

HD
1694
.N8
N6
no.242

Report No. 242



METHODOLOGY FOR ASSESSMENT OF CONTAMINATION OF THE UNSATURATED ZONE BY LEAKING UNDERGROUND STORAGE TANKS

By

Francis A. DiGiano

Cass T. Miller

Anne C. Roche

Edward D. Wallingford



Department of Environmental Sciences and Engineering
University of North Carolina at Chapel Hill

November 1988



Water Resources Research Institute
OF THE UNIVERSITY OF NORTH CAROLINA



Price—\$8.00

Copies available from: Water Resources Research Institute
of The University of North Carolina
North Carolina State University
Box 7912
Raleigh, North Carolina 27695-7912

THE UNIVERSITY OF NORTH CAROLINA *is comprised of the sixteen public senior institutions in North Carolina.*

METHODOLOGY FOR ASSESSMENT OF CONTAMINATION OF THE
UNSATURATED ZONE BY LEAKING UNDERGROUND STORAGE TANKS

By

Francis A. DiGiano
Professor

Cass T. Miller
Assistant Professor

Anne C. Roche
Research Assistant

Edward D. Wallingford
Research Assistant

Department of Environmental Sciences and Engineering
The University of North Carolina
Chapel Hill, North Carolina 27599

The research on which this publication is based was supported by funds provided by the Water Resources Research Institute of The University of North Carolina.

WRRI Project No. 70057

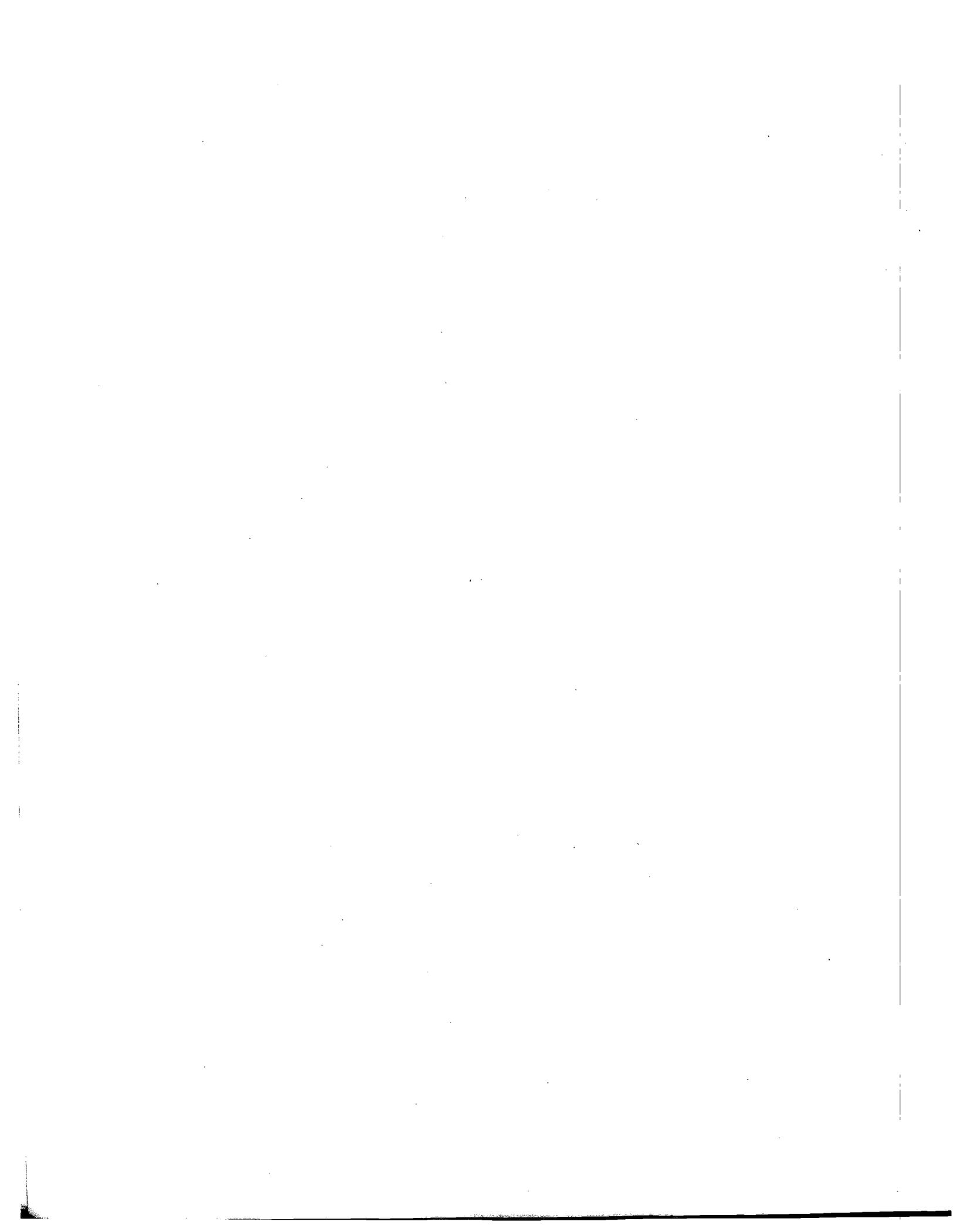
LIBRARY
Appalachian State University
Boone, North Carolina 28608

HD
1694
.N8
N6
ms. 242

df 5/18/90

ACKNOWLEDGMENTS

This work was performed within the Department of Environmental Sciences and Engineering of the School of Public Health at the University of North Carolina at Chapel Hill. We wish to thank Dr. Aziz Amoozegar-Fard, from the Soil Science Department of North Carolina State University, for his cooperation and assistance on the sampling aspects of this project. We were fortunate in receiving first-class treatment and excellent cooperation from Marine Corps Base Camp Lejeune—specifically Mr. Robert E. Alexander and Colonel T. J. Dalzell. The Base contractors deserve thanks for their cooperation as well: Bert Lea and James Gonzales of Specialized Marine, Inc.; and Richard Catlin of Richard Catlin & Associates. We are indebted as well to the staff of the Department of Natural Resources and Community Development—Perry Nelson, Douglas Dixon, Charles Wakild, and Rick Shiver to name but a few—for their assistance in site location, needs assessment, and the monitoring well permitting aspects of the project.



ABSTRACT

The groundwater resources of the U.S. have been contaminated by a variety of volatile organic pollutants that include solvents, petroleum products, and pesticides. Groundwater monitoring and renovation must be founded on the measurement of a contaminant concentration distribution in the subsurface environment. Many common volatile organic contaminants typically exist in several phases of the subsurface environment: as a nonaqueous phase liquid, as a solute dissolved in the aqueous phase, as a solute volatilized in the vapor phase, and as a solute sorbed to a solid phase. Determination of a contaminant distribution in the subsurface environment requires measurement or theoretical computation of the concentration in each phase—or some combination of the two approaches.

This work focuses on the investigation of three methods for measuring a contaminant distribution in the subsurface: an ultrasonic, mixed-solvent, solid-core extraction method; a nitrogen-purge, solid-core extraction method; and a driveable ground-probe, vapor-phase sampling method. Laboratory results demonstrate the theoretical basis and performance of each method, while an investigation at a Camp Lejeune site provides a field trial. Method development and testing are presented in detail for all methods. The results show all methods to have theoretical appeal. The best results in the field were obtained with the ultrasonic, mixed-solvent, solid-core extraction method and the driveable ground-probe, vapor-phase sampling method. Field data results show that concentrations in each phase may be roughly predicted by assuming equilibrium among all phases.

DISCLAIMER STATEMENT

The contents of this publication do not necessarily reflect the views and policies of the Department of Interior, nor does mention of trade names or commercial products constitute their endorsement by the United States Government.

