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Aknowledgments

Abstract

Monitoring of contaminant vapors in the unsaturated zone is a convenient method for detecting volatile organic contaminants in the subsurface. This technique can be used for optimizing the placement of monitoring and recovery wells. The most common method uses a driveable ground probe (DGP) to extract vapor sample followed by direct injection into a portable gas chromatograph (GC). However, many regional offices of regulatory agencies do not have ready access to such equipment. This research evaluates an alternative method- the carbon adsorption method- in which vapor is withdrawn by the DGP but concentrated on a small activated carbon trap (150 mg). The carbon traps can be returned to a central laboratory for solvent extraction and GC analysis. This provides the advantage of a reduction in field equipment and convenience of in-lab analyses (multiple GC injections are possible) and also increased sensitivity because any volume of soil vapor may be collected. A simple DGP and carbon trap system was constructed and tested at a field site. Soil vapor concentrations of target compounds present in gasoline were conveniently mapped; the

concentrations ranging from 10,000 ug/ liter of soil vapor to
less than 10 ug/ L. These concentrations were also shown to
to decrease in the direction of the ground surface as
expected. Measurements of target compounds in soil indicated
that the soil vapor contributed a large fraction of the total
contaminant mass where a non aqueous phase layer (NAPL) had
been identified. As important is the rather uniform
contamination of soil outside the NAPL region. Finally, the
concentrations of target compounds in the soil vapor and
ground water could be related in a manner roughly described
by a simple equilibrium model, although exceptions were
noted.

Introduction

A majority of the existing underground gasoline storage
tanks were installed throughout the United States during the
1950's and 1960's. By some estimates these tanks have
reached maximum life (18 years) and are now or may soon be
leaking (14). Those currently leaking are estimated to
number 75,000 to 100,000 (22). Those expected to leak in the
next five years are estimated as 350,000 (41). Clearly,
leaking underground storage tanks (UST's) have been
identified as an important environmental concern.

The scope of technologies available for contaminant
detection and site assessment is beginning to be developed in
answer to this problem. Conventional investigative
techniques employed for the evaluation of subsurface
contamination have been primarily limited to the installation
of groundwater monitoring wells and soil borings. These
methods are, however, inherently expensive and time
consuming. Moreover, given limited information, the initial
locations of these monitoring points are seldomly sufficient
to assess site conditions. Sampling techniques and
analytical methods for monitoring pollutants in the

unsaturated, or vadose, zone offer an alternative. Petroleum distillates such as gasoline, which contain a multiplicity of volatile components, will partition significantly in the soil atmosphere of the unsaturated zone. By using sampling methods that collect soil vapors, the volatile fraction of these multi-component compounds can be detected. Soil vapor sampling affords a fast, economical avenue for detecting the presence of leaked or spilled volatile contaminants. Moreover, it can be used as a reconnaissance tool for location of monitoring/recovery wells and soil borings. This sampling method can also yield information regarding the areal extent of contamination in the unsaturated and capillary zones. Since contamination in these zones can serve as a source of future groundwater contamination, knowledge of the amount of this contamination is an important criterion for the evaluation of long-term contaminant risk.

The objective of this research was to evaluate a carbon sorption method for the measurement of gasoline vapors in the unsaturated zone. This particular method involves a driveable ground probe (DGP) to withdraw soil vapors for collection/concentration on an activated carbon adsorbent. The trapped vapors are then solvent desorbed and analyzed by gas chromatography. This method was first described by Thorburn et al. (44) and Colenutt and Davies (6) for the detection of organic vapors in landfills, but has not been thoroughly evaluated with regard to its applicability for the measurement of gasoline components. The method offers

improved sensitivity over the more common procedures that withdraw a discrete volume of vapor into a gas tight syringe for injection into a portable gas chromatograph. This feature is a result of the ability to concentrate contaminant vapors from a larger volume of the soil atmosphere. This volume-integrated sampling period also avoids the effects of localized soil heterogeneities and thus a more accurate measurement is obtained for delineating the areal extent of contamination.

Literature Review

2.1 Subsurface Contaminant Movement and Distribution

Immiscible organic liquids that have leaked from an UST percolate by gravitational forces through the unsaturated zone in primarily a vertical direction. The rate of contaminant migration is largely determined by its density and viscosity (31). The amount of liquid retained by the porous media is dependent upon the height above the free liquid surface; the final distribution of contamination becomes an equilibrium condition between gravity and capillary forces (22). Figure 1 illustrates a typical immiscible contaminant leak from a UST. Contaminants such as hydrocarbons (e.g. petroleum distillates), have specific gravities as low as 0.7, and evidence exists as to the "floating" of these and other such low density liquids on the water table (31). For large spills, a local depression of the ground water table occurs as a result of the immiscible fluid presssure (22). Bulk movement of organic contaminants in the capillary fringe is due to fluid pressure and
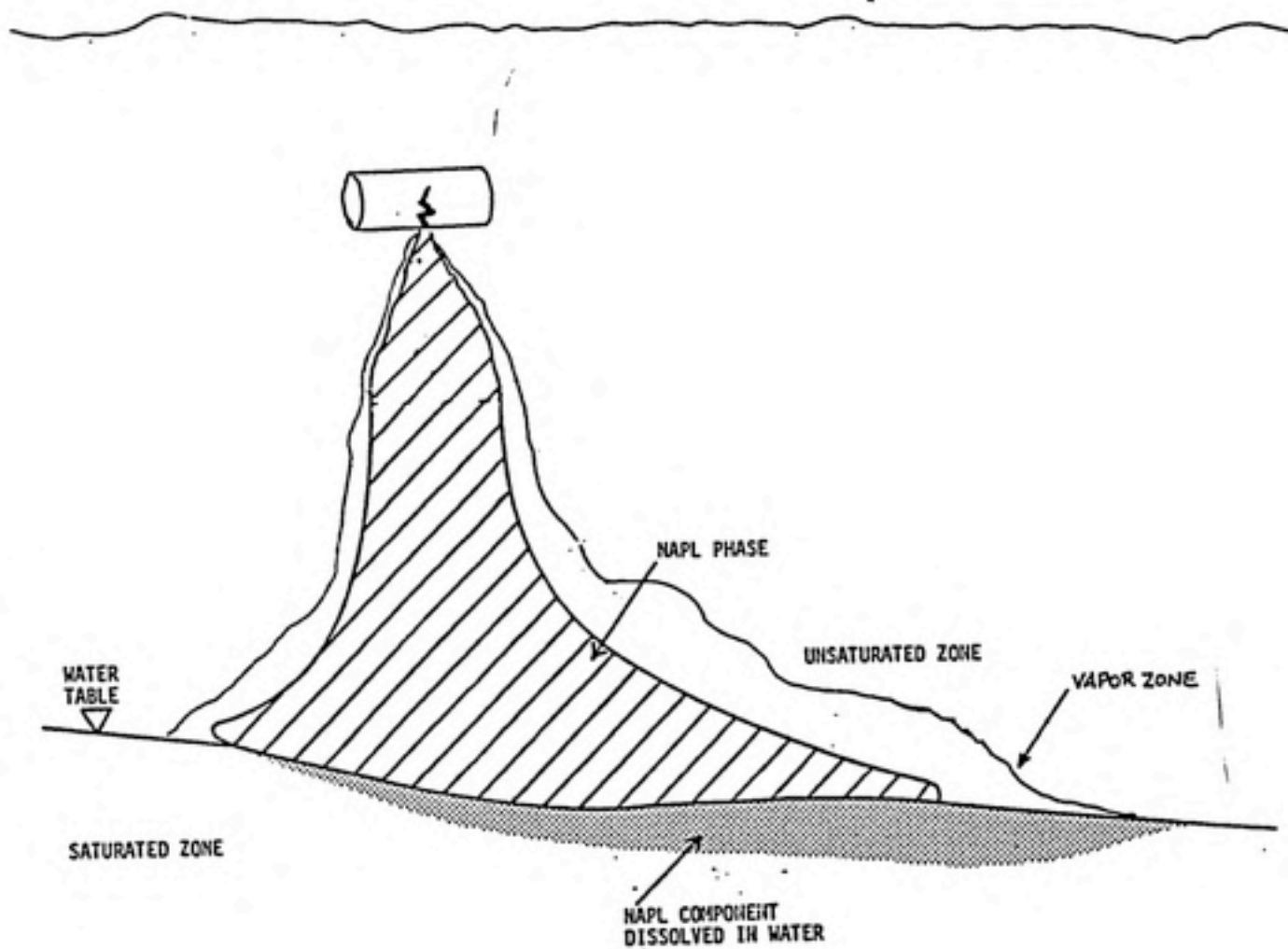
Figure 1. Typical Gasoline Distribution from a Leaking
Underground Storage Tank

capillary forces. This primarily down-gradient migration occurs as a discrete nonaqueous phase, although movement (partitioning) of some contaminant components into the adjacent groundwater may occur during this period.

2.1.1 Contaminant Sorptive Interactions

Sorption is a generic term that is used to describe the uptake of a compound (either vapor or solute) by soil, without reference to a specific mechanism. Goring and Haymaker indicate that organic compounds are sorbed onto soil particles by the following intermolecular forces: Van der Waals, London, hydrophobic repulsion, ion exchange, and hydrogen bonding (17). The mechanisms of sorption include both partitioning (Van der Waals, London, hydrophobic repulsion) and adsorption (ion exchange, hydrogen bonding).

In adsorption, the adsorbate only occupies surficial sites on the adsorbent media. Chiou distinguishes adsorption into two categories: physical adsorption - chiefly Van der Waals forces between adsorbate and adsorbent, and "chemisorption" - adsorption related to chemical bonding forces (5). In contrast, partitioning refers to the dissolution or volatilization of sorbate into a phase by solution forces (e.g. Van der Waals forces). The descriptive indicator of partitioning, the partitioning coefficient, is a function of the distribution of a compound between two phases. Considering the forces involved in both adsorption

and partitioning, it is obvious that the tenacity of any contaminant/soil interaction is very much dependent on the physical and chemical characteristics of both the soil and the organic compounds involved.

In designing a sampling and analytical method for determining subsurface fate and transport of organic contaminants, it is necessary to understand these processes of sorption. Numerous studies have been made concerning the sorption of hydrophobic organic compounds in soil and sediment systems. Many of these studies have shown the existence of a linear relationship between a compound's sorption coefficient and soil organic carbon and octanol-water partitioning coefficients (25, 17, 4). Karikoff et al. (25) researched hydrophobic contaminant interaction on sediments and reported that an estimate of sorptive partitioning could be made using the organic carbon content of the soil (K_{oc}) and the octanol/water coefficient (K_{ow}) of the analyte. The authors found the functional relationship between the organic carbon content of the soil, Koc, and the octanol-water partitioning coefficient of the organic solute, Kow, to fit the empirical formula:

$$\log K_{oc} = \log K_{ow} - 0.21$$

Additional research by the authors confirmed this relationship as a critical parameter to consider when estimating subsurface contaminant transport.

If, however, the soil has a very low organic carbon content (e.g., many sandy soils), alternative sorptive

mechanisms may predominate. Although the existing literature is sparse, some studies indicate that one such mechanism may be adsorption of the contaminant onto the mineral surface of the soil particles (18, 49, 21). Considering both of these mechanisms of contaminant attenuation, the soil media can probably best be described as a dual sorbent where the mineral content acts as a conventional adsorbent and the organic matter as a partitioning medium (5).

Moisture content has been shown to limit the sorptive capacity that soil has for certain organic compounds. Chiou et al. investigated the effects of soil humidity on the sorptive mechanism and capacity for six aromatic compounds (4). Chiou's research data indicates that an increase in water vapor (relative humidity) sharply reduces the sorption uptake of organic vapors on unsaturated soils. This reduction was attributed to adsorptive displacement by water on mineral surfaces. Since the relative humidity in the capillary fringe is higher than in the intermediate and soil zones, then the retentive capacity of this region would also be expectedly less. Thus, if the goal of vapor-phase sampling in the unsaturated zone is to elucidate the distribution relationship with the capillary and saturated zones, this phenomenon of moisture attenuation warrants consideration.

2.1.2 Contaminant Volatilization

As the contaminant mass is distributed in the unsaturated and capillary zones, there is a concurrent volatilization of organic compounds into the overlying pore spaces from this mass. The predominant mechanism for this contaminant distribution is gas-liquid partitioning. Understanding this mechanism of volatile contaminant distribution in unsaturated systems is necessary for valid interpretation of soil vapor measurements obtained from sampling in the unsaturated zone.

Partitioning from a liquid phase to a gaseous phase is termed volatilization. The degree of volatilization for a particular compound in a gas-liquid system can be described by Henry's Law:

$$c_g = K_h \, c_l$$

where c_g is compound concentration in the gas phase

c_l is compound concentration in the liquid phase

K_h is Henry's Law constant

Henry's Law states, that in a dilute solution, the partial pressure of a solute is proportional to its concentration. Typical Henry's Law constants as well as other physical characteristics for selected components of gasoline are presented in Table 1. The high vapor pressures for most of these components indicate that these components are volatile.

Table 1. Physical and Chemical Constants for Selected Gasoline Components

	Benzene	Toluene	m-Xylene	o-Xylene	p-Xylene
Molecular Weight (g/mol)	78.12	92.14	106.17	106.17	106.17
Specific Gravity	0.8765	0.8669	0.8642	0.8802	0.8611
Henry's Law Constant ($atm*m^3$/mol)	5.5E-3	6.68E-3	--	5.27E-3	--
Log Octanol-Water Partition Coefficient	1.86	2.46	3.20	2.95	--
Vapor Pressure (mm Hg @ 20°C)	76	22	6	5	6.5
Solubility in H_2O (mg/l @20°C)	1780	150	200	175	198

In the unsaturated zone, contaminants will partition between the soil matrix, soil solution, and soil atmosphere as illustrated in Figure 2. Gas/liquid/soil partitioning is a measure of the tendency of these compounds to move into a particular phase and is represented by the physio-chemical functions termed partitioning coefficients. Henry's Law constants are specific partitioning coefficients that can be used to describe a linear partitioning relationship of the contaminant between liquid and gaseous phases.

Volatile organics tend to have larger values of Henry's Law constants and thus contaminant partitioning favors the

LOCALIZED CONTAMINANT EQUILIBRIA
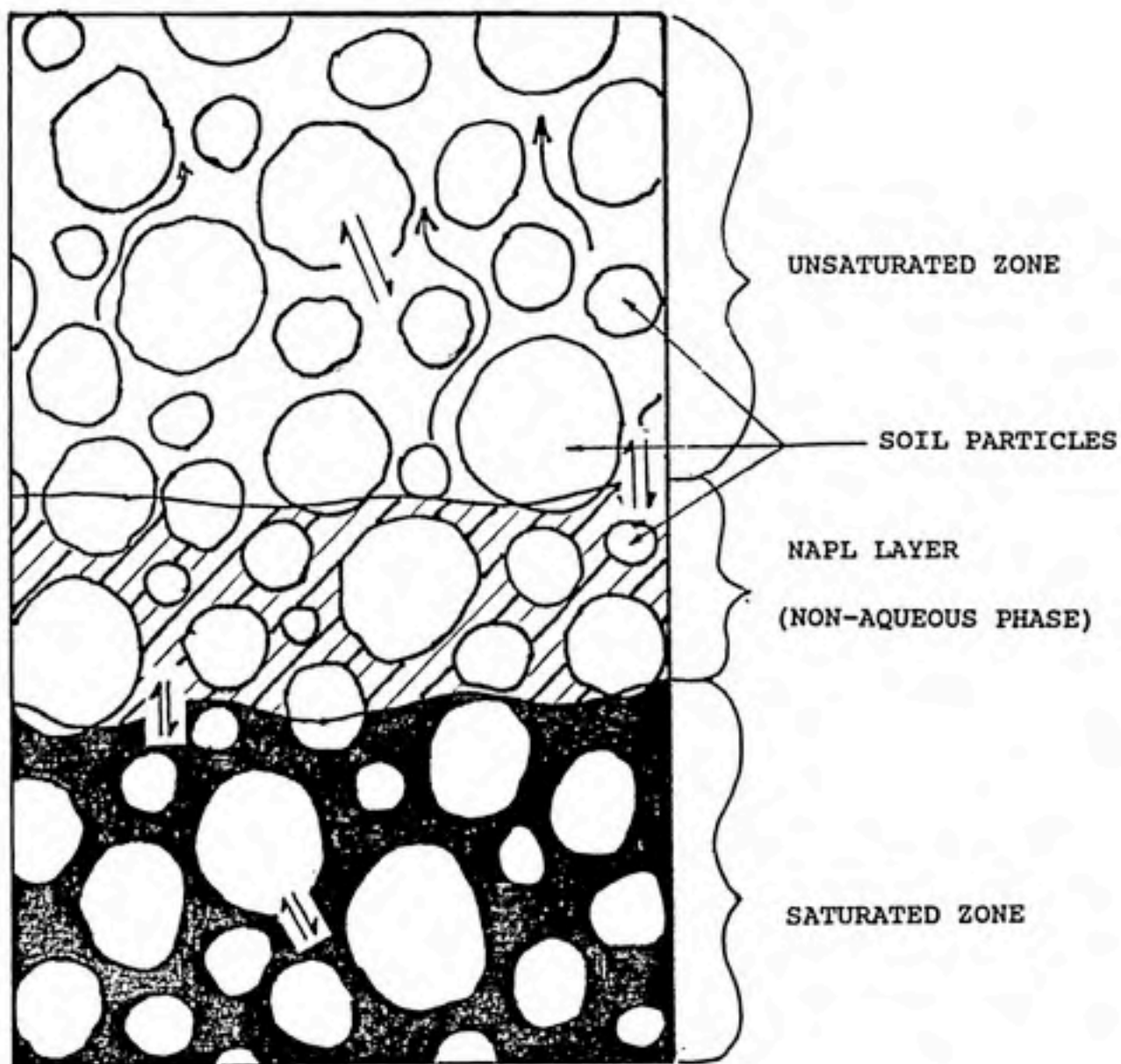
Figure 2. Localized Contaminant Equilibria (arrows indicate
partitioning between phases).

gaseous phase, assuming the two-phase system previously described. However, when a third phase (i.e. solid) is introduced into the system, partitioning values must be derived for describing movement into this third phase from the other two phases. This multi-phase problem is further complicated by the occurrence of biological and chemical transformations if simulation of field conditions is desired in a partitioning model. Considerable research attention has been devoted to this multi-phase problem (24, 21, 38, 36), yet it is clear that considerable work remains to be done. Nevertheless, gross estimates of total contaminant mass can be made if interphase equilibrium distributions and mass transfer rates are known or can be estimated using diffusion and partitioning relationships.

The chief mechanism for mass transfer of volatilized contaminants in the unsaturated zone is diffusion through interstitial pore spaces of the soil. Assuming one dimensional diffusion for simplicity, the concentration of contaminants in air as a function of time and distance, can be described by Fick's Second Law :

$$dC/dt = Dd^2C/ dz^z$$

where:

C is concentration of contaminant in air

D is the diffusion coefficient

z is the distance of travel

Jury et al. indicate that for intermediate molecular weight compounds an estimated diffusion coefficient for a volatile organic compound in air is 0.43 m^2/d (23). However, because of the existence of a solid phase, this function cannot be applied to describe subsurface diffusion. Nevertheless, Jury et al. derived a formula using Fick's Second Law for estimating diffusion coefficients for volatile pesticides in soil (24). This diffusion formula accounts for the decreased cross-sectional flow area and the increased length of travel due to increased tortuosity when compared to similar models for air diffusion :

$$D_G = Da^{10/3} / n^2$$

where D_G is the diffusion coefficient in soil gas

   D is the diffusion coefficient in air (e.g. 0.43 m^2/d)

   a is the volumetric air content of the soil

   n is total soil porosity

Experimental studies conducted by the authors indicate that the coefficient for gaseous diffusion in soils is several orders of magnitude greater than the liquid phase diffusion coefficient (24).

The incorporation of Fick's Law and Henry's Law into a mathematical model for describing volatile organic compound behavior in soil can be seen in models developed by Jury et al. (23) and Swallow and Gswend (42).

2.2 Unsaturated Zone Monitoring

Detection of a leaking UST event has primarily been
limited to the installation of groundwater monitoring wells
and soil borings. From these wells, a groundwater sample is
removed and analyzed by a procedure such as purge and trap
with subsequent GC/MS identification (46). The installation
of monitoring wells as a reconnaissance tool in order to
sample from the saturated zone can be both time consuming and
economically unfeasible. In response to these problems, an
increasing amount of research has been devoted to developing
faster and less expensive monitoring techniques. These newer
techniques have primarily focused on monitoring in the
unsaturated zone.

Two review articles by Everett et al. and Wilson discuss
several unsaturated zone sampling techniques, and thus serve
as good introductory reference sources (13, 47). The choice
of a suitable sampling methodology should be governed mainly
by the chemical nature (e.g., hydrophobicity, volatility) of
the suspected contaminant. Moreover, the type of sampling
matrix, required sampling volume, method simplicity and
reliability, and other additional sampling considerations are
important, as discussed by Everett et al. (13).

Unsaturated soil matrix sampling often is necessary for
monitoring hydrophobic, non-volatile contaminants such as
PCBs and halogenated pesticides that will not be present in

the soil solution or the soil atmosphere at appreciable concentrations. Obtaining samples from these latter phases would prove inferior to a soil matrix sampling technique such as soil boring. A tabulation of criteria for selection of suitable soil solids sampling equipment is presented in an American Petroleum Institute publication (10).

Contaminants that have an appreciable solubility in water are often present in the soil solution in unsaturated soils. These compounds can be sampled with an apparatus such as a vacuum lysimeter. Vacuum lysimetry removes available water under capillary forces from the unsaturated zone, which can subsequently be analyzed by conventional aqueous methods. Unfortunately, this method often results in an inadequate sample volume because of the inability of the vaccuum pump to withdraw water held under strong hygroscopic and capillary forces.

For situations where the contaminant is of a volatile nature, soil vapor-phase sampling in the unsaturated zone is a viable alternative. Previous investigations into soil vapor-phase sampling have produced many techniques potentially applicable to leaking UST detection and assessment. A state of the art review of shallow soil vapor-phase detection methods for hydrocarbons is compiled in an API publication (10). This literature search separates the unsaturated zone sampling techniques into five categories: (1) grab sampling of soil cores, (2) surface flux chambers, (3) downhole flux chambers, (4) acccumulator devices, and (5) ground probes.

These techniques are discussed below.

