25 scfm. During that time the vacuum measured at the extraction manifold was ~15 in Hg (0.5 atm). As is shown conceptually in Figure 3.8, the pressure dropped rapidly with distance away from the trenches. This was thought to have occurred primarily due to preferential flow and leakage to ground surface (despite the presence of a "good" concrete cap on the system).

Another possible explanation for the rapid decrease in vacuum with distance was the accumulation of water at the extraction points. Water in the fractures appears to have played a major role in controlling air flow in the system. Given the shallow water table, nearly all of the fractures should have been water filled due to capillary rise prior to initiation of the SVE system. Application of the SVE vacuum caused significant changes in the distribution of water as evidenced by the fact that ~3000 L of water was removed from the system during 2.5 months of active remediation. Cumulative water recovery along with flow rate and vacuum are shown in Figure 3.9. Generally, the system yielded significant water every time that the vacuum was increased. However, as discussed

above, the vacuum dropped rapidly with distance from the extraction trench, thus it is likely that the changes in water content were localized along preferred pathways. Therefore, the water content of the fractures in much of the soil within the cell may have been relatively unaffected by the applied vacuums. Since the fracture aperture and frequency tend to increase near to ground surface, it is not surprising that vertical short-circuiting of the induced air flow was a problem.

At the conclusion of the 1993 field season, a series of tracer tests were conducted to evaluate air flow in the cell. As with previous tests at the site (see Chapter 2), sulfurhexafluoride (SF_6) was used as the tracer gas. The tests were conducted during the regular course of extraction by the addition of 50 mL of SF_6 at one of the vertical wells. The concentration of the SF_6 in the air extracted from the trenches was measured using a HP 5890 GC with an electron capture detector. Because the volume injected into the soil represents a potentially long-term source of the gas and because of the potential for retardation of the SF_6 (Gupta, 1994; Fry, et al., 1994), the travel time for each test was taken at the point where the SF_6 concentration first began to increase significantly (i.e., ~5% of the maximum value). An example tracer breakthrough curve is shown in Figure 3.10.

The tracer tests indicated that air flow through the cell was very non-uniform. Tests were conducted at five locations across the cell (C-2, C-9, C-14, C-20 and V-7), located at distances of approximately 0.8, 2.7, 3, 4, and 5 meters from the extraction trench. During each of the tests air was being extracted from the west trench at 22 scfm. Data in Table 3.1 indicate that travel time to the extraction trench was not directly related to distance from the trench. The data also indicate that travel times were much longer than would be anticipated based on the air volume extracted and the effective porosity previously determined at the site. Based on the data in Table 3.1, the effective SVE air flow porosity ranges from 1 to ~8 (compared to ~0.001-0.006 in Chapter 2). This suggests the effective porosity exceeds 100% and indicates that significant leakage was occurring. As a consequence, it is estimated that <<10% of the air was used effectively in the extraction. The conclusion from these data is that significant short-circuiting of the air (more than 90%, probably from ground surface), occurred during SVE.

Mass Removal from the Trenches

During the 1993 field season, a total of approximately 11 kg of the 40.6 kg spilled was removed by SVE, as determined by vapor offgas measurements. At the same time, the measured concentrations in the extracted air dropped by about an order of magnitude (e.g., see the benzene and toluene data in Figure 3.11). Superimposed on Figure 3.11 are the flow rates which were active during the various stages of pumping along with the SVE trench configuration. This concentration drop is due to a number of factors which are difficult to decouple from one another, including that: 1) gasoline became increasingly less available with time; 2) changes in the composition of the NAPL as the result of weathering reduced the overall vapor pressure of the mix; 3) flow rates (and applied vacuums) were changed; 4) water levels changed as the result of precipitation; and 5) air flow changed due to the probable establishment of preferential pathways in the soil.

At most SVE remediation sites, concentrations drop relatively quickly at the onset of remediation. In many cases this probably is because the most easily removed mass (i.e., the most volatile or the most accessible) is quickly extracted from the system, leaving progressively less volatile and less-accessible mass to be removed. This process almost certainly occurred at the Sarnia site. Preferential removal of the more volatile contaminants from the mixture would result in an overall reduction in the volatility of the gasoline. As a consequence, under steady-state flow conditions, the recovery rate of the gasoline would be expected to go down. This decrease should also be reflected in changes in the composition of the extracted hydrocarbons. As will be discussed below, evidence of these changes in composition is indicated by the ratios of compounds removed by the SVE system.

As discussed in the previous section, tracer tests conducted at the conclusion of the 1993 field season indicated that air flow within the cell was irregular. It is likely that some of these pathways existed at the onset of the SVE process; however, it is also likely that some of these pathways changed due to the SVE process itself. As a result, it is likely that large portions of the soil were not effectively vented. All of the above factors probably played a role in controlling mass removal. From the practical perspective, it can

be concluded that greater emphasis should be placed on hydraulic control and achieving uniform air flow than simply on the volume of air removed from the system. Several means of improving hydraulic control and air flow through the system will be discussed below. Assessing the uniformity of air flow based on vacuum measurements is difficult, but in general, tracer tests are the most reliable.

Water level within the cell changed significantly during the extraction period (Figure 3.12). In addition to regional water level changes, the SVE system had some localized impact on the water levels. It is quite likely that these water level changes impacted mass recovery. This is particularly true when the system was operating at an ~ 0.5 atm vacuum. During the SVE process, the trenches were pumped, using the 1-inch PVC dewatering wells, as an additional attempt to lower the water level within the cell. However, the volume of water collected from the dewatering wells was small in comparison to the volume of water extracted by the Roots (positive displacement) blower connected to the SVE system.

The cumulative mass recovery in the SVE offgas is presented in Figure 3.13. The Figure shows that mass recovery is fairly steady throughout a variety of changes in extraction conditions. Close inspection of the data indicates that there is some increase in mass recovery at the higher flow rates, but generally the higher flow rate also resulted in increased problems with water production. Mass recovery of individual gasoline components is more revealing. Figure 3.14 shows the recovery of isooctane, trichloroethane (TCE), toluene and benzene as a function of time. Isooctane, the least soluble of the four, showed the highest recovery. TCE, whose solubility is intermediate to toluene and benzene, showed greater recovery than either of those two compounds. This could be the result of biodegradation, but the uncertainties in mass recovery are on the same order as the observed differences.

The fraction of each compound in the gasoline recovered at the end of the first season of remediation is presented in Figure 3.15. As expected, the less soluble and more volatile compounds were recovered to the greatest extent. Figure 3.16 shows how the mass recovery ratios of TCE and methyl-tert-butyl-ether (MTBE) to isooctane changed over the course of the extraction process. The ratios of MTBE and isooctane to TCE are

shown in Figure 3.17. The figures indicate that both TCE and MTBE respond similarly (Figure 3.16), while MTBE and isooctane have opposite responses (Figure 3.17). TCE has an intermediate response and also has an intermediate mix solubility compared to MTBE and isooctane (TCE, 61.3 mg/l; MTBE, 2017.8 mg/l; and isooctane 0.2 mg/l). Also, demonstrated on the figures are the changes that occurred when system operating conditions were changed. For example, changes in air flow resulted in large changes in response for MTBE and isooctane (Figure 3.17). At initial SVE system startup for both trenches, the isooctane to TCE mass ratio increased dramatically while the MTBE to TCE ratio was approximately zero. However as the system continued to operate the isooctane ratio decreased and the MTBE ratio increased.

The cumulative recovery of MTBE by the SVE system was greater than might have been expected considering that it should have partitioned almost entirely into the soil matrix (see Chapter 2). However, if partitioning to the gas phase occurred via diffusion through the aqueous phase, then the high solubility of MTBE would have caused it to have the highest flux from the water. In addition, if a significant portion of the recovered mass came from the matrix, then MTBE would also have had the greatest flux out of the matrix since it has the largest effective diffusion coefficient. Figure 3.18 shows the ratio and inverse ratio of MTBE to isooctane. Isooctane was chosen for comparison because it is the least water soluble and is unlikely to biodegrade. At the time of system start-up isooctane recovery is much greater than MTBE. This is probably because most of the isooctane was in the fractures, while most of the MTBE was in the matrix. This Figure indicates that as time progressed, the ratio of MTBE to isooctane increased to ~0.5 which indicates that most of the mass transfer at that point was coming from the matrix. This situation continues until extraction was switched to the other trench, at which point the isooctane again increased dramatically.

At the beginning of the 1994 field season, the SVE system was restarted using the two extraction trenches and similar extraction conditions to those at the end of the 1993 season. Hydrocarbon concentrations of ~0.02 to 0.04 g/m³ were observed for the two week period over which these conditions were maintained (Figure 3.19). This corresponds to a total mass removal rate of only ~22 g/day. As a result, over the two

week period ~0.3 kg of mass was removed from the cell. Following this the system was shut down for conversion to a high vacuum pump and vertical wells.

The SVE system removed ~3000 liters of water during the course of the 1993 field season. During that same period $\sim 3 \times 10^7$ liters of air was also extracted with the SVE system. Since the air-water ratio was so large, the water drawn in by the SVE system should have been thoroughly stripped by the air, and the concentrations in the water and air were probably at equilibrium. Therefore, the masses of each of the mixture components removed in the water can be calculated from the corresponding air concentrations and the volume of water removed. The Table 3.2 indicates that mass removal in the water was small (10.5 g), even for the more soluble components, and therefore this pathway is not considered to be significant for hydrocarbon removal.

Soil Vapor Extraction from the Vertical Wells

Pressure and Flow Measurements

During the 1994 field season air was extracted from the vertical wells using a high vacuum (liquid ring) pump. Figures 3.20-21 display pressure readings across the cell during SVE from the five wells (W-wells, see Figure 3.1 for locations). Observed vacuums during extraction with the liquid ring pump were quite small (Figure 3.21). In this case the air flow rate was ~4 scfm and the vacuum at the manifold was ~27" Hg (~0.75 atm). SVE from the W-wells using the positive displacement blower indicated significantly better vacuums despite the lower vacuum at the manifold (~10-15" Hg or ~0.5 atm). This may be due to the water level in the cell being lower during the latter case.

As air was extracted from the trenches, air flow measurements were made using an inline flow meter. However when very-high vacuum extraction from the vertical wells was initiated the entire extraction system became coated with a layer of fine particles which made direct air flow measurements very difficult. As an alternate approach, helium was used as a tracer to directly measure air flow. Once a particular flow configuration

(e.g., the liquid ring pump on the W-wells) was established, helium was injected at a known rate into the extraction manifold near the well head. A small fraction of the extracted air stream was then withdrawn from the extraction manifold near the pump (the same system used for sampling hydrocarbons). The concentration of helium in the air was measured using a Mark Products helium detector and the flow rate was calculated. The measured flow rates for the W-wells using both the Roots blower and liquid ring pump are shown in Figure 3.22. The Figure indicates that flow rates from the vertical wells were fairly low, especially given the high vacuum the system was generating.

Mass Removal from the Vertical Wells

Once the SVE system was converted to the liquid ring pump and the vertical W-wells, it was restarted and the initial mass recovery was $\sim 0.4 \text{ g/m}^3$. This large concentration spike suggests that the W-wells were accessing fractures which still contained LNAPL or that new fracture pathways were being accessed by the SVE system. The high concentrations persisted for only a day and then dropped to $\sim 0.01\text{-}0.02 \text{ g/m}^3$ levels indicating the "clearing out" of the newly accessed fractures and weathering of the spill mixture. Similar low concentration levels were observed when the SVE system was switched back to the positive displacement blower on the trenches. As can be seen from the Figure 3.19, concentrations in the offgas remained very low for the duration of the 1994 field season.

Figures 3.23-24 shows offgas concentrations for individual compounds under all of the flow conditions during the 1994 field season. Behaviors of the individual compounds are generally the same as the total concentration data in Figure 3.19. However, the ratios of individual compounds indicate some interesting trends. Figure 3.25 displays the mass ratios of MTBE and isooctane to TCE. There were significant changes in these ratios when the flow configuration was turned from the trenches to the vertical wells. The isooctane to TCE ratio was higher when the system was on the trenches but when the system was moved to the vertical wells the MTBE to TCE ratio was higher and remained higher when the system was changed back to the trenches. It

is also interesting to note that these ratios during the second field season are closer together than in the first field season (Figure 3.17). This probably indicates that the isooctane was becoming less available with time and that the MTBE became relatively more available with time probably due to its greater mobility in the matrix (i.e., larger solubility and therefore greater flux).

Figure 3.26a presents the total mass recovered during the 1994 field season for each compound in the spill mix. The total mass recovered for each compound expressed as the fraction of the spilled mass of that compound is shown in Figure 3.26b. As indicated in the figures, the recovery for all compounds was low, with only MTBE approaching 10% recovery during the 1994 field season.

Figure 3.27 shows the cumulative mass recovered during the 1994 field season. A total of ~1 kg was recovered. Approximately 0.8 kg of the mass came from the relatively short interval at the beginning of the season when air was extracted from the trenches. The remainder of the mass came from the vertical wells and the well intersecting the hydrofracture (discussed below).

Total mass released and cumulative mass recovered for each compound recovered during both the 1993 and 1994 seasons are presented in Figure 3.28. The data once again indicate that the 1994 mass recoveries were low. However, the combined data for the 1993 and 1994 field seasons do show that recoveries of a number of compounds, including MTBE, hexane, TCE and isooctane were significantly greater than 50%. To close the mass balance on all of the compounds a compound-by-compound analysis of soil cores was carried out during the 1995 field season (see Mass Balance Analysis below).

Mass Recovery During Air Sparging

In 1993 following extraction from each of the trenches in situ air sparging was conducted in the 5 AS-wells near the center of the cell (see Figure 3.1 for locations). The air injection rate was 1 scfm while the air extraction rate from both trenches was 25 scfm. Each of the wells was sparged individually and sequentially. The locations of the sparge

points were selected during the initial coring process, prior to any analysis of data on the distribution of contaminants within the system. However, the wells are reasonably well distributed throughout the zone of contamination.

Pressure measurements made during the sparging process indicated that the center of the cell was approximately at atmospheric pressure. In the case of AS-3, a number of sampling points indicated pressures greater than one atmosphere (e.g. +0.5 inches of water). Thus it is likely that some mass was lost from the system to the atmosphere during sparging. It is significant to note that this occurred even with an extraction to injection flow rate ratio of 25:1.

Tracer tests were conducted to assess the extent to which sparged air was lost to the atmosphere. The tests were conducted by injecting helium at a known concentration in with the sparge air and measuring the helium concentration in the SVE offgas. By knowing the rates of air injection and air extraction the percent recovery of the IAS air can be calculated. The estimated percent recovery values for each of the sparge wells is shown in Table 3.3.

It was anticipated that increased air pressure during the sparging process would "clear out" additional fractures and improve mass recovery. Offgas concentrations during sparging are shown in Figure 3.29. In all cases except AS-3, mass recovered from the sparging process was initially small and in all cases the concentrations dropped within 24 hours. AS-3 is located at the center of the spill zone and yielded the majority of the mass due to sparging. It was estimated that the total additional mass recovered as a result of the sparging process was 0.96 kg, with 0.65 kg from AS-3. This mass represents a relatively minor contribution to the total 1993 mass recovery. However the tracer tests, indicated that only 13-45% of the sparge air was recovered by the SVE system. Therefore, the actual mass removed from the subsurface was probably closer to 5.7 kg. The estimated mass recovery from each of the sparge wells is listed in Table 3.3. The conclusions drawn from the sparging data at this site are that it may be possible to remove significant mass when the sparge well is placed within the source zone, however collecting the sparge air (offgas) may be difficult.

Hydrofracturing and Water Removal

The hydraulic fracture was created to increase water removal within the cell, which in turn should improve air flow. Figure 3.30 presents the rate of water recovery from the trenches and hydraulic fracture during the 1994 field season. As seen in the Figure, significant volumes of water were extracted from the trenches when the SVE system was started up (e.g., days ~680-695 and ~705-715). However, once the initial volume of water was removed, the removal rate dropped dramatically. In contrast, water removal rates from days 720 to 740 from the hydraulic fracture were sustained over a longer period of time. This may be due, in part, to the higher vacuums maintained in the hydraulic fracture by the liquid ring pump. It should be noted that a significant volume of water was recovered from the hydraulic fracture while only a small amount of water was collected from the vertical wells (W-wells, days ~700-705) under the same vacuum conditions. The larger volume of water removed from the hydraulic fracture may, in part, be due to the depth and extent of the fracture. Since the hydraulic fracture is below the water table (typically between ground surface and 2 m) and extends laterally under most of the cell, it has access to a greater volume of water, both from above and below, than either the trenches or vertical wells. Cumulative water volume removal for the 1994 field season is presented in Figure 3.31.

Water level data from monitoring wells MW-1 and MW-2 located near the northeast corner of the cell (see Figure 3.1 for the locations) are shown in Figure 3.32. Both the 1993 (Figure 3.12) and 1994 data show the influence of individual rain events both inside (MW-2) and outside (MW-1) the sheetpile cell. Water levels outside the cell dropped more than inside the cell. This is probably as result of lateral drainage outside the cell and reduced evaporation inside the cell due to the concrete surface cover. Surprisingly, water removal from the hydraulic fracture appears to have had a very small effect on the water level within the cell. While this may be due in part to the location of the hydraulic fracture, it also suggests that the effect of dewatering within the cell was relatively localized.

Mass Balance Analysis

Soil Core Analysis

Pre-remediation soil samples were taken at 30 cm vertical intervals at 12 locations to determine the initial distribution of the hydrocarbons within the soils (see Chapter 2 for details). If the soil concentration data is integrated over the volume of contaminated soil, the total mass accounted for is ~13.1 kg or 32% of the mass spilled. Given the density of the sampling grid, it is unlikely that significant quantities of hydrocarbons migrated out of the sample region. Underestimation of the mass may have resulted from several sources of error in the sampling process. An error could have arisen because the fractures are primarily vertical, as was the coring process, and therefore the small (2" diameter) cores may not have sampled a representative number of fractures. Given what is known about air and water flow in the till, it is also likely that the mass was not uniformly distributed within the medium. Compaction during the coring process may have been forced NAPL out of the fractures being sampled resulting in an underestimation of the mass in the fractures.

Following the first season of SVE/IAS remediation, when 16.3 kg (41%) of the mass was removed, additional soil cores were collected and analyzed. As with the "pre-remediation" data, the concentration contours for the 90 cm depth interval have been plotted (Figure 3.33) along with specific data for each sample location. Note that the concentration contours are almost double in the post-remediation plot compared to the pre-remediation contours (Figure 2.15). This second set of soil cores accounted for 14 kg (34%) of the spill. This is somewhat more than the mass estimated from the pre-remediation coring. Therefore, with the 41% removed by SVE/IAS, 75% of the original mass was now accounted for. The soil and SVE/IAS masses accounted for at the various stages of the study are summarized in Table 3.4. The difference between the mass released and the measured total accounted for is once again thought to be due to the sampling process.

Prior to the second season (1994) SVE operations 4" soil cores were taken. These

samples were collected to resolve the discrepancy in the mass balance for the spill. Locations of the cores are indicated on Figure 3.1 as W-1 through W-5 and the hydrofracture well (HF-1). The larger 4 " soil cores were collected using a hydraulic ram in an attempt to minimize bias during sampling. It was anticipated that this approach would be less damaging to the cores than the jackhammer driven approach used in 1993 and that the larger-diameter cores would provide a more representative sample. A number of large-volume (i.e., 1-L) samples were collected in addition to the standard 40 mL samples. This comparison showed no significant difference in soil concentrations based on sample size. The data indicated 9.9 kg (24%) of the spill remained in the ground. Along with the 41% removed by SVE, this accounts for 65% of the original mass.

In general, the 1994 GRO values for the soil samples are less than those taken at the end of the 1993 field season. In the vicinity of the center of the spill, concentrations in 1994 are approximately half of the post-1993 values. This is somewhat surprising since it was believed that "less-biased" samples were collected in 1994. The reasons for the differences are most likely explained by biodegradation and variability in the sampling process.

Final sampling in 1995 involved obtaining samples by digging into the walls of large trenches that had been excavated in the contaminated zone at the site. A comprehensive compound-by-compound GC/MS analysis was preformed at OGI, with several replicate samples sent to a commercial laboratory (Kemron, Inc.) for GRO analysis. In order to compare the two methods the GC/MS samples were adjusted by removing the contributions of pentane, MTBE, TCE and naphthalene (i.e., non-GRO compounds) from the total compound analysis. Figure 3.34 presents a plot of the GC/MS GRO data versus the Kemron GRO data and indicates there is significant scatter between the two data sets ($r^2=0.16$). The large amount of scatter between the two data sets probably reflects sampling variability in the soil over the scale of centimeters. The slope of the regression line is 0.63. Plotting the Kemron GRO data versus the total GC/MS analyses (Figure 3.34) gives a slope of 2.45, suggesting that a compound by compound analysis of the Kemron data would lie somewhere between the two sets of GC/MS data (i.e., GRO and total analysis). This is likely to be the case since some non-GRO

compounds may have been counted to some extent in the Kemron analyses.

The final mass of individual compounds at each sample level for 1995 is presented in Table 3.5. Concentration contours for the 90 cm level based on the Kemron GRO data are shown in Figure 3.35. The Kemron GRO data is presented in order that direct comparison with previous soils data (i.e., 1993 and 1994) analyzed in a similar manner is possible. Figure 3.36 displays concentration contours from a vertical section along one of the trenches for the Kemron GRO data. A complete set of soils data based on the GC/MS data (GRO and all compounds) along with the Kemron data can be found in Appendix C. The distribution of contaminants based on the 1995 data is generally consistent with data from previous years and indicates that contamination levels are continuing to decrease.

Data from the compound specific GC/MS analyses have been combined with the SVE and IAS analysis data from the previous years to calculate the mass balance for each compound in the spill mixture (Table 3.6 and Table 3.7). The data indicate that from ~20 to 120 percent of the mass of each compound can be accounted for. In general the BTEX compounds have the lowest recovery percentages (benzene, 25%, toluene, 35%, ethylbenzene, 19%, and xylenes, 20-30%), while the less-volatile and more recalcitrant compounds have the highest recoveries (naphthalene, 121%, isooctane, 109%, TCE 80%, hexane, 69%, MTBE, 67%, and 2-methylpentane 63%). As will be discussed below, the data indicate that a significant fraction of the BTEX compounds may have degraded while in the subsurface.

The GC/MS soils data indicate that essentially all of the naphthalene released at the site was still present in the subsurface at the conclusion of active remediation (121% of the initial mass). If it is assumed that the final distribution of the naphthalene is the same as it was initially and that it also reflects the initial distribution of the LNAPL as a whole, then the initial LNAPL concentrations can be scaled from the naphthalene data. Figure 3.37 presents the calculated initial concentrations of LNAPL distribution based on the naphthalene data. The percent of LNAPL remaining in the soil based on the calculated initial LNAPL distribution is shown in Figure 3.38 while the final concentration of LNAPL in the soil is shown in Figure 3.39. The data show that the

fraction of LNAPL remaining increases with depth. This is consistent with other data from the site (e.g., decreasing fracture frequency, increasing water content with depth) which would indicate better air flow characteristics nearer the ground surface. Table 3.6 lists the average percent remaining in the soil for each compound based on the final GC/MS soils analyses. The data indicate that greater than 90% of the spilled mass has been removed from the soil through active remediation or degradation. For the BTEX compounds the percent removals were significantly higher (95-99%).

Biodegradation Measurements

Geochemical and microbiological characterization of soil samples from the site generally showed conditions which favor biological activity (ORNL, 1995). The geochemical factors are summarized in Table 3.8. Microbial analysis of the soils indicated that a variety of populations capable of degrading hydrocarbons were present in the soil at levels which could produce modest intrinsic biodegradation rates (Table 3.9). The ORNL team concluded that sustained rates of 0.5 to 1 mg/kg/day were likely in this soil. A complete copy of both geochemical and microbial characterization is contained in Appendix B.

To estimate the percent of each compound that could have been biodegraded at the site the mass removed by SVE (1993 and 1994) and the final mass remaining in the soil was subtracted from the total mass spilled (Table 3.6 and Table 3.7). As discussed previously the BTEX data suggest that 70 to 80% of their mass could have been biodegraded. In contrast the naphthalene, isooctane and TCE data indicate that less than 20% of their mass was biodegraded.

CONCLUSIONS

In this field study soil vapor extraction (SVE) and in situ air sparging (IAS) were used to remediate a fractured clay till contaminated with gasoline-range organics. SVE using trenches and IAS were able to remove ~40% of the spilled mass during the initial two months of operation. During that time vapor concentration decreased by approximately one order of magnitude. However, as the result of increasingly aggressive extraction conditions, mass recovery remained fairly constant during the two months of extraction/injection. At the conclusion of the initial field season, the SVE was removing air at a rate of ~25 scfm and the vacuum at the extraction trench was ~0.5 atm. These conditions represented the capacity of the Roots (positive displacement) pump system used for the SVE system, thus the observed mass recovery rate could not have been sustained.

Following the initial remediation activities soil cores were collected at the site. They showed that ~39% of the original mass remained in the soil after SVE/IAS. However, there is considerable uncertainty in these data (e.g., pre-remediation soils analysis was able to account for only ~25% of the mass released into the soil). The combination of mass removed and soils analysis accounted for ~75% of the mass initially released into the cell.

Remediation during a second field season (1994) focused on extraction from vertical wells, including one which intersected a hydraulically-induced horizontal fracture. In all cases, mass removal from the wells was small (i.e., <1 kg or <2% of the released mass).

Following active remediation (1995), a detailed analysis of soil cores from the site was made using gas chromatography/mass spectrometry (GC/MS). These data indicated that primarily the low-volatility compounds (e.g., naphthalene, 1,2,4-trimethylbenzene and o-xylene) remained in the soil while little 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 reasonable for a number of compounds, including isooctane, TCE, and to a somewhat lesser extent MTBE, hexane, and several other alkanes. In contrast, overall mass balances 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 conclusion of the ORNL study which was done in conjunction with this project.

Final naphthalene soils data were used to estimate the initial distribution of the NAPL at the site and were compared with the final compound specific soils data. These data indicate that greater than 90% of the spilled mass had been removed from the soil at the site. For the BTEX compounds the percentage removed was significantly higher (95-99%). In the context of the BTEX compounds, it must be concluded that remediation at the site was successful. At the same time, the naphthalene data suggest that it is difficult to remediate less volatile contaminants such as the polynuclear aromatic hydrocarbons using air flushing in low-permeability soils.

Both SVE and IAS were initially able to remove a significant mass of contaminants, especially if the mass was still present in the fractures. They may also have improved aerobic biodegradation at the site. Also, even at modest biodegradation rates, the relatively low contaminant levels in the soil (i.e., residual saturation of 2 L/m³) may mean that biodegradation has the potential to account for a significant mass removal even within the "source" zone. Finally, the combination of air flushing and biodegradation removed nearly all of the benzene and toluene from the soil. Removal of the lower vapor pressure compounds (e.g., naphthalene) was less successful.

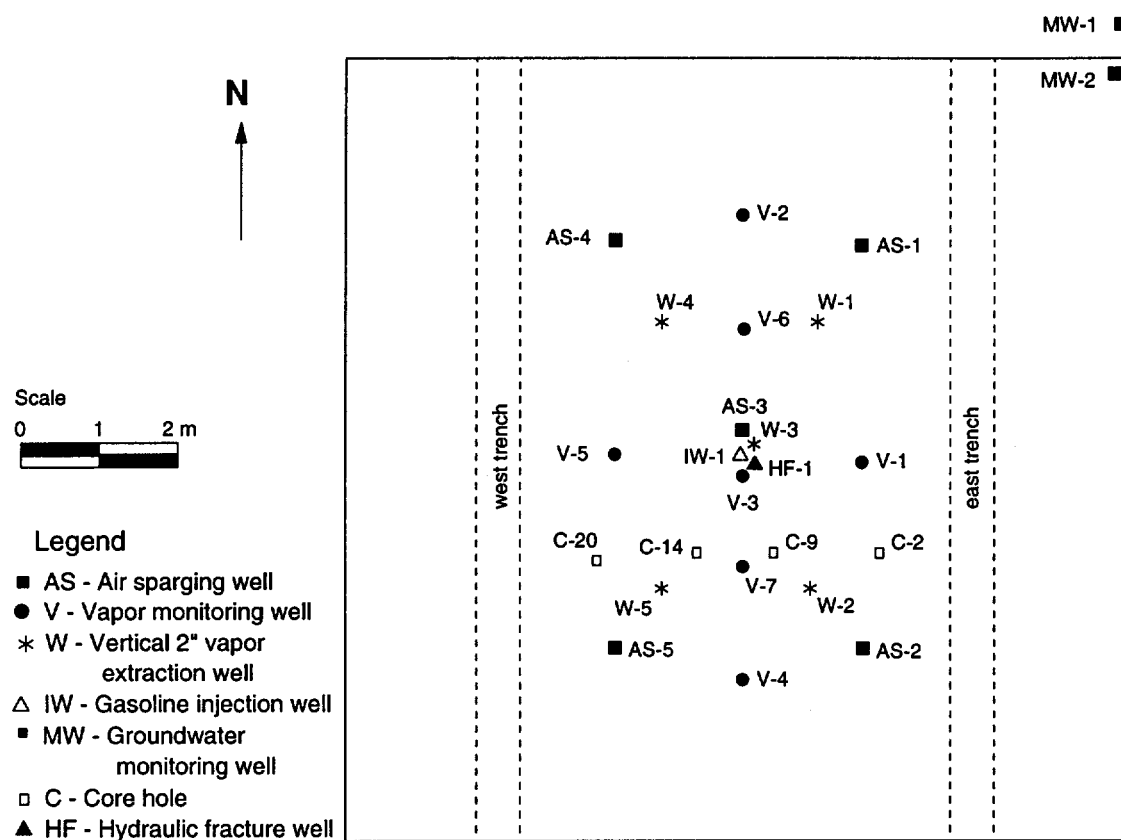
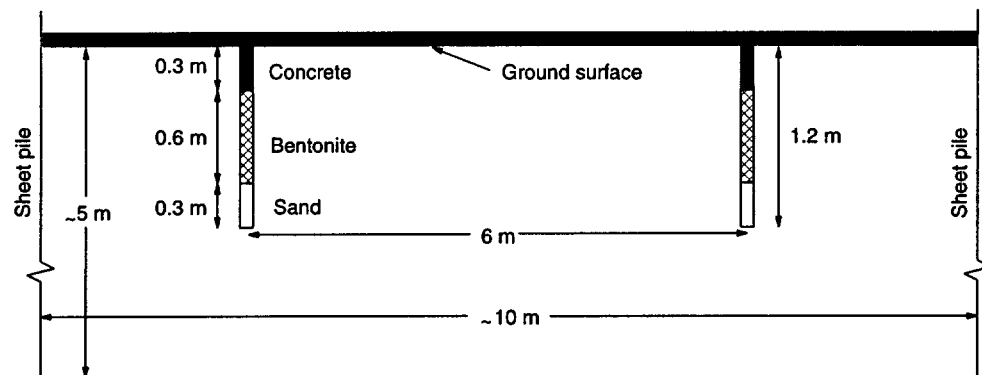


Figure 3.1. Plan view of the cell showing the locations of the trenches and wells.

a) Cell Cross-section Perpendicular to Trenches



b) Trench Cross-section

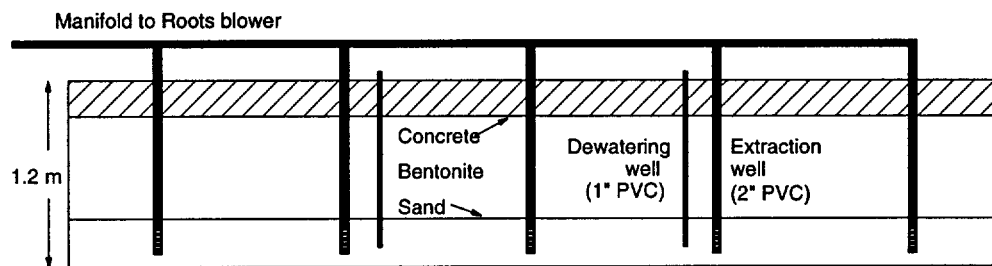


Figure 3.2. Schematic "as built" diagrams of the SVE extraction trenches. a) Cell section view b) trench section view

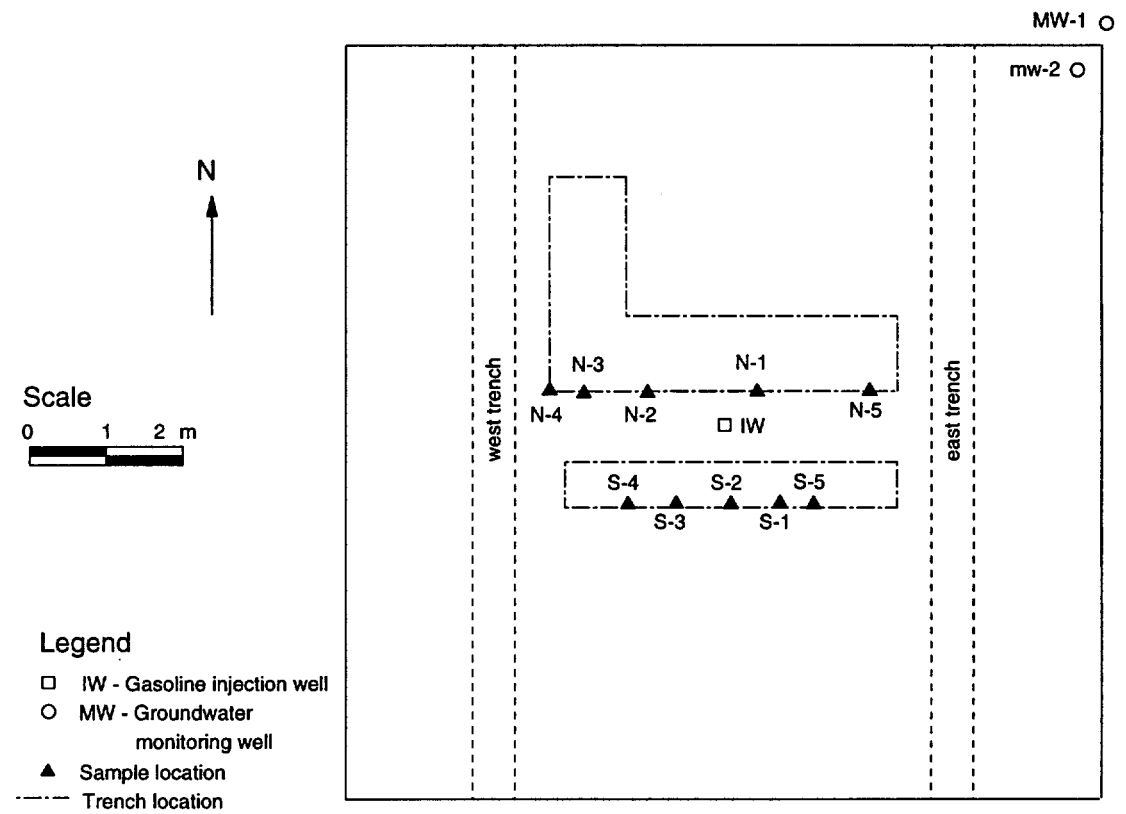


Figure 3.3. Plan view of the site showing the locations of the sampling trenches and the specific sample locations.

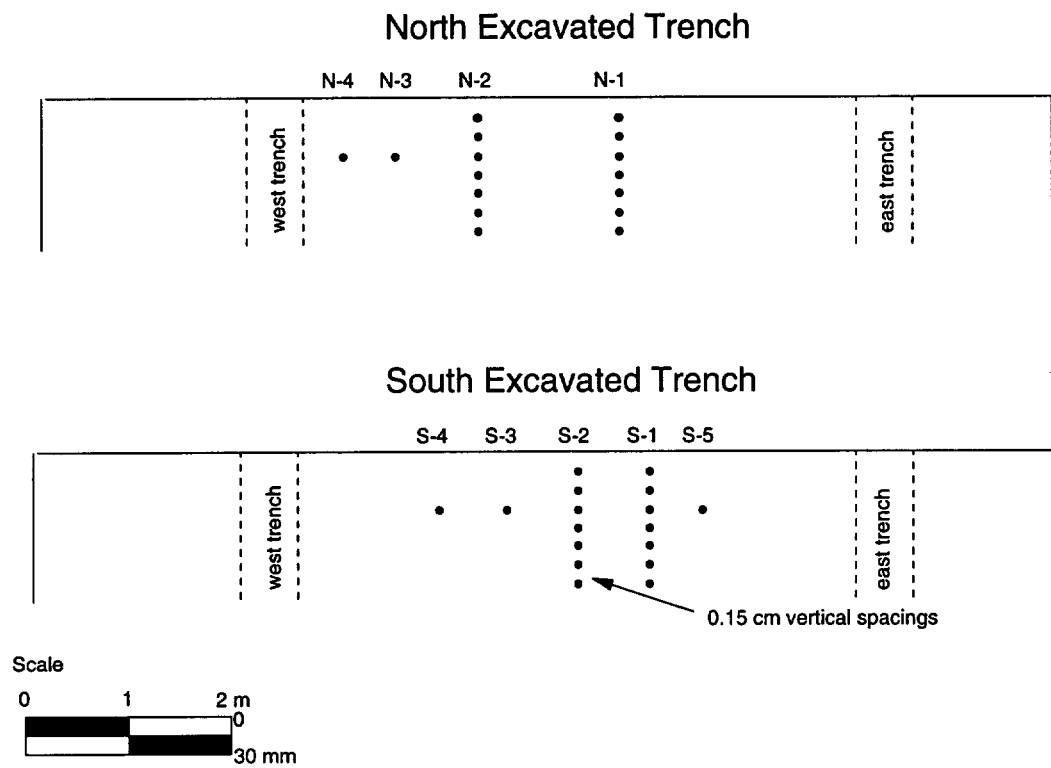


Figure 3.4. Profile of soil sample locations in the excavated trenches.

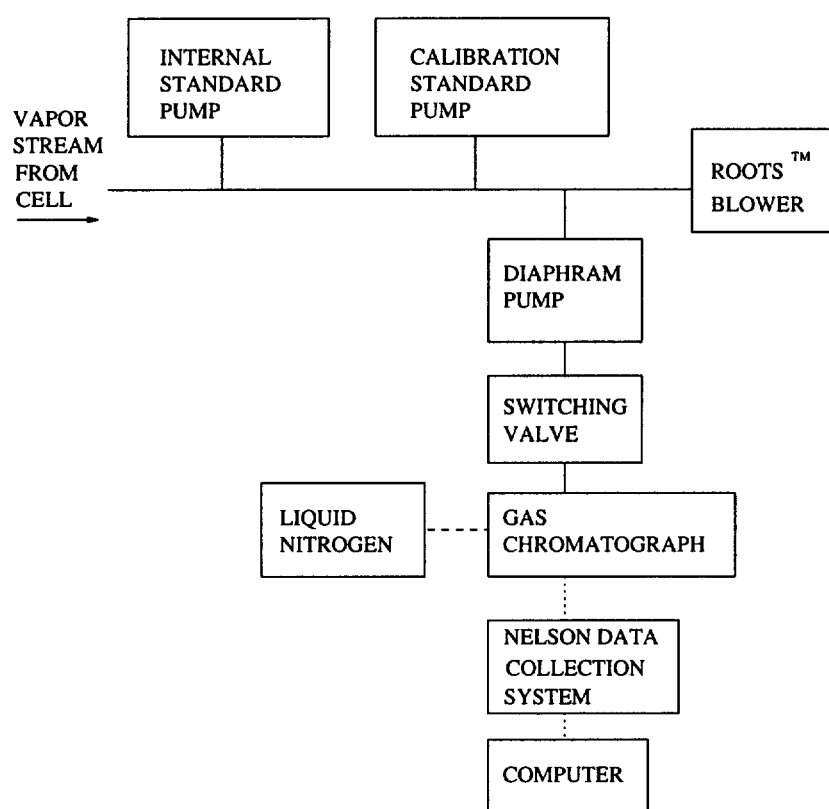


Figure 3.5. Block drawing of the analysis system.

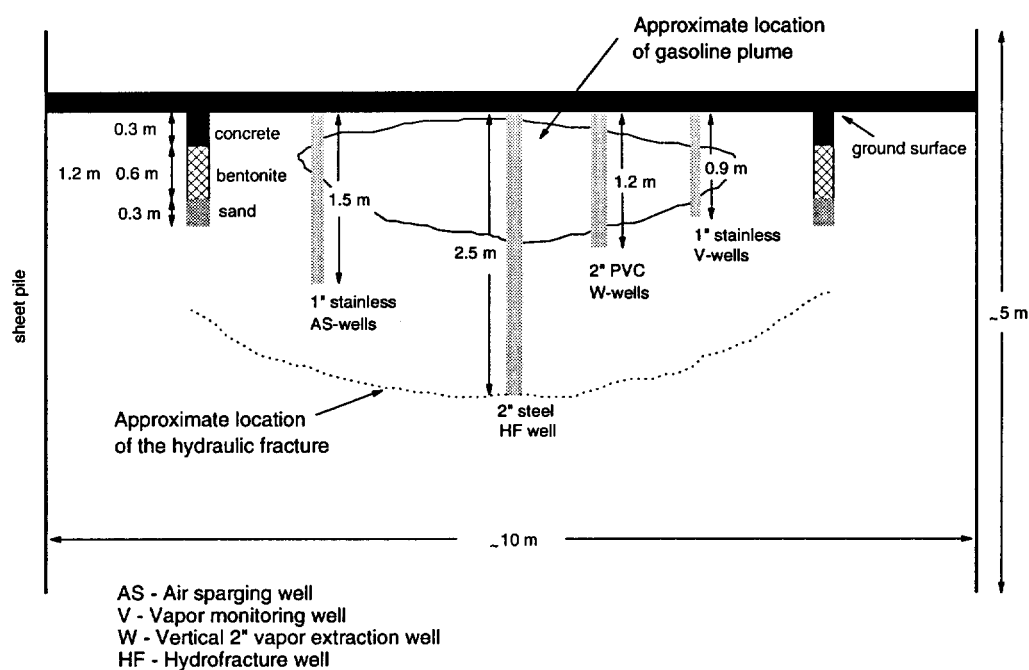
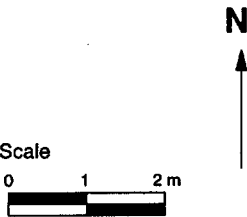


Figure 3.6. Cross-section view of the experimental cell showing the location of the wells, trenches and hydraulic fracture.

SVE on trenches with ROOTS

pressures in "in H₂O"
July 23 (-0.10)
July 30 -0.14



- Legend
- AS - Air sparging well
 - V - Vapor monitoring well
 - △ IW - Injection well
 - MW - Groundwater monitoring well
 - C - Core hole
 - ▲ HF - Hydraulic fracture well
 - * W - Vertical 2" vapor extraction well

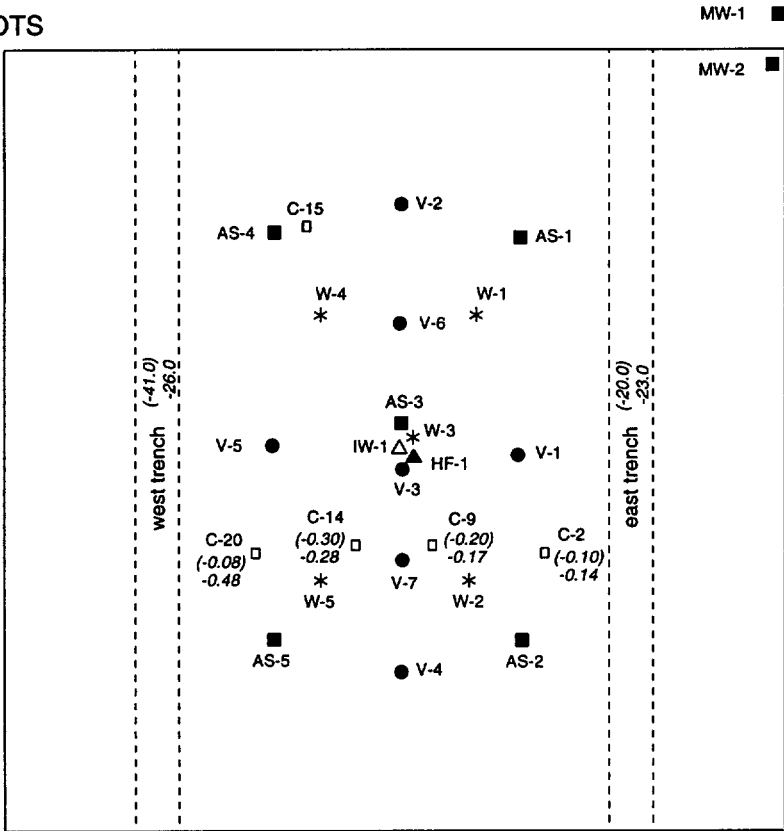


Figure 3.7. Distribution of soil vacuum during extraction with the Roots pump from the trenches at 25 scfm during the 1993 field season.

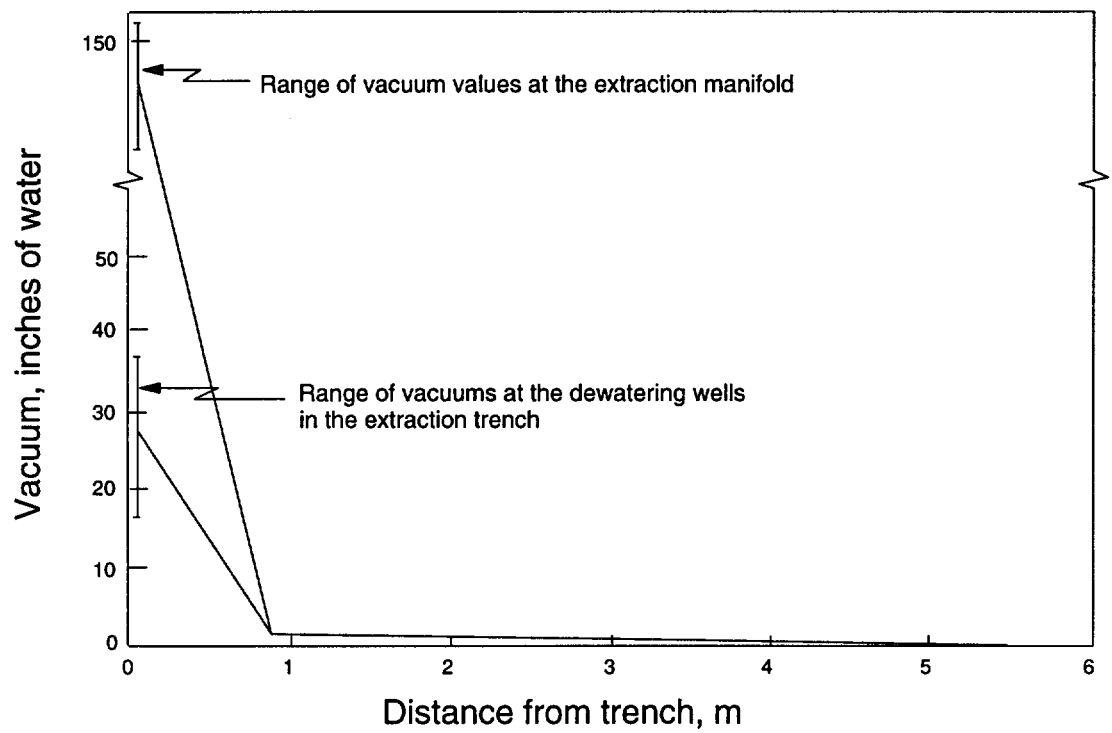


Figure 3.8. Schematic drawing of vacuum decreases with distance from the extraction trenches.

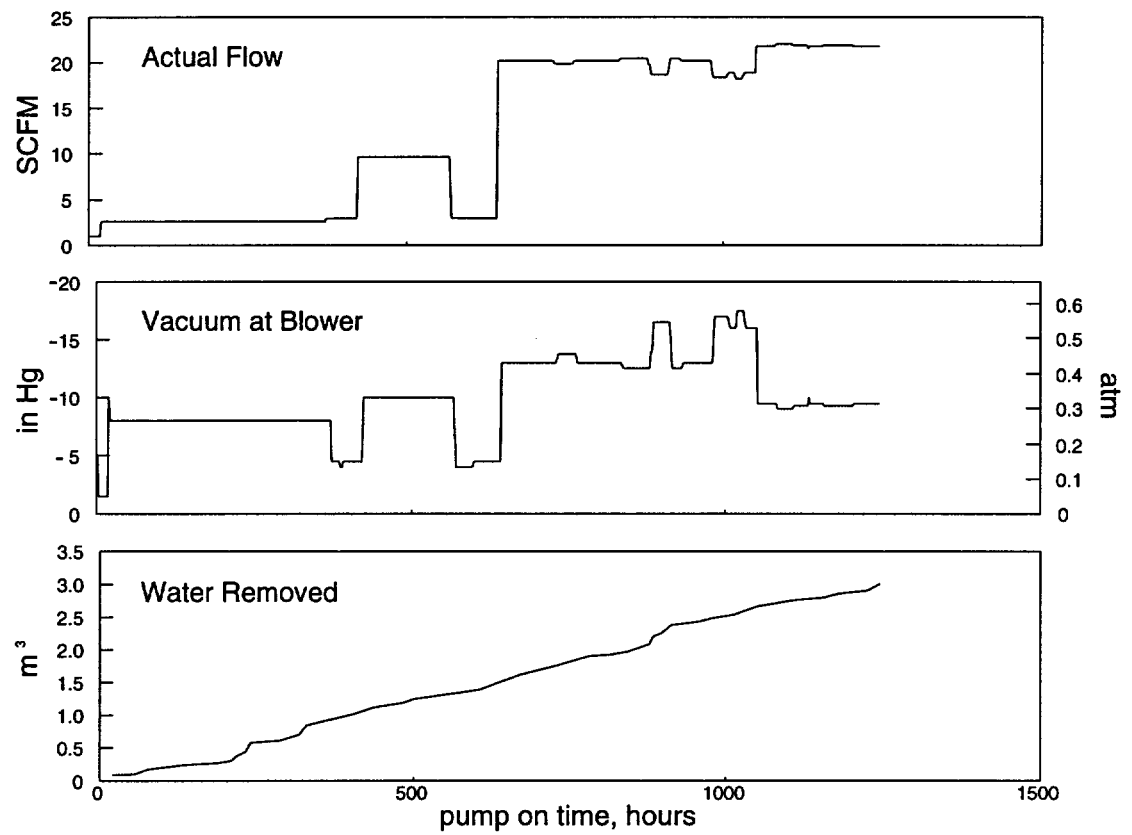


Figure 3.9. Flow, applied vacuum and water removed during extraction as a function of time during the 1993 field season.

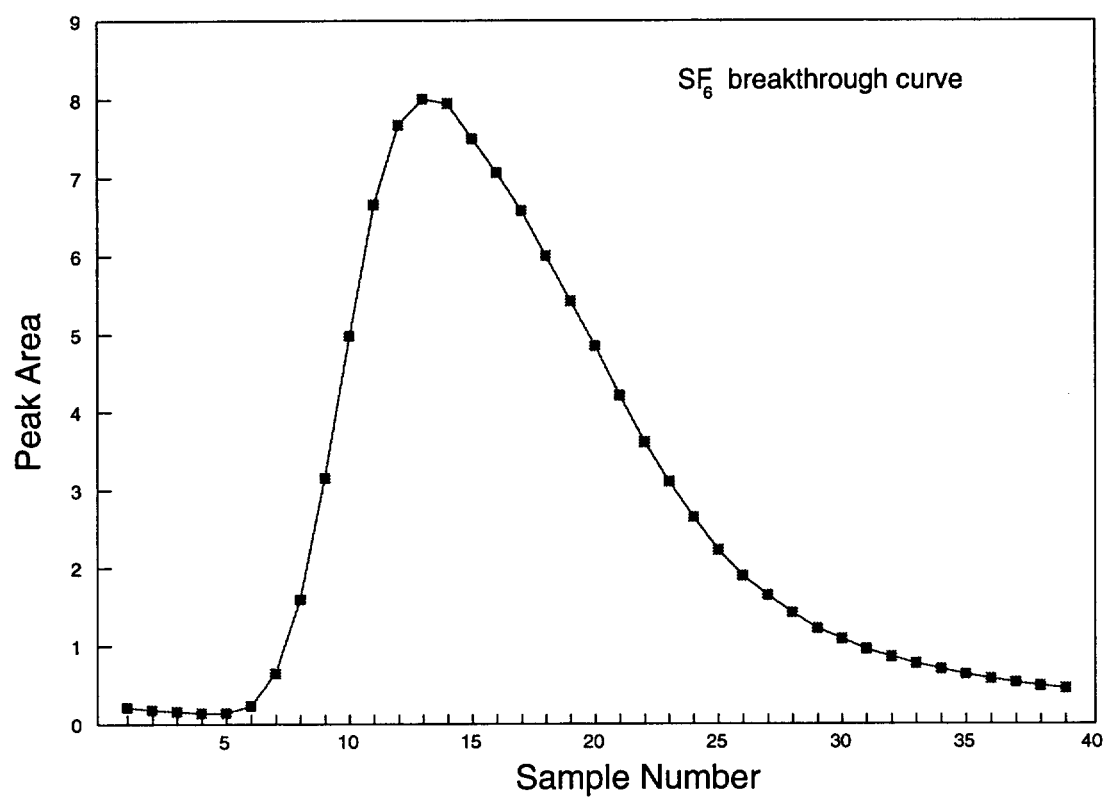


Figure 3.10. Breakthrough of SF_6 injected at point C-9. Each cycle represents 10 minutes.

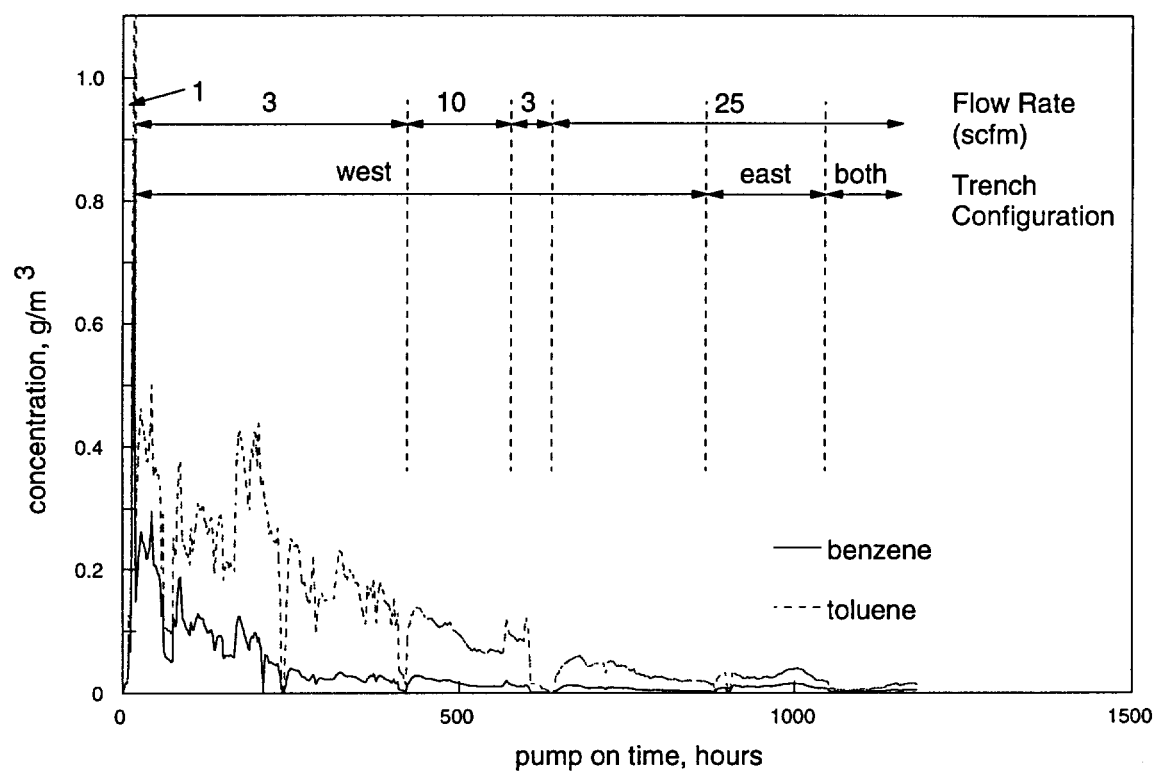


Figure 3.11. Offgas concentrations (g/m^3) of benzene and toluene and the SVE conditions during the 1993 field season.

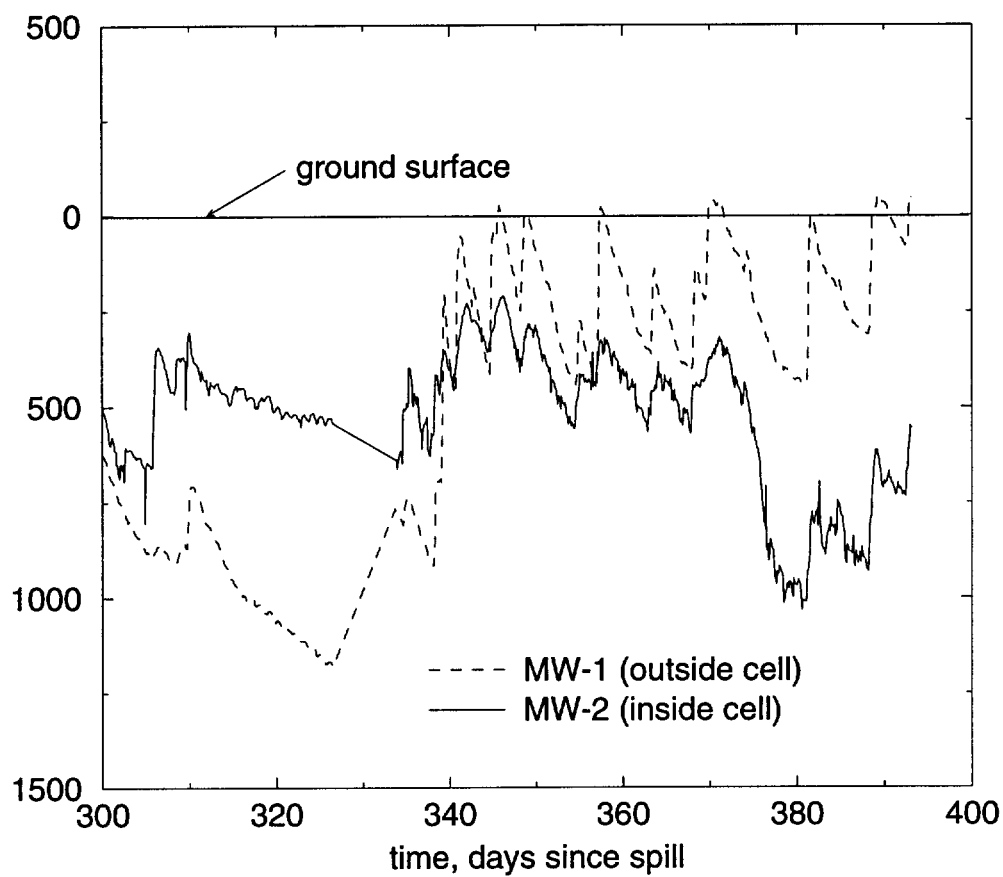


Figure 3.12. Water levels in monitoring wells MW-1 and MW-2 during the 1993 field season.

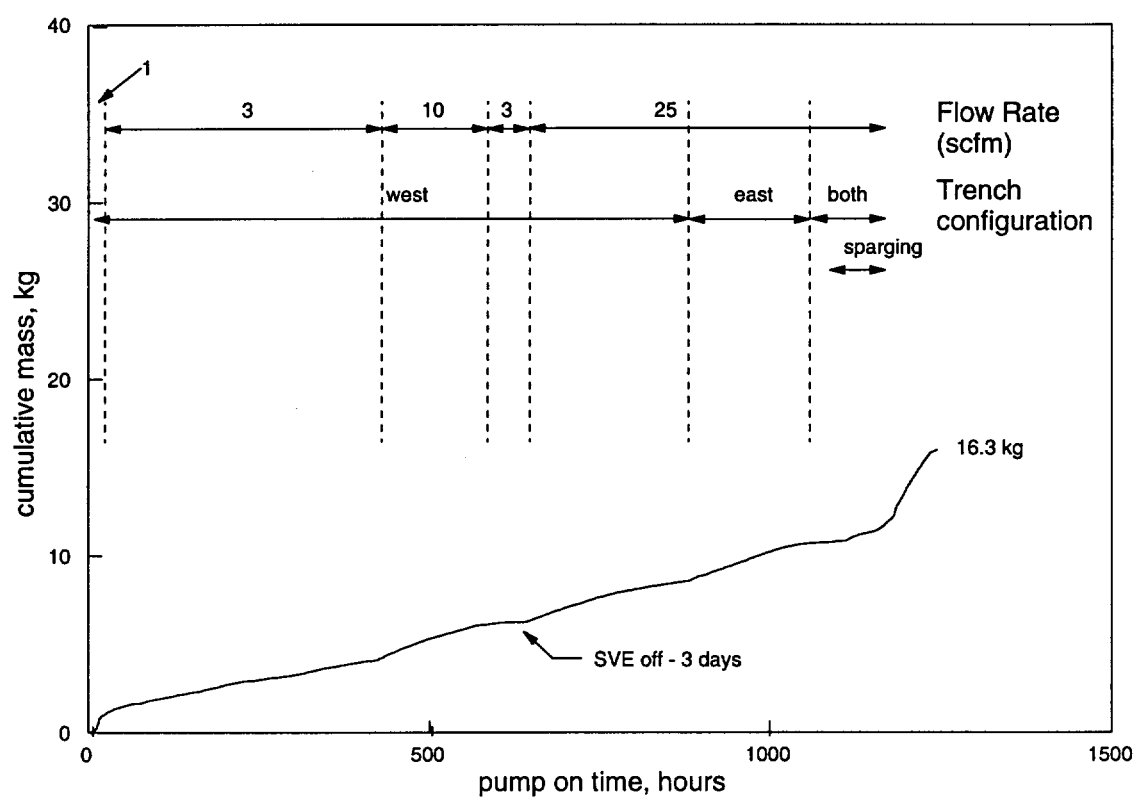


Figure 3.13. Cumulative mass of hydrocarbons recovered (kg) and the SVE conditions during the 1993 field season.