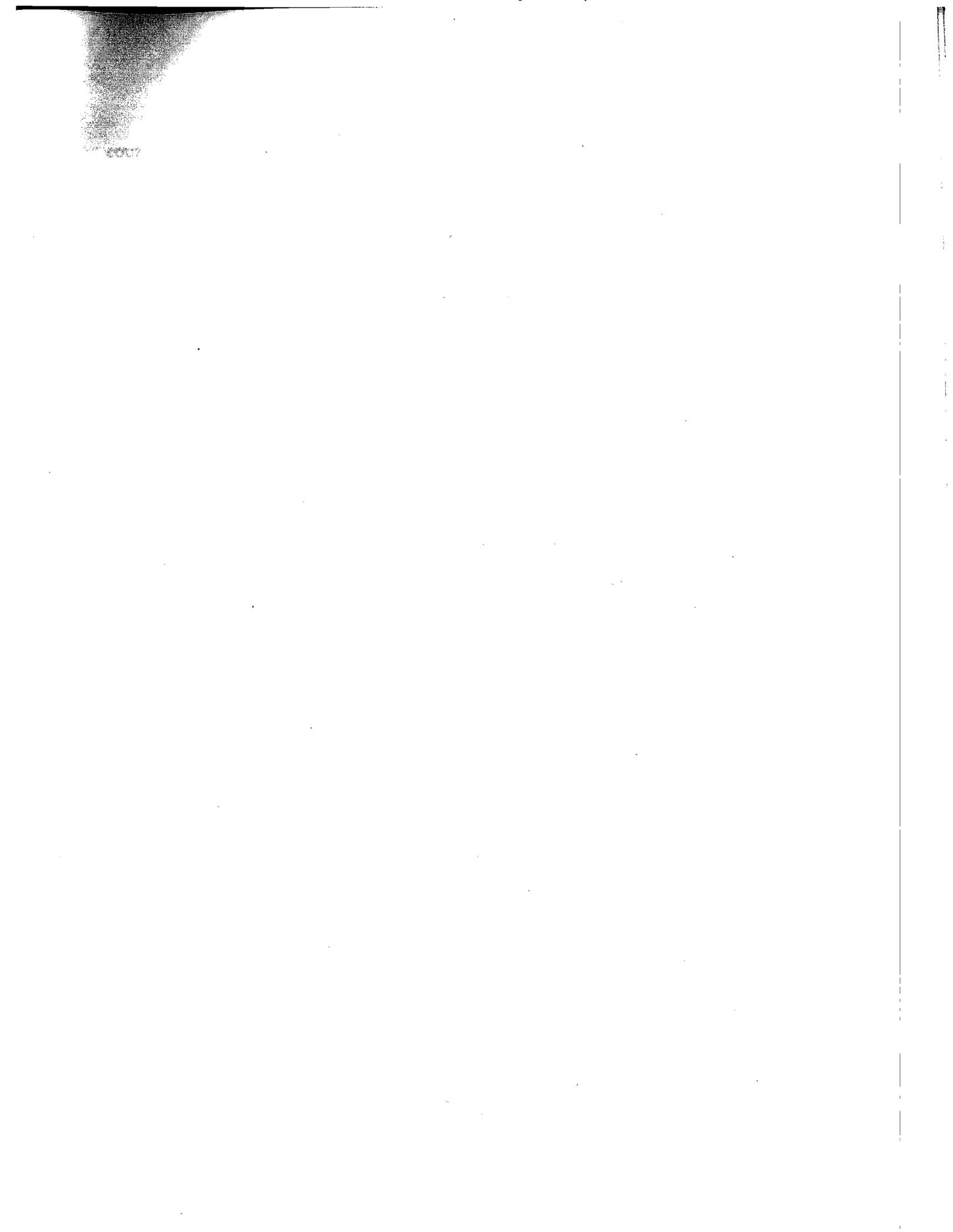
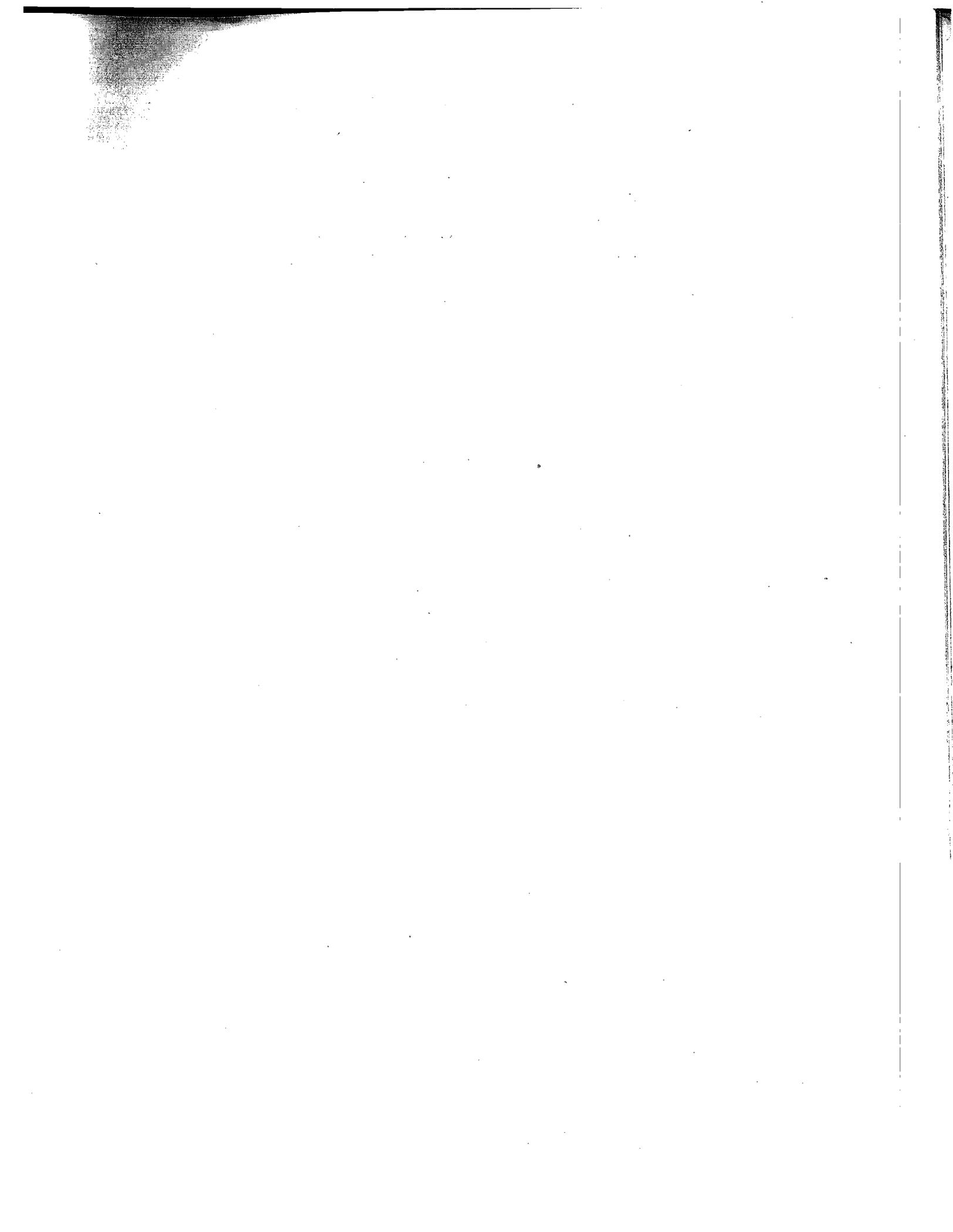


TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	ii
ABSTRACT	iii
LIST OF FIGURES	vi
LIST OF TABLES	viii
SUMMARY AND CONCLUSIONS	ix
RECOMMENDATIONS	xii
INTRODUCTION	1
PREVIOUS RESEARCH	2
GENERAL	2
EXTRACTION OF CORES	4
VAPOR-PHASE SAMPLING	7
METHODS	15
GENERAL	15
DESIGN OF CORE-SAMPLING SYSTEM	15
DESIGN OF VAPOR-PHASE SAMPLING SYSTEM	15
EXTRACTION OF SAMPLES	17
Core Samples	17
Aqueous Samples	21
Activated Carbon Samples	21
MEASUREMENT OF GASOLINE COMPONENTS	21
SELECTION OF TARGET COMPOUNDS	22
LABORATORY RECOVERY EXPERIMENTS	27
Recovery of Contaminants from Cores	27
Activated Carbon Traps	28
FIELD INVESTIGATION	32
SITE DESCRIPTION	32
CORE SAMPLING	35
VAPOR-PHASE SAMPLING	42
RESULTS	43
LABORATORY RESULTS	43
Recovery of Contaminants from Cores	43
Vapor-Sampling Method Development	47
FIELD RESULTS	51
Core Sampling and Extraction	51
Vapor-Phase Sampling	55

1111

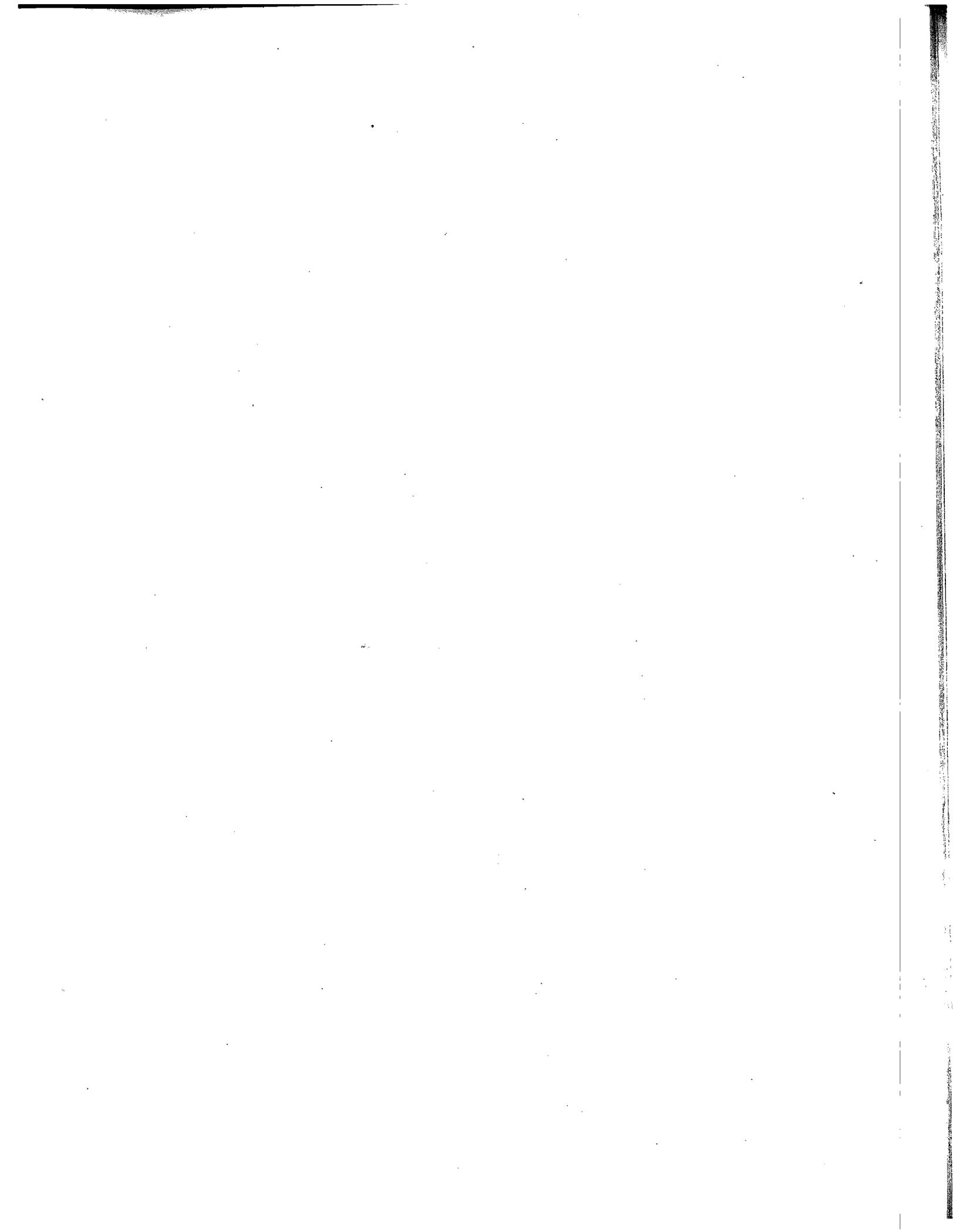
SOLUTE PARTITIONING	<u>Page</u> 63
REFERENCES	68



LIST OF FIGURES

1. Schematic, macroscopic illustration of a typical low-density NAPL multi-phase system.	3
2. Schematic, microscopic-scale illustration of four-phase system.	5
3. Surface flux chamber.	9
4. Down-hole flux chamber.	9
5. Cutaway view of passive dosimeter sampler.	11
6. Driveable ground-probe (DGP) designs used (a) by Neglia and Fav- eratto (1962) and (b) by Thorburn et al. (1979).	12
7. Schematic illustration of core sampling procedure.	16
8. Design of the vapor-phase sampling system.	18
9. Ultrasonication solvent extraction procedure.	19
10. GC/MS total ion chromatogram from vapor-phase sample BB.	24
11. Comparison of TMP spectrum to library spectrum.	25
12a. Apparatus for circulating the spiked solution through the core sample to sorb solutes.	29
12b. Apparatus to purge sorbed solutes from core sample and concentrate them on activated carbon.	29
13. Laboratory apparatus used to determine the adsorption characteris- tics of the carbon trap.	31
14. Location of Tarawa Terrace site at Camp Lejeune, Jacksonville, North Carolina.	34
15. Piezometric head distribution resulting from operation of the purge- well recovery system.	36
16. Contour map of apparent product thickness measurements collected from the monitoring well network.	38
17. Location of monitoring wells at Tarawa Terrace site at Camp Lejeune, Jacksonville, North Carolina.	40
18. Subsurface core sampling scheme.	41
19. Effect of storage of carbon trap at -13°C.	49

20. Effect of storage of carbon trap at 27°C.	49
21. Breakthrough curves for target compounds from a gasoline vapor mixture.	50
22. Comparison of nitrogen purge and ultrasonication analyses for samples collected between 20–21.5 ft below ground surface.	56
23. Estimated, vapor-phase concentration distribution based on 26 discrete measurements and universal kriging interpolation.	59
24. Toluene concentration as a function of depth for the 4 BB sampling locations.	60
25. Octane concentration as a function of depth for the 4 BB sampling locations.	61
26. Ethylbenzene concentration as a function of depth for the 4 BB sampling locations.	61
27. Total m- and p-xylene concentration as a function of depth for the 4 BB sampling locations.	62
28. Total o-xylene concentration as a function of depth for the 4 BB sampling locations.	62
29. Relationship between vapor-phases and groundwater concentrations for target compounds (in duplicate) at each monitoring well. Solid lines are equilibrium.	66