2.2.1 Grab Sampling

Grab sampling of soil cores involves obtaining a soil core by augering or hydraulically driving a tube into the suspected area of contamination. The removed cores are sealed, allowing a minimal volume of headspace. Subsequently, the remaining headspace gas is evacuated by the introduction of an inert carrier gas and the outflow is analyzed by gas chromatography. A comparison of three soil core analytical techniques by Slater et al. illustrates typical methodologies involved in grab sampling (40). Figure 3 illustrates the apparatus used by Slater et.al. to desorb contaminant vapors from soil cores. Unfortunately, spike and recovery experiments for the three organic analytes yielded highly variable recoveries ranging from 42.56% to 164.40%. Grab sampling of soil cores offers the advantages of being simple, inexpensive, and quick. The main disadvantage is that adsorbed contaminants, and those associated with bound water are measured in addition to contaminants present in the interstitial pore spaces of the soil; thus phase distributional information is lost. Adsorbed contaminants are desorbed from the soil using a continuous carrier gas flow to create a concentration gradient which favors the gaseous phase. In addition, analyte loss during the sample transfer steps, poor suitability to rocky soils and the time

FROM N₂ TANK

TO ATM

REGULATOR

CHARCOAL COLLECTING SERIES

CHARCOAL FILTER

SEPTUM

SEPTUM

SEALED GLASS SAMPLE JAR WITH TEFLON LINED LID

HEATING TAPE

N₂ INJECTION NEEDLE

SOIL TUBE (SEE DETAIL LEFT)

BRASS SAMPLING TUBE

SOIL SAMPLE
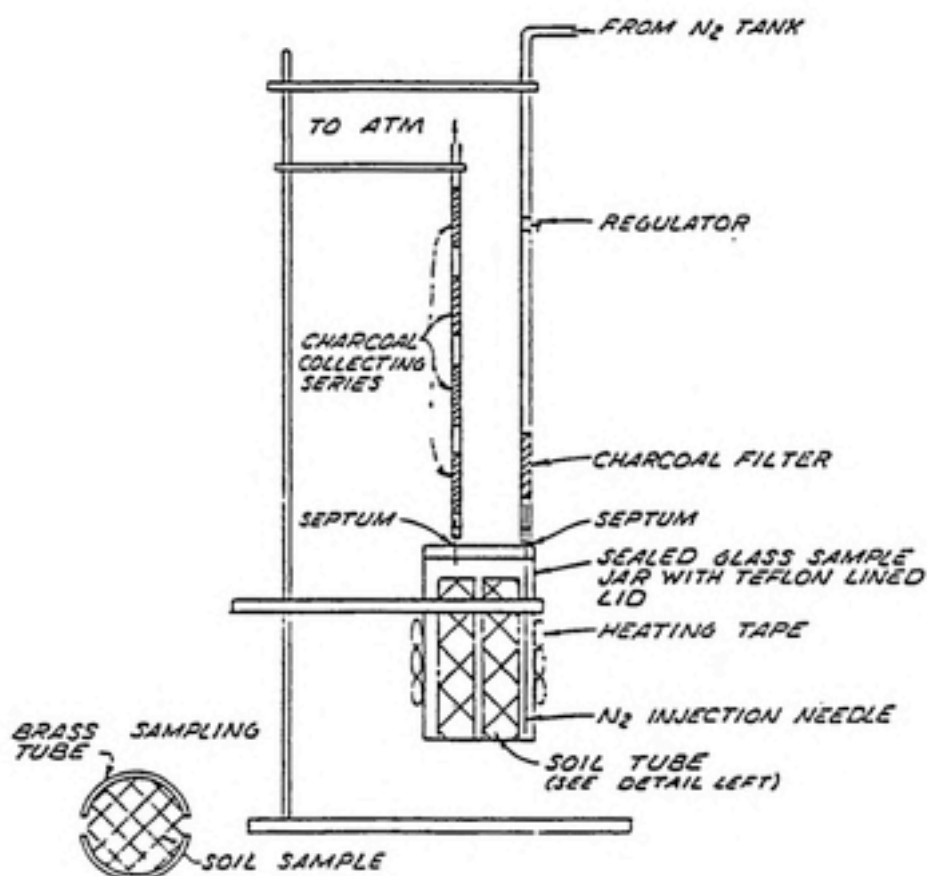
Figure 3.   Apparatus Used by Slater et.al. to Desorb
            Contaminant Vapors from Soil Cores

delay between sampling and analysis are other considerable
disadvantages.

2.2.2 Surface Flux Chambers

Surface flux chambers incorporate an enclosure device
over a defined area of ground surface. An example of a
surface flux chamber is illustrated in Figure 4. Gases
originating from the subsurface are sampled as they emit from
the surface. Carrier gas is directed into the chamber to
purge the vapor emmisions from the device. The exit gases
are then analyzed by GC. Previous research into surface
flux chambers is reviewed by Eklund and Schmidt (9)
Advantages of these designs are: undisturbed sampling of the
soil, a rapid sampling time, a suitability to all soil types,
and equipment simplicity. Principal disadvantages include:
dilution of the vapor sample with carrier gas and possible
hindrance of vapor transport by water saturated soil or
certain geologic heterogeneties.

2.2.2 Downhole Flux Chambers

Downhole flux chambers operate on the same principle as
surface flux chambers. However, downhole flux chambers are
modified to sample from the subsurface. Schmidt et al.
descibes such a chamber for sampling organic flux
measurements from hazardous waste sites (39) The device,
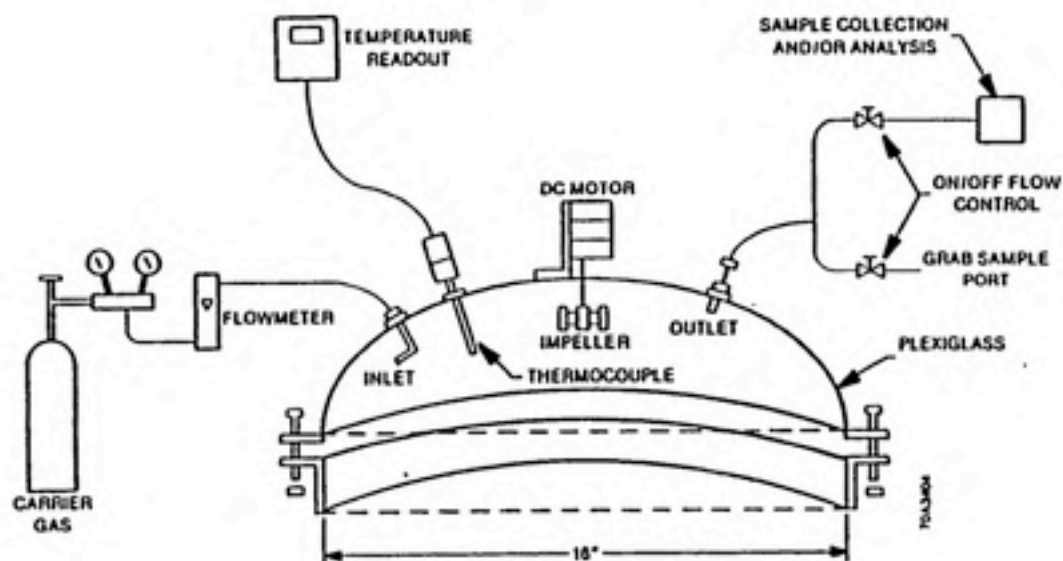
Figure 4. Surface Flux Chamber and Associated Equipment Used by Eklund et.al.
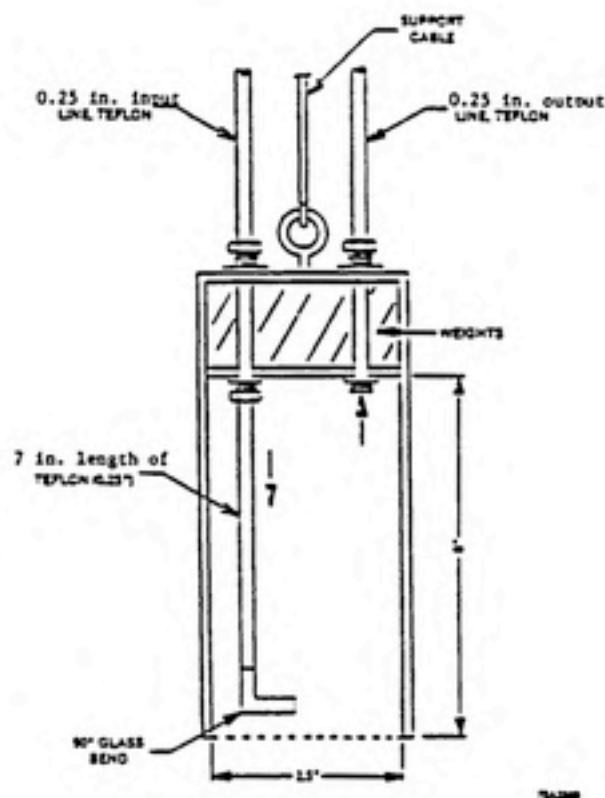
Figure 5. Downhole Isolation Flux Chamber Used by Schmidt et.al.

shown in Figure 5 is emplaced in the ground using a hollow-stem auger, although a hand auger could be utilized at shallower depths. The advantages and disadvantages of these techniques are similar to those for surface flux chambers; the difference being that sampling occurs in the subsurface where vapor concentrations are higher.

2.2.3 Accumulator Devices

Accumulator devices are used to collect soil vapors by a mechanism of static or dynamic concentration. A typical accumulator device is shown in Figure 6. The sensitivity of the method can be increased by extending the length of sampling time. False-negative results caused by temporary fluctuations in soil vapor concentrations are minimized by taking time integrated samples. Kerfoot et al. describe a passive soil vapor sampling technique which incorporates industrial hygiene samplers, suspended inside of metal cans (26). The method was successful when applied to detect chloroform in a contaminated aquifer. Voorhees et al. describe a surface static collection device made of an activated carbon coated ferromagnetic wire (46). The collectors are analysed by Curie point desorption mass spectroscopy. Application of this method to a tetrachloroethylene (PCE) contamination site proved successful in detecting subsurface vapors. Advantages of these techniques include: simplicity, relatively low-cost
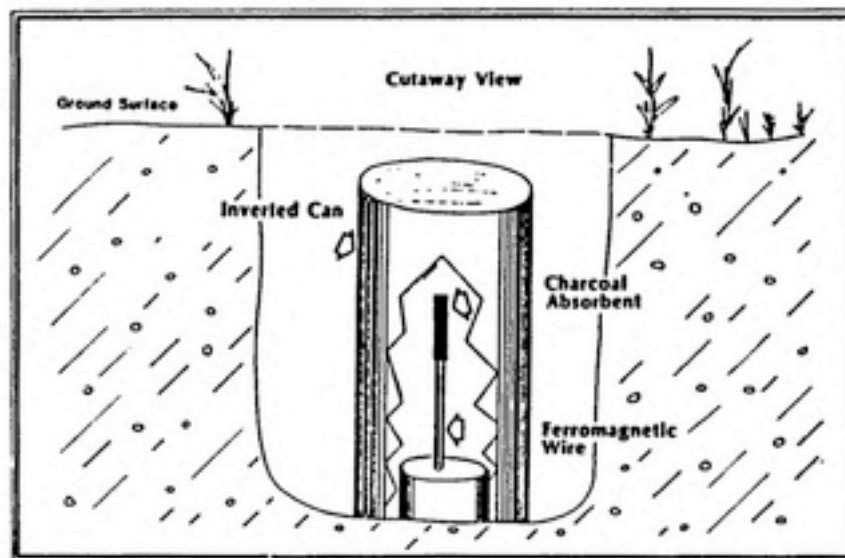
Figure 6. Accumulator Device Used by Vorhees et.al.

sampling and analysis, suitability to various site conditions (e.g. wet soils, rocky soils). Disadvantages include: long sampling times (days), potential interference from background concentrations, and undefined soil vapor sample volume.

2.2.4 Driveable Ground Probes

According to an API report (10), the preferred vapor sampling technique for groundwater and soil contamination investigations is the driveable ground probe technique (DGPT). This technique uses a hollow tube that has been hydraulically driven or hammered to a desired depth in the unsaturated zone above the suspected site of contamination. The tube has an opening(s) in the base to allow subsurface vapors to enter the tube from the surrounding soil media. Soil vapor-phase samples are pumped through the tube and exit from an opening at the upper end of the tube. This method alters the interstitial soil vapor composition adjacent to the tube less than passively emplaced ground probe methods, which require soil excavation (10).

Neglia and Favretto sampled subsurface vapors using ground probes for surface geochemical prospecting of petroleum and natural gas deposits (33). The researchers used a driveable ground probe which was driven to depths of 2-3 meters and then raised 20-30 cm to allow an opening for soil gas flow (see Figure 7a). A pump was used to withdraw vapors, which were collected in glass containers for in-lab

gas chromatographic analysis with flame ionization detection. Although the results were inconclusive, hydrocarbon vapors were detected and measured at the part per million level.

Soil probe vapor sampling techniques have also been developed for assessment of hazardous waste contaminations; some of these have been amended to leaking UST investigations (44, 6, 29). Sampling methane and other vapors from landfill sites, Thorburn et al. utilized a ground sampling probe which consisted of an aluminum tube 1.2-cm diameter x 0.8-cm bore x 2-m length with 0.3-cm holes along the side (44). Individual tubes were inserted with the aid of a pointed steel rod with a pounding block on one end (see Figure 7b). The rod was inserted in a tube and the two were hammered into the ground. Once in place the rod was withdrawn to leave an evacuated tube buried in the ground. The researchers used activated carbon as an adsorbent to concentrate the vapors from the subsurface. The trapped vapors were desorbed in CS_2 and analyzed in-lab by gas chromatography. Colenutt and Davies also utilized a sampling device similar to the device of Thorburn et al. in their study of organic vapors from landfill sites (6).

A ground-probe method developed by Tracer Research Corporation was successfully applied by Lapella and Thompson for the detection of trichloroethylene (TCE) in unsaturated zones that ranged in thickness from a few meters to over 30 meters (28)(see Figure 8). With their method, 10-milliliter samples are collected by inserting a gas-tight syringe into

(a)

(b)

Diameter
0.2 in.

|1 in|

2 in.

6.6 ft

6.7 ft

Sampling
Tube
(Aluminum)

Steel Rod
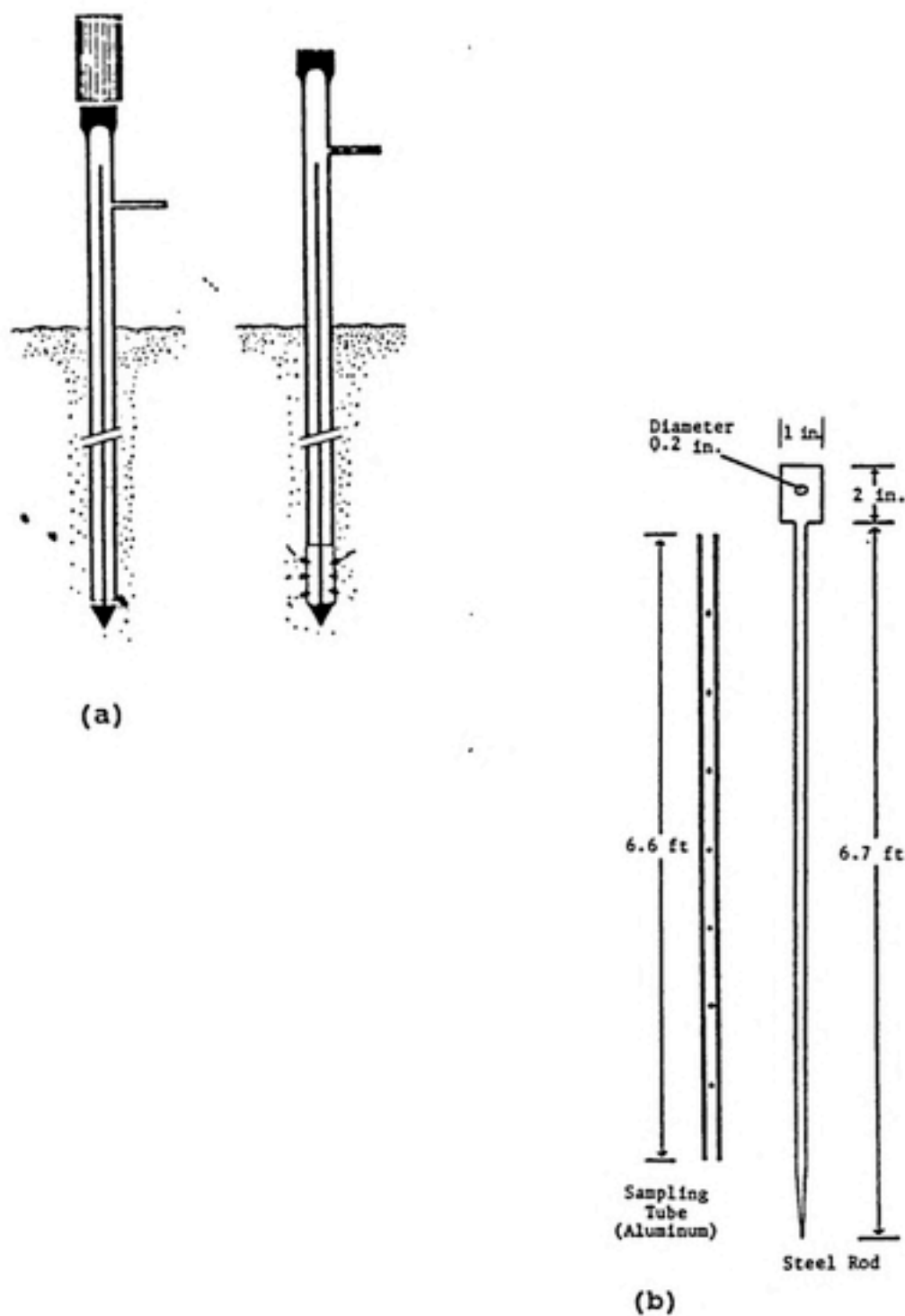
Figure 7. (a) Driveable Ground Probe used by Neglia and
Favretto and (b) Ground Probe Design Used
by Thorburn et.al.

1A   1B

10 CC GLASS SYRINGE

SILICONE RUBBER TUBE CONNECTION
TO VACUUM PUMP

SYRINGE
NEEDLE

ADAPTER FOR SAMPLING SOIL-GAS PROBE

HOSE
CLAMP

SILICONE RUBBER
TUBE

CLEAR TUBING SLEEVE CONNECTOR
(DISPOSABLE)

SOIL-GAS FLOW DURING SAMPLING

1/4 IN. TUBING

3/4 IN. GALVANIZED PIPE

5-7 FT.

DETACHABLE DRIVE POINT
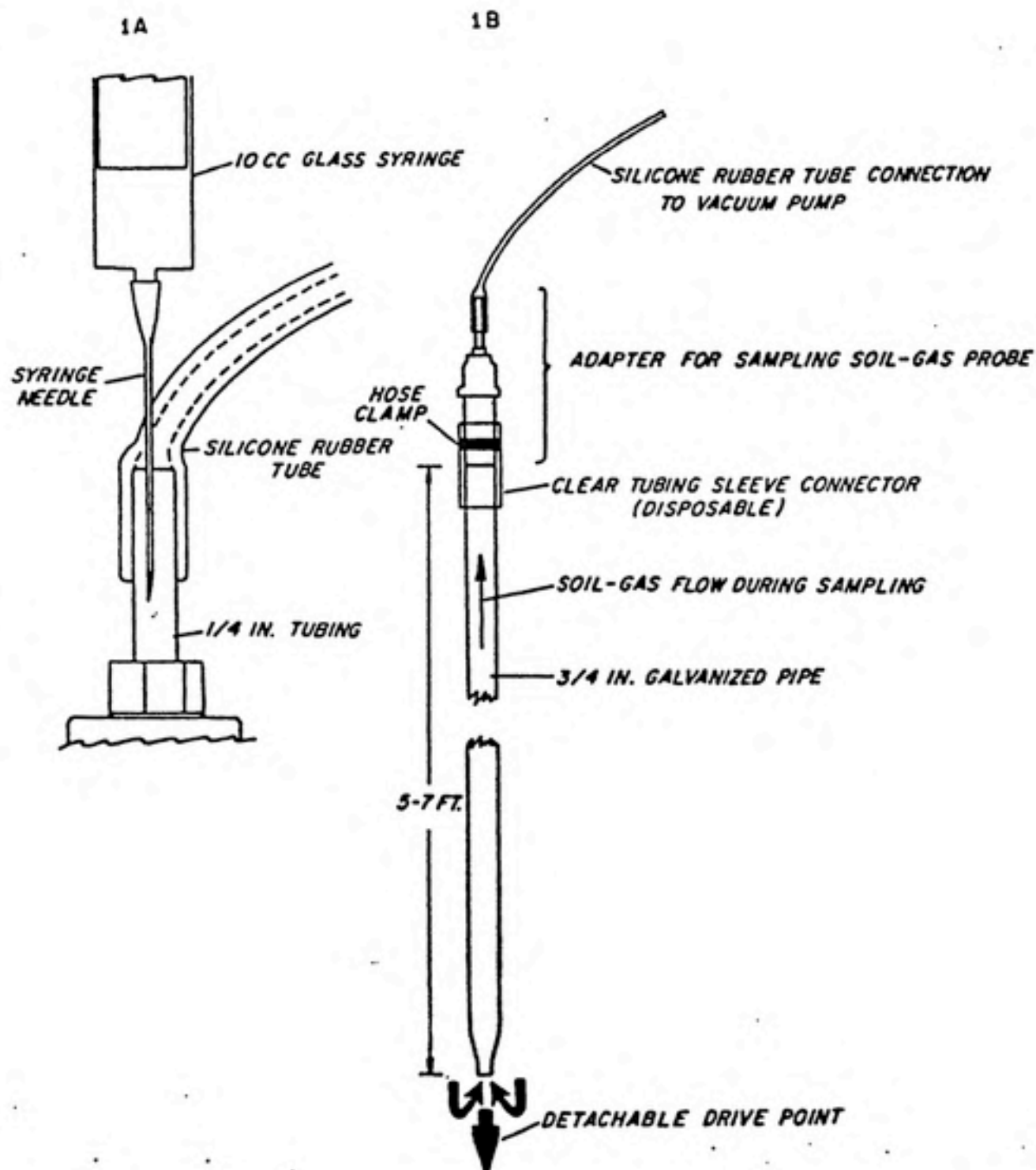
Figure 8.   Soil Vapor-phase Sampling Apparatus of Lapella and
            Thompson: (a) Close-up view of syringe sampling
            through an evacuation line, (b) vapor flow through
            the soil probe.

the evacuation line, which runs inside the length of the ground probe. The samples are immediately analyzed by injection into a gas chromatograph which is located in an equipped analytical field van. Although sensitivity is reported to be high (0.01 ppb for total hydrocarbons), it is limited by the syringe volume. Further inquiry into the this method indicated that 2-ml sub-samples are injected into the GC and that the sensitivity of the GC is 70-picograms for petroleum hydrocarbons (11). This level of sensitivity may not be sufficient for adequate peak separaion from the baseline. Evans and Thompson utilized the Tracer method to delineate the areal extent of two subsurface petroleum hydrocarbon spills (12). The researchers indicated that total hydrocarbon concentrations in the soil vapor-phase decreased rapidly outside of the edge of the groundwater contamination plume.

Radian Corporation reported that a ground probe sampling program, implemented at the site of a subsurface hydrocarbon spill, was able to detect contaminant plume advancement, but that only the lighter fraction of gasoline was detected near the surface (37).

2.3 Vapor Sample Acquisition

2.3.1 Preconcentration vs. Direct Injection

Procedures for the analysis of vapor samples taken from

a gaseous stream or evacuation vessel involves either a direct injection or a preconcentration step. Direct injection involves withdrawing an aliquot of the vapor-phase sample using a gas-tight syringe for injection into a portable gas chromatograph. The principal advantage of using this method is a minimal number of sample workup procedures. The use of gas-tight syringes has produced some satisfactory quantitative results if proper direct injection handling techniques are used (see Grob and Remhards (15)). More commonly, quantitative results via direct injection are less than satisfactory and should be used only as empirical or preliminary results (35). This is due in part to higher detection limits when compared with preconcentration methods, since analytes of moderate vapor pressure would be found in lower concentrations relative to compounds with higher vapor pressures. Since gasoline contains components with a wide spectrum of vapor pressures, this may preclude its use in this application.