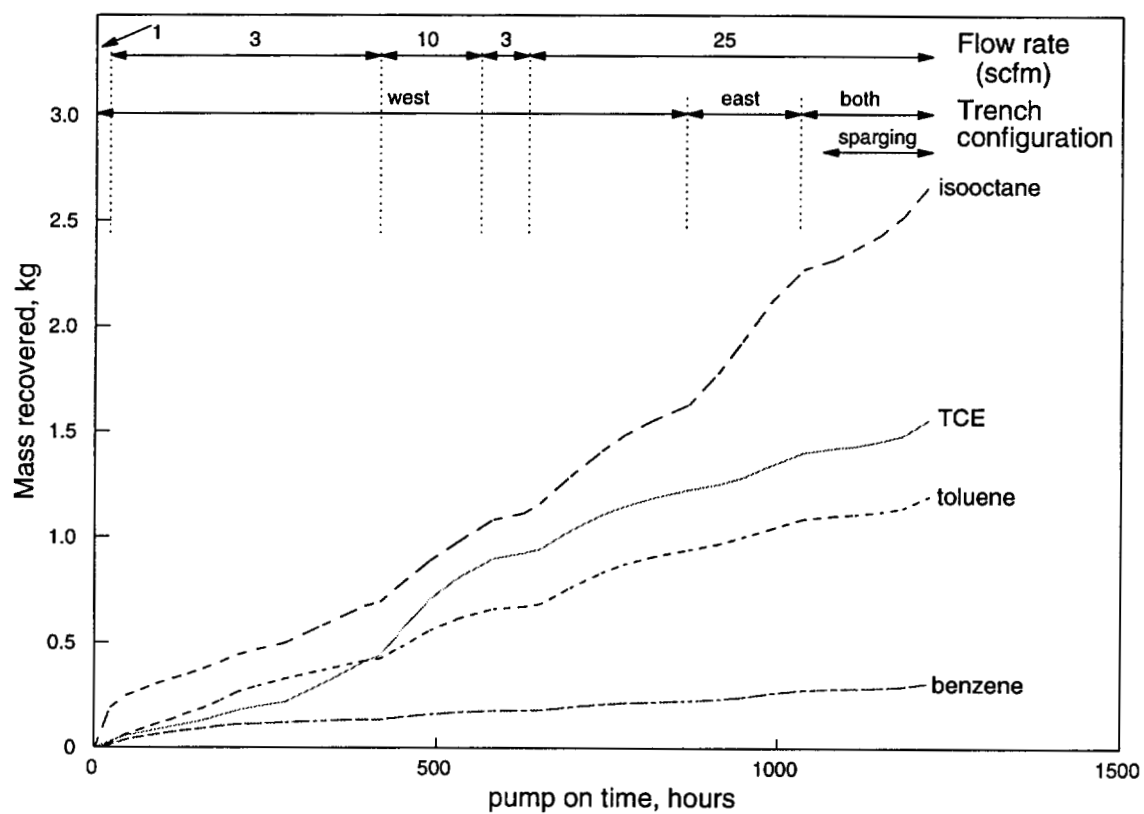


Figure 3.14. Mass recovery of isooctane, TCE, toluene and benzene and SVE conditions during the 1993 field season.

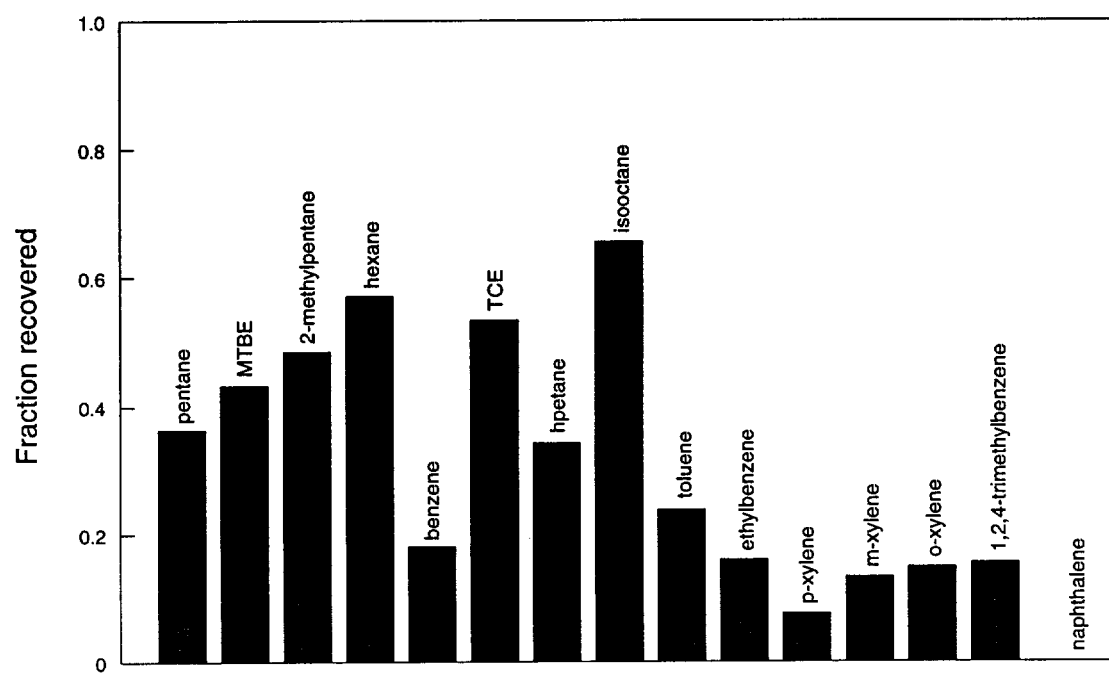


Figure 3.15. Fraction of mass recovered for each of the NAPL components in 1993.

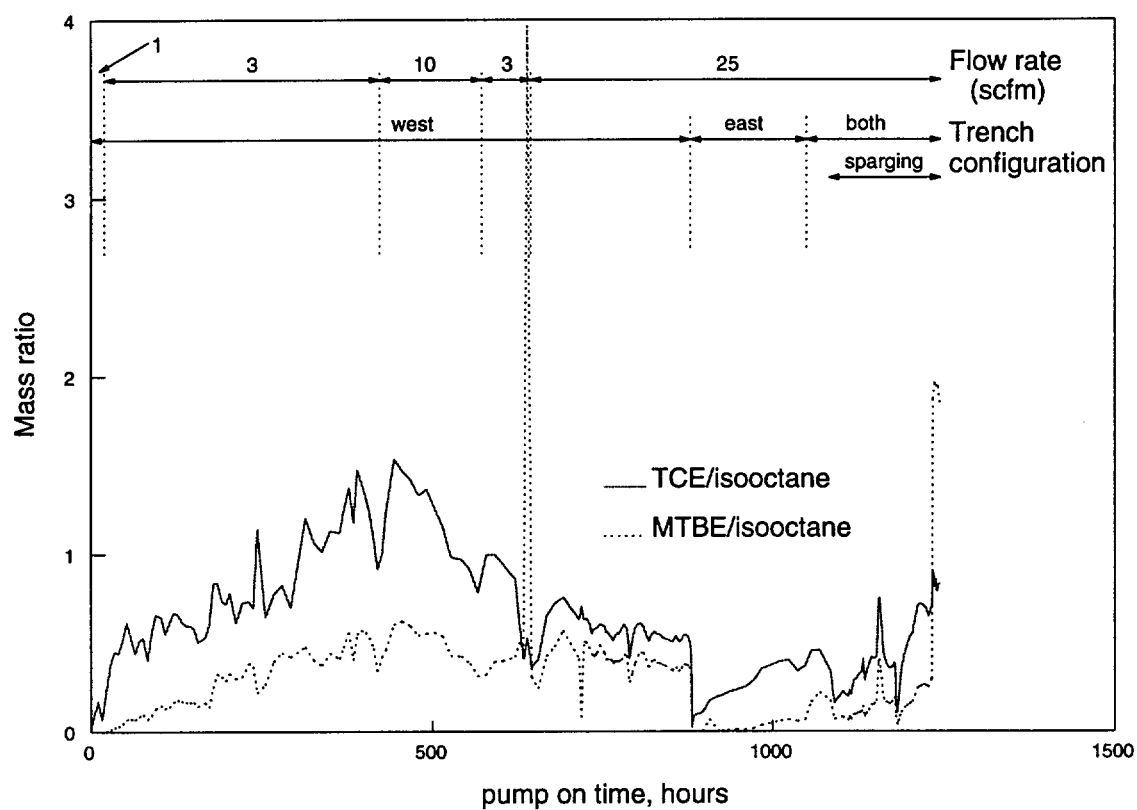


Figure 3.16. Ratios of TCE and MTBE to isooctane and SVE conditions during the 1993 field season.

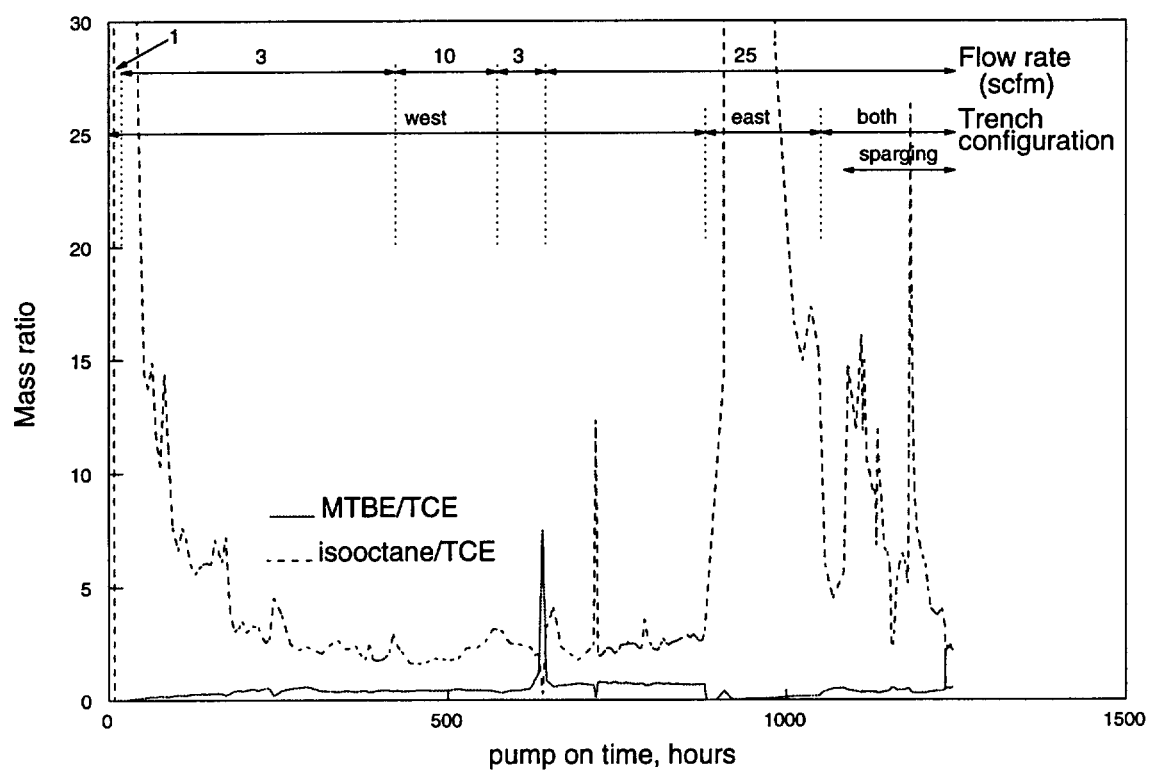


Figure 3.17. Ratios of MTBE and isooctane to TCE and SVE conditions during the 1993 field season.

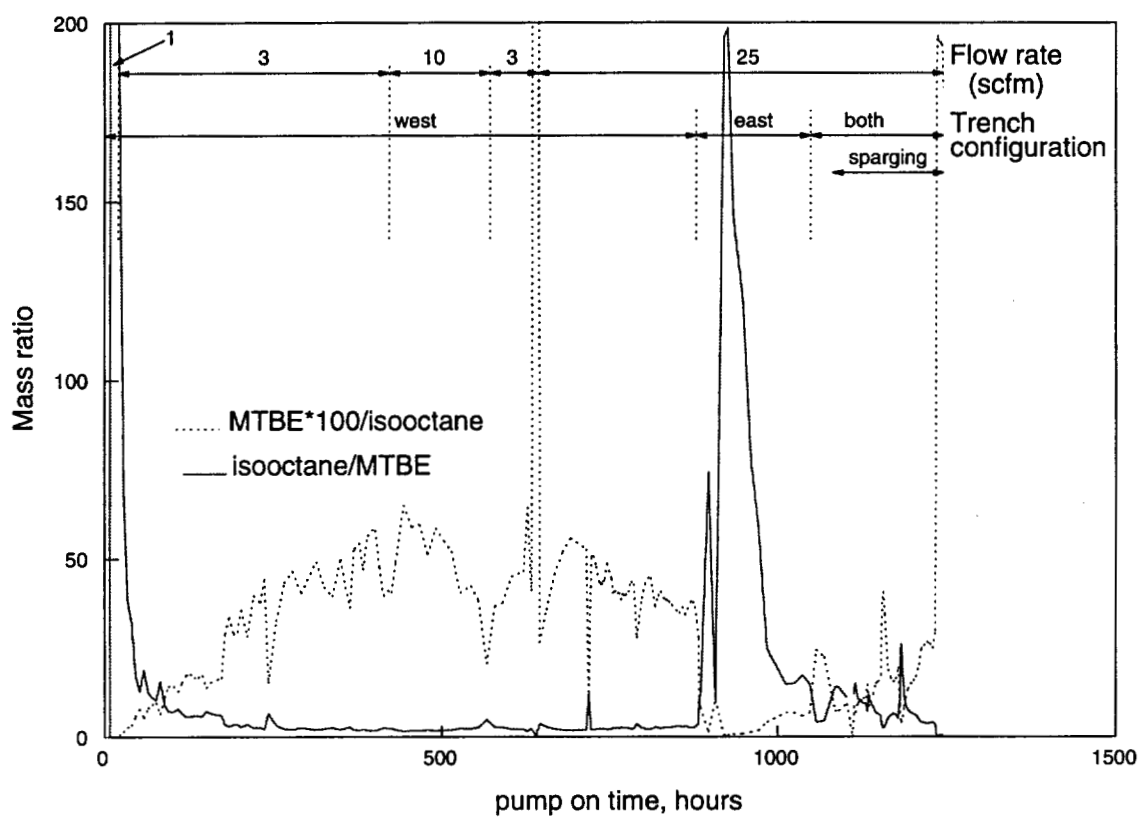


Figure 3.18. Ratios of MTBE to isooctane and isooctane to MTBE and SVE conditions during the 1993 field season.

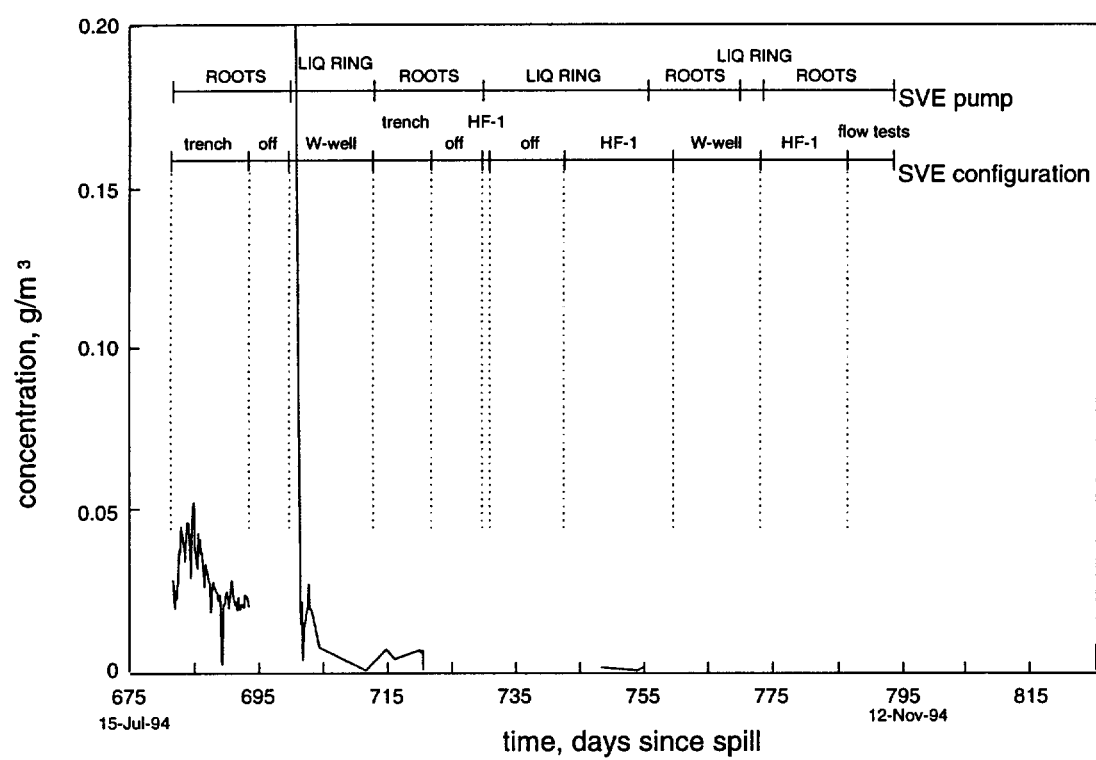


Figure 3.19. Total hydrocarbon concentrations in the offgas during the 1994 field season.

SVE on W-wells with ROOTS

pressures in "in H₂O"

Oct 07 (-0.19)

Oct 17 -0.63

N

Scale



Legend

- AS - Air sparging well
- V - Vapor monitoring well
- △ IW - Gasoline injection well
- MW - Groundwater monitoring well
- C - Core hole
- * W - Vertical 2" vapor extraction well

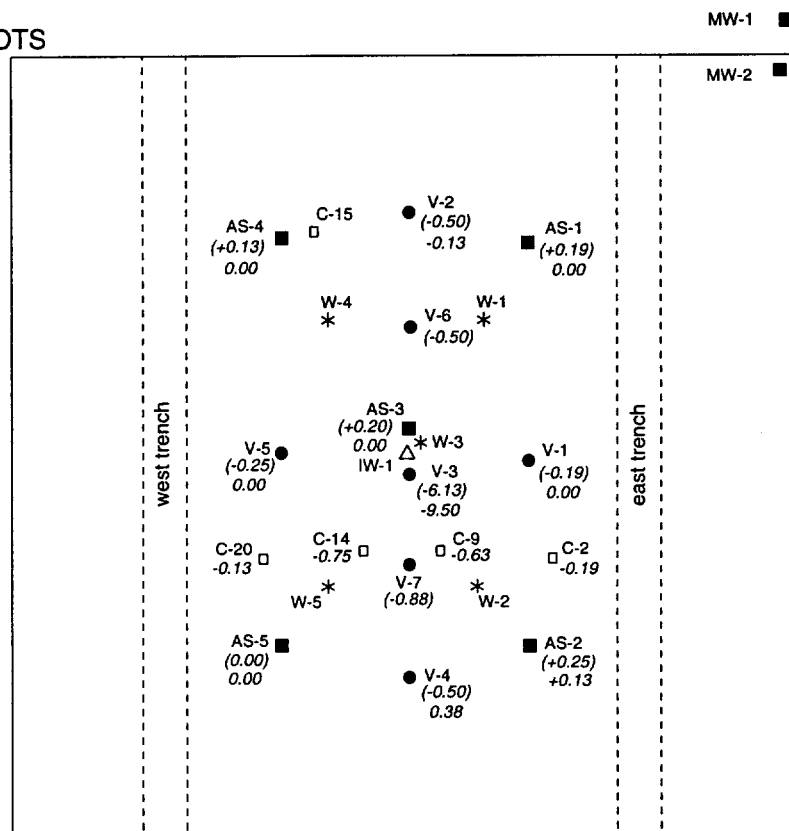


Figure 3.20. Vacuum distribution during extraction from the W-wells using the Roots pump during the 1994 field season.

SVE on W-wells with Liquid ring

pressures in "in H_2O "
 Aug 08 (0.00)
 Aug 15 -0.01

N


Scale


Legend

- AS - Air sparging well
- V - Vapor monitoring well
- △ IW - Gasoline injection well
- MW - Groundwater monitoring well
- C - Core hole
- ▲ HF - Hydraulic fracture well
- * W - Vertical 2" vapor extraction well

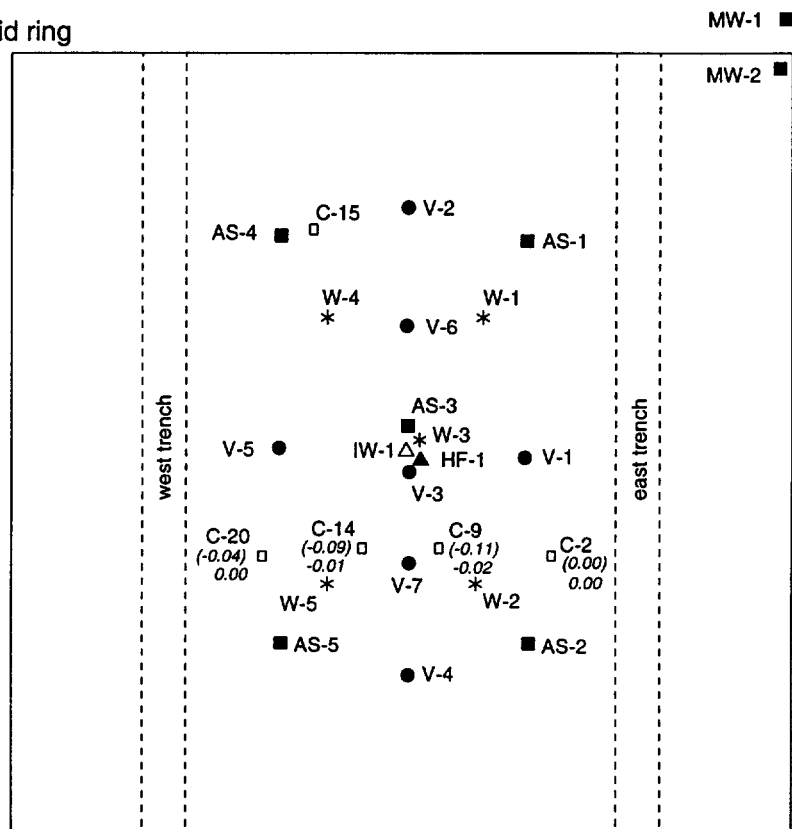


Figure 3.21. Vacuum distribution during extraction from the W-wells using the liquid ring pump during the 1994 field season.

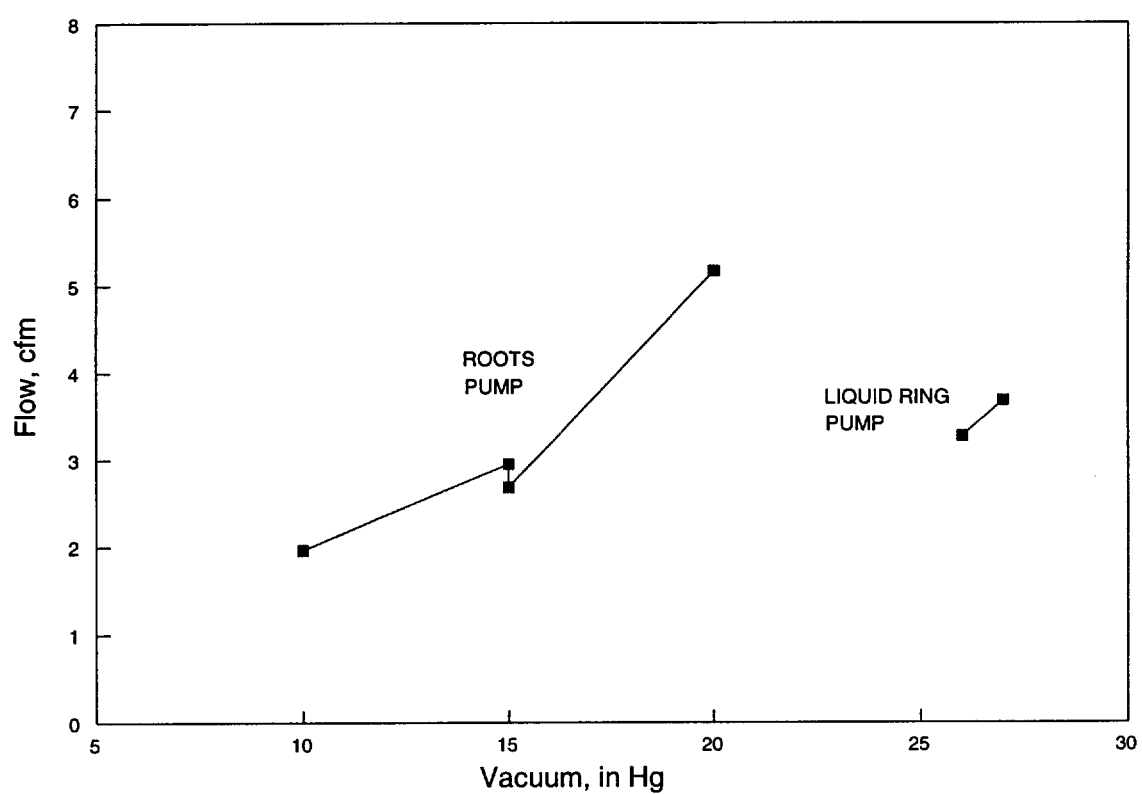


Figure 3.22. Air flow from the W-wells as determined by helium tracer test during the 1994 field season.

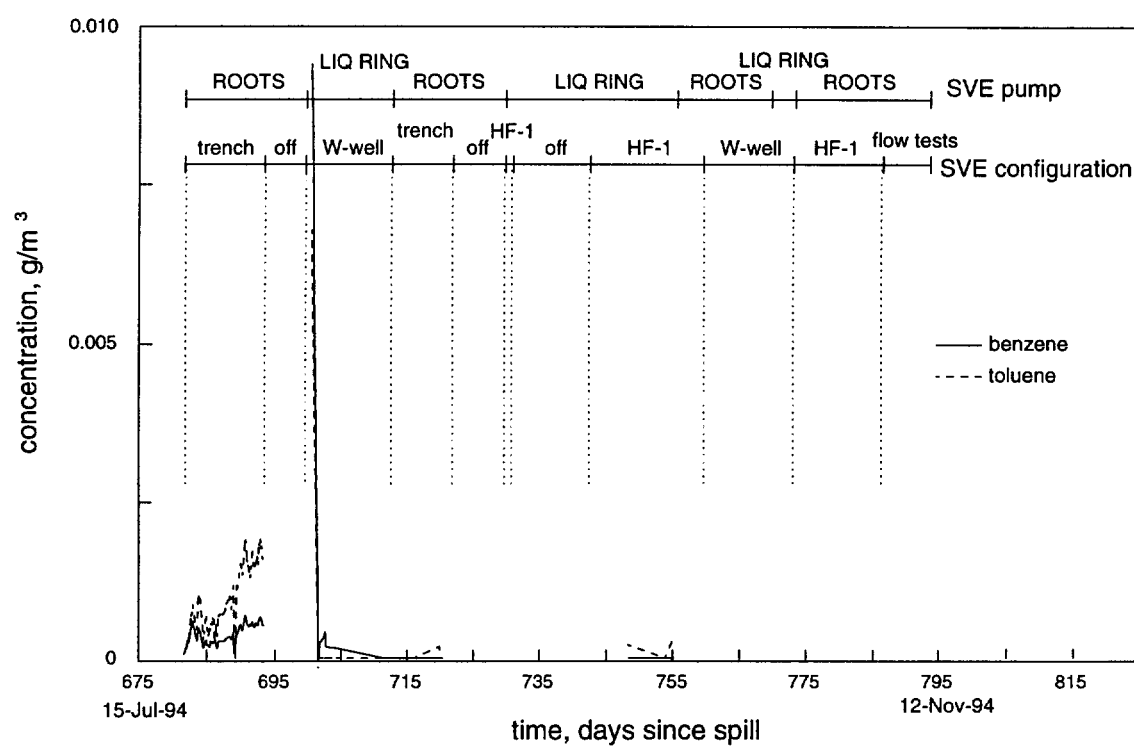


Figure 3.23. Offgas concentrations of benzene and toluene and SVE conditions during the 1994 field season.

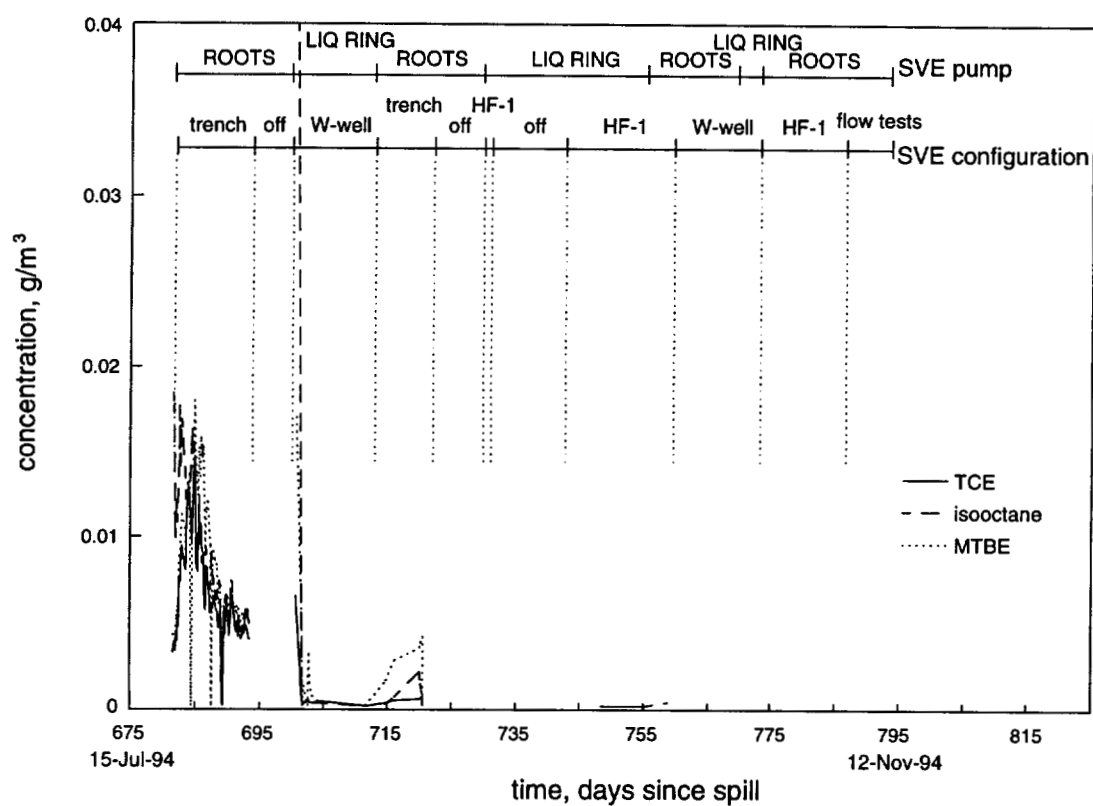


Figure 3.24. Offgas concentrations of TCE, MTBE and isooctane and SVE conditions during the 1994 field season.

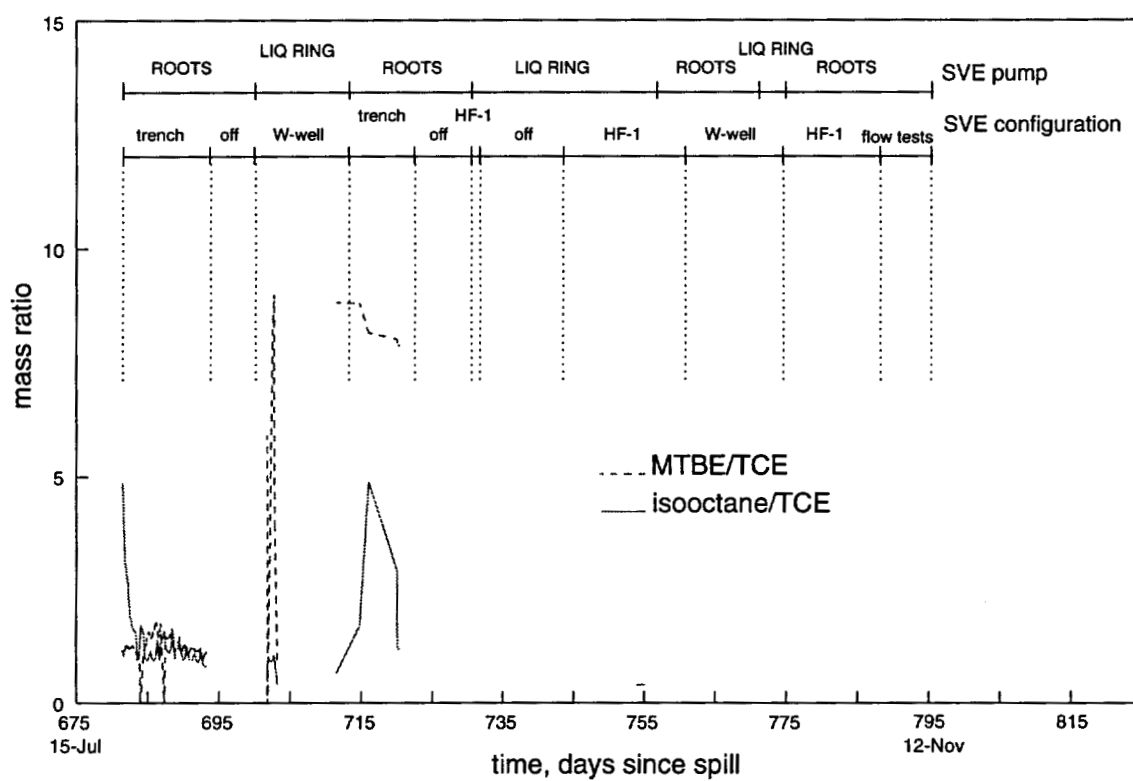


Figure 3.25. Ratios of MTBE and isooctane to TCE and SVE conditions during the 1994 field season.

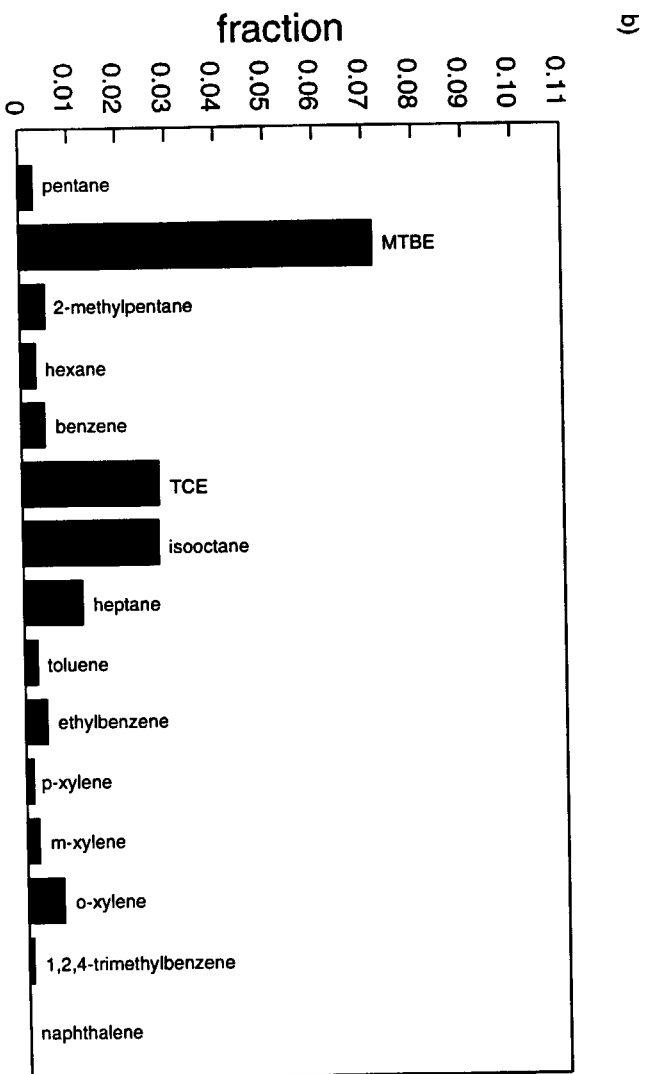
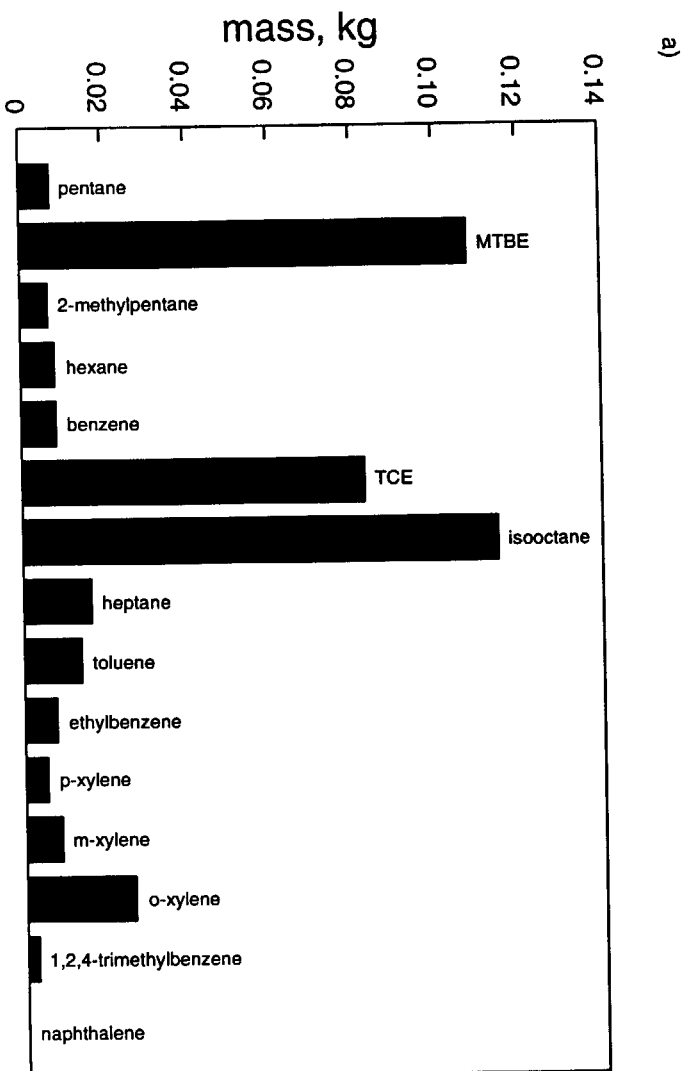


Figure 3.26. a) Masses of individual compounds recovered during the 1994 field season,
 b) Fractions of masses of each compound recovered during the 1994 field season.

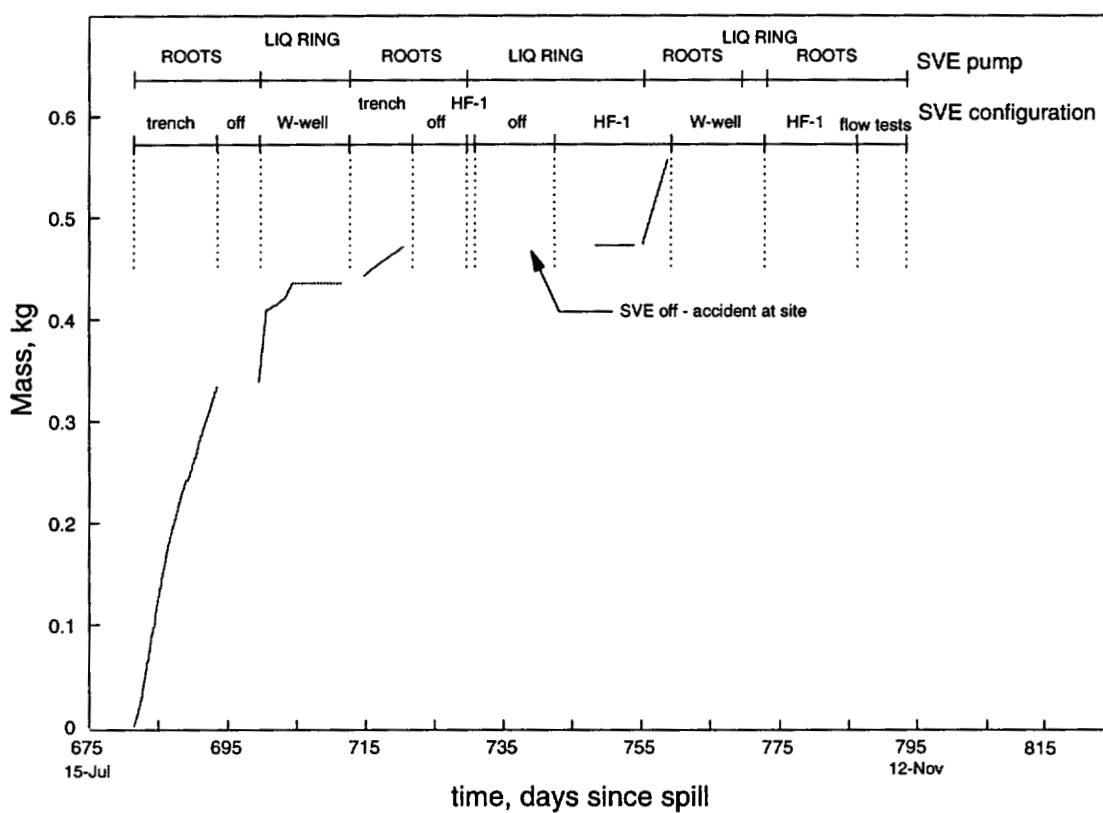


Figure 3.27. Cumulative mass recovered and SVE conditions during the 1994 field season.

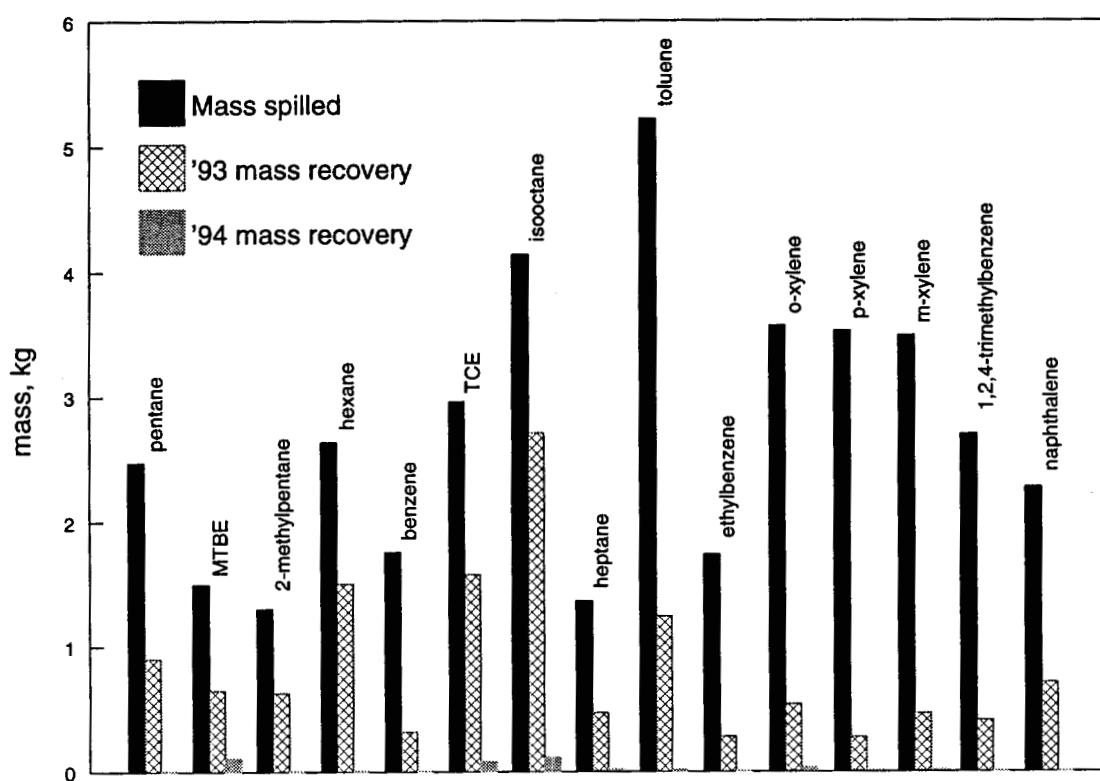


Figure 3.28. Total mass of each compound in the spill mix released, removed in 1993 and removed in 1994.

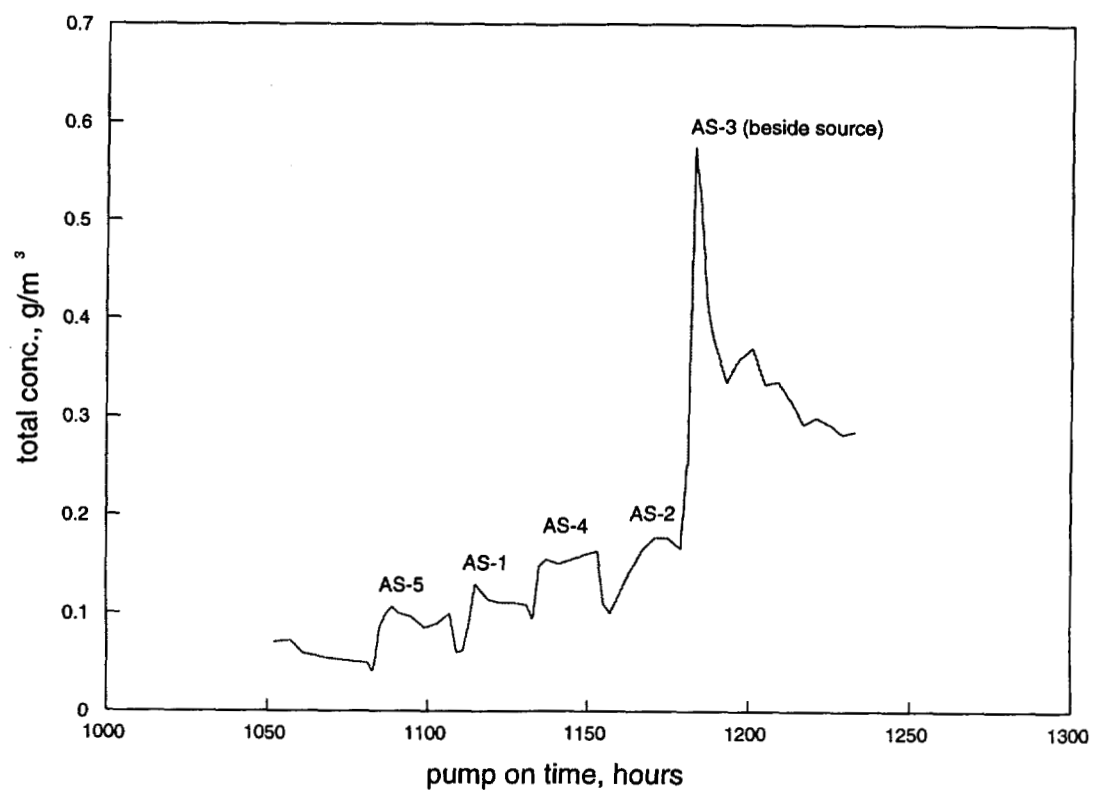


Figure 3.29. SVE concentrations during air sparging as a function of time and the SVE conditions during the 1993 field season.

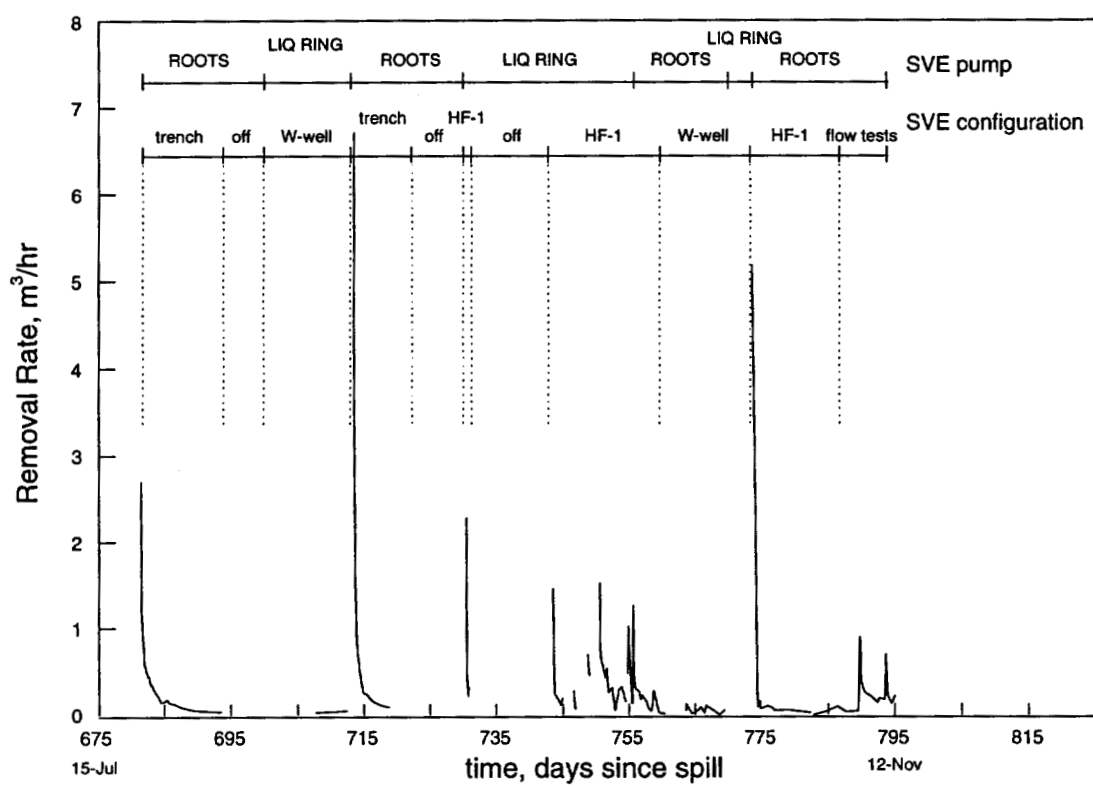


Figure 3.30. Rate of water recovery from the trenches and hydrofracture and SVE conditions during the 1994 field season.

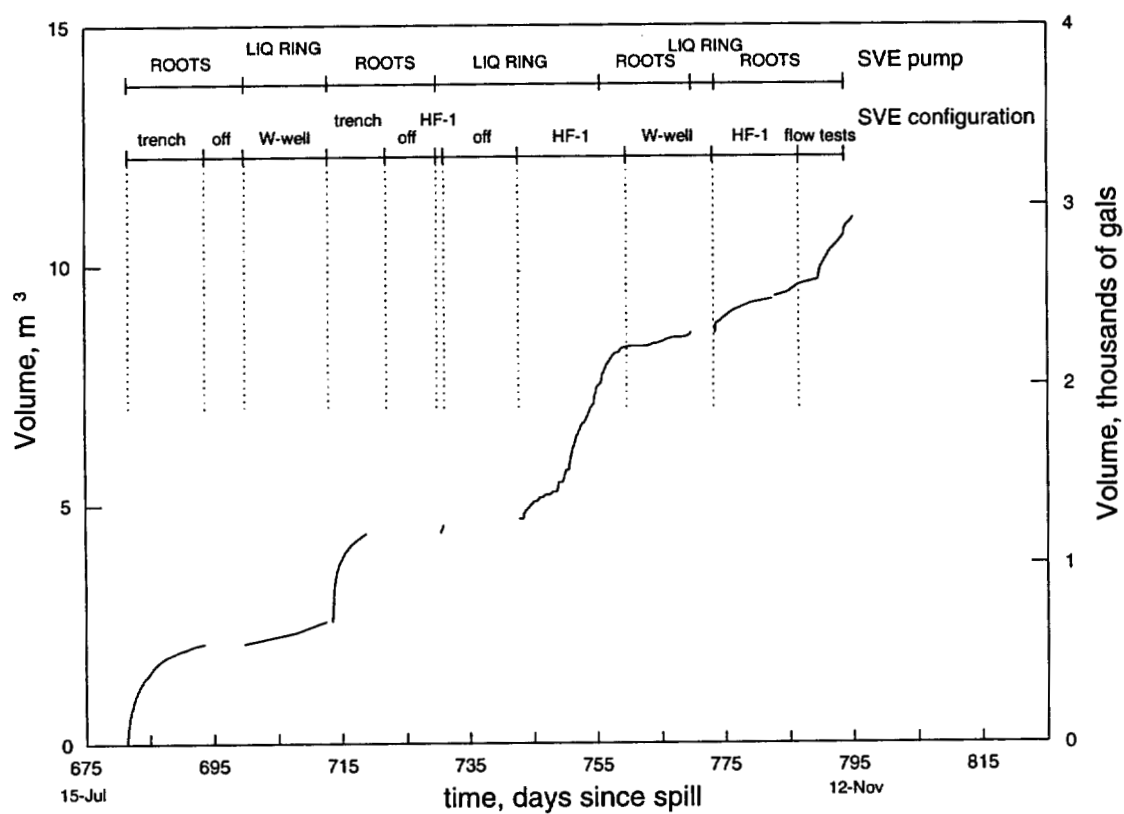


Figure 3.31. Cumulative water recovery and SVE conditions during the 1994 field season.

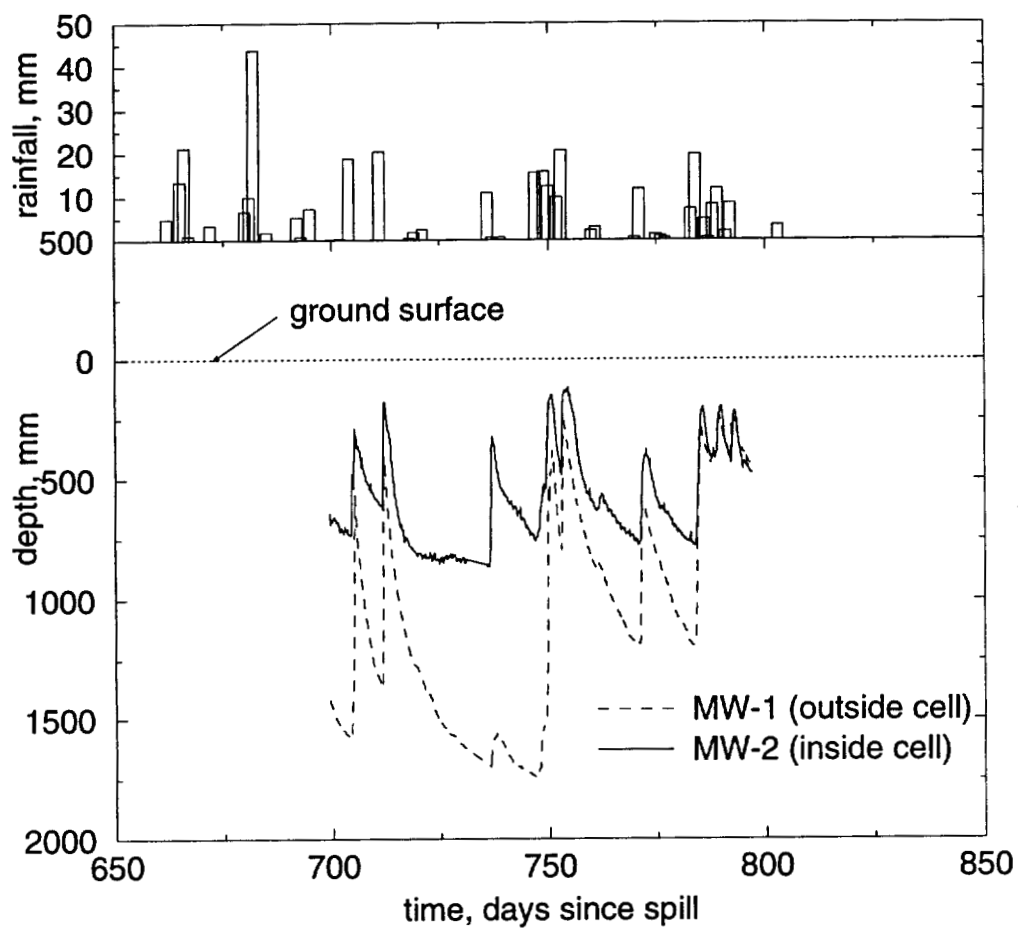


Figure 3.32. Water levels in monitoring wells MW-1 and MW-2 along with daily rainfall data during the 1994 field season.

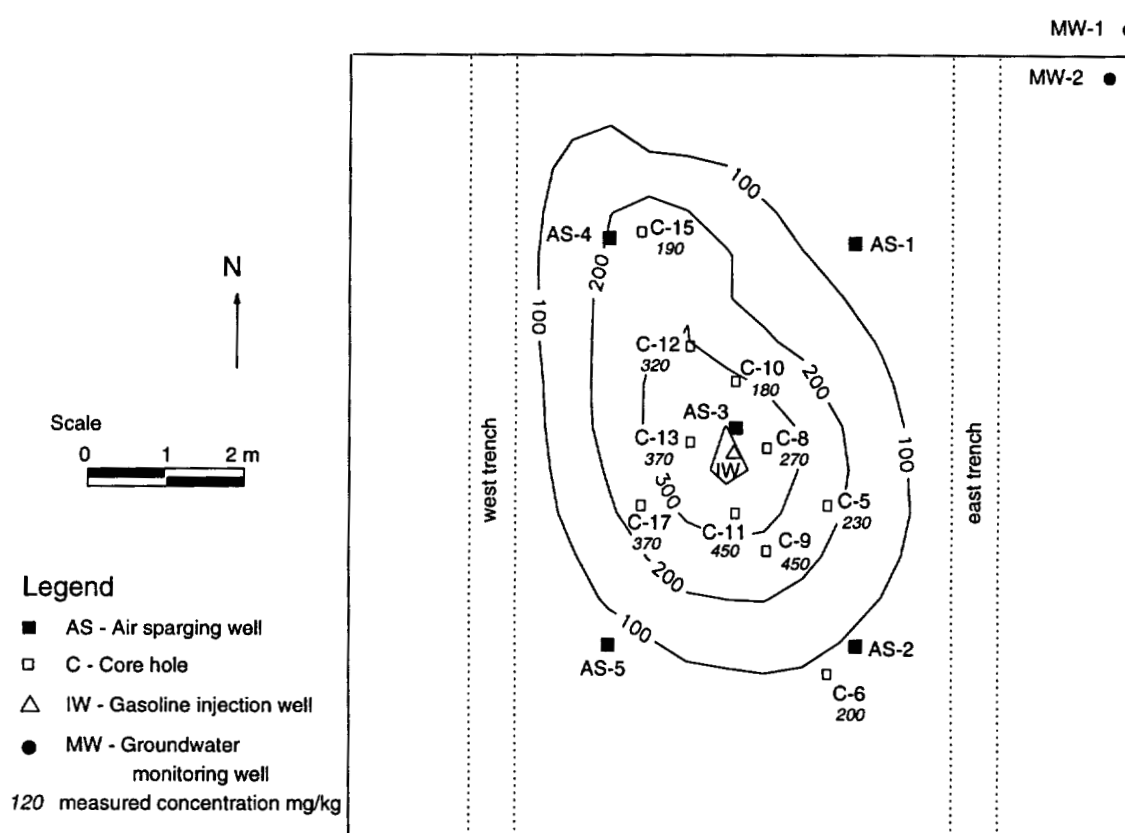


Figure 3.33. Hydrocarbon concentration contours following the 1993 field season at the 90 cm depth (mg/kg).

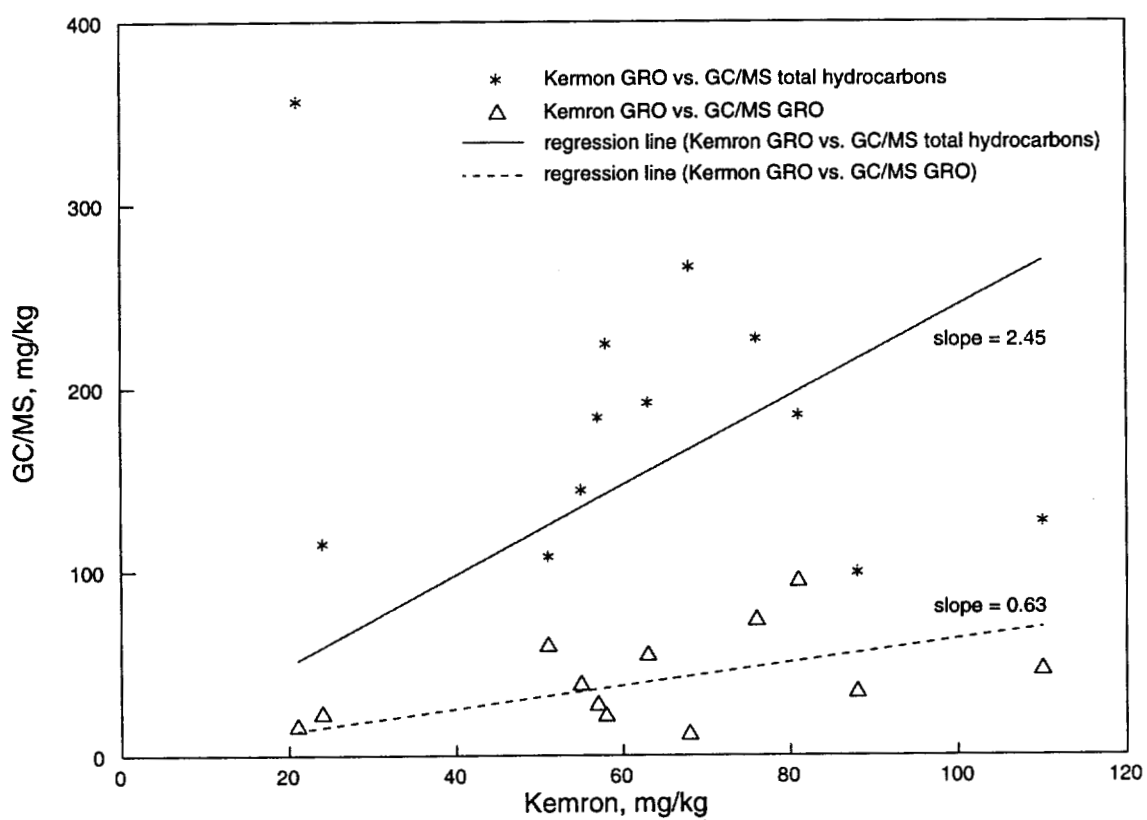


Figure 3.34. Scatter plot showing Kemron GRO analyses versus OGI GC/MS totals (mg/kg).

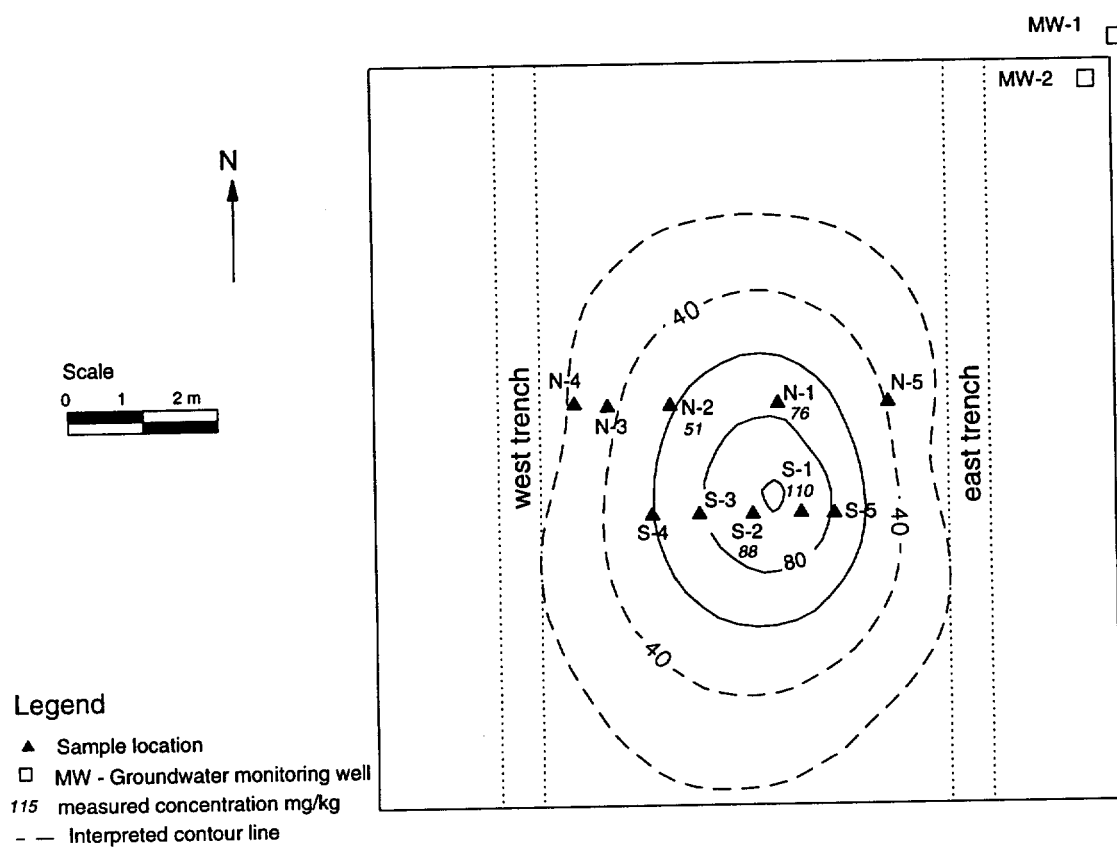


Figure 3.35. GRO concentration contours following remediation, taken in 1995 at the ~90 cm depth (mg/kg).