LIST OF TABLES

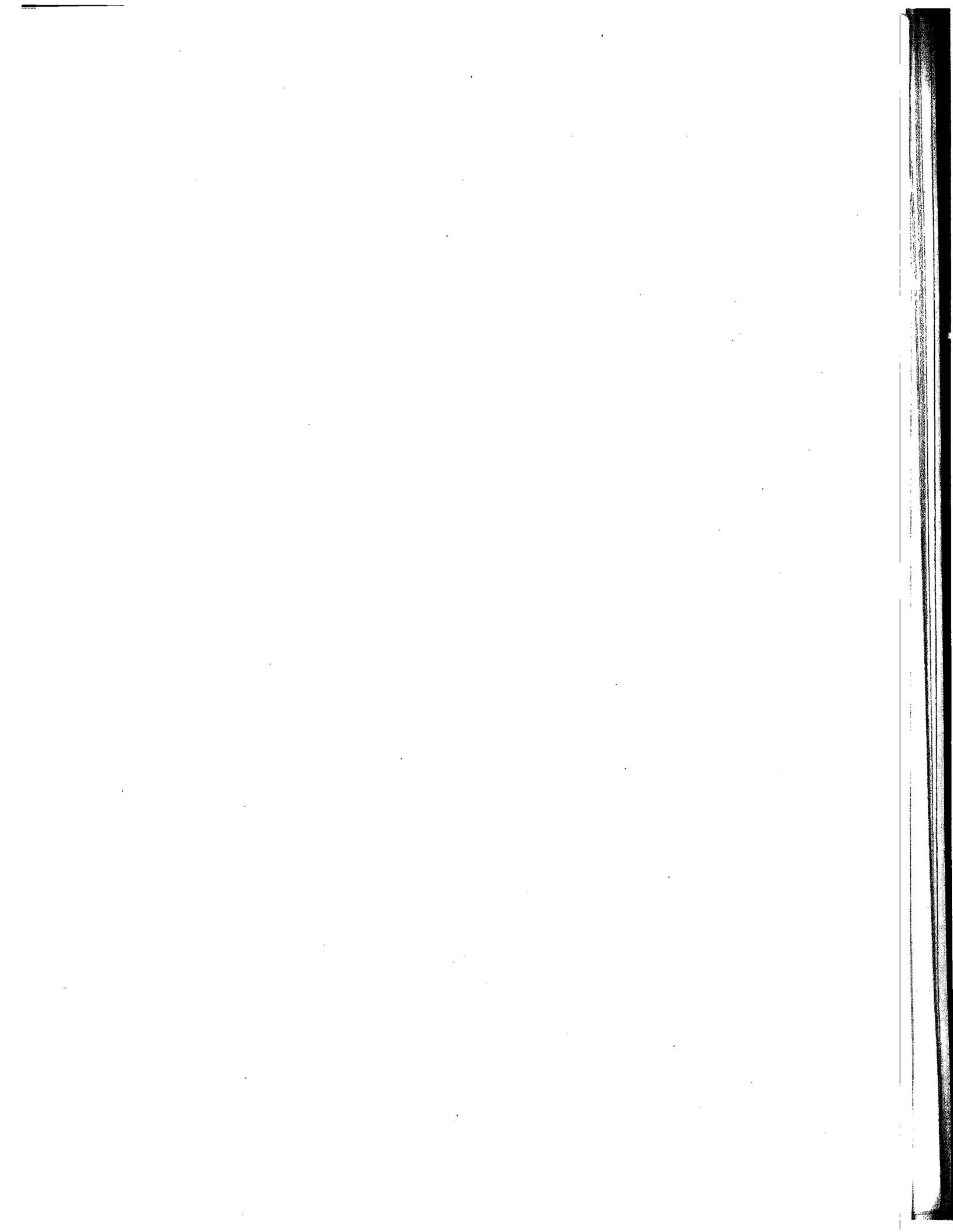
1. Major Components of Gasoline Detected by GC/MS Analysis of Vapor-Phase Sample BB.	23
2. Physical and Chemical Properties of Target Compounds.	26
3. Camp Lejeune Contamination and Cleanup Event Chronology.	37
4. Mass-Recovery Results by Ultrasonication.	44
5. Mass-Recovery Results by Nitrogen Purge.	46
6. Nitrogen-Purge Mass Recovery from Field Samples.	52
7. Comparison of Target Solute Concentrations and Moisture Content for Samples Analyzed Using the Nitrogen-Purge Method.	54
8. Target Solute Concentrations from Ultrasonic Analysis of 20-g Field Samples Collected at Depth of 21 Feet Below Ground Surface.	55
9. Comparison of Concentrations from Multiple Ultrasonication Analyses Performed on Samples Collected at 20.5 Feet Below Ground Surface.	57
10. Temporal Variation in Contaminant Concentrations Expressed as Percent Change Between 1 April 1987 and 18 June 1987.	58
11. Calculation of Fraction of Target Compound in Vapor Phase Based on Independent Measurements of Vapor Phase and Vapor, Solid, and Aqueous Phases Combined.	65



SUMMARY AND CONCLUSIONS

This research investigated three methods of measuring contamination of the partially saturated zone by leaking underground fuel tanks. Two of the methods relied upon obtaining a soil core from the field. These differed in the method of extraction: (1) by nitrogen purge of the entire core, followed by adsorption-solvent extraction and gas chromatographic (GC) analysis and (2) by sonication of a small sub-sample from the core, followed by solvent extraction and GC analysis. The third method focused on determining the contaminants present in the vapor phase of the partially saturated zone. This required use of a driveable ground probe (DGP) and activated carbon trap (to concentrate the contaminants), followed by solvent extraction and GC analysis. While each of these methods has been reported in the literature, there is little experience with them. Each has a number of system parameters that affect performance and their practical implementation for measuring the extent of subsurface contamination. This research combined laboratory study of the methods under controlled conditions with field study at the Marine Corps Base Camp Lejeune.

The soil core procedures required construction of a sampling tube that proved quite successful to use in the field, while also permitting convenient operation of the nitrogen purge system upon return to the laboratory. Extensive laboratory investigation was undertaken to determine the conditions that maximized recovery of a series of target compounds (toluene, octane, ethylbenzene and m,p xylene) known to be present in gasoline. Recoveries approaching 100% were achieved in the nitrogen purge procedure by: heating the soil core to 100°C; trapping water exiting the soil core prior to the adsorption step; and using activated carbon instead of Tenax as the adsorbent. Similar, high recoveries were achieved in the sonication procedure by: minimizing exposure of the sample to the atmosphere; using a series of two sonications (each 10 min. at 500 watt power) and extractions. The sonication procedure was advantageous because it requires far less time than either nitro-

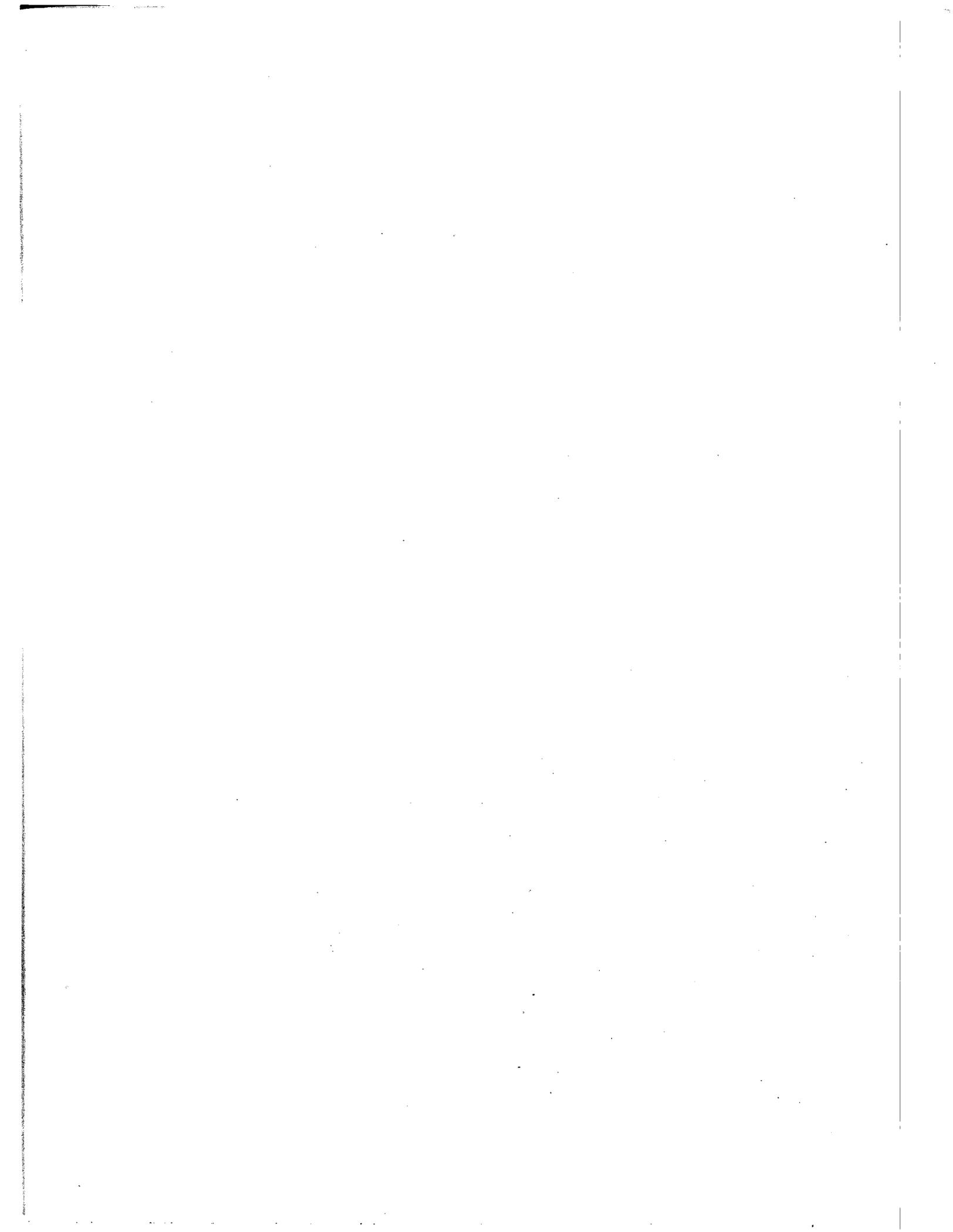


gen purge of the soil core or conventional soxhlet extraction. A comparison of the nitrogen purge and sonication procedures on field samples taken from the Marine Corps Base Camp Lejeune showed that the nitrogen-purge procedure gave lower recoveries of gasoline components selected as target compounds. One unavoidable problem with nitrogen purging is variability in hydraulic conductivity of cored sample; this means that uneven nitrogen purging may result.