Preconcentration involves the physical sorption of analytes on a solid adsorbent, which are subsequently desorbed. Desorption of analytes from the adsorbent is achieved by either solvent or thermal means. In a review on analyses of vapor phase compounds, Nunez indicates that activated carbon, carbonaceous materials, molecular sieves, and porous polymers offer the most promise as vapor adsorbents for preconcentration (35). Preconcentration is the most commonly used procedure for analyzing headspace

volatiles and has been extensively applied in air pollution studies. In order to properly implement this procedure, knowledge of analyte breakthrough volumes for each analyte is required. The breakthrough volume is dependent on: (1) type of adsorbent, (2) mass and specific surface area of the adsorbent, (3) chemical nature of the analytes(s) and (4) complexity of the sample. Therefore, prior to implementing this procedure into a soil vapor sampling methodology, breakthrough times for the analytes should be determined.

Solvent desorption is made possible by the propensity of the analyte to partition from the adsorbent into the eluent. The primary advantage of solvent desorption is the opportunity for multiple injections of the same eluate. Often when handling samples of unknown concentration, the possibility for saturation of the chromatographic column warrants the neccessity of a second injection in order to obtain an accurate analysis. This advantage is conditional upon a sufficient concentration of analyte in the extract. Solvent desorption would, however, be an unfavorable method when the solvent elution time approaches that of the absorbate(s). The resulting chromatogram from such a combination would show incomplete chromatographic resolution or coelution of the analyte with the solvent peak; quantitative and qualitative determinations would thus be hindered. A further disadvantage of solvent desorption is the possibility for artifact introduction from the solvent, glassware and storage vials (35).

Alternatively, thermal desorption involves heating the solid adsorbent and directing the desorbed analytes onto a GC column. Advantages of thermal desorption include: no coelution or chromatographic interference from a solvent peak and the elimination of a dilution factor since all of the adsorbate is desorbed. However, the hardware required for thermal desorption of analyte to chromatographic column is often expensive and complex. Since the entire sample is desorbed, only one chromatogram is obtained per sample. This may be a problem if the instrument settings (e.g. attenuation) are improper resulting in the loss or inaccuracy of the measurement. Furthermore, the storage of undesorbed samples for extended periods of time may jeopardize the retention and chemical integrity of the adsorbate(s).

2.3.2 Solid Adsorbents

The proper choice of solid adsorbent is essential for successful soil vapor sample aquisition and should be governed by the objectives of the analysis and the characteristics of the sample. Unfortunately, there is no ideal adsorbent that is applicable to all analytical situations. For soil gas, researchers have primarily utilized adsorbent compounds such as porous polymers (e.g.Tenex) (42), and granular activated carbon (GAC)(6). A discussion of the properties of these and other solid adsorbents when used for headspace analysis of organic

compounds is presented in an review article by Nunez et al. (35).

Because water actively competes for sorption sites on the solid adsorbent, water vapor adsorption can possibly hinder the adsorption of the analyte vapor. Sampling in relative humidities greater than 50% has been shown to decrease the adsorptive capacity of activated carbon (AC) (35). Porous polymers have less affinity for water than activated carbon. Nevertheless, Grob (1978) has shown AC "capable of adsorbing organic compounds from a stream of steam, a far more severe test than that likely to be encountered with (soil) gases from landfill sites" (6). Novotny et al. noted significant displacement effects when trapping volatiles on Tenax (35) which is a less significant problem with AC. This phenomenon was observed in complex samples containing analytes of different chemical potentials and present in different concentrations. Generally, the less volatile compounds were more effectively collected. Thus, the use of porous polymers as tools for monitoring volatiles may be precluded in such complex samples because of its demonstrated low capacity.

AC has been extensively used for air sampling due in part to its low cost and the problems with other adsorbents such as those previously described. The adsorbent has a much greater surface area and specific activity than porous polymers which lessens displacement and may often more than compensate for its tendency to adsorb water. These

properties also allow the use of small traps which can be desorbed with minimal solvent dilution. However, because of excessive surface activity, irreversible adsorption may lead to recovery problems with certain organic compounds on AC (35). Contrary to this observation, Colenutt and Davies report 94% - 100% recovery of 16 organic compounds from AC (6). Similarly, Colenutt and Thorburn obtained good recoveries for hydrocarbons in the part per million range (7). If thermal techniques are to be used for desorption, porous polymers adsorbents are preferential to AC adsorbents. This is because thermal desorption requires temperature so high that many compound may thermally decompose if adsorbed on AC (35).

Experimental Methodology

3.1 <u>Laboratory Investigations- Supporting Studies</u>

3.1.1 Analyte Recovery

A study was undertaken to determine the recovery efficiency of "select" components of gasoline from the type of carbon traps which were used in the soil vapor-phase sampling method. For this research, these "select" components are referred to as the "target compounds" and the motivation for their selection is discussed in section 3.5.2. This study was necessary because recovery of an adsorbate(s) from an adsorbent is often hindered by a strong sorptive reaction. Although usually more of a problem with polar organics, certain non-polar compounds are recovered poorly from activated carbon adsorbents (36).

The carbon traps consisted of a small glass tube sealed at both ends and containing 150 mg of carbon. A known quantity of target compounds (76 ug of each component) was injected with a 10-ul syringe directly into an open end of the carbon traps. Recovery controls were prepared by directly injecting the same known quantity into 2 ml of CS_2. The traps (front and back sections of carbon) were desorbed in 2 ml of CS_2 for an equilibration period of 24 hours. The samples and controls were then analyzed by gas chromatography

with the following temperature program: 35°C for 8 minutes, then temperature programmed to 145 ^{o}C at 4°C/minute.

3.1.2 Sorptive Capacity of the Carbon Trap

A laboratory experiment was devised to determine the sorptive breakthrough characteristics of the activated carbon traps which were used in the field vapor sampler. This experiment was necessary because sorption kinetics and/or equilibrium sorptive capacity can limit the practical application of such trap devices. If sorption kinetics are slow, some target compounds may escape adsorption. If the equilibrium sorptive capacity is too low, the adsorbent may saturate quickly and allow the target compounds to pass through the carbon trap- severely restricting the sampling time of the trap. In either case, the vapor-phase concentration calculated from the mass recovered from the trap may be lower than the actual concentration because not all of the target compound introduced to the trap is captured. The apparatus for studying breakthrough characteristics is shown in Figure 9.

A vapor-phase of either unleaded gasoline (100 ml) or individual components of gasoline (Burdick and Jackson Laboratories Inc.) was produced by purging with zero grade air, using a 500-ml glass, gas washing bottle. The vapor flow was directed into a second evacuation flask via a ball and socket connecting joint from which it passed through a
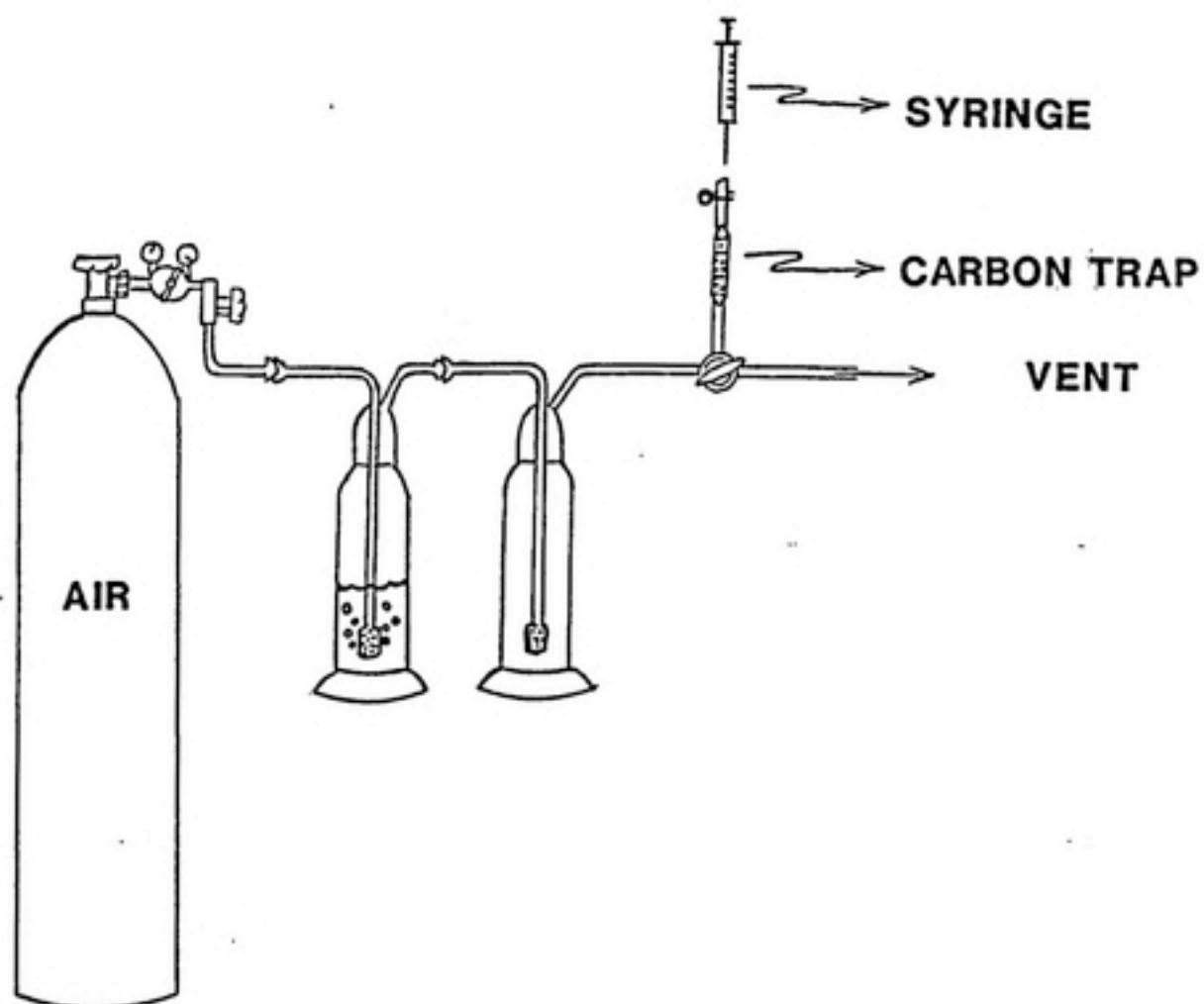
Figure 9. Apparatus Used for Sorptive Capacity Studies

glass T-valve either to the carbon trap or into a fume hood. This flow rate was adjusted to the rate of the field sampler. Samples of vapor leaving the carbon trap were taken at timed intervals using a gas-tight syringe (Precision Sampling Corporation) and immediately injected into a Varian 3700 gas chromatograph with a flame ionization detector. Splitless injection onto a capillary column was employed, with an initial temperature of $50^{\circ}C$, temperature programming $10^{\circ}C$ per minute, to a final temperature of $165^{\circ}C$. Compound identification was obtained through retention time indices.

3.1.3 Analyte Loss from Activated Carbon Trap

The purpose of this study was to determine if there was any loss of analytes from the time of field sampling until desorption of the trap. The utility of this study can be appreciated in a field situation, where the investigator may not return to the laboratory for several days or may have stored the field samples in a freezer for later analysis.

Five of the "target" compounds were selected for evaluation of loss over time. A spiking solution of the standards was prepared in CS_2 from solutions of the individual compounds with 1-chlorodecane as an internal standard. Carbon traps were then injected with 10 ul of spiking solution so that when desorbed in 1 ml of CS_2, the final concentration of the eluate was 17.5 ppm (12.5 ppm for octane). Duplicate spiked traps were then capped and stored

either at -13°C or 27°C. Four traps (two at -13°C and two at 27°C) were desorbed at 0, 1, 3.5, 6.5, 10 and 15 days. GC-FID areal responses were quantitatively compared to a prepared standard curve.

3.2 Soil Vapor-Phase Sampling Method

Figure 10 illustates the design of the soil vapor-phase sampling probe system. The 12-foot driveable ground probe is constructed of 0.675-inch O.D., 0.475-inch I.D., hollow, 304 grade stainless-steel tubing. A 0.375-inch diameter internal rod, fitted with a hardened-steel driving point, is screwed in place during probe insertion. The probe system is fitted with a hammer block to facilitate probe insertion. Stainless steel Swagelock[R] fittings are used to connect 0.125-inch stainless-steel tubing between the probe and the vacuum pump. The pump (Thomas Industries model 115) is fitted with teflon-faced diaphragms to minimize adsorption of contaminant vapors. The outflow of the pump is directed through a 150 milligram (100 mg plus 50 mg backup) coconut-shell activated-carbon trap (Environmental Compliance Corporation). The flow rate is regulated with a rotameter (Dwyer Corporation) which is positioned after the carbon trap.

Soil vapor-phase samples are collected by driving the probe into the ground and extracting vapors from the tube via the vacuum pump. Prior to positioning the probe, a 1.12-inch pilot hole is augered to a depth 0.5 to 1-foot above the

①

Ground Surface

② Hammer Block

③ Inner Rod

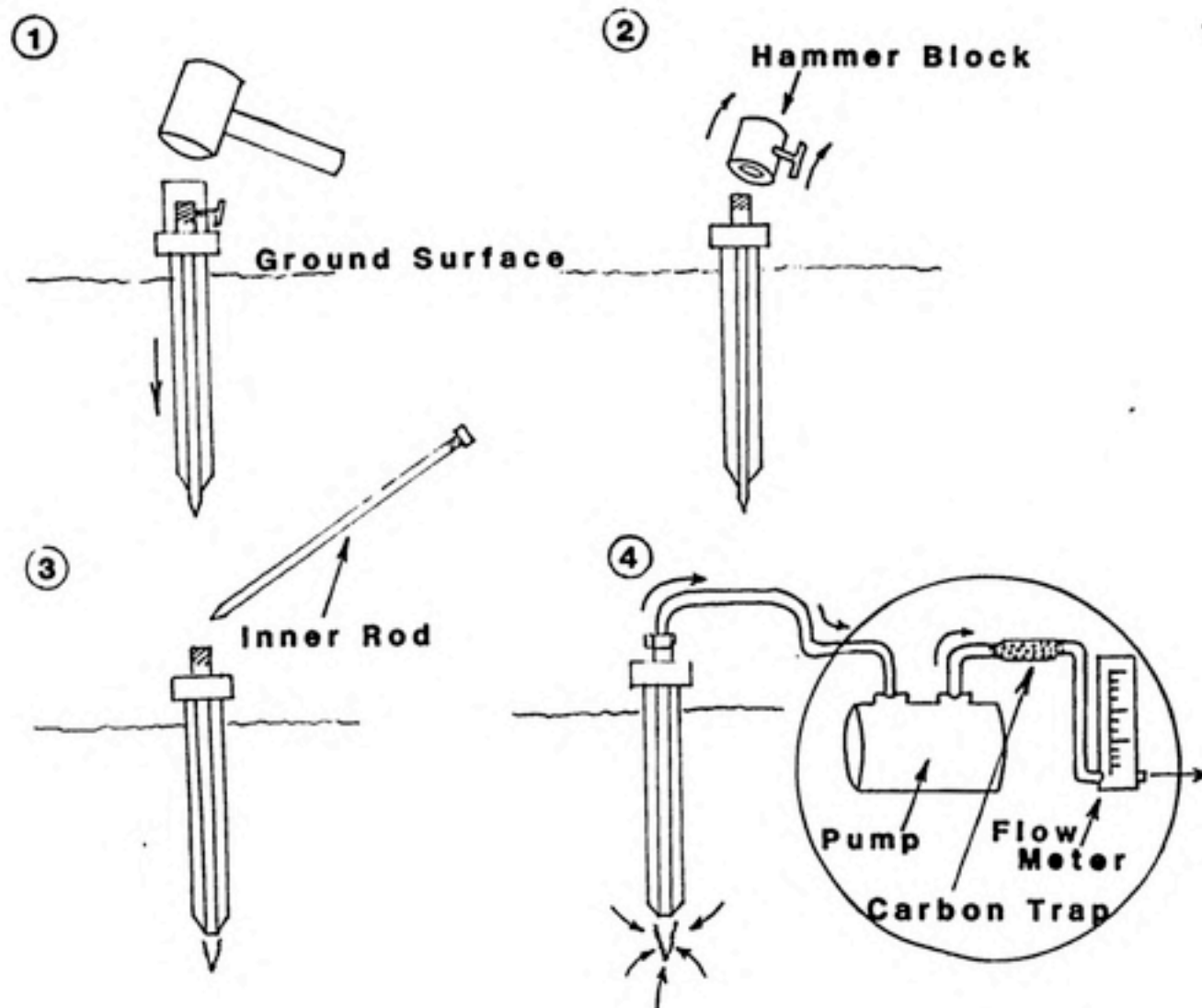**④** Pump Flow Meter Carbon Trap

Figure 10. Soil Vapor Sampling System

sampling depth. The inner driving rod is then removed to reveal a 1-cm opening at the driving end of the probe; it is from this opening that vapors are withdrawn. This design eliminates the possibility of clogging the tube opening with soil and since all parts of the probe are removed from the ground no field equipment is left behind after sampling is completed.

3.3 Field Site Description

An extensive field site investigation was conducted at a gasoline station on the Marine Corps Base - Camp Lejeune, in Jacksonville, North Carolina. A chronology of the gasoline contamination and cleanup effort is given in Table 2. Although this account may not be complete, it is the best that can be construed from the limited information available.

Soil drilling logs, taken during monitoring and recovery well installation, reveal 8-10 feet of yellow-brown clay with a moderate silt content, underlain by 10-35 feet of medium to fine grained, well sorted sands. The thickness of the unsaturated zone is approximately 24-28 feet. Groundwater flow within the immediate vicinity of the site is currently governed by the cone of depression that is created by the recovery pump. Under quiescent conditions, the direction of flow was in the east direction. This slight gradient was indicated from data collected prior to the recovery period, and during times of pump shutdown.

Table 2. Camp Lejeune Contamination and Cleanup Event Chronology

Period	Event
• Late 1940's–1950's	Gas station built and underground gasoline tanks installed.
• 1950's–Present	Small leaks of product may occur.
• 21 September 1985	4,400 gallon loss of premium unleaded gasoline occurs.
• Late September 1985	Leaking tank taken out of service.
• January 1986	Recovery system and 11 monitoring wells installed.
• 17 January 1986	Recovery system begins operation. Monitoring of water levels and product thickness in monitoring wells begins.
• July 1986	Testing of recovered product reveals the presence of leaded product.
• 23 July 1986	3,000 gallon leaded gasoline tank confirmed to be leaking and is taken out of service.
• September 1986–Present	Recovery system continues to operate but with numerous periods of system shutdown due to equipment failures.
• 10 December 1986	Remaining two underground gasoline tanks (unleaded) tested for leaks. No leaks are found in tanks, but delivery pipes from tanks to gasoline dispensers are found to be leaking.
• December 1986–Present	Gas station closed to customers for indefinite period.

Although artificial conditions (i.e. cone of depression) created by the concurrent recovery effort should have some effect on the distribution of contaminant vapors, this site was chosen because of its accessibility.

3.4 Field Sampling Procedures

At the Camp Lejeune site, vapor-phase samples were taken at depths between 7-11 feet. The variability of sampling depths is in response to a lack of specific information about the lithology at each sampling point, prior to the actual sampling. The depths of the sampling points were varied in an attempt to sample from an approximately consistent pedologic formation, a white sandy layer directly underneath the upper clay layer. A site map indicating the locations of these sampling points is presented in Figure 11.

Subsurface vapors were pumped for 5 to 30 minutes through a carbon trap to collect volatile contaminant compounds. Most often, 10- and 30-minute sampling time periods were taken from each hole, except in close proximity to the suspected source where 5-minute samples were taken. The vapor-phase sample volumes that were drawn through the traps measured between 235 and 1410 cubic centimeters. The adsorption traps were then capped for return to the laboratory. Precautions were taken to eliminate cross-contamination of samples by rinsing the sampling probe with acetone between sampling locations and allowing it to dry.
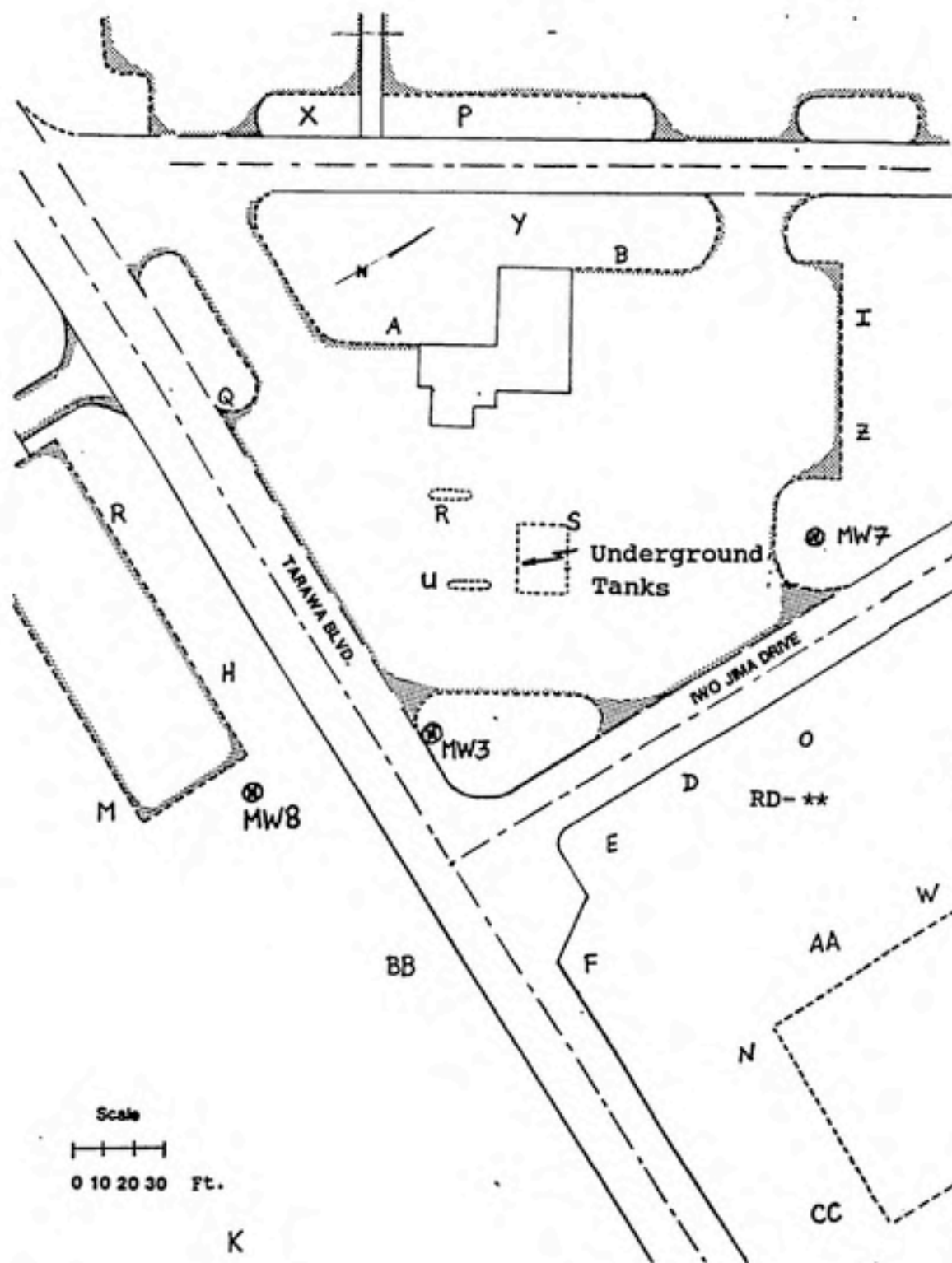
Figure 11. Site Map Indicating the Locations of Sampling
Points

The pumping system was then purged with ambient air for 2-minutes to remove any residual contamination.