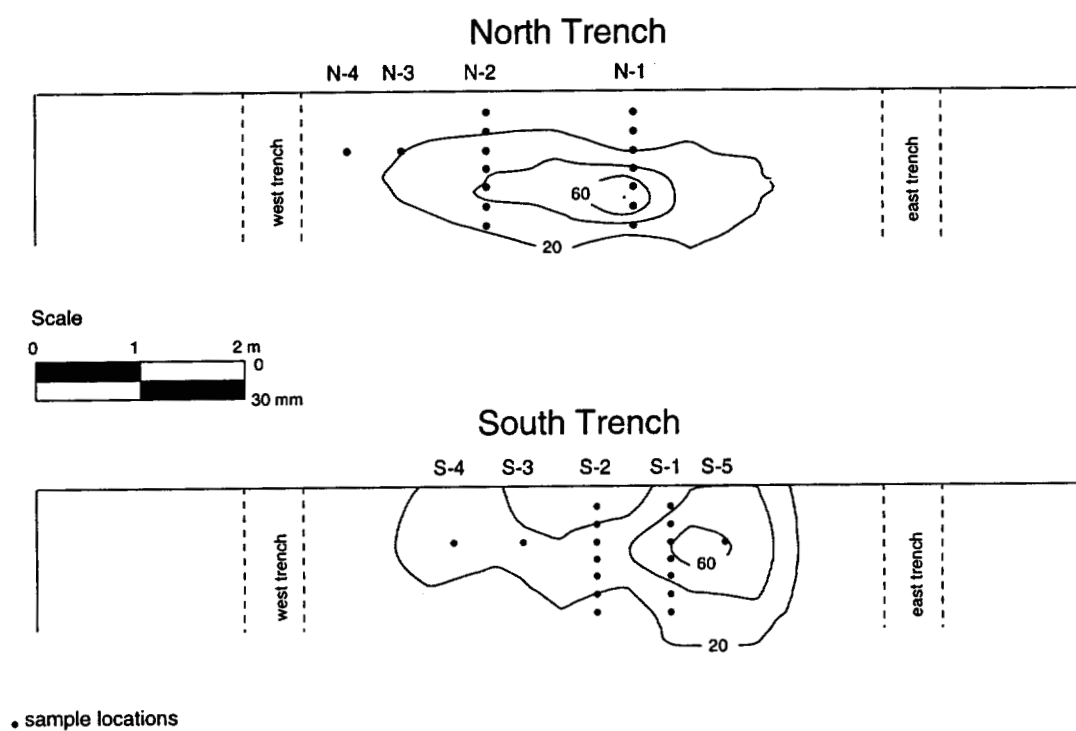


Figure 3.36. OGI GRO based soil concentration profiles for the north and south excavated trenches (mg/kg).

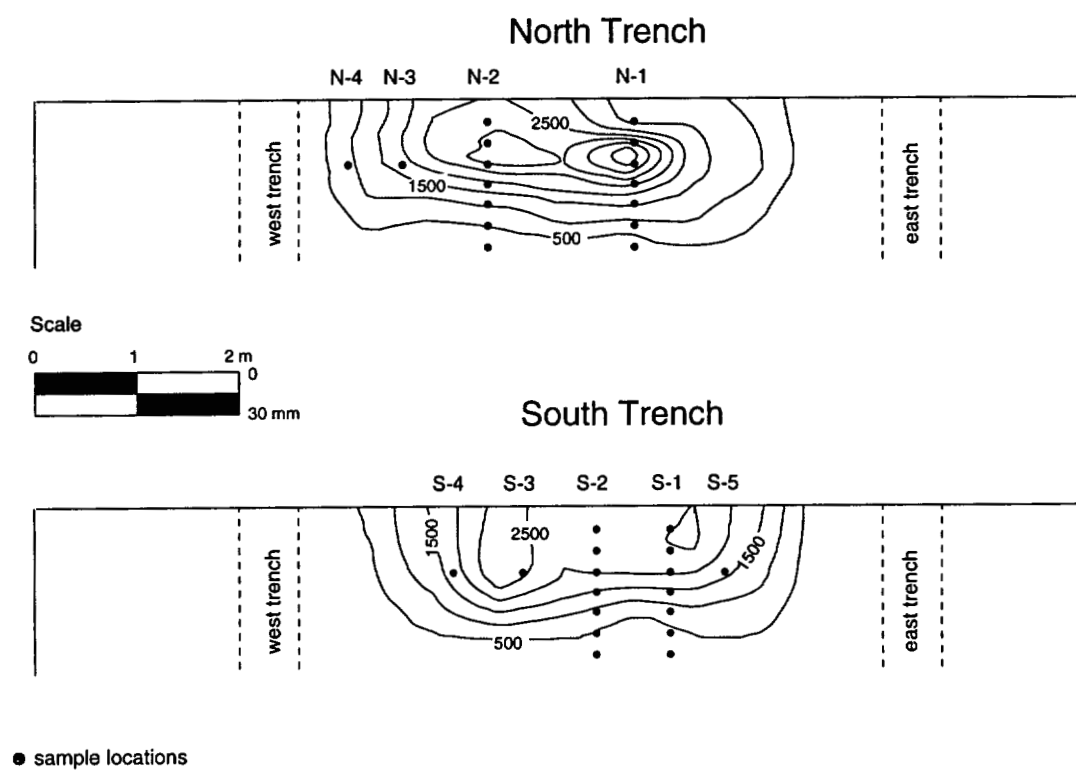


Figure 3.37. Estimated initial mass distribution based on the final naphthalene distribution (mg/kg).

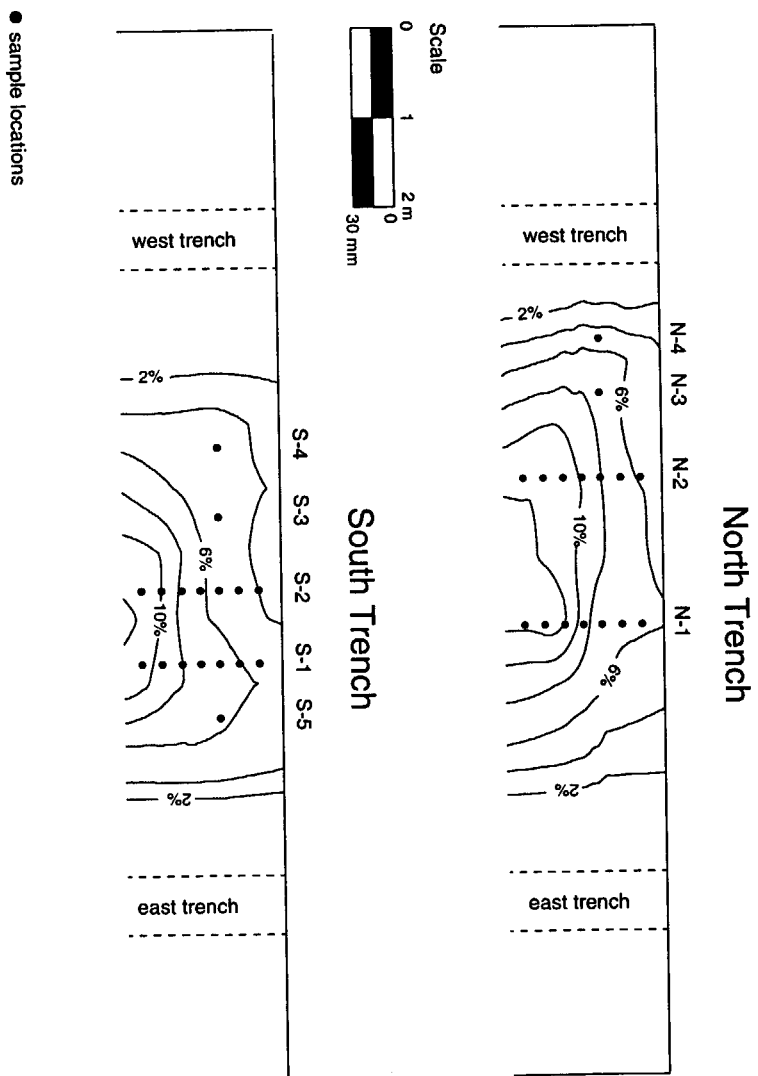


Figure 3.38. Percent of initial mass remaining in the soil based on the estimated initial distribution and final GC/MS soils analyses.

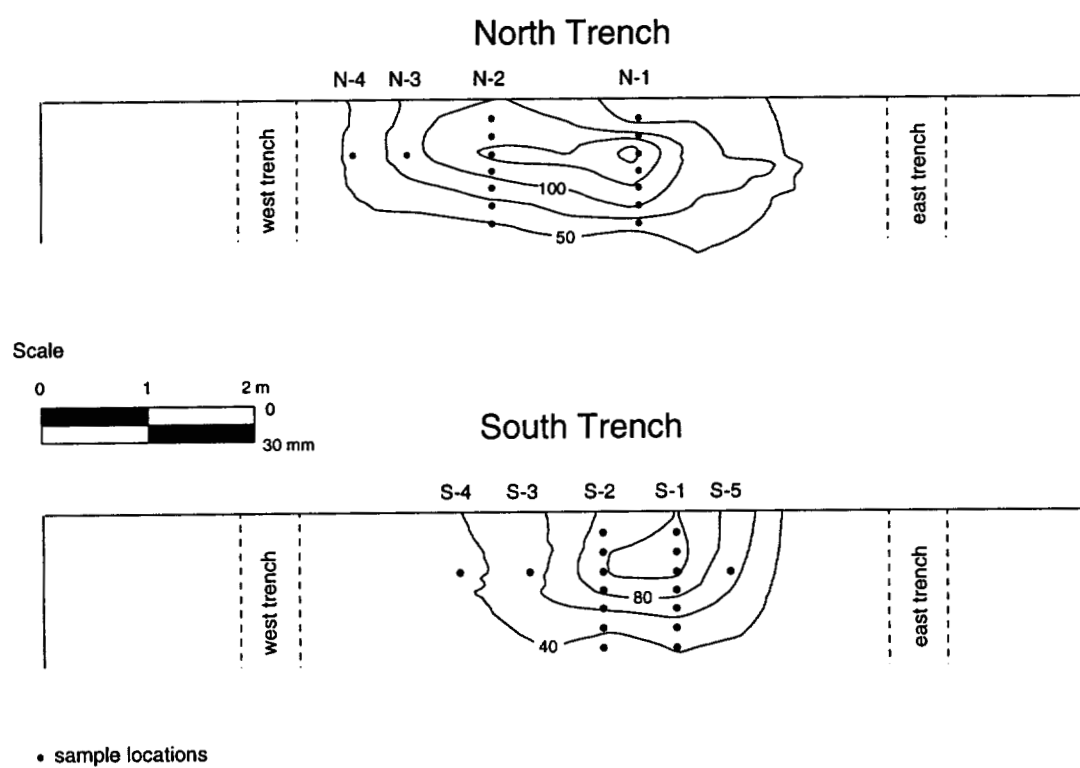


Figure 3.39. Final mass distribution in the soil after remediation based on GC/MS analyses (mg/kg).

Table 3.1. Breakthrough times for the SF₆ tracer tests

Well	Distance from trench (m)	Break-through time (hours)	Effective porosity (%)
C-2	5	11:40	813
C-9	4	1:05	107
V-7	3	2:10	197
C-14	2.7	1:36	261
C-20	0.8	1:45	805

Table 3.2. Mass removed in the extracted water.

Compound	Mass (g)
pentane	0.01
MTBE	5.64
2-methylpentane	0.00
hexane	0.04
benzene	0.60
tce	0.84
isooctane	0.00
heptane	0.01
toluene	1.25
ethylbenzene	0.39
p-xylene	0.37
m-xylene	0.54
o-xylene	0.49
1,2,4-trimethylbenzene	0.35
naphthalene	0.00
Total mass (g)	10.55

Table 3.3. Calculated mass recovery for air sparging.

Sparge location	% sparge air recovered	Mass collected (kg)	Adjusted mass (kg)
AS-3	16	0.65	4.00
AS-1	13	0.06	0.44
AS-2	13	0.11	0.82
AS-4	45	0.09	0.20
AS-5	45	0.05	0.11
		total	5.67

Table 3.4. Mass of Hydrocarbons Accounted for by Soil Core Analysis

Remediation Conditions	Mass Accounted for from soil analysis	Mass removed	Total mass accounted for
spill			40 kg (100%)
pre-first season - no remediation	13.1 kg (32%)		13.1 kg (32%)
post-first season - SVE from trenches	14.0 kg (34%)	10.6 kg (26%) SVE 5.7 kg (15%) Air Sparging	30.3 kg (75%)
pre-second season	9.9 kg (24%)	16.3 kg (40%)	26.2 kg (64%)
pre-third season - SVE finished	3.3 kg (8%)	<1 kg+16.3 kg (43%)	20.6 kg (51%)

Table 3.5. Final compound-specific analyses for all sample levels.

	level a (g)	level b (g)	level c (g)	level d (g)	level e (g)	level f (g)	level g (g)	'95 soil (g)	'95 soil (kg)
pentane	-	-	-	-	-	-	-	0.00	0.00
MTBE	-	-	1.73	5.68	7.45	11.62	5.90	32.39	0.03
2-methylpentane	-	-	0.30	-	-	0.60	-	0.90	0.00
hexane	-	-	0.85	0.58	-	1.47	0.88	3.77	0.00
benzene	-	-	-	0.72	-	4.18	2.07	6.97	0.01
TCE	-	0.32	2.01	4.52	6.36	11.59	5.99	30.79	0.03
isooctane	17.71	32.02	23.33	16.17	6.91	7.42	1.26	104.82	0.10
heptane	0.92	1.76	2.42	1.00	0.53	0.68	-	7.30	0.01
toluene	-	-	0.65	1.19	4.40	-	-	6.23	0.01
ethylbenzene	0.51	1.06	11.93	19.30	23.29	22.81	6.45	85.34	0.09
p-xylene	0.59	1.90	20.05	19.51	22.37	31.64	0.42	96.48	0.10
m-xylene	-	1.60	6.53	5.87	6.57	5.77	0.88	27.22	0.03
o-xylene	3.15	29.57	206.24	56.16	48.45	42.91	2.19	388.68	0.39
1,2,4-trimethylbenzene	7.43	33.77	49.31	50.47	39.58	32.63	8.80	222.00	0.22
naphthalene	507.49	1080.38	825.55	390.14	242.34	148.09	44.73	2765.00	2.77
GRO	37.84	147.25	182.42	243.18	196.63	184.49	32.72	1024.54	1.02
Total hydrocarbons	537.79	1182.38	1150.90	571.31	408.24	321.40	79.56	4417.27	4.42

Table 3.6. Compound-specific mass balance (in kg).

	Mass initially spilled (kg)	'93 SVE mass removed (kg)	'93 IAS mass removed (kg)	'94 SVE mass removed (kg)	'95 mass remaining in soil (kg)	Total mass acc't for (kg)	Total mass unacc't for (kg)
pentane	2.5E-0	8.8E-1	1.4E-1	8.0E-3	0.0E-0	1.0E-0	1.5E-0
MTBE	1.5E-0	6.1E-1	2.6E-1	1.1E-1	3.2E-2	1.0E-0	4.9E-1
2-methylpentane	1.3E-0	5.9E-1	2.1E-1	7.0E-3	1.0E-3	8.1E-1	4.9E-1
hexane	2.6E-0	1.4E-0	3.6E-1	8.0E-3	4.0E-3	1.8E-0	8.3E-1
benzene	1.8E-0	3.0E-1	1.2E-1	9.0E-3	7.0E-3	4.3E-1	1.3E-0
TCE	3.0E-0	1.4E-0	8.2E-1	8.3E-2	3.1E-2	2.4E-0	5.9E-1
isooctane	4.1E-0	2.4E-0	1.9E-0	1.2E-1	1.0E-1	4.5E-0	-3.9E-1
heptane	1.4E-0	4.3E-1	2.0E-1	1.6E-2	7.0E-3	6.5E-1	7.1E-1
toluene	5.2E-0	1.1E-0	5.9E-1	1.4E-2	6.0E-3	1.8E-0	3.5E-0
ethylbenzene	1.7E-0	1.8E-1	5.7E-2	8.0E-3	8.5E-2	3.3E-1	1.4E-0
p-xylene	3.5E-0	2.2E-1	2.9E-1	5.0E-3	9.6E-2	6.1E-1	2.9E-0
m-xylene	3.5E-0	3.9E-1	4.2E-1	9.0E-3	2.7E-2	8.5E-1	2.6E-0
o-xylene	3.6E-0	4.9E-1	2.2E-1	2.6E-2	3.9E-1	1.1E-1	2.4E-0
1,2,4-trimethylbenzene	2.7E-0	4.1E-1	1.0E-3	3.0E-3	2.2E-1	6.3E-1	2.1E-0
naphthalene	2.3E-0	0.0E-0	0.0E-0	2.0E-3	2.8E-0	2.8E-0	-4.9E-1

Table 3.7. Compound-specific mass balance (in % of initial mass).

	Total percent removed by air flushing (%)	'95 percent remaining in soil (%)	Total percent acc't for (%)	Total percent unacc't for (%)
pentane	41.2	0.0	41.2	58.8
MTBE	65.0	2.2	67.1	32.9
2-methylpentane	62.6	0.0	62.6	37.4
hexane	68.5	0.1	68.7	31.3
benzene	24.2	0.4	24.6	75.4
TCE	79.2	1.0	80.2	19.8
isooctane	106.8	2.5	109.4	-9.4
heptane	47.4	0.5	47.9	52.1
toluene	33.5	0.1	33.6	66.4
ethylbenzene	14.2	5.0	19.0	81.0
p-xylene	14.7	2.7	17.4	82.6
m-xylene	23.7	0.8	24.5	75.5
o-xylene	20.9	10.9	31.8	68.2
1,2,4-trimethylbenzene	15.3	8.2	23.5	76.5
naphthalene	0.0	121.3	121.4	-21.4

Table 3.8 Geochemical soil characteristics.

Soil Characteristic	
pH	7-8.2
organic carbon (by weight)	0-0.5%
nitrogen (by weight)	0.03-0.17%
phosphorous	0.065-0.076%
bulk density	1.5-1.8 g/cm ³
total porosity	~45%

Table 3.9. Microbial soil characteristics of the contaminated soil (cells/g).

Heterotrophic Aerobes	$10^5 - 10^7$
Heterotrophic Anaerobes	$10^4 - 10^6$
Hydrocarbon Utilizers	$10^2 - 10^5$

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CHAPTER 4

NUMERICAL MODELING OF LNAPL MOVEMENT AND REMOVAL BY SOIL VAPOR EXTRACTION

INTRODUCTION

Clay aquitards overlying sand, gravel and bedrock aquifers are common in many areas of Europe and North America. These low permeability soils are often considered a protective barrier in preventing the contamination of an underlying aquifer. The presence of fractures in these soils is an important factor in the transport of contaminants. The fractures provide an effective and a relatively fast pathway for transport, while the intact matrix blocks provide the bulk of the storage volume and therefore act as a retardation mechanism.

The analysis of contaminant transport in fractured low permeability media is important, since it may be used to predict the consequences of spills in these soils. However, the numerical modeling of groundwater flow and contaminant transport in these soils is a complicated problem due to a number of factors (Sudicky and McLaren, 1992). Numerical difficulties arise from the different time scales involved when modeling rapid advection through the fractures and the slow, but tenacious diffusion in the matrix blocks. Also, finite element and finite difference models based on a discrete fracture will require close nodal spacing at the fracture-matrix interface. The high concentration gradients that

exist at the fracture-matrix interface along with the contrast in time scales will limit the ability of a model to handle field scale problems. Practical difficulties arise when trying to characterize the fracture network and the physical and chemical transport properties of the media (Sudicky and McLaren, 1992).

Discrete fracture models can be analytical, semianalytical or numerical. The early analytical models (Neretnieks, 1980; Grisak and Pickens, 1980, 1981; Sudicky and Frind, 1982; and Rasmuson, 1984) look at either single fractures or a family of equally spaced fractures. The mass transport interactions between the fracture and matrix are typically neglected which limits the usefulness of these models for simulating mass transport in fractured media (Schwartz and Smith, 1988). Semianalytical models use analytical solutions to simulate transport within the matrix and numerical solutions to simulate contaminant movement within the fractures (Bibby, 1981). The disadvantage to Bibby's approach is the use of analytical solutions to describe transport in the porous media. Numerical discrete fracture models that account for matrix diffusion include; Berkowitz, et. al., 1988, Germain and Frind, 1989; and Rasmussen and Evans, 1989. A finite difference approach was used by Berkowitz, et. al. (1988) to step through time. This leads to numerical dispersion in the model unless a fine nodal spacing is employed. Germain and Frind, 1989, used a 2-D hybrid analytical-numerical solution to simulate diffusion between the fractures and the matrix. This scheme did not involve time stepping, however, it involved an infinite number of source/sink terms to represent diffusion along the fractures. Rasmussen and Evans, 1989, employed a 3-D variably saturated model using the boundary element method. Although this approach did not rigorously account for matrix diffusion it did allow fluid exchange between the fractures and the matrix.

An approach that avoids some of these difficulties is to treat the fractured media as a single continuum (Berkowitz, et. al., 1988; Schwartz and Smith, 1988). This continuum or equivalent porous media (EPM) approach assumes the scale of the problem is sufficiently large that meaningful, but average, flow and transport properties adequately describe the system. Early models used surface reaction and bulk reaction concepts (Neretnieks, 1980). Surface reaction models allow solutes to react on the fracture faces

only and the matrix block is not considered as a sink. On the other hand, bulk reaction models view the entire bulk medium as being accessible to the solute. A densely fractured porous media was represented as a single continuum by Bibby (1981) with diffusion into the matrix blocks simulated as a sink term. Double porosity or dual porosity theories bridge the gap between EPM and discretely fractured approaches by viewing the fracture and matrix systems as two overlapping continua. Huyakorn, et. al. (1983), used a dual porosity model following the work of Bibby (1981) and developed an exchange term to represent radioactive decay. An EPM model was developed by Pankow, et. al., (1986) simulated transport in two very different fractured field situations. The field sites had different fracture apertures, spacings, and interconnectiveness along with different porosities and molecular diffusion coefficients. They found that the EPM approach was effective in formations with higher fracture connectivity, higher block porosity and smaller fracture spacings. The continuum or EPM approach is a feasible way of simulating mass transport in field-scale systems. However, by using simple matrix geometry (i.e., uniform size and shape) to describe a complex process many important transport mechanisms are also averaged and simplified (Schwartz and Smith, 1988).

Other modeling approaches for simulating transport in fractured porous media include particle tracking (Schwartz and Smith, 1988), stochastic modeling (Smith and Schwartz, 1984) and Laplace transform Galerkin techniques (Sudicky and McLaren, 1992). Recent models have included multiphase flow in a variable aperture fracture. Murphy and Thomson (1993) simulated dynamic two-phase, two-dimensional flow in a single variable aperture fracture using a finite volume approach. Their model is being further developed to accommodate intersecting fractures and the processes of hydrodynamic dispersion and dissolution along with the dynamics of remediation techniques.

All of the aforementioned approaches have their advantages and disadvantages. With few exceptions, the models only have simulated transport of single component spills and until recently multiphase flow has not been attempted in great detail. A one-dimensional finite difference model described in this chapter was developed to simulate

transport of an LNAPL release into a fractured clay till at a field site in Sarnia, Ontario. The model simulates diffusive movement of a multicomponent gasoline mix initially present in the fractures into or out of the adjacent matrix from a single fracture face. Vaporization due to air flushing in the fracture is also accounted for along with adsorption within the matrix. The model results are then compared with soil vapor extraction (SVE) data from the site in order to better understand the preferential removal of the spill components from the media and the role of reverse diffusion from the matrix into the fracture.

NUMERICAL MODEL AND EQUATIONS

The numerical model used for the initial LNAPL distribution between the fractures and the matrix and subsequent removal of the LNAPL by SVE is capable of simulating the aqueous diffusion of multicomponent LNAPL from a fracture to the matrix in one-dimension and LNAPL removal by vaporization. The model considers dissolution of the LNAPL out of the fractures, aqueous phase diffusion and sorption onto the soil. The system is assumed to be diffusion controlled and therefore advection is not considered. A Crank-Nicholson finite difference numerical approach is used to approximate the governing equation, which is,

$$\frac{\delta C_a}{\delta t} = D_a \frac{\delta^2 C_a}{\delta x^2} \quad (1)$$

where: $\delta C_a / \delta t$ = change in concentration of compound "a" with time (M/L³/T)

D_a = apparent diffusion coefficient of compound "a" (L²/T)

$\delta^2 C_a / \delta x^2$ = change in concentration gradient of compound "a" (M/L³/L²).

Diffusion coefficients were calculated using data determined at the field site (Johnson, et., al., 1989), along with the molecular weights and densities of the individual components. The model uses the following equation to calculate the apparent diffusion

coefficients for each compound (Johnson, et. al., 1989; Wilke and Chang, 1955),

$$D_a = \left(\frac{MW_{benz} \rho_a}{MW_a \rho_{benz}} \right)^{0.6} D_{benz} \quad (2)$$

where: D_a = free-solution diffusion coefficients of compound "a" (L^2/T)

D_{benz} = free-solution diffusion coefficient of benzene ($2 \times 10^{-7} \text{ cm}^2/\text{s}$)

MW_a = molecular weight of compound "a" (M/mol)

MW_{benz} = molecular weight of benzene (M/mol)

ρ_a = density of compound "a" at its boiling point (M/L^3)

$\rho_{a,benz}$ = density benzene at its boiling point (M/L^3).

Mix solubilities are calculated to account for dissolution of the LNAPL out of the fractures into the water-saturated matrix. As individual compounds preferentially diffuse into the matrix, the LNAPL composition and consequently the mix solubility of each compound changes. Therefore, the mole fractions of each compound are determined and updated every time step as the LNAPL composition changes. Mix solubilities are calculated using the following relationship,

$$S_M = \frac{Mol_a}{Mol_T} S_a \quad (3)$$

where: S_M = mix solubility of compound "a" in LNAPL mixture (M/L^3)

Mol_a = moles of compound "a" in LNAPL mixture (mol)

Mol_T = total moles in NAPL mixture (mol)

S_a = solubility of compound "a" (M/L^3).

Once the mix solubility of each compound is calculated it is used as the initial aqueous phase concentration which is then diffused into the matrix. Since the matrix is assumed to be water saturated, the contaminants are either in the aqueous phase or sorbed onto the soil while in the matrix.

Sorption onto the soil is assumed to be an equilibrium process that follows a linear Freundlich isotherm (or Langmuir isotherm),

$$S_a = K_{D_a} C_a \quad (4a)$$

$$K_{D_a} = K_{oc_a} f_{oc} \quad (4b)$$

where: S_a = sorbed concentration of compound "a" (M/L³)

K_{D_a} = partitioning coefficient (L³/M)

C_a = aqueous concentration of compound "a" (M/L³)

K_{oc_a} = organic carbon partitioning coefficient of compound "a" (L³/M)

f_{oc} = fraction of organic carbon.

Equation 1 determines the aqueous phase concentration at each node in the system and then the sorbed concentration is determined using Equations 4a and 4b. Both aqueous and sorbed concentrations at each node are totaled and the mass at the fracture face is then calculated by subtracting the original fracture mass from the mass diffused and sorbed in the matrix.

SVE was simulated by removing mass from the fracture according to each compounds mix vapor pressure, an assumed air velocity through the fracture, and an average path length through the contaminated region.

$$n = \frac{P*V}{R*T} \quad (5a)$$

$$M = n*MW*v \quad (5b)$$

where: n = number of moles of compound (mol)

P = mix vapor pressure of compound (atm)

V = volume (L³)

R = universal gas constant (0.082 L-atm/mol-atm)

T = temperature (K)

M = mass (M)

MW = molecular weight of compound (M/mol)

v = velocity of SVE air (L/T).

The mole fraction of each compound was determined using Equation 3 again and then the mix vapor pressure calculated. As the more volatile compounds were removed from the fracture, the LNAPL composition changed and therefore the mix vapor pressure of each compound was updated every time step. An average air velocity through the fracture was determined based on tracer tests conducted in the field (see Chapter 3). Removal is based on volume of air flow through the fracture and vapor pressure using Equation 5. The removal efficiency of the SVE air was assumed to be less than 100% for several reasons including, the preferential nature of flow through the till and the availability of the LNAPL to the SVE air. Removal efficiency is also assumed to decrease in proportion to the fraction of the initial LNAPL remaining in the fracture.

METHOD

Numerical simulations of a 50 L release of an LNAPL into a naturally fractured till were performed using porous media properties determined at the field site (Table 4.1). The conditions for the numerical model taken from field experiments translate in to an effective porosity of 0.1% (fracture aperture 20 μ m and fracture spacing, 2 cm), which is in the same order of magnitude as the field determined effective porosity. A schematic drawing of the one-dimensional grid used for the simulations is shown in Figure 4.1. The matrix was assumed to be saturated during the simulations. Initially the fractures contained the LNAPL mixture only and the mass at the fracture face was calculated based on the residual saturation (2 L/m³) determined from field experiments (see Chapter 2). As the LNAPL compounds diffused into the matrix the mass and mix solubility in the fractures was recalculated.

The LNAPL was allowed to migrate into the clay matrix for 300 days, which corresponds to the time from release to initiation of the SVE system. From days 300 to

360 the mass in the fractures was removed by vaporization due to SVE air. The mass recovered at each time step during SVE was calculated and totalled in order to maintain a mass balance in the system (i.e., no mass losses in the system except during SVE). Following the 60 days of remediation, the simulation continued for 500 days allowing the remaining mass to move between the fractures and the matrix.

RESULTS

Pre-Remediation Simulations

As presented in Chapter 2, the one-dimensional diffusion model was used to determine the phase distribution of the LNAPL components 10 months (300 days) after the LNAPL release. The following is a more detailed analysis of the pre-remediation results.

Figure 4.2 shows the percent of the mass spilled of several compounds that remained in the fractures during the first 300 days. The model indicates that the more soluble compounds (MTBE (methyl-tert-butyl-ether), toluene, and TCE (trichloroethylene)) disappear fairly quickly into the soil matrix. Less than 25% of these compounds remain in the fractures while >70% of the less-soluble compounds (naphthalene and isooctane) persist. The effect of differing solubilities can be seen by comparing MTBE and isooctane. The initial mix solubility of MTBE (2026.5 mg/L) is four orders of magnitude greater than that of isooctane (0.2 mg/L). Therefore, MTBE will move quickly into the matrix (99%) while the isooctane moves very slowly into the matrix (<4%).

The ratio of aqueous phase concentrations to original LNAPL mix solubilities throughout the matrix (at 300 days) is presented in Figure 4.3. As the more soluble compounds move into the matrix the mixture solubility of the less soluble compounds in the fractures increases. For example, the mole fraction of naphthalene increased from 0.06 to 0.1, and as a consequence its mix solubility has also increased. On the other

hand, the mole fractions of MTBE, toluene and TCE have decreased and so have their mix solubilities. Figure 4.3 also indicates that MTBE is essentially at equilibrium between the fracture and the matrix at 300 days. Nevertheless, small changes in the MTBE aqueous concentrations will still occur as the LNAPL composition in the fracture changes, resulting in changing the mix solubility of MTBE.

Nodal concentrations taken at various times for several compounds are plotted in Figure 4.4a-d. As mentioned above, MTBE is at equilibrium in the system at 300 days, with equilibrium almost reached by 100 days (Figure 4.4a). In contrast, naphthalene (Figure 4.4d) is not close to equilibrium and has only moved about 0.4 cm into the matrix in 300 days. This again has to do with the difference in MTBE's and naphthalene's solubilities (48,000 mg/L and 33 mg/L, respectively). Also, differing retardation factors effect the rate of movement within the matrix. The retardation factor for MTBE is ~ 4 and therefore it moves 40 times faster than naphthalene whose retardation factor is ~ 160 . Both toluene and TCE have similar solubilities (92 and 131 mg/L, respectively) and retardation factors (20 and 21, respectively) and as a consequence have similar concentration profiles over time (Figure 4.4b-c).

Remediation Simulations

Once partitioning of the LNAPL between the fracture and the matrix had been simulated the numerical model then simulated SVE from the fracture. Figure 4.5 shows the percent remaining in the fracture from days 0 to 360 for several compounds. SVE was initiated at day 300 and continued until day 360. A dramatic decrease in pentane and isooctane mass in the fracture occurred within the first 10 days of remediation. Pentane has the highest vapor pressure (0.57 atm) of all the compounds simulated and as a result was removed rapidly from the fracture. Isooctane's vapor pressure (0.051 atm) is an order of magnitude smaller than pentane's and therefore would not be expected to be removed as quickly. However, the mole fraction of isooctane in the fracture is high at the start of SVE. This translates into a high mix vapor pressure, which in turn increases isooctane's vapor removal rate.

On the other hand MTBE's vapor pressure (0.26 atm) is ~5 times that of isooctane, but very little of its mass was removed during the remediation simulation. This is because most (>99%) of the original MTBE mass was in the matrix at the initiation of SVE and therefore was not as accessible to the extraction system as was pentane and isooctane. Naphthalene has the lowest vapor pressure (0.00014 atm) of all the LNAPL compounds and therefore SVE is not expected to be as effective at removal as it was for the more volatile compounds. The decrease in naphthalene mass in the fracture, due to vaporization and diffusion into the matrix, is ~42% while for isooctane (~94%) the decrease is substantially higher. Both TCE and toluene have similar vapor pressures (0.075 and 0.035 atm, respectively), and show the same decreasing trend.

Figures 4.6a-d are plots of aqueous phase concentration in the matrix for days 300 and 360 for several compounds. As seen in Figure 4.6a, MTBE is at equilibrium in the matrix in 300 days. However, at the end of SVE MTBE is essentially being "pulled" from the matrix as its mass in the fracture is decreasing due to SVE. The opposite is happening to the naphthalene concentration (Figure 4.6d). Since very little of the naphthalene mass is volatilized its mole fraction, and therefore solubility, increases in the fracture (see previous section) causing it to move into the matrix. Again, TCE and toluene (Figures 4.6b-c) show similar trends in their behavior due to their similar vapor pressures and pre-remediation mass distribution in the matrix (Figures 4.4b-c)

The cumulative percent of the original compound mass removed in the SVE offgas for several compounds is shown in Figure 4.7. Also included on this Figure is the total percent of the original LNAPL mass removed (~36%) during the SVE simulation. As indicated the mass removal rates of the compounds decrease with time as the fracture becomes "cleared-out". However, the mass removal rate of naphthalene increases with time, despite of its low vapor pressure, as it becomes more available as its mole fraction increases in the fracture. The overall LNAPL mass removal rate is also decreasing with time indicting that the SVE system has removed the most volatile compounds (i.e., pentane) while the less-volatile compounds (i.e., naphthalene) remaining in the system. As simulated by the numerical model, isooctane was effectively removed from the fracture (~95%). This is due to isooctane largely remaining in the fracture (>96%) at the

start of SVE and therefore it is accessible to SVE.

The effect of differing solubilities and vapor pressure for various compounds can be seen in Figure 4.8a-d, which presents the percent of the original compound mass in the fracture, matrix and removed in the SVE offgas. As mentioned previously, the large difference in solubilities between MTBE and isooctane lead to dramatic and contrasting mass distribution and removal rates in the system. The removal rates of MTBE, TCE and isooctane (Figure 4.8a-c) all indicate a decreasing rate of removal since they are being preferentially removed at the initiation of SVE and become less available with time compared to naphthalene (Figure 4.8d). Naphthalene is becoming more available with time and its removal rate is therefore increasing. Again, this is a result of naphthalene's low vapor pressure (0.00014 atm) and moderate solubility (33 mg/L).

Physical and Numerical Model Comparison

The percent removal of the LNAPL components that was actually removed by SVE during the first field season along with simulated percent removal are summarized in Table 4.2. In general, the numerical model over-estimates the mass removed. There are several possible reasons for the differences between the numerical and physical model results. First, the SVE system in the field was not operating 100% of the time as was simulated in the numerical model. Second, preferential flow paths that exist in the field (see Chapter 3 for discussion) influence the LNAPL and SVE air distribution in the soil. As was demonstrated by tracer tests in the experimental cell, these preferential pathways decrease the efficiency of the SVE system, whereas the numerical model simulated constant air flow through a fracture. Third, and the most difficult to quantify or model, is the impact of biodegradation. Finally, the effect of a fluctuating water table as observed at the field site, was not accounted for in the numerical model.

Although there are discrepancies between the numerical model and the field data, the trends simulated by the model are informative. The model indicates which compounds will move more readily into the matrix along with the fluxes associated with the diffusive driving force and the time to reach steady state concentrations between the

fracture and the matrix. Except for the compounds with the highest or lowest solubilities or vapor pressures, the model over-predicts mass removal by SVE by approximately 50%, but the preferential removal of the compounds is similar to those measured at the field site. In other words, the weathering of the LNAPL observed in the field was consistent with the numerical simulations.

Table 4.3 presents the final soil core analysis (1995) along with the numerical estimation of the mass remaining in the soil. For all the compounds, except naphthalene, the percent remaining in the soil estimated by the numerical model is substantially greater than that measured in the field. Because naphthalene is fairly resistant to biodegradation and because it has the lowest vapor pressure of the compounds in the LNAPL spill the loss of mass to unaccounted sinks (i.e., biodegradation and non-SVE volatilization) is minimal and the agreement between the numerical model (82.7%) and physical model (100%) is reasonable.

CONCLUSIONS

A one-dimensional finite difference model was developed to simulate transport of a multicomponent LNAPL release in a fractured clay till. Diffusion and adsorption of the LNAPL between a fracture face and the adjacent matrix block were accounted for using physical soil properties measured at the field site. The model indicates that the most soluble compounds move rapidly into the matrix while the less soluble compounds remain in the fracture. MTBE has the highest solubility in the LNAPL and ~99% of its original mass diffused into the matrix, whereas, <4% of isooctane (lowest solubility) moved into the matrix.

Following 300 days of diffusion, vaporization due to SVE in the fractures was simulated for 60 days. During this time ~36% of the LNAPL was removed. The simulated total mass removed agrees reasonably well with the field results (~40% removed). The most volatile compounds (i.e., pentane) and the compounds with high mole fractions in the fracture and moderate vapor pressure (i.e., isooctane) were removed

quickly from the fracture. On the other hand, naphthalene which has by far the lowest vapor pressure was "enriched" in the fracture and moved into the matrix as other compounds were preferentially removed from the fracture. MTBE concentrations indicated that mass was diffusing back into the fracture from the matrix as SVE continued to remove other compounds from the fracture.

Comparison of the numerical model and physical model results highlight the complexities of both systems. The numerical model idealizes an extremely complex physical system that is difficult to characterize. The influence of preferential flow paths, biodegradation and water table fluctuations all complicate the field situation and were not accounted for in the numerical model. Also, the numerical model had difficulties handling the fluxes of the most soluble compounds in the LNAPL mixture. This is probably due to its low vapor pressure and resistance to biodegradation in the physical model. In general however, the model simulated similar trends to those observed in the field.

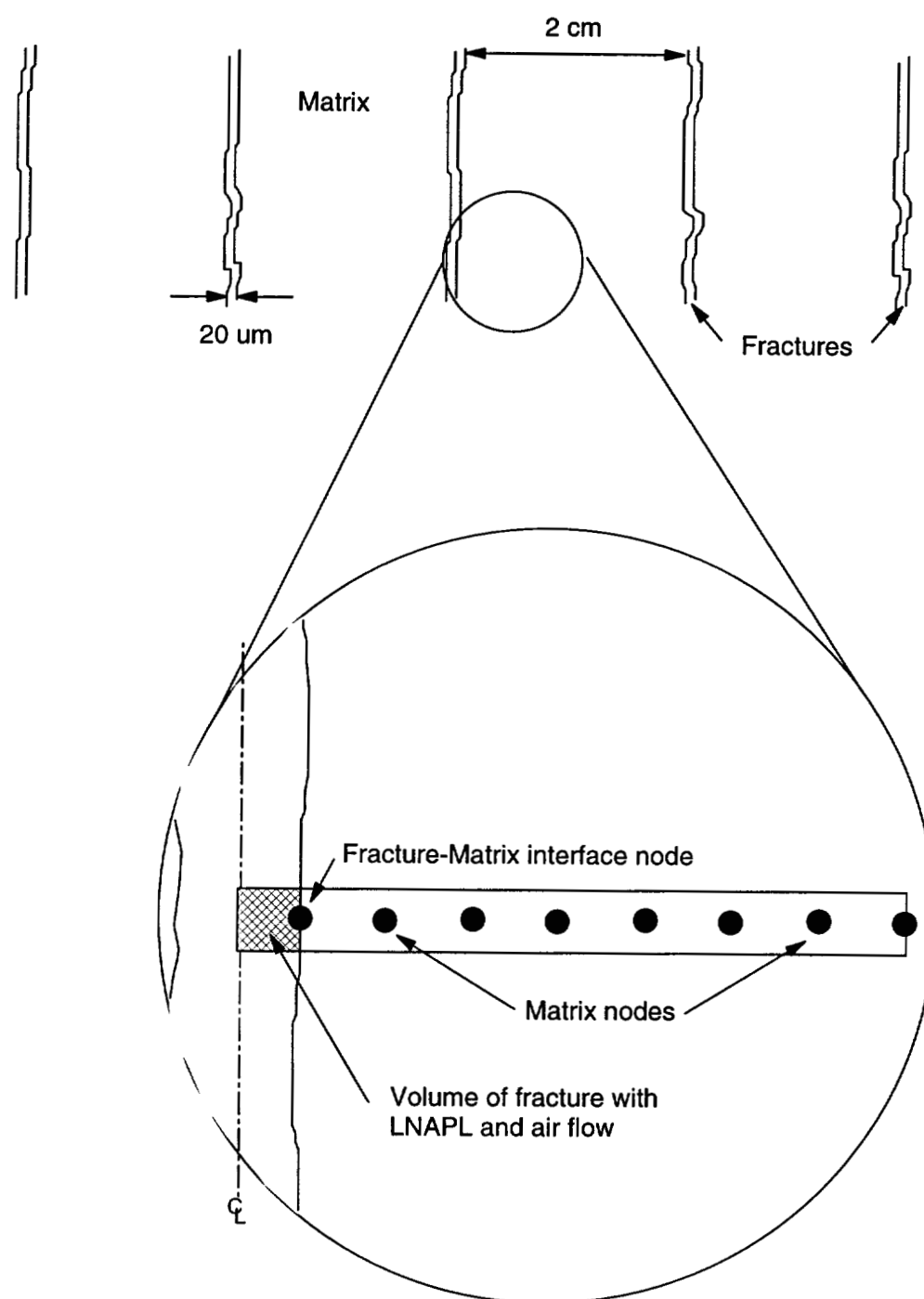


Figure 4.1. Schematic drawing of 1-D grid for LNAPL simulations.

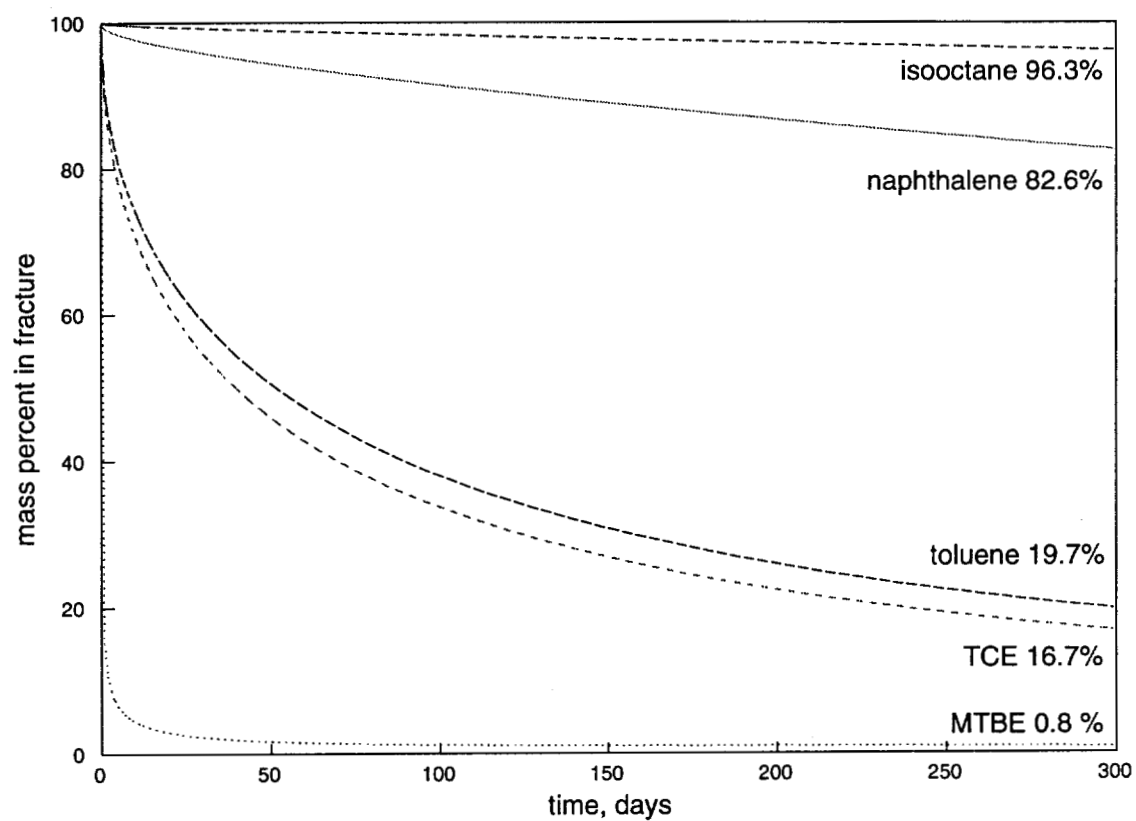


Figure 4.2. Estimated percent of initial mass remaining in the fractures prior to remediation as a function of time for the base case numerical diffusion model (isooctane, naphthalene, toluene, TCE and MTBE).

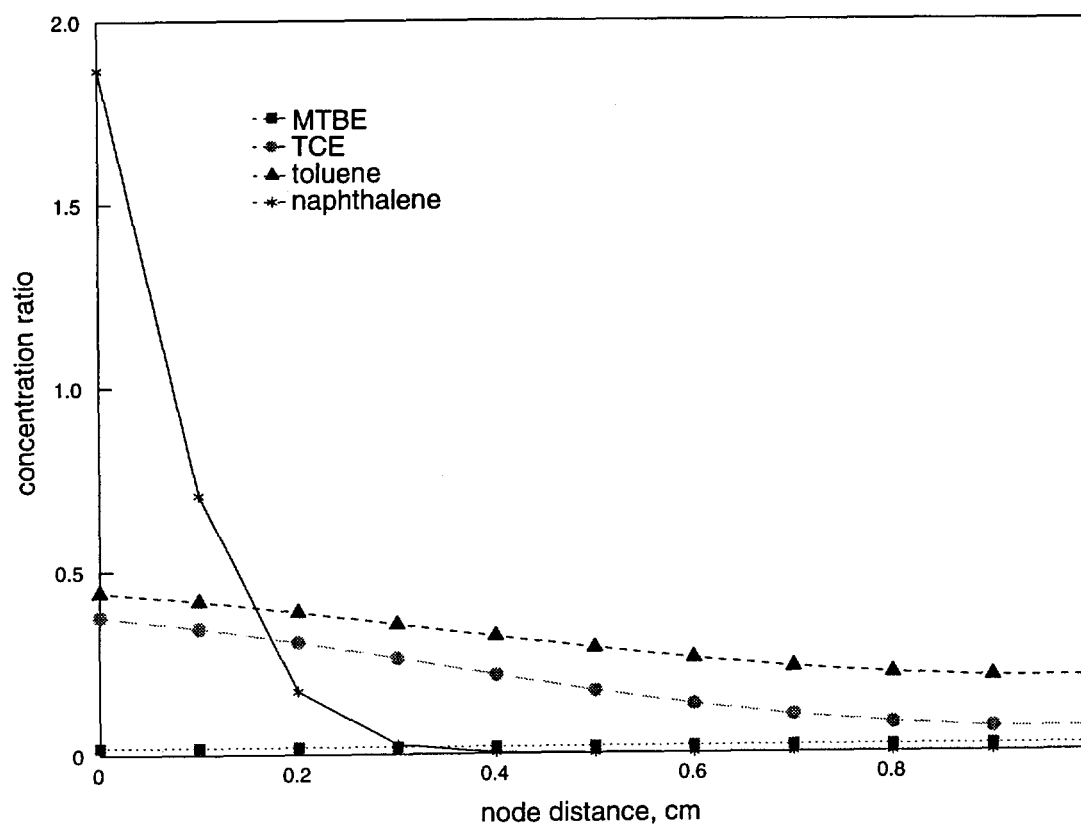


Figure 4.3. Estimated ratio of aqueous concentration to original mix solubility throughout the matrix prior to remediation (MTBE, TCE, toluene and naphthalene).

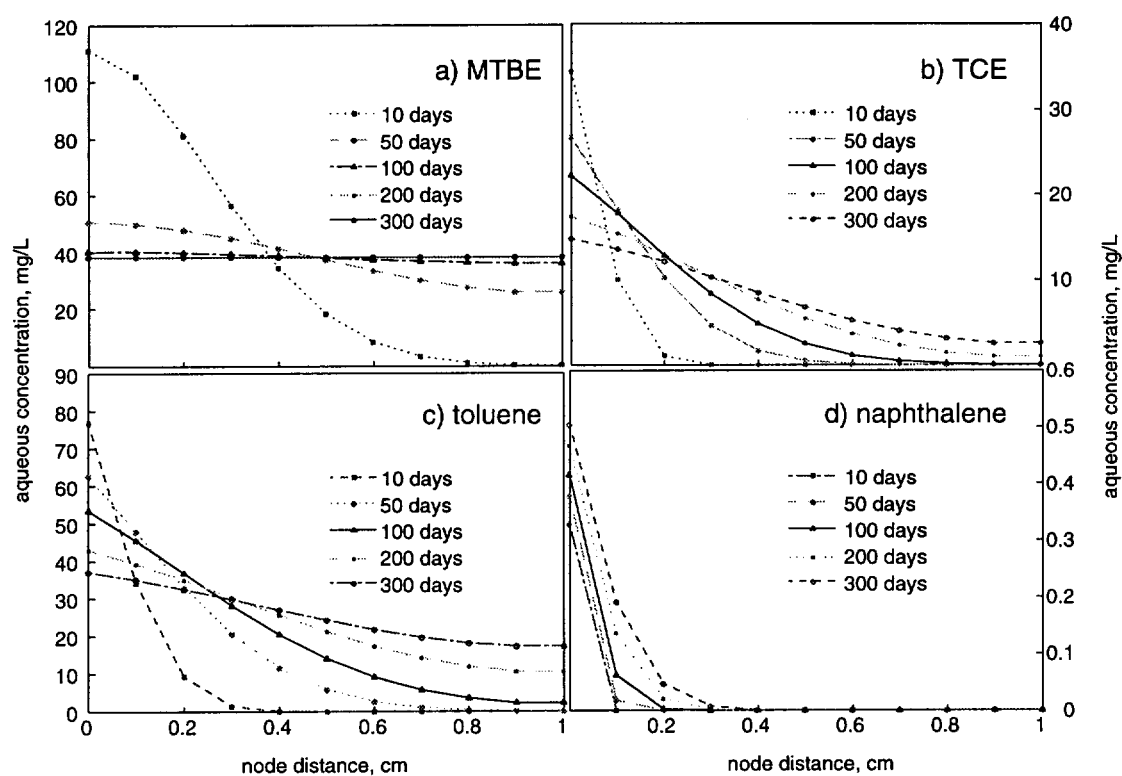


Figure 4.4. Estimated node concentrations at days 10, 50, 100, 200 and 300, prior to remediation (MTBE, TCE, toluene, and naphthalene).

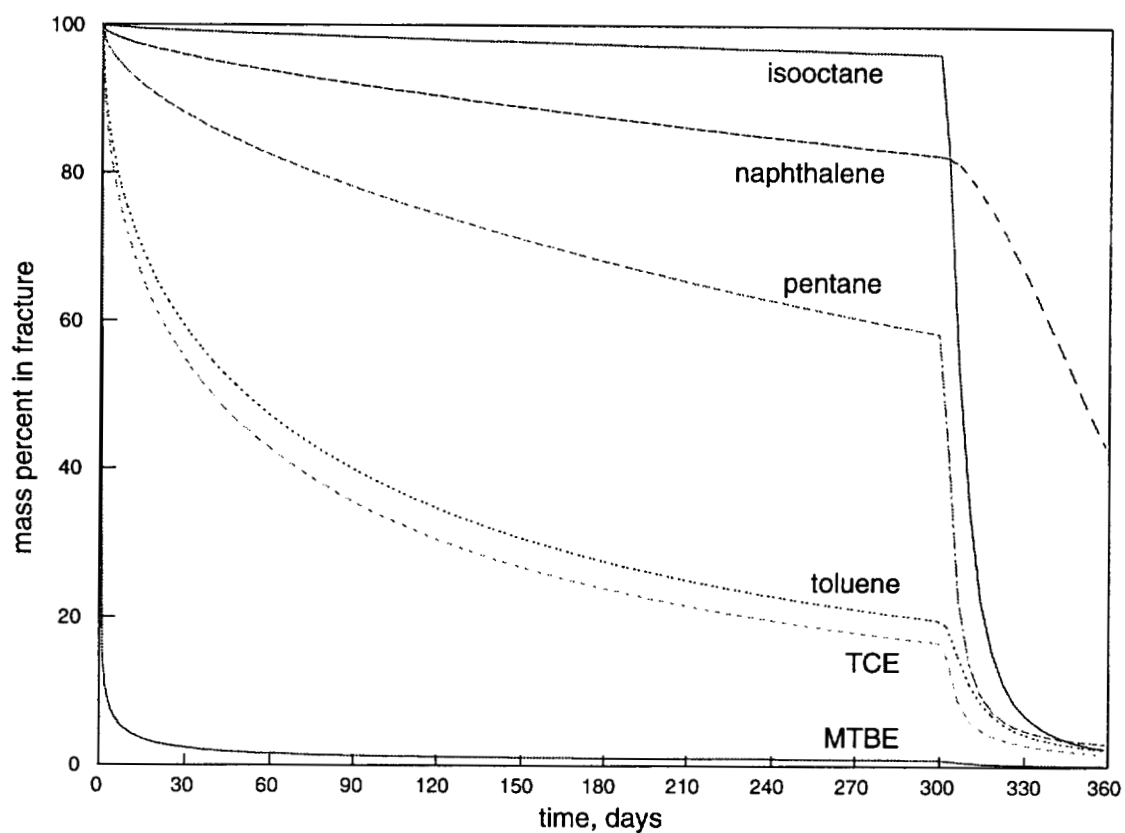


Figure 4.5. Estimated percent of initial mass remaining in the fracture as a function of time prior to (0-300 days) and during (300-360 days) remediation (isooctane, naphthalene, toluene, TCE, MTBE, and pentane).

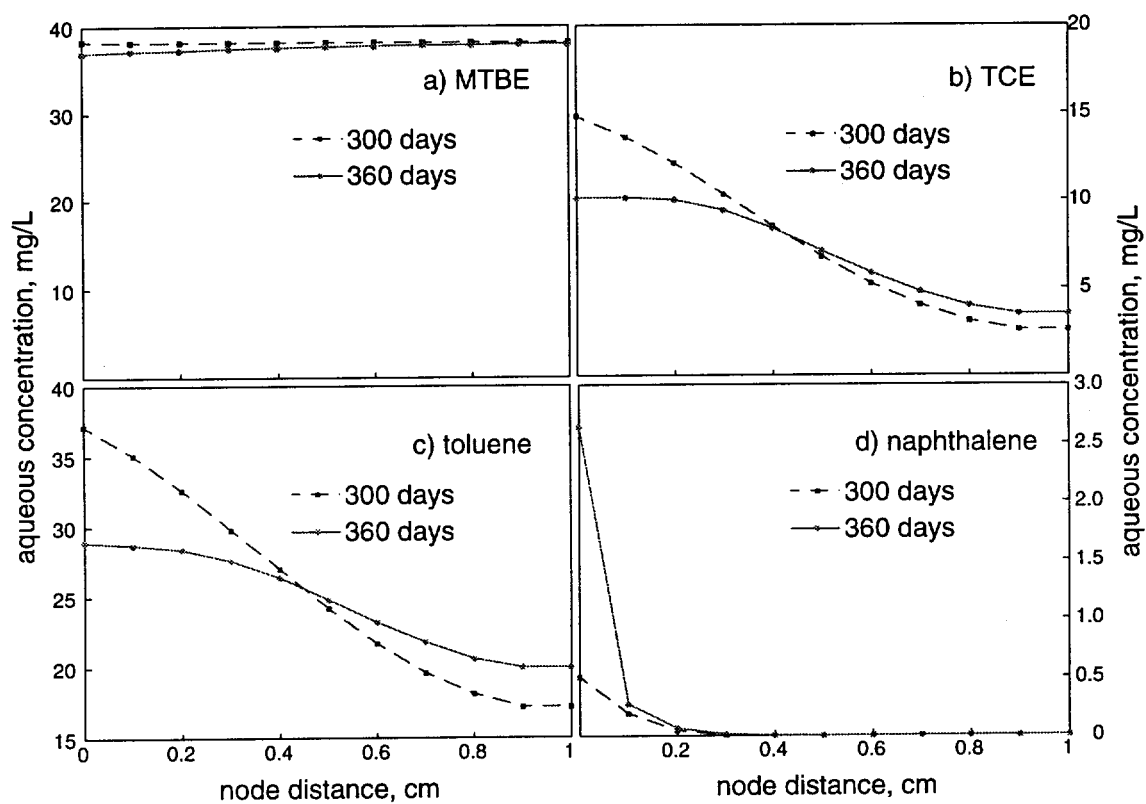


Figure 4.6. Estimated node concentrations at days 300 and 360, start and end of remediation (MTBE, TCE, toluene, and naphthalene).

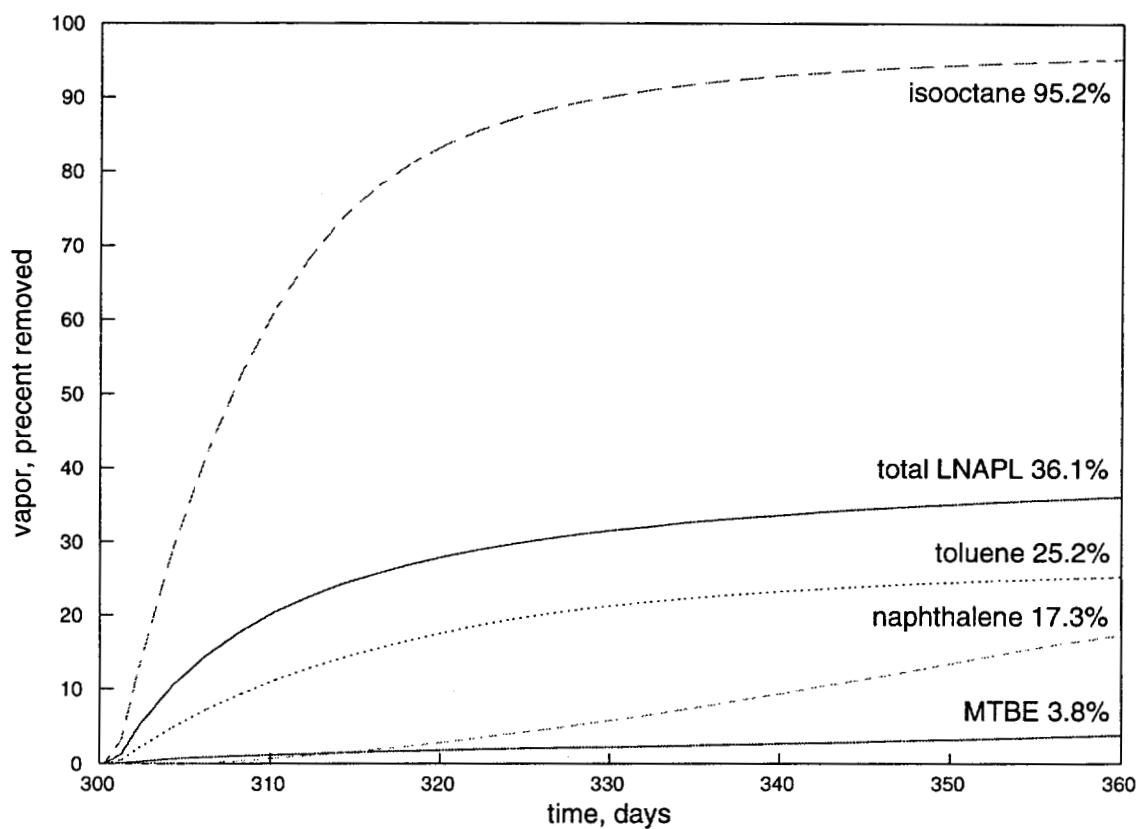


Figure 4.7. Estimated percent removed during SVE as a function of time during remediation (total LNAPL, naphthalene, MTBE, isooctane, and toluene).

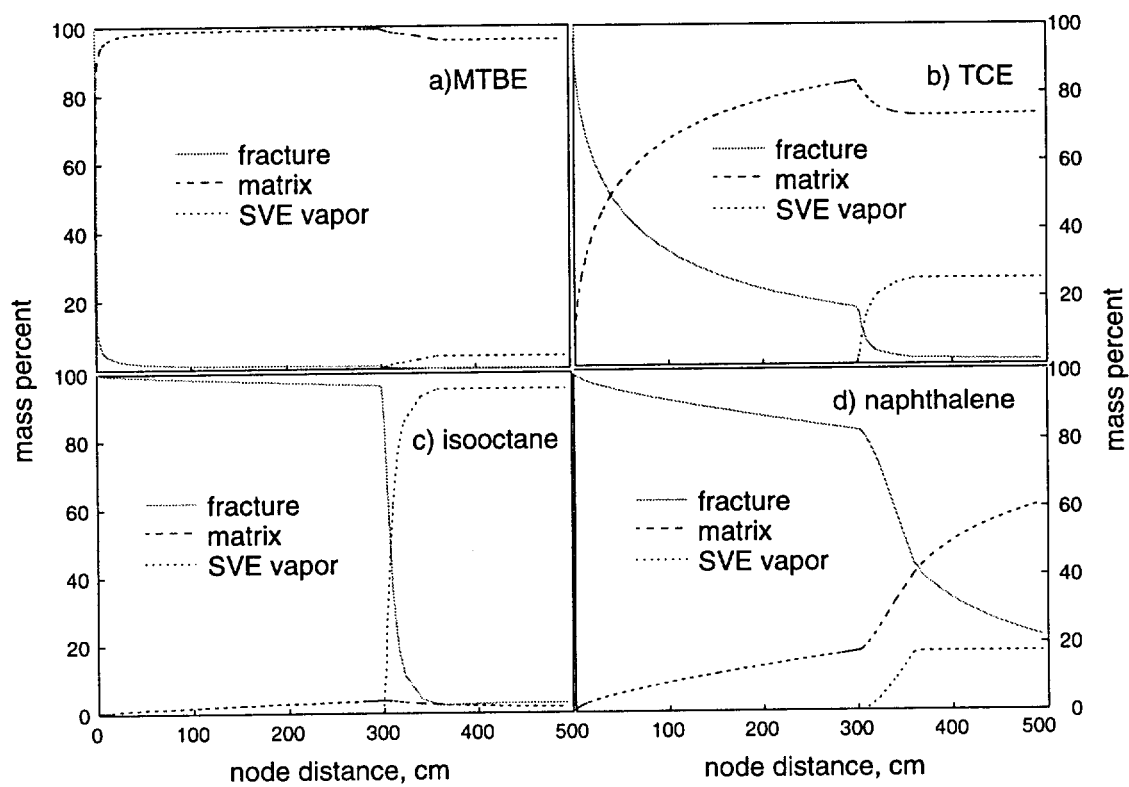


Figure 4.8. Estimated mass percentages in the fracture, matrix and removed in the SVE offgas as a function of time for 0 to 500 days (MTBE, TCE, isooctane and naphthalene).