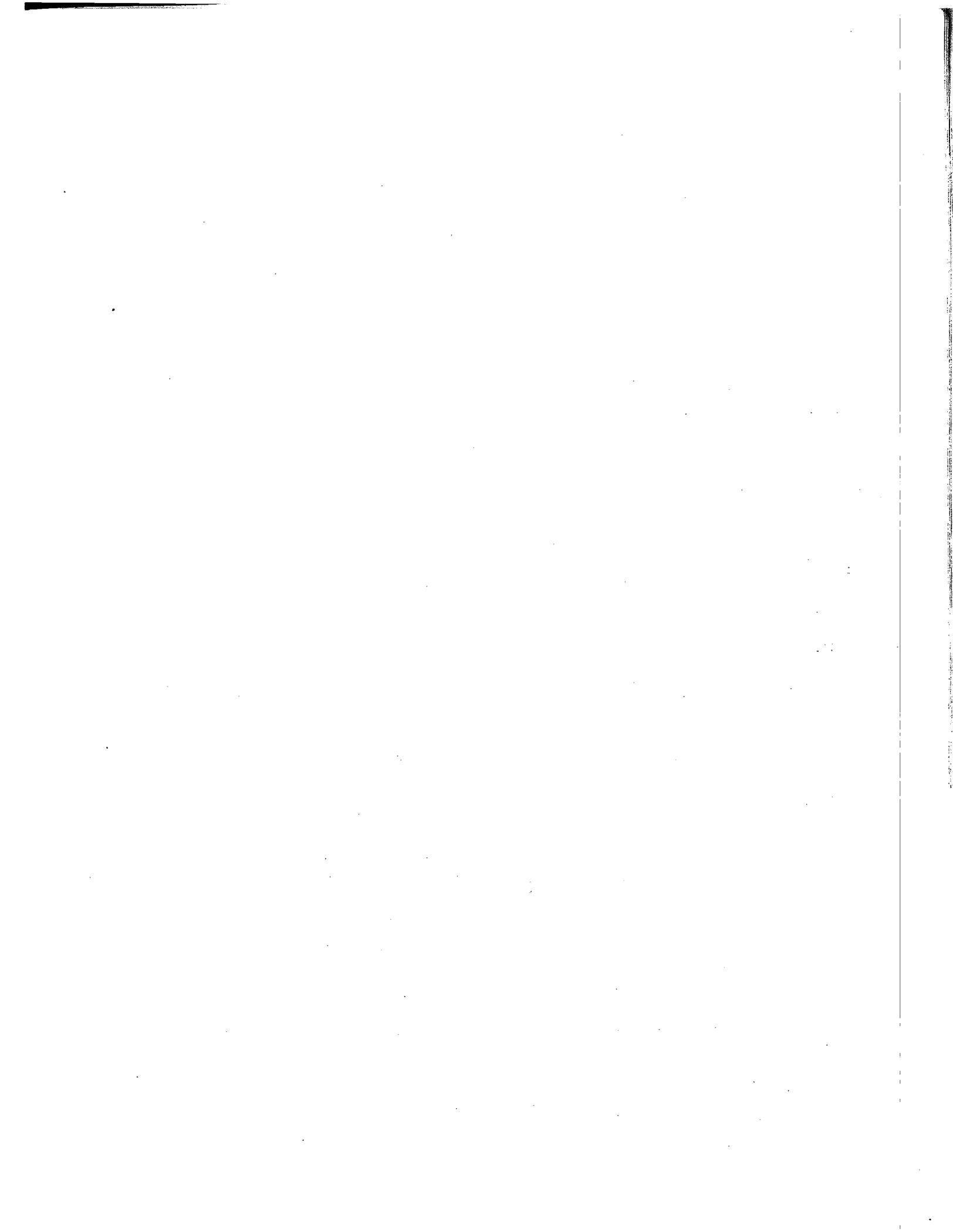
The soil core method, regardless of the subsequent sample handling by either nitrogen purge or sonication, was very useful in mapping the extent of contamination of the subsurface near leaking underground storage tanks. These contaminants recovered by such a device can be present in the vapor, solid, or aqueous phases within the core. A theoretical analysis based on literature values of partition coefficients and some field data suggests further that the aromatic hydrocarbons are rather uniformly distributed among all three phases. Thus the effectiveness of clean-up efforts cannot be properly assessed unless the nature of residual soil contamination is recognized.

The DGP with sorptive trap provides a practical alternative to the commercially available DGP with direct injection of vapor phase into a field GC. Although results may not be available immediately in the field, the method provides offsetting advantages. It seems particularly well-suited for use by regional, regulatory offices that may lack crew experienced in analytical methods and a budget to purchase a field GC. A two-person crew could easily obtain vapor-phase samples from say 10 to 20 locations in one day and mail the samples back to a central laboratory for processing; the samples can be stored (several weeks) without significant loss of analytes. Typical sampling times may be on the order of 5 or 10 minutes, as demonstrated by laboratory studies of controlled systems and the results of field tests.

Vapor-phase measurements provided a convenient way to map the extent of contamination from a leaking underground gasoline storage tank at the Camp Lejeune site. Concentrations of target compounds ranged from 10,000 ug/l to less than 10 ug/l of vapor



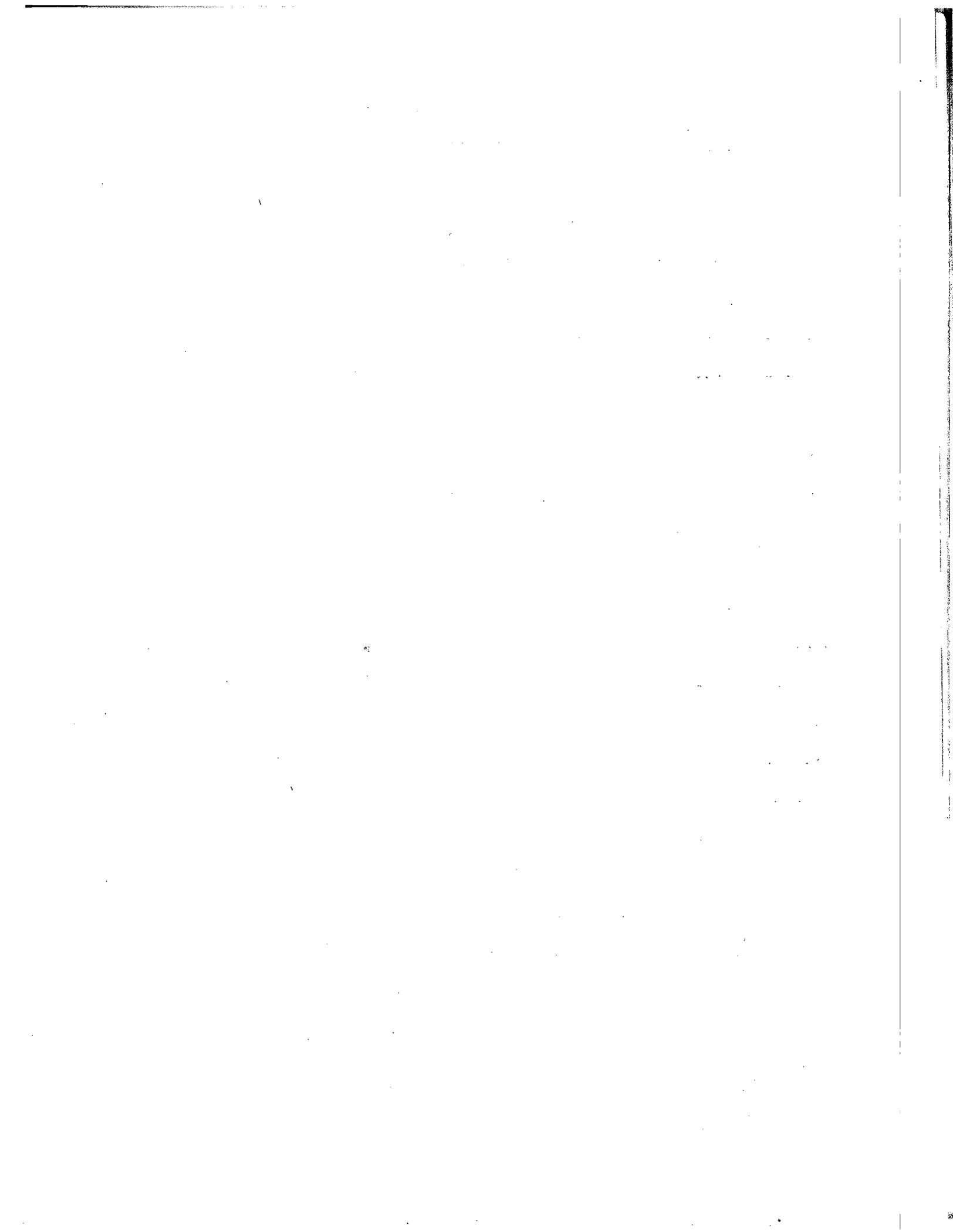
phase. The highest concentrations were found above the NAPL as was expected. However, the method was also able to show that contamination exists well beyond the NAPL, albeit the concentrations drop off precipitously. Attempts to relate the vapor-phase concentrations to those in the soil and the groundwater proved difficult. Core concentration, which included contaminant in the solid, aqueous, and vapor phases, was about the same regardless of whether the sample was taken from within or without the non-aqueous-phase liquid (NAPL) region. However, the vapor-phase contribution to the total decreased on either side of the NAPL region. Although there were exceptions, the data appeared to support equilibrium partitioning between the vapor and aqueous phases, despite the fact that vapor samples were obtained 10 ft or more above the groundwater. Thus it may be possible to use Henry's law and a vapor-phase solute concentration to estimate a groundwater solute concentration.



RECOMMENDATIONS

The work summarized in this document suggests several recommendations: some that are immediately applicable, and some that require additional research. These recommendations may be summarized by:

1. Routine use of the driveable ground-probe method investigated in this research should be considered by State personnel and consultants, because it is a rapid and economical method of investigating the distribution of subsurface contamination.
2. The ultrasonic extraction method investigated in this research should be used by State personnel and consultants for cases where an estimate of total contaminant mass and distribution in the subsurface is needed.
3. Vapor-phase mass transfer is an important process in the subsurface, which leads to the distribution of contaminant in all directions from an initial source. This distribution can result in a substantial mass of solute retained within the partially saturated zone—complicating source identification and aquifer restoration. This process requires further investigation at the laboratory, field, and theoretical levels.
4. Additional research is needed to define experimentally and theoretically the significance of nonequilibrium phase partitioning in the subsurface. It seems likely that the rate of interphase mass transfer and equilibrium hysteresis are important areas of research—areas where advancement can and should be made in order to more accurately predict contaminant movement in the subsurface.



INTRODUCTION

Leaking underground storage tanks are one of the most frequent causes of groundwater pollution in the United States. For example, a recent survey estimated that more than 75,000 gasoline storage tanks were leaking (Mackay et al., 1985), while many other tanks are approaching their design life (Sun, 1986). Upon release of gasoline in the subsurface, each of the many organic components in gasoline is transported by bulk movement and inter-phase transfer (i.e., to the groundwater, soil and vapor); some of these components may also be degraded or transformed by either biotic or abiotic processes. The result is a spatial and temporal distribution of contaminants in the subsurface environment. The challenge for regulatory agencies and clean-up firms is to obtain and interpret measurements of this distribution in order to take corrective action. If the proper data are obtained, it is possible to: evaluate the severity of the contamination; rank sites for clean-up priority; predict future distributions of contaminants; and perform risk-assessment analysis.