3.4.1 Changes in Vapor-Phase Concentrations Over Time

Sample aquisition at the Camp Lejeune site covered a four month period. During this time, the contaminant recovery operation may have significantly affected the gasoline vapor concentrations. Therefore, a check was needed in order to ascertain if temporal variations caused by this and other factors such as biodegradation and volatilization loss had any affect on vapor-phase concentrations. This required taking replicate samples from three specific locations, at the beginning and end of the sampling period. These samples were taken at the same depths and within 2 feet of their original sites. Analytical procedures for these samples is described under Methods 3.5.1.

3.4.2 Effect of Depth on Vapor-Phase Concentration

The effect of sampling depth on measured concentration should be in accordance with the laws of diffusive flux. The closer samples are taken to the source, the higher the expected concentration of contaminant. Although the sensitivity of the method is increased by sampling deeper, more time and expense is required in order to take these samples. Therefore, determining a reasonable balance between

sampling costs and sensitivity requirements must be made. The variance in concentration measurements resulting from sampling within a window of depths can also be evaluated as accountable error if this type of study is made prior to the actual sampling regime.

For this study, vapor samples were obtained from three different depths (6.5, 9.5, 11.5-feet) from the sandy layer. Consecutive replicate samples could not be taken from the same sampling point because re-equilibration of contaminant vapors would not occur immediately following devaporization (sampling). Therefore, samples were taken at four points located in an approximately six-foot circular area (designated collectively as location RD** on Figure 11); this distance also eliminated transverse devaporization between sample locations, while obtaining as close to a replicate sample as possible. The sampling and analytical procedures were identical to those used for the other field vapor samples.

3.4.3 Multi-Phase Contaminant Distribution

Soil and water samples were taken in addition to the vapor sampling at the Camp Lejeune site. The motivation for obtaining samples from these latter two phases was to observe whether a relationship could be established between contaminant concentrations in each phase.

3.4.3a Ground Water Sampling

Samples of groundwater were taken from monitoring wells in close proximity to corresponding soil and vapor-phase sampling points. A bailer was used to take water samples from monitoring wells. In order to prevent cross contamination of wells, the bailer was rinsed thoroughly with acetone and distilled water, respectively, and dryed between wells. Samples were transferred to 40-ml glass vials, topped off with pentane to eliminate headspace, and capped with teflon-faced septa. The samples were then returned to the laboratory and stored at $6^{\circ}C$.

3.4.3b Soil Sampling

Soil samples were also taken at points adjacent to monitoring well and vapor sampling points. A hand auger with a coring attachment was used to remove intact cores from the desired depths. Soil cores were retreived at depths as close as possible to corresponding vapor-phase sampling depths. Upon withdrawl from the borehole, samples were immediately transferred into 40-ml glass vials, covered with n-pentane (pesticide grade), and sealed with teflon-faced septa screw caps. Samples were returned to the laboratory and stored at $-13^{\circ}C$ until analysis.

3.5 Analytical Methodology

3.5.1 GAC Extraction/Analysis Procedure

The field samples were processed in the laboratory by desorbing the activated carbon into 1 ml of carbon disulfide (CS_2). Two internal standards (IS), 1-chlorooctane and 1-chlorodecane, were added at 35-ppb to the CS_2 stock before the solvent aliquots were delivered to the desorption vials. These ISs were added in order to account for differences in sample injection volumes so that samples could be corrected to a mean value of IS area response. The solvent extracts from the carbon traps were analyzed using a Varian 3700 high-resolution gas chromatograph with a flame-ionization detector (FID). Separation was achieved on a Supelco 30-meter SPB-1 fused-silica capillary column with splitless injection and temperature programming: the initial temperature of $35^{\circ}C$ was held for 8 minutes, and then programmed to a final temperature of $200^{\circ}C$ at a rate of $6^{\circ}C$ per minute. The injector temperature was set at $285^{\circ}C$; the flame ionization detector temperature was set at $300^{\circ}C$; and the helium carrier gas flow rate at 1.7 milliliters per minute. If hydrocarbons were not detected by the GC analyses, the samples were evaporated under a gentle stream of nitrogen to 0.1-ml. These concentrated samples were then rerun under the same conditions.

Gas chromatography/mass spectrometry (GC/MS) compound identification was performed on a Hewlett-Packard 5895

quadrupole mass spectrometer with a Hewlett-Packard data system. Electron ionization (EI) was employed (70-electron volt source potential) with a scan range of 40 to 400 atomic mass units. The same temperature program used in the gas chromatographic analyses was also used for the GC/MS runs. Library spectral matching was employed for identification purposes and included 25 major peaks after 6 minutes, and before 18 minutes, of the temperature program.

3.5.2 Target Compounds

If the quantitative analysis was only for one compound, sample measurements could easily be extrapolated to the define a mass of contaminant per volume of soil gas. However, gasoline is a mixture of many different component compounds. A representative group of compounds must be selected in order to gain some quantitative description of the extent of contamination. These "target compounds" were chosen from among those selectively identified by GC/MS library spectral matching and determined by gas chromatography to be present in high concentrations in vapor samples; additionally, they must sorb well onto activated carbon. Unfortunately, the percentage of individual components of gasoline vary markedly from commercial brand to brand and from season to season. Thus a calculation of the original total mass of gasoline based on these percentages is impossible. While some quantitative information is lost, the

selection of target compounds does provide important "markers" for describing the extent of subsurface contamination.

3.5.3 Ground Water Extraction/Analysis Procedure

Samples of water from the monitoring wells were stored at $6^{o}C$ prior to extraction. Each vial of water was transferred to a 125-ml separatory funnel in addition to 40-ml aliquots of pentane used as vial rinsates. These water/solvent samples were shaken for 2 minutes and allowed to separate for 10 minutes. After the separation period, the water (which has a higher density than pentane) was eluted from the funnel back into the vial. The pentane extract was added to 500-ml Kurderna-Danish (KD) concentrator apparatus. The water eluates were returned to the separatory funnels and the procedure was repeated two additional times. The samples were concentrated in the KD apparatus to approximately 5 ml. Further concentration to 2 ml was performed under a gentle stream of nitrogen gas. Gas chromatographic analysis of the concentrates employed the same capillary column, instrument conditions and temperature program as those used in the soil vapor analyses.

3.5.4 Soil Extraction/Analysis Procedure

The soil-pentane mixtures were transferred with a

spatula and 30-ml of acetone to 25-ml glass centrifuge bottles; 100-ml aliquots of pentane were added to the mixtures. In order to remove soil moisture, 30-g of sodium sulfate (Na_2SO_4) was mixed into the soil for approximately 2 minutes with a teflon stirring bar.

The soil-solvent mixtures were then capped and placed in a water bath with a sonicator probe (Tekmar model TM-500) submerged 3.8 cm below the water surface. Sonication was applied at 90% pulsed duty and full power output (500 watts) for 10-minutes. Each sample was centrifuged at 2300 rpm for 10-minutes; the supernatant was then added to a KD apparatus for concentration to approximately 5 ml. A gentle stream of nitrogen gas was used for final concentration to 3-ml. Chromatographic analysis was the same as used in the water analyses.

Results and Discussion

4.1 Laboratory Analyses

4.1.1 Sorptive Capacity of Carbon Trap

The results from the sorptive capacity experiment gave
an indicaton of the maximum allowable sampling time to assure
complete analyte recovery of the target compounds. Figure 12
shows the breakthrough of toluene and xylenes (o-,m- and p-)
when introduced to the carbon trap as single vaporized
components. Figure 13 shows the breakthrough of these same
components when present in a gasoline mixture. Figures 12 and
13 can be used to understand the effects of competitive
adsorption and more importantly, the proper selection of
target compounds and sampling durations. If the chosen
components to be monitored break through before the end of
the sampling period, the sorptive capacity of the trap has
been exceeded and subsequent analysis of the extract from the
trap will underestimate the concentration of the contaminant.

The results presented in Figures 12 and 13 are not
directly comparable for two reasons. First, the
chromatographic peak originally identified by retention time
indices as toluene was found to be a coelution product of
toluene and 2,3,3- trimethylpentane. Secondly, because the

Toluene Breakthrough
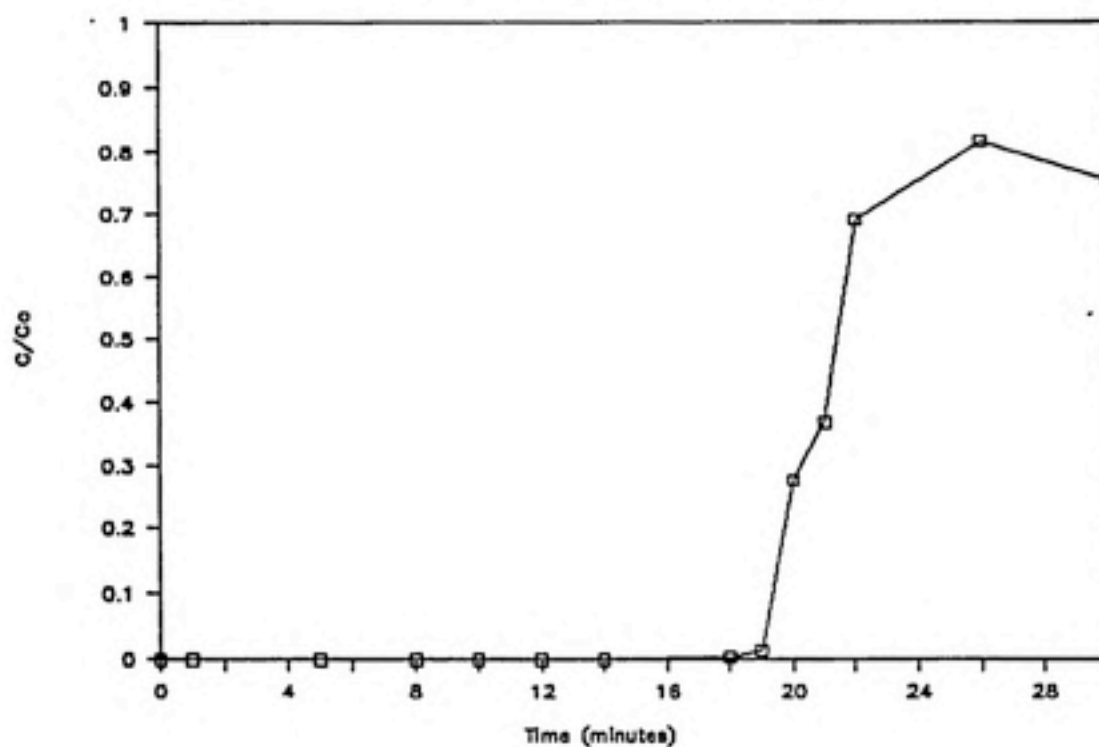
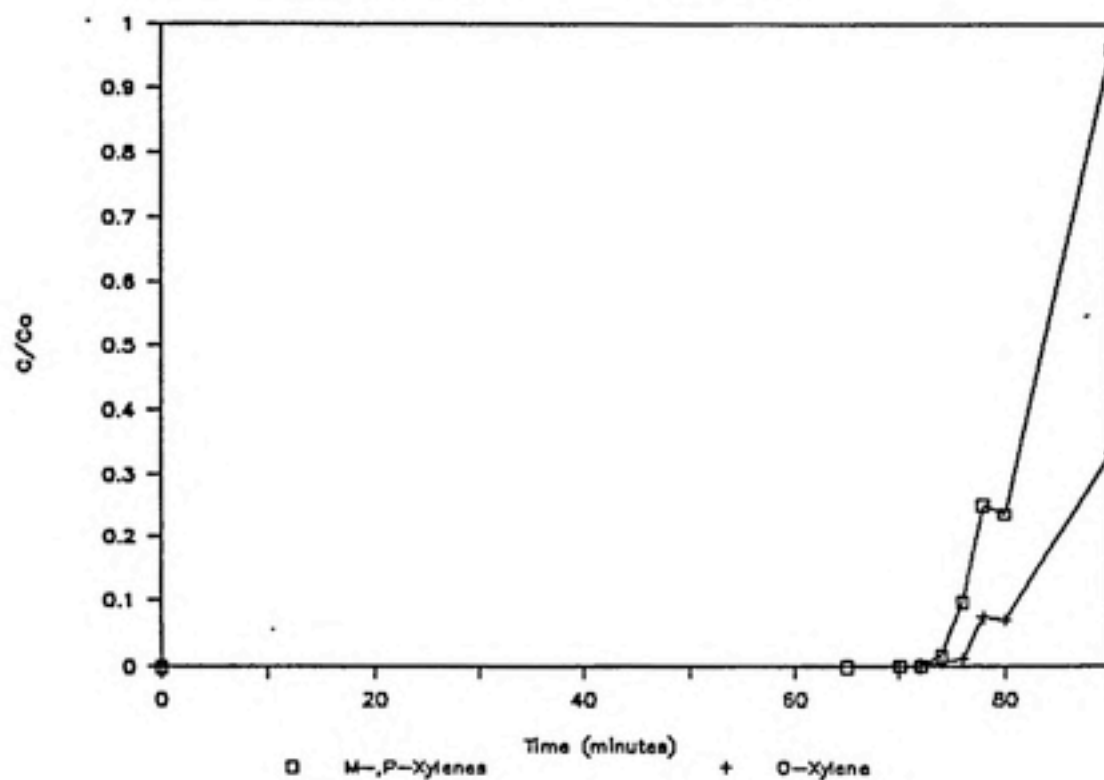## Xylene Breakthrough

Figure 12. Breakthrough Curve for Toluene and Xylenes from an (150-mg) Activated Carbon Trap
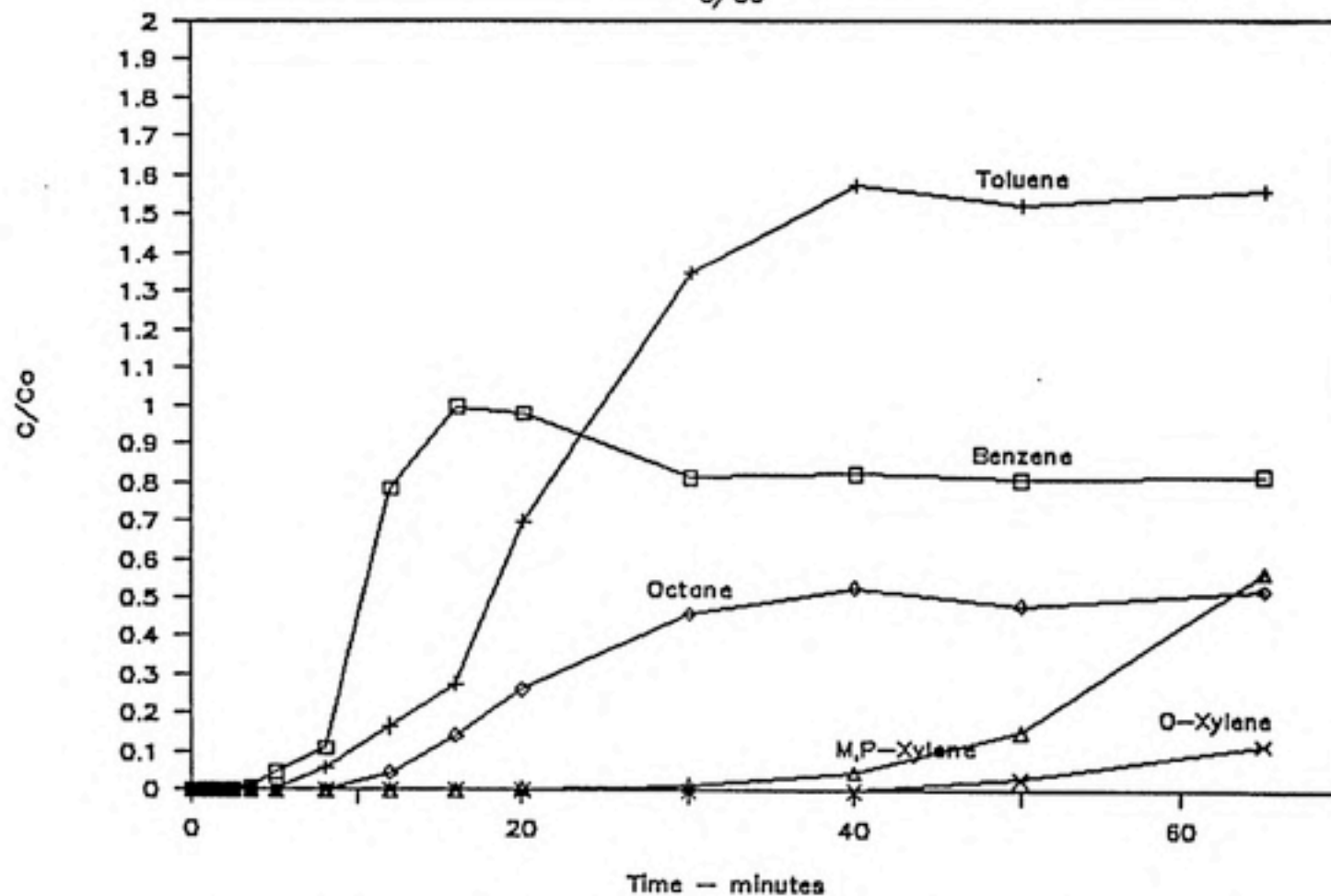
GASOLINE BREAKTHROUGH

C/Co

Figure 13. Breakthrough Curve for Selected Components of a Gasoline Matrix from an Activated Carbon Trap

vapor phase concentrations introduced to the carbon traps were not the same in both experiments, the time to breakthrough will necessarily be different even if competitive adsorption did not occur. Nonetheless, the relative ordering of breakthrough is given from the single component experiments (Figure 12) and the same ordering is seen in the mixture (Figure 13). The relative ordering of adsorbability (from weakest to strongest) is: toluene/trimethylpentane; octane; ethylbenzene; m- and p-xylene (treated as one because of poor chromatographic resolution); and o-xylene. That the concentration of toluene leaving the trap exceeds that being introduced is proof of competitive displacement by more strongly adsorbed components. Here, the exit concentration rises above the feed concentration, i.e. $C/C_o > 1$ because the previously sorbed toluene/TMP is displaced by the xylenes and other more strongly sorbed components. Although displacement of weakly adsorbed components is apparent, further interpretation of the shape of the curves is impossible because C_o may not have remained constant over time. Evidence of this anomaly is illustrated by the failure of the benzene breakthrough curve to approach $C/C_0 = 1$ as must occur when sorptive capacity is exhausted.

These laboratory experiments nevertheless suggest that the xylenes are excellent components to field monitor because breakthrough does not occur within 40-minutes or more of sampling; however, since xylenes have a lower vapor pressure,

they will not be present in as high concentrations as the
other analytes. Octane, and toluene/TMP are also good
choices if sampling times are limited to less than
approximately 10-minutes in highly concentrated areas. These
are conservative estimates of allowable sampling time because
the experiment was conducted by volatilizing pure gasoline;
thus the feed concentrations were maximized and breakthrough
times were minimized. In actual field situations, some
gasoline partitioning into the soil and aqueous phases will
occur and thus, the vapor phase concentrations will be
accordingly lower. The possibility also exists for
increasing the mass of carbon in the trap if longer sampling
times are desired. However, increasing the mass of adsorbent
necessitates using a larger volume of solvent for desorbing
the traps, thus introducing additional dilution of the
sample.

4.1.2 Analyte Loss from Carbon Traps

One of the major advantages of the proposed sampling
methodology is the elimination of expensive, sophisticated
field equipment. However, this advantage would be diminished
if additional handling procedures restricted the convenience
of the method. Most often, access to refrigeration and
chemical stocks is usually unavailable at remote field
locations. Thus, any adsorbent employed in field sampling
must not allow self-desorption at moderate temperatures or

over the duration of the sampling trip. The results from this experiment indicates the degree of tenacity to which activated carbon adsorbs the "target" compounds. Figure 14 a) and b), respectively indicate no significant change in concentration can be seen over the ten day experimental period at either room or freezer temperatures.

4.2 Gas Chromatographic Calibration for Target Compounds

A standard curve, a plot of peak area response versus mass injected, was prepared for each of the target compounds. All curves showed excellent linearity (r > 0.998), although some deviation was seen at the lower concentrations. Response factors (RFs), generated from these curves for each target compound, were used to convert peak area responses to mass measurements. Since the instrument was not dedicated exclusively to hydrocarbon analysis, standard curves were prepared for each run of sample analyses to avert any changes in FID sensitivity. Moreover, standard solutions were prepared prior to each analytical run because of the high volatility of CS_2, the solvent used to prepare these solutions.