Table 4.1. Base case parameters for the numerical diffusion model.

Parameter	Value
porosity	0.37 ^a
bulk density	1.5 g/cm ³ ^a
soil organic content	0.011 ^a
fracture spacing	2 cm ^b
fracture aperture	20 µm ^b
air velocity through fracture	1 cm/min ^c
SVE removal efficiency	50% ^c
residual saturation	2 L/m ³ ^c

^a Johnson, et. al., 1989

^b McKay, et. al., 1993a

^c This report

Table 4.2. Percent removed by SVE during the 1993 field season and the numerical simulation.

Compound	Percent removed by SVE: numerical simulation	Percent removed by SVE: 1993 field season
pentane	66.8	35.4
MTBE	3.8	40.0
2-methylpentane	80.8	45.5
hexane	84.3	54.7
benzene	10.6	17.0
TCE	25.2	48.8
isooctane	95.2	57.4
heptane	93.0	31.7
toluene	25.2	21.9
ethylbenzene	18.9	10.4
o-xylene	18.3	13.9
p-xylene	21.2	6.2
m-xylene	16.3	11.2
1,2,4-trimethylbenzene	11.5	15.1
naphthalene	17.3	0

Table 4.3. Percent remaining in the soil at the end of the numerical simulation and the end of the field work.

Compound	Percent remaining in soil: numerical simulation	Percent remaining in soil: 1995 field data
pentane	33.2	0.0
MTBE	96.2	2.1
2-methylpentane	19.2	0.1
hexane	15.7	0.2
benzene	89.4	0.4
TCE	74.8	1.0
isooctane	4.8	2.5
heptane	7.0	0.5
toluene	74.8	0.1
ethylbenzene	81.1	4.9
o-xylene	81.7	10.9
p-xylene	78.8	2.7
m-xylene	83.7	0.8
1,2,4-trimethylbenzene	88.5	8.2
naphthalene	82.7	100

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CHAPTER 5

SUMMARY, CONCLUSIONS AND IMPLICATIONS

SUMMARY

The research presented here has three main components: 1) characterization of a light non-aqueous phase liquid (LNAPL) release into a naturally fractured clay till; 2) in-situ remediation by air flushing of the LNAPL contaminated soil; and 3) numerical modeling of both the distribution of the LNAPL in the till and remediation by air flushing. The 15 component LNAPL release provided an opportunity to examine the physical and chemical limitations of in-situ remediation in a fractured clay till. The air flushing experiments, because of the controlled experimental cell at the field site, provided quantitative understanding of the effectiveness of air flushing in a fractured till soil. Modeling the movement of the LNAPL between the fractures and matrix was compared to the field results and provided a means of understanding the preferential removal rates of the various components in the LNAPL release.

To conduct this research an LNAPL was released into an experimental cell at a field site. Prior to remediation effective porosity and air permeability were measured using tracer tests and pneumatic pumping tests. The extent of the spill was determined from soil cores. The expected phase distribution of the individual compounds between the fractures and the matrix was determined using a one-dimensional diffusion model.

Ten months after the LNAPL release, an air flushing system consisting of two soil vapor extraction (SVE) trenches, five air sparging wells and five vertical SVE wells were installed at the field site. The ground surface within the experimental cell was covered with concrete to prevent surface leakage. Active and passive control of the trenches and wells was achieved by ball valves installed along the SVE manifold. The first field remediation season used various trench configurations and air flow rates to maximize mass removal rates. The second field season used high vacuums on the vertical wells. To improve hydraulic control within the experimental cell a hydraulic fracture was induced below the contaminated zone. Mass removal was continuously monitored by collecting and analyzing offgas samples using a gas chromatograph. A mass balance was determined using mass removal rates, soil core analysis and microbiological sampling data.

The LNAPL movement between the fractures and the matrix was numerically simulated in one-dimension using a finite difference approximation of the diffusion equation. The multicomponent model was used to simulate LNAPL movement and mass removal during SVE. The numerical model's ability to reproduce remediation observations in the field was evaluated by comparing both the numerical and physical data.

CONCLUSIONS

Pre-remediation Experiments

Prior to the release of a 50 L (40.6 kg) LNAPL spill in the clay till, air permeability and effective porosity were determined in the field. Pneumatic pumping tests indicated an air permeability of $\sim 10^{-16}$ m². This is several orders of magnitude greater than the permeability of the solid matrix and suggests that fluid (air, water and NAPL) movement in the till will largely be through the fractures. An effective porosity of <0.01 was determined from tracer tests and is similar to values calculated using fracture spacings and fracture apertures. After the contaminant was in the subsurface for

10 months (time to allow partitioning between the fractures and the matrix) soil cores were taken to determine the extent of the spill. The soil data indicated that approximately 25 m³ of the till was contaminated, which is equivalent to a residual saturation of 2 L/m³. Integration of the soil core data over the spill zone accounted ~25% of the spilled mass. Sampling difficulties and biodegradation probably explain the missing mass.

Remediation Experiments

In the first two months of active remediation, SVE from trenches and SVE combined with in-situ air sparging (IAS) recovered ~40% of the spilled LNAPL mass. In general, offgas concentrations decreased over time. More aggressive extraction (i.e., higher vacuums) kept mass recovery at a fairly constant level. Soil cores taken at the end of the first season's remediation showed ~35% of the LNAPL remained in the subsurface. Combining mass recovery with soil core analysis accounted for 30.3 kg (~75%) out of the 40.6 kg spilled. Mass removal during the second season concentrated on applying a high vacuum to vertical wells. At the same time, to improve air flow within the experimental cell, a hydraulic fracture was induced to dewater the contaminated zone. However, mass removal during the second season was only ~2% (<1 kg).

At the end of remediation a detailed soil analysis along freshly exposed trench walls within the contaminated zone was made. These data indicated that compounds with relatively low volatilities (naphthalene and 1,2,4-trimethylbenzene) remained in the soil to a greater extent than the higher volatile compounds (benzene and toluene). Mass balances for the less volatile compounds were >60% (e.g., MTBE, hexane, and isooctane). However, overall mass balances for the BTEX (benzene, toluene, ethylbenzene and xylenes) compounds were ~20% suggesting that the remaining mass underwent in-situ degradation. Removal of the BTEX compounds from the soil was high (95-99%) mainly due to biodegradation and therefore remediation of these compounds was considered successful. In contrast, essentially all of the naphthalene remained in the soil.

Numerical Modeling

A diffusion model indicated that the more soluble compounds in the LNAPL mixture would move into the matrix (>75%) and therefore would be less accessible to active remediation; in contrast, the less soluble compounds would remain largely in the fractures. The diffusion model also indicated that preferential removal of compounds from a fracture by SVE would increase the solubility of compounds with low vapor pressures, thereby driving these compounds into the matrix during remediation. Comparison of physical and numerical modeling results is difficult given the complexities in both systems and the uncertainties associated with field experiments. However overall results indicated that ~34% of the mass was removed during the simulated mass removal, which compares favorably with the ~40% removed in the same time frame from the field site.

IMPLICATIONS

The research presented here illustrates the difficulties in remediating a contaminated fractured clayey till. In the controlled release studied here, less than 40% of the spill mass was recovered using air flushing. The initial mass removal rate was high, however, the mass removal rate at the end of the first season was difficult to maintain suggesting that significant additional mass removal was unlikely. The research also indicates that the physical characteristics of fractured low permeability soils play an important role in the effectiveness of air flushing performance.

The low effective porosity and high water content of the soil matrix caused the initial release of LNAPL to spread laterally through the fractures into a large soil volume. In addition vertical smearing of the LNAPL will occur since relatively small volumes of water can cause large water table fluctuations. As a result, hydrocarbon levels in the soil were generally <1000 mg/L.

Tracer test data collected during extraction indicates that significant "short-circuiting" occurred as air flowed to the extraction points. Less than 10% of the extracted

air flowed through contaminated zones decreasing the effective mass removal rate. Mass removal data indicated that the extraction trenches performed better at removing the contaminants and propagating a vacuum than the vertical wells even though the wells were spaced more closely than the trenches. These results are in contrast to earlier tracer tests done at the site that showed air moved relatively efficiently between closely spaced vertical well extraction points.

To improve air flow through the till better hydraulic control (i.e., dewatering) was necessary. A hydraulic fracture induced below the contaminated zone provided some hydraulic control, however the presence of preferential flow paths and matrix diffusion still dominated transport in the till. Air sparging on the other hand, was more effective at dewatering and at the same time it also removed mass from the source zone. However, the air sparging data indicates that the SVE system was unable to capture the injected air which largely escaped through the surface cap. Fractures in the concrete surface cap appear to have acted as flow paths implying that the air preferentially flowed through these fractures as opposed to fractures in the till. Therefore, a surface cover that prevents surface leakage would be necessary to improve air flow through the fractured soil. This study indicates the difficulties and importance of controlling water and air movement in a fractured clay till.

The preferential flow paths in the clay also impacted the LNAPL distribution and soil core analysis. Soil coring at the site prior to remediation accounted for ~25% of the spilled mass. The under-estimation of the mass resulted from several possible sources of error in the sampling process. Given what is known about non-uniform air and water flow in the till, it is likely that the mass was not uniformly distributed within the soil. Also, since the fractures and coring process are both vertical it is possible that the cores may not have sampled a representative number of contaminated fractures. Compaction during the sampling process could also have forced LNAPL out of the portions of the fractures being sampled. The various soil core analysis conducted at the site demonstrate the difficulty in determining the amount of contaminant in the subsurface at an uncontrolled release site.

The field data and numerical modeling data indicate that active remediation of an

LNAPL by flushing air through the fractures and intrinsic biodegradation can remediate a contaminated fracture till. Air flushing techniques would remove the more volatile compounds (i.e., BTEXs) from the fractures while the less volatile compounds (i.e., naphthalene) would remain in the soil. However, once the contaminants have diffused into the matrix, the reverse diffusion process may be slow enough to reduce the risk to a potential receptor.

APPENDIX A

SUMMARY OF HYDRAULIC FRACTURING ACTIVITIES AT THE LAIDLAW SITE, SARNIA, ONTARIO

This appendix contains a summary of hydraulic fracturing activities at the Sarnia site by personnel for FR_x and the University of Cincinnati. As discussed in Chapter 3 several hydraulic fractures were induced at the field site, including one in the experimental cell to improve hydraulic control.

Summary of Hydraulic Fracturing Activities at the
Laidlaw Site, Sarnia, Ontario

October, 1994

prepared for
American Petroleum Institute
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Summary of Hydraulic Fracturing Activities at the Laidlaw Site, Sarnia, Ontario

Hydraulic fractures were created at the Laidlaw site, Sarnia, Ontario, by personnel from FRX and the University of Cincinnati during two trips in August, 1994. The purpose of the effort was to establish the feasibility of creating hydraulic fractures at the site, evaluate possible interactions between fractures and sheet pile, create several fractures outside the cell for future evaluation, and create one fracture inside the cell for dewatering.

Currently, there are 15 fractures at 9 locations either within or in the vicinity of the sheetpile cell at the site (Fig. 1). Five fractures were created at 2 locations during the first trip and 10 fractures were created at 7 locations during the second trip. All but one of the fractures appear to be gently dipping features that remain within the subsurface and are equant to slightly elongate in plan. The deepest fracture apparently was steeply dipping, climbing rapidly and reaching the ground surface roughly a meter from the point of injection.

The following document describes essential details of the hydraulic fractures that were created, the process of creating the fractures is described elsewhere. An overview of the fractures and two tables summarizing key parameters is followed by brief descriptions of individual fractures. Data describing the uplift of the ground surface and the injection pressure as a function of time are appended.

Hydraulic fractures are designated as follows: SAR3-2.0; the first three letters indicate the site, the next number indicates the location, and the number after the dash indicates the depth of initiation in meters. The decimal point in the depth of initiation has been omitted in some cases, such as designation of disk files.

OVERVIEW

Fractures were initiated at depths between 1.2 and 5.6 m, with most of the work occurring between 2 and 3 m. They were filled with between 100 and 300 L of sand (bulk volume) that was suspended in 230 to 600 L of gel per fracture. The ratio of bulk volume of sand to total volume of slurry was 0.4 to 0.5. The fractures created broad, gentle domes, which roughly indicate the location and thickness of sand at depth. The maximum uplift ranged from 1.1 to 4.65 cm, with uplift increasing with volume of injected slurry.

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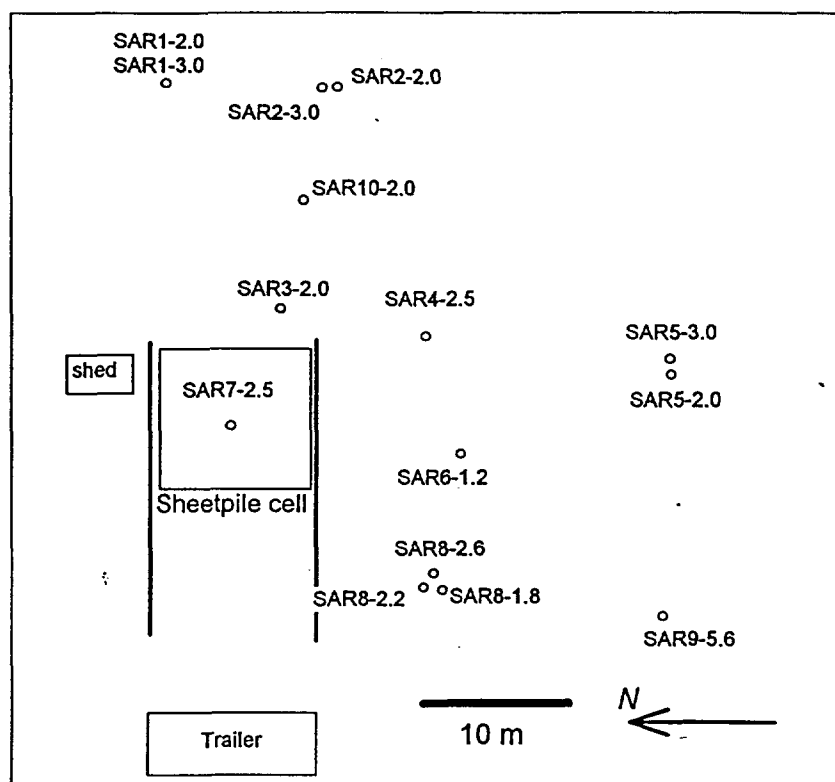


Figure 1. Approximate locations of hydraulic fractures, Laidlaw site, Sarnia, Ontario.

Specifications of the fractures are given in the following table. Depth is the distance from the current ground surface to the point of initiation of the fracture. The bulk volume of sand and volume of gel were estimated during field operations. The maximum uplift was obtained by leveling and the maximum thickness of sand is approximately the maximum uplift times the ratio of bulk sand volume to total slurry volume. The maximum diameter of the fracture that contains sand was estimated as the maximum distance between the 0.3 mm contour of uplift (a minimum aperture of approximately 3 mm is required for sand to enter the fracture).

Summary data for hydraulic fractures created at the Laidlaw site, Sarnia, Ontario, during August 1994

Fracture	Depth	Vol. sand	Vol. gel	Max. up	Diameter	Comments
	m	L (ft ³)	L (gal)	cm	m	
SAR1-2.0	2	220 (8)	375 (100)	3.2	7	contains poorly sorted sand
SAR1-3.0	3	330 (12)	600 (160)	3.5	12	asymetric uplift, scrap sand
SAR2-2.0	2	100 (3.5)	340 (90)	1.1	6	well-sorted sand
SAR2-3.0	2	160 (6)	600 (160)	3.5	11	asymetric, well-sorted sand
SAR3-2.0	2	160 (6)	375 (100)	1.7	6	next to sheet pile
SAR4-2.5	2.5	125 (4.5)	230 (60)	1.2	7	test sheet pile recipe
SAR5-2.0	2	160 (6)	280 (75)	2.0	7	symetric uplift
SAR5-3.0	3	270 (10)	450 (120)	2.6	8	asymetric
SAR6-1.2	1.2	110 (4)	240 (65)	3.1	6	shallow
SAR7-2.5	2.5	110 (4)	260 (70)	1.6	7	in sheet pile cell
SAR8-1.8	1.8	160 (6)	375 (100)	3.05	8	three fractures same volume
SAR8-2.2	2.2	160 (6)	375 (100)	2.0	7	three fractures same volume
SAR8-2.6	2.6	160 (6)	375 (100)	2.35	9	three fractures same volume
SAR9-5.6	5.6	55 (2)	230 (60)	0.5	-	deepest fracture reached g.s.
SAR10-2.0	2	300 (11)	720 (190)	4.65	9	large volume relative to depth

Fractures were created for several purposes and have several possible future applications, which are summarized in the following table.

Fracture	Purpose	Potential application
SAR1-2.0	Fracturing feasibility, poorly sorted sand	Excavation for geometry
SAR1-3.0	Fracturing feasibility, poorly sorted sand	Excavation for geometry
SAR2-2.0	Fracturing feasibility, well-sorted sand	Possible flow studies
SAR2-3.0	Fracturing feasibility, well-sorted sand	Possible flow studies
SAR3-2.0	Effects of sheet pile and casing	Already excavated and filled
SAR4-2.5	Evaluate recipe used in cell	Flow studies
SAR5-2.0	Pair for flow studies	Flow studies
SAR5-3.0	Pair for flow studies	Flow studies
SAR6-1.2	Evaluate shallow depth application	Flow studies
SAR7-2.5	Fracture in sheet pile cell	Flow studies
SAR8-1.8	Triplet for flow studies	Flow studies
SAR8-2.2	Triplet for flow studies	Flow studies
SAR8-2.6	Triplet for flow studies	Flow studies
SAR9-5.6	Evaluate moderate depth applicatio	Possible flow studies
SAR10-2.0	Larger volume application	Flow studies

INDIVIDUAL FRACTURES

The first two fractures were created to evaluate general feasibility of fracturing. They were filled with poorly sorted sand to avoid the cost of processed sand should the feasibility tests be negative. The tests showed that creating useful fractures at the site was feasible, and a second set of tests (SAR2-2.0 and SAR2-3.0) showed that the fractures could be filled with coarse-grained sand. Equipment problems resulted in fluctuations in sand concentration during creation of the first 4 fractures, so we recommend that they be used primarily to evaluate general fracture form; other fractures should be used to evaluate effects on subsurface flow.

SAR3-2.0

SAR3-2.0 was created to evaluate interactions with sheet piling and driven casing. The fracture was created between the sheet pile and the driven casing, approximately 2 m from both. It was initiated at a depth of 2 m and the nearby casing was driven to 2.8 m. The vicinity of the injection casing was excavated to map the location and thickness of the fracture and to inspect the vicinity where the fracture intersected the sheet pile and the driven casing.

Sand distribution

The greatest observed thickness of sand was 10 mm, and occurred approximately 0.5 m east of the injection point. Sand thickness varied along the length of the fracture, with changes in thickness of several mm commonly occurring over lengths of several dm. In general, however, the sand isopach (inferred from trench

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exposures and uplift) forms a roughly equidimensional lens extending to the northeast of the injection point (Fig. 2).

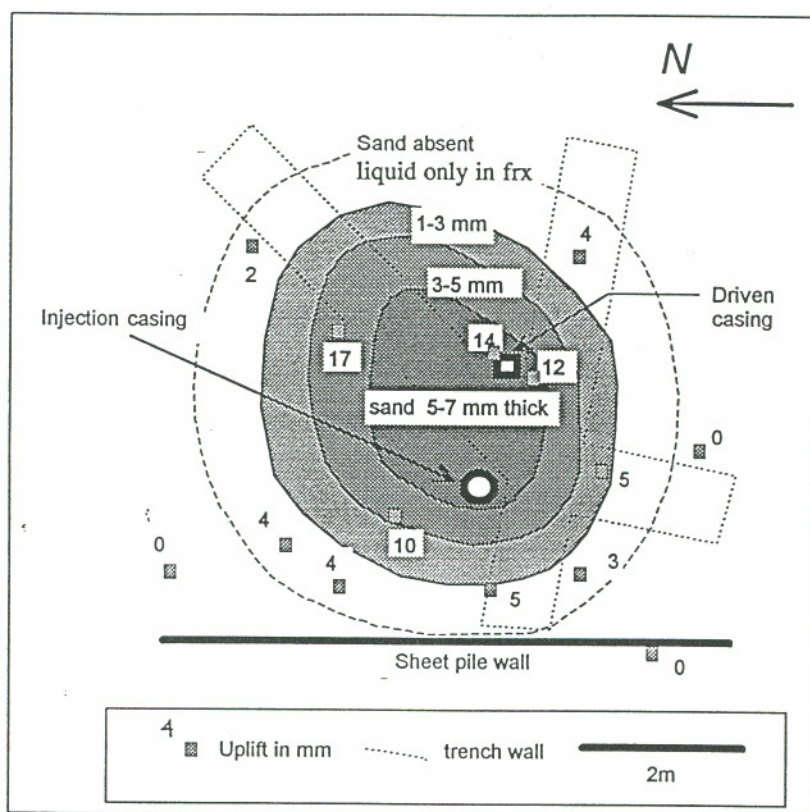


Figure 2. Distribution of sand in fracture created in vicinity of sheet pile. Based on measurements of sand thickness along wall of trenches and inferred from uplift.

General form

The fracture was slightly elongate and asymmetric with respect to the injection casing. The preferred direction of propagation was to the northeast, away from the sheet pile and to the north of the driven casing. Sand filling the fracture was observed 4m from the northeastern side of the injection point, whereas sand was limited to within 1 to 1.5 m from the southern and western sides of the injection point (Fig. 3).

This fracture was slightly more asymmetric than others at a similar depth at Sarnia, although it was similar to the degree of asymmetry of fractures created at 3.0 m depth.

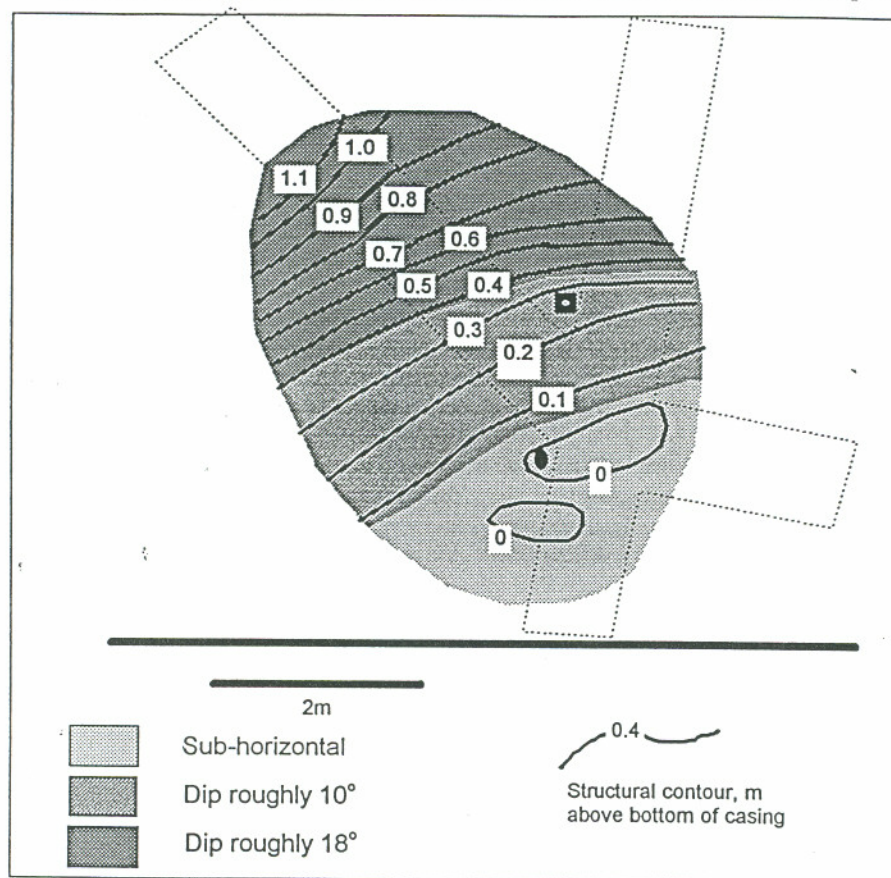


Figure 3. Structural contours and approximate dip of hydraulic fracture

Dip

In general, the fracture dipped gently toward the injection point, with the dip angle increasing with distance from the injection point. The fracture was flat-lying within roughly 1 m of the point of injection, it curved upward to approximately an 10° dip 1 to 2 m northeast of the injection point, and it dipped approximately 18° from 2 to 4 m from the injection point (Fig. 3).

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Liquid in the vicinity of the fracture

Water flowed from the fracture when it was intersected during excavation, and water was observed beneath the fracture in many locations. In addition, saturated areas were observed as much as a meter from the leading edge of the sand-filled fracture. Presumably, the decomposed gel flowed into open fractures beneath the sand-filled fracture. It is unclear whether this occurred under ambient conditions or only when natural fractures opened in response to stress relief following excavation of the trench. It is clear, however, that the induced fracture extended at least a meter beyond the most distal limit of sand. This tip zone apparently was filled with water and remained open for at least a day after fracturing.

Sheet pile

Thickness of sand decreased as the fracture approached the sheet pile and sand was absent within a few dm of the wall. The fracture was difficult to identify where it lacked sand so excavation was discontinued a few dm short of the sheet pile. The sheet pile was exposed approximately 1.3 m above the fracture revealing a gap of several mm to a cm between the metal and the soil. The width of this gap may have increased after excavation. The gap was filled with a watery liquid that contained petroleum hydrocarbons, presumably a residual from the pile driving process. The liquid adjacent to the sheet pile was slightly slippery, an indication that it was at least partly derived from fluid injected during fracturing.

The available data suggest that the leading edge of the hydraulic fracture probably reached the sheet pile. The aperture of the fracture was less than a few mm, however, because there is no evidence that sand reached the sheet pile.

Driven casing

The fracture intersected a driven casing approximately 2 m from the point of injection. The thickness of sand in the fracture decreased from 5 to 6 mm within a few cm of the casing to 1-2 mm or less adjacent to the casing. The fracture did appear to thin adjacent to driven casing, but the effect appeared to be limited to within a few cm.

The local form of the fracture may have been affected by the driven casing. The fracture stepped upward by a few to 10 cm in the vicinity of the driven casing. This upward step was the only major step observed in the excavation, although upward steps have been observed in other locations where the fracture did not intersect a driven casing.

It appears that the driven casing probably caused a localized thinning and perturbation in the fracture form, presumably because it tended to pin the walls of the fracture together. However, these effects influenced a small part of the overall fracture and I expect that they would have negligible effect on the performance of a fracture used for delivery or recovery. The localized thinning may be a problem if the driven casing were a screened well that was to be used for recovery. In this case, the

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localized thinning could increase head losses in the vicinity of the well, however, this is only speculation because the localized thinning may not occur in the vicinity of a well.

SAR4-2.0

This fracture was created to evaluate the approach to be used in the sheet pile cell. It contains a relatively small volume of sand compared to other fractures at similar depth. This was done in order to limit the possibility of intersecting trenches or monitoring wells in the sheet pile cell. The fracture is slightly asymmetric with respect to the injection point. It has a maximum uplift of 2.0 cm and a maximum dimension of 7 m. This was considered appropriate for application within the sheet pile wall.

SAR5-2.0 AND SAR5-3.0

This is a pair of fractures spaced 1 m apart vertically. The lower fracture is asymmetric and may have a steeper dip than the upper fracture. These pair of fractures is a candidate for assessing subsurface flow.

SAR6-1.2

This is the shallowest fracture created during the trip. It was filled with approximately 110 L of sand during initial creation. An additional 15 L was injected the next day to ensure adequate thickness in the vicinity of the access casing. This fracture is a candidate for assessing subsurface flow.

SAR7-2.5

This fracture was created at the center of the sheet pile cell. Surface displacement consists of a symmetric dome, suggesting that the distribution of sand is approximately symmetrically distributed around the injection point. The extent of sand, as defined approximately by the 2 to 3 mm uplift contour, forms a 7-m-diameter circle. Sand thickness in the subsurface is expected to be approximately one half of the uplift. A few hairline cracks were observed after creation of the fracture, with most displacement occurring as normal-type faults along the seams where the trenches were placed.

SAR8-1.8, SAR8-2.2, SAR8-2.6

This is a series of fractures of the same volume stacked at 0.4 m intervals with depth. The uplift associated with SAR8-2.2 is less than expected based on the results at the other two fractures. This may be a result of settling of an upper fracture interfering with uplift measurements. These fractures are candidates for evaluation of subsurface flow.

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SAR9-5.5

This fracture showed minimal uplift and reached the ground surface as a steeply dipping fracture several m in length. I would recommend against using this fracture for studies intended to characterize the effects of fractures on subsurface flow.

SAR10-2.0

This fracture contains nearly twice the volume of sand as other fractures created at 2 m depth. The maximum dimension of this fracture is slightly greater than that of the others, however, the maximum uplift is roughly twice that of other fractures at similar depth. Apparently the extra volume injected into SAR10-2.0 primarily increased the thickness and had a lesser effect on maximum dimension.

CONFIGURATION OF WELLS

Casing driven to create the hydraulic fractures was left in place to access the fracture during recovery. The fractures will be 1 to 2 cm below the bottom of the casing, and there will be natural soil below the fracture. A conical, sand-filled cavity will occur where the drive point was held below the casing. Sand filling the fracture should be roughly 1 cm thick at the bottom of the casing, although sand may be several cm thick within 5 to 15 cm of the bottom of the casing as a result of water jet cutting prior to fracturing.

All casing at Sarnia is 1.5-inch nominal black iron pipe with NPT thread at the ground surface. The casings stick up above the ground surface by a few dm.

The casing will probably contain some sand and it may be nearly completely filled with sand following fracturing (Fig. 4a). If vapor or minor amounts of water are

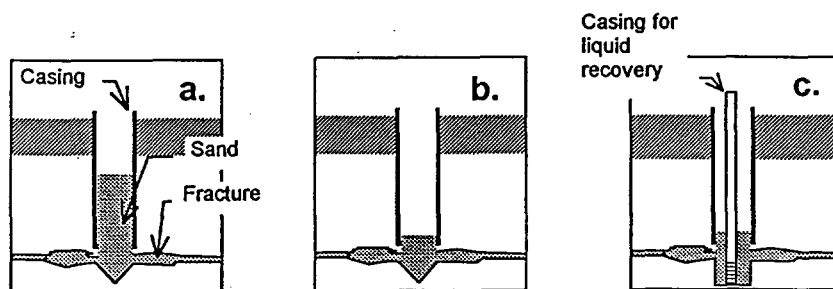


Figure 4. a. Schematic of the vicinity of the borehole after fracture is created. B. Sand removed from casing for vapor extraction. C. Sand and soil removed from bottom of casing to install slotted screen for liquid recovery.

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to be recovered from the well, we recommend that the sand be removed to within a few cm of the bottom of the casing, either by flushing with water or using a small auger. If significant volumes of water are expected or encountered, it may be worthwhile to auger 1 to 2 dm below the fracture to place a small well screen and gravel pack. The top of the screen should be below the bottom of the fracture if vapor and liquid are to be recovered simultaneously. This will enhance the flow of vapor by draining liquid from the point where the fracture meets the casing. The bottom of the casing should always contain gravel or sand to inhibit mobilization of fine-grained sediment.

CONCLUSIONS

1. Hydraulic fractures suitable for affecting subsurface flow can be created and filled with sand at the Laidlaw site, Sarnia, Ontario.

2. A hydraulic fracture was initiated at a depth of 2.5 m and filled with approximately 110 L of sand within the sheet pile cell. The fracture created surface displacement that was symmetric about the point of injection, suggesting that the sand was distributed symmetrically.

3. Forms of hydraulic fractures appear to change with depth. Hydraulic fractures initiated at depths equal to or shallower than 2.5 m are roughly symmetric about the point of injection, whereas those initiated at 3.0 m are highly asymmetric. The only fracture initiated below 3.0 m was markedly different than the others. It was initiated at 5.5 m and climbed steeply to reach the ground surface after injection of a relatively small volume.

The available information suggests that the dip of hydraulic fractures increases with the depth of initiation when that depth is greater than 2.5 m. Fractures initiated at 3.0 m should be useful for delivery or recovery, although they are asymmetric and one should expect that their effects will be asymmetrically distributed. The fracture initiated at 5.5 m will be of limited value for delivery and recovery.

The reason for the change in orientation with depth, and the actual depth where hydraulic fractures change from gently to steeply dipping are unclear based on available information. We expect that the change in orientation of the hydraulic fractures is related to changes in the in situ stress and perhaps changes in the fabric and material properties of the till with depth.

4. Interaction with sheet pile and driven casing

The fracture created near the sheet pile and driven casing exhibited a preferred direction of propagation that was roughly 140° from the line between the injection point and the sheet pile and 40° from the line between the injection point and the driven casing. The observations are consistent with the sheet pile and driven casing

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influencing the preferred direction of propagation of the fracture; the sheet pile being a major influence and the driven casing a more minor one.

Sand filled the hydraulic fracture within a few dm of the sheet pile and within a few cm of the driven casing. It appears that injected fluid reached the edge of the sheet pile, although there is no evidence that sand reached the pile. Sand probably did reach, or at least came within a few mm from, the driven casing.

There was no evidence that either the sheet pile or the driven casing affect the dip of the fracture.

The results of this study indicate that it should be feasible to propagate hydraulic fractures initiated at 2m depth in the vicinity of, and probably up to, the sheet pile at Sarnia. We should expect that as the sheet pile wall is approached, the propagation rate in the vicinity of the sheet pile should diminish and the rate elsewhere should increase. It follows that this effect will tend to cause hydraulic fractures to be centered within the cell.

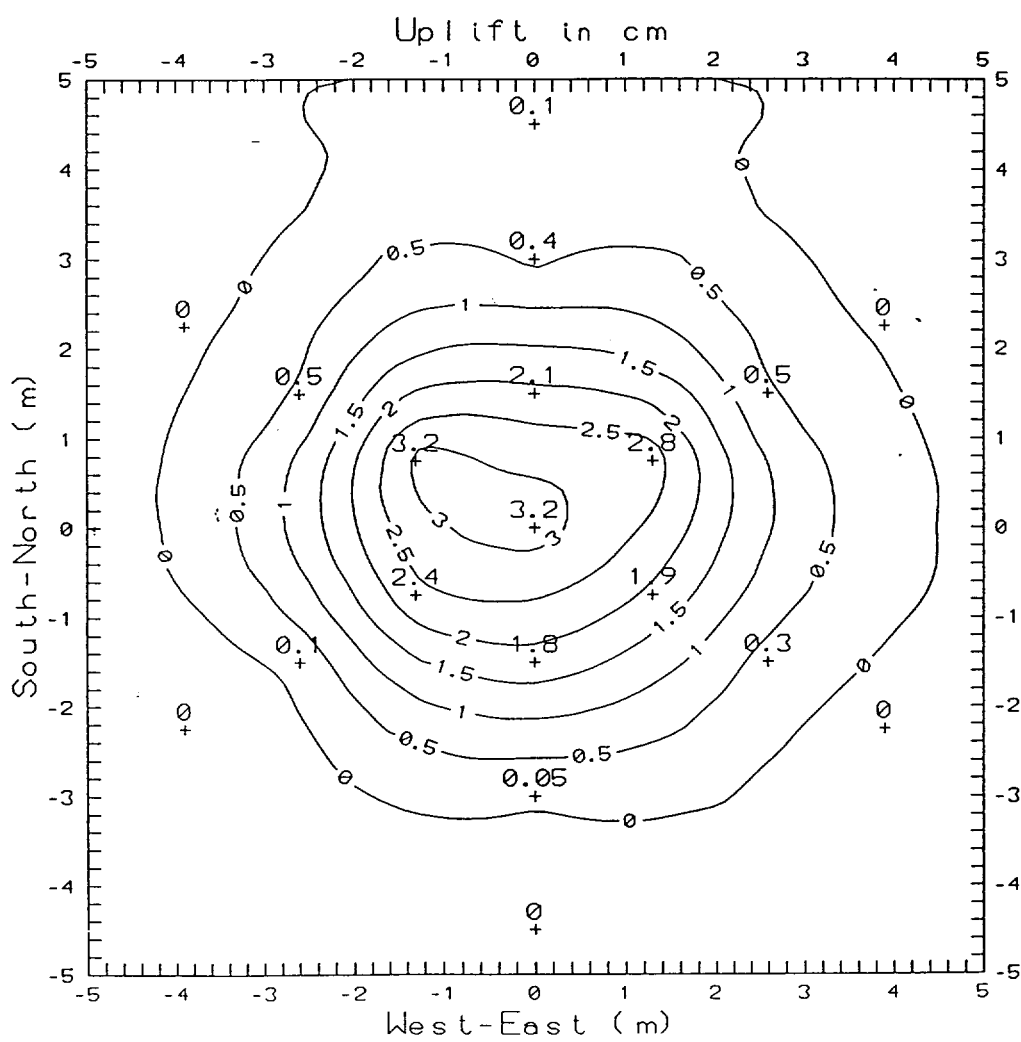
The effect of a preexisting borehole 2 m from the point of injection appear to be minor. This suggests that interactions with monitoring wells that are relatively narrow, temporarily sealed, and more than 2m from the point of injection should have minor effects on the fracture. Pinching of the fracture aperture in the vicinity of the driven casing may result in excessive head losses if the driven casing were pumped as a well (assuming the driven casing was a gravel-packed well). However, interaction with a gravel-packed well may be considerably different than with a driven casing (e.g. the pinching effect may be absent), so effects on a gravel-packed well are speculative.

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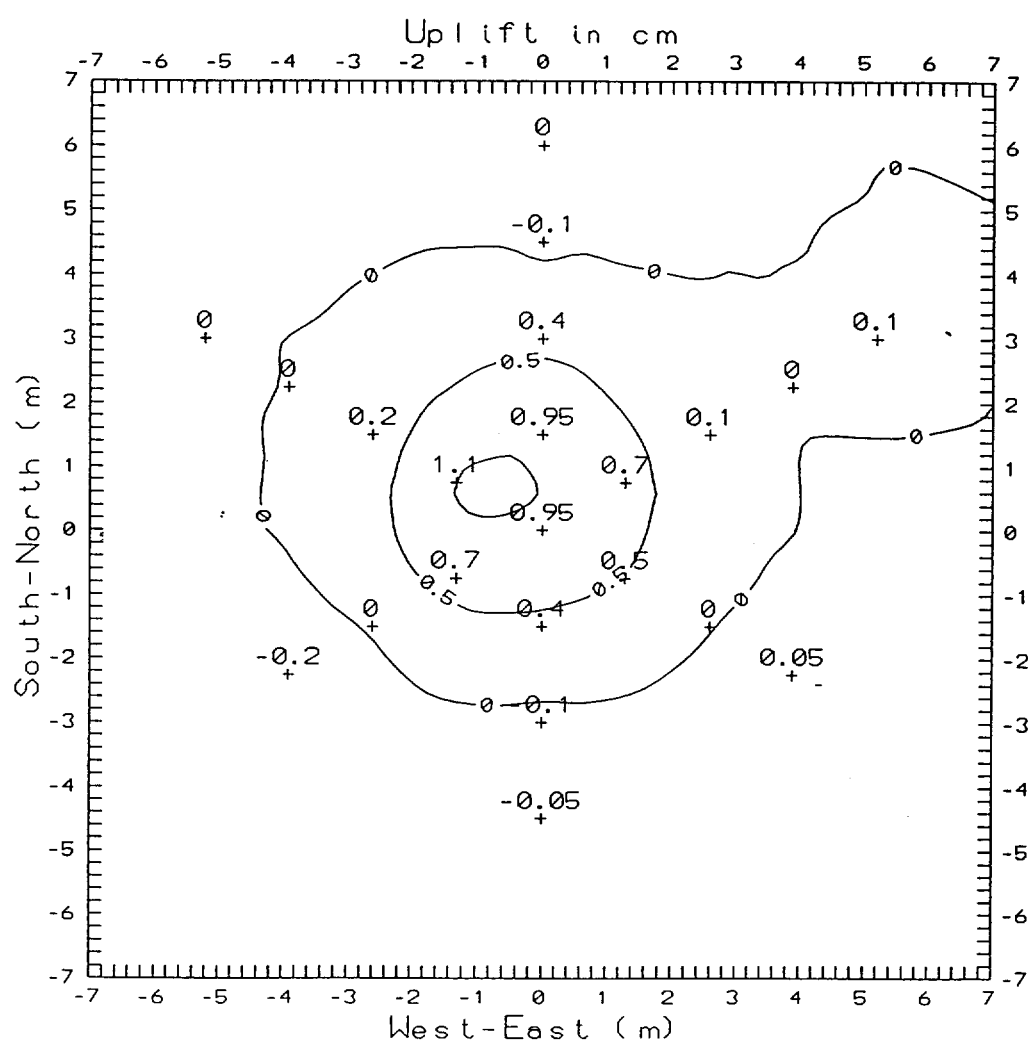
APPENDIX A
UPLIFT MAPS AND PRESSURE LOGS

Pressure logs and maps of uplift for each fracture follow. The thickness of sand in the fracture can be estimated as the uplift times the volumetric sand content of the slurry (0.4 to 0.5 for the fractures created at Sarnia).

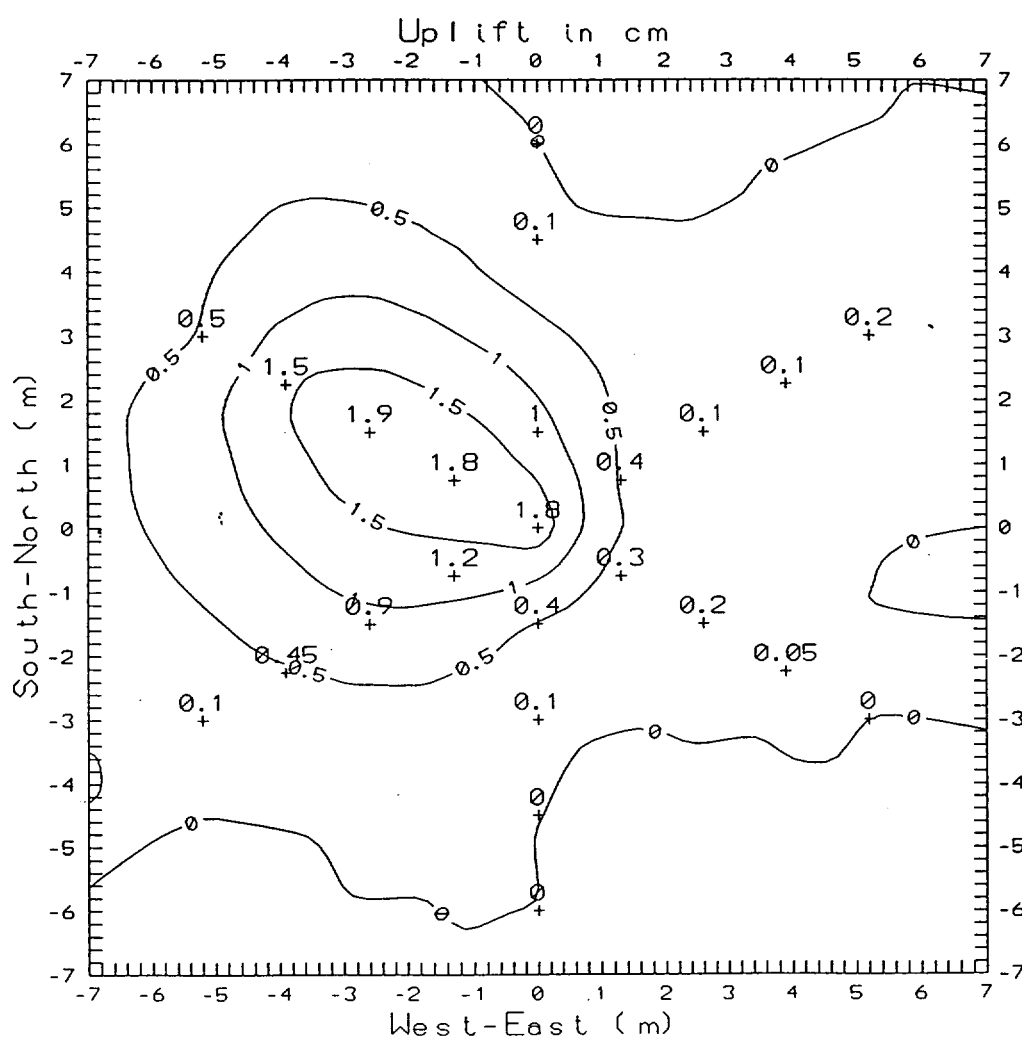
SAR1-20 Uplift Map



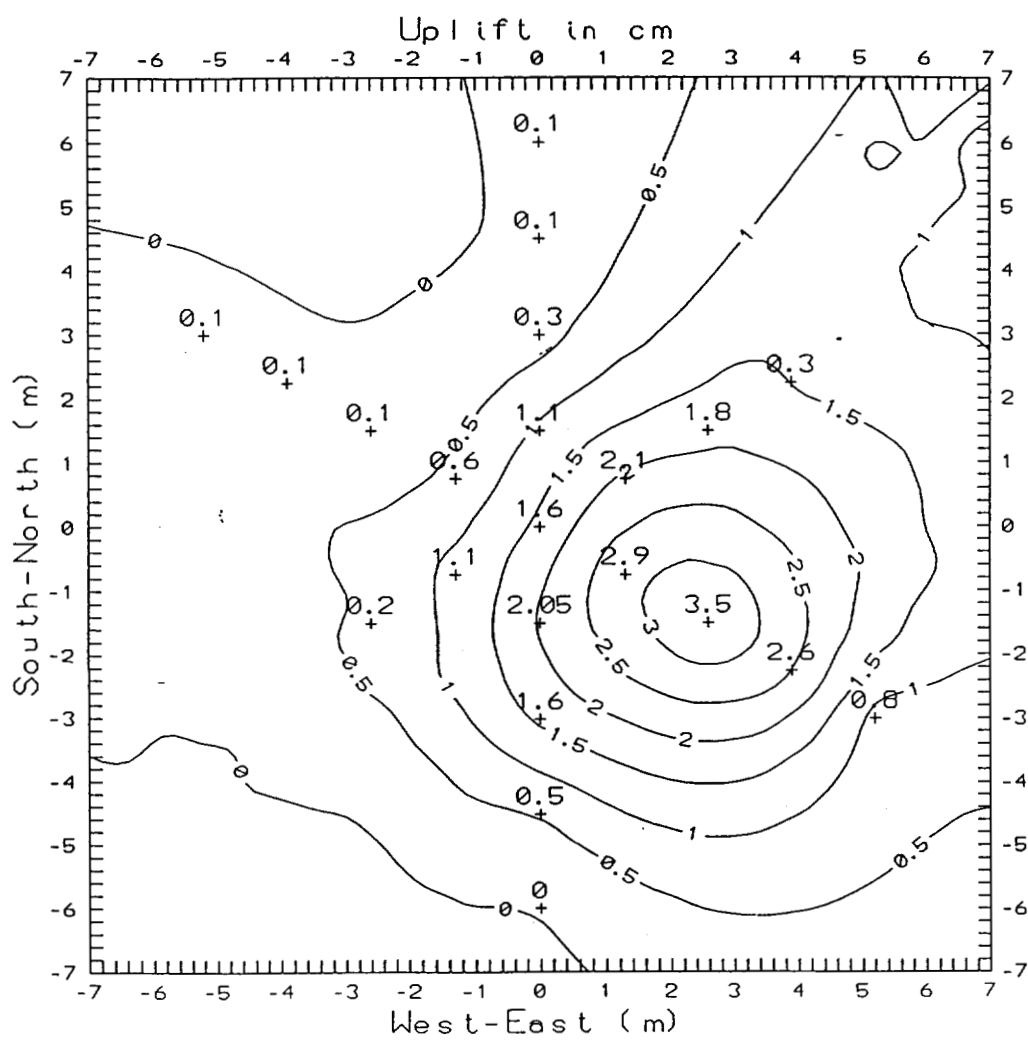
SAR2-20b Uplift Map



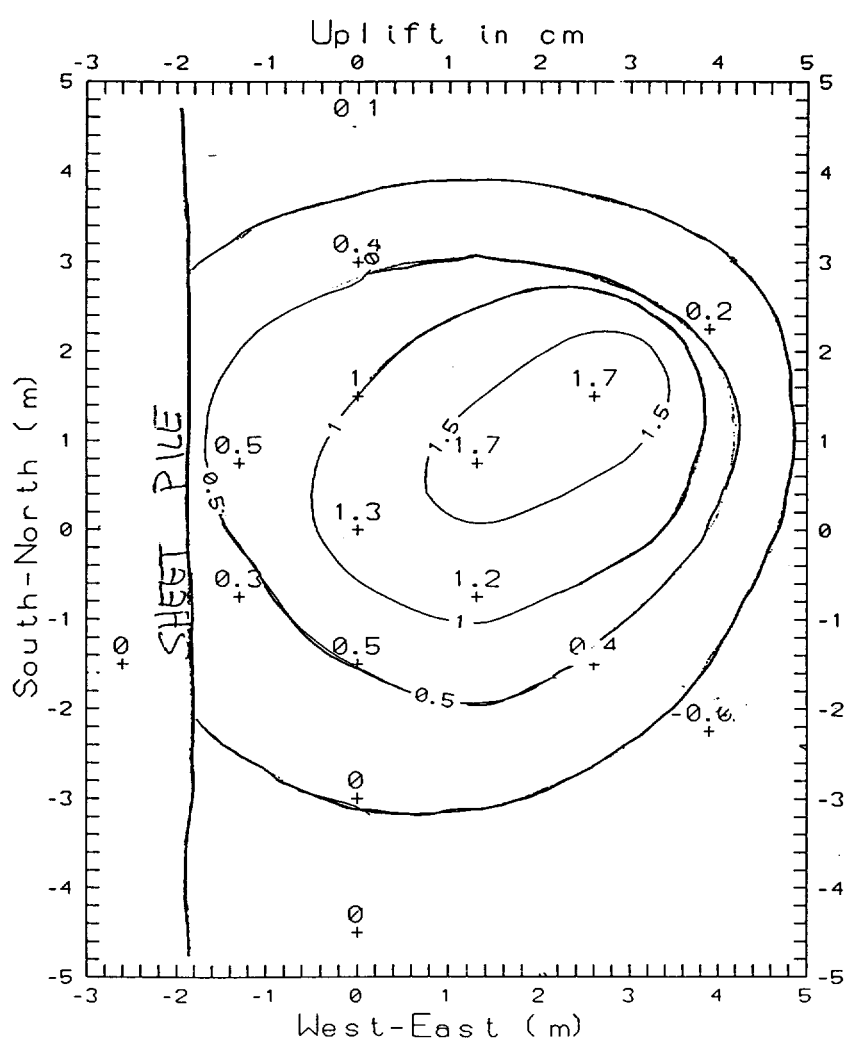
SAR2-30 Uplift Map



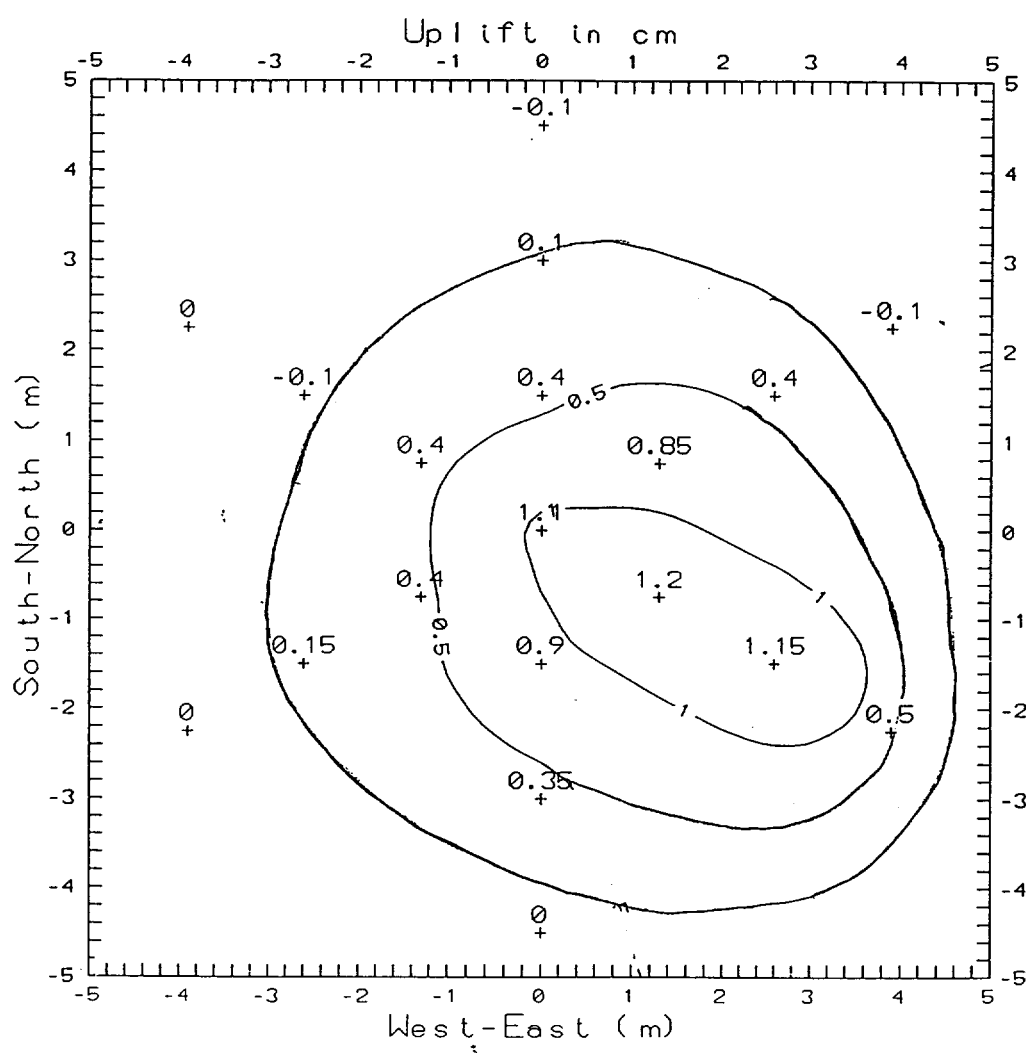
SAR2-30 Uplift Map



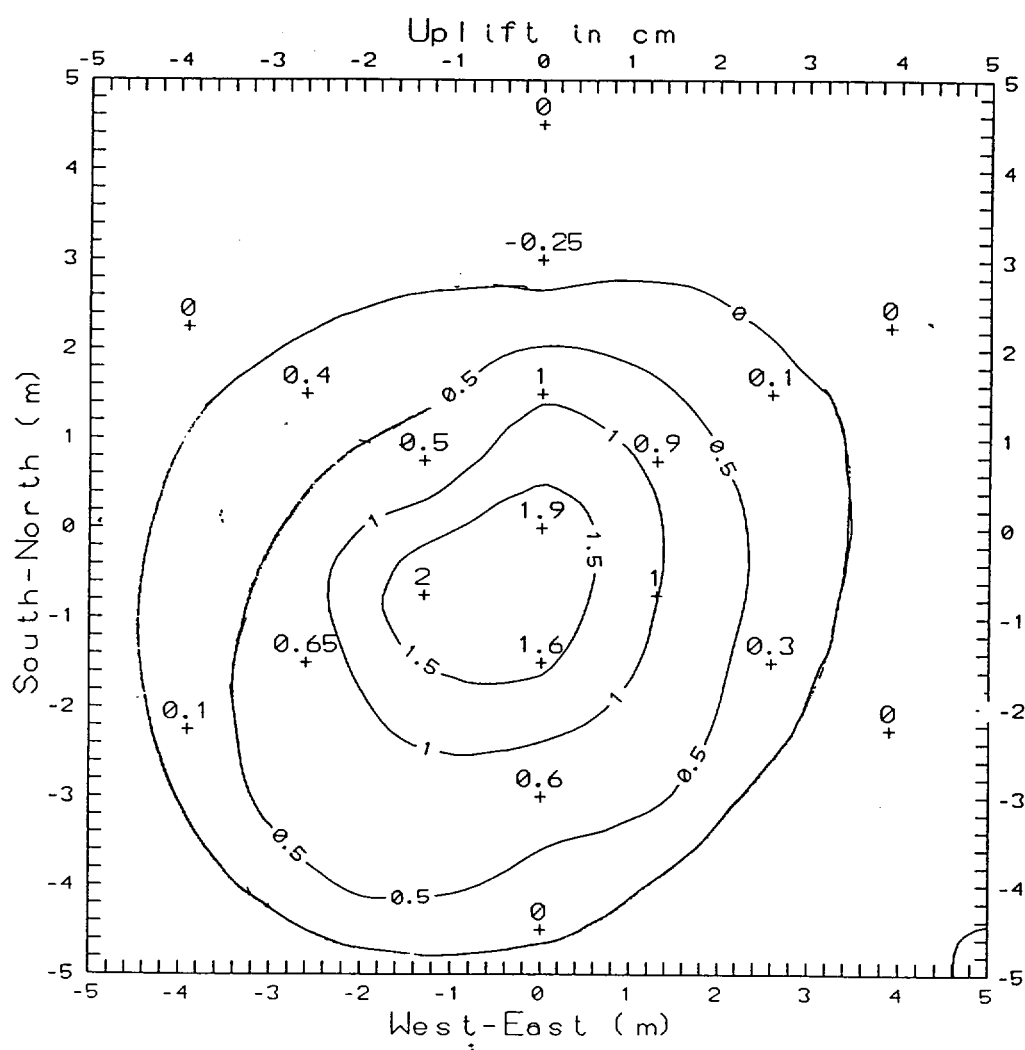
SAR3-20 Uplift Map



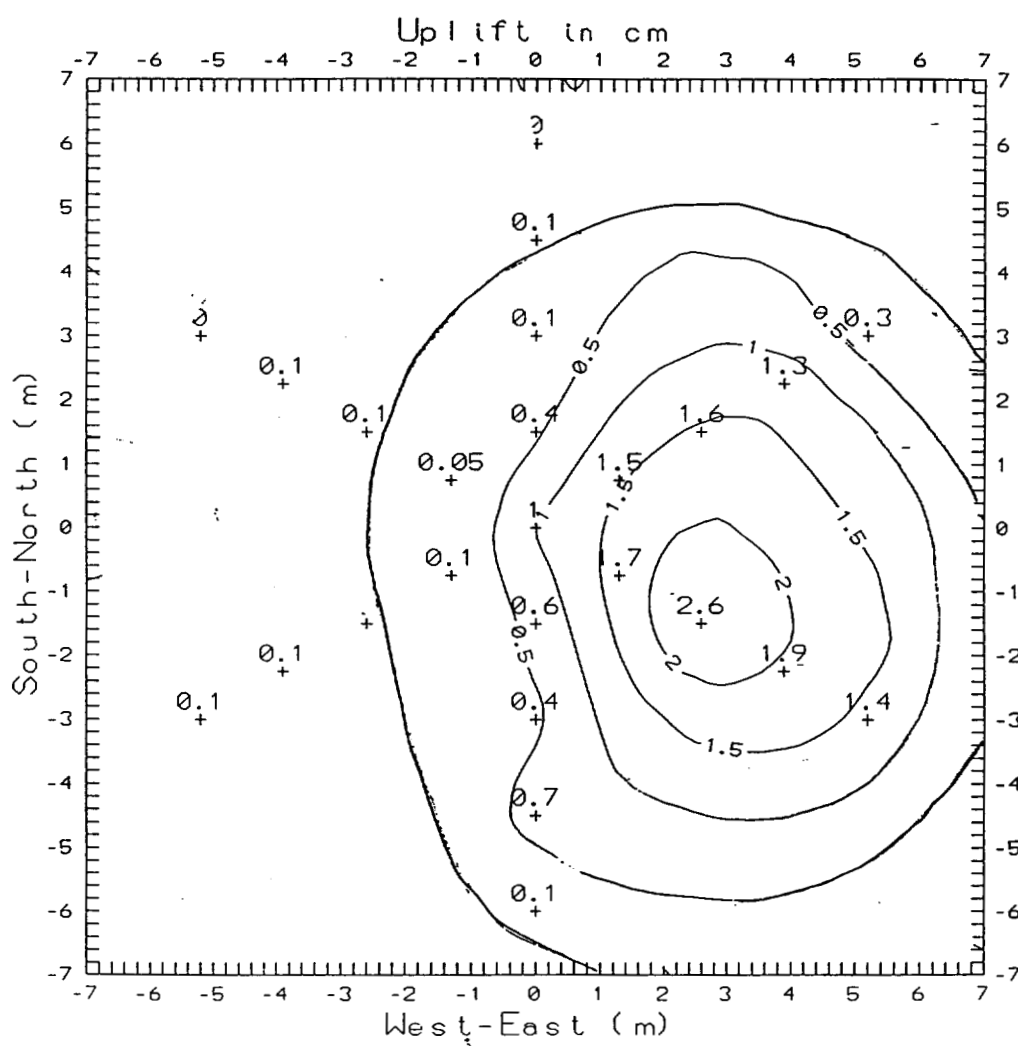
SAR4-25 Uplift Map



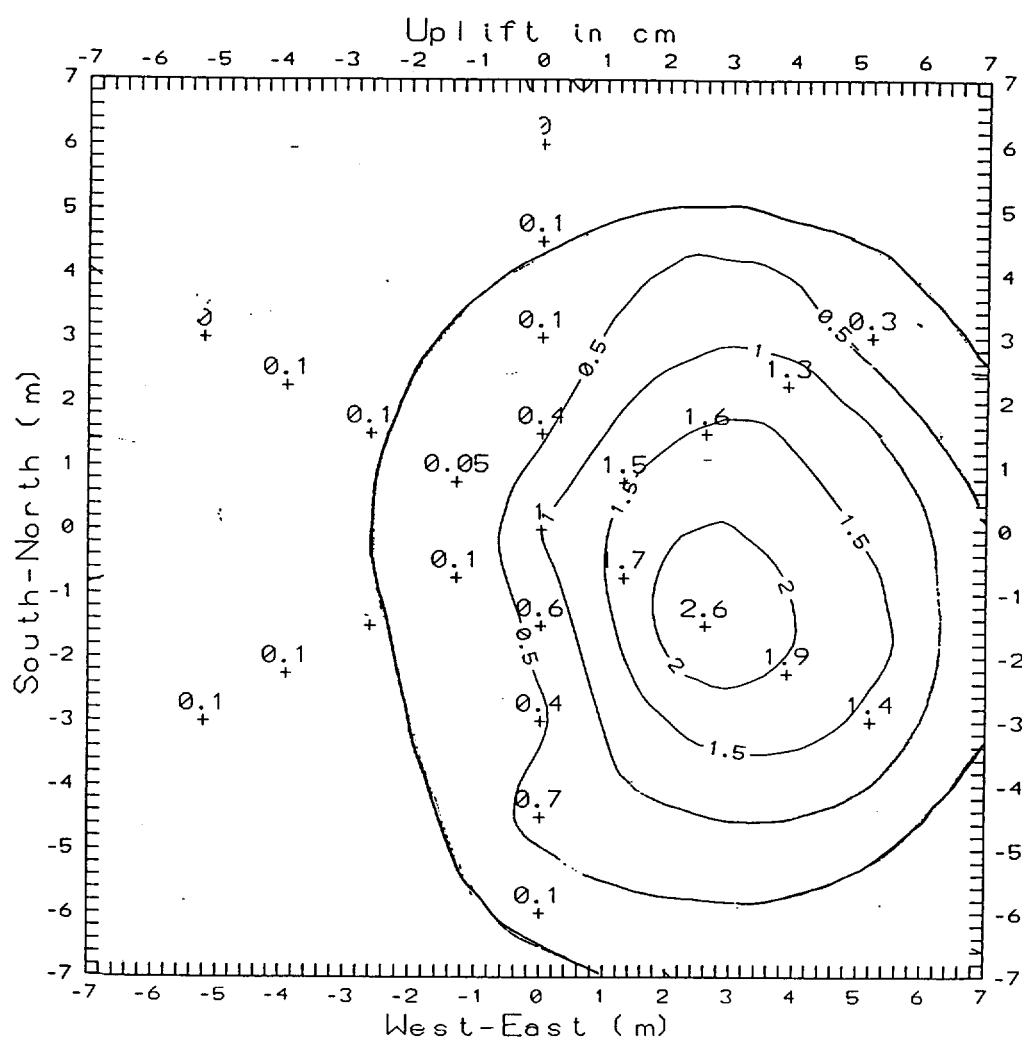
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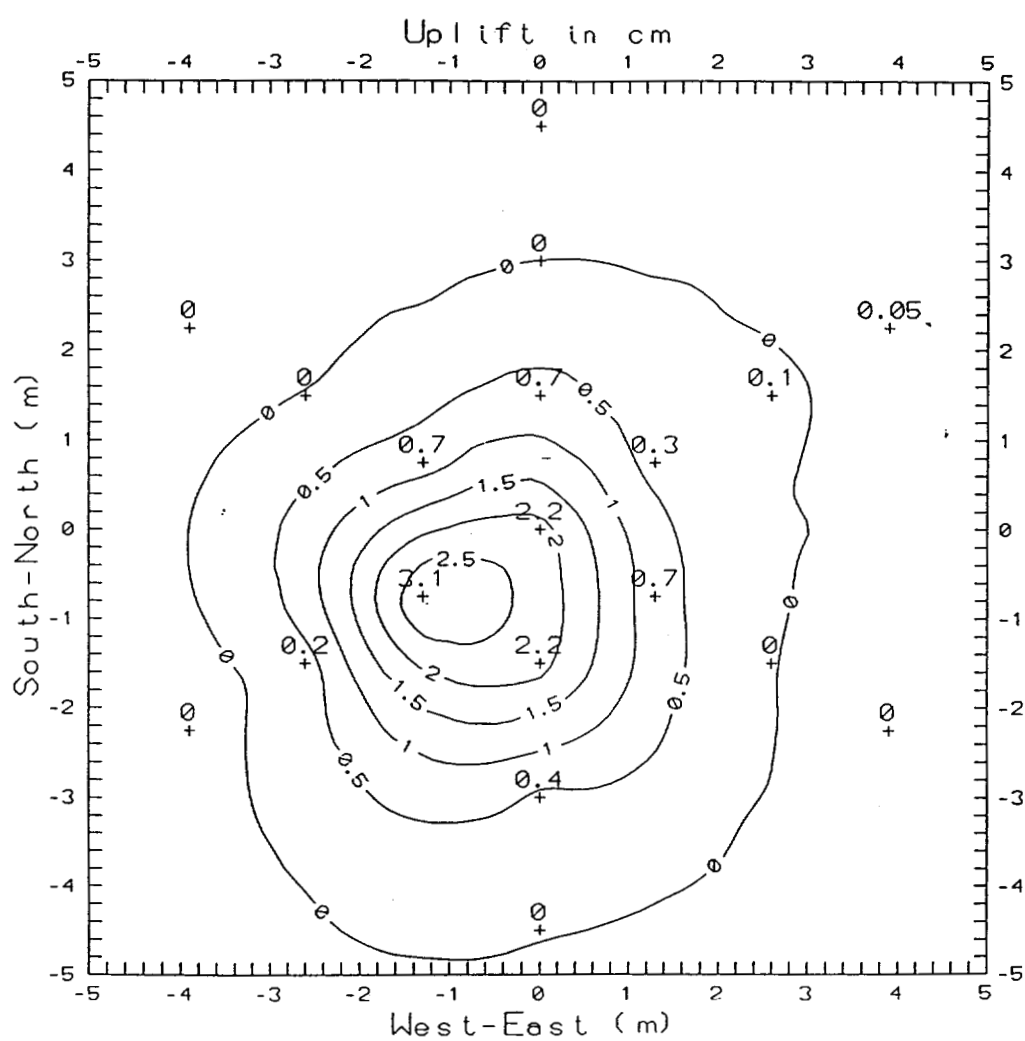
SAR5-30 Uplift Map