While the ultimate use of contaminant measurements is to assess the extent of groundwater contamination, the problem of leaking underground storage tanks begins in the partially-saturated zone. Thus, measurements of contaminant distribution within this zone can be worthwhile for assessing the proper corrective action provided that convenient techniques are available.

The objectives of this research were to develop and test two methods for measurement of organic contaminants in the partially-saturated zone. These methods involved sampling and analysis of subsurface cores and vapor withdrawn from the sub-surface. Method investigation included laboratory control experiments and field-scale testing.

The results of this work are: (1) a design and an operational protocol for a sensitive vapor-phase sampling probe; (2) a comparison of methods for subsurface core contaminant extraction—along with an analytical protocol; (3) and a field-scale comparison of the results from application of both methods.

PREVIOUS RESEARCH

GENERAL

The terminology used in this report is somewhat different than that often noted in the literature. For example, this report will use *subsurface core* or simply *core* samples to describe samples collected from the subsurface that typically include 3 phases: solid, aqueous, and vapor. Such samples are frequently called *soil cores*. *Vapor-phase* or *gas-phase* concentration will be used to describe the mass of solute per volume of vapor in the interstices of the subsurface solid matrix—a quantity which is often termed the *soil gas* concentration. The reasons for this divergence are twofold: the common name is a misnomer, because soil is a solid phase and not a gas or vapor phase; and the analysis performed in this work included samples from the soil zone, from the intermediate zone, and from locations in excess of 20 ft below ground surface—approaching the phreatic surface. Therefore, use of the term *soil* infers an overly restrictive description of the work performed here and the methods used to perform that work.

A fluid that is immiscible with water is termed a non-aqueous-phase liquid (NAPL). NAPL's may be either less dense (e.g. petroleum products) or more dense (e.g. chlorinated solvents) than water. Consider the spill of a low-density NAPL released into the subsurface environment from a leaking underground storage tank, which is illustrated by Figure 1. After release the NAPL moves primarily vertically through the partially-saturated zone (unsaturated zone) in response to gravity forces. As the NAPL moves vertically: a portion of the immiscible fluid is retained by capillary forces in the pore spaces (Schwille, 1967); soluble components of the NAPL are transferred to the pore water phase; volatile components of the NAPL are transferred to the vapor phase; and the NAPL eventually intercepts the water table and begins migration in the direction of groundwater movement—if a sufficient volume of NAPL is released.

The above scenario leads to the distribution of contaminants in four phases: the NAPL

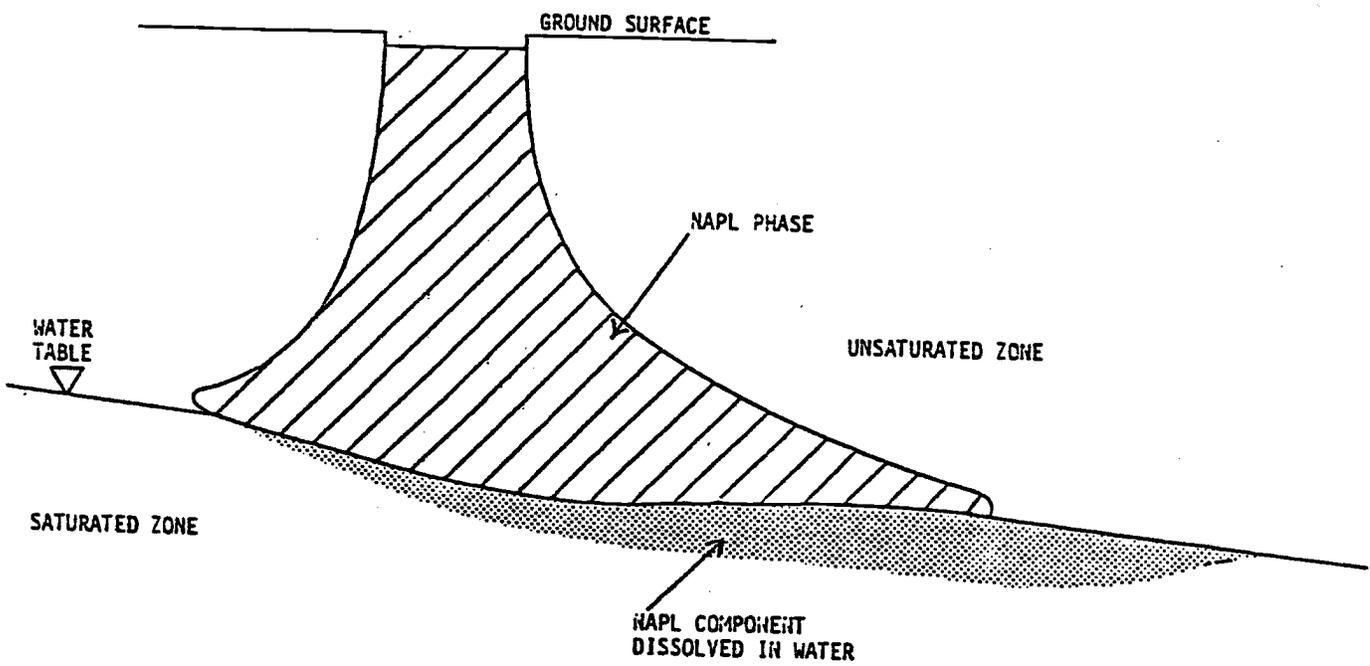


Figure 1. Schematic, macroscopic illustration of a typical low-density NAPL multi-phase system.

phase, the aqueous phase, the vapor phase, and the solid (soil, partially-saturated sands, silts, or clays, and aquifer materials) phase. A schematic, microscopic-scale illustration of a four-phase system is given by Figure 2. The amount and distribution of contaminant in each phase is an important consideration for evaluating and implementing clean-up plans.

A body of literature exists describing the distribution of contaminants among all phases for a variety of hydrogeological conditions and solute contaminants. A thorough review of this literature is beyond the scope of this report. Rather, a brief review of two areas key to this research follows: methods of subsurface core extraction, and methods of measuring the vapor-phase concentration.

EXTRACTION OF CORES

The measurement of contaminants in a core sample requires the removal of contaminants from all phases of the sample: solid, aqueous, and vapor. Therefore, measurement of contaminant levels in a subsurface core is a composite measurement of levels in all phases present in the sample. Methods of contaminant concentration extraction typically rely on some combination of: (1) elevated temperature or other sources of energy input to the system—to encourage desorption, an endothermic process; (2) introduction of an organic solvent—to concentrate hydrophobic solutes; and (3) circulation of fluid with a small concentration of the contaminants of concern—to impose nonequilibrium conditions that yield solute mass transfer to the circulated fluid.

Soxhlet extraction is the most widely used solvent extraction method for volatile organic recovery from solid-phase samples. In this method, a solid sample is placed in a glass thimble and continuously extracted with an appropriate solvent through a repetitive closed distillation-condensation process. The usual extraction time in this method is 24–48 hr, providing exhaustive extraction of the sample. However, this lengthy extraction time is not practical for a large volume of samples.

Ultrasonication of a natural solids-solvent mixture is another method by which volatile

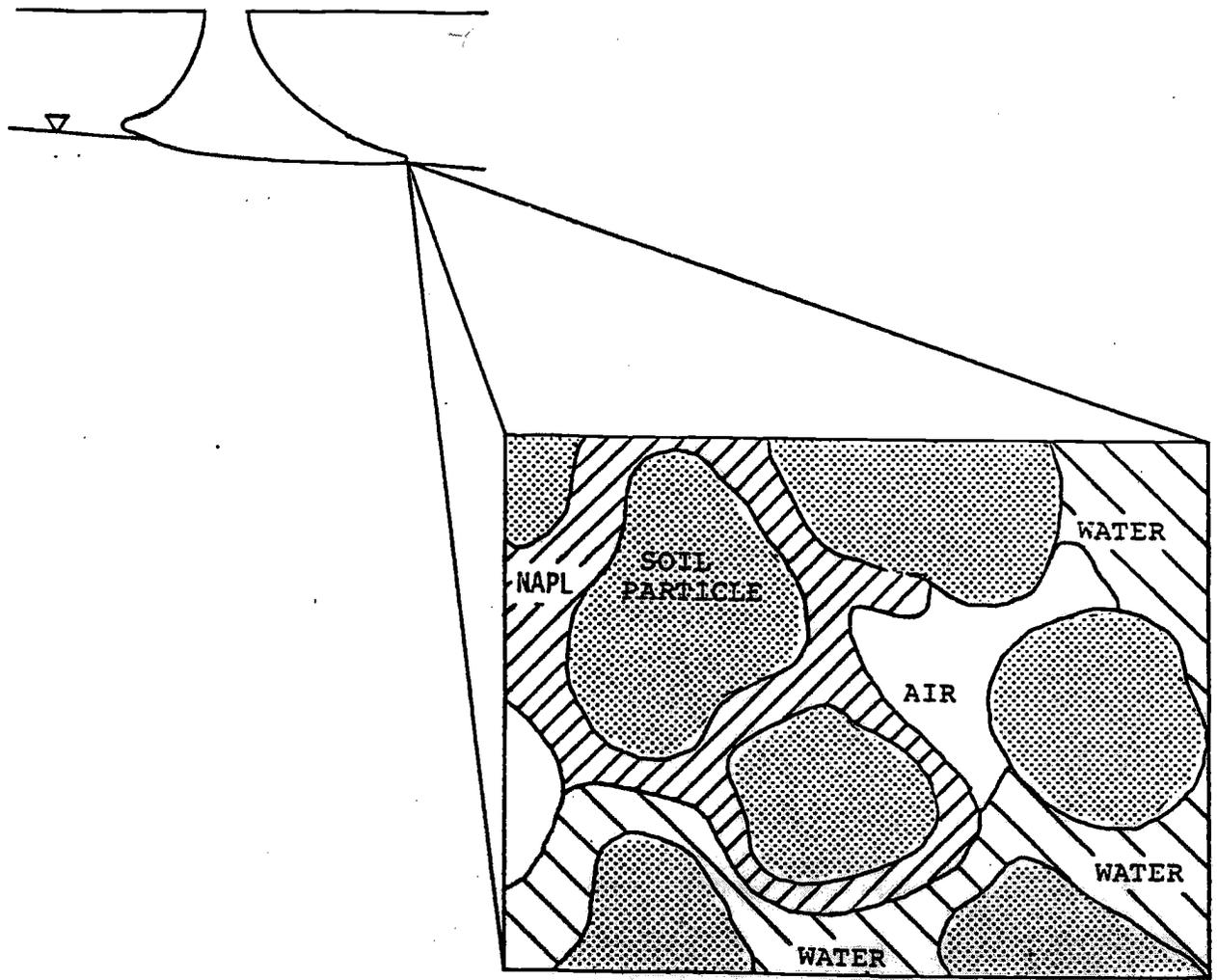


Figure 2. Schematic, microscopic-scale illustration of four-phase system.

organic compounds can be extracted. Ultrasonication involves the agitation and disruption of solute particles from the solid phase by means of high frequency sound waves. Johnsen and Starr (1972) first developed this method for the recovery of pesticides (dieldrin and heptachlor) from sediments.