4.3 Selection and Analysis of Target Compounds

At the onset of this study, the following were chosen as target compounds based on their known presence in

Analyte Loss @ 27 Degrees Celcius

LEGEND

□ Toluene/ TMP
◇ n-Octane
△ Ethylbenzene
+ m,p-Xylene
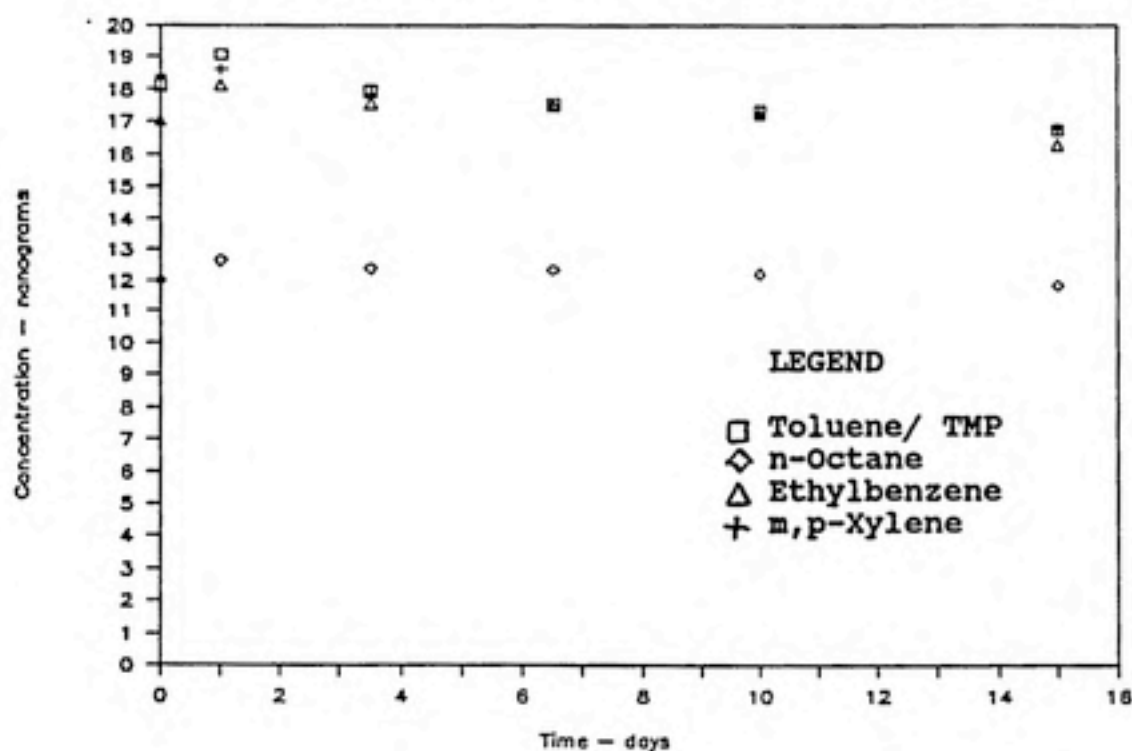
Analyte Loss at −13 Degrees Celcius

LEGEND

□ Toluene
◇ n-Octane
△ Ethylbenzene
+ m,p-Xylene

Figure 14. Target Compound Loss from Activated Carbon Trap Over a Ten Day Period at 27oC and −13oC.

gasoline: toluene, octane, ethylbenzene, m,p-xylene and o-xylene. Several initial field samples were analyzed and compared to the retention times of these five target compounds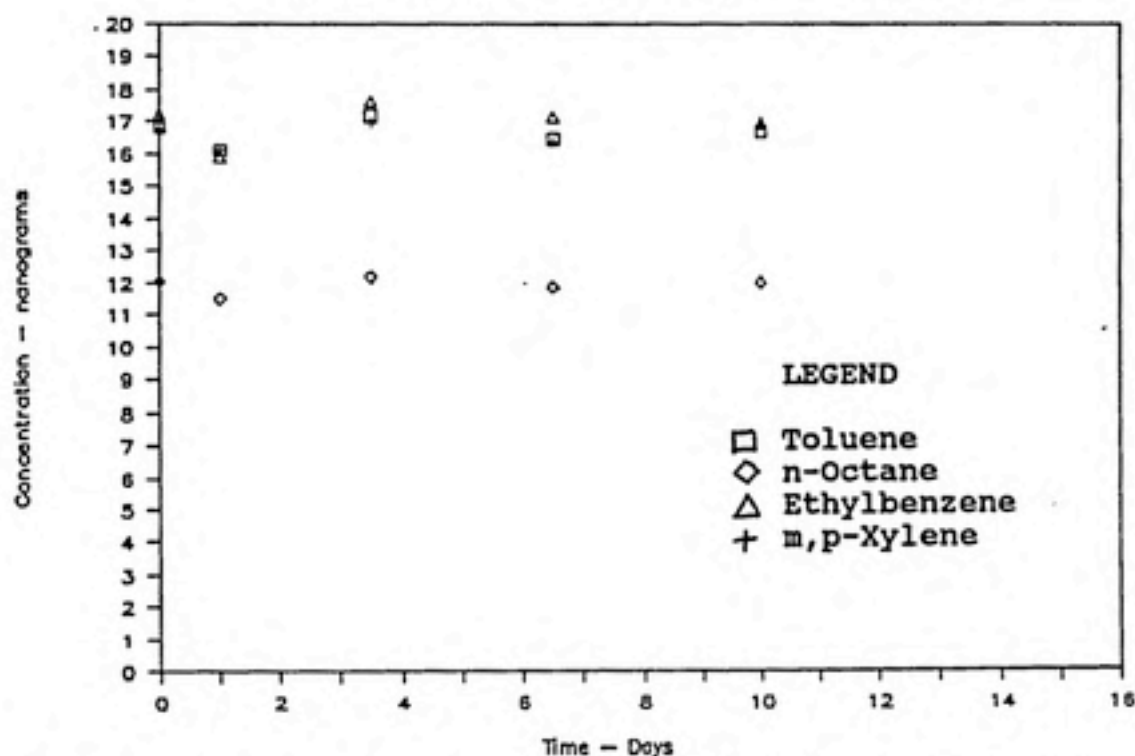. All five of these compounds were tentatively identified in field samples by retention time indices. However, retention time matching is not confirmation. Later in the research, samples of vapor eluant, from two sampling locations (BB and W on Figure 11) at the Camp Lejeune site, were submitted to the North Carolina State University GC/MS facility for identification. A GC/MS total ion chromatogram for one of the samples-location BB, is shown in Figure 15. Table 3 lists 27 major components found by this analysis; the conditions of the specified search range can be found in Section 3.2.2. All of the selected target compounds (designated by an asterisk) were confirmed.

Table 3. Major Gasoline Components Selectively Identified by GC/MS

1. Hexane	13. 2,3,4-Trimethyl Pentane	*25. m-Xylene
2. 2,2-Dimethyl Pentane	14. 4-Methyl Heptane	*26. p-Xylene
3. 2-Methyl Hexane	*15. 2,3,3-Trimethyl Pentane	*27. o-Xylene
4. 3-Methyl Hexane	*16. Toluene	
5. 2,2,4-Trimethyl Pentane	17. 3,3-Dimethyl Hexane	
6. 2,2-Dimethyl Hexane	18. 2-Methyl Heptane	
7. 3-Methyl Hexane	19. 3,4-Dimethyl Hexane	
8. 2-Methyl Hexene	20. 3-Methyl Heptane	
9. 3-Methyl Hexene	21. 2,4-Dimethyl Hexane	
10. 1,1,3-Trimethyl Cyclopenetane	22. 2,4,4-Trimethyl Hexane	
11. 2,5-Dimethyl Hexane	23. 3,4-Dimethyl Octane	
*12. n-Octane	*24. Ethylbenzene	

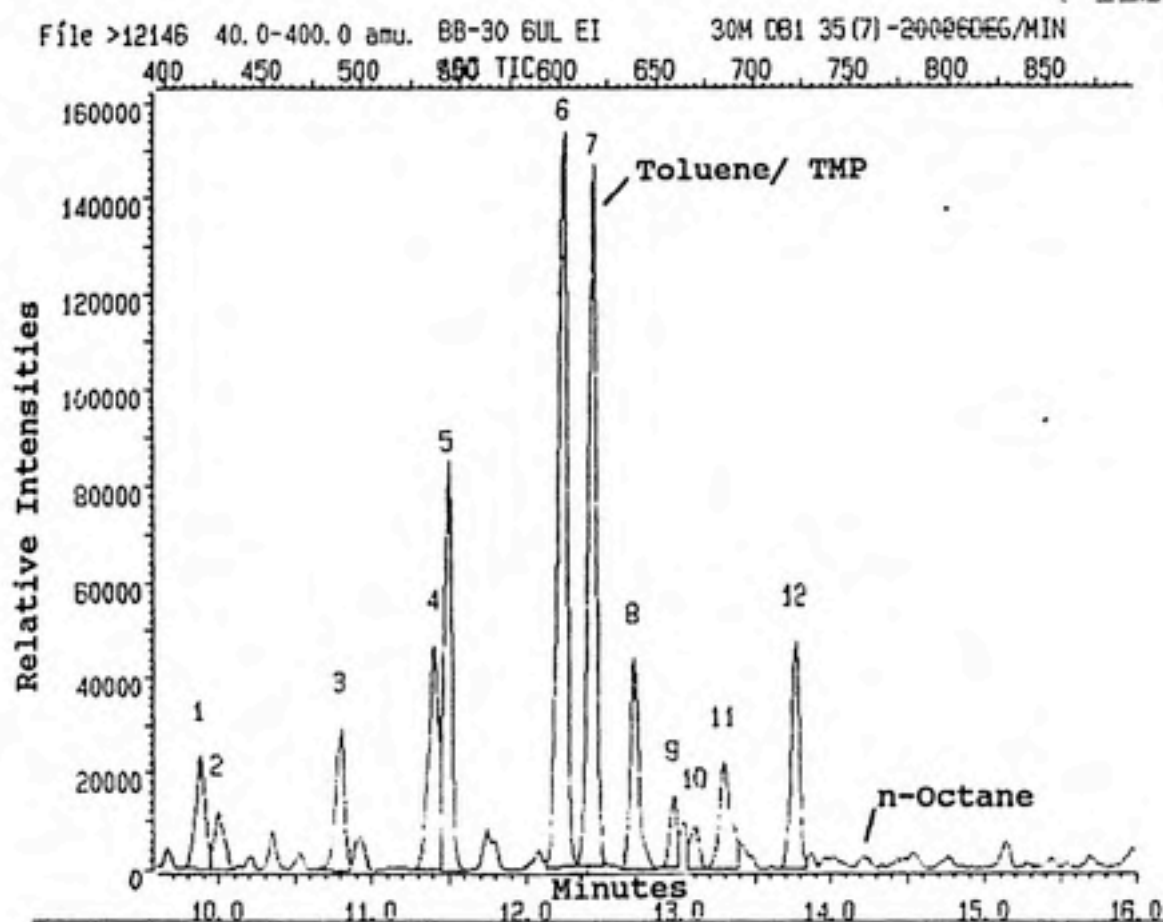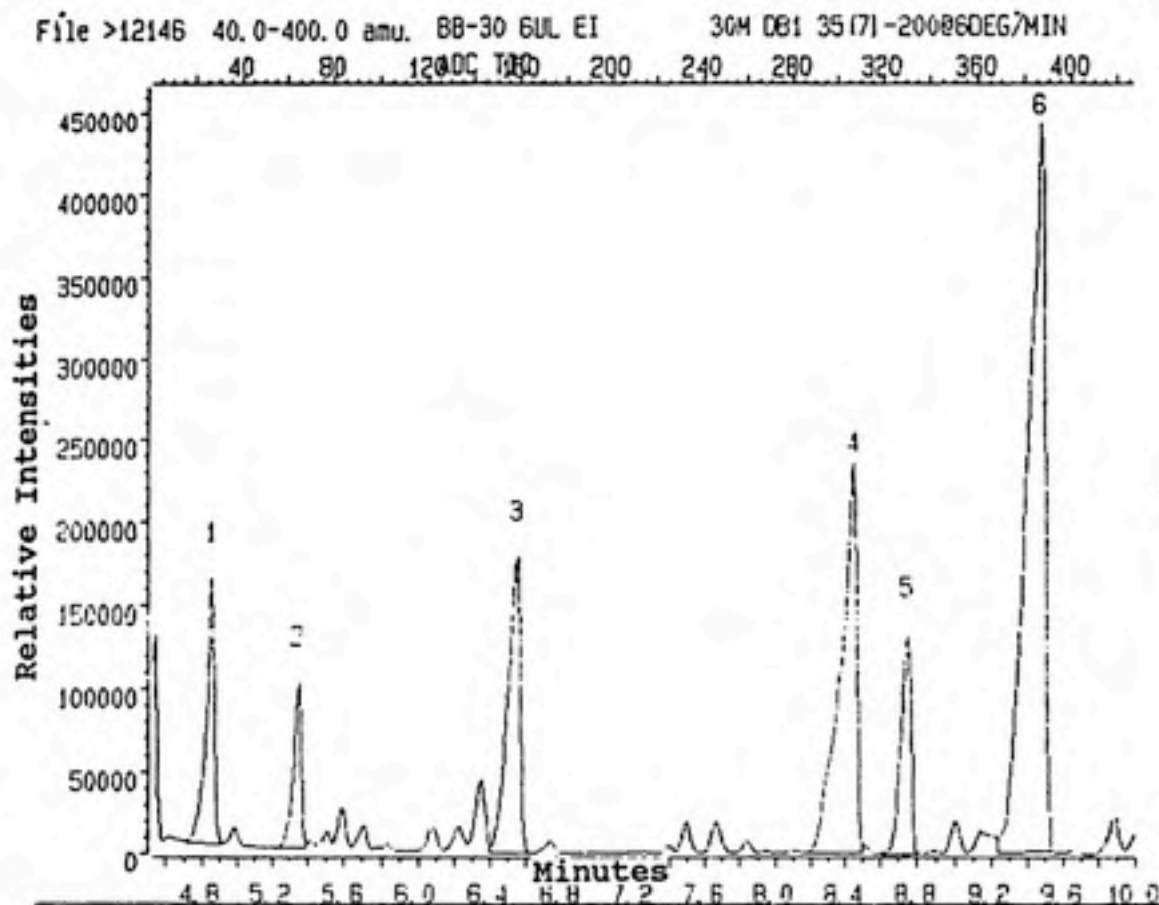However, the mass spectral analyses showed that toluene and

58

Figure 15. GC/MS Total Ion Chromatogram of Vapor Sample at Location BB

Figure 15. GC/MS Total Ion Chromatogram of Vapor Sample at
Location BB

60
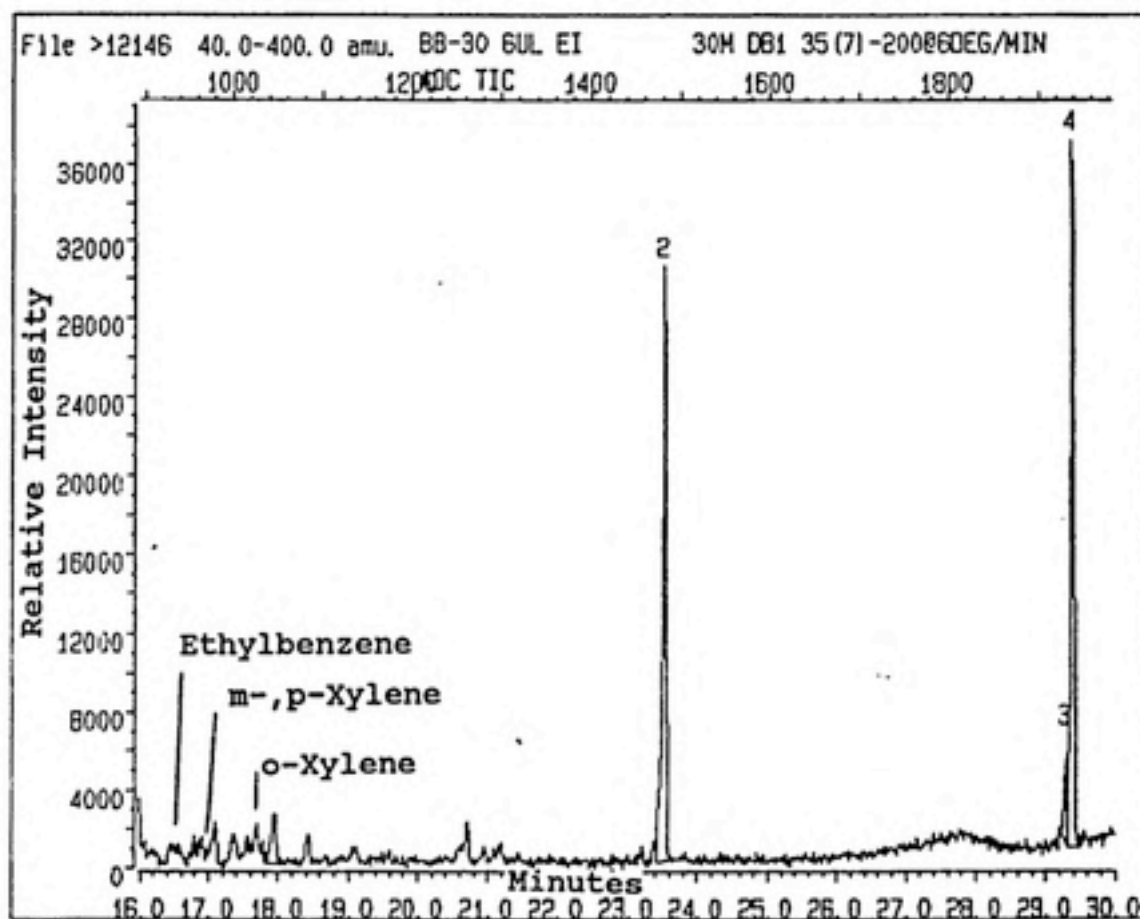
an aliphatic hydrocarbon- trimethyl pentane (TMP)- coelute. Matching of the TMP spectra (Figure 16) to library reference spectra tentatively identifies this compound as 2,3,3 trimethyl pentane. In order to resolve the problem of distinguishing toluene from the TMP for quantitative determination of each, samples samples were analyzed on a more polar capillary column. The percentage contribution of each compound to the total peak area was estimated by reanalyzing three field samples, AA, BB and W. These samples were re-analyzed in duplicate pairs, first on a Supelco Inc. SPB-1 (non-polar) 30-meter capillary column and subsequently on a J&W Scientific Inc. DB-5 (slightly polar) 30-meter capillary column. Because toluene is a slightly polar compound, its retention time is increased on the more polar column. Thus the lowering of response of the co-elution peak using the DB-5 column was attributed to the toluene eluting later. The results of this analysis indicate that toluene accounts for 23.2%, 1.5%, and 1.5% of the toluene/TMP peak seen using the SPB-1 non-polar column for samples AA, BB, and W, respectively. Analytical variability between duplicate samples from each location was between 0.00% and 0.82%.

Chromatographic response factors, which are a relative measure of the response of the FID to a known mass of analyte are 1.07 and ⁻1.0 for toluene and TMP, respectively (8), so that quantification of the peak area response for the two can be calculated with no more than 7% additional error. Therefore since this condition of coelution was not detected
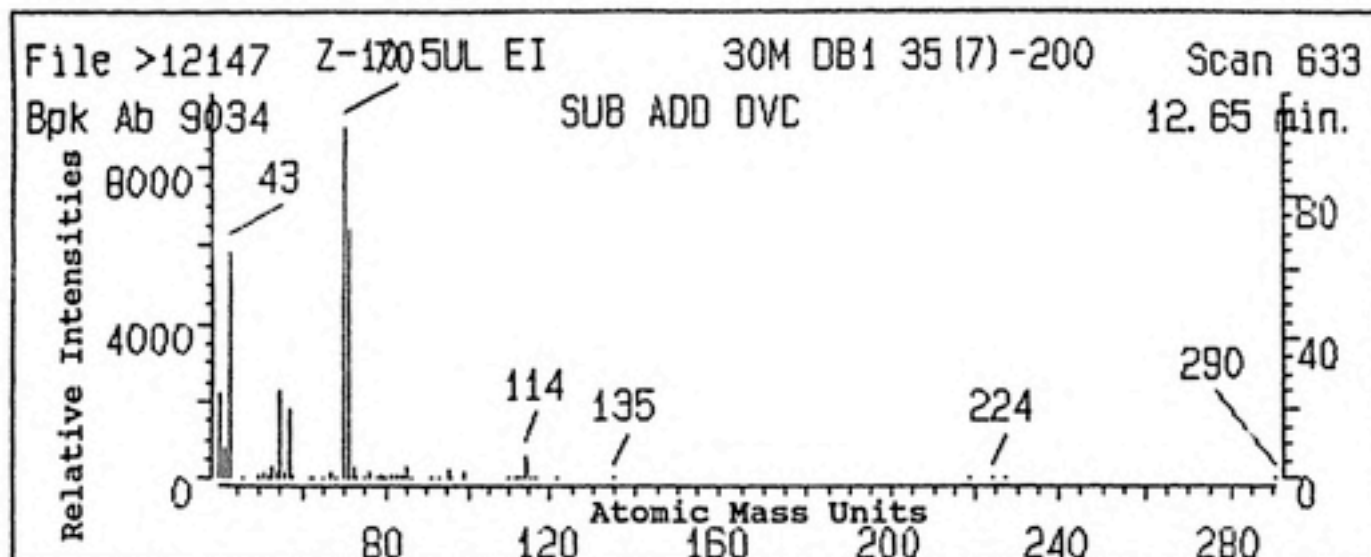
Figure 16. Mass Spectrum of (2,3,3-) Trimethyl Pentane Showing Characteristic Ion Fragmenting Pattern (Peak #7 on Figure 15).

until after samples had been run, the areal integration of the peak that represents both toluene and TMP will be reported as such.

It is interesting to note that since toluene makes up about 6-7 volume per cent of most gasolines (45), it would be expected that a correspondingly high concentration of toluene in the soil vapor samples would be seen. However, this was not the case. The possibility of preferential toluene biodegradation over aliphatic compounds is unlikely because aromatic ring cleavage is a less favored pathway compared to alkane side chain cleavage (1, 27). It is possible that toluene partitioning occurs onto soil particles and its associated pore and hygroscopic water with greater affinity than TMP.

4.4 Detection Limits of Target Compounds

The following values for vapor-phase detection limits are given as parts per billion by volume (ppbv). This descriptor is a common method of expressing concentration in air chemistry and may be confusing to readers of other disciplines. Ppbv is a volume per unit volume measurement e.g., ul analyte per liter gas. On the other hand, parts per billion (ppb) is a mass per unit mass measurement; by convention, water phase concentrations are reported as mass per volume because one milliliter of water weighs about one gram. The conversion of mass per volume meaurements to ppbv

is:

ppbv = (X ug of analyte/ L gas) x (mole/Y grams) x (10E6 grams/ug) x (22.4E6 ul/mole gas)

At an air flow rate of 47-cm^3 per minute and a
sampling time of 30 minutes, the soil vapor sampling method
produced a detection limit of 0.04-ppbv for the "target"
compounds. Moreover, the limits of detection for this
research method can be increased if the sampling time is
increased- a feature not available to techniques involving
the analysis of a discrete volume of gas (e.g. direct
injection into a chromatograph). Lowering the limit of
detection by increasing the sampling time is illustrated in
Table 4.

Table 4. Limits of Detection as a Function of Sampling Time

	Sampling Time	Limit of Detection (ppbv)*
	1 minute	1.19
	3 minutes	0.40
	10 minutes	0.12
	30 minutes	0.04
	60 minutes	0.02
	90 minutes	0.01
Kerfoot et al.	14 days	0.02**
Evans & Thompson	***	0.01***

*   GC detection limit of 1-ng of 100-g/mole compound
** Accumulator Device
*** Instantaneous injection from vapor stream; GC detection
    limit of 70-picograms

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In comparison to literature values, Kerfoot et al. (26) indicated a lower detection limit- 0.02-ppbv- for an accumulator device; however, an exposure period of 14-days was required. Evans and Thompson indicated a detection limit of 0.01-ppbv for their ground probe/ direct injection technique (12). Evans (11) reports that this level is acheivable for any C_4 through C_9 aliphatic or aromatic hydrocarbon using a two milliliter sample. Response factors, generated for benzene, were used for calculating concentrations from chromatographic peak area measurements of these compounds. At this level of detection, the sensitivity of the GC (Varian 3300 with FID) would be 70-picograms injected. This is a questionably small quantity for insuring adequate chromatographic baseline resolution for a typical hydrocarbon detected with an FID.