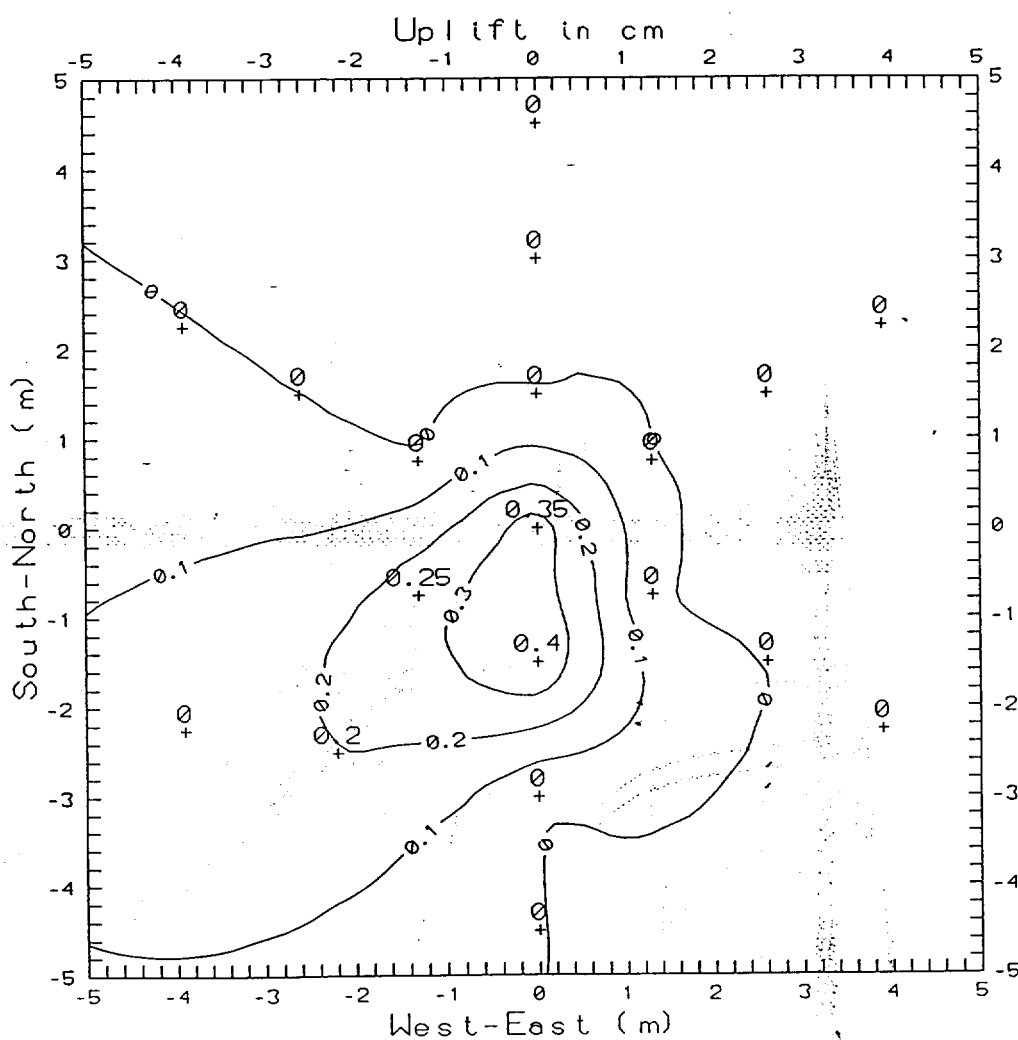
SAR5-30 Uplift Map



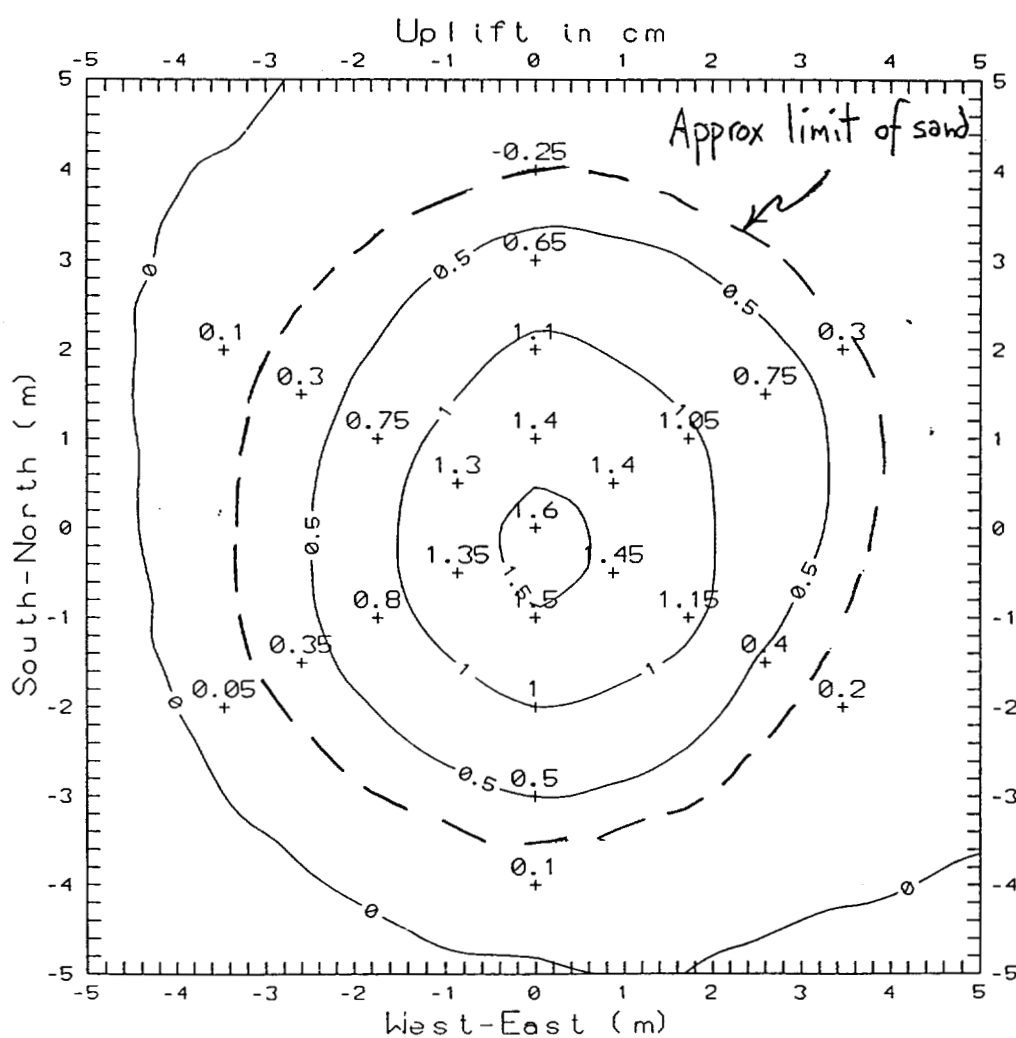
SAR6-12 Uplift Map



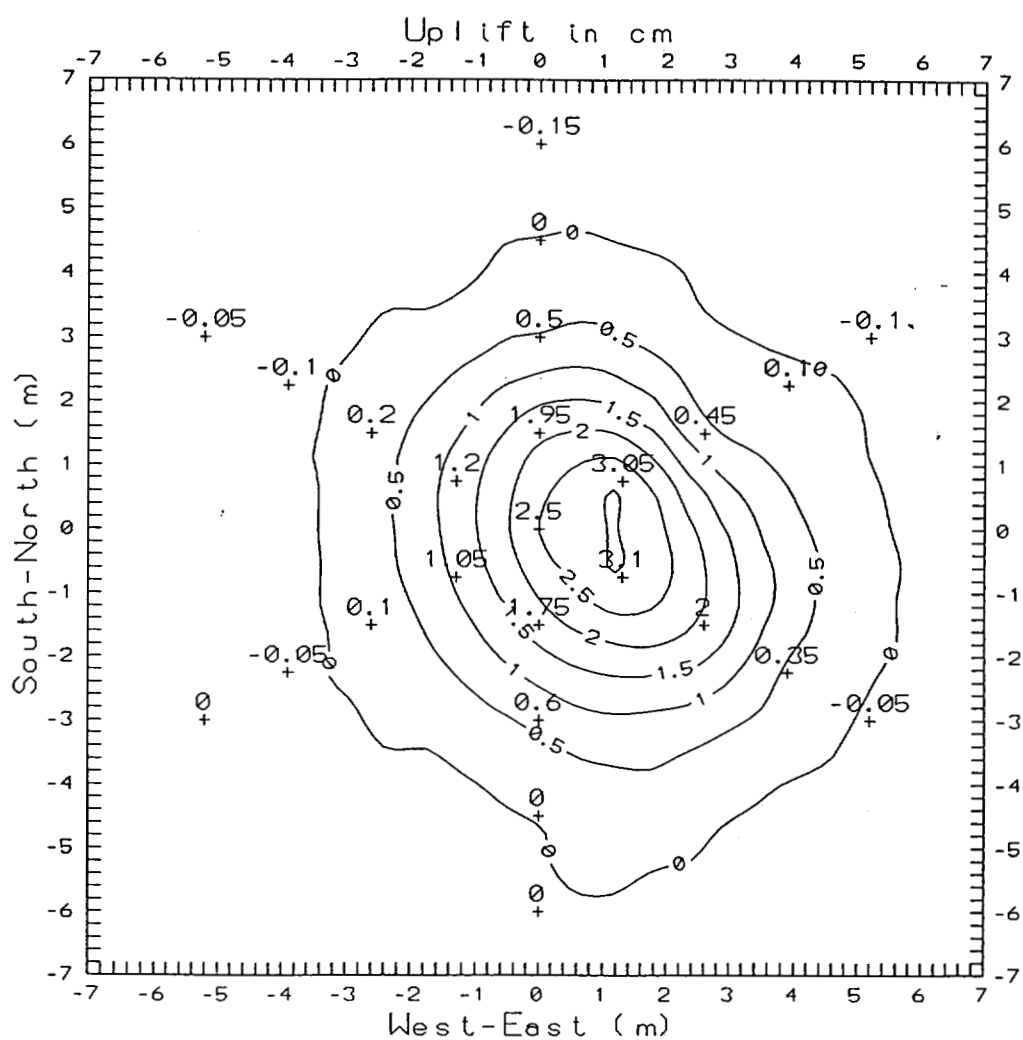
SAR6-12a Uplift Map



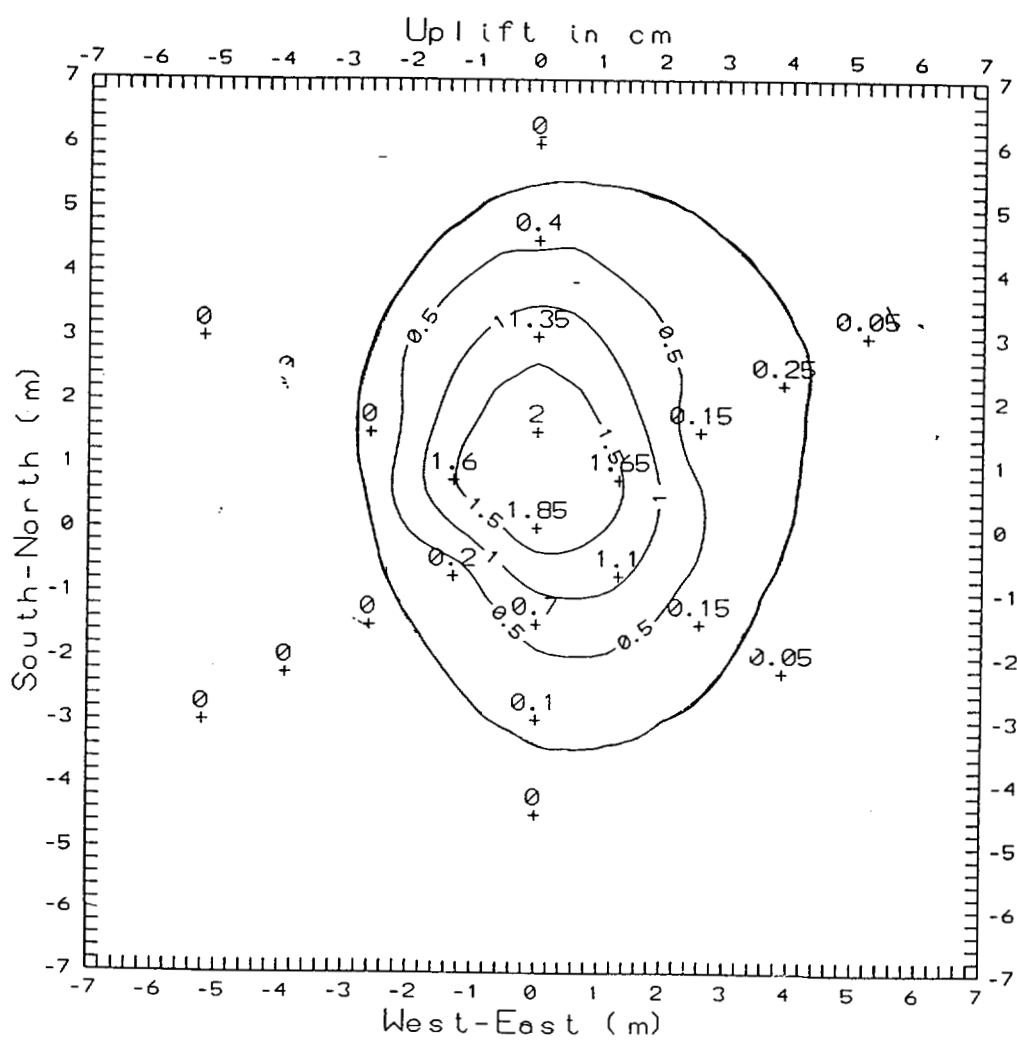
SAR7-25 Uplift Map



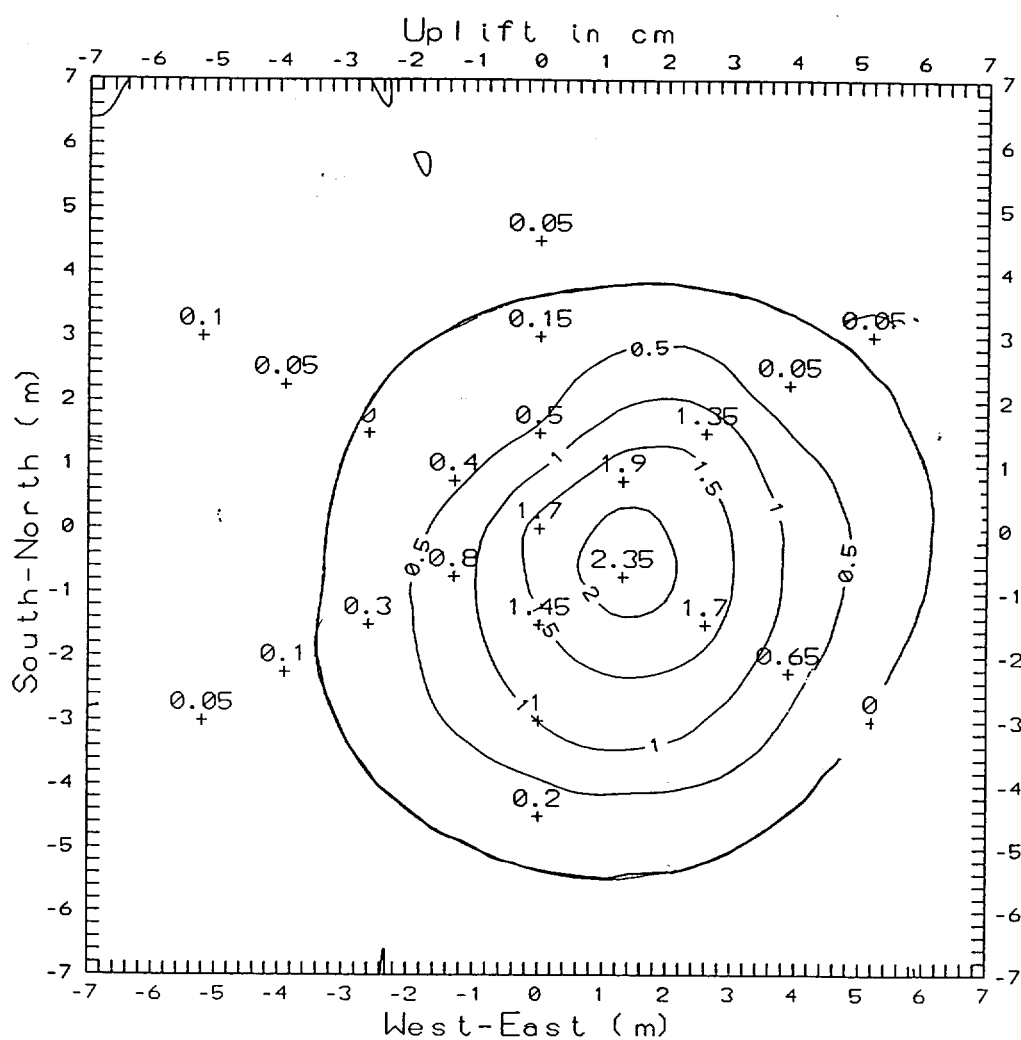
SAR8-18 Uplift Map



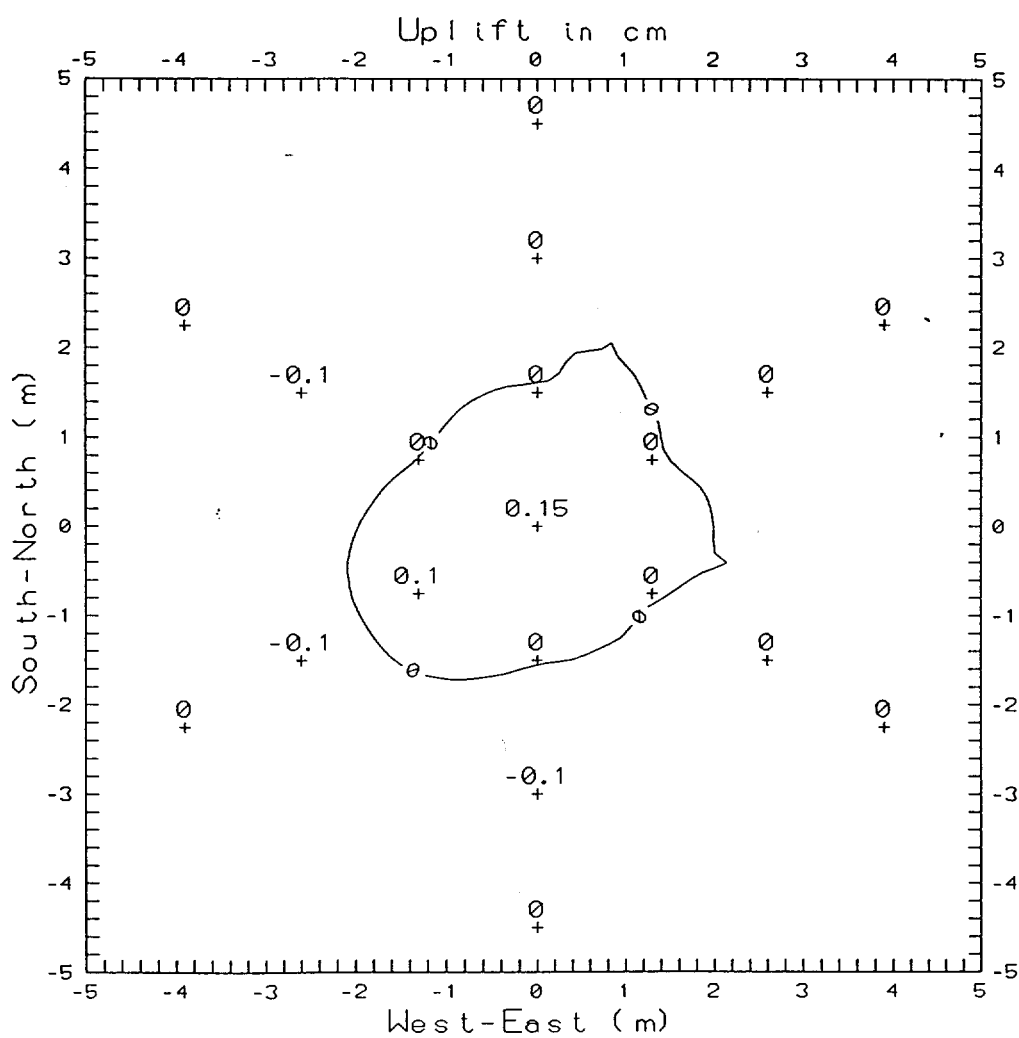
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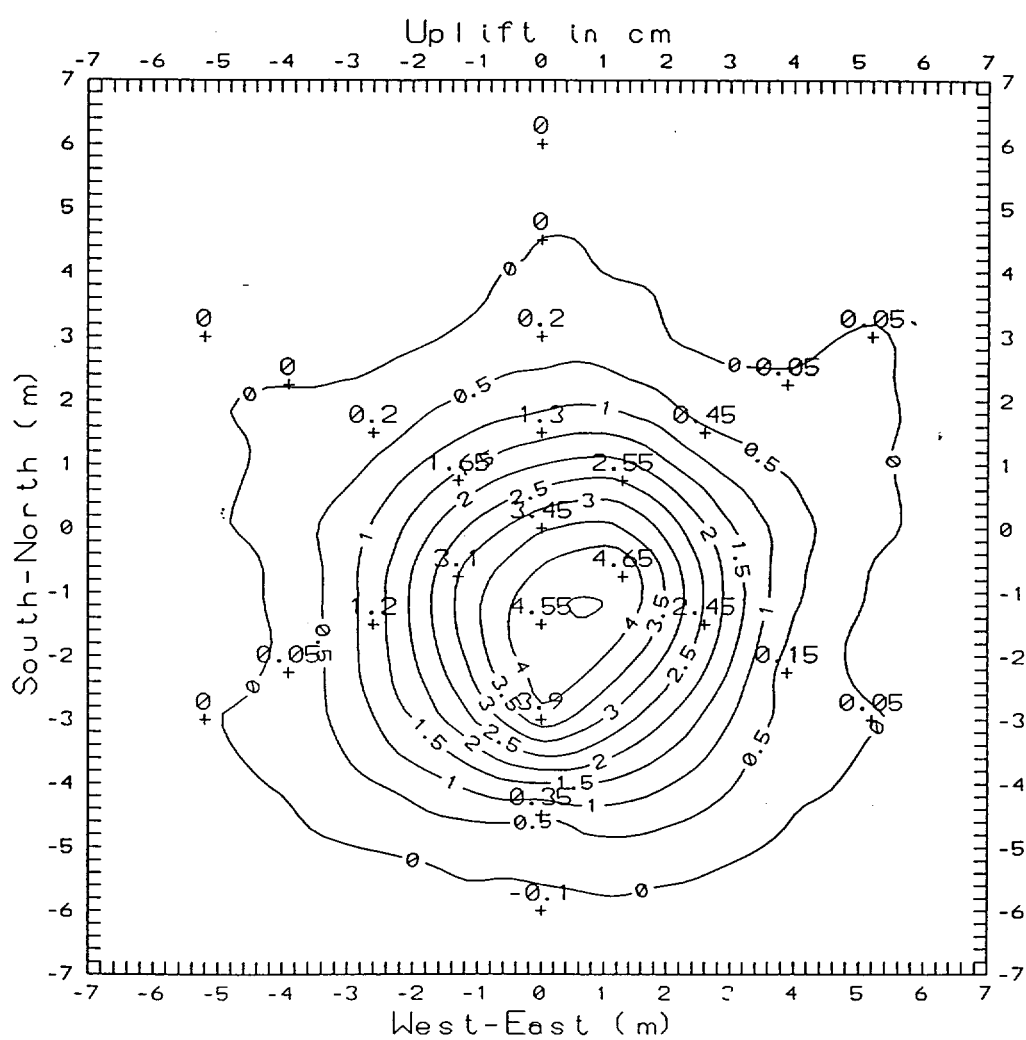
SAR8-26 Uplift Map



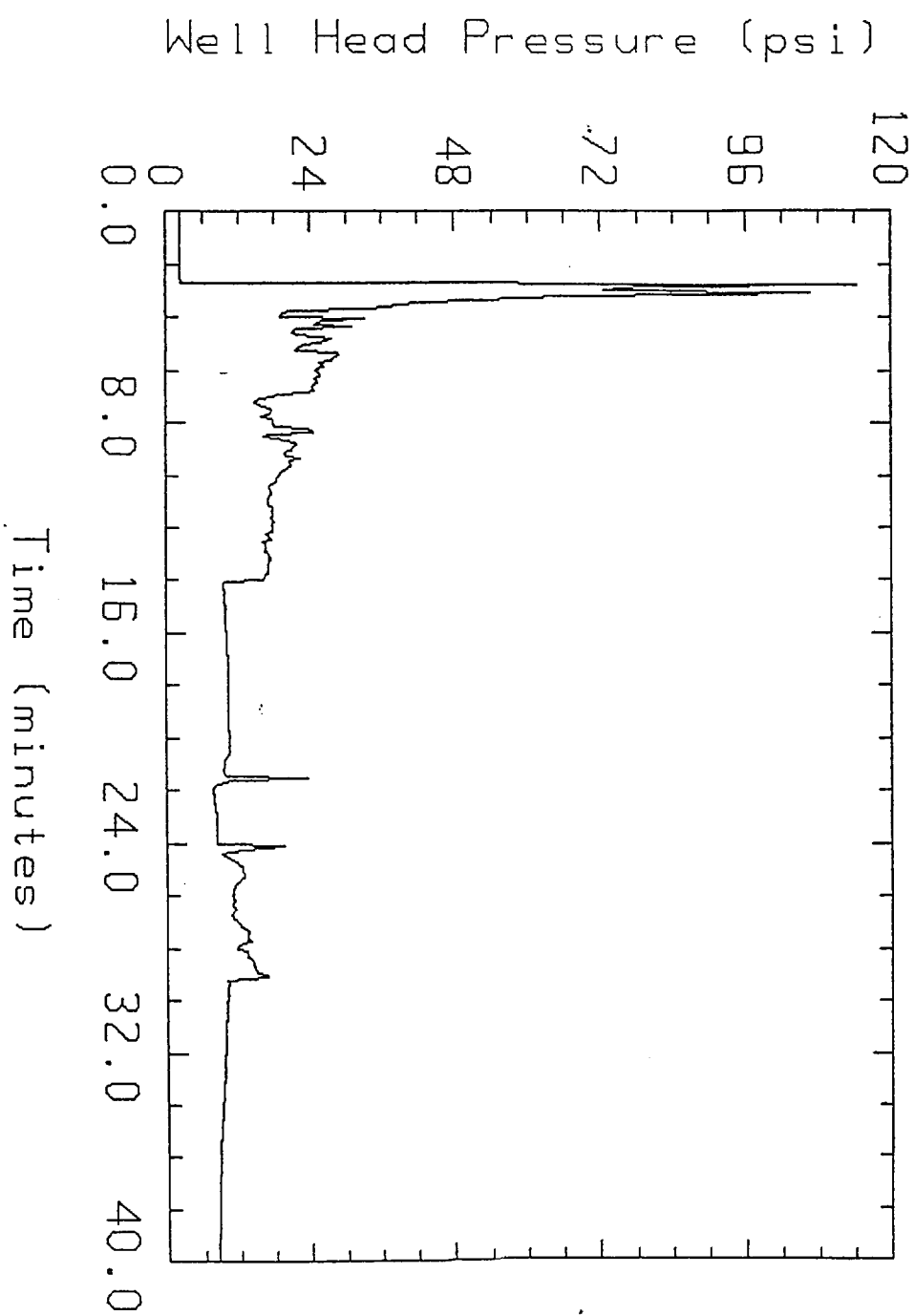
SAR9-55 Uplift Map



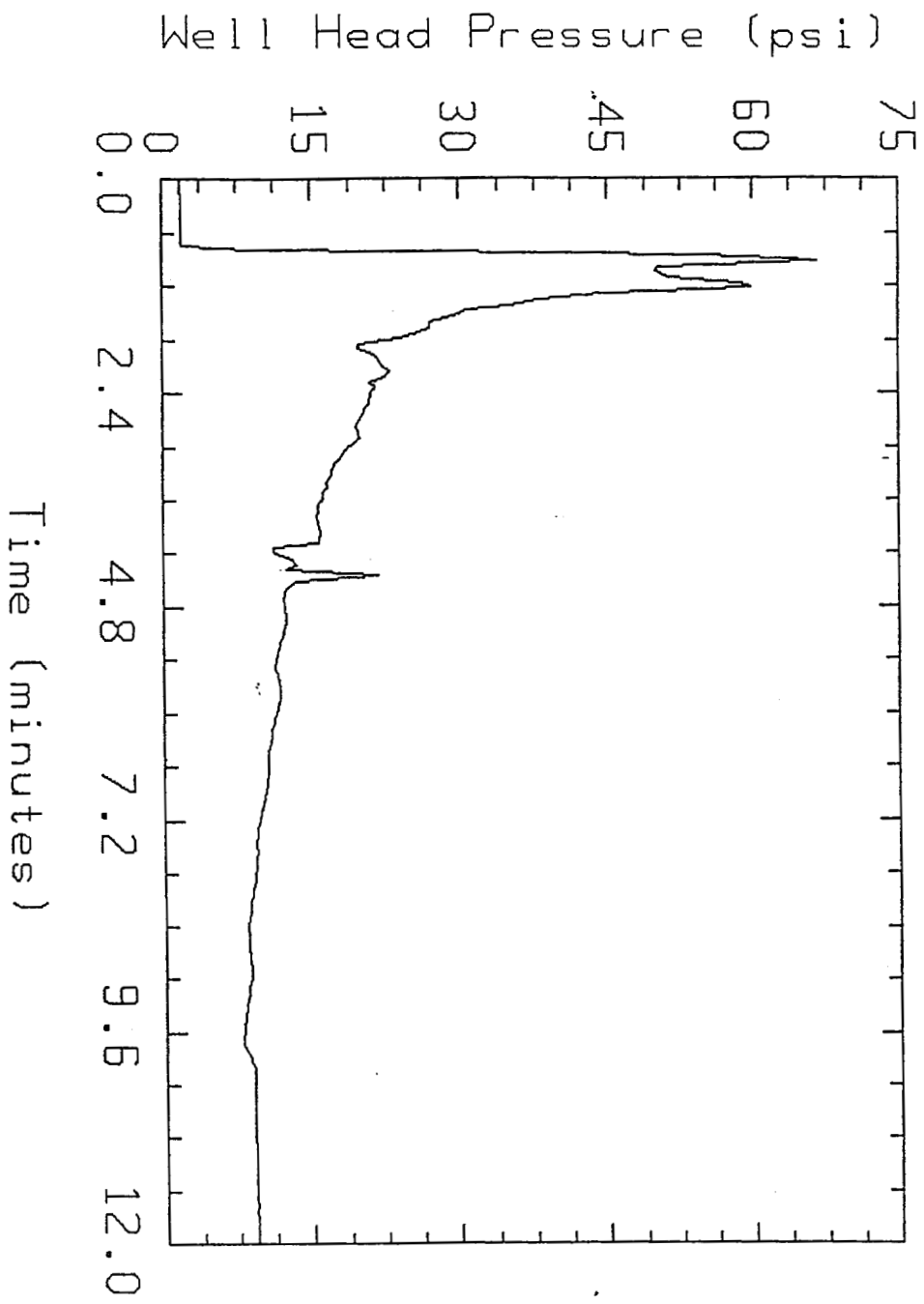
SAR10-20 Uplift Map



Pressure Log For: SAR1-30

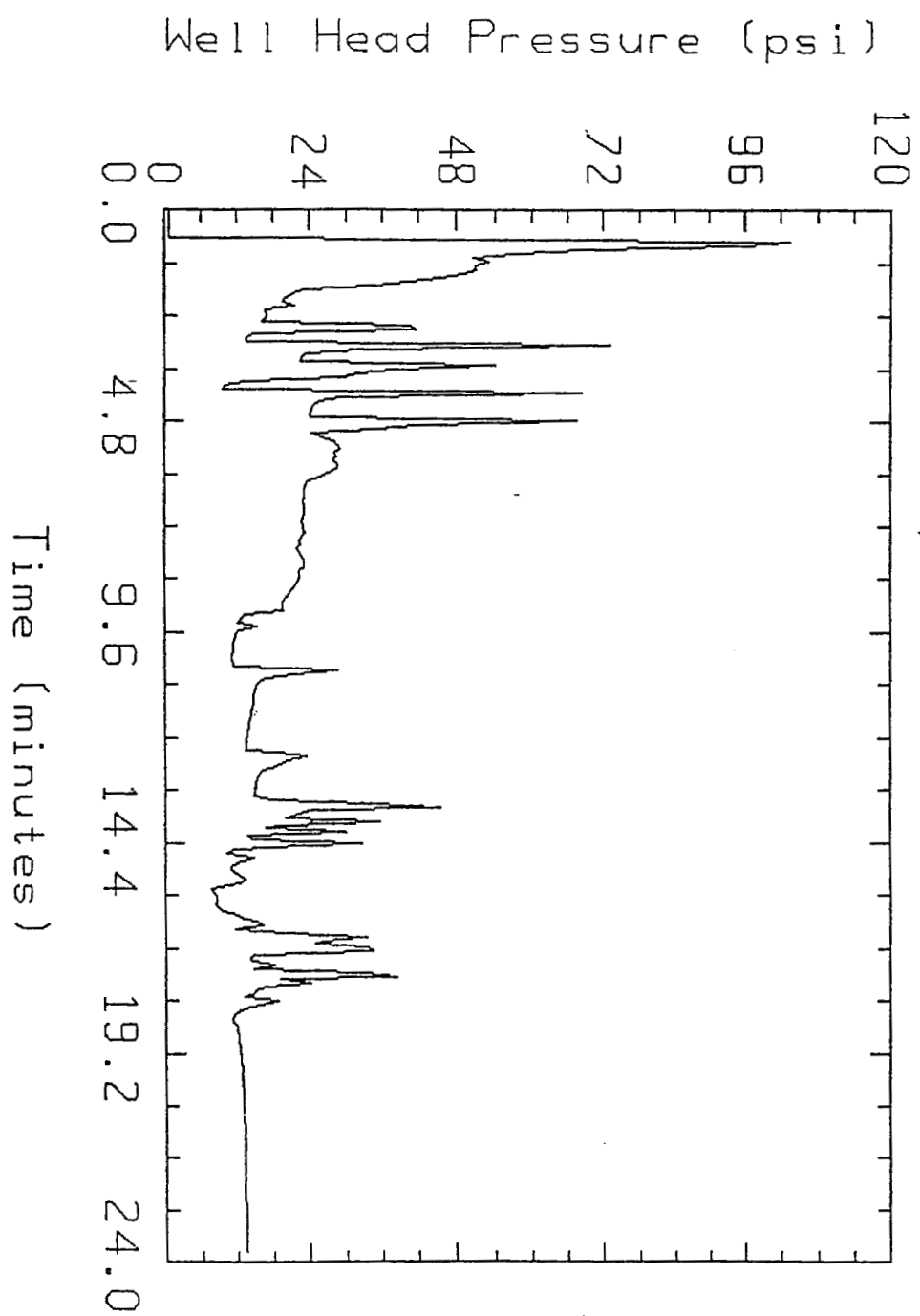


Pressure Log For: SAR2-20

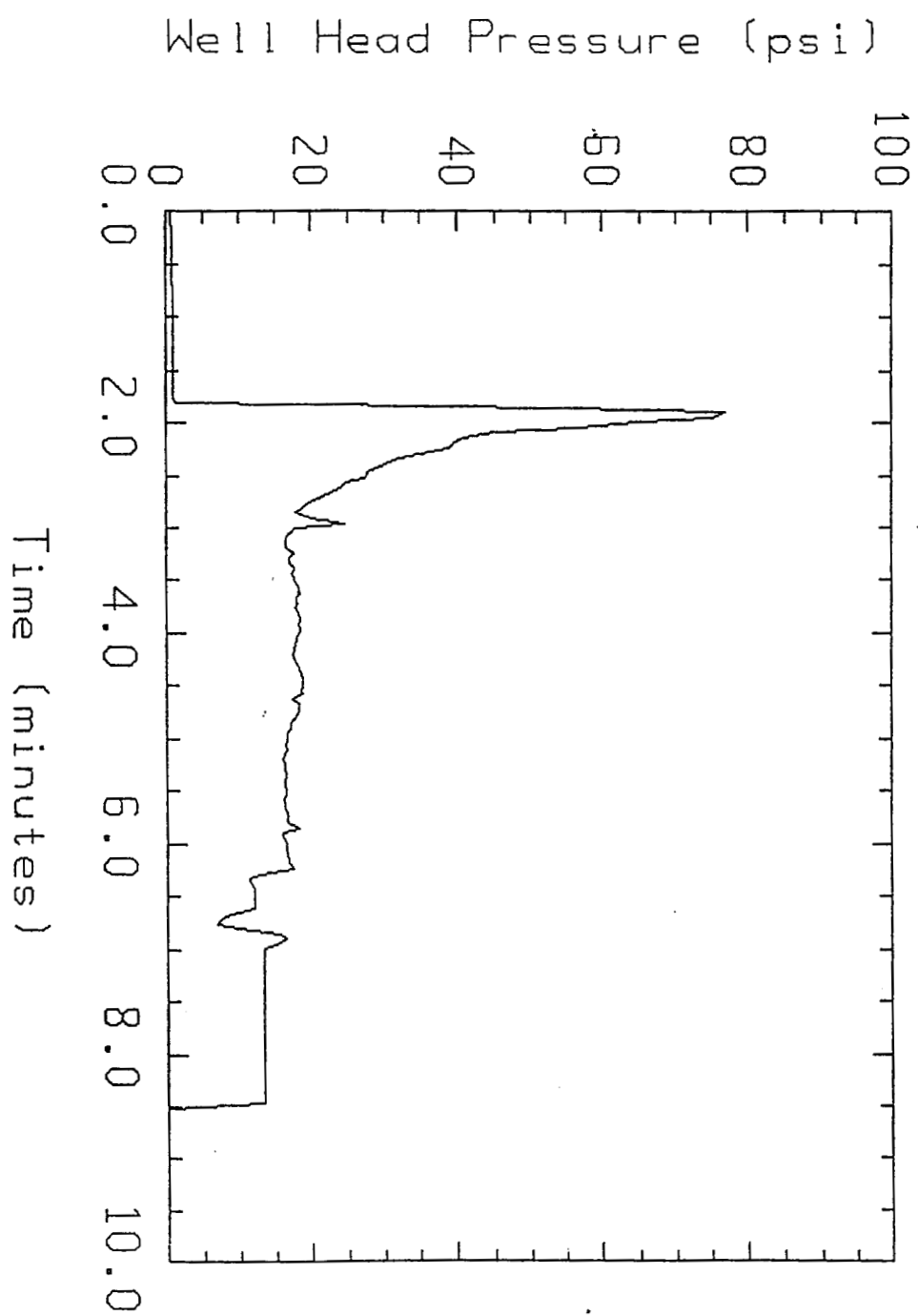


File: SAR2-20.DAT

Pressure Log For: SAR2-30

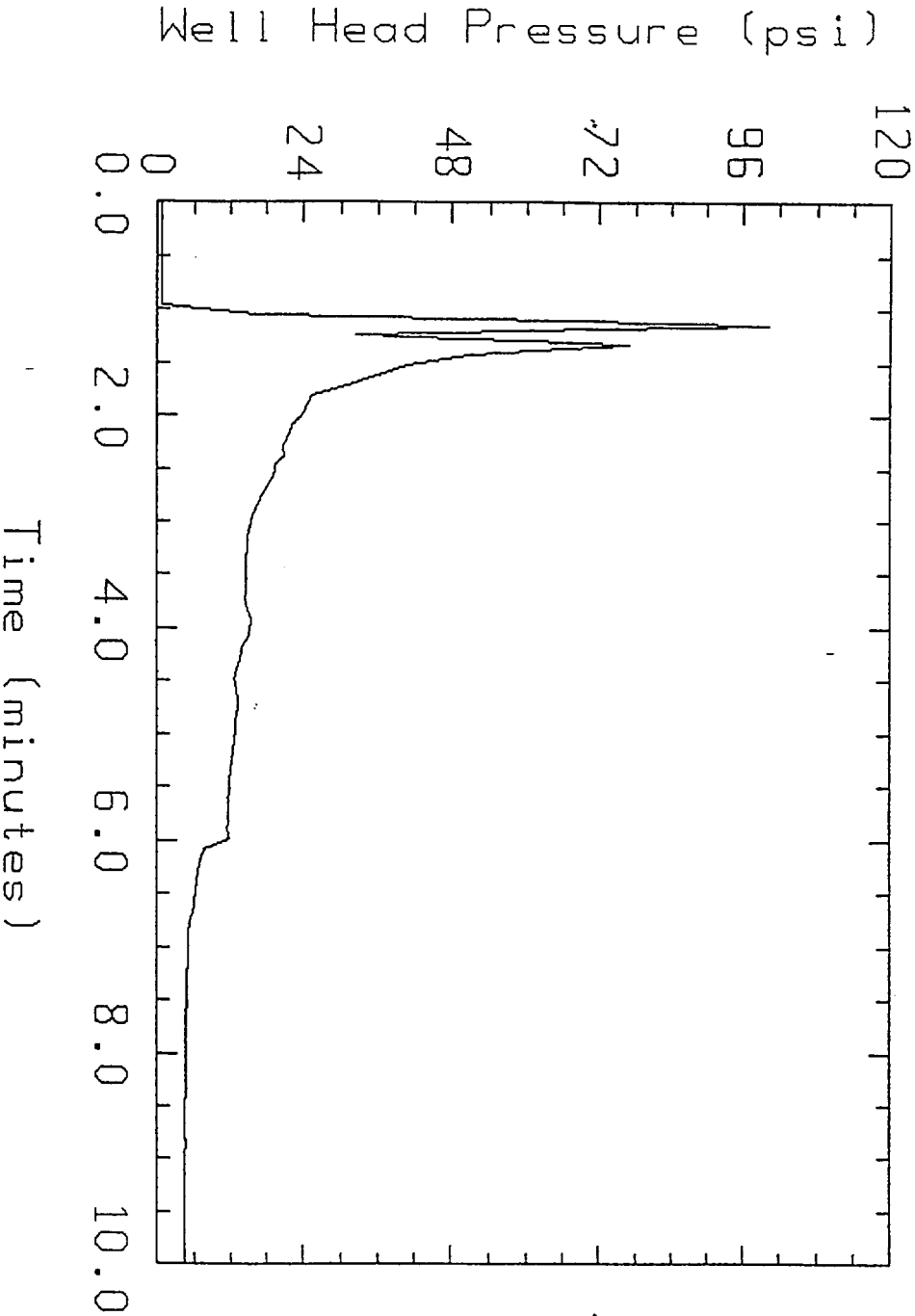


Pressure Log For: SAR3-20



File: SAR3-20.DAT

Pressure Log For: SAR4-25



Pressure Log For: SAR5-20

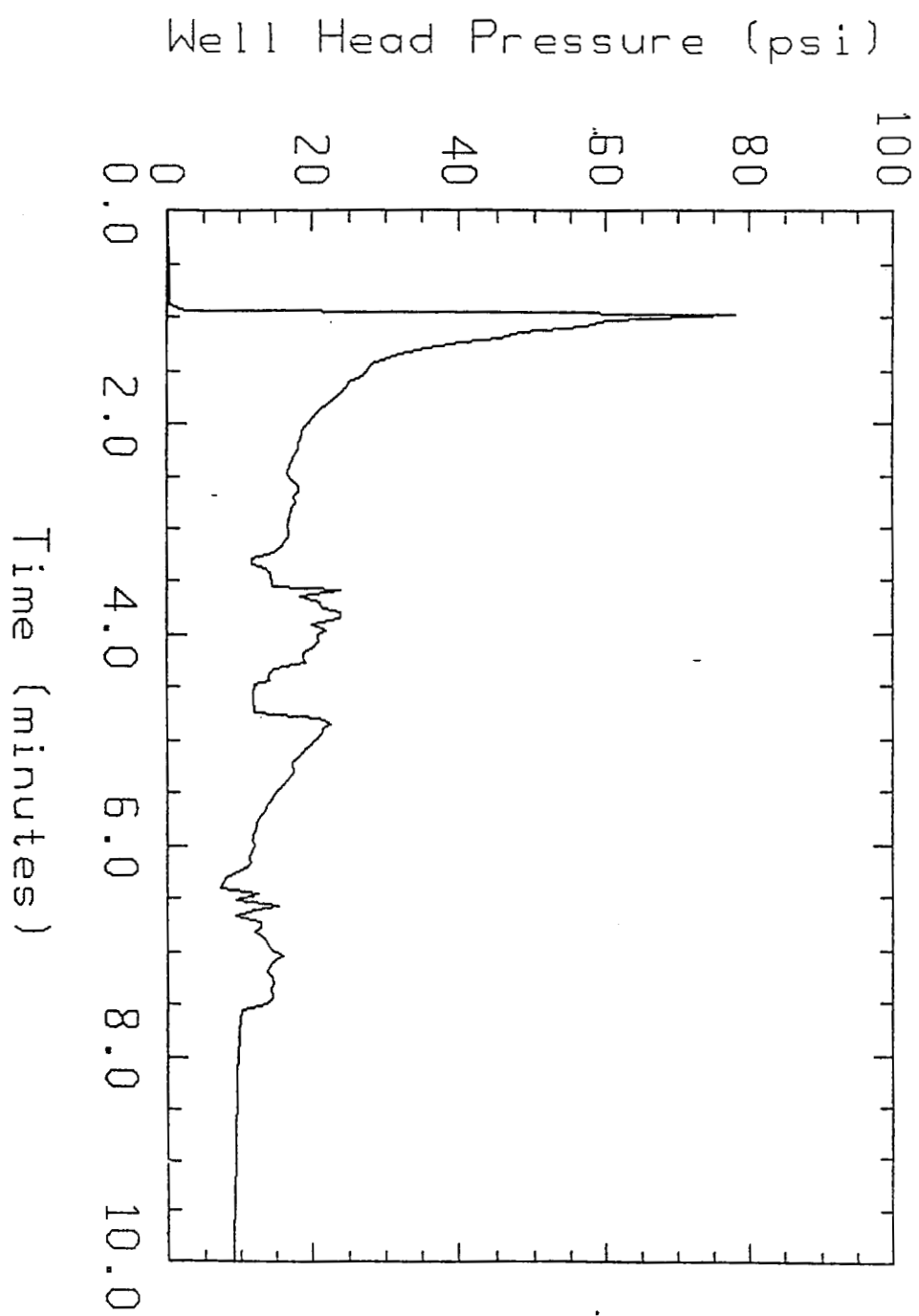
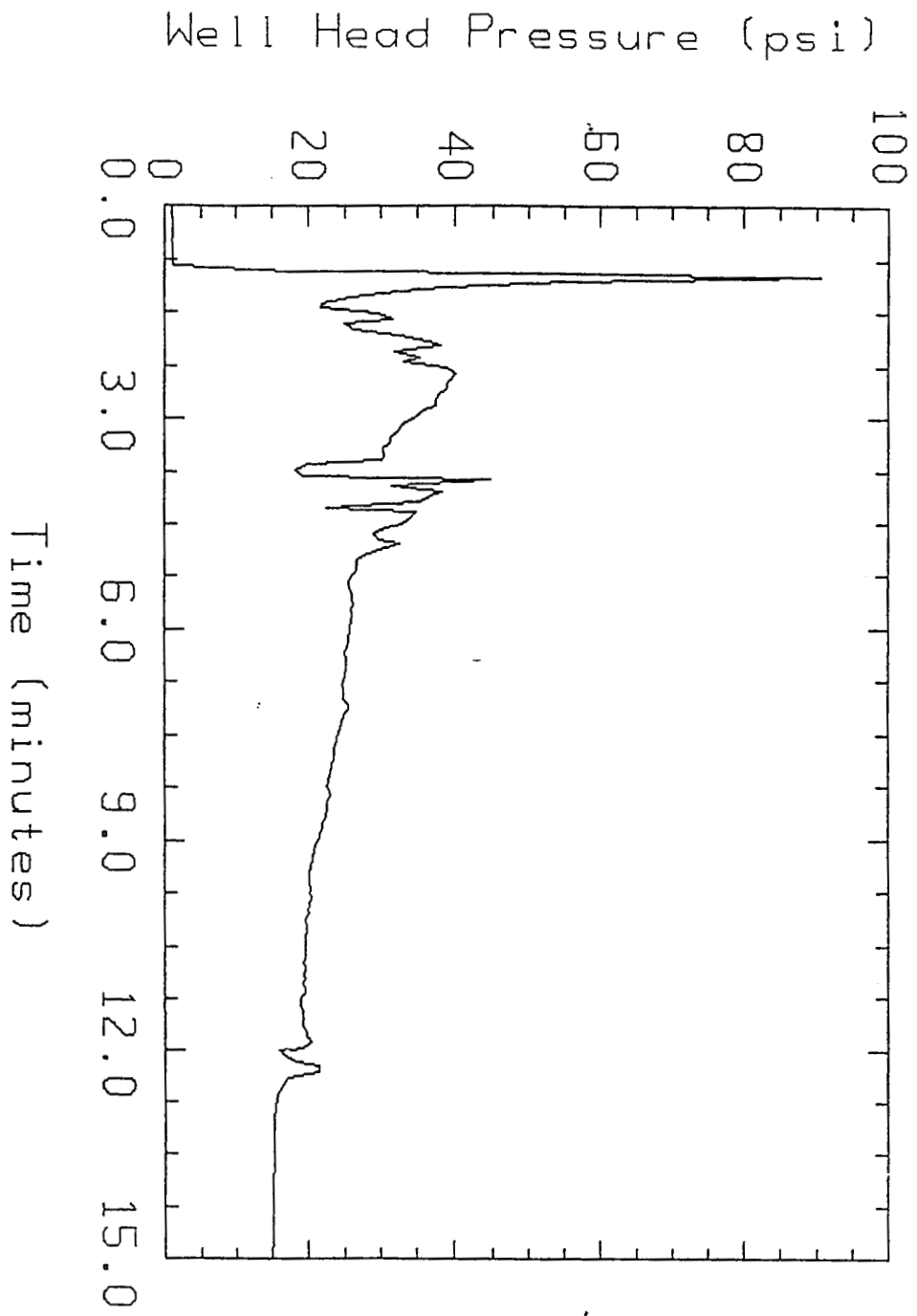


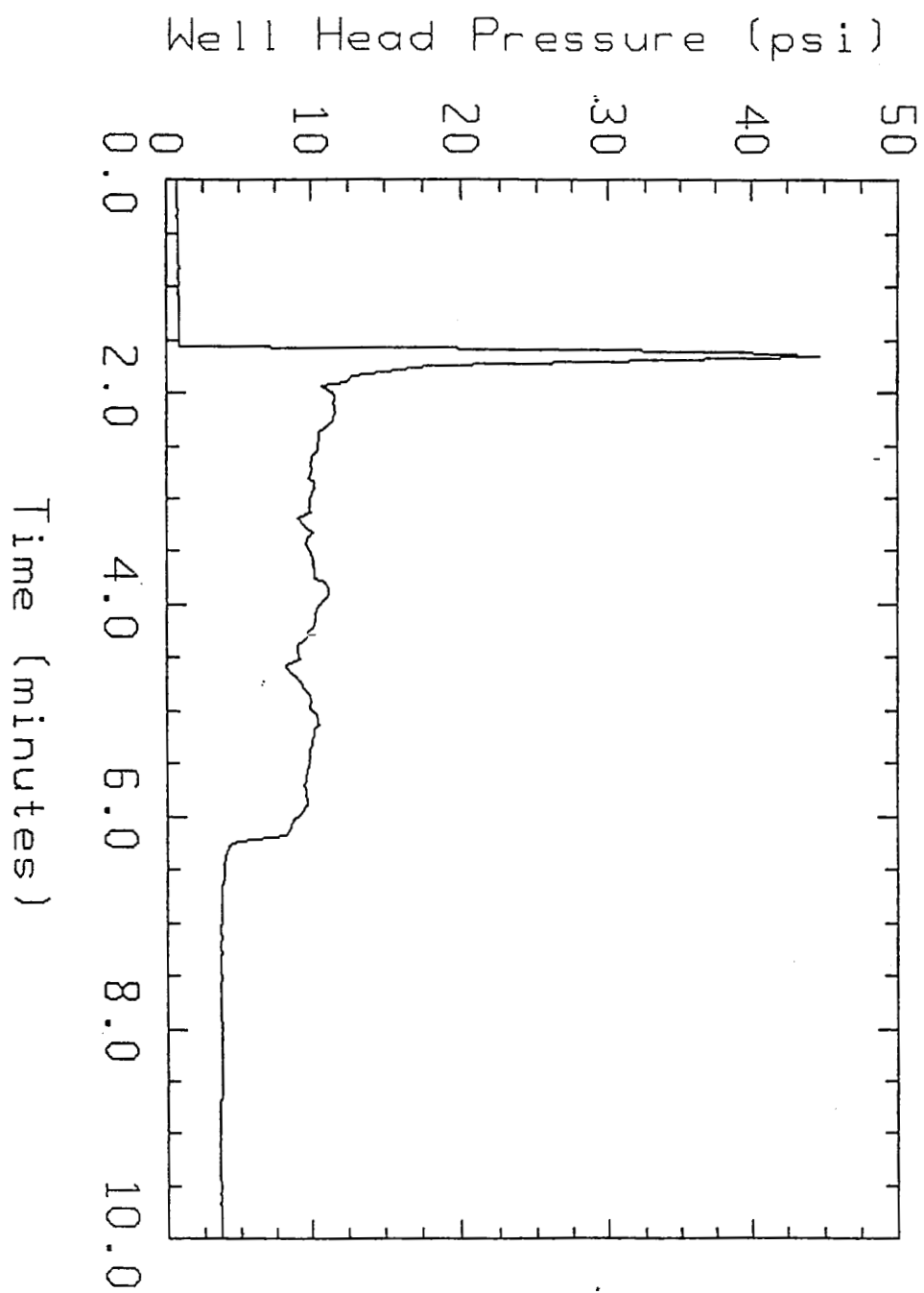
Fig: SAR5-20 DAT

Pressure Log For: SAR5-30



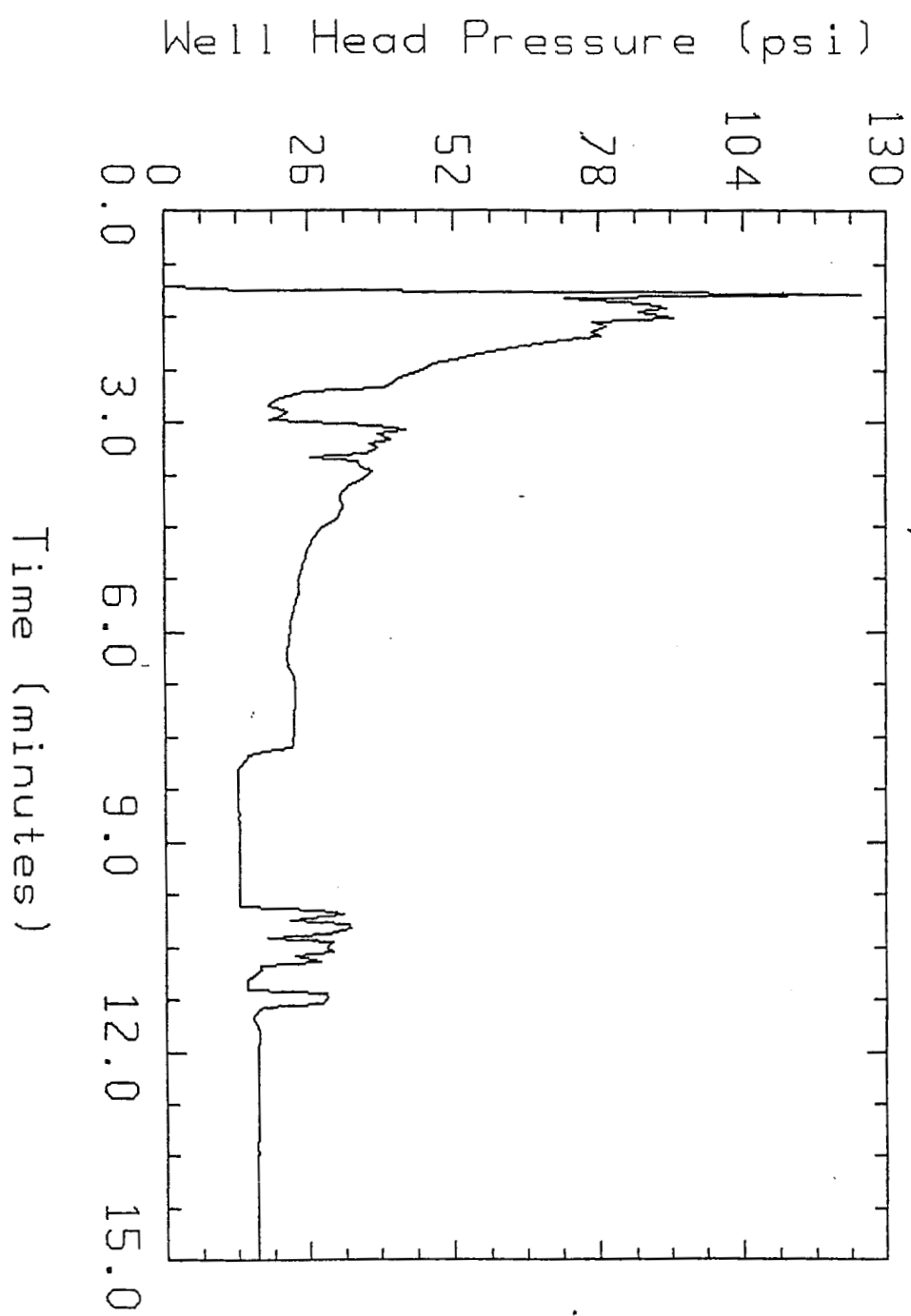
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Pressure Log For: SAR6-12