Petersen and Freeman (1982) used soxhlet and sonication extraction to extract phthalates from wet and dry subsurface materials. They found low recoveries and high variability using soxhlet extraction, with dry solid-phase samples yielding better recoveries than initially wet samples. Sonication extraction gave better recoveries than soxhlet extraction for both the wet and the dry samples.

Hamilton et al. (1984) investigated soxhlet extraction of hydrocarbons from river sediments. The extractions were carried out for 48 hr with a solvent mixture (65% methylene chloride and 35% methanol). Recoveries of 97% were reported for total extractable hydrocarbons.

Laseter et al. (1980) also employed a rapid solvent extraction method. They obtained subsurface solid-phase samples via a split-spoon sampler, added 1 ml of hexane to a 1 g subsample from the core, and equilibrated the sample on a vortex mixer for 30 seconds. Recoveries ranged from 80–90% for aromatic chlorocarbons.

Another study compared soxhlet extraction of aromatic and aliphatic hydrocarbons for 76 hr with ultrasonication extraction. Recoveries for this experiment were 92% for the aromatic hydrocarbons and 96% for the aliphatic hydrocarbons, using soxhlet extraction as the reference method. The ultrasonic extraction was performed by extracting the solid-phase sample with a solvent pair (2:1 volume ratio of methylene chloride and methanol, respectively) six separate times, followed by concentration with a rotary evaporator and a gentle stream of nitrogen (Grimalt et al., 1984).

Jenkins and Grant (1987) performed a comparison study using 2 different solids, 2 different target compounds (trinitrotoluene and trinitrobenzene), 2 different solvents (acetonitrile and methanol), and four different techniques (soxhlet extraction, ultrasonic bath

extraction, mechanical shaker extraction, and a homogenization sonicator extraction). The ultrasonicator bath method was recommended because: more samples could be processed at one time, recoveries were comparable with the soxhlet extraction, less time was necessary for the extraction procedure, and the water content of the sediments did not seem to affect the extraction efficiency of this method.

Slater et al. (1983) used a dry purge method of a clayey solid-phase sample to detect volatile organics. An undisturbed representative sample (800 g) was collected by means of a split-spoon drive sampler and a hollow-stem, continuous-flight auger. The heated sample was purged with a 40 cc/min of nitrogen for 20 hr onto an activated carbon trap. The recoveries for this method ranged from 60-110% for freon, 1,1,3-trichloroethylene, and perchloroethylene. The advantages of this method are: the large sample volume reduces the effects of small-scale sample heterogeneity; and less handling of the sample is required.

VAPOR-PHASE SAMPLING

The state-of-the-art of vapor-phase sampling is described in a recent American Petroleum Institute publication (Eklund, 1985). Sampling methods are divided into the following categories:

- surface flux chambers
- downhole flux chambers
- accumulator devices
- driveable ground probes (DGPs)

While these appear to offer the user a wide choice, none of the methods has been tested extensively enough to date to establish what may be termed an acceptable standard procedure. Some have been brought to commercial development but these are "first generation" designs.

A surface flux chamber is shown in Figure 3. A vapor-phase sample is trapped in the chamber located at the ground surface. The vapor is then passed to a field gas chro-

matograph (GC) by purging the chamber with an inert carrier gas. Use of this device is reviewed by Eklund and Schmidt (1983). Being an in-situ measurement, it simplifies sample handling greatly thus being fairly rapid. Because augering is not required, it can be applied to any field condition. However, the main disadvantages are that only vapor near the surface can be measured and dilution of the vapor collected by the carrier gas results in a loss of sensitivity in GC analysis.

Down-hole flux chambers are similar in principle to surface flux chambers but allow measurement of vapor concentrations for any depth thereby overcoming one disadvantage of surface flux chambers. The device, as shown in Figure 4, is placed in the ground using a hollow-stem auger, although a hand auger could also be used for shallow depths. This method has been used at hazardous waste sites (Evans and Thompson, 1986).

Accumulator devices offer an alternative in-situ method of vapor-phase sampling. The objective is to eliminate purging of the vapor phase into a GC. Instead, the organic compounds in the vapor phase are concentrated directly onto a sorbent material implanted in the subsurface. The organic compounds reach the sorbent material by molecular diffusion. In the air and industrial hygiene field, these devices are known as passive dosimeters. In fact, Kerfoot, et al. (1986) recently reported the use of such commercially available, organic vapor monitors to measure chloroform in the vapor phase. A cutaway view of the sampler-manifold assembly is given in Figure 5. The monitor itself is made of activated carbon; in this application, it was suspended inside a 1-quart metal can at a depth of 1 ft below the surface. After a 2-wk exposure, the dosimeters were retrieved and extracted for GC analysis of the organic compounds of interest. The concentration in the vapor phase is computed from Fick's Law of steady-state diffusion. Voorhees, et al. (1984) describe a similar method, differing only in the technique used to desorb the organic compounds collected on the dosimeter. The sorbent (activated carbon) is coated onto a ferromagnetic wire, which makes it possible to use Curie-point desorption mass spectroscopy and thus eliminates extraction by an organic solvent. This method was used to measure tetra-

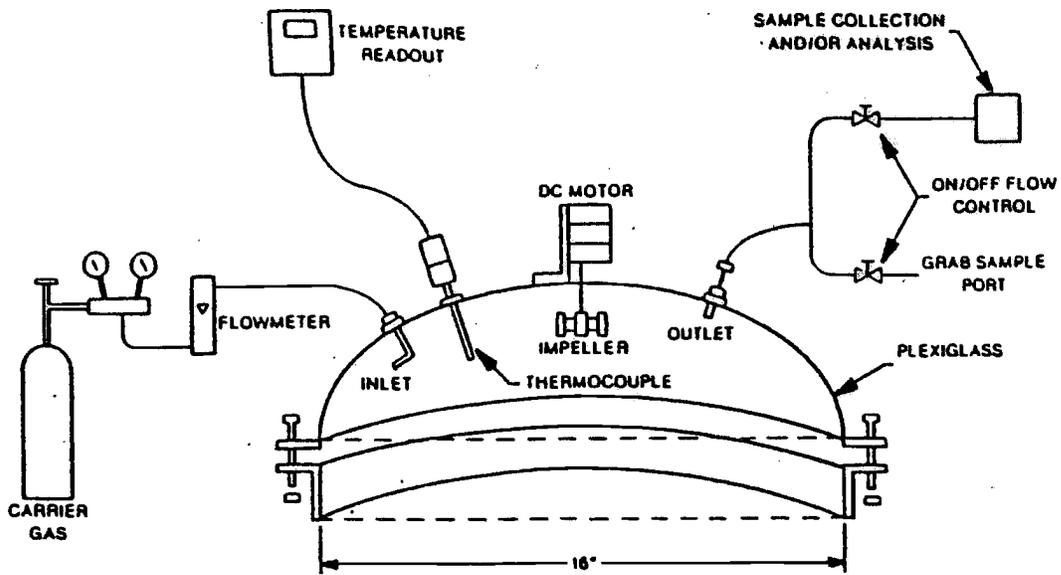


Figure 3. Surface flux chamber.

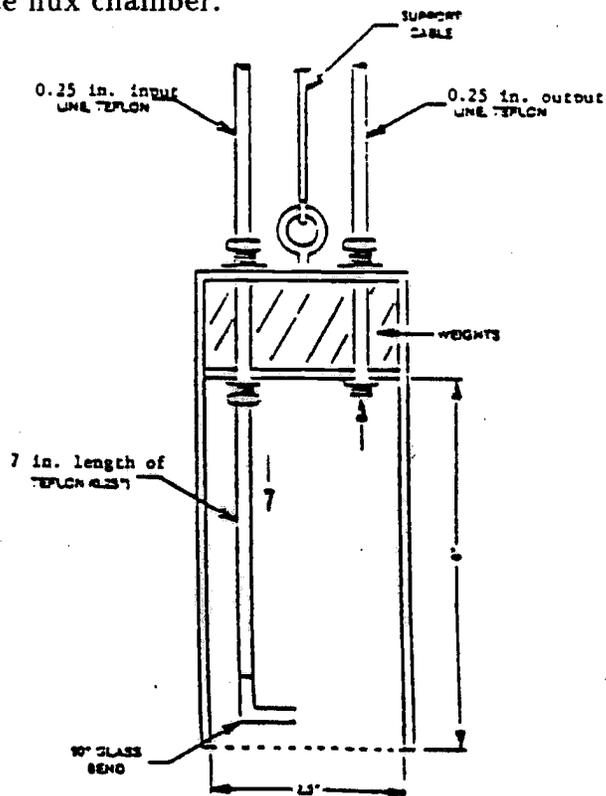


Figure 4. Down-hole flux chamber.

chloroethylene in the vapor phase.

Accumulator devices offer advantages of simplicity, relatively low-cost and suitability for various site conditions. However, sampling times tend to be quite long (on the order of weeks) in order to accumulate sufficient mass of organic compounds to detect; this is because such passive samplers rely on molecular diffusion for vapor-phase collection.

The driveable ground probe (DGP) method is, according to a recent American Petroleum Institute report (Eklund, 1985), recommended over all the others. A hollow tube is hydraulically driven or hammered to a desired depth as illustrated in Figure 6. The tube has an opening(s) at the bottom to allow vapors to enter the tube from the surrounding media. A pump is used to bring a vapor phase to the surface where a small aliquot (a few ml) is withdrawn for GC analysis on-site. This method has been used for decades in oil exploration (Neglia and Favretto, 1962) to detect hydrocarbons at ppm levels.

The DGP method has been adapted for various field site investigations (Thorburn et al., 1979; Colenutt and Davies, 1980; Colenutt and Thorburn, 1980; Lapella and Thompson, 1983; Swallow and Gschwend, 1983; Radian, 1984). Several organic solvents (trichloroethylene, perchloroethylene and trichloroethane) were measured above a contaminated aquifer in Santa Clara, California (Lapella and Thompson, 1983). The amounts found in the vapor phase were in rough agreement with predictions based on gas-liquid partitioning coefficients. In another application, the areal extent of 2 subsurface petroleum spills was determined (Evans and Thompson, 1986). In both instances, the total hydrocarbon concentration (i.e. the sum of all the detectable volatile components of the petroleum) decreased rapidly beyond the edge of the groundwater plume. Thus the hydrocarbons in the vapor phase originated from volatilization from the non-aqueous-phase layer. Radian Corporation (1984) reported success in using the method to detect the advancement of a contaminant plume; however, only the lighter fraction of the gasoline components could be detected in the vapor phase.