4.5 Field Sample Analyses

4.5.1 Gasoline Vapor Concentrations at Camp Lejeune Site

Known components of gasoline were detected in 24 out of 26 samples taken at the Camp Lejeune site explicitly for the preparation of contaminant vapor concentration contours. Only those components designated as "target" compounds were quantified, although many other components were detected. Figure 17 shows typical gas chromatograms of subsurface
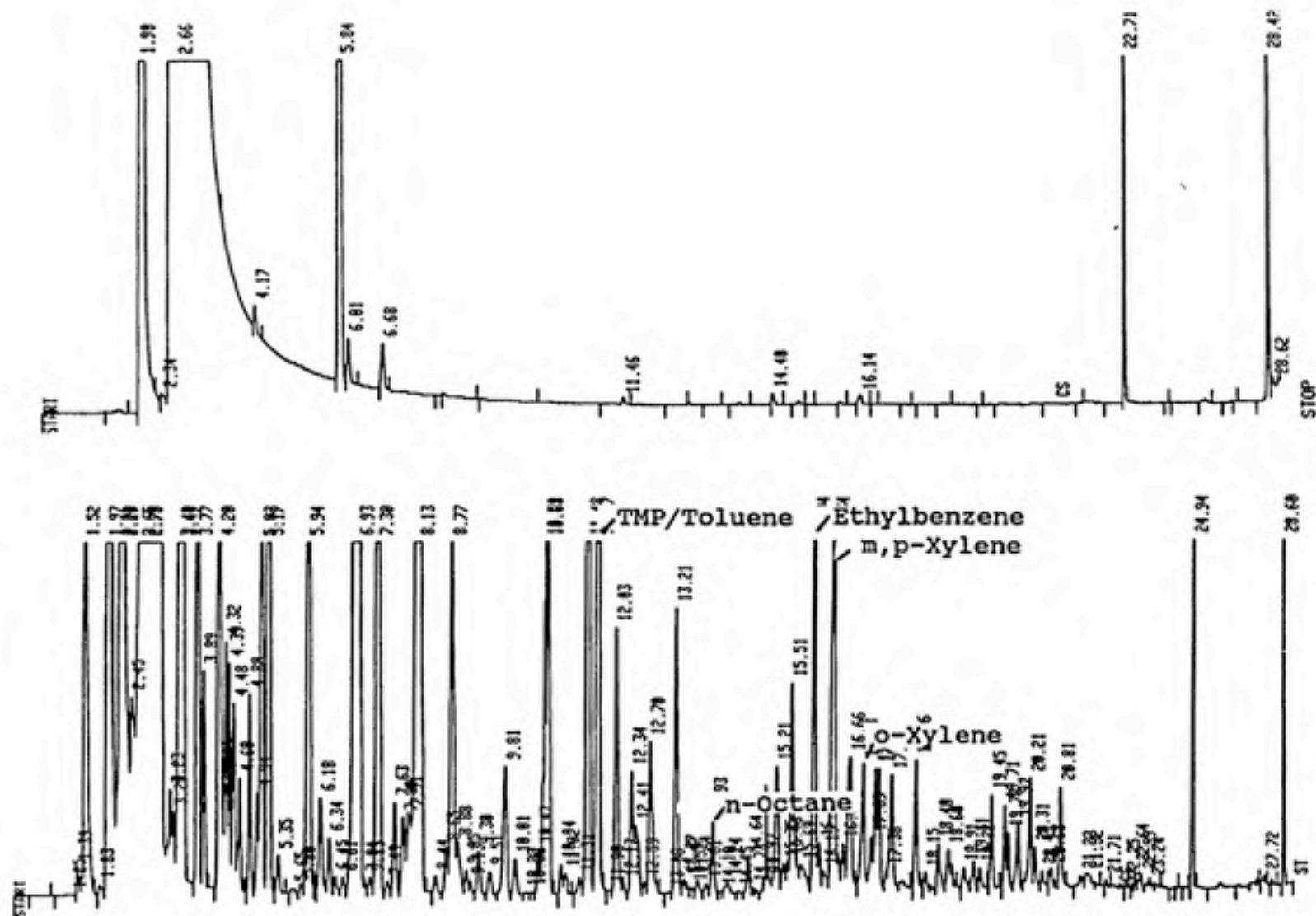
Figure 17. Gas Chromatographic Traces of Vapor Sample at
Locations K (30 min) and D (30 min)

65

gasoline vapors for sampling locations K30 and D30, respectively.

Vapor concentration contours were mapped for three sampling dates (4-1-87; 5-1-87; 6-27-87) over a four month period. These maps were constructed by linearly interpolating between target compound concentrations at each of the sampling points. Interpolations were accomplished on a microcomputer using a technique known as Kriging, which delivers a best linear unbiased estimate of the data. The accuracy of the contour lines for predicting the actual field conditions increases with the number of data points.

The first sampling trip was used to estimate the variability in vapor-phase concentration in the area around the site of the leaking tanks. Data collected from these sampling points were used in constructing the vapor contour map shown in Figure 18. From this figure, a trend of contaminant vapor distribution in the east direction is suggested, although the boundaries of this vapor "plume" are not well defined.

The areal extent of the vapor plume was further defined on the second sampling trip (Figure 19). These data give further definition of the contour perifery, particularly in the east and southeast directions. Extensive perimeter sampling in the north and northwest was not possible because much of the area is covered by a large parking lot.

Data taken during the third sampling trip added further definition to the vapor contours. The concentration contours

Figure 18.   Vapor Concentration Contour Map for 4-1-87
             Sampling Trip. Measurements in log ug of target
             compounds per liter of soil vapor.

Figure 19. Vapor Concentration Contour Map for 5-1-87 Sampling Trip. Measurements in log ug of target compounds per liter of soil vapor.

for the third data set are shown in Figure 20. The contours
lines for the highest concentrations are positioned similarly
to those of the first data set (Figure 18). However, the
center of maximal contamination has shifted due to a very
large concentration found at a location in close proximity to
the tanks.

Contour lines derived from combining all three sets
together over the four-month sampling period are shown in
Figure 21. From this figure, the trend of vapor distribution
towards the east is more distinctly seen than in the previous
contour maps. Moreover, the outer perimeter contours,
especially in the east and southeast give added definition to
the areal extent of the vapor-phase contamination.

The cone of depression created by the recovery pump,
controls the direction of groundwater movement in the
immediate vicinity of the tanks. Therefore, the shape of the
contaminant vapor plume in Figure 21 cannot be considered
indicative of that for a typical site of gasoline
contamination prior to remedial efforts. Furthermore,
temporal changes, such as active withdrawls of free-product
and biodegradation, were likely over the 3-month sampling
period. Thus, combining all three data sets to construct
these contour lines may lack rigor. However, Figure 21 does
represent the type of information that can be attained by
using soil vapor sampling and a technique such as Kriging,
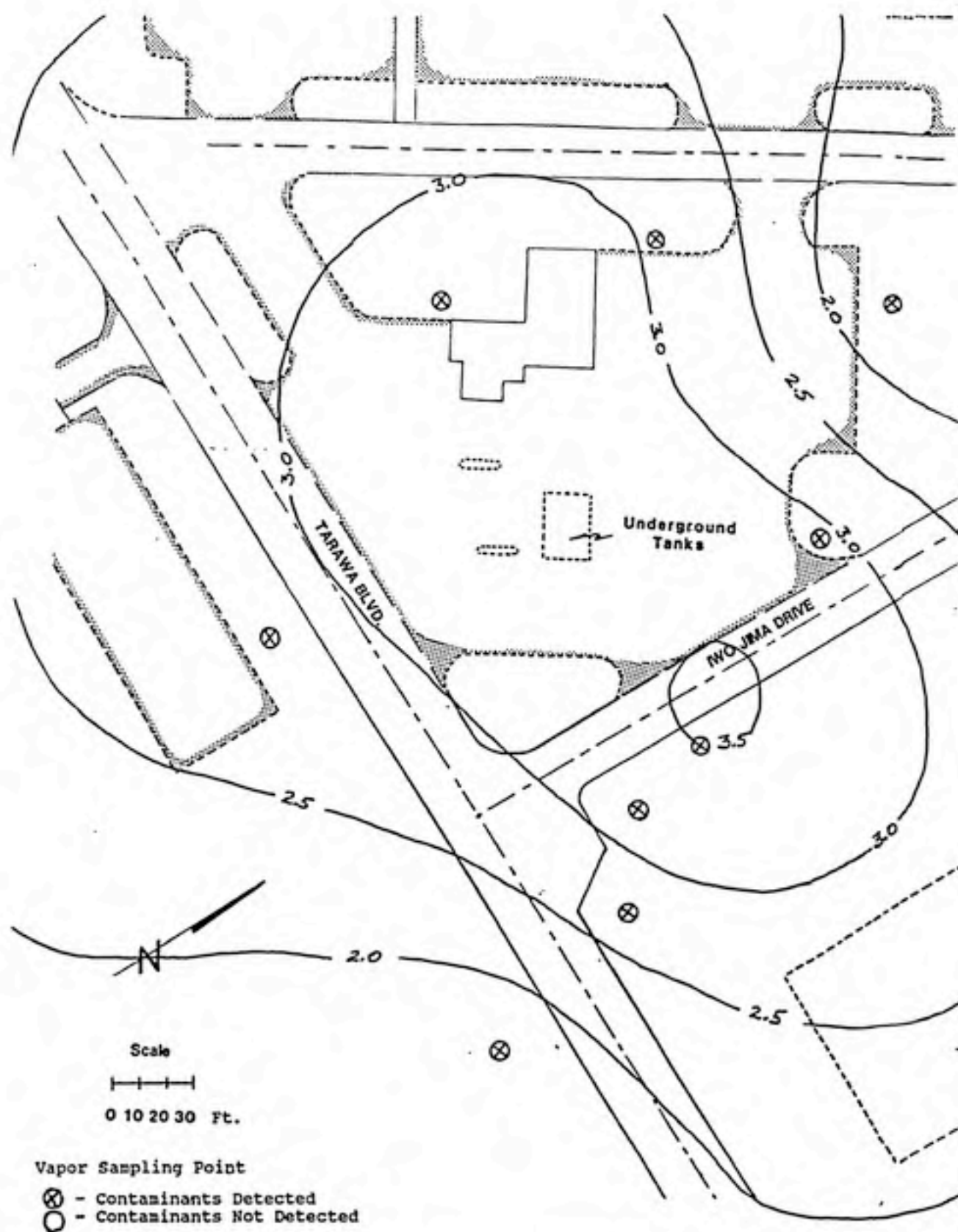for interpolatons of concentrations.
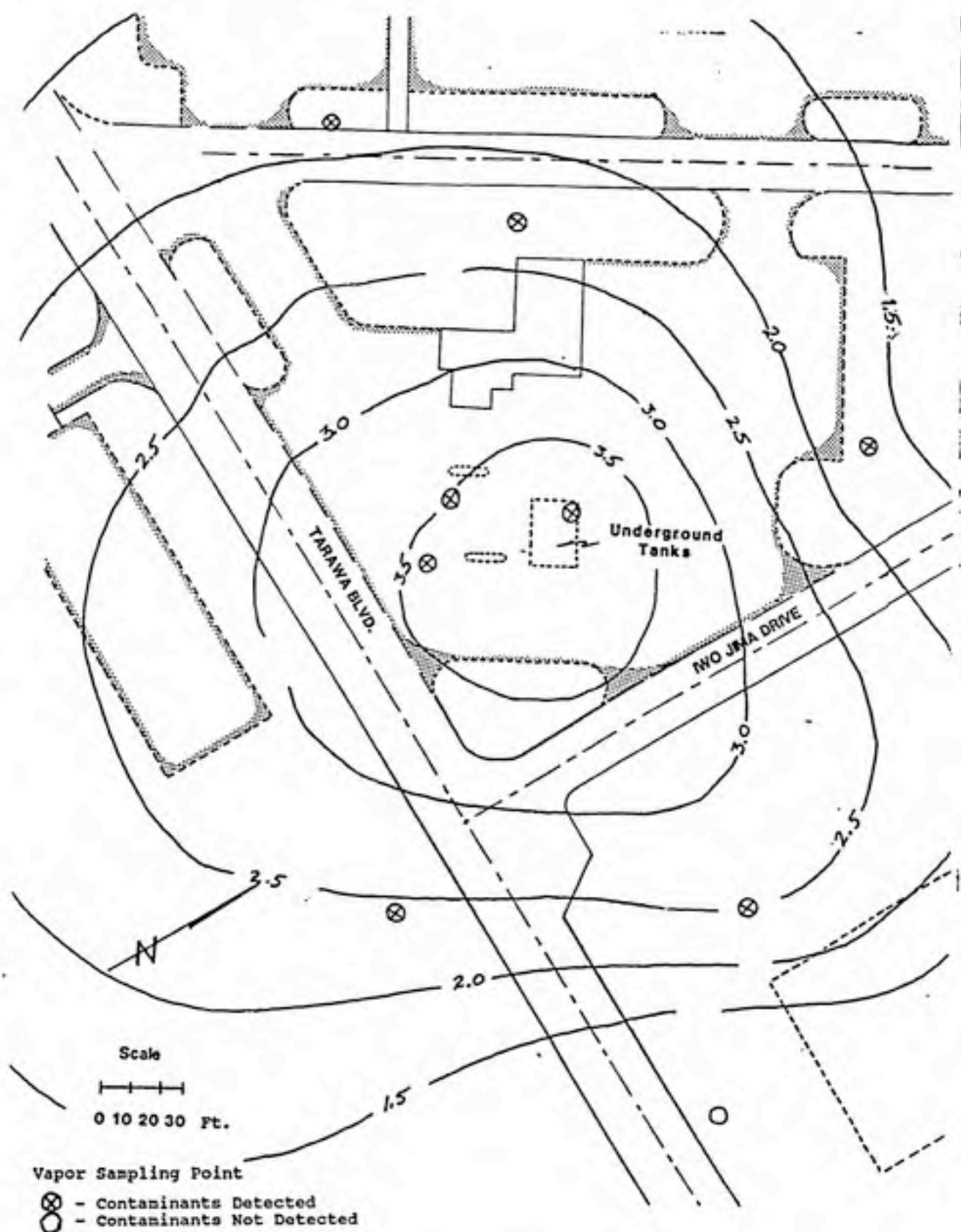
Figure 20. Vapor Concentration Contour Map for 6-27-87
Sampling Trip. Measurements in log ug of target
compounds per liter of soil vapor.

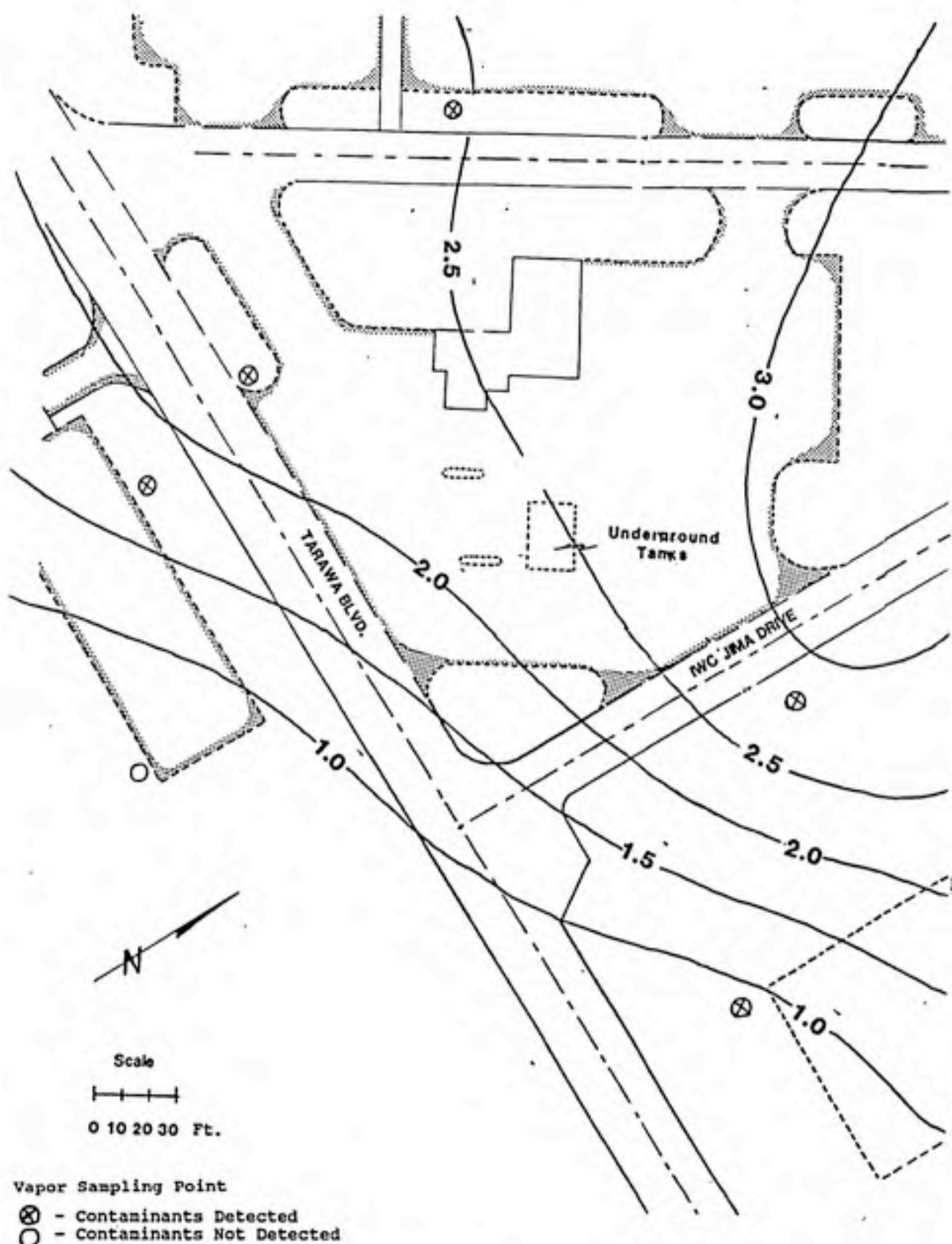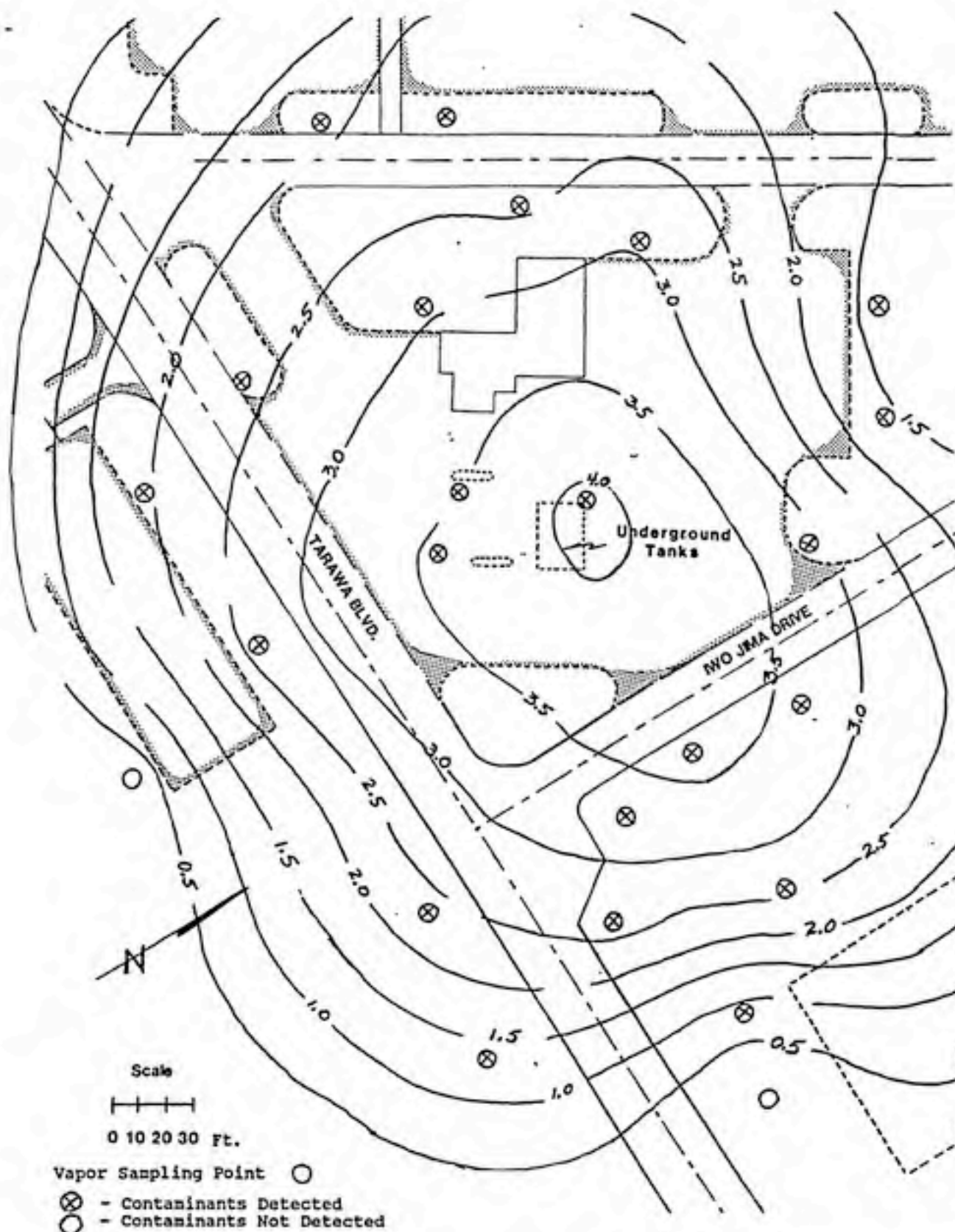Figure 21. Vapor Concentration Contour Map using measurements made over a three-month period (4-1-87, 5-1-87 and 6-27-87). Measurements in log ug of target compounds per liter of soil vapor.

4.5.2 Relationship of Vapor-Phase Concentrations to the NAPL

The distribution of the vapor-phase contaminant "plume"
should reflect the distribution of the source of the vapors,
primarily, the non aqueous phase liquid (NAPL). Distribution
of the NAPL occurred mostly under pre-recovery conditions.
During this time, the hydraulic gradient was likely towards
some point of discharge, which as seen in Figure 22, is
likely to be the Northeast Creek, lying east and southeast of
the site. Data collected before the recovery effort began
and during periods of pump shutdown indicate a slight
hydraulic gradient in the southeast direction, consistent
with the Northeast Creek being the discharge area.