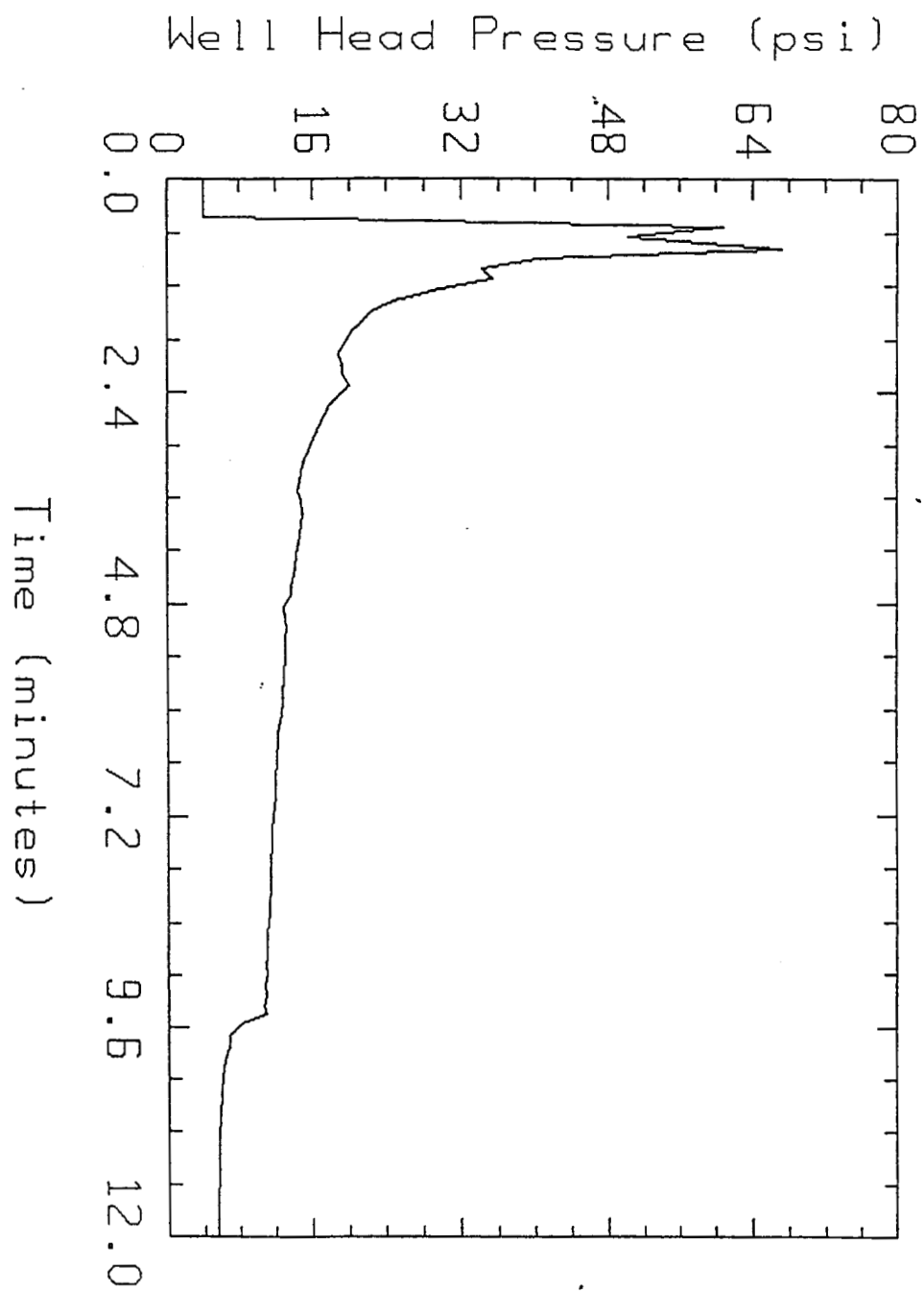
FILE: SAR6-12

Pressure Log For: SAR7-25



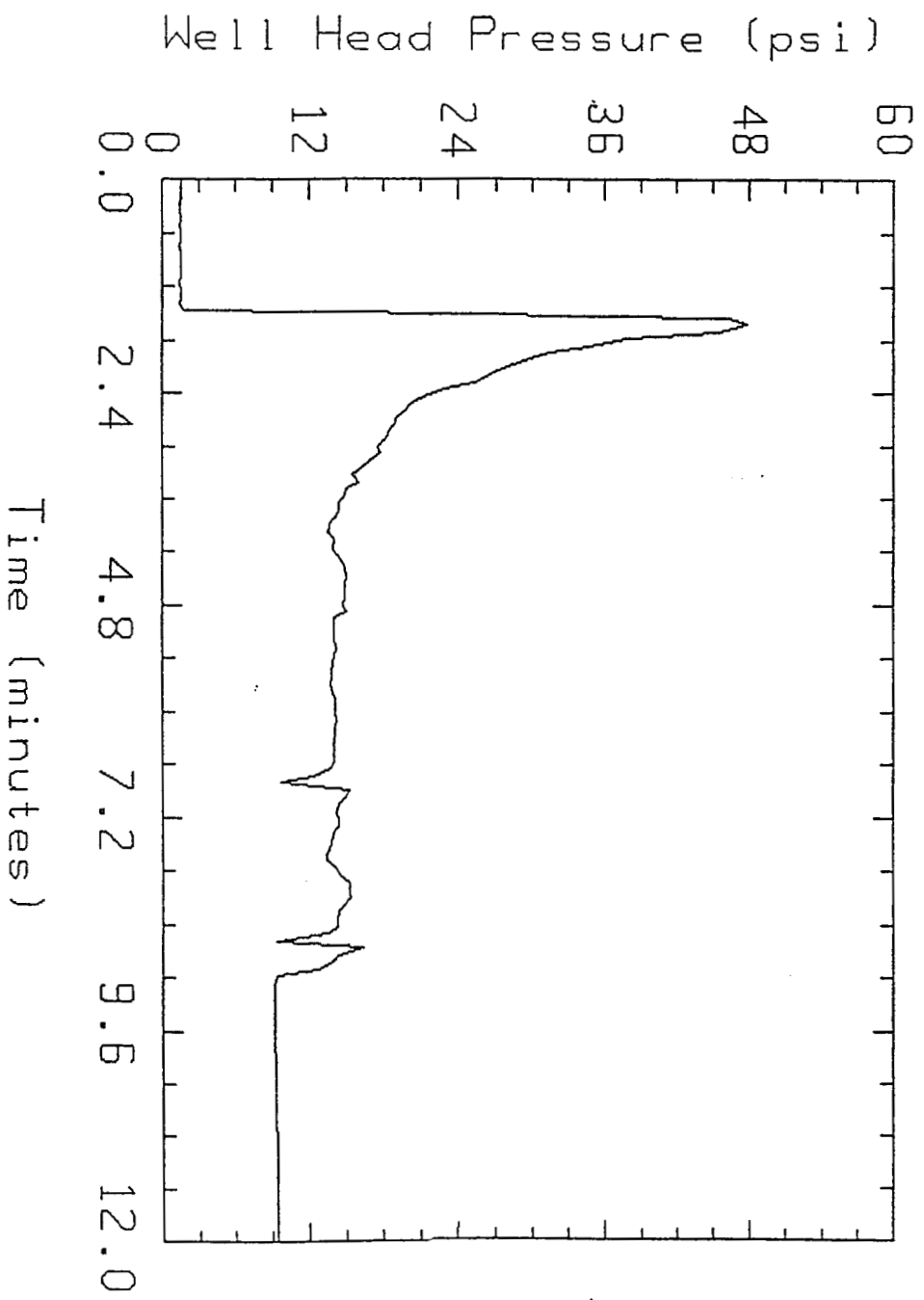
F11: SAR721.DAT

Pressure Log For: SAR8-18



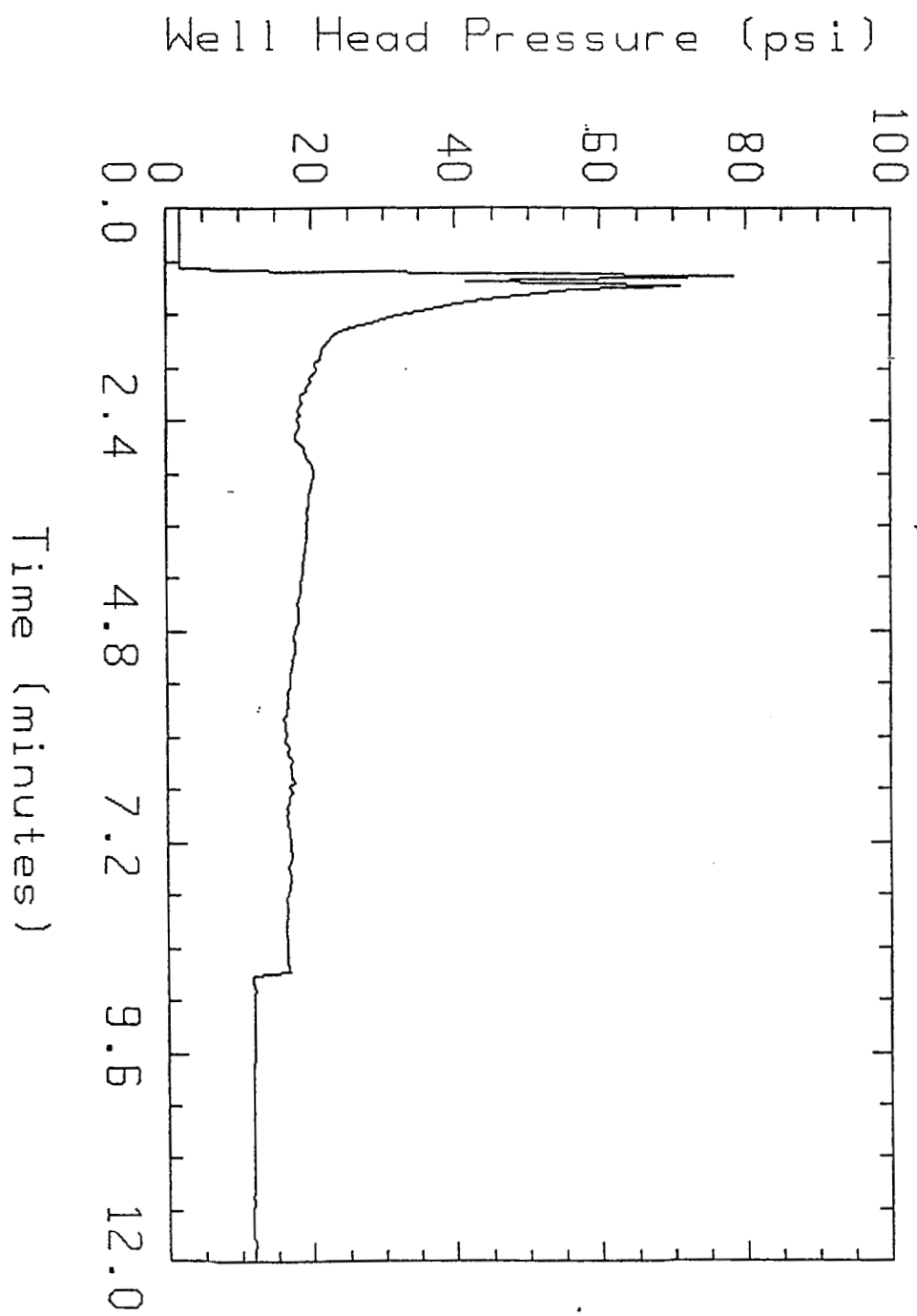
File: SAR8-18.DAT

Pressure Log For: SAR8-22



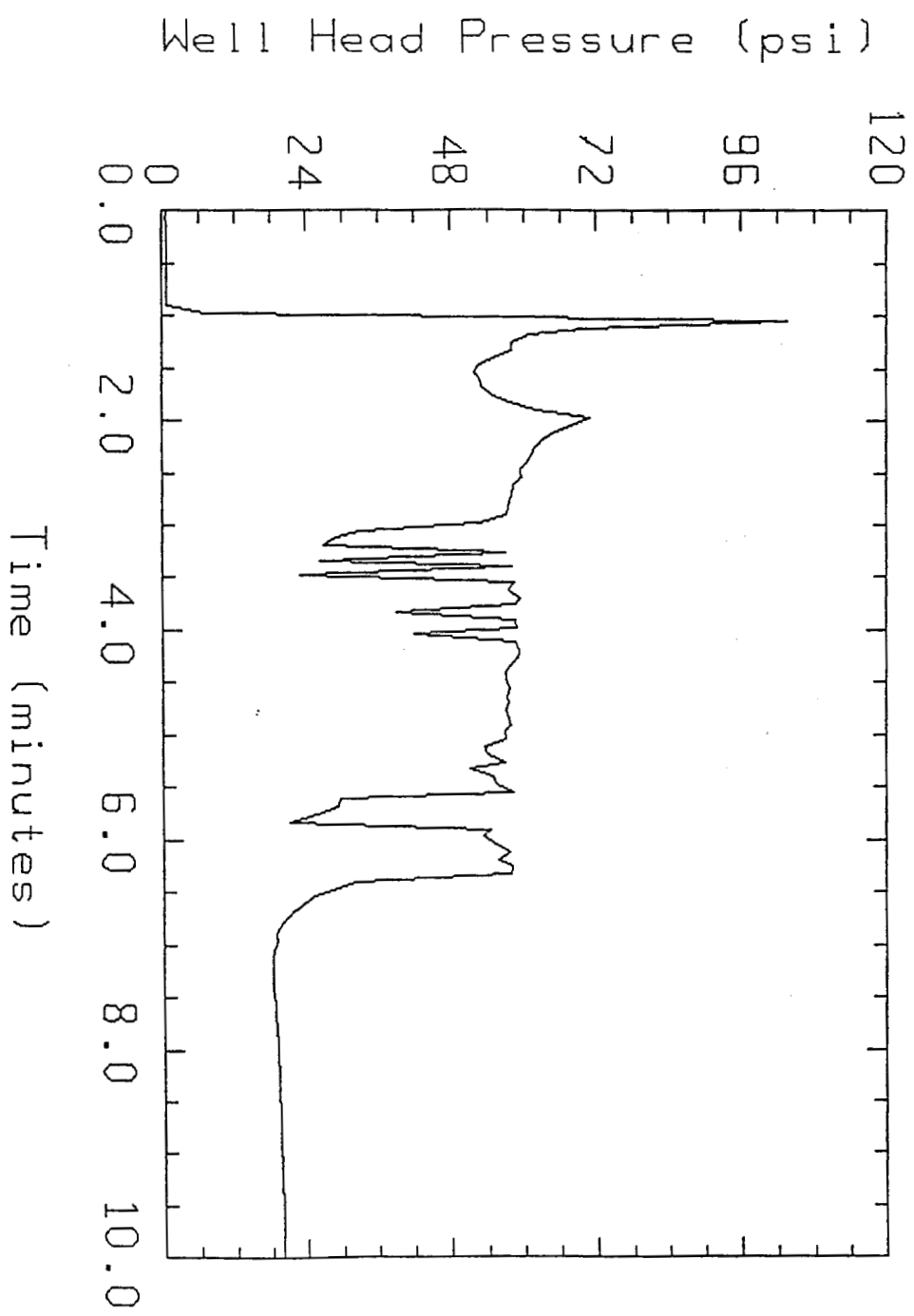
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Pressure Log For: SAR8-26



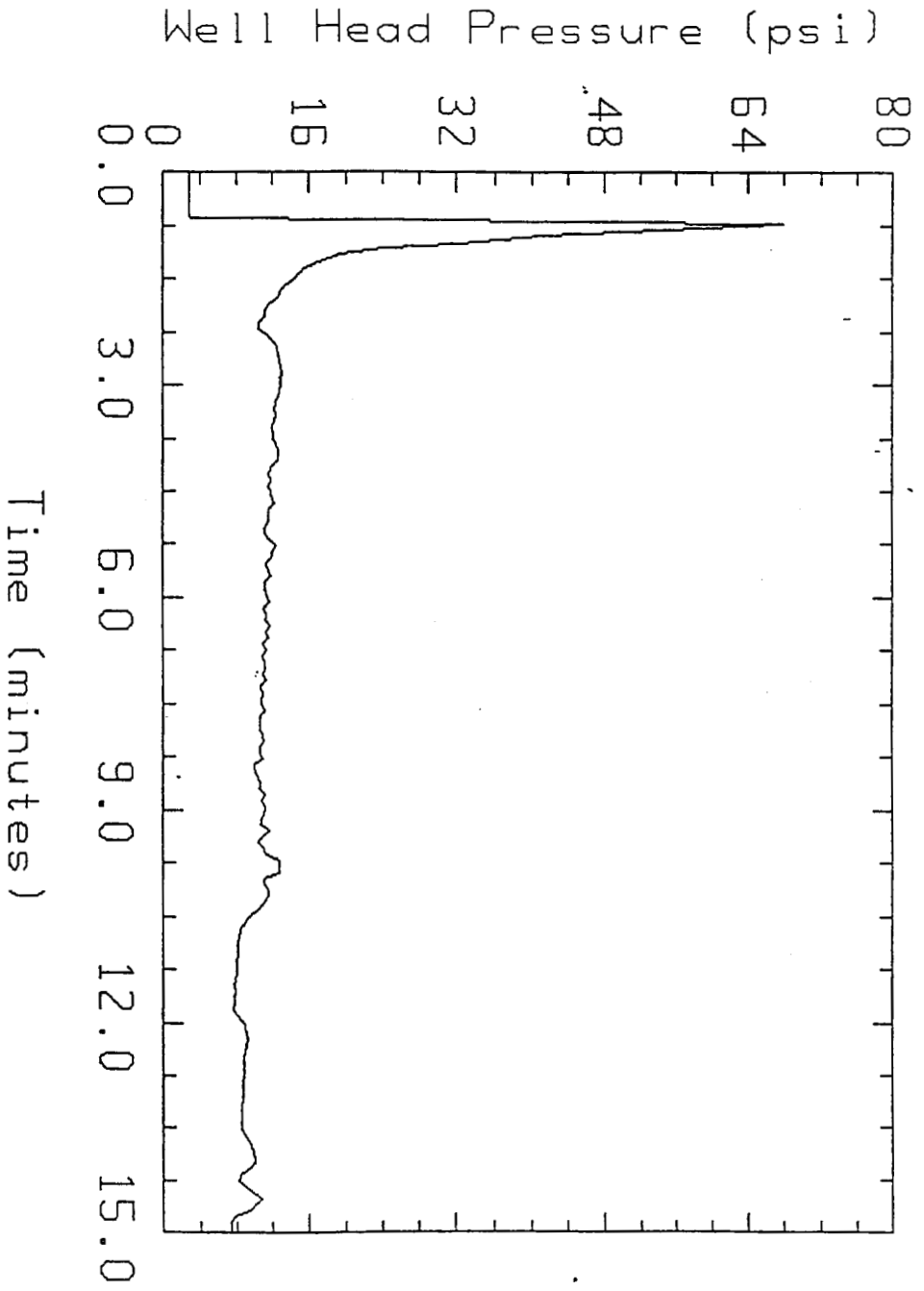
FILE: SAR8-26.DAT

Pressure Log For: SAR9-55



File: SAR955.DAT

Pressure Log For : SAR10-20



File: SAR10A37.DAT

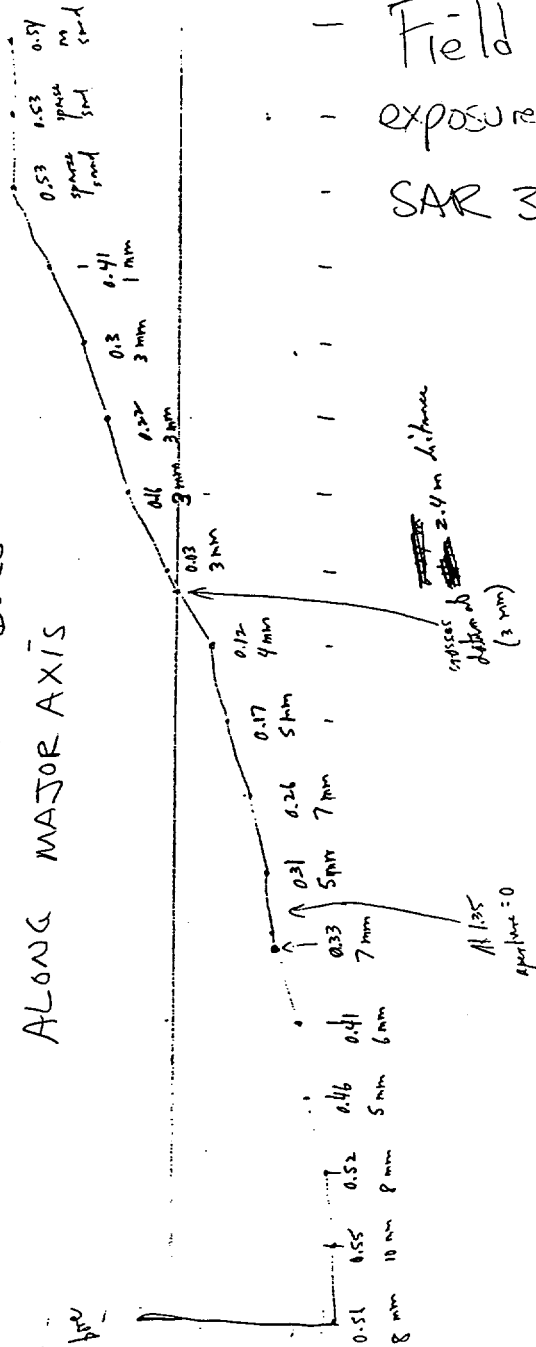
42 SHEETS 3 SQUARE
43 SHEETS 3 SQUARE
44 SHEETS 3 SQUARE
45 SHEETS 3 SQUARE
NATIONAL

trench trends 045 (Direct Face)

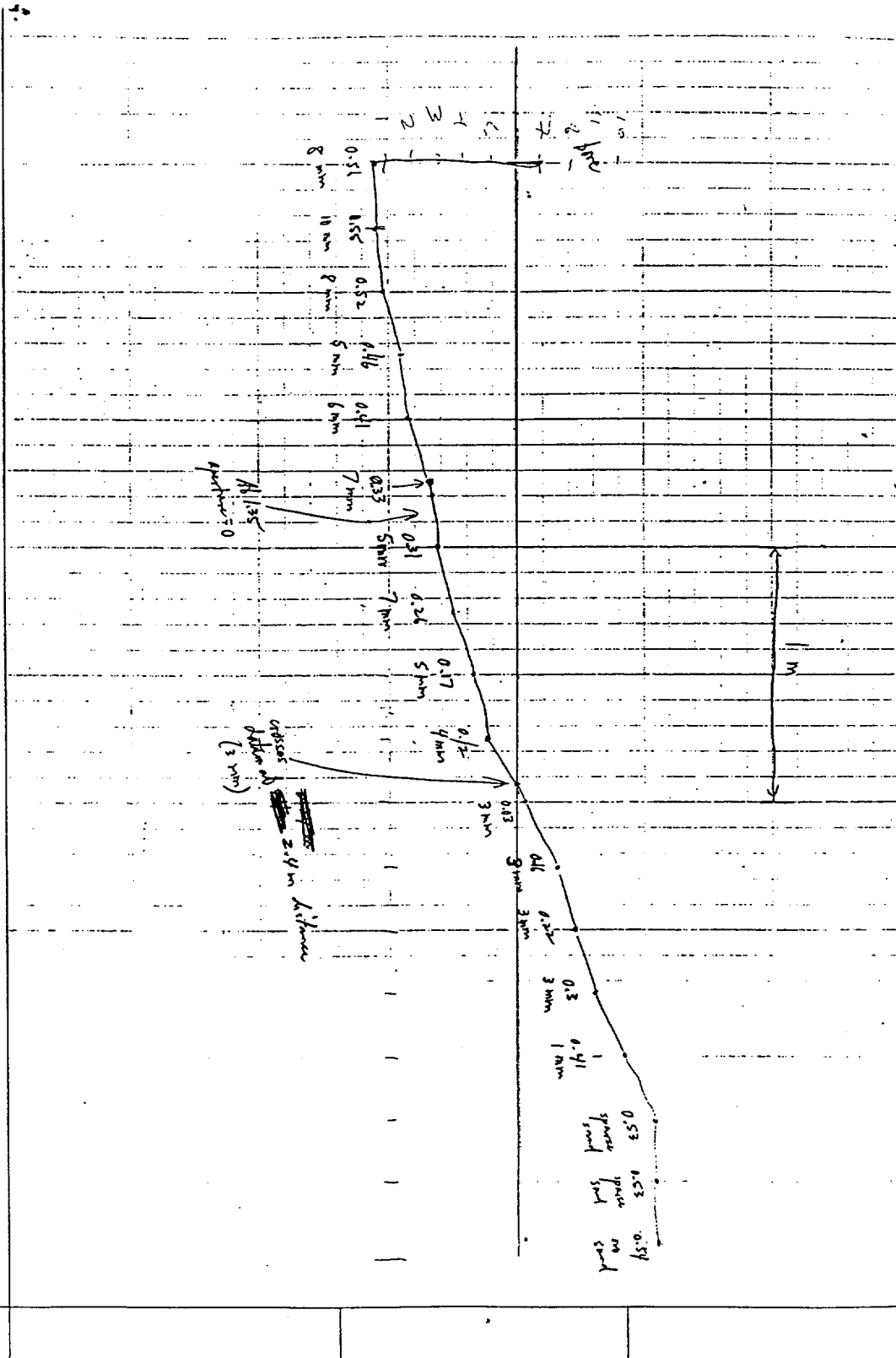
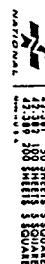
A

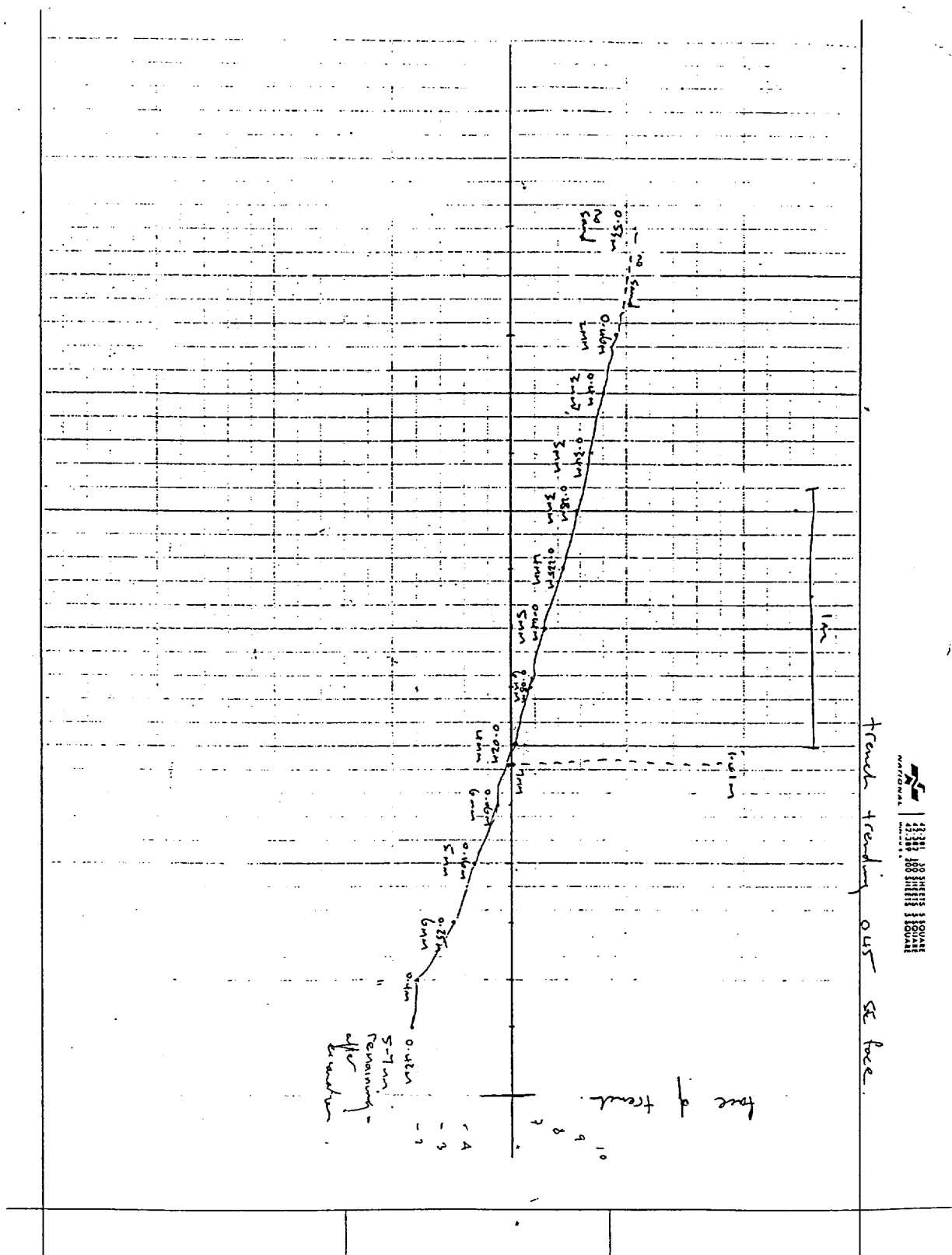
1 m

CROSS SECTION FROM BORE
ALONG MAJOR AXIS



trough trends 045 (West Face)



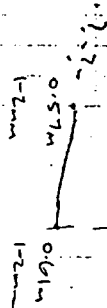


track track 200°

23.181 30 SHEET SQUARE
23.181 30 SHEET SQUARE
23.181 30 SHEET SQUARE
23.181 30 SHEET SQUARE

edge of track

interior base



APPENDIX B

MICROBIAL CHARACTERIZATION AND BIOACTIVITY ASSESSMENT AT THE LAIDLAW SITE, SARNIA, ONTARIO

This appendix contains a summary of microbial characterization and bioactivity assessment at the Sarnia site by personnel from Oak Ridge National Labs (ORNL). As discussed in Chapter 3 assessment of biological activity was undertaken to determine the biodegradation capabilities of the native microbes.

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***In Situ Remediation of DNAPL Compounds
in Low Permeability Media***

**A Joint Initiative of the Department of Energy
and American Petroleum Industry**

Interim Report

Compiled by:

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K. S. Lowe²

With Major Contributions From An Ad Hoc Team of
Scientists and Engineers From DOE
National Laboratories, Academia, and Industry

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3. ENHANCED SOIL VAPOR EXTRACTION

3.1. Introduction

The LNAPL in tight soils project initiated by API was focused largely on field-scale testing of in situ SVE at a test site located near Sarnia, Canada (Fig. 3.1). In this work, field activities at the Sarnia site were initiated in 1992 by Dr. Rick Johnson et al. of the OGI under sponsorship from API. The purpose of the work was to evaluate the feasibility of remediating LNAPLs from a fractured fine-grained soil using in situ SVE potentially aided by air sparging. In addition, several SVE design criteria were to be evaluated to determine the most effective conditions for NAPL mass removal. Field experiments with SVE were completed during the summer of 1993 and the summer and fall of 1994. During the summer of 1995, the Sarnia site was decommissioned. The decommissioning of the test cell enabled collection of large-diameter cores for laboratory column testing at OGI.

Companion activities were completed at the site by ORNL, UCinn, and UT with funding from DOE OTD. These activities included a pilot-scale hydraulic fracturing test completed during August 1994 (see Sect. 5.0) and microbial characterization of the test cell completed during the summer of 1994 and 1995.

This section first provides a brief overview of the Sarnia site and the API work completed there. The information presented on the API work has been largely abstracted from progress reports submitted to API by Dr. Rick Johnson et al. from OGI (Johnson and Grady 1994, 1995). For more up to date and/or detailed information, readers are referred to these progress reports and forthcoming API project reports prepared by OGI. Following the synopsis of the Sarnia site characteristics and the SVE testing, a detailed discussion is given regarding the microbial characterization work completed there by ORNL and UT with DOE OTD funding. A discussion of a portion of the hydraulic fracturing pilot test completed by UCinn is given in this section, while additional details are provided in Section 5.

3.2. Sarnia Site Characteristics

The study site is located about 10 km southeast of Sarnia, Ontario on private property owned by Laidlaw, Inc. (Fig. 3.1). Prior to establishment of the test cell, the site was cultivated for agricultural purposes. Current land use on the property and immediately adjacent to the test cell site involves a major hazardous waste landfill operated by Laidlaw. The surface topography around the test cell is level and there are no major surface water drainage features.

The Sarnia test site has been studied extensively by McKay et al. (1993a, 1993b). The site is within 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). The lithology is described as a clay-rich till (25 to 40% clay particles with silt, sand and a few pebbles) that extends to ~50 m thick and underlain by marine shale (McKay 1993a). The upper zone extending from ground surface to about 5 m depth is highly weathered, oxidized and contains a network of pronounced desiccation fractures (Fig. 3.2). The saturated hydraulic conductivity in the upper zone ranges from 10^{-8} to 10^{-4} cm/s with typical values falling between 10^{-6} and 10^{-5} cm/s. The lower zone beneath ~5 m depth is unweathered with a low hydraulic conductivity ($\sim 10^{-8}$ cm/s) (McKay et al. 1993a, 1993b).

Water movement in the shallow subsurface zone is rapid due to the extensive fracture system. Some of the fractures are visible to the naked eye and exhibit carbonate staining (Fig. 3.2). The reported effective hydraulic apertures range from 10 to 100 μ m and the fracture spacings

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increased from a few centimeters at the surface to a meter or more at a depth of 4 m (McKay et al. 1993a, 1993b). In contrast, groundwater movement in the lower subsurface zone is very limited and reportedly due primarily to diffusion.

The water table at the site generally fluctuates from near ground surface to a depth of about 2 m. The clay matrix between the fractures is probably completely saturated due to capillary effects (McWhorter 1994). In addition, much 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.

3.3. Soil Vapor Extraction and Dewatering Tests

3.3.1. Purpose and Scope

With funding provided by API, OGI designed and completed a series of field experiments to evaluate the performance capabilities of conventional and enhanced SVE to remove NAPL mass from the Sarnia clay till (Johnson and Grady 1994, 1995). This work was focused on gasoline range organic compounds although ~7.3% of the mass of the mixture (mole fraction = 0.0557) was TCE (Table 3.1).

3.3.2. Methods and Results

In September 1992, 50 L (40.6 kg) of a synthetic gasoline blend (with TCE as a tracer) was released from a constant head reservoir near ground surface (~0.6 m bgs) at the center of a 10-m by 10-m sheet-pile enclosed test cell (Fig. 3.1 and 3.3) (Johnson and Grady 1994, 1995). The composition of the synthetic gasoline released at the site is listed in Table 3.1. The site was left undisturbed and allowed to equilibrate over the winter. In July 1993, the site was characterized by soil core collection and analysis of gasoline concentrations. This was done to provide a baseline for subsequent SVE treatment tests. To provide some control over airflow patterns and to minimize surface volatilization and precipitation infiltration, the test cell was subsequently covered with a thin concrete cap.

In August 1993, attempts to recover the gasoline were initiated using SVE with air flow from an inlet trench to a outlet trench ~6 m apart within the experimental cell (Fig. 3.3). The trenches were installed to ~1.5 m depth and were carefully prepared to minimize smearing of the fine-grained soil on the trench sidewalls. The trenches were filled with gravel aggregate and air delivery/recovery vents and piping.

During SVE operation between August and October 1993, analyses of the SVE off-gas revealed that the hydrocarbon concentrations were approaching asymptotic levels in the off-gas, but only ~30% of the mass of released gasoline had been removed (Johnson and Grady 1994). After three months of various SVE tests (e.g., air extracted from one or both trenches at different flow rates), SVE operation was terminated and the cell was resampled at the end of October. The results from this soil sampling indicated that only ~39% of the mass of gasoline that was released could be accounted for in the soil. Thus, in addition to relatively low mass recoveries (i.e., ~30%), over 30% of the released mass was unaccounted for.

Based on the results of the 1993 experiments, OGI field activities for summer 1994 were planned to determine: (1) if additional mass could be removed by SVE by continuing extraction using the same trench system used during the 1993 season; (2) if hydrofractures could improve hydraulic control and mass removal; (3) if higher vacuums produced using a liquid ring pump

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could improve hydraulic control and mass removal; and (4) if vertical wells could improve mass removal.

At the beginning of the 1994 field season, the SVE system was restarted using the two extraction trenches and operating conditions similar to those used during 1993. The SVE off-gas concentrations rose quickly but only to values similar to those observed at the close of the 1993 field season (i.e., 0.03 g/m^3 or a total mass removed per day of 21.6 g/day) (Johnson and Grady, 1995). For most of the compounds in the spill mix, these concentrations dropped during the course of two weeks of SVE operation. Performance of the SVE trenches was attributed in part to surface leakage and poor access to a large portion of the mass which was either in inaccessible fractures or had dissolved and diffused into the soil matrix.

With funding provided by DOE OTD, a pilot-scale fracturing test was completed at the Sarnia site in August 1994 (more discussion in Section 5). As part of this work and in an attempt to increase water removal and improve air flow through the fine-grained soil, a hydrofracture was placed by Dr. Larry Murdoch of the UCinn beneath the contaminated soil zone at a depth of $\sim 2.5 \text{ m}$. The hydrofracture was also used as an air injection and extraction point in order to minimize surface leakage. Water removal from the cell was significantly increased by the combination of the hydrofracture and a high vacuum, liquid-ring pump. However, the overall effects of the hydrofracture in reducing the water content and improving air flow were minimal. Air flow from the hydrofracture was quite small ($\sim 1 \text{ scfm}$) even at very high vacuums (e.g., 27 in. Hg) and the extent that the vacuum was propagated from the hydrofracture was less than anticipated. This was attributed to the fact that the hydrofracture was installed at a depth (i.e., 2.5 m) where the vertical fracture density was relatively low.

Additional SVE tests extracted air from a network of vertical wells concentrated in the center of the test cell near the point of gasoline release. These wells were screened just below the zone of highest contamination. Air flow from a total of five wells was $\sim 5 \text{ scfm}$ at $10\text{-}27 \text{ in. Hg}$ (ave. $\sim 15 \text{ in. Hg}$). However, sustained off-gas concentrations were quite small and overall mass removal rates were well below those obtained from the trenches.

3.3.3. Summary

The conclusions derived from the SVE tests completed during the 1993 and 1994 field seasons were summarized by Johnson and Grady (1995) as follows: "(1) trenches performed better than the vertical wells for removing contaminant mass; (2) significant contaminant mass could be removed, however the total was significantly less than 50%; (3) attempts to improve air flow by dewatering and an increased density of vertical wells were largely unsuccessful; (4) soils data cannot account for all of the mass which was not removed in the extracted air and water, and the reasons for this remain unclear; and (5) the overall benefit of air flushing to remove contaminants and reduce risk is unclear."

In 1995, activities were designed to explore potential reasons for the inability to account for all the spilled mass in the SVE off-gas and in the clay till (~ 30 to 50%) and to collect intact soil cores for laboratory studies at OGI. The specific activities included: (1) placement of a trench in the experimental cell to measure mass flux from the test cell soil due to volatilization, (2) collection of large-diameter cores for laboratory leaching experiments, and (3) collection of a final set of soil samples for detailed chemical analysis. The test cell at Sarnia was decommissioned in summer 1995, and as of this writing, all field activities have been completed at the Sarnia site. Results from the 1995 activities are not yet available. During fall 1995 and into 1996, API funded laboratory studies are planned and/or in progress at OGI to assess the mobility of LNAPL residuals in the low permeability soil after SVE has achieved varying levels of mass removal.

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3.4. Microbial Characterization and Bioactivity Assessment

3.4.1. Purpose and Scope

A companion DOE activity was linked to the API work at Sarnia. The goal of this work was to develop an understanding of the microbiology of the Sarnia deposit and the effects of exposure to gasoline and SVE treatment. This information was deemed important as it would provide some insight into the potential for natural or passive bioremediation of residual NAPLs in fine grained deposits. Specific objectives of the work included determination of the microbial biomass, activity, and NAPL degradative capacity as affected by varying degrees of exposure to NAPLs. This work was completed by Drs. Susan Pfiffner (UT) and Robert Siegrist, Kathryn Lowe, and Tony Palumbo (ORNL) with assistance from Dianne Grady (OGI) and Terry Walden (BP).

3.4.2. Methods

The microbial and geochemical characterization of the subsurface at the Sarnia site was designed to provide insight into the microbial community structure, activities, and degradative capacities of the existing subsurface microbial populations. Assays to assess microbial biomass included microbial enumeration (by colony forming units [CFU] and most probable number [MPN]), and microbial community structure and nutritional status (by phospholipid fatty acid methyl ester analysis [PLFA]). Microbial activities and degradative capacities can be assessed using acetate incorporation, glucose utilization, and hydrocarbon degradation. Key physical/chemical properties were also assessed including bulk density, particle size distribution, water content, pH, total organic carbon (TOC), nitrogen and phosphorus. Samples were preliminarily acquired from the Sarnia site from soil cores collected by BP during field activities in 1994. A second set of samples were acquired by ORNL aseptically and under controlled conditions during July 1995.

Sampling and Analysis Methods - 1994. Three of the soil cores that were collected by BP and OGI during July 1994 for characterization of total petroleum hydrocarbons (TPH) were retrieved and analyzed at ORNL and UT for geochemical properties and microbial activity. These cores were collected in ~10 cm diameter aluminum tubes driven into the test cell. After small plugs of soil were removed for TPH analyses, the cores were archived under ambient temperature conditions. It is noted that these cores were not collected specifically for microbial analyses under aseptic procedures and more than a month had passed since core collection. Nevertheless, it was felt that analyses of these cores on hand would be valuable and provide preliminary information on site geochemical and microbial properties. This information would aid in subsequent sampling and analysis efforts.

The soil cores were collected from the site at three areas of varying LNAPL exposure: outside the test cell in an adjacent background area (0 ppm TPH), inside the cell but near one edge of where contamination was low (200 ppm TPH), and near the center of the cell where TPH contamination was high (1000 ppm TPH) (Fig. 3.3). Upon receipt at ORNL, the cores were kept refrigerated until soil could be retrieved from the 10 cm aluminum tubes. Soil was recovered from the cores using sterile spatulas, knives and spoons and placed into sterile petri dishes. This process was done in an anaerobic glove bag under a nitrogen and hydrogen atmosphere (95% / 5% mixture, respectively). The soil was cut into fine pieces before initiating anaerobic enumerations and activity studies. The petri dishes containing the sediments were then brought out of the glove bag for aerobic enumeration and activity studies.

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Microbial biomass was evaluated using MPN techniques for aerobic heterotrophic populations. Aerobic heterotrophic enumerations were based on turbidity being exhibited over a 5 dilution range in 1% PTYEG medium in screw-capped test tubes (Pfiiffner 1994). The aerobic enumerations were also set up in a single-series dilution scheme over 9 dilutions. Anaerobic heterotrophic enumerations utilized the same media with the addition of cysteine hydrochloride as the reducing agent, resazurin as the Eh indicator and nitrogen/CO₂ as the headspace gas mixture (Pfiiffner 1994).

Duplicate plate counts were also performed using the pour plate technique with 1% PTYEG medium without toluene, and phosphated buffered basal medium with the addition of yeast extract (3 mg/L) and toluene (20 µL). Plates and test tubes were observed at two and four weeks.

Microbial activity was assessed by measuring acetate incorporation in time course experiments as described previously. Sterile polypropylene centrifuge tubes were used for aerobic acetate incorporation experiments. Anaerobic crimp-top tubes (Bellco Glass Co., Vineland, NJ) were used for anaerobic acetate incorporation experiments. Acetate incorporation experiments used 2 g soil and 2 mL containing 5 µCi [³H]-acetate. Final acetate concentrations in experimental tubes were 30 ng/g. Incubations were at room temperature. At time zero (t₀) and after 2 days, duplicate tubes were inhibited with 5.0 mL of a phosphate-buffered chloroform-methanol solution and frozen.

Sampling and Analysis Methods - 1995. In July 1995, the test site was again sampled to determine microbial characteristics present in three areas of LNAPL exposure (high, medium, and low TPH) at up to each of three depths (0.1, 0.5, and 1 m). Based on the controlled release in the center of the 10 x 10 meter cell, soil core samples were collected on a transect including one location near the center of the test cell (M3), one inside the cell but near the edge of the zone of influence of the release (M2), and one inside the cell but outside the suspected zone of influence of the release (M1) (Fig. 3.3 and 3.4). Existing trenches recently dug at the site for core sampling facilitated access for microbial sampling. At each of the three locations along the transect, soil samples were collected at each of three depths (0.1 m, 0.5 m and 1.0 m). A second sampling transect (M6, M5, M4) was made ~1.2 m away from and parallel to the first transect, thus providing insight into the longer-range heterogeneity within the test cell. In total, soil samples were collected from 18 locations (2 transects * 3 locations * 3 depths = 18).

Soil samples were collected following controlled aseptic procedures as follows. Pre-sterilized stainless steel tubes (~5 cm diameter and 30 cm long) were driven into the trench face at each location using a hydraulic jack. A 20 cm core segment was then retrieved within each tube. The core end was removed to expose fresh soil surface and the core was extruded and cut into desired sample lengths using pre-sterilized utensils. Subsamples of ~25 to 75 g each were then removed and immediately placed into sterile polyethylene bags (Whirlpak). Samples for PFLA analyses were stored on dry ice. Samples for CFU, MPN, acetate incorporation and hydrocarbon utilization, and samples for geochemical properties were stored at 4°C. The soil samples were shipped by overnight courier to ORNL and the UT Center for Environmental Biotechnology for subsequent laboratory analyses. Sampling equipment was sterilized between sample collection by an isopropyl alcohol rinse and subsequent flaming of the residual alcohol on the sample utensils and cores. Sampling utensils and cores were then wrapped in aluminum foil. Two water equipment rinsate samples were collected for field quality assurance/quality control. Rinsates were collected by pouring a small amount (< 1 liter) of de-ionized water over the sterilized equipment and collecting the water in whirlpaks and 125 ml glass jars. These samples were then placed on ice and shipped to ORNL/UT for analysis.

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3.4.3. Results

Geochemical Properties. Results of physical and chemical analyses of the soil samples collected in July 1994 are summarized in Table 3.2 while comparable data for July 1995 (some analyses still pending) are presented in Table 3.3. The subsurface soils contained from 67 to 87% silt and clay sized particles (i.e., < 0.05 mm) and alkaline in pH (7.0 to 8.2). Soil bulk densities were estimated at ~1.5 to 1.8 g/cm³ field moist soil. Soil water contents were high within the test cell (~10 to 20% by wt.) but relatively lower (7.3%) in the shallow background soil (Tables 3.2-3.3, Fig. 3.5). Soil water contents were also substantially and significantly higher ($\alpha=0.05$) at 0.1 m depth as compared to the 0.5- or 1.0-m depths. These differences may have been attributable to the enclosure of the test cell and indicate that the fine-grained soil was not "dried out" during SVE operation. The estimated bulk densities and water contents yielded a crude estimate of total porosity at 45% v/v with approximately half of the pores water-filled and the other half air-filled.

The total carbon content was quite high at ~2.5 to 5% by wt., but the vast majority of this was inorganic carbon, likely present as carbonates (Table 3.2). The TOC concentrations typically ranged from non-detectable to ~0.5% by wt. (Fig. 3.6). Nitrogen and phosphorus were present at 0.03 to 0.17 % and 0.065 to 0.076 % by wt., respectively (Table 3.2). Thus, the subsurface appeared to have ample water and nutrients for biological activity (assuming they were bioavailable) but may have been limited in organic carbon. The partition coefficient for TCE, K_d , was measured at 0.8 to 1.35 mL/g.

Microbial Properties. Microbial analysis results from the 1994 archived core samples are summarized in Table 3.3. Aerobic heterotrophic enumerations from both plate counts and broth culture indicated aerobic populations of 10⁴ cells/g in the high LNAPL exposed soil, 10⁵ cells/g in the low LNAPL exposed soil, and 10⁵⁻⁶ in the uncontaminated soil (Table 3.2). There appeared to be no difference between the two types of plate count methods used suggesting that most of the microorganisms that grew could utilize toluene or were not inhibited by toluene at the concentrations used. Dilutions in broth cultures with toluene as the sole carbon source showed positive growth at 10⁴⁻⁶ (however the 10⁰⁻³ tubes showed questionable growth) for uncontaminated soil, 10⁴⁻⁵ for 200 ppm contaminated soil, and 10³⁻⁴ for 1000 ppm contaminated soil. This toluene broth data is considered preliminary and is difficult to interpret.

Microbial activity as measured by acetate incorporation into microbial lipids showed an interesting pattern in that the aerobic and anaerobic activities (in dpm/g/d) was similar for both the uncontaminated and 200 ppm contaminated soil (Table 3.2). Lower rates for the anaerobic tests were expected. It is possible that the anaerobic test tubes were not strictly anaerobic since no reducing agent was used as in the enumerations. It is interesting to note that the 200 ppm soil demonstrated a 1.5 times greater incorporation than that of the uncontaminated sediment. This may be due to the increase in a readily available carbon source (i.e., synthetic gasoline) at a level that was not toxic for microbial activity. The heavily-contaminated soil (1000 ppm) showed aerobic acetate incorporation activity that was similar to that of the uncontaminated soil, but dropped to near detection limits under anaerobic conditions. Lack of activity in the soil contaminated at 1000 ppm may suggest a toxic effect of the gasoline on the ability of anaerobic bacteria to incorporate acetate into their membranes.

In July 1995, soils were carefully collected from the Sarnia test site at six sample locations and at 0.1, 0.5, and 1 m depths from each location. Two equipment rinsate water samples were also tested for quality control. Microbial enumerations for all depths at sample locations M1-M3 and at the 1 m depth for sample locations M4-M6 included single series dilution schemes for aerobic and anaerobic heterotrophic broth enrichments, aerobic hydrocarbon-degrading enrichments, and heterotrophic plate counts. Activity studies covered aerobic and anaerobic tritiated acetate incorporation with time points of 0, 8, and 24 hours, and ¹⁴C-toluene mineralization (with and without nutrients) with time points of 0, 3, and 10 days. Plate counts and activity studies were

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performed in duplicate. All remaining soil and water samples were set up for broth enumeration of aerobic heterotrophs and hydrocarbon degraders.

The microbial growth for one week incubations at 25°C showed that for transect 1 (M1-M3) the plate counts revealed 10^6 heterotrophs per gram of soil at the 0.1 and 0.5 meter depths, while the 1 m depth showed slightly lower counts of 10^5 heterotrophs per gram of soil (Table 3.4). Similar levels of soil heterotrophs (i.e., 10^5 cells/g) were also measured at 1 m depth in samples from M4 to M6. This decrease in bacteria with depth was as expected. The heterotrophic aerobic broths indicated 10^{6-7} cells/g for the 0.1 m depth, and 10^5 cells/g at the 1 m depth for all sample locations with the exception of M6 which showed 10^7 cells/g at the 1 m depth. Aerobic broth enrichments usually result in higher cell estimates than with plate counting techniques. Interestingly, at the 0.5 m depth, the heterotrophic aerobic broths showed 10^5 cells/g for M1, 10^7 for M2, and 10^6 for M3-M6 (Table 3.4, Fig. 3.7). It is unknown if the differences in heterotrophs at this depth are significant and if so, if they are due to the concentration of contamination present or to a geochemical factor such as water content. Heterotrophic aerobes were seen in the water samples at 10^6 and 10^7 cells/mL. It is assumed that this is due to contamination by soils on the equipment.

The microbial enumeration based on one month incubations and culture transfer data indicated that in general, the heterotrophic population decreased with depth with the exception of M6 at 1 m depth (Table 3.4). Pour plate counts on dilute PTYEG medium indicated 1.7 to 2.8×10^7 heterotrophs per gram of soil at the 0.1 m depth for M1 and M3. At 0.5 m, heterotrophic counts ranged from 7.9×10^5 to 3.6×10^6 to 1.8×10^7 cells/g for M1, M3, and M2, respectively. CFU's at 1 m were 4.9 to 6.2×10^5 heterotrophs for M4 and M5, while M6 showed 1.5×10^6 heterotrophs/g.

Based on one month incubations, the heterotrophic aerobic broths indicated $\geq 10^7$ cells/g for the 0.1 m depth at all sample locations (Table 3.4, Fig. 3.7). At 0.5 m, 10^6 cells/g were demonstrated with the exception of M2 which showed greater than 10^8 cells/g. Soils from 1 m for M1 through M4 showed heterotrophs at 10^5 cells/g, while M5 and M6 had 10^6 and 10^7 cells/g, respectively. The heterotrophic broth enrichments, which resulted in slightly higher cell estimates than plate counts, corresponded well with the heterotrophic plate counts.

Anaerobic heterotrophs were more abundant than expected (Table 3.4, Fig. 3.8). The anaerobic enrichments at 0.1 m depth for M1 and M2 indicated 10^4 cells/g, while M3 showed 10^6 cells/g. At the 0.5 m depth, anaerobic heterotrophs enumerations varied from 10^4 , 10^6 , and 10^5 cells/g from M1, M2, M3 respectively. The most surprising anaerobic enrichment were at 1.0 m depth where M1 showed 10^3 anaerobes/g and M3-M6 showed 10^4 anaerobes/g. Furthermore, these enrichments for heterotrophic anaerobes show strong evidence for the presence of sulfate reducers by the production of black precipitate in the culture tubes.

After one month incubation anaerobic heterotrophs in soils M2 (0.1 and 0.5 m) and M6 (1 m) had the highest populations with greater than 10^6 anaerobes/g. At the 0.1 m depth there were 10^4 cells/g for M1 and 10^5 cells/g for M3, an up to 10^6 cells/g for M2. At the 0.5 m depth, were indicated at 10^3 cells/g for M1 and at 10^4 cells/g for M3. At 1 m depth, anaerobic counts ranged from 1 to 10^4 cell/g with the soils listed in order of increasing (by factor of 10) cells/g for M4, M5, M1, M2, and M3. Of the twelve enrichments for heterotrophic anaerobes, nine enrichments have shown growth in sulfate-reducing medium.

Hydrocarbon utilizers, as expressed by visible microbial turbidity in minimal medium supplemented with gasoline, were most abundant in M2 at 10^4 cells/g at the 0.1 and 0.5 m depths and 10^3 for the 1 m depth (Table 3.4, Fig. 3.9). Other samples showing 10^3 cells/g were M3 and M5 at 0.1 depth and M3 and M6 at 1 m depth. The remaining soils tested showed 100 cells/g, while the water samples showed no hydrocarbon utilizers.

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After one month incubation, the aerobic hydrocarbon utilizers showed considerable heterogeneity with locations and depth (Fig. 3.9). The most abundant populations were shown in M3 (0.5 m) and M5 (0.1 m) at 10^5 cells/g. M2 (1 m), M4 (0.1 m), and M6 (all depths) revealed 10^4 hydrocarbon utilizers/g. M3 at 1m indicated 10^3 cells/g, while 10^2 cells/g were shown in M2 (0.1 and 0.5 m), M3 (1 m) and M5 (0.5 m). Soils which showed 1 to 10 cells/g included M1 (0.5 and 1 m), M4 (1 m), while soils M1 (0.1 m), M4 (0.5 m) and the water samples showed no evidence of hydrocarbon utilizers. It appears that M6 had the largest population of hydrocarbon utilizers with respect to depth. It is interesting that M4 had a relatively high abundance (10^4 cells/g) of hydrocarbon degraders at the 0.1 m depth.

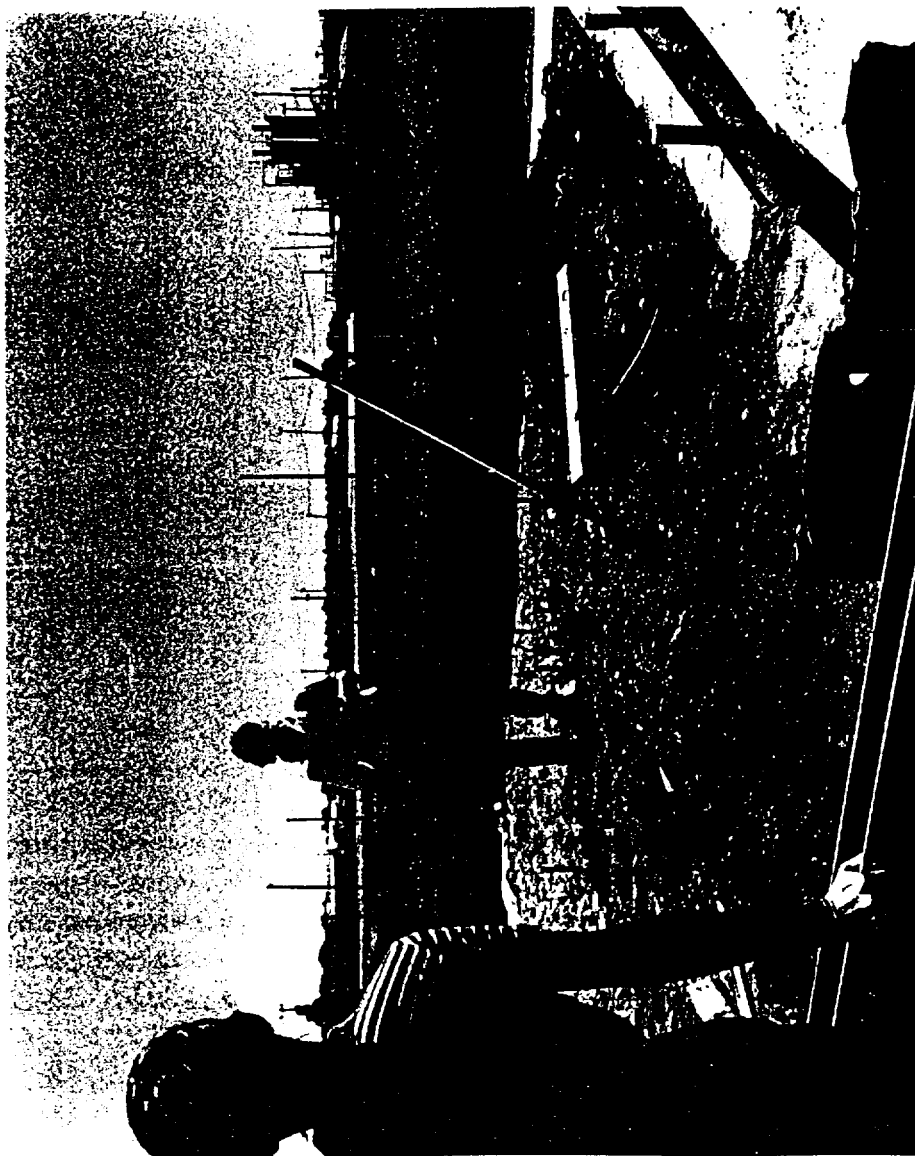
Samples collected for PLFA analysis are still being interpreted.

3.4.4. Summary

The microbial characterization of the Sarnia clay till revealed that it contained an appreciable microbial biomass (e.g., 10^5 org./g) comprised of active and potentially capable hydrocarbon degraders. Given this, calculations were made to determine if the mass of released gasoline that was not removed by SVE (i.e., ~50%) could have conceivably been removed by biological degradation. These calculations revealed that even if the biodegradation rate were extremely low (e.g., <1 mg/kg/day) relative to that observed for more permeable sandy sites (e.g., 5 to 50 mg/kg/day), biological degradation could have removed the unaccounted for mass of gasoline. It is speculated that bioremediation of some LPM systems might be achieved passively or through mild stimulation (e.g., bioventing). This is a very important observation, as the ability to rapidly and extensively remove/degrade NAPLs in LPM may be very constrained, but it is possible that the rate of migration is low enough due to diffusion-limited mass transfer, and if passive biodegradation can be expected, no further action might be warranted. Obviously the potential for biodegradation with LNAPLs like gasoline is likely considerably greater than for DNAPL compounds like TCE.

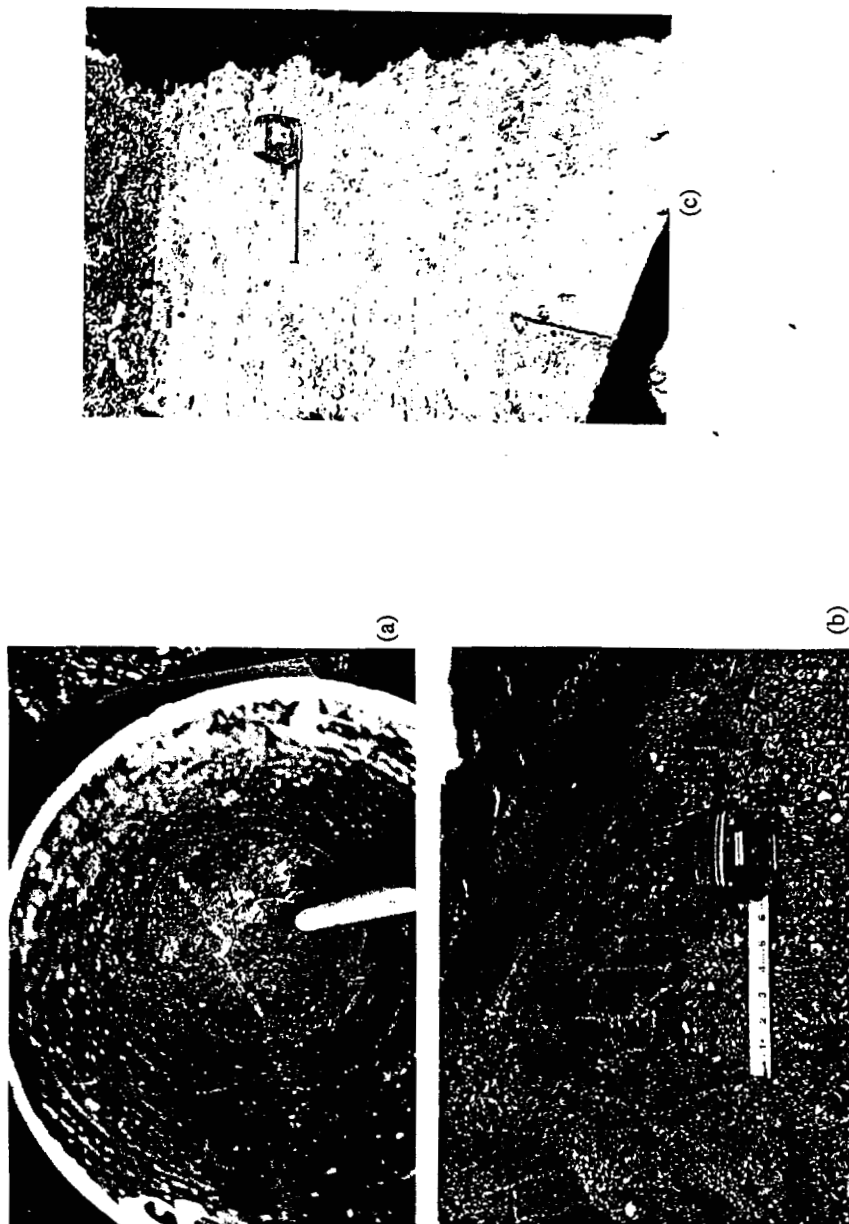
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Figure 3.1. Photograph of the Sarnia test cell and Dr. Rick Johnson of OGI during a site visit in summer 1993.