The DGP method has been modified to allow for concentration of organic compounds

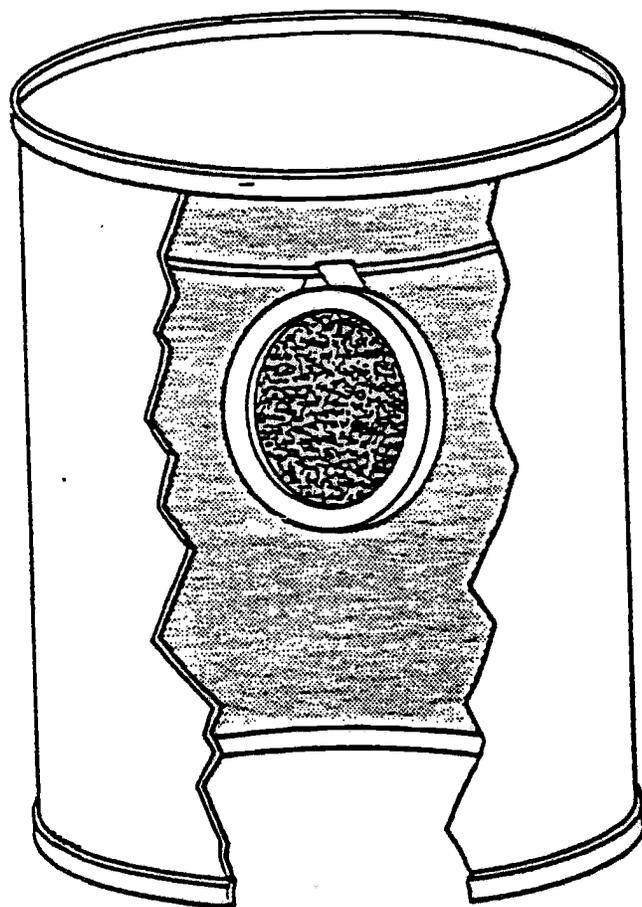


Figure 5. Cutaway view of passive dosimeter sampler.

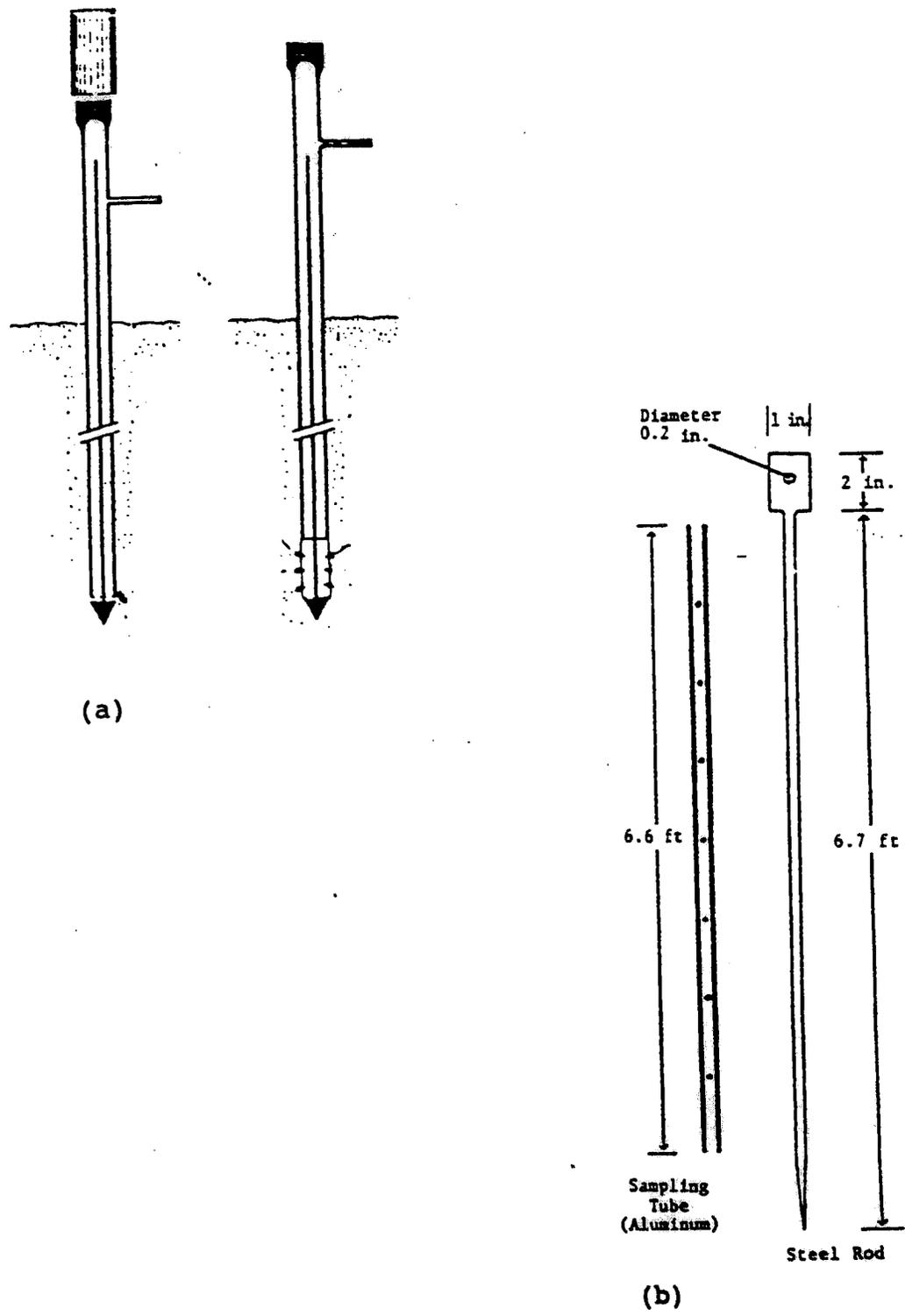


Figure 6. Driveable ground-probe (DGP) designs used (a) by Neglia and Faveratto (1962) and (b) by Thorburn et al. (1979).

in the vapor phase (Thorburn et al., 1979; Colenutt and Davies, 1980; Colenutt and Thorburn, 1980; Swallow and Gschwend, 1983). Instead of withdrawing a vapor-phase sample for injection into a GC, it is continuously passed through an adsorption trap for a period of time ranging from minutes to hours. The organic compounds are then desorbed for GC analysis, which is performed in a laboratory rather than in the field. The first report of this approach appeared in 1979 for detection of methane and other gases from landfill sites (Thorburn et al., 1979). Reports that followed from the same investigators in 1980 discussed the application to detection of other organic compounds at a landfill site (Colenutt and Davies, 1980; Colenutt and Thorburn, 1980). In each instance, the adsorbent was activated carbon.

A synthetic, porous polymeric adsorbent (Tenax) has been used instead of activated carbon for concentration of vapor-phase contaminants above a contaminated aquifer (Swallow and Gschwend, 1983). The Tenax trap is desorbed thermally rather than with an organic solvent. This is accomplished by attaching the trap directly to the inlet port of a GC and heating it to sweep the organic compounds into the GC column for detection. This eliminates the interference of a solvent peak and increases sensitivity because there is no dilution of the organic compounds by the solvent. The disadvantages, however, are that the hardware to adapt a GC for thermal desorption is expensive and complex; only one opportunity for analysis is provided (the trap is desorbed completely); thermal decomposition of some organic compounds may occur; and finally, the sorptive capacity for Tenax is much less than that of activated carbon for a wide variety of compounds.

While the literature does contain some reports of the DGP method modified to include a preconcentration step using an adsorption trap, there is little information on its applicability to detection of gasoline vapors, the specific point of interest in this research. Moreover, the method is still in the development stage with more work needed on the design of the DGP itself, verification of the sorptive capacity of the trap for specific organic compounds, and application to actual field conditions.

Preconcentration may not be necessary in many applications because direct injection offers enough sensitivity. However, direct injection requires use of a fairly expensive, portable GC and a field crew skilled in analytical techniques. On the other hand, preconcentration usually means that samples are not analyzed in the field but instead must be sent back to a laboratory. In addition, preconcentration requires that the adsorption and desorption characteristics of each compound of interest be known in order to calculate concentrations correctly. For example, it has been shown that water vapor can decrease the adsorption of many volatile organic compounds due to competition (Chiou and Shoup, 1985; Tang, 1986). A more detailed comparison of direct injection vs. preconcentration from the analytical perspective is given by Nunez et al. (1984). In general, quantitative results obtained by direct injection are not as accurate. This is especially true when analyzing for many compounds in a mixture such as gasoline; less volatile components may have lower concentrations in the vapor phase and will not be easily detected by direct injection (Nunez et al., 1984).

METHODS

GENERAL

Methods included design of field equipment for collection of cores and vapor-phase samples and development of laboratory methods for subsequent analysis of these field samples. The following sections detail these methods, while discussions of the field site and application of these monitoring methods in the field are presented in the next chapter.

DESIGN OF CORE-SAMPLING SYSTEM

Subsurface core samples were collected using a hollow-stem auger drilling method and a split-tube sampling method. A schematic illustration of this core sampling procedure is shown on Figure 7. The hollow-stem auger was used to advance drilling to the point immediately above where a sample was desired. The drilling rig was disconnected from the auger string and a split-tube sampler was connected to a string of drill rod and lowered down the hole. The sampler was then advanced into the undisturbed region of the subsurface by pounding the drill rod repeatedly with a drop hammer. After the sampler was advanced 1.5 feet the sampler was removed from the hole with the in situ samples retained in the split-tube sampler. The ends were then removed from the split-tube sampler, and the sampler was disassembled. Inside the sampler 3 brass sleeves (2.5-in diameter by 6-in long) filled with the subsurface core material remained. The brass sleeves and their contents were removed from the sampler, and the sleeves were capped with vapor-tight polyethylene caps and stored at 4°C.

DESIGN OF VAPOR-PHASE SAMPLING SYSTEM

Figure 8 illustrates the design of the vapor-phase sampling system. A DGP was constructed of 0.675-in OD, (0.2-in wall) 304 stainless-steel tubing with a conical tip (0.4-in opening) at one end to allow entrance of vapor and a 0.375-in diameter inner rod fitted with

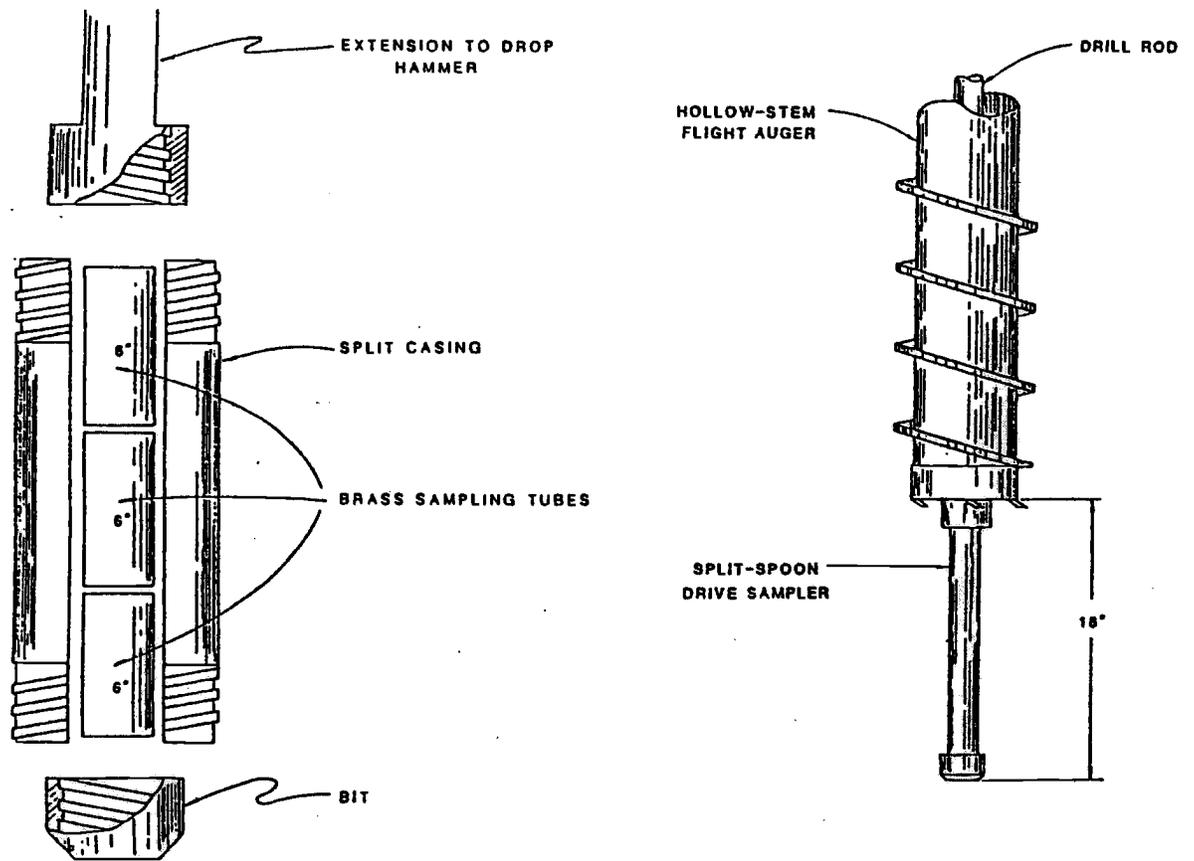


Figure 7. Schematic illustration of core sampling procedure.