A relationship between the positioning of the vapor-
phase concentration contours and the position of the NAPL may be
reasoned intuitively. The concentration of vapors would be
expected to be greatest above NAPL where vertical diffusion
accounts for the bulk of the vapor movement. Outside the
area of NAPL contamination, contaminant vapors are present due
to transverse diffusion and vertical diffusion from
contaminated groundwater. Therefore, a large decrease in
vapor-phase concentration would be expected beyond the edge
of the NAPL plume. Figure 23 illustrates the contours
generated from measurements of free gasoline product (NAPL)
taken form nine monitoring wells located at the site. Figure
24 shows the position of the NAPL (as indicated by the shaded
area) superimposed over the combined vapor-phase contour map

Figure 22. Areal Map of the Camp Lejeune Site Indicating the
Northeast Creek Controlling Boundary (shaded area).
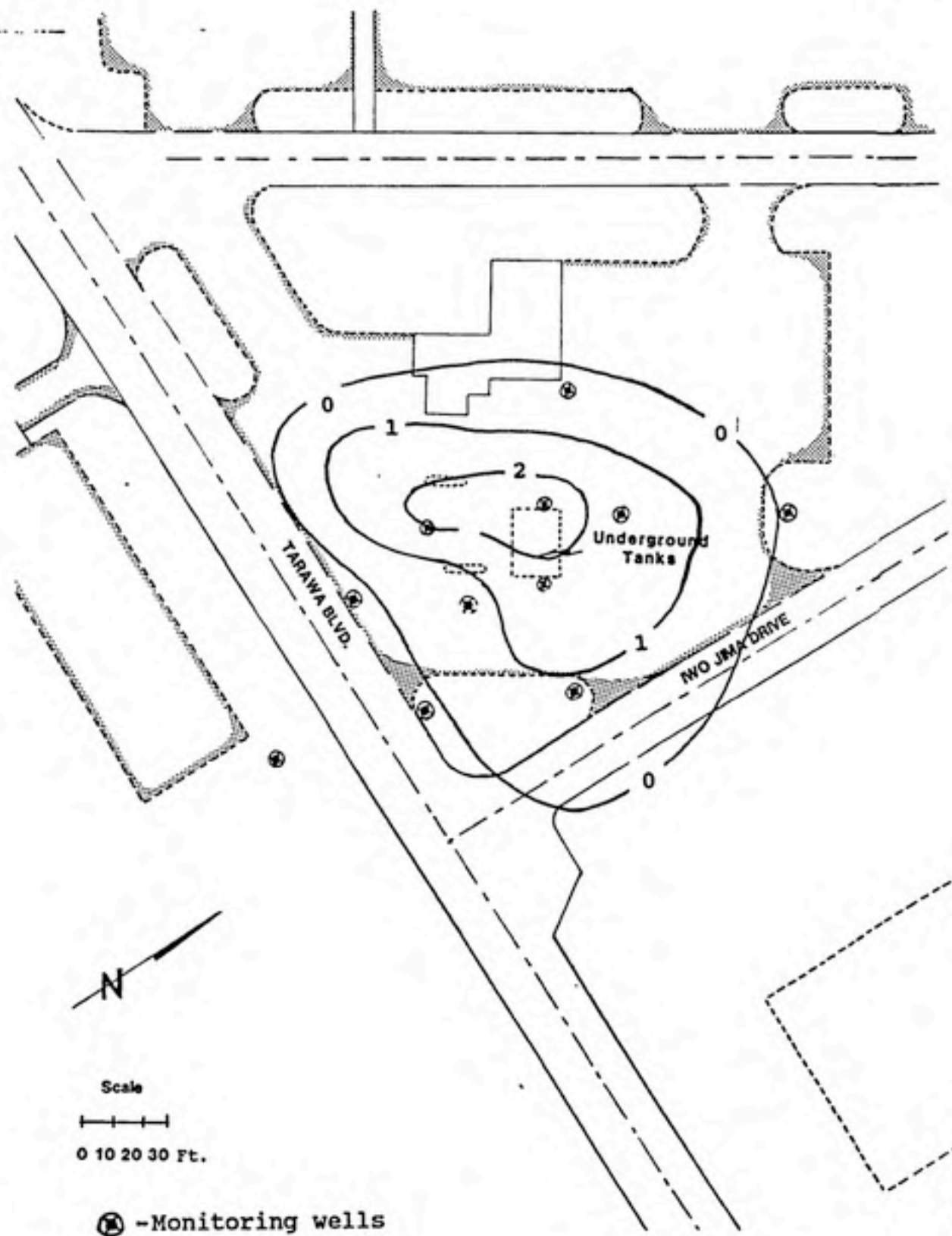
Figure 23.   Concentraion Contour Map of Free Gasoline
Product i.e. NAPL (in inches).
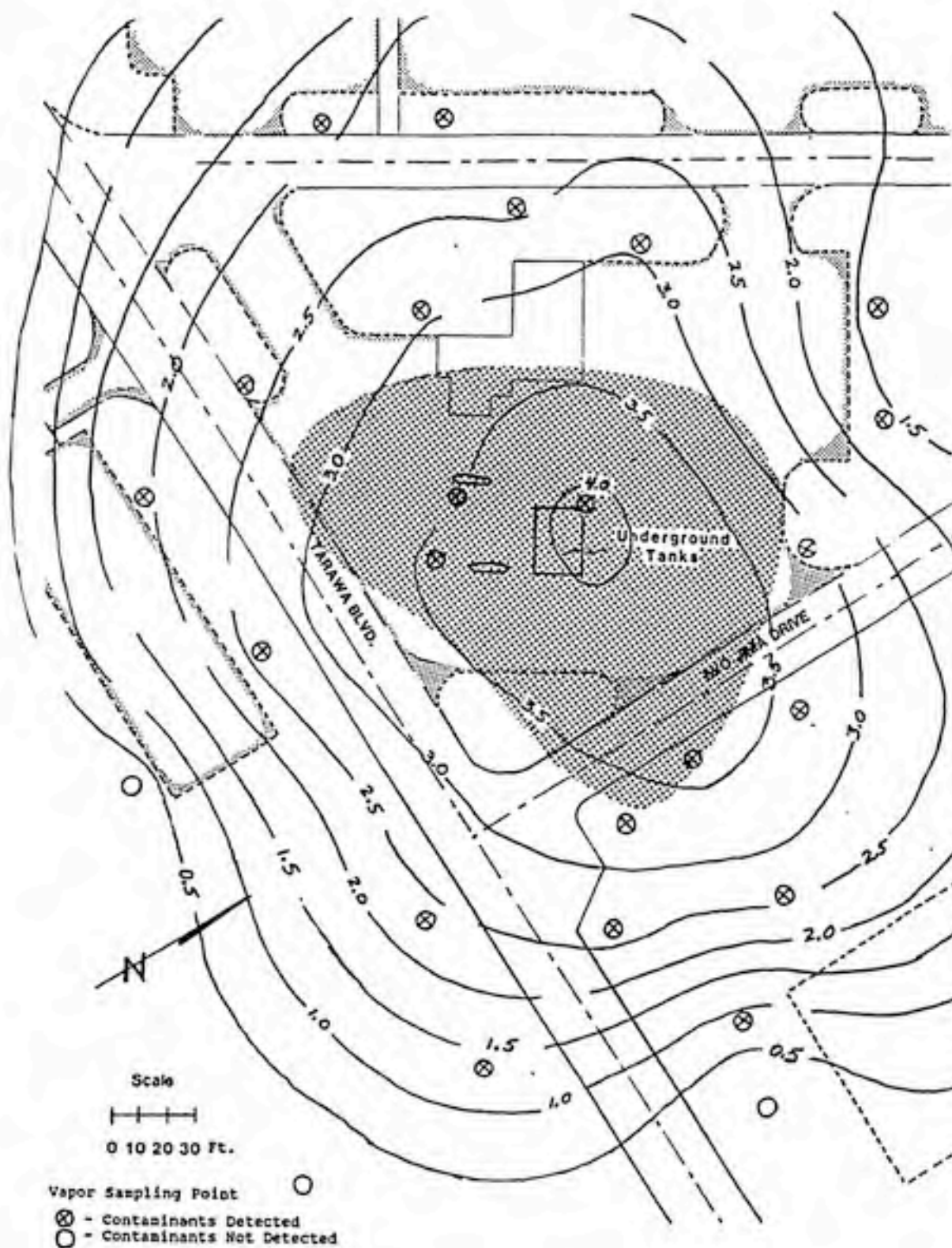
Figure 24. Areal extent of NAPL (Shaded) superimposed over Vapor-Phase Concentration Contours.

(Figure 21). The position of the NAPL was derived from measurements of free gasoline product (NAPL) taken from nine monitoring wells located at the site. Inspection of Figure 24 shows that the vapor-phase contour intervals become increasingly narrower past the edge of the NAPL plume (i.e. the vapor-phase concentration decreases rapidly beyond the edge of the NAPL).

4.5.3 Temporal Variation in Contaminant Concentrations

Measuring the extent of temporal variation in vapor-phase concentration over the four month sampling period was critical to judging whether all three data sets could be combined for construction of the contour lines in Figure 21, as discussed above. With an active recovery operation in progress, it seems unlikely that temporal variation could be avoided. To determine the extent of variation, vapor-phase samples were taken at the same location at the beginning and end of the sampling period. The results from this study are shown in Table 5.

Table 5. Temporal Variations in Contaminant Concentrations
(Percent change from 4-1-87 through 6-18-87)

Sample location	Toluene/TMP	Octane	Ethylbenzene	m,p-Xylene	o-Xylene
C	-22%	-30%	-23%	-4%	+22%
D	+43%	-74%	-65%	+343%	-1%
F	+4%	+122%	+60%	+95%	+39%

Two of the three sampling locations (D and F on Figure 11) showed considerable change in vapor-phase concentration over four months. At sample location C (Figure 11), reproducibility was within 30% of the initial concentration for all of the "target" compounds, with a range of -4% change for m,p-Xylene to a - 30% change for octane. Reproducibility was much worse at sample location D, where precision ranged from -1% for o-Xylene to +343% for m,p,-Xylene. Location F proved to also show considerable variability. Toluene/TMP showed the least change at +4% and octane showed the most at +122%. Even though the changes in concentration were less than an order of magnitude, the variability in concentration over the duration of the field investigation was indeed extensive, but not unexpected because of the active recovery operation. It is also plausible that location C may have had less change because it under less influence from the cone of depression due to its spatial orientation.

4.5.4 Depth Profile of Gasoline Vapor Concentrations

Figures 25 a,b,c,d,e show the target compound concentrations as a function of depth from the surface of the ground surface. There is considerable variability in concentration among the four sampling locations at each of the two lower depths. Nonetheless, taking the average concentration at each depth shows that concentration decreases towards the surface as would be expected if
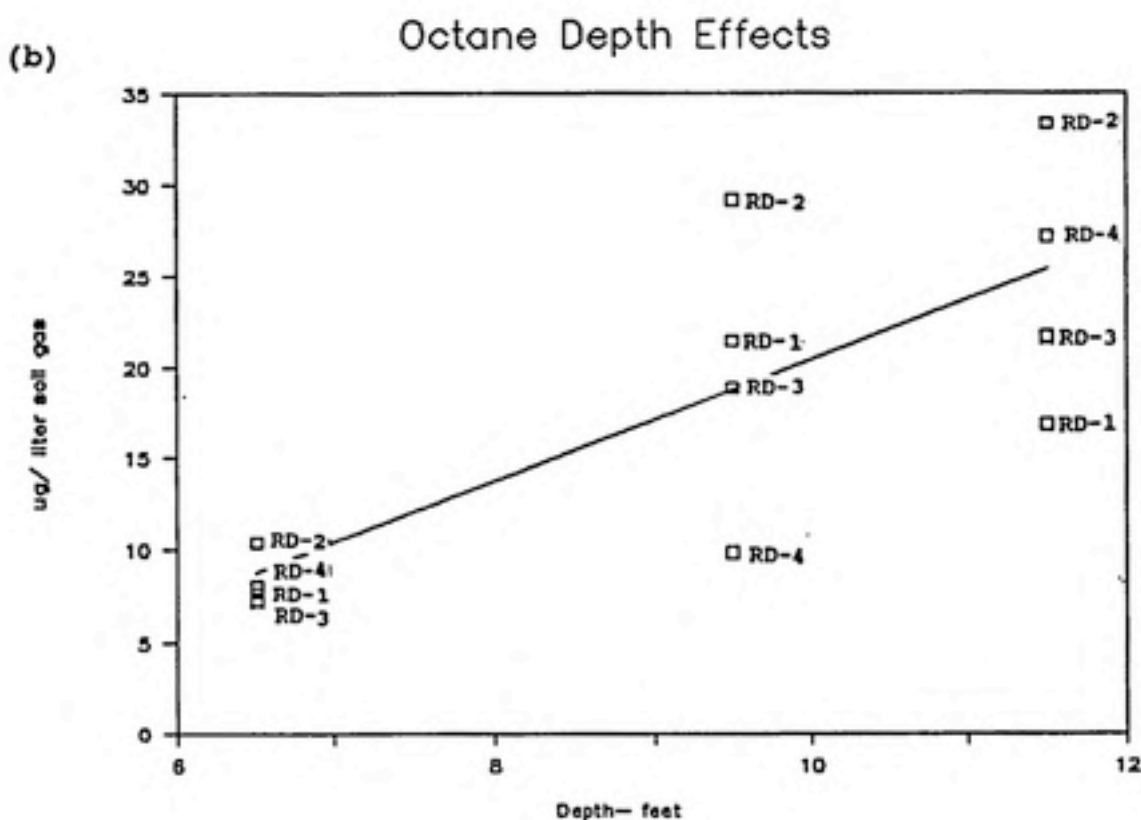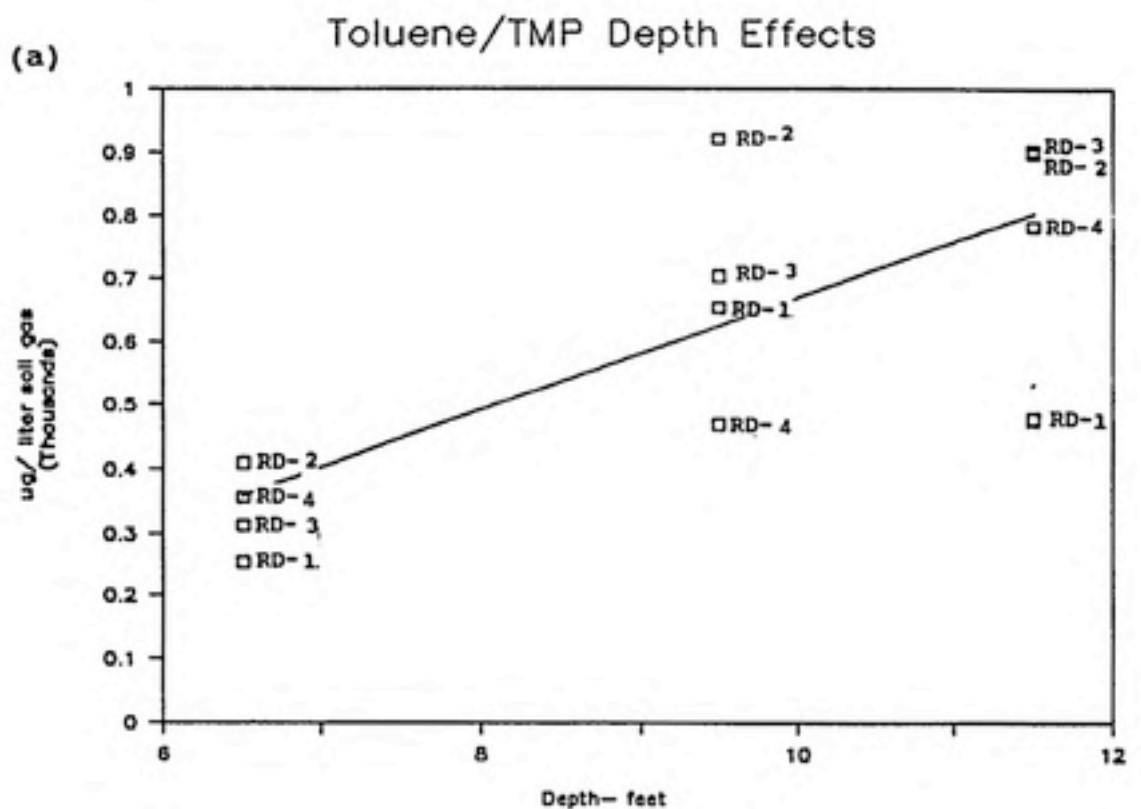
(a)

Toluene/TMP Depth Effects

(b)
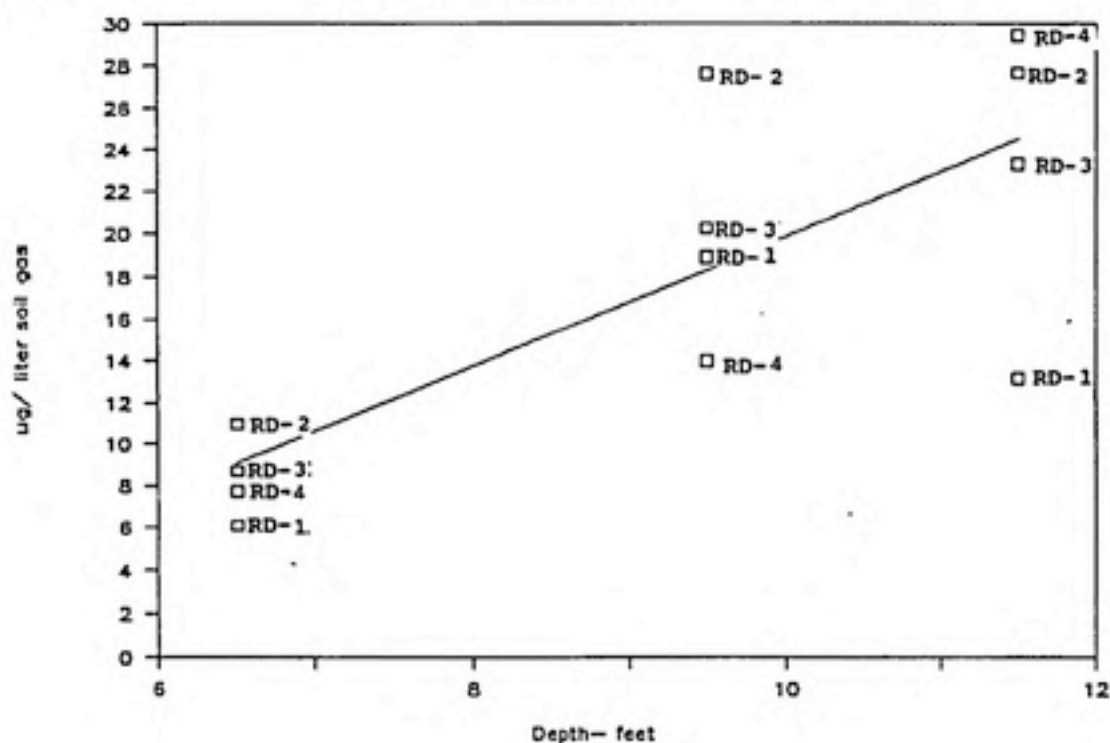
Octane Depth Effects

Figure 25. Vapor Concentration Measurements of Target
Compounds as a Function of Depth from the Surface.
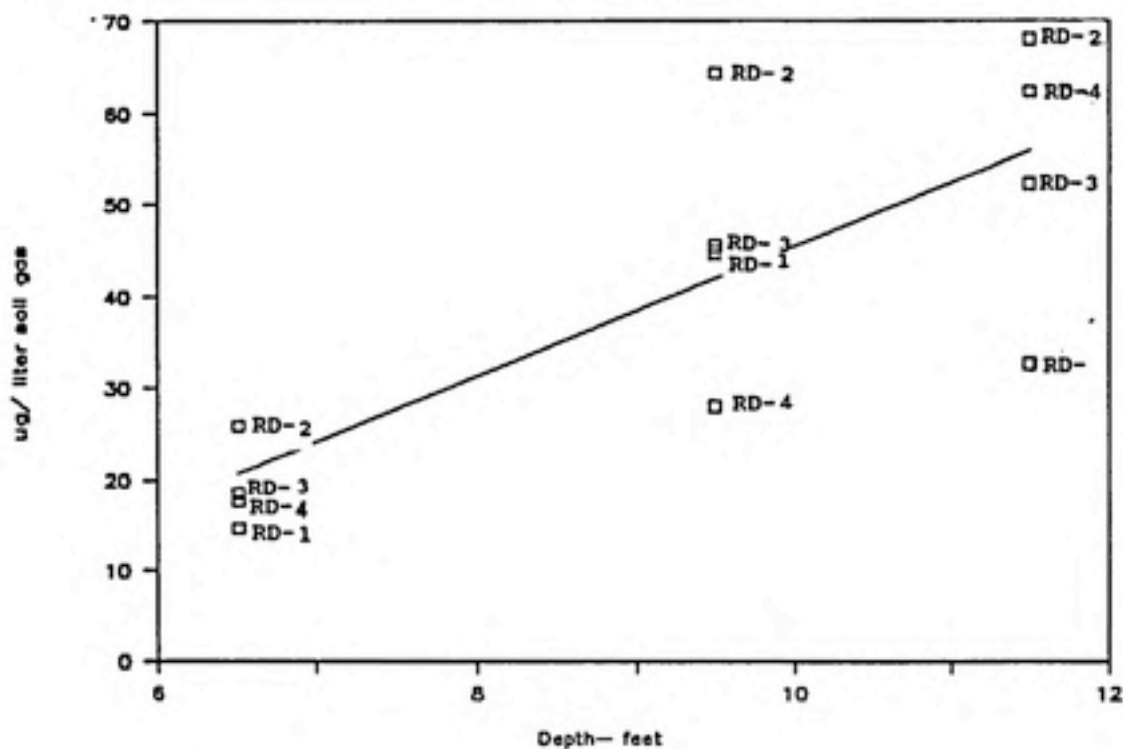
Figure 25. Vapor Concentration Measurements of Target
Compounds as a Function of Depth from the Surface.

(e)
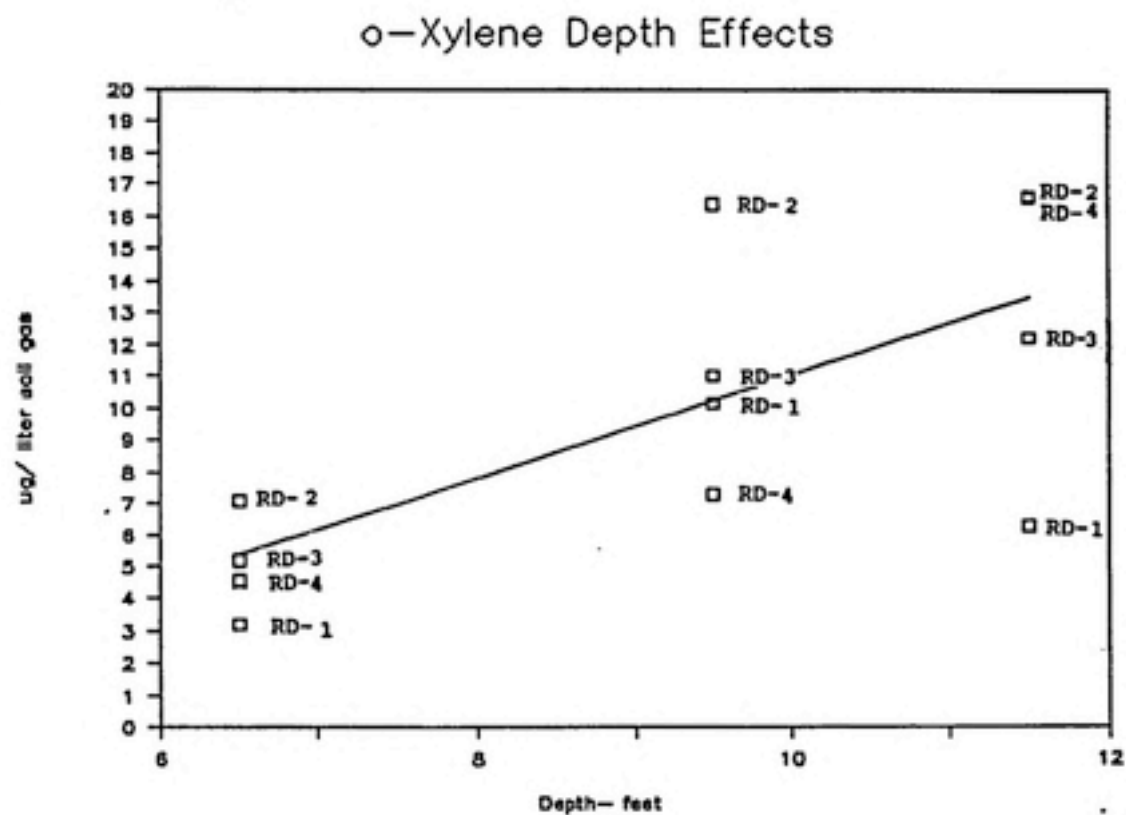
Figure 25. Vapor Concentration Measurements of Target
Compounds as a Function of Depth from the Surface.

verticle diffusion from the NAPL was important.
Biodegradation near the ground surface may contribute to the
concentration gradient. Evans and Thompson recently reported
a similar observation and indicate that petroleum
hydrocarbons are particularly susceptible to biodegradation
in the shallow regions of the soil profile (12). Aerobic
biodegradation is more likely near the ground surface because
there is more oxygen available to the petroleum degrading
microorganisms. The authors point out the importance of
depth profiling as a means of determining adequate sampling
depths in order to insure significant hydrocarbon
concentration while minimizing probe emplacement time.
Subsurface hydrocarbon vapors are most effectively detected
when samples are collected as close to the water table as
possible if the vapors originate from the water.