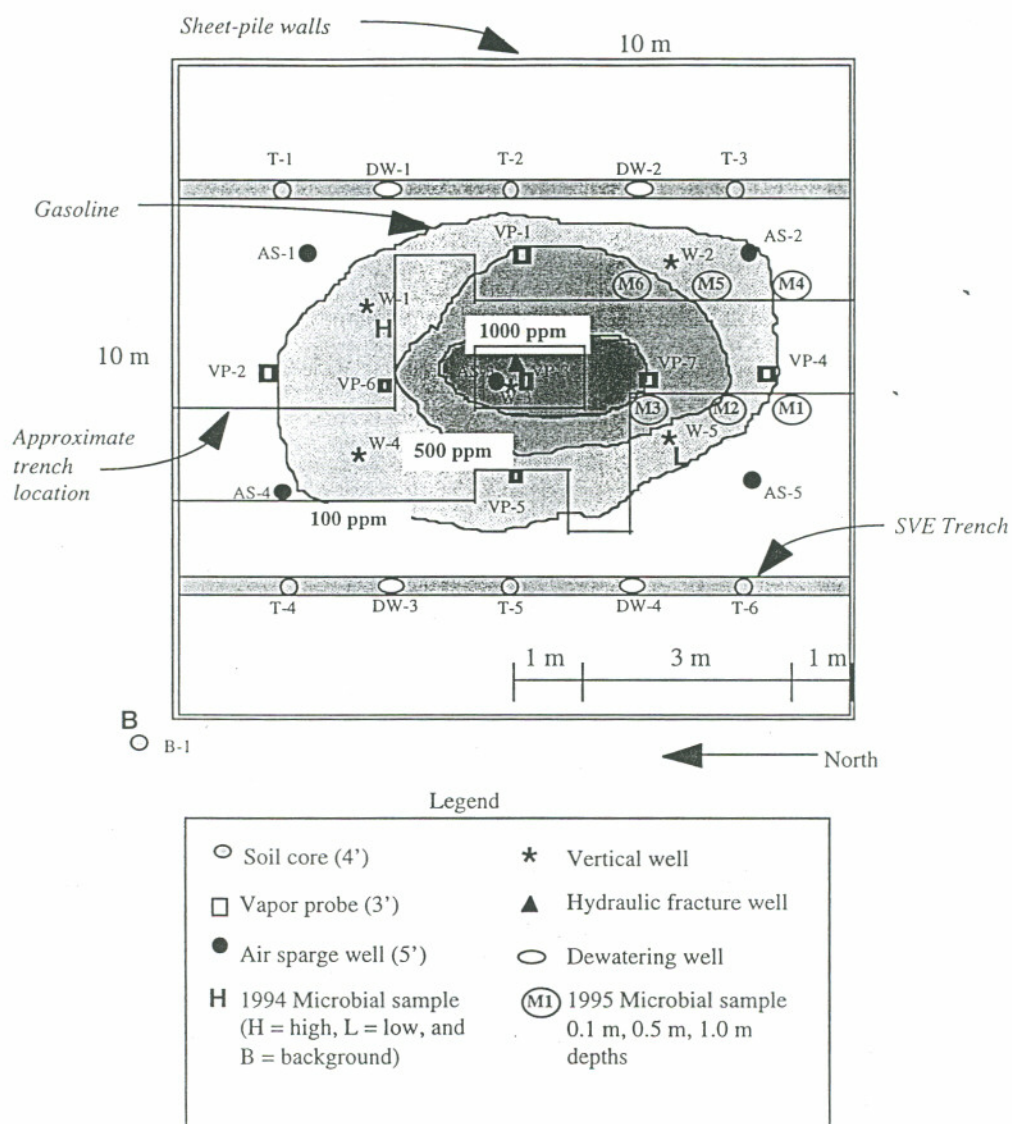
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Figure 3.2. Photographs of the Sarnia clay till taken during microbial characterization studies in July 1994 and 1995: (a) soil core collected from location W5-D in July 1994; (b) testpit profile during July 1995 with fractures apparent in a vertical plane; and (c) testpit profile during July 1995 with fractures apparent throughout a horizontal plane.



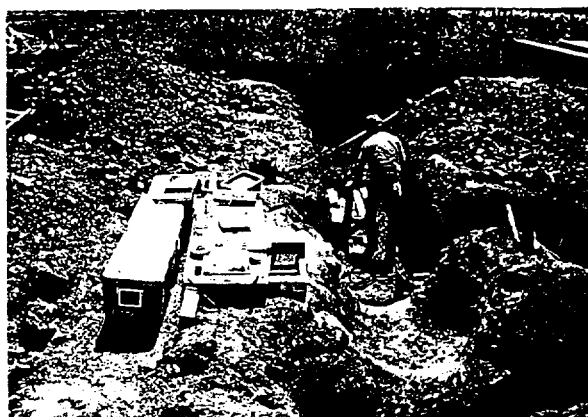
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Figure 3.3. Site schematic of the Sarnia test cell with the post-release TPH concentration contours and monitoring and measurement locations (modified from Johnson and Grady, 1994).



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Figure 3.4. Photographs of the microbial sampling in July 1995: (a) sample collection; (b) sample location profile with samples collected at 0.1, 0.5, and 1.0 m bgs; and (c) location of transects in test cell.



(a)



(b)



(c)

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Figure 3.5. Soil water content in samples collected at the Sarnia site during July 1995.

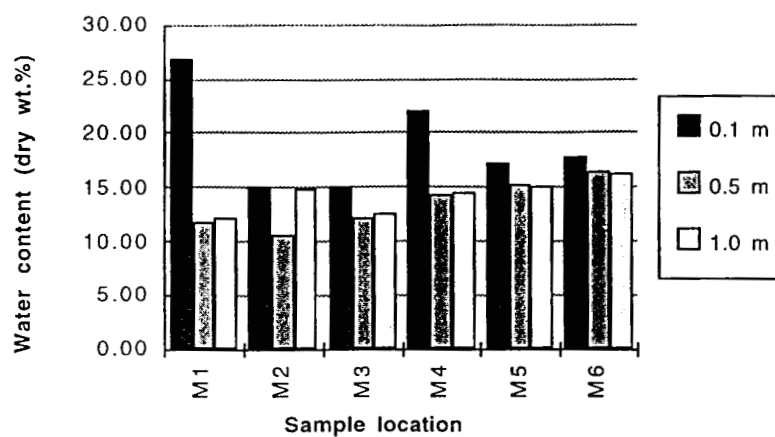
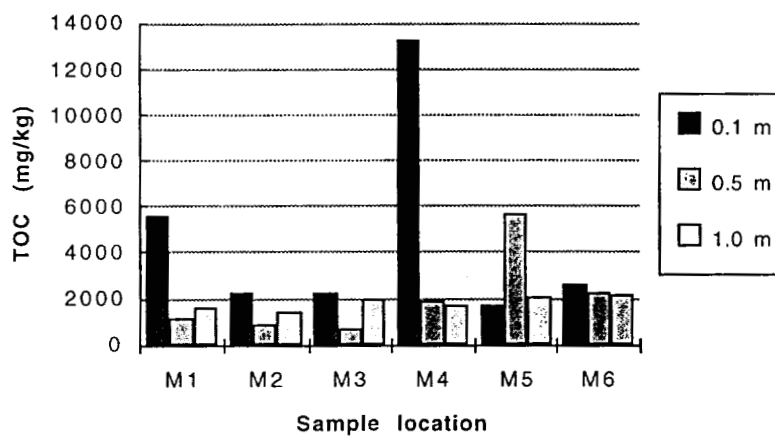


Figure 3.6. Total organic carbon content in soil samples collected at the Sarnia site during July 1995.



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Fig. 3.7. Spatial distribution of aerobic heterotrophs in soil samples collected at the Sarnia site during July 1995.

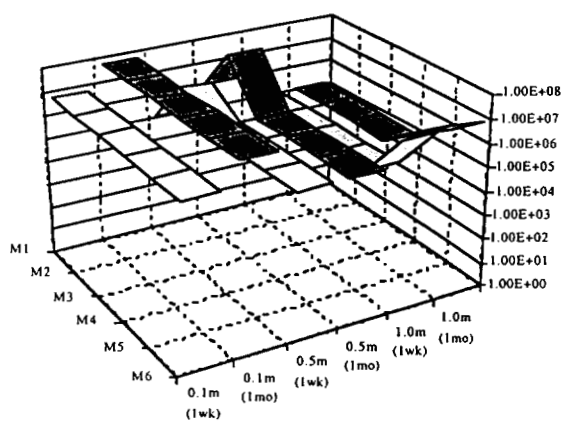
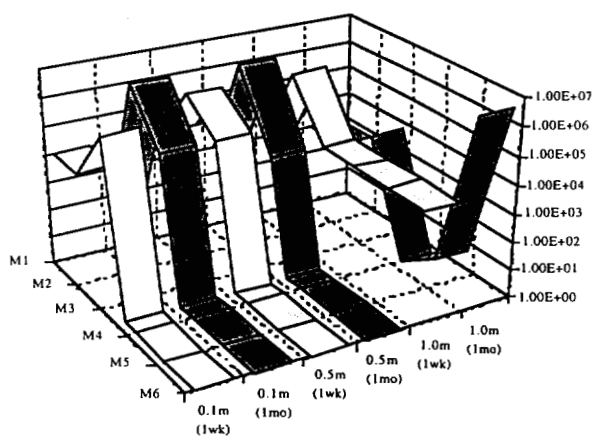
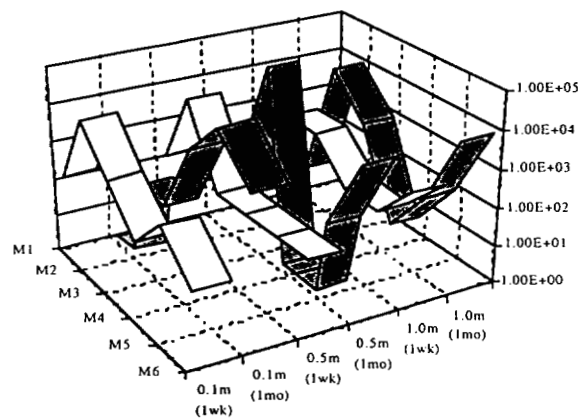


Fig. 3.8 Spatial distribution of anaerobic heterotrophs in soil samples collected at the Sarnia site during July 1995.



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Fig. 3.9 Spatial distribution of hydrocarbon utilizers in soil samples collected at the Sarnia site during July 1995.



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Table 3.1. Composition of the synthetic gasoline mixture spilled at the Sarnia site during September 1992 (Johnson and Grady, 1994).

Organic compound	Mass spilled (kg)	Mole fraction
pentane	2.48	0.0849
MTBE	1.5	0.0420
2-methylpentane	1.3	0.0373
hexane	2.64	0.0757
benzene	1.76	0.0556
trichloroethylene ^a	2.96	0.0557
heptane	1.36	0.335
isooctane	4.14	0.896
toluene	5.22	0.1399
ethylbenzene	1.74	0.0405
p-xylene	3.52	0.0819
m-xylene	3.48	0.0810
o-xylene	3.56	0.0828
1,2,4-trimethylbenzene	2.7	0.0555
naphthalene	2.28	0.0439
Total =	40.64	1.0000

^a TCE was added to the gasoline blend by OGI as a tracer.

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Table 3.2. Geochemical and microbiological properties of the Sarnia site as determined in archived cores collected during July 1994. ^a

Parameter	Units	High LNAPL (W1-C)	Low LNAPL (W5-D)	Background
Sample depth	m	0.6 to 0.9	0.9 to 1.2	0.6 to 0.9
TPH concentration ^b	mg/kg	1000	200	~0
Soil color (Munsell)		10YR3/6	10YR4/5	10YR2/5
Grain size distribution:				
Sand (0.05 - 2.0 mm)	wt. %	12.9	12.9	33.2
Silt (0.002 - 0.05 mm)	wt. %	48.8	48.1	48.8
Clay (< 0.002 mm)	wt. %	38.3	39.1	18.0
Bulk density (field moist)	g/cm ³	1.47	1.84	nd
Water content	dry wt. %	16.23	15.73	7.33
pH	-	8.21	8.19	7.03
Total carbon	dry wt. %	5.17	5.13	2.49
TOC	dry wt. %	0.22	0.36	nd
Kd	mL/g	1.15	1.35	0.84
Total iron	dry wt. %	2.19	2.29	1.67
Total nitrogen	dry wt. %	0.03	0.05	0.17
Total phosphorus	dry wt. %	0.065	0.072	0.076
Gross C:N:P ratio	-	3.4: 0.4: 1.0	7.2: 0.7: 1.0	-
Aerobic heterotrophs	CFU/g wet	6.7 x 10 ⁴	8.0 x 10 ⁵	2.0 x 10 ⁶
w/ Toluene	CFU/g wet	7.7 x 10 ⁴	5.0 x 10 ⁵	2.0 x 10 ⁶
Anaerobic heterotrophs	CFU/g wet	≥ 10 ³	≥ 10 ³	≥ 10 ³

^a Sample collected prior to any SVE operation during that season.

^b TPH analyses conducted by BP Oil as part of the API LNAPL project.

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Table 3.3. Geochemical properties of the Sarnia site as determined in soil samples collected during July 1995. ^a

Location ^b	Depth (m)	On-site Hnu PID (ppmv)	Bulk Density (g/cm ³)	Water Content ^c (wt.%)	pH (units)	TOC ^c (ug/g)	Total N ^c (ug/g)	Total P ^c (ug/g)
M1 (fringe)	0.1	0.2	NA	26.82	7.30	5616	NA ^d	NA
	0.5	0.3	NA	11.8	8.14	1129	NA	NA
	1.0	0.2	NA	12.07	8.20	1641	NA	NA
M2 (interm.)	0.1	0.2	NA	15.02	7.84	2229	NA	NA
	0.5	0.2	NA	10.54	8.31	919.2	NA	NA
	1.0	6.8	NA	14.77	8.21	1449	NA	NA
M3 (center)	0.1	0.2	NA	15.04	8.02	2264	NA	NA
	0.5	7.2	NA	12.23	8.32	676.5	NA	NA
	1.0	114	NA	12.46	8.33	1976	NA	NA
M4 (fringe)	0.1	0.2	NA	21.99	7.54	13270	NA	NA
	0.5	0.2	NA	14.20	8.24	1874	NA	NA
	1.0	0.2	NA	14.46	8.28	1685	NA	NA
M5 (interm.)	0.1	- ^e	NA	17.14	8.24	1728	NA	NA
	0.5	0.2	NA	15.26	8.25	5695	NA	NA
	1.0	0.4	NA	15.14	8.29	2096	NA	NA
M6 (center)	0.1	-	NA	17.74	8.07	2605	NA	NA
	0.5	-	NA	16.32	8.27	2216	NA	NA
	1.0	-	NA	16.19	8.34	2143	NA	NA

^a Samples collected prior to any SVE operation during that season.

^b See Fig. 3.3 for sample locations. Information in () refers to plume soil TPH concentrations.

^c Results expressed on a dry soil weight basis.

^d "-" indicates measurement not collected due to equipment malfunction.

^e NA indicates sample not analyzed but analysis pending.

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Table 3.4. Microbiological properties of the Samia site as determined in soil samples collected during July 1995. ^a

Location ^b	Depth (m)	On-site Hnu PID (ppmv)	Heterotrophic Aerobes: Plate Counts (cells/g)		Broths (cells/g)		Heterotrophic Anaerobes (cells/g)		Hydrocarbon Utilizers (cells/g)	
			<i>1 wk</i>	<i>1 mo</i>	<i>1 wk</i>	<i>1 mo</i>	<i>1 wk</i>	<i>1 mo</i>	<i>1 wk</i>	<i>1 mo</i>
<i>Incubation:</i>										
M1 (fringe)	0.1	0.2	10 ⁶	10 ⁷	10 ⁶⁻⁷	≥10 ⁷	10 ⁴	10 ²	10 ²	0
	0.5	0.3	10 ⁶	10 ⁵	10 ⁵	10 ⁶	10 ⁴	10 ³	10 ²	1-10
	1.0	0.2	10 ⁵	NA ^c	10 ⁵	10 ⁵	10 ³	10 ³	10 ²	1-10
M2 (interm.)	0.1	0.2	10 ⁶	10 ⁷	10 ⁶⁻⁷	≥10 ⁷	10 ⁴	>10 ⁶	10 ⁴	>10 ²
	0.5	0.2	10 ⁶	10 ⁶	10 ⁷	10 ⁸	10 ⁶	>10 ⁶	10 ⁴	10 ²
	1.0	6.8	10 ⁵	NA	10 ⁵	10 ⁵	10 ⁶	10 ³	10 ³	10 ⁴
M3 (center)	0.1	0.2	10 ⁶	10 ⁷	10 ⁶⁻⁷	≥10 ⁷	10 ⁶	10 ⁵	10 ³	10 ²
	0.5	7.2	10 ⁶	10 ⁷	10 ⁶	10 ⁶	10 ⁵	10 ⁴	10 ²	10 ⁵
	1.0	114	10 ⁵	NA	10 ⁵	10 ⁵	10 ⁴	10 ⁴	10 ³	10 ³
M4 (fringe)	0.1	0.2	NA	NA	10 ⁶⁻⁷	≥10 ⁷	NA	NA	10 ²	10 ⁴
	0.5	0.2	NA	NA	10 ⁶	10 ⁶	NA	NA	10 ²	0
	1.0	0.2	10 ⁵	10 ⁵	10 ⁵	10 ⁵	10 ⁴	1	10 ²	1-10
M5 (interm.)	0.1	- ^d	NA	NA	10 ⁶⁻⁷	≥10 ⁷	NA	NA	10 ³	10 ⁵
	0.5	0.2	NA	NA	10 ⁶	10 ⁶	NA	NA	10 ²	10 ²
	1.0	0.4	10 ⁵	10 ⁵	10 ⁵	10 ⁶	10 ⁴	10	10 ²	10 ²
M6 (center)	0.1	-	NA	NA	10 ⁶⁻⁷	≥10 ⁷	NA	NA	10 ²	10 ⁴
	0.5	-	NA	NA	10 ⁶	10 ⁶	NA	NA	10 ²	10 ⁴
	1.0	-	10 ⁵	10 ⁶	10 ⁷	10 ⁷	10 ⁴	>10 ⁶	10 ³	10 ⁴

^a Sample collected prior to any SVE operation during the prior 12 months.

^b See Fig. 3.3 for sample locations. Information in () refers to plume soil TPH concentrations.

^c "-" indicates measurement not collected due to equipment malfunction.

^d NA indicates sample not analyzed.

APPENDIX C

SOIL CORE ANALYSIS AND DISTRIBUTION OF THE LNAPL SPILL WITHIN THE EXPERIMENTAL CELL AT VARIOUS STAGES OF REMEDIATION

This appendix contains the results of soil core analysis determined prior to and subsequent to remediation, and at various stages during the remediation process. Soil core concentrations are tabulated followed by contour plots of the data.

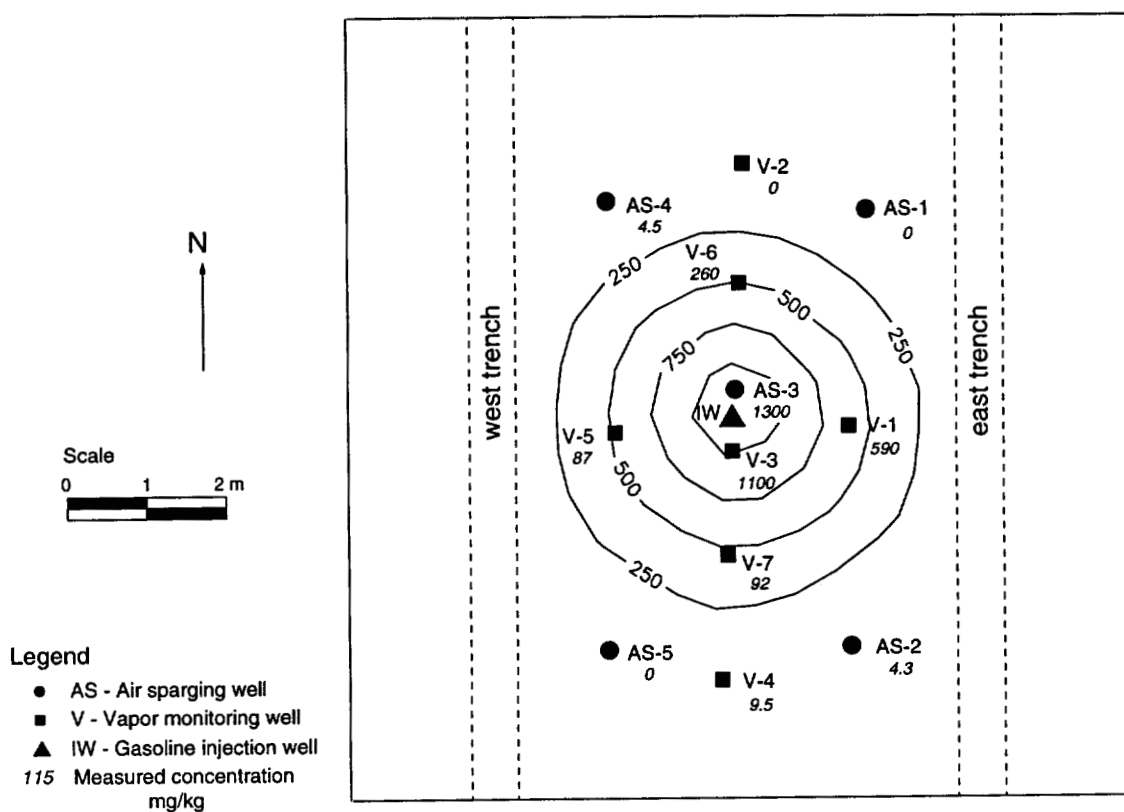


Figure C.1. Pre-remediation (July, 1993) hydrocarbon concentrations (mg/kg) at the 30 cm depth (GRO analysis by Kemron Lab.).

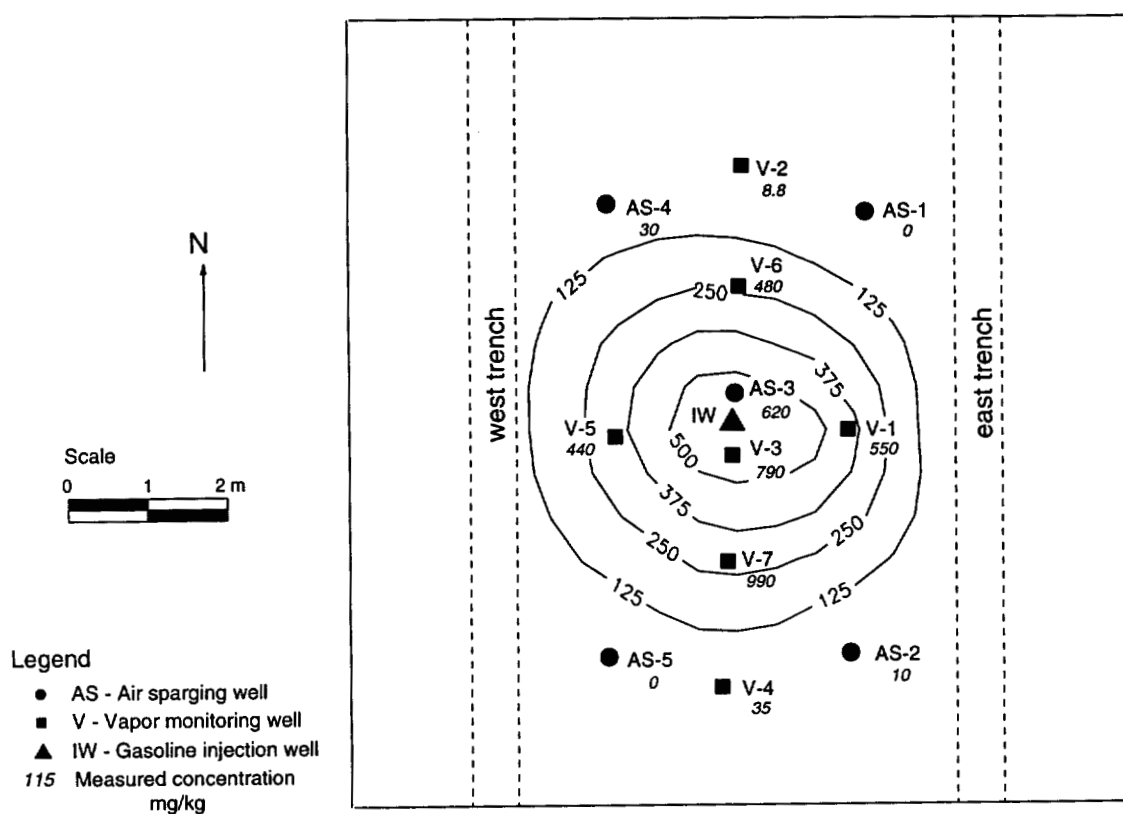


Figure C.2. Pre-remediation (July, 1993) hydrocarbon concentrations (mg/kg) at the 60 cm depth (GRO analysis by Kemron Lab.).

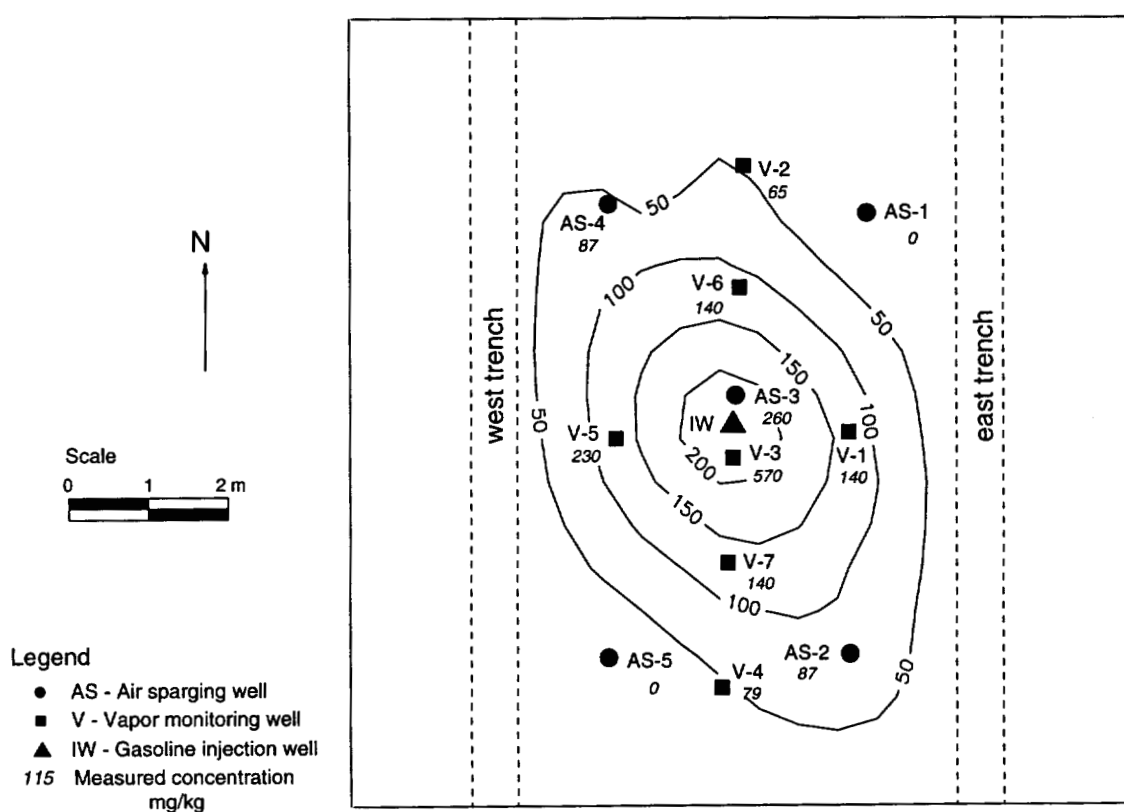


Figure C.3. Pre-remediation (July, 1993) hydrocarbon concentrations (mg/kg) at the 90 cm depth (GRO analysis by Kemron Lab.).

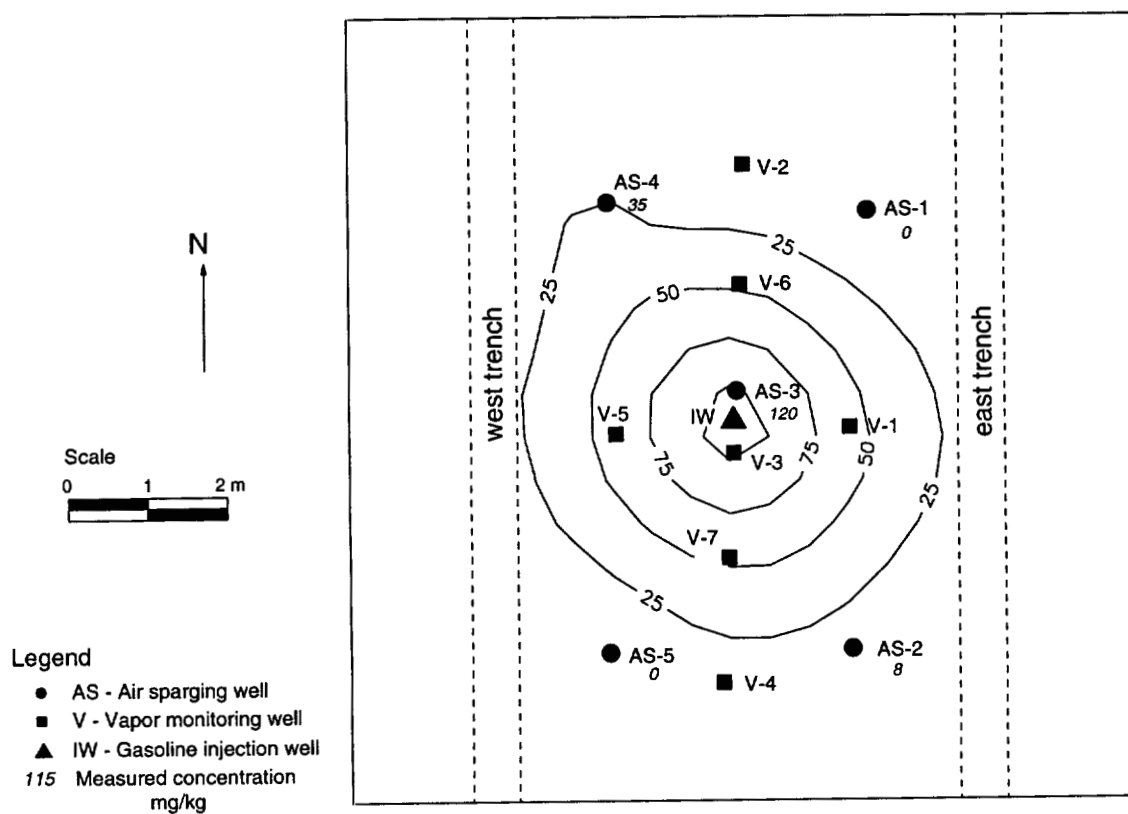


Figure C.4. Pre-remediation (July, 1993) hydrocarbon concentrations (mg/kg) at the 120 cm depth (GRO analysis by Kemron Lab.).

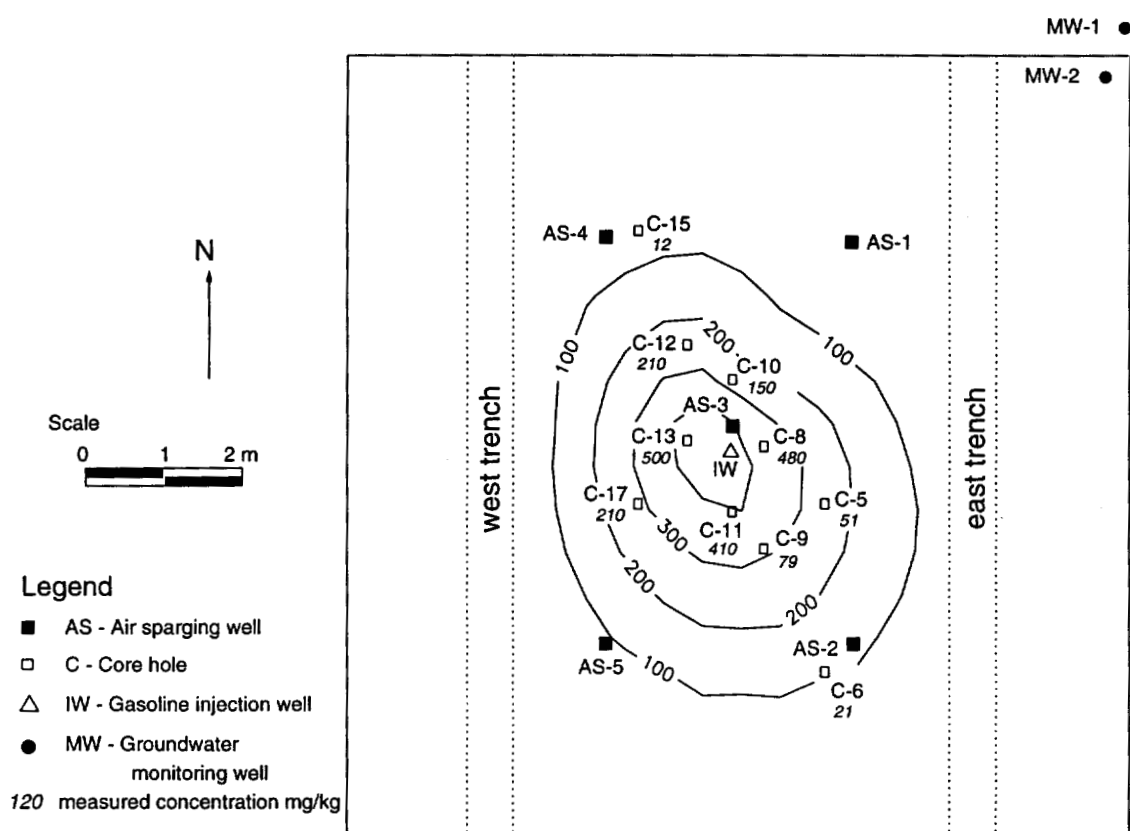


Figure C.5. Post first season (Oct., 1993) hydrocarbon concentrations (mg/kg) at the 30 cm depth (GRO analysis by Kemron Lab.).

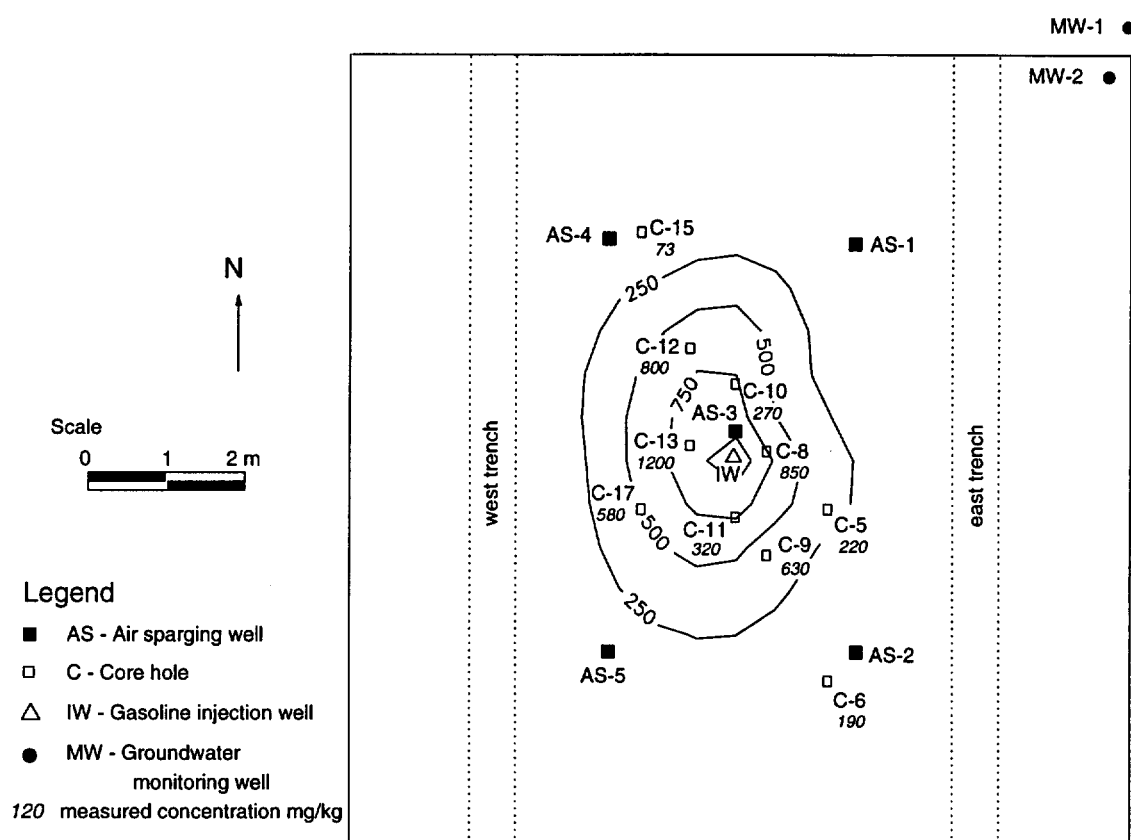


Figure C.6. Post first season (Oct., 1993) hydrocarbon concentrations (mg/kg) at the 60 cm depth (GRO analysis by Kemron Lab.).

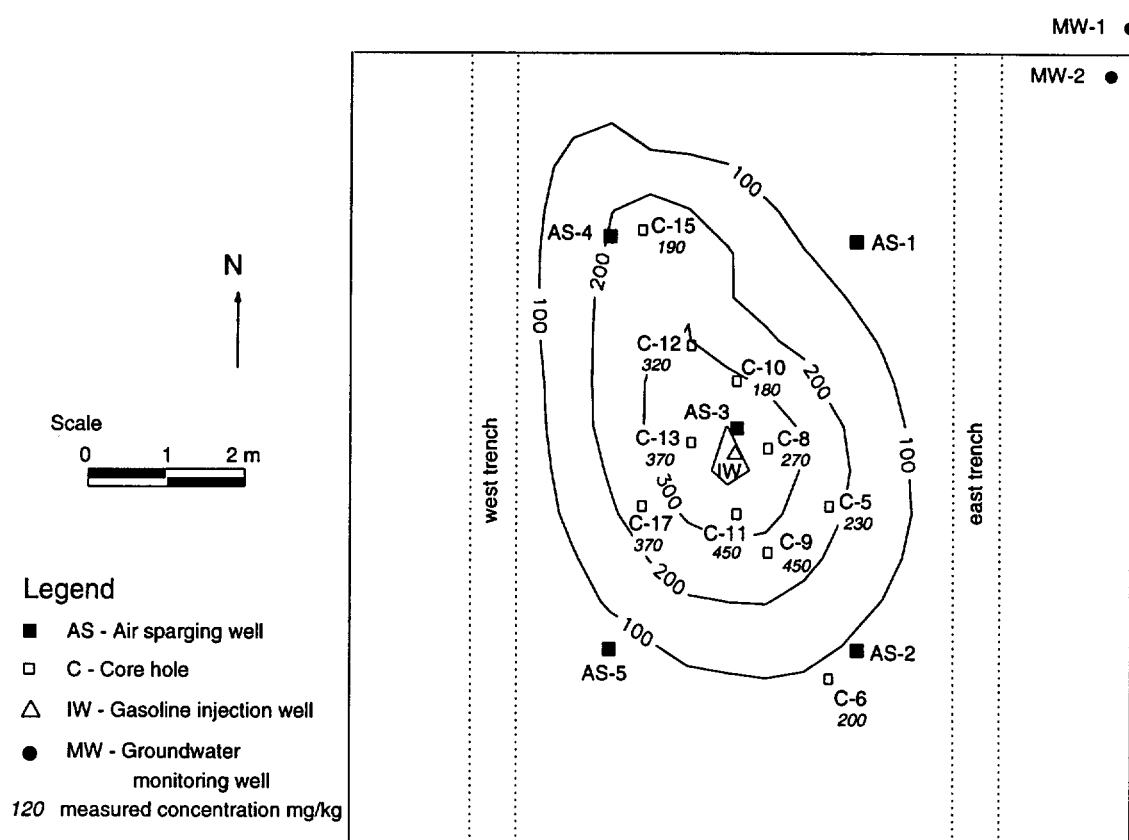


Figure C.7. Post first season (Oct., 1993) hydrocarbon concentrations (mg/kg) at the 90 cm depth (GRO analysis by Kemron Lab.).

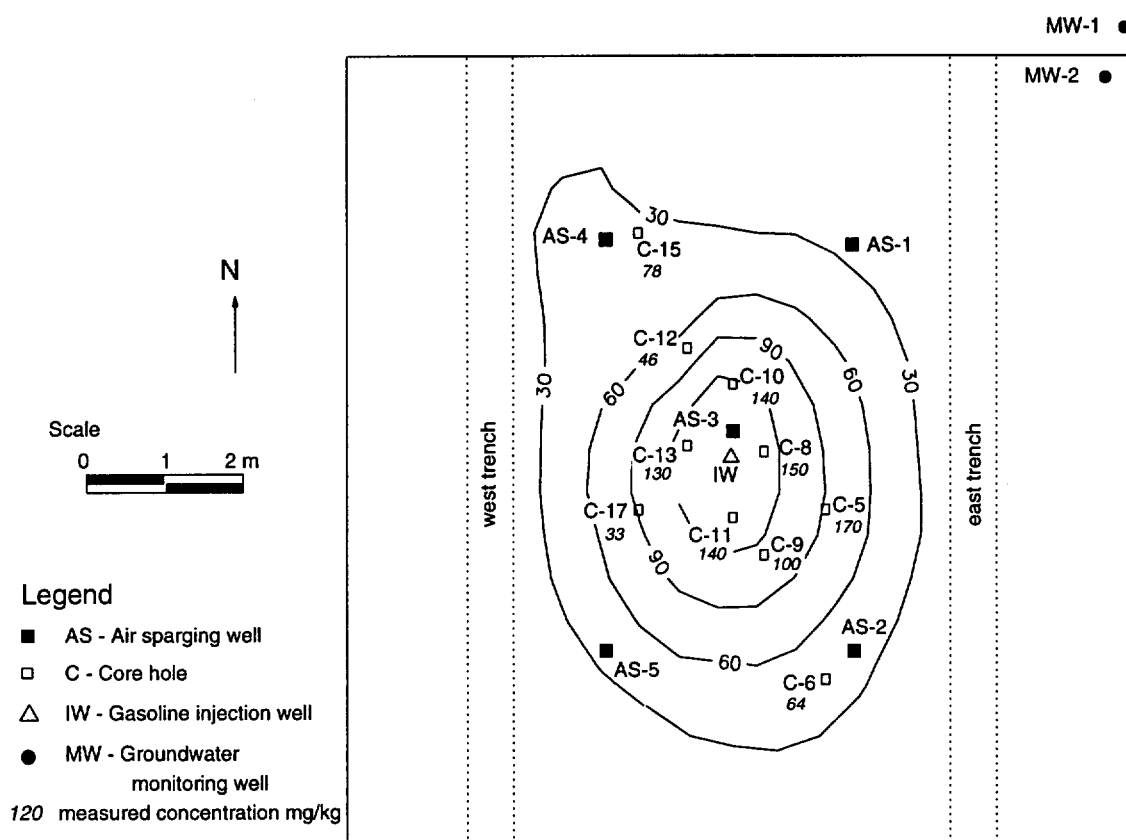


Figure C.8. Post first season (Oct., 1993) hydrocarbon concentrations (mg/kg) at the 120 cm depth (GRO analysis by Kemron Lab.).

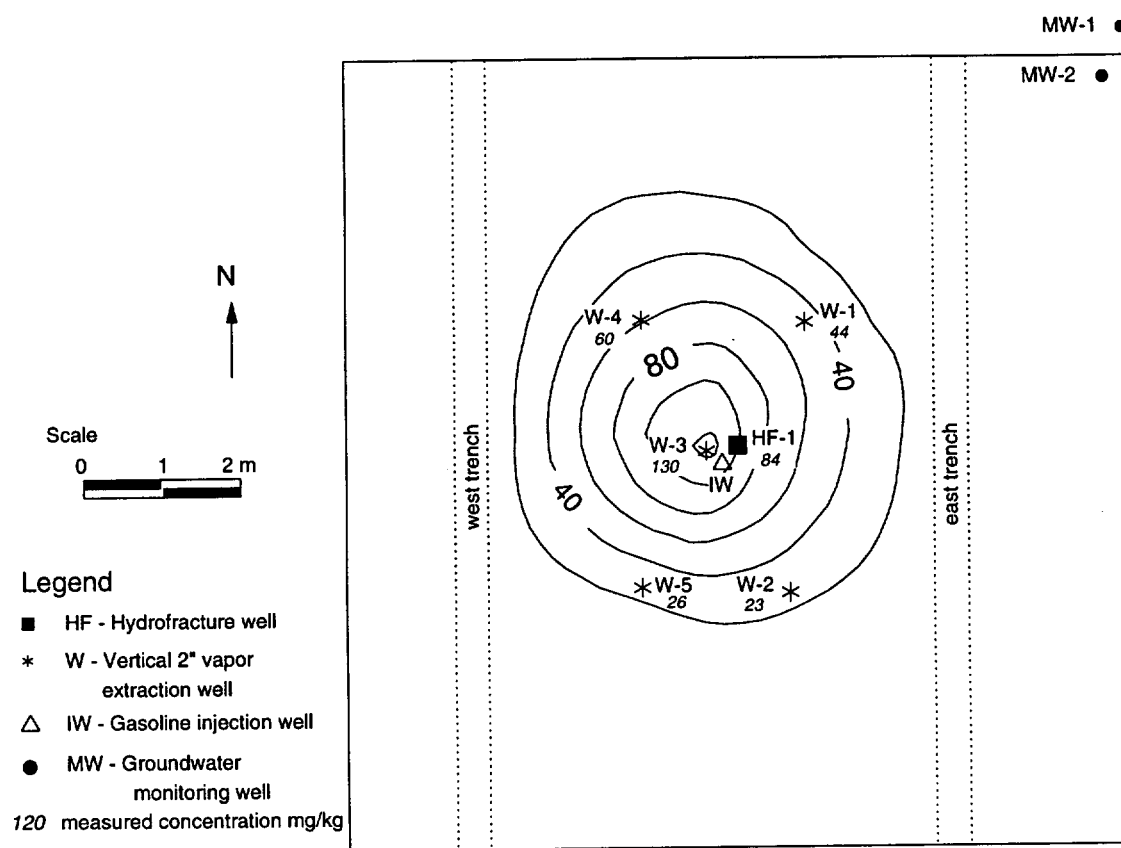


Figure C.9. Pre-second season (June, 1994) hydrocarbon concentrations (mg/kg) at the 30 cm depth (GRO analysis by Kemron Lab.).

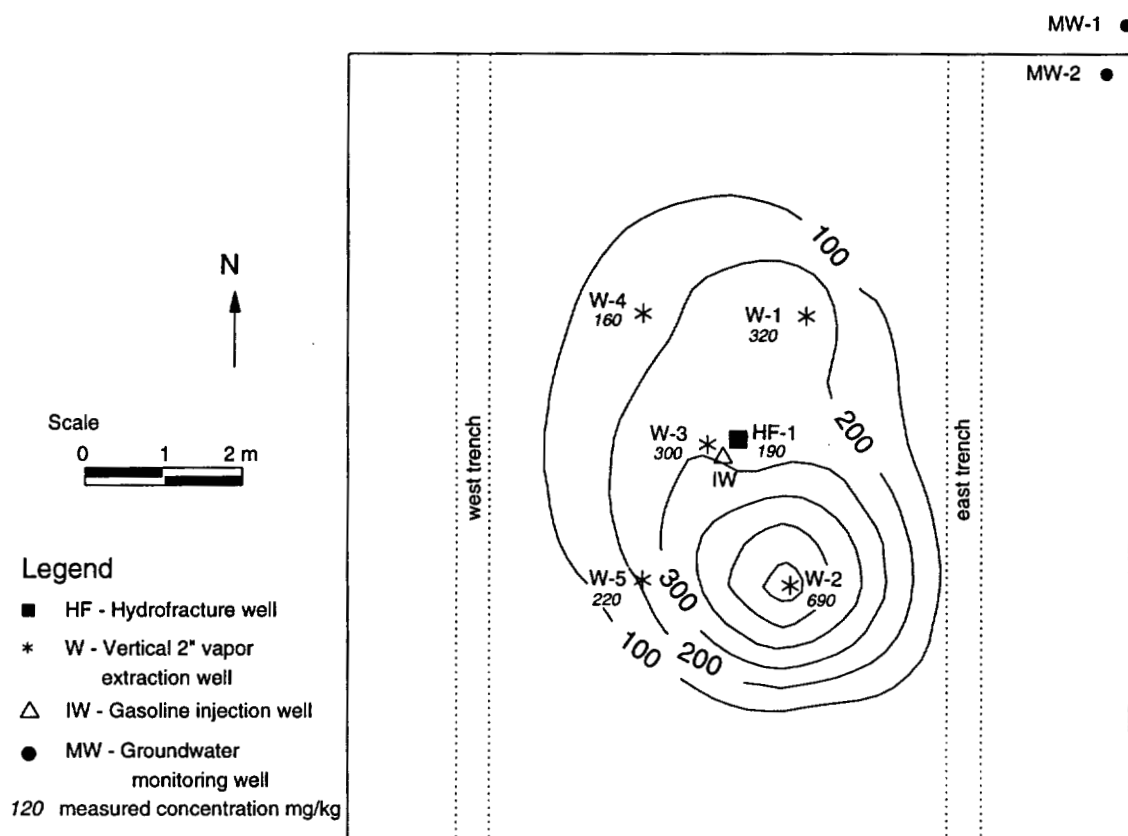


Figure C.10. Pre-second season (June, 1994) hydrocarbon concentrations (mg/kg) at the 60 cm depth (GRO analysis by Kemron Lab.).

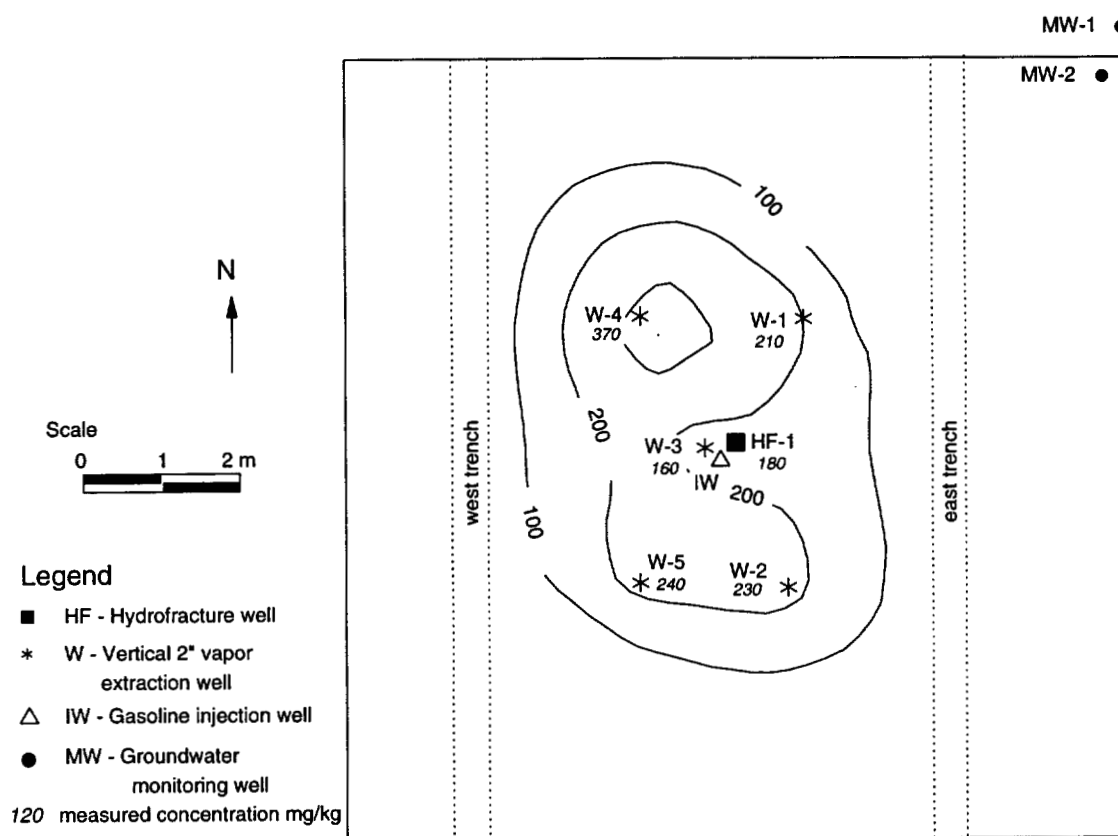


Figure C.11. Pre-second season (June, 1994) hydrocarbon concentrations (mg/kg) at the 90 cm depth (GRO analysis by Kemron Lab.).

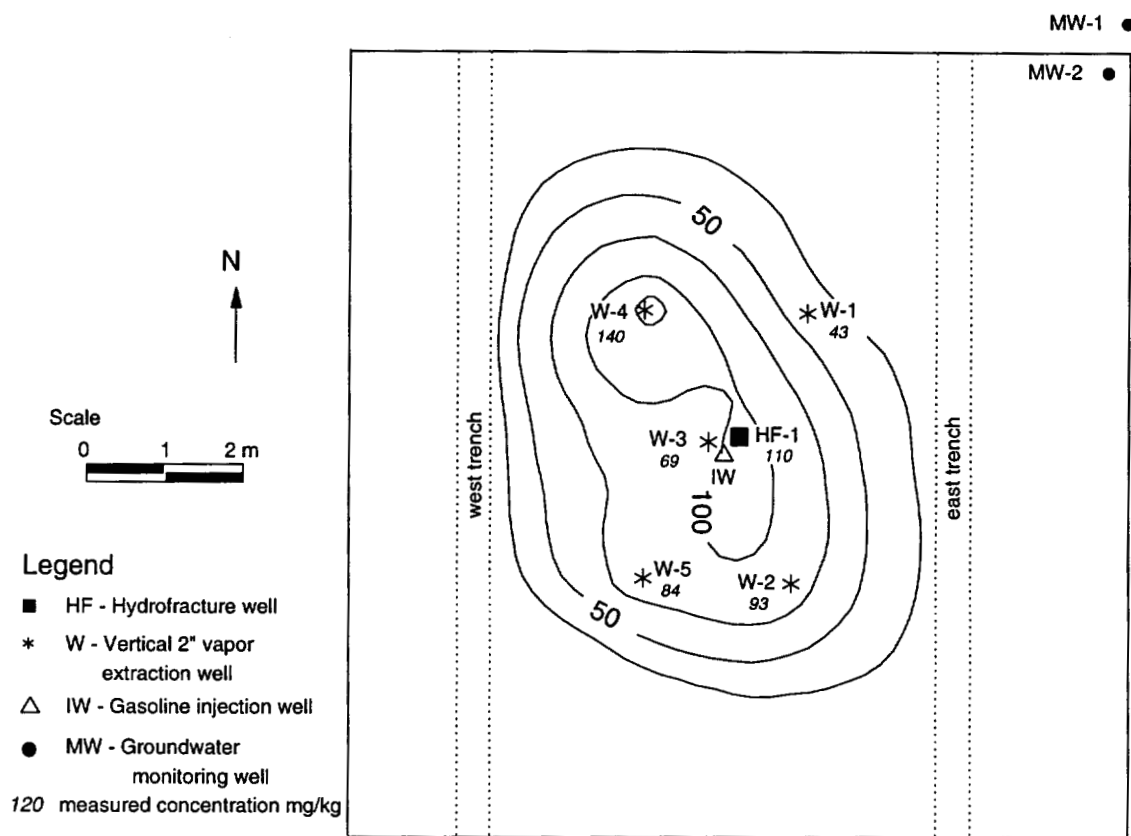


Figure C.12. Pre-second season (June, 1994) hydrocarbon concentrations (mg/kg) at the 120 cm depth (GRO analysis by Kemron Lab.).

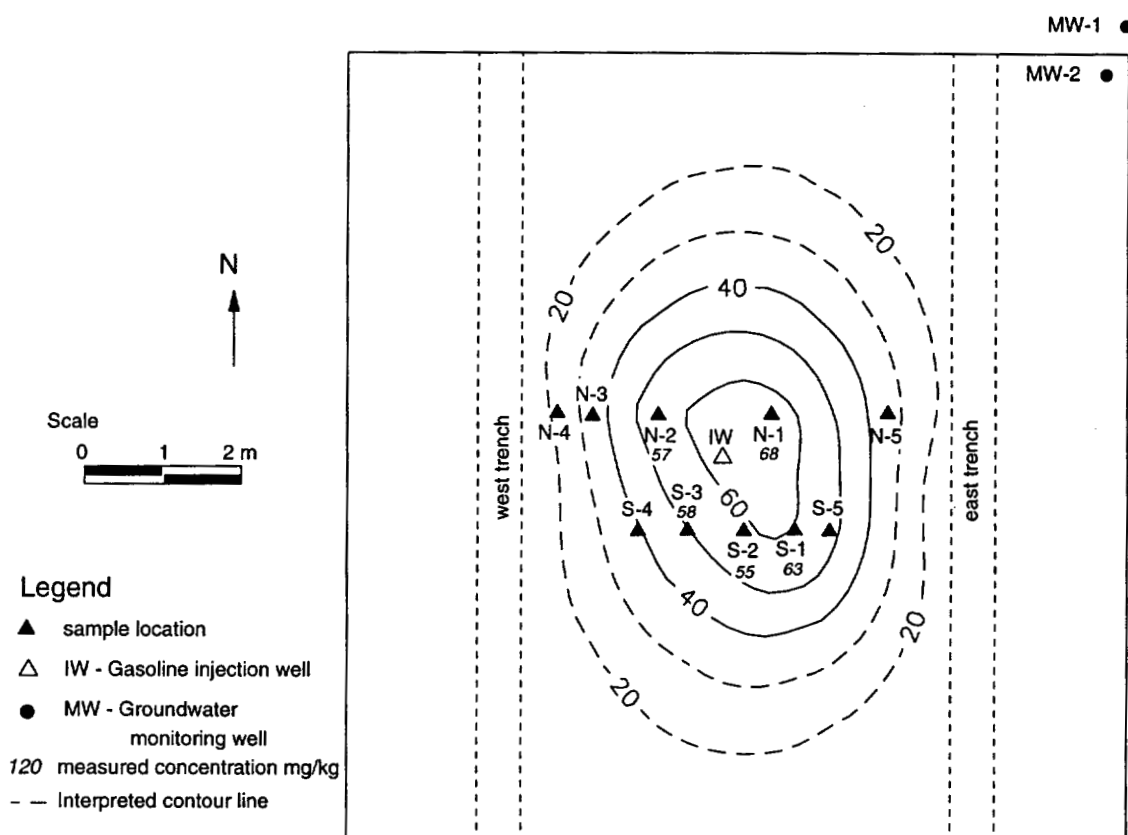


Figure C.13. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 60 cm depth (GRO analysis by Kemron Lab.).

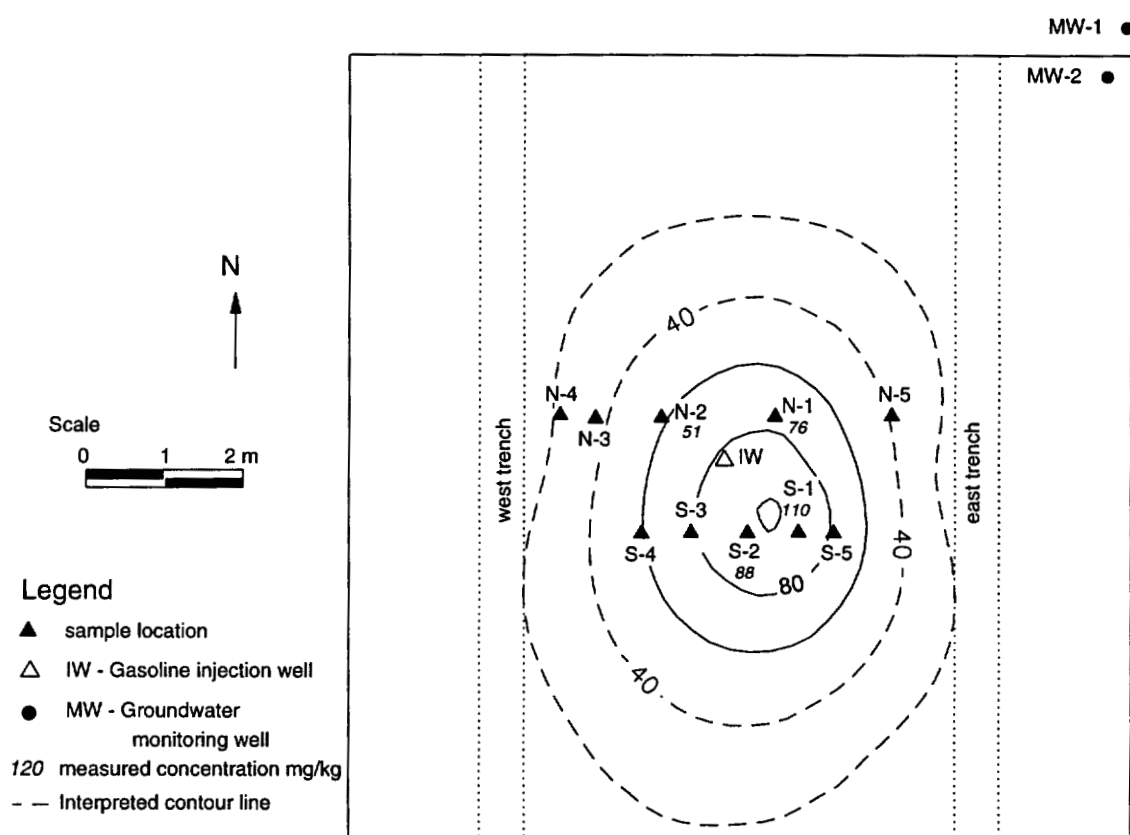


Figure C.14. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 75 cm depth (GRO analysis by Kemron Lab.).

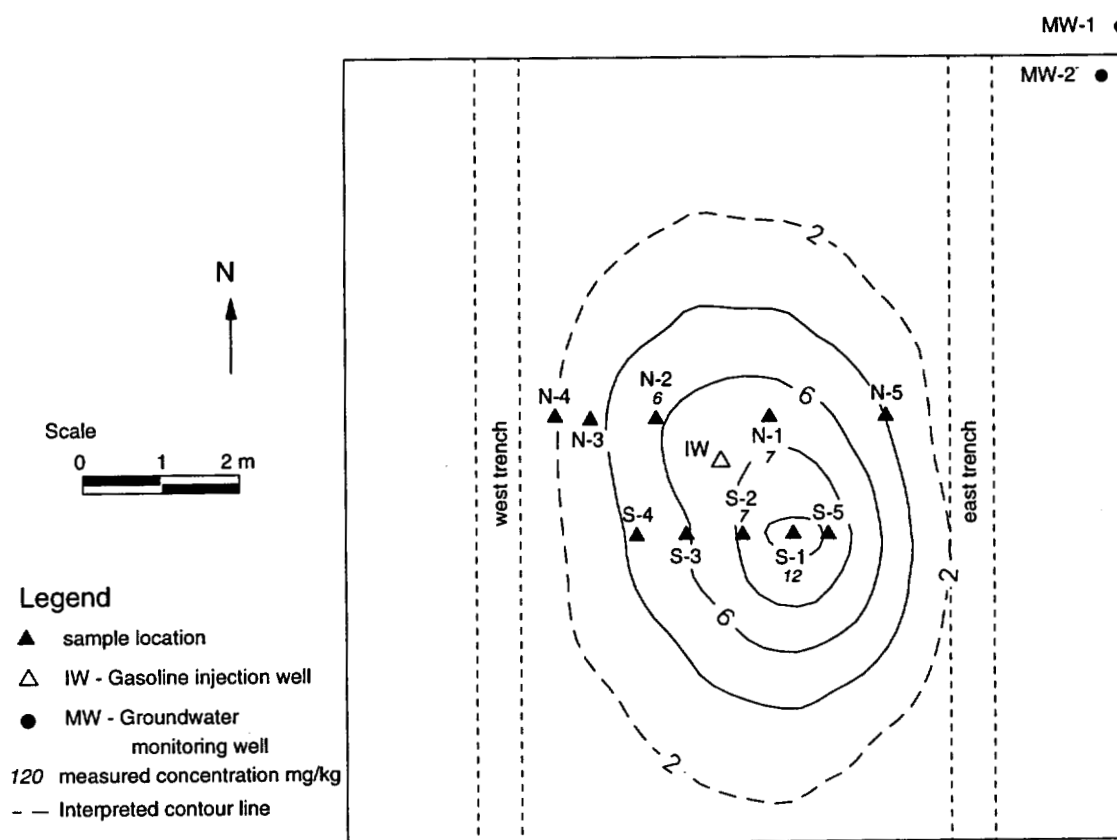


Figure C.15. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 30 cm depth (GRO analysis by OGI GC/MS).

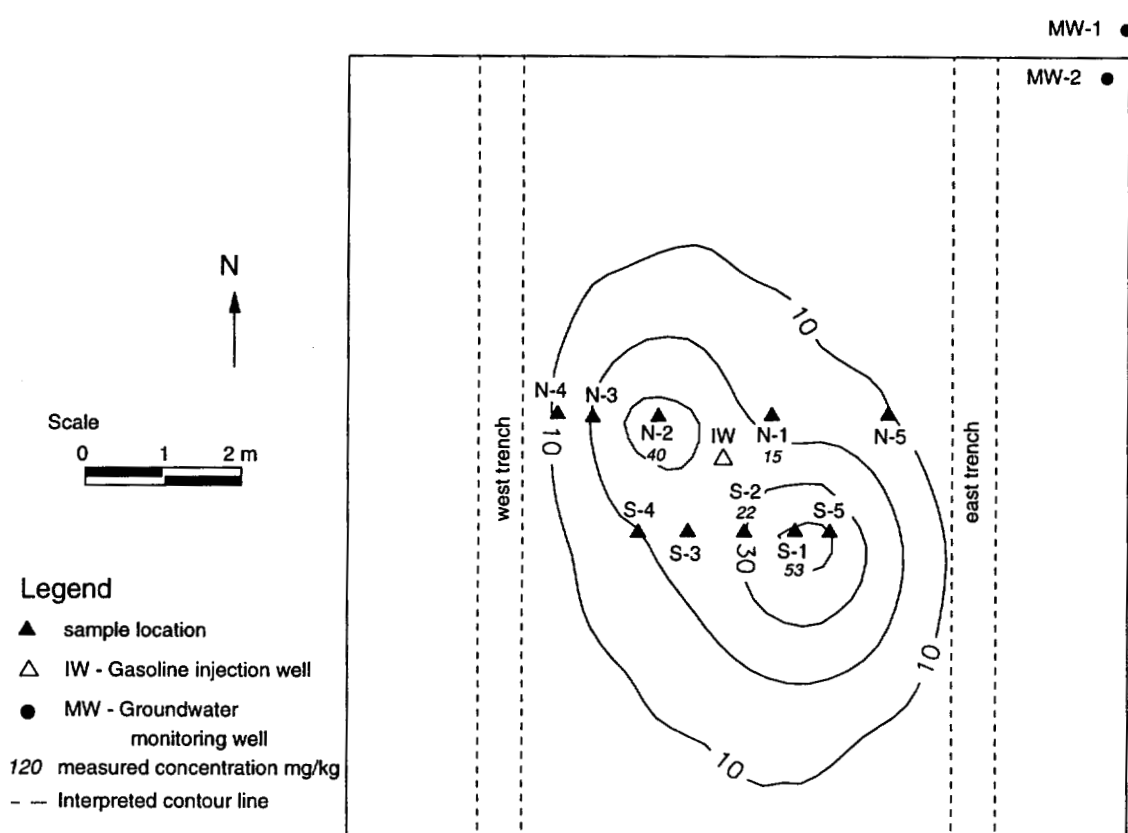


Figure C.16. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 45 cm depth (GRO analysis by OGI GC/MS).

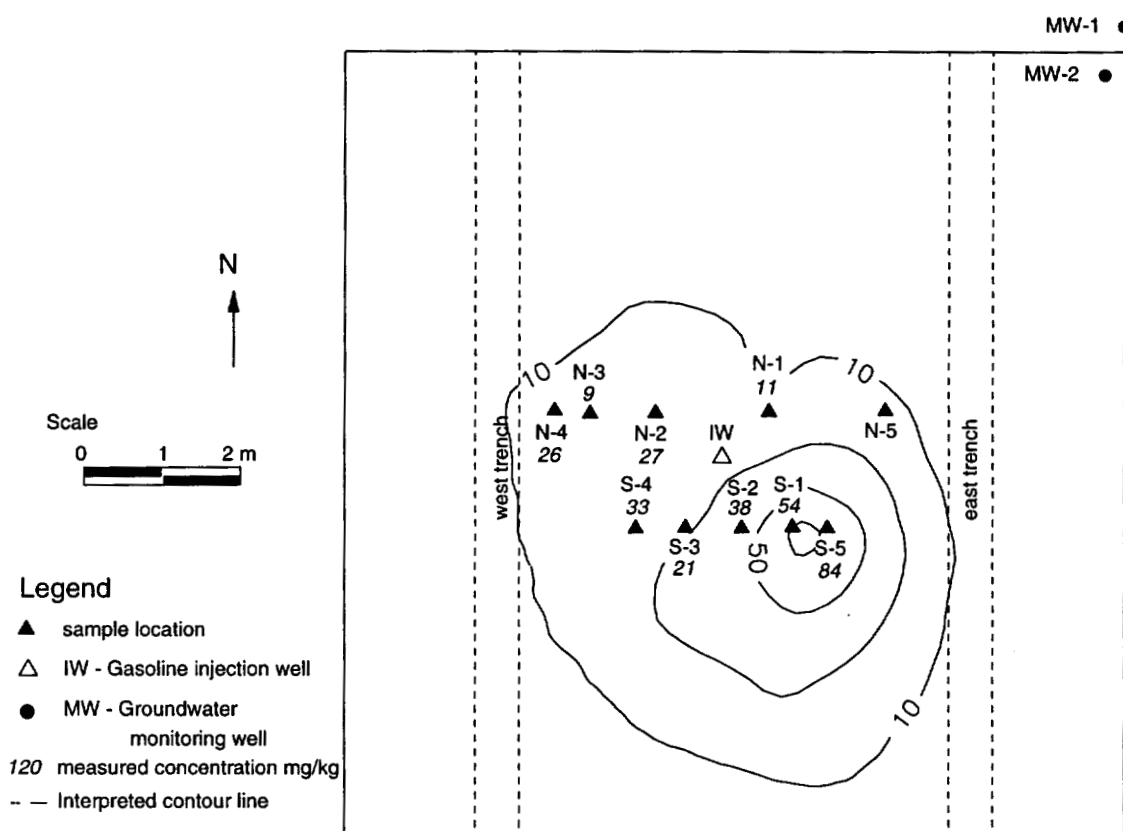


Figure C.17. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 60 cm depth (GRO analysis by OGI GC/MS).

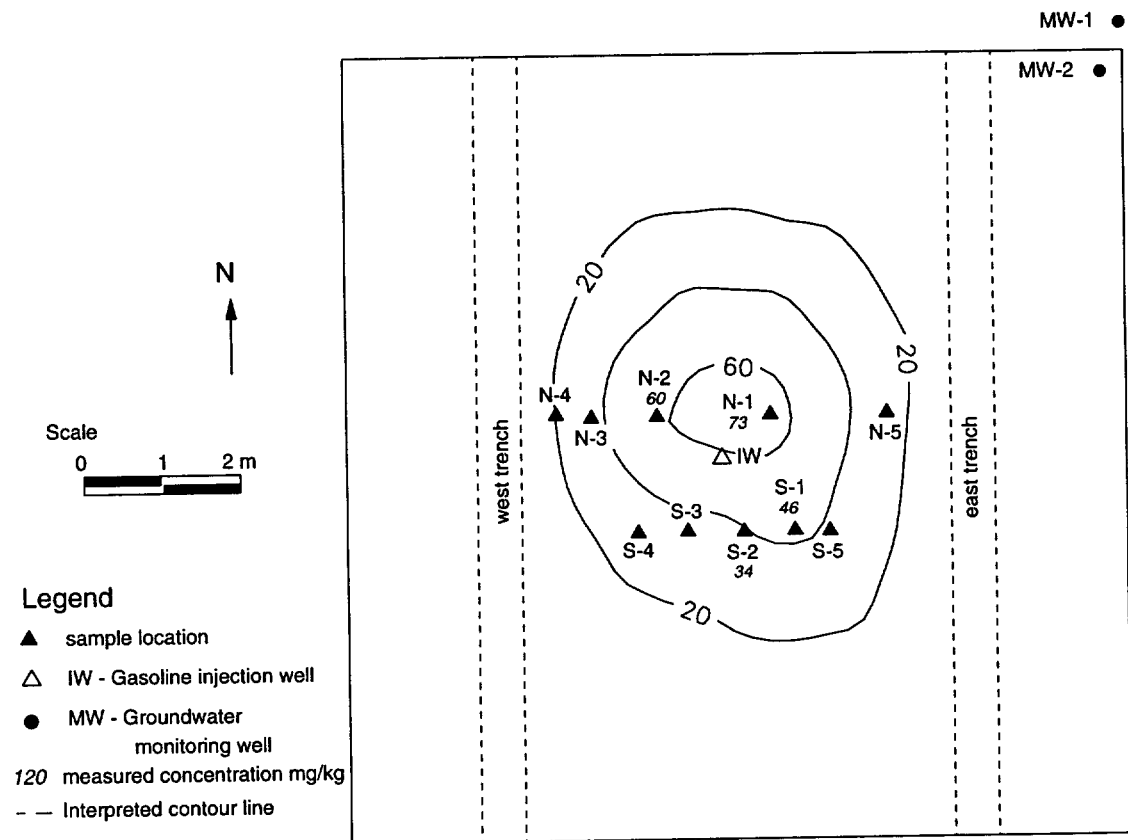


Figure C.18. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 75 cm depth (GRO analysis by OGI GC/MS).

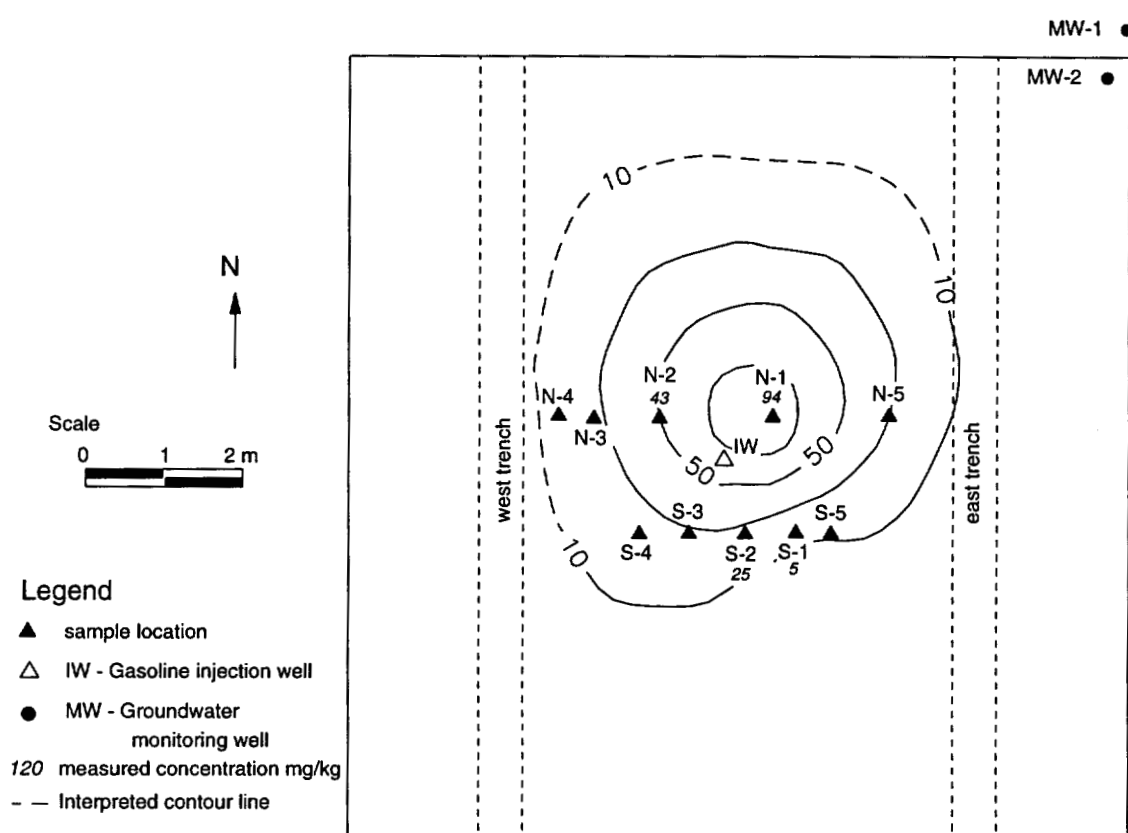


Figure C.19. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 90 cm depth (GRO analysis by OGI GC/MS).

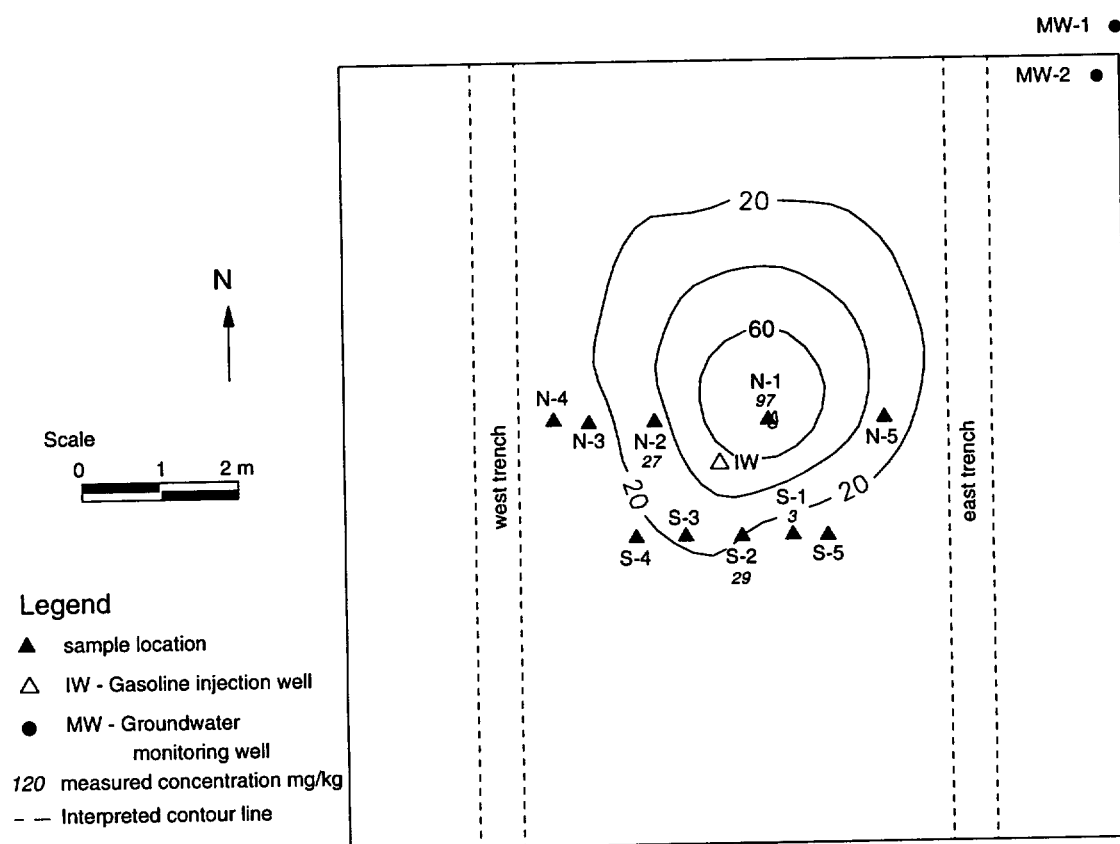


Figure C.20. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 105 cm depth (GRO analysis by OGI GC/MS).

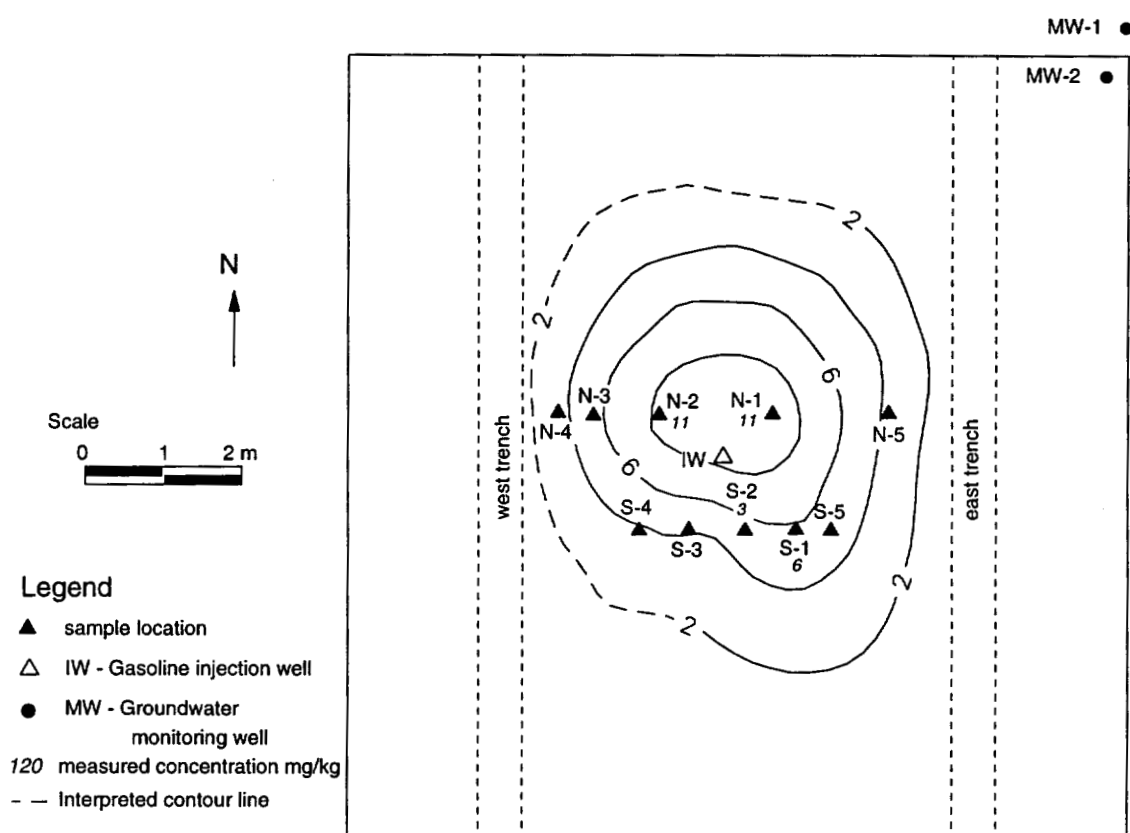


Figure C.21. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 120 cm depth (GRO analysis by OGI GC/MS).

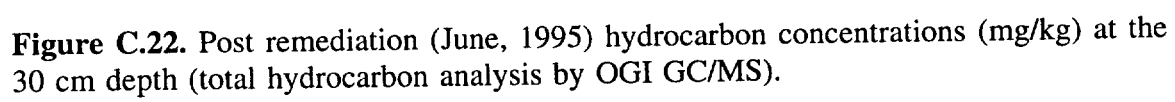


Figure C.22. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 30 cm depth (total hydrocarbon analysis by OGI GC/MS).

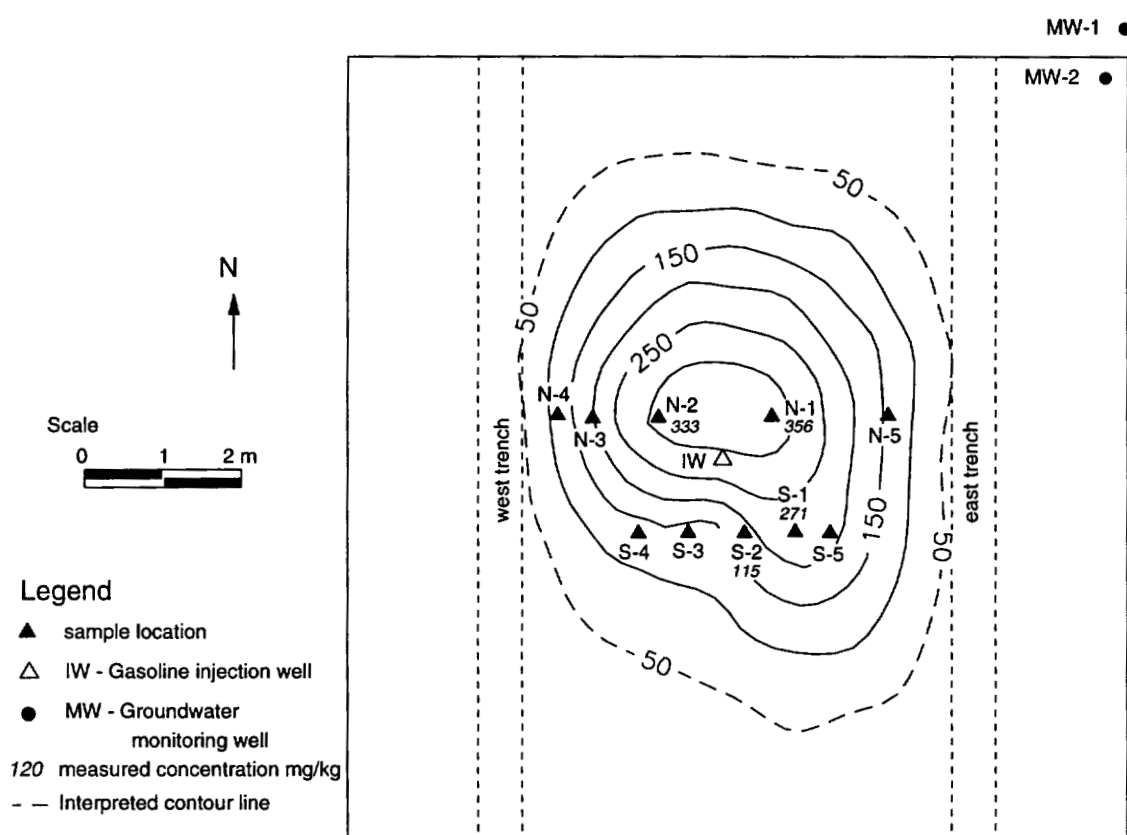


Figure C.23. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 45 cm depth (total hydrocarbon analysis by OGI GC/MS).

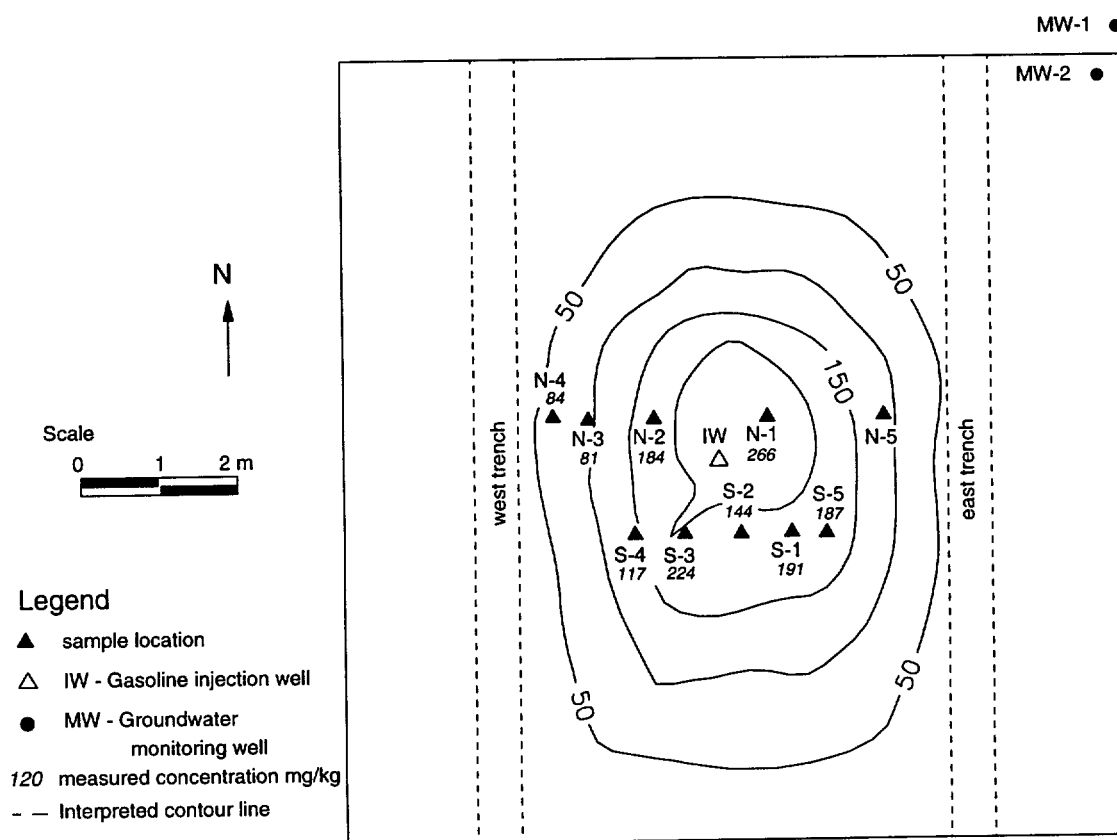


Figure C.24. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 60 cm depth (total hydrocarbon analysis by OGI GC/MS).

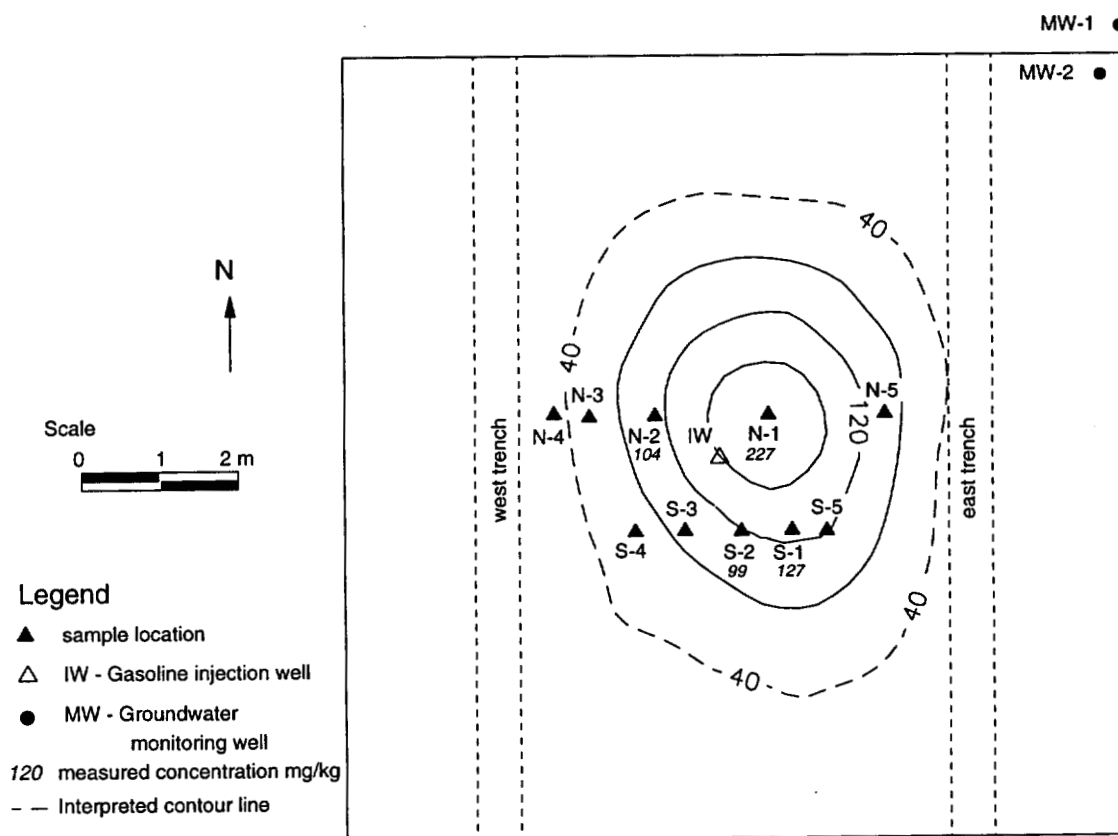


Figure C.25. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 75 cm depth (total hydrocarbon analysis by OGI GC/MS).

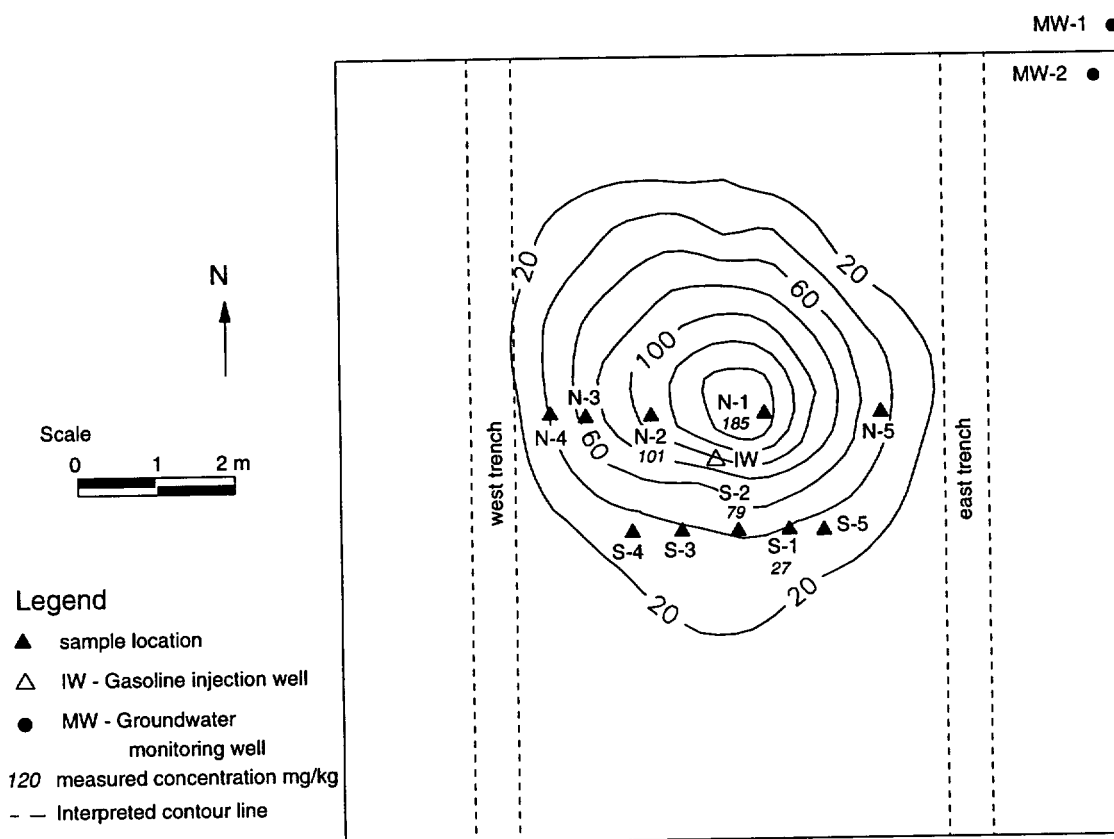


Figure C.26. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 90 cm depth (total hydrocarbon analysis by OGI GC/MS).

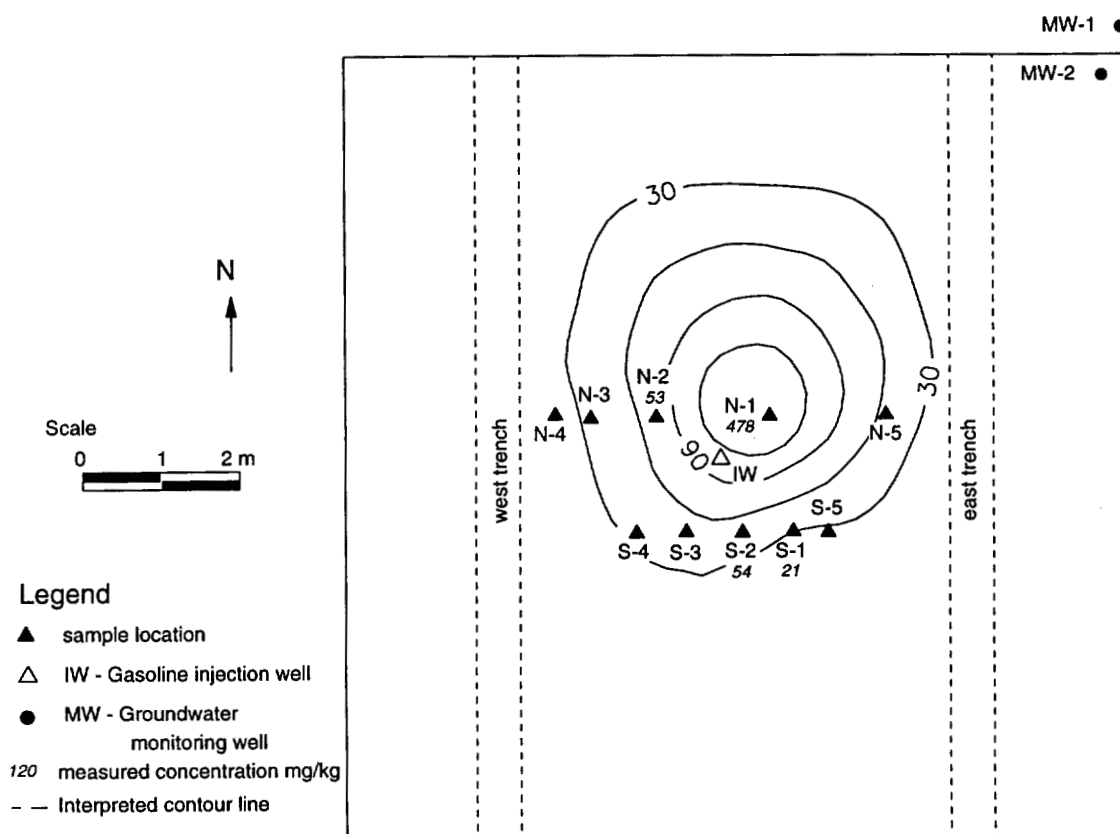


Figure C.27. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 105 cm depth (total hydrocarbon analysis by OGI GC/MS).

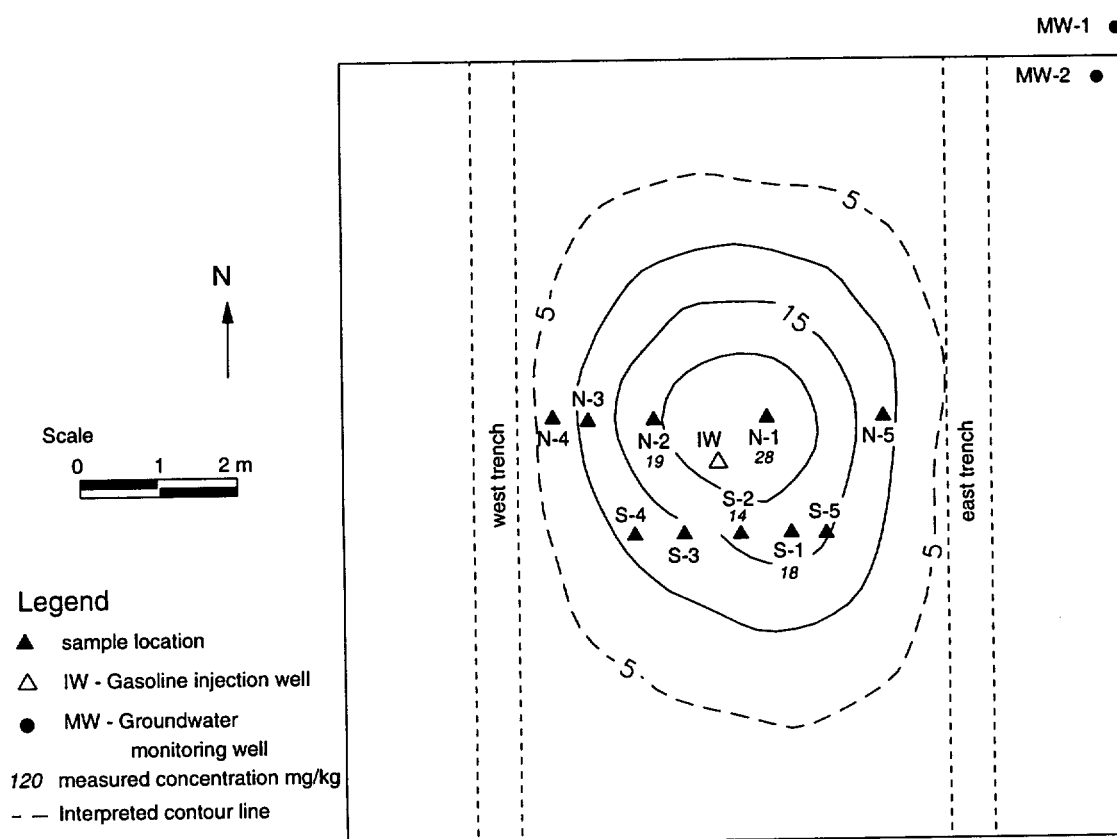


Figure C.28. Post remediation (June, 1995) hydrocarbon concentrations (mg/kg) at the 120 cm depth (total hydrocarbon analysis by OGI GC/MS).

APPENDIX D
ONE-DIMENSIONAL NUMERICAL-MODEL CODE

This appendix contains the Fortran code for the one-dimensional finite-difference diffusion numerical model discussed in Chapter 4. Also included is the input file ("sample.dat") and an output file ("header.out") containing parameters initially calculated in the code and used through out numerical model.

```

c      One dimensional diffusion Finite Difference Model
c      Fully implicit, fully explicit or Crank-Nickolson methods available
c      Diffusion of the Sarnia gasoline mixture from the
c      fracture into the matrix and subsequent remediation by SVE

```

```

c      Diane E. Grady and Richard L. Johnson
c      15-Nov-1996

```

```

c      **** Definition of terms ****

```

```

c      K = compound counter
c      I = node counter

c      D = diffusion
c      R = retardation factor
c      SOL = solubility g/ml
c      M = mass kg
c      P = compound density
c      MOL = moles
c      MW = molecular weight
c      MS = mix solubility
c      MX = mole fraction
c      TMASS = total mass spilled
c      FACE = fracture face area in cm^2 per m^3 block of clay
c      RS = residual saturation
c      VA = velocity of SVE air cm/min
c      VP = vapour pressure atm
c      VMP = mix vapour pressure
c      TMP = average ground temperature C
c      C & C0 = aqueous phase concentrations mg/l
c      S = sorbed phase concentration mg/l
c      OLDVAL = old aqueous phase concentration mg/l
c      M, FNEW & FOLD = mass in fracture mg/cm^2
c      MAT,MNEW & MOLD = mass in matrix mg/cm^2
c      VM, VNEW, VOLD & VMAX = mass in vapor mg/cm^2
c      M0 = initial mass in fracture mg/cm^2
c      NN = number of moles in vapor phase
c      TMAS = total mass in fracture in current time step mg/cm^2
c      DELTA = change in mass in the matrix
c      DT, DTO, DDAY, TIME = time counters and steps

DOUBLE PRECISION C(1001,15),C0(1001,15),S(1001,15)
DOUBLE PRECISION FPER(15),MOL(15),VP(15),VMP(15),OLDVAL(1001,15)

DOUBLE PRECISION KOC(15),R(15),KD(15),D(15),P(15),R1(15)
DOUBLE PRECISION SOL(15),M(15),MW(15),MS(15),MX(15),M0(15)
DOUBLE PRECISION VPER(15),MPER(15),VNEW(15),VM(15),VOLD(15)
DOUBLE PRECISION FNEW(15),FOLD(15),MNEW(15),MOLD(15),DELTA(15)
DOUBLE PRECISION MAT(15),VMAX(15),NN(15)
DOUBLE PRECISION IT,ST,FRAC,TIME,DTO,DDAY,MINIT,RF,TMAS
DOUBLE PRECISION EL,ET,DX,DT,BD,FOC,N,MOLES,TOR,TOL,AMAX,ERR
DOUBLE PRECISION TMASS,FACE,RS,TMP,VA,FW,VOL
INTEGER NX,NC,PC,NF,NUMIT
INTEGER I,K,IRST
CHARACTER*10 CMP(15)

```

```

c      Open files

```

```

OPEN (2,FILE = 'sample.dat')
OPEN (3,FILE = 'frx.out')
OPEN (7,FILE = 'header.out')
OPEN (10,FILE = 'delta.out')
OPEN (11,FILE = 'matrix.out')
OPEN (12,FILE = 'vapour.out')
OPEN (13,FILE = 'totals.out')
OPEN (14,FILE = 'ms.out')
OPEN (16,FILE = 'restart.in')

```

```

c      Read in data file and echo

```

```

READ (2,*) EL      !length of system in cm

```

```

      READ (2,*) ET      !time of solution in days
      READ (2,*) BD      !bulk density
      READ (2,*) FOC     !fraction of organic carbon
      READ (2,*) N       !total porosity
      READ (2,*) TOR     !tortuosity
      READ (2,*) NX      !number of nodes (# of spacial intervals +1)
      READ (2,*) DT      !time step (d)
      READ (2,*) IT      !day which SVE starts (mass removed in fractures)
      READ (2,*) ST      !day which SVE stops (no mass removed from fractures)
      READ (2,*) RS      !residual saturation L/m^3
      READ (2,*) NF      !number of fractures per meter (ie.50/m=2cm spacings)
      READ (2,*) FW      !fracture width (microns)
      READ (2,*) VA      !velocity of SVE air m/min
      READ (2,*) TMP      !average ground temperature C
      READ (2,*) NC      !number of cmpds solved for
      READ (2,*) PC      !cmpd number to print results for
      READ (2,*) FRAC    !maximum fraction of mass removed per day
      READ (2,*) IRST    !if IRST=1 then read "restart.in"
      READ (2,*) ALPHA   !0=explicit, 0.5=Crank-Nickolson, 1=implicit
      READ (2,*) TOL     !Solution tolerance C-N iteration
      DO 10 K=1,NC
        READ (2,161) CMP(K),MW(K),SOL(K),M0(K),KOC(K),P(K),VP(K)
10    CONTINUE

      DX = EL/DFLOAT(NX)
      VOL = FW/2*1.0D-6*0.01D0*1.0D0 !volume of air for 1m long fracture
      DDAY = 2.0D0

c      Set initial conditions

      DO 20 K=1,NC
        DO 15 I=1,NX
          C(I,K) = 0.0D0
          C0(I,K) = 0.0D0
          S(I,K) = 0.0D0
15    CONTINUE
        VM(K) = 0.0D0
        MOLD(K) = 0.0D0
        DELTA(K) = 0.0D0
        VOLD(K) = 0.0D0
        FOLD(K) = 0.0D0
        DTO = DT
        TIME = 0.0D0
20    CONTINUE

      WRITE (7,*) 'INPUT DATA FOR 1-D FINITE DIFFERENCE SOLUTION'
      WRITE (7,*) ' '
      WRITE (7,*) 'LENGTH OF SYSTEM (cm) : EL = ',EL
      WRITE (7,*) 'TIME OF SOLUTION (days): ET = ',ET
      WRITE (7,*) 'NUMBER OF NODES : NX = ',NX
      WRITE (7,*) 'SPACIAL INCREMENT (cm) : DX = ',DX
      WRITE (7,*) 'TIME INCREMENT : DT = ',DT
      WRITE (7,*) 'DAY OF SVE INITIATION : IT = ',IT
      WRITE (7,*) 'DAY OF SVE SHUTOFF : ST = ',ST
      WRITE (7,*) 'NUMBER OF COMPOUNDS : NC = ',NC
      WRITE (7,*) 'TORTUOSITY : TOR = ',TOR
      WRITE (7,*) 'POROSTIY : N = ',N
      WRITE (7,*) 'RESIDUAL SAT. (L/m3): RS = ',RS
      WRITE (7,*) 'NUMBER OF FRACTURES/M : NF = ',NF
      WRITE (7,*) 'FRACTURE WIDTH (micron): FW = ',FW
      WRITE (7,*) 'VEL. OF SVE AIR (m/min): VA = ',VA
      WRITE (7,*) 'AVG. GROUND TEMP. (C) :TMP = ',TMP
      WRITE (7,*) 'ALPHA :ALPHA = ',ALPHA
      WRITE (7,*) 'ITERATION TOLERANCE :TOL = ',TOL
      WRITE (7,*) ' '
      WRITE (7,*) 'COMPOUND MW SOLUB. MASS KOC DEN.
+VPRESS'
      DO 30 K=1,NC
        WRITE (7,5) CMP(K),MW(K),SOL(K),M0(K),KOC(K),P(K),VP(K)
30    CONTINUE
      WRITE (7,*) ' '

```

```

c      Calculate eff. diffusion, distb'n and retard. coeff's

DO 35 K=1,NC
  D(K) = (78.0D0/MW(K)*P(K)/0.88D0)**0.6D0*2.0D-07*86400.0D0  !in cm^2/day

  KD(K) = FOC*KOC(K)
  R(K) = 1+BD/N*KD(K)
  R1(K) = D(K)/R(K)*DT/(DX*DX)  !used in Explicit iteration
35 CONTINUE

c      Check for stability constraint for fully explicit iteration

DO 40 K=1,NC
  IF (R1(K) .GT. 0.5 .AND. ALPHA .EQ. 0.0D0) THEN
    WRITE (*,*) '---- SOLUTION IS UNSTABLE ---- ABORT'
    WRITE (*,*) 'AT ',CMP(K)
    WRITE (*,*) 'R1 =',R1(K), 'DX =',DX, 'DT =',DT, 'D =',D(K)
    GOTO 200
  END IF
40 CONTINUE

c      Calculate initial mass of each compound at fracture face

TMASS = 0.0D0
DO 41 K=1,NC
  TMASS = M0(K)+TMASS
41 CONTINUE

FACE = NF*2.0D0*100.0D0*100.0D0  !fracture face area in cm^2/m^3
DO 42 K=1,NC
  M(K) = M0(K)*RS/TMASS*P(K) !mass in kg/m^3
  M(K) = M(K)/FACE*1.0D06
42 CONTINUE
  MINIT = 0.0D0
DO 52 K=1,NC
  M0(K) = M(K)
  FNEW(K) = M(K)
  MINIT = MINIT+M(K)
52 CONTINUE

c      check for restart file (i.e. not starting at day one)

IF (IRST.EQ.1) THEN
  READ (16,*) TIME
  DO 16 K=1,NC
    READ (16,*) FNEW(K)
16 CONTINUE

  DO 18 I=1,NX
    READ (16,19) (C0(I,K),K=1,NC)
18 CONTINUE
  DO 48 I=1,NX
    DO 48 K=1,NC
      C(I,K) = C0(I,K)
      S(I,K) = C(I,K)*KD(K)
48 CONTINUE
  DO 49 K=1,NC
    MOLD(K) = 0.0D0
    DO 51 I=1,NX-2
      MOLD(K) = MOLD(K)+((C(I,K)+C(I+1,K))/2.0D0*N
+      + (S(I,K)+S(I+1,K))/2.0E0*BD)*DX*0.001D0
51 CONTINUE
49 CONTINUE
  ENDDIF

  DO 43 K=1,NC
    FOLD(K) = FNEW(K)
43 CONTINUE

c      Initialize boundary conditions

WRITE (7,*) ' '
WRITE (7,*) 'COMPOUND   MOLE X   MIX SOL.   RETDN   MASSo

```

```

+ (mg/cm^2)      MIX VP      KD'

      MOLES = 0.0D0
      DO 45 K=1,NC
        MOL(K) = M(K)/MW(K)/1000.0D0
        MOLES = MOL(K)+MOLES
45      CONTINUE
      DO 46 K=1,NC
        MX(K) = MOL(K)/MOLES
        MS(K) = SOL(K)*MX(K)
        VMP(K) = VP(K)*MX(K)
        WRITE (7,9) CMP(K),MX(K),MS(K),R(K),MO(K),VMP(K),KD(K)
        DELTA(K) = 0.0D0
46      CONTINUE

c      ***** Time loop *****

47      IF (TIME .GE. ET) GOTO 200

      DO 111 K=1,NC
        VNEW(K) = 0.0D0
111      CONTINUE

c      ***** SVE loop *****

      IF ((TIME .GE. IT) .AND. (TIME .LE. ST)) THEN
        SIN = 0.0D0
        STOT = 0.0D0
        DO 104 K=1,NC
          NN(K) = VMP(K)*VOL*1000.0D0/0.082057D0/(TMP+273.0D0)
          VM(K) = NN(K)*MW(K)*1000.0D0
          VMAX(K) = VM(K)*VA*1440.0D0*DT/100.0D0 !calc. max removal possible
          VNEW(K) = VMAX(K)*FRAC*RF
          IF (DELTA(K).LT.0.0D0) SIN = -DELTA(K)
          IF (VNEW(K) .GT. FNEW(K)*FRAC*DT*RF)
+          VNEW(K) = FNEW(K)*FRAC*DT*RF !calc. effective removal mass
          IF (SIN .GT. VNEW(K)) VNEW(K)=SIN !adjust if amt diffusing too large
          IF (VMAX(K).LT.VNEW(K)) VNEW(K)=VMAX(K) !adj if amt removed too large
104      CONTINUE

          MOLES = 0.0D0
          DO 106 K=1,NC !calc. new fracture solubility
            MOL(K) = 0.0D0
            FNEW(K) = FNEW(K)-VNEW(K)
            MOL(K) = FNEW(K)/MW(K)/1000.0D0
            MOLES = MOL(K)+MOLES
106      CONTINUE
          DO 110 K=1,NC
            MX(K) = MOL(K)/MOLES
            MS(K) = SOL(K)*MX(K)
            FOLD(K) = FNEW(K)
            VNEW(K) = VNEW(K)+(KD(K)+1)*(C(1,K)-MS(K))
+            *DX*N/2.0D0/1000.0D0 !readjust mass removed based on...
            C0(1,K) = MS(K) !conc change in t
he matrix
            C(1,K) = MS(K)
            STOT = STOT+VNEW(K)
110      CONTINUE
          ENDIF

c      ***** end of SVE loop *****

c      ***** Concentration and sorbed loop *****
c      Loop over points - avoid initial node (fracture)

c      Calculate aq. conc. and sorbed mass in matrix

50      CONTINUE
      DO 82 K=1,NC
        NUMIT = 0
55      AMAX = 0.0D0

```

```

NUMIT = NUMIT+1

DO 83 I=2,NX-1
  OLDVAL(I,K) = C(I,K)
  R1(K)=D(K)*DT/R(K)/DX/DX
  C(I,K) = R1(K)/(1.0D0+2.0D0*ALPHA*R1(K))*(ALPHA*(C(I+1,K)+
+   C(I-1,K))+C0(I,K)/R1(K)+(1.0D0-ALPHA)*(C0(I+1,K)
+   -2.0D0*C0(I,K)+C0(I-1,K)))
  S(I,K) = KD(K)*C(I,K) !mg/kg sorbed conc.
  ERR = DABS(C(I,K)-OLDVAL(I,K))
  IF (ERR .GT. AMAX) THEN
    AMAX = ERR
  ENDIF
83  CONTINUE
  C(NX,K) = C(NX-1,K) !set end bdry conditions (zero flux)
  S(NX,K) = S(NX-1,K)
  S(1,K) = KD(K)*C(1,K)
  IF (ALPHA .LT. 0.1) GOTO 60
  IF (AMAX .GT. TOL) GOTO 55
60  MNEW(K) = 0.0D0
  MAT(K) = 0.0D0
  DO 84 I=1,NX-2
    MAT(K) = MAT(K)+((C(I,K)+C(I+1,K))/2.0D0*N
+   +(S(I,K)+S(I+1,K))/2.0E0*BD)*DX*0.001D0
84  CONTINUE
  MNEW(K) = MAT(K)
  DELTA(K) = MNEW(K)-MOLD(K)
  IF (DELTA(K) .GT. FNEW(K)) THEN !readjust if change in...
    C(1,K) = C(1,K)*(FNEW(K)-DELTA(K))/FNEW(K)/2.0D0 !matrix too large
    IF (C(1,K) .LT. 1.0D-10) C(1,K) = 0.0D0
    DO 81 I=2,NX
      C(I,K) = C0(I,K)
81  CONTINUE
    GOTO 55
  ENDIF
82  CONTINUE

  INEG = 0
  DO 86 K=1,NC
    FNEW(K) = FOLD(K)-DELTA(K)
    IF (FNEW(K) .LT. 0.0D0) INEG = 1
86  CONTINUE

  IF (INEG.EQ.1) THEN !adjust if too much mass taken out of fracture
    WRITE (*,*) 'INEG'
    DO 87 K=1,NC
      DO 87 I=1,NX
        C(I,K) = C0(I,K)
87  CONTINUE
    DT = DT/10.0D0
    IF (DT .LT. 1.0D-5) THEN
      DO 88 K=1,NC
        IF (FNEW(K) .LT. 0.0D0) FNEW(K) = 0.0D0
88  CONTINUE
    ENDIF

    GOTO 50
  ENDIF

91  TIME = TIME+DT
  DT = DTO

c  Update - Initial conc. in matrix for next time step

  MOLES=0.0D0
  TMAS=0.0D0
  DO 85 K=1,NC
    MOL(K) = FNEW(K)/MW(K)/1000.0D0
    MOLES = MOL(K)+MOLES
    TMAS = TMAS+FNEW(K)
    DO 85 I=1,NX
      C0(I,K) = C(I,K)
85  CONTINUE

```

```

DO 89 K=1,NC
  MX(K) = MOL(K)/MOLES
  MS(K) = SOL(K)*MX(K)
  VMP(K) = VP(K)*MX(K)
  C0(1,K) = MS(K)
  C(1,K) = MS(K)
89  CONTINUE
  RF = TMAS/MINIT

```

c Calculate percent of mass remaining in fractures

```

DO 130 K=1,NC
  VOLD(K) = VOLD(K)+VNEW(K)
  MPER(K) = MNEW(K)/M0(K)*100.0D0
  FPER(K) = FNEW(K)/M0(K)*100.0D0
  VPER(K) = VOLD(K)/M0(K)*100.0D0
130 CONTINUE

  IF (DDAY .GT. 1.0D0) THEN
    WRITE (3,131) TIME, (FPER(K),K=1,NC)
    WRITE (10,131) TIME, (DELTA(K)/DT,K=1,NC)
    WRITE (11,131) TIME, (MPER(K),K=1,NC)
    WRITE (12,131) TIME, (VPER(K),K=1,NC)
    WRITE (13,131) TIME, TMAS, STOT
    WRITE (14,131) TIME, (MS(K),K=1,NC)
    WRITE (*,*) TIME

    DDAY = 0.0D0
    OPEN (15, FILE='restart.out')
    WRITE (15,*) TIME
    DO 135 K=1,NC
      WRITE (15,*) FNEW(K)
135  CONTINUE

    DO 136 I=1,NX
      WRITE (15,19) (C0(I,K),K=1,NC)
136  CONTINUE
    CLOSE (15)

    ELSE
      DDAY = DDAY+DT
    ENDIF

    DO 141 K=1,NC
      FOLD(K) = FNEW(K)
      MOLD(K) = MNEW(K)
141 CONTINUE

    GOTO 47

c **** end of time loop ****

c Format statements

4  FORMAT (A31,1X,F10.5)
5  FORMAT (A10,1X,F5.1,2X,F7.1,2X,F7.2,2X,F7.1,2X,F4.2,2X,F7.5)
6  FORMAT (A31,1X,F10.2)
7  FORMAT (A31,1X,I10)
8  FORMAT (F6.1,11(1X,F11.4))
9  FORMAT (A10,2X,F6.4,3X,F8.2,3X,F8.2,6X,F5.3,10X,F8.7,2X,F6.2)
11 FORMAT (A10,5X,F10.2)
19 FORMAT (15E12.4)
131 FORMAT (F6.1,15(2X,E10.5))
161 FORMAT (A10,1X,E7.3,2X,E10.3,2X,E9.4,2X,E9.3,2X,E6.4,
+ 2X,E9.7)
200 CONTINUE

  OPEN (15,FILE='restart.out')
  WRITE (15,*) TIME
  DO 210 K=1,NC
    WRITE (15,*) FNEW(K)

```

210 CONTINUE

DO 220 I=1,NX

WRITE (15,19) (CO(I,K),K=1,NC)

220 CONTINUE

CLOSE (2)

CLOSE (3)

CLOSE (7)

CLOSE (10)

CLOSE (11)

CLOSE (12)

CLOSE (13)

CLOSE (14)

CLOSE (15)

CLOSE (16)

STOP

END


```

1.0      'length of system (cm)'
300.     'time of solution (days)'
1.5      'bulk density (g/cm^3)'
0.011    'fraction of organic content'
0.37     'total porosity'
0.25     'tortuosity'
100      'number of nodes (# of spacial intervals +1)'
0.001    'time step'
301.     'day at which SVE starts (mass removed from fractures)'
360.     'day at which SVE stops (no mass removal from fractures)'
2.       'residual saturation (L/m^3)'
50       'number of fractures per m (50=2cm spacings)'
20.      'fracture width (microns)'
1.       'velocity of SVE air (m/min)'
15       'average ground temperature (C)'
15       'number of cmpds to solve for'
5        'cmpd number to print results for'
0.5      'maximum vapour to remove per day'
0        'read restart.in if IRST=1'
0.5      'ALPHA value for finite difference iteration'
0.001    'Tolerance value for Crank-Nickolson iteration'
pentane   72.1E0   40.0E0   2.48E0   2162.0E0   0.62E0   0.57000E0
MTBE      88.0E0  48000.0E0   1.50E0    66.4E0   0.75E0   0.26000E0
2-methylp 86.0E0   14.0E0   1.30E0   6242.0E0   0.65E0   0.21000E0
hexane    86.0E0   13.0E0   2.64E0   4404.0E0   0.66E0   0.16000E0
benzene   78.0E0  1780.0E0   1.76E0    348.6E0   0.88E0   0.10000E0
tce       131.0E0 1100.0E0   2.96E0    453.8E0   1.48E0   0.07500E0
isooctane 114.0E0    2.2E0   4.14E0  18306.0E0   0.69E0   0.05100E0
heptane   100.0E0    3.0E0   1.36E0   8993.0E0   0.68E0   0.04600E0
toluene    92.0E0   515.0E0   5.22E0    415.1E0   0.87E0   0.03500E0
ethylbenz 106.0E0   180.0E0   1.74E0   1464.0E0   0.87E0   0.00750E0
o-xylene  106.0E0   198.0E0   3.56E0    881.0E0   0.88E0   0.00800E0
p-xylene  106.0E0   162.0E0   3.52E0   1060.0E0   0.87E0   0.00860E0
m-xylene  106.0E0   175.0E0   3.48E0   1003.0E0   0.89E0   0.00660E0
1,2,4-TMB 120.0E0    57.0E0   2.70E0   2317.0E0   0.88E0   0.00190E0
naphth    128.0E0    33.0E0   2.28E0   3559.0E0   1.14E0   0.00014E0

```

INPUT DATA FOR 1-D FINITE DIFFERENCE SOLUTION

LENGTH OF SYSTEM (cm) : EL = 1.0
 TIME OF SOLUTION (days): ET = 300.0
 NUMBER OF NODES : NX = 100
 SPACIAL INCREMENT (cm) : DX = 1.0E-002
 TIME INCREMENT : DT = 1.0E-003
 DAY OF SVE INITIATION : IT = 301.0
 DAY OF SVE SHUTOFF : ST = 360.0
 NUMBER OF COMPOUNDS : NC = 15
 TORTUOSITY : TOR = 2.5E-001
 POROSITY : N = 3.7E-001
 RESIDUAL SAT. (L/m3): RS = 2.0
 NUMBER OF FRACTURES/M : NF = 50
 FRACTURE WIDTH (micron): FW = 20.0
 VEL. OF SVE AIR (m/min): VA = 1.0
 AVG. GROUND TEMP. (C) : TMP = 15.0
 ALPHA : ALPHA = 5.0E-01
 ITERATION TOLERANCE : TOL = 1.0E-003

COMPOUND	MW	SOLUB.	MASS	KOC	DEN.	VPRESS
pentane	72.1	40.0	2.48	2162.0	.62	.57000
MTBE	88.0	48000.0	1.50	66.4	.75	.26000
2-methylp	86.0	14.0	1.30	6242.0	.65	.21000
hexane	86.0	13.0	2.64	4404.0	.66	.16000
benzene	78.0	1780.0	1.76	348.6	.88	.10000
tce	131.0	1100.0	2.96	453.8	.48	.07500
isooctane	114.0	2.2	4.14	8306.0	.69	.05100
heptane	100.0	3.0	1.36	8993.0	.68	.04600
toluene	92.0	515.0	5.22	415.1	.87	.03500
ethylbenz	106.0	180.0	1.74	1464.0	.87	.00750
o-xylene	106.0	198.0	3.56	881.0	.88	.00800
p-xylene	106.0	162.0	3.52	1060.0	.87	.00860
m-xylene	106.0	175.0	3.48	1003.0	.89	.00660
1,2,4-TMB	120.0	57.0	2.70	2317.0	.88	.00190
naphth	128.0	33.0	2.28	3559.0	.14	.00014

COMPOUND	MOLE X	MIX SOL.	RETDN	MASSo (mg/cm^2)	MIX VP	KD
pentane	.0704	2.82	97.41	.076	.0401438	23.78
MTBE	.0422	2026.50	3.96	.055	.0109769	.73
2-methylp	.0324	.45	279.36	.042	.0068142	68.66
hexane	.0669	.87	197.39	.086	.0107054	48.44
benzene	.0656	116.72	16.55	.076	.0065575	3.83
tce	.0358	39.40	21.24	.070	.0026863	4.99
isooctane	.0828	.18	371.40	.141	.0042204	91.37
heptane	.0305	.09	402.04	.046	.0014049	98.92
toluene	.1630	83.95	19.51	.223	.0057057	4.57
ethylbenz	.0472	8.49	66.29	.074	.0003537	16.10
o-xylene	.0976	19.33	40.29	.154	.0007808	9.69
p-xylene	.0954	15.46	48.27	.151	.0008205	11.66
m-xylene	.0965	16.89	45.73	.152	.0006369	11.03
1,2,4-TMB	.0654	3.73	104.33	.117	.0001242	25.49
naphth	.0082	.27	159.71	.016	.0000012	39.15

VITA

The author was born on October 11, 1960, in Oakville, Ontario, Canada. In 1969 she and her family moved to New Westminster, British Columbia, Canada, where she finished high school in 1978. After two years of college she enrolled in the Landscape/Horticulture program at the British Columbia Institute of Technology (B.C.I.T.). Upon graduation in 1982 she worked for four years as a gardener at the University of British Columbia.

Realizing that gardening was not for her, she then enrolled in the Civil and Structural Engineering program at B.C.I.T. where she received a Diploma of Technology in 1988. Having found a discipline she enjoyed she then entered the Civil Engineering program at the University of Waterloo, Ontario. The co-op program at the University reinforced the choice of engineering and the desire to continue in school. Therefore, after earning her bachelors degree in 1992 she moved to Portland, Oregon to start her Ph.D. in Environmental Science and Engineering at the Oregon Graduate Institute (OGI). Her research involved travelling to Sarnia, Ontario to a hazardous waste landfill. This research included living in Petrolia, Ontario for a total of 12 months and shipping 1.5 tons of clay back to OGI for additional experiments. In November 1996 she defended her dissertation.

She is now enjoying a postdoc at OGI (and one last ski season in Oregon) before moving to either Europe or Canada and getting a "real" job.