a hardened steel driving point. The probe assembly was inserted by driving on a hammer block. Withdrawal of the inner rod left a void space in the media where the driving point had protruded below the outside tubing, thus giving an opening to the sampling tube that was not clogged by solid particles. The probe assembly was connected to the vacuum pump (Thomas Industries Model 115), adsorption traps (two in series) and flow meter (Dwyer) with 0.125-in diameter, flexible, stainless-steel tubing and appropriate fittings. The adsorption traps are simply small glass tubes containing a known amount of coconut-shell activated carbon (Environmental Compliance Corporation); the first adsorption trap contained 100 mg and the second trap 50 mg. The two trap series was used so that the ability of the first trap to capture all the vapor-phase contaminants could be ascertained, i.e., in normal operation, no contaminants would be recovered from the second trap.

EXTRACTION OF SAMPLES

Core Samples

The ultrasonication solvent extraction procedure illustrated by Figure 9 was developed and consisted of the following protocol.

1. A 20-g sample or subsample was removed from *in situ* liner sample and placed in a 40-ml Pierce vial—filling the vial to the top with water and storing at 4°C to prevent volatilization losses.
2. At analysis time, the Pierce vial contents were transferred to 250-ml borosilicate centrifuge bottles, and the vial was rinsed three times with 10 ml of acetone. The acetone rinse was placed in the centrifuge bottle that contained the original sample.
3. The centrifuge bottle was amended with: 35 g of sodium sulfate—a drying agent; and 100 ml of pentane—the organic solvent used for extraction. The centrifuge bottle was then capped with a Teflon^(R)-lined screw-cap and stirred with a magnetic stirrer and a Teflon-coated stir-bar for 5 min.
4. The centrifuge bottle was placed in a water bath equipped with a sonic horn (Tekmar

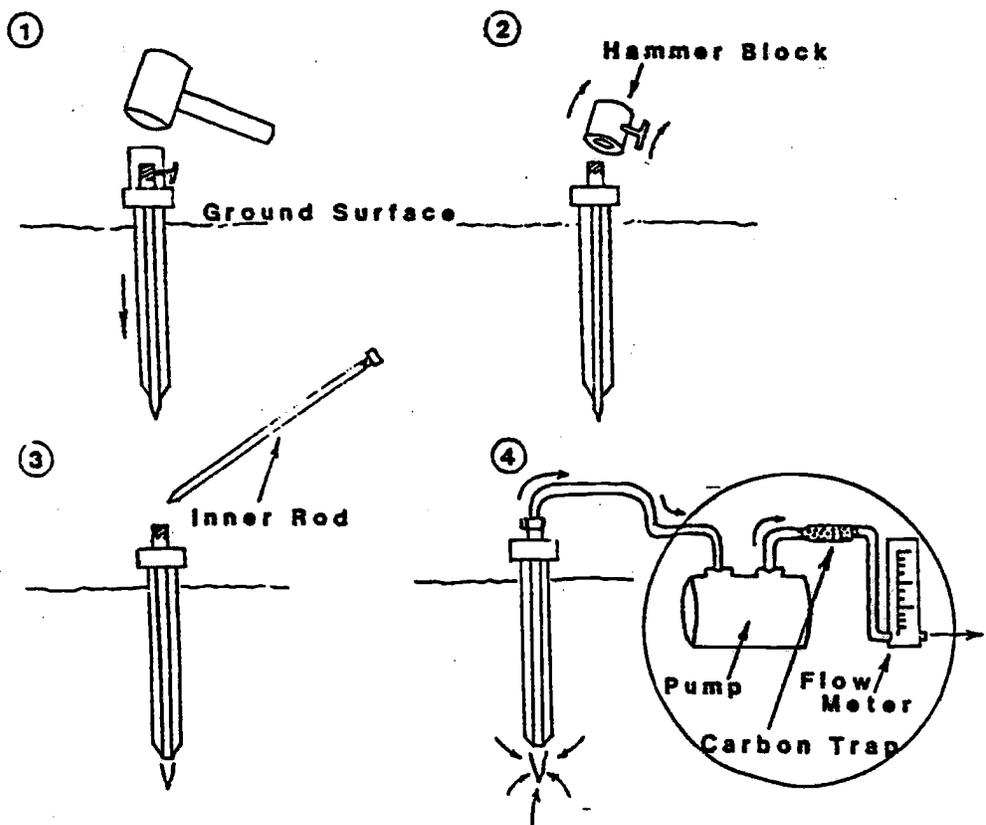


Figure 8. Design of the vapor-phase sampling system.

ULTRASONICATION PROCEDURE

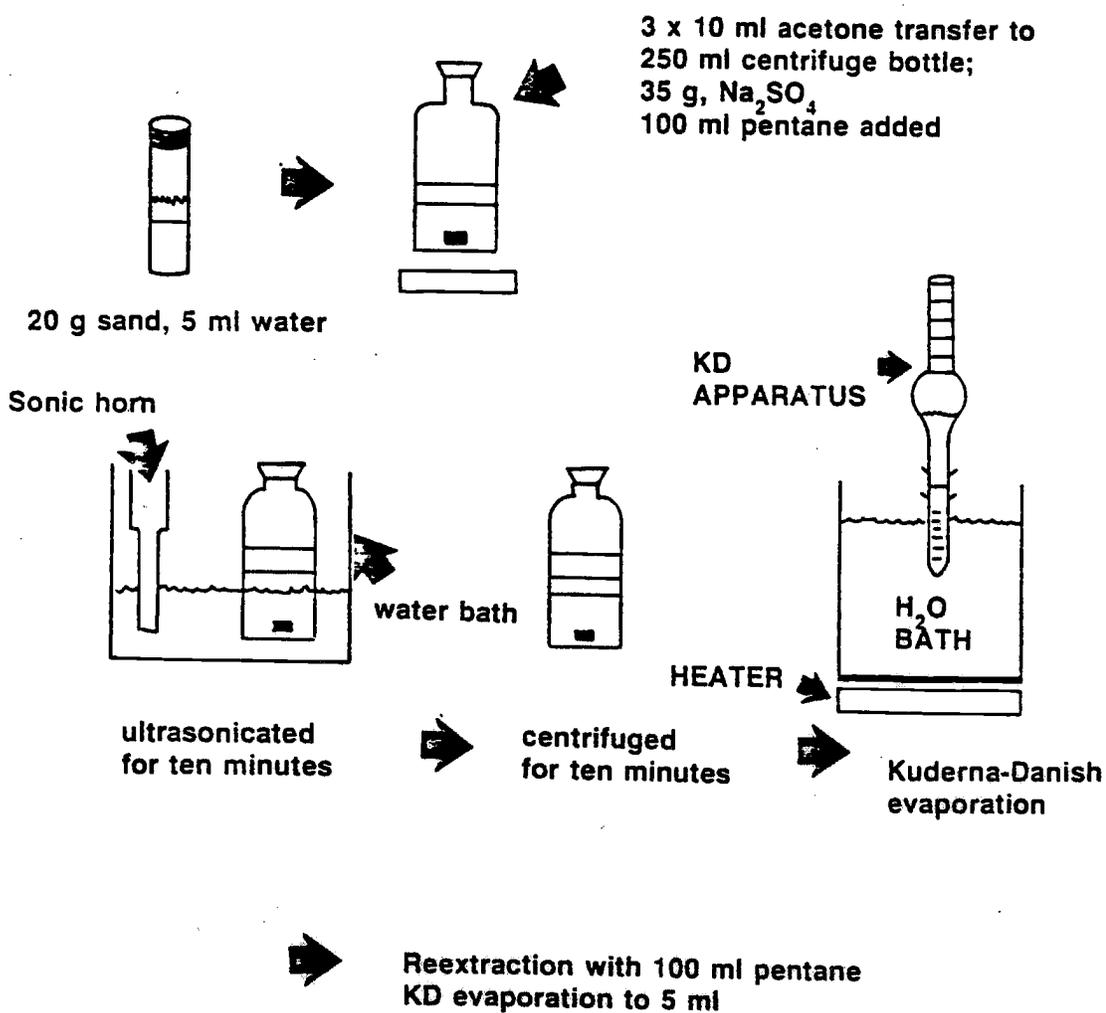


Figure 9. Ultrasonication solvent extraction procedure.

disruptor horn, 500 watts), and ultrasonicated for 10 min at full power.

5. The sample was centrifuged (CRU 5000 centrifuge) for 10 min at 2899 rpm and 4°C and the supernatant was decanted into a Kuderna-Danish evaporation flask.
6. An additional 100 ml of pentane was added to the centrifuge bottle. The contents were stirred for 5 min; ultrasonication was performed for 10 min at 500 watts power; phase separation was accomplished by centrifugation for 10 min at 2899 rpm; and the pentane supernatant was added to the original fluid mixture.
7. The combined solvents were dried with anhydrous sodium sulfate and evaporated to about 5 ml using the Kuderna-Danish method and brought to a 10-ml volume by adding pentane to the concentrate in a volumetric flask.
8. Extracts (1 μ l) were analyzed by capillary gas chromatography using a 30- m, SPB-1 capillary column. Chromatographic conditions were 33°C (2 min), 4°C/min, 100°C (3 min). An external calibration curve of the target compounds was used to calculate percent recoveries.

The second subsurface-sample extraction method investigated was a heated nitrogen purge of an *in situ* liner sample. The method consisted of the following protocol.

1. At analysis time, the polyethylene caps were removed from the field-collected *in situ* liner sample and machined, brass caps, which were equipped with an o-ring seal, were placed on each end of the brass liner.
2. The assembly was placed into a custom-made oven, which was capable of accommodating 4 samples simultaneously. The inlet line was connected to a nitrogen tank, and the effluent line discharged through two, 150-mg activated carbon traps to an exhaust hood. Included in the effluent line was a separatory funnel that was used to trap moisture prior to discharge through the activated carbon traps.
3. Extraction was accomplished by adjusting the oven temperature to