Concentration measurements from samples used to
construct the vapor contours were taken at depths of 7-10
feet. Considering the concentration gradient revealed in the
aforementioned study, these concentration measurements can be
expected to have an inherent window of variance of less than
100%.

4.6 Contaminant Distribution in the Three Phase System

4.6.1 Soil Mass/Vapor-Phase Distribution

Subsurface vapor-phase measurements can be used to estimate

the total mass of target compound present per volume of soil in the unsaturated zone. If the system is equilibrated, the ratio of soil vapor-phase concentration to soil-mass concentration is described by a partition coefficient between these two phases. At low concentrations, this ratio may be a constant, the specific value of which depends on chemical properties of the compound. An analysis of the fraction of each target compound found in the vapor phase is given in Table 6. These fractions were calculated from vapor-phase and soil mass (solid, vapor and aqueous phases combined) taken at locations MW3, MW7, and MW8 in Figure 11. The mass of any target compound in the vapor-phase is:

$$M_V = C_V \ e_V \ V_T$$

where C_V is the concentration (ug/M^3) in the vapor-phase; e_V, the fraction of voids filled with vapor-phase (0.24 has been estimated based on field measuremnts); and V_T is the total unit volume of the soil mass (1 M^3 in Table 6). The total mass, M_T, in all three phases is calculated from measurement of mass in the soil sample:

$$M_T = C_T \ P_S \ (1 - e)$$

where C_T is is the concentration (ug/kg) of target compound per dry weight of soil; p_S, the density of dry soil (2.65 g/cm^3) and e, the void fraction (estimated as 0.35 from field

Table 6. Calculation of the fraction of target compound in vapor-phase based on independent measurements of vapor-phase and soil mass (solid, aqueous, and vapor-phase combined)

Target Compound	Well No.	Concentrations		Mass per m^2		Fraction in Vapor-Phase
		Vapor-Phase C_V (ug/cm^3) x 10^{-2}	Soil Mass C_T (ug/kg)	Vapor-Phase M_V (ug) x 10^{-2}	Soil Mass M_T (ug) x 10^{-2}	F
Toluene/TMP	3	1960	203			
			233	470	349	1.35
	7	1206	151		402	1.17
			168	289	259	1.12
	8	143	221		290	1.00
			168	34	381	0.09
					289	0.12
n-Octane	3	98	72			
			62	24	123	0.19
	7	90	64		108	0.22
			74	22	109	0.20
	8	13	63		127	0.17
			83	3	109	0.03
					144	0.02
Ethylbenzene	3	117	284			
			291	28	488	0.06
	7	59	388		501	0.06
			247	14	669	0.02
	8	3	259		426	0.03
			278	0.7	447	0.001
					479	0.001
m,p-Xylene	3	231	35			
			19	55	60	0.92
	7	73	18		33	1.66
			18	18	32	0.55
	8	5	17		31	0.56
			ND	1.3	30	0.04
					ND	

measurements). The fraction of target compound, F, found in the vapor-phase is:

$$F = M_V/M_T$$

When all of the target compound is in the vapor-phase, the maximum possible value of F is unity. However, Table 6 shows that four values larger than unity were obtained. These anomalous values occurred because F is calculated from independent measurements - one from the vapor-phase directly, and the other of the soil sample. The value of F for any given target compound decreases roughly an order of magnitude from MW3 to MW8, which also is in increasing distance from the source of contamination. Toluene/TMP and m,p-xylene show the greatest tendency to be in the vapor-phase i.e. they have the largest F values.

Theoretically, a linear equilibrium relationship exists between M_V and M_T regardless of concentration. However, Table 6 shows values of F which vary markedly. This immediately suggests that the system being tested was not at equilibrium. A non-equilibrium condition could exist due to aerobic biodegradation or to the kinetics of sorption/ desorption. Biodegradation has been shown to significantly reduce the level of hydrocarbon contaminants sorbed on the soil particles in unsaturated systems. As an example, Kuhlmeier and Sunderland (27) recently showed that non- nutrient enhanced, natural microbial flora decreased the levels of toluene, ethylbenzene, and m,p-xylene from 214,

11.7, 92.4 ppb contamination levels to below detection limits (1ppb) for a respirometer vessel study of naturally contaminated soil. The kinetics of sorption may also limit the sorptive uptake of contaminant vapors from the soil atmosphere to soil particles and associated water. Even considering these factors, the concentration in the soil-sorbed phase should not be completely independent of the vapor-phase concentrations. Thus, considering the limited amount of this data, a strong conclusion is difficult to make.

4.6.2 Ground Water/ Vapor-Phase Distribution

Figure 26 shows the relationship observed between the subsurface vapor-phase and ground water concentrations for selected compounds at three monitoring well locations (locations MW3, MW7, MW8 on Figure 11) likely located within the NAPL region. A logarithmic plot was necessary to accommodate the full range of data. If the expected results were a constant ratio of vapor-phase to ground water phase concentration, at equilibrium, the relationship is described by Henry's Law:

$$C_v = Kh \ C_w.$$

Logarithmic transformation to facilitate data presentation gives:

$$\log C_v = \log Kh + \log C_w$$
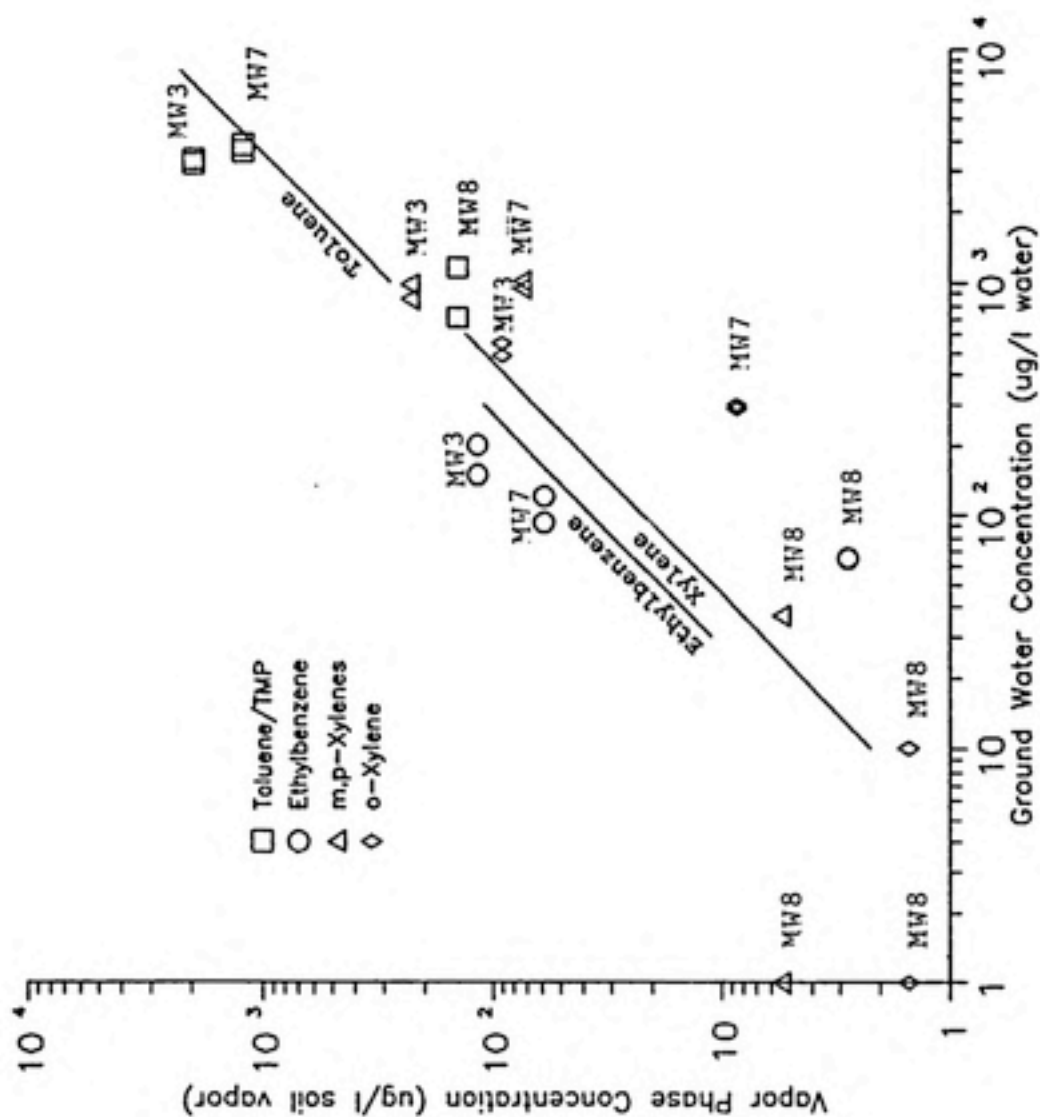
Figure 26. Distribution of Target Compounds Between Soil Vapor-Phase and Ground Water. Solid Lines Are Equilibrium Distributions Predicted by Henry's Law.

For Henry's Law to hold, the slope of the plots shown in Figure 26 should all equal one; theoretical partitioning lines with slopes of one and Kh values from the literature are included for comparison. Table 7 lists the slopes and R^2 values calculated from the data used in constructing Figure 26, in addition to literature vaues for Henry's constants.

Table 7. Comparison of Vapor / Water Partitioning Data to Henry's Law

	Slope	R^2 Value	Henry's (50) Constant (unitless)
Toluene/TMP[*]	0.54	0.89	0.28
n-Octane	(not detected in water)		136
Ethylbenzene	0.23	0.81	0.37
m,p-Xylene	0.86	0.84	0.22
o-Xylene	0.79	0.71	0.22

* Henry's Constant for Toluene/TMP was calculated for toluene. Trimethyl Pentanes, like other alkanes would have a larger value (e.g. n-octane)

As shown by Figure 26 most of the data for ground water/soil vapor-phase partitioning were fairly close to that predicted by Henry's Law, although the logarithmic scales may distort the extent of agreement in some instances. The most

notable discrepancies from equilibrium predictions were for ethylbenzene (at MW8), m,p-xylene (at MW8) and o-xylene (at MW7). As shown in Figure 23, MW7 and MW3 were located on the edge of the predicted region of NAPL contamination, while MW8 is well outside of the NAPL region. Thus, contaminant vapors at MW3 and MW7 vapors may have originated from the ground water and transverse diffusion of vapors from the NAPL region, while at MW8 likely originated from contaminated ground water only.

Much of the non-compliance of the data in Figure 26 with Henry's Law may be due to the violation of the assumption of dilute solutions (i.e. the concentrated mass of contaminant existing in the NAPL layer) and the distance that the vapor samples were taken from the water table (approximately 10 feet). Contrary to the results reported here, Evans and Thompson reported vapor-phase concentrations 1-2 orders of magnitude less than ground water concentrations as predicted by Henry's Law (12) in a similar field study comparison.

4.7 Cost and Efficiency Comparison of Vapor-Phase vs. Ground Water Assessment

Table 8 lists the estimated costs and efficiency of using this vapor-phase sampling method versus a typical ground water monitoring application. These figures show that soil vapor-phase sampling is much less expensive and time

consuming means of detecting and delineating the distribution of subsurface contamination than obtaining similar information from ground water samples.

Table 8. Estimated Cost and Efficiency Comparison: Vapor-Phase Sampling vs. Monitoring Wells

Monitoring Wells		Vapor-Phase Sampling	
23-ft x 2" Stainless Steel Casings (8) .	$1120	12-ft Stainless Steel Tubing ...	$ 75
Well Screens	600	Inner Rod and Welding Supplies .	25
Well Installation (8 wells)	8000	Stainless Steel Fittings	30
Teflon Water Bailer	100	3/8" Stainless Tubing	10
Riser and Iron Caps	200	Teflon-diaphram Air Pump	275
Grout, Bentonite, and Concrete	240	Flow Meter	50
Development Costs	160	Construction Costs	120
		Carbon Traps per 50	50
Total	10520	Total	635
Wells per Day	2	Vapor Wells per Day	8

Conclusions

The carbon sorption technique can serve as a rapid, inexpensive means of detecting and delineating the distribution of subsurface gasoline contamination. With a two-person sampling crew, the amount of data that can be collected per day of vapor-phase sampling would take several days with conventional drilling and sampling techniques. Vapor-phase sampling is even more cost effective as the depth to ground water increases because the costs of conventional drilling methods increase while the cost of vapor-phase sampling remains relatively constant. Remediation efforts would benefit by using the technique as an aid for effective location of monitoring and recovery wells.

The addition of an activated carbon trap to the conventional ground probe apparatus provides the following advantages over conventional vapor sampling methodologies: (1) a reduction in necessary field equipment, (2) the convenience of in-lab analyses, (3) the opportunity for replicate analyses of samples, and (4) the possibility for increased sensitivity. The importance of increased sensitivity may not be as apparent in the case of a gross contamination, however, its utility can be realized in the case of a small leakage over a period of time or when used to

define plume boundaries. In addition to the carbon trap advantages, fitting the ground probe with a removeable inner rod assures unrestricted flow of vapors from the subsurface, which is not always guaranteed with other probe designs.

While the methodology is a very practical and useful tool for detecting and delineating subsurface contaminant vapors, two disadvantages are worthy of mention. First, is the possibility of puncturing underground utilities if their locations are not known presents a safety hazard to the field crew; it is essential to have records of these utilities prior to sampling. Second, this vapor sampling procedure requires return of the field samples to the laboratory for analyses. Therefore, it does not allow for selection or alteration of sampling locations as would be possible with a real time measurement. The disadvantage could be overcome with a portable gas chromatograph and a mobile laboratory in which to perform extractions and analyses. However, the simplicity of the field procedure as it is now designed is well suited to use by field crews lacking laboratory or analytical skills such as would be found in small, regional offices of state agencies.

Soil vapor-phase measuremnets provided a convenient way to map the extent of contamination from a leaking underground storage tank at the Camp Lejeune site. Concentrations of target compounds ranged from 10,00 ug/l to less than 10 ug/l of soil vapor. The highest concentrations were found above the NAPL as was expected. The method also showed that

contamination exists well beyond the NAPL, although the concentrations drop off precipitously. This type of information is especially valuable when deciding on the locations of monitoring and recovery wells.

This research also showed vapor concentrations of toluene, as revealed by GC/MS analysis, that were much lower than expected from compositional analyses of toluene in gasoline. Therefore, monitoring only of aromatic hydrocarbon mixtures such as the widely reported BTX (benzene, toluene, xylenes) mixture may not truly represent the distribution and amount of the bulk of gasoline contamination present. Indeed, using this aromatic hydrocarbon monitoring mixture to describe the status of remedial progress may lead to the conclusion that remedial efforts are complete. Curtailing clean-up efforts based on this information could result in accumulations of straight and branched chain alkane vapors in overlying structures that could be explosive.

Attempts to relate vapor-phase concentrations to those in the soil proved difficult. Soil concentration, which includes the solid, vapor and aqueous phases, was roughly the same regardless of whether the sample was taken within or outside the NAPL region; however, vapor-phase contribution to the total decreased outside the of the NAPL. Although, there were exceptions, the vapor-phase/ground water data appeared to support equilibrium partitioning predeicted by Henry's Law, despite the fact that vapor-phase samples were obtained 10 feet or more above the ground water. Thus it may be

possible to use Henry's Law and vapor-phase concentrations to estimate ground water concentrations.

Recommendations for further investigation include using a larger carbon trap for monitoring hydrocarbons that are less effectively sorbed onto activated carbon (e.g. butanes, pentanes, hexanes). Because of the high volatility and low water solubility of these compounds, they would likely be seen near the surface soon after the spread of contamination. Although these compounds were not monitored in this study, they were seen in much higher concentrations than those that were monitored.

In addition, much more work is required in order to explain why toluene was seen in such low concentrations relative to the other compounds, which chromatographically elute at similar retention times.

Additional research into multi-depth sampling would be beneficial for indicating optimal sampling depth. This would minimize the time needed for placement of the probe while assuring adequate sensitivity for delineating the extent of contamination accurately.

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Appendix

Camp Lejeune Soil Vapor-Phase Analyses

6-24-87

ug/ 1000 cm3 soil vapor-phase

Sample	toluene/TMP	octane	ethbenz	mp-xyl	o-xyl
Travel Blank	0.000	0.000	0.000	0.000	0.000
AA	3239.710	19.252	14.098	38.177	5.939
BB	240.445	11.576	2.466	3.210	3.743
CC	0.000	0.000	0.000	0.000	0.000
R	1806.347	91.060	97.001	398.009	117.669
S	9594.073	425.018	826.608	3111.939	993.904
T	502.955	76.325	30.203	207.777	65.949
U	3235.674	133.464	191.447	705.484	234.954
W	227.169	7.080	2.214	3.668	3.352
X	65.996	1.063	0.504	0.697	0.691
Y	156.912	11.121	1.572	2.411	1.979
Z	22.689	0.000	0.000	0.678	0.000

4-4-87

Camp Lejeune Soil Vapor-Phase Analyses

ug/ 1000 cu3 soil vapor-phase

	Toluene	Octane	Eth-Benz	M,P-Xyl	O-Xyl	Cumulatives
A 9 min	977.823	119.696	9.700	18.584	3.739	1129.542
B 5 min	1329.741	145.866	6.831	9.570	NA	1492.008
C 15 min	1606.101	155.432	56.208	60.769	11.825	1891.334
D 10 min	5063.061	378.621	145.762	42.393	61.737	5691.574
E 10 min	1156.198	85.537	27.783	25.316	7.173	1302.006
F 10 min	677.395	28.316	4.583	5.139	NA	715.433
G 30 min	42.798	1.957	NA	NA	NA	44.754
H 10 min	637.783	88.921	10.497	21.052	5.417	763.670
I 30 min	NA	15.405	NA	0.265	NA	15.670

5-4-87

Camp Lejeune Soil Vapor-Phase Analyses
ug/ 1000 cu3 soil vapor-phase

	Toluene	Octane	Eth-Benz	M,P-Xyl	O-Xyl	Cumulatives
K 30 min	0.000	0.000	0.000	0.000	0.000	0.000
M 30 min	0.000	0.000	0.000	0.000	0.000	0.000
N 30 min	2.526	0.000	0.000	0.822	0.000	3.348
O 10 min	1884.000	138.000	49.000	125.000	21.642	2217.642
P 30 min	236.080	5.595	0.651	0.645	0.000	243.171
R 30 min	0.090	0.795	0.000	0.000	0.000	0.885
W 30 min	192.000	10.975	1.372	2.066	1.091	207.504

REPRODUCIBILITY/ DEPTH EFFECTS
ug/liter

SAMPLE	toluene	octane	ethbenz	m,p,-xyl	o-xyl	depth
RD1-6.5	253.27	7.69	6.15	14.63	3.21	6.5
RD2-6.5	408.61	10.36	10.97	25.90	7.08	6.5
RD3-6.5	355.79	7.98	7.78	17.67	4.54	6.5
RD4-6.5	311.99	7.26	8.74	18.56	5.17	6.5
Std Dev	65.91	1.39	2.03	4.78	1.61	
Mean	332.42	8.32	8.40	19.19	5.00	
95%Upper C.I	437.28	10.54	11.63	26.80	7.56	
95%Lower C.I	227.55	6.11	5.17	11.59	2.44	
RD1-9.5	652.96	21.42	18.85	44.72	10.15	9.5
RD2-9.5	920.68	29.11	27.59	64.23	16.38	9.5
RD3-9.5	467.13	9.80	13.92	28.01	7.28	9.5
RD4-9.5	703.83	18.82	20.23	45.52	11.02	9.5
Std Dev	186.54	7.96	5.65	14.80	3.80	
Mean	686.15	19.79	20.15	45.62	11.21	
95%Upper C.I	982.93	32.46	29.14	69.17	17.25	
95%Lower C.I	389.37	7.12	11.16	22.07	5.16	
RD1-11.5	474.86	16.82	13.09	32.70	6.24	11.5
RD2-11.5	897.90	33.31	27.60	67.97	16.61	11.5
RD3-11.5	902.85	27.15	29.41	62.29	16.55	11.5
RD4-11.5	781.33	21.64	23.28	52.26	12.20	11.5
Std Dev	200.92	7.11	7.31	15.49	4.90	
Mean	764.24	24.73	23.34	53.80	12.90	
95%Upper C.I	1083.90	36.04	34.97	78.46	20.69	
95%Lower C.I	444.57	13.42	11.72	29.15	5.11	

Ground Water / Vapor-Phase Distribution

Water	ug/L of water sample				
	toluene/TMP	octane	ethbenz	mp-xyl	o-xyl
Well #3a	3191.564	ND	149.0110	844.9663	482.1440
Well #3b	3342.056	ND	200.1093	974.5342	547.1859
Well #7a	3861.679	ND	92.48094	940.5658	285.3105
Well #7b	3621.586	ND	119.7800	1013.209	296.9582
Well #8a	708.3531	ND	17.35942	ND	ND
Well #8b	41.07766	ND	64.81786	ND	ND

Vapor	ug/ 1000 cu3 vapor				
	toluene/TMP	octane	ethbenz	mp-xyl	o-xyl
Well #3 (10 min)	1959.462	98.27005	116.8253	230.5840	90.80932
Well #7 (10 min)	1205.686	89.95831	58.69983	73.21035	8.545287
Well #8 (10 min)	142.7218	13.43459	2.779683	5.428417	1.509076

Comparison of Duplicate Samples Separated By Time (3 Months)
(peak area measurements)

SAMPLE	toluene	octane	ethbenz	mp-xyl	o-xyl
C15(4-4-87)	653202	48042	40165	41843	8450
C15(6-24-87)	510208	33843	30839	40180	10315
% CHANGE	-22	-30	-23	-4	+22
F30(4-4-87)	871149	26877	10470	10292	12388
F30(6-24-87)	908009	59698	16740	20054	17170
% CHANGE	+4	+222	+60	+95	+39
D10(4-4-87)	1372767	77520	69439	·19460	29411
D10(6-24-87)	745109	19918	24102	86154	29148
% CHANGE	-46	-74	-65	+443	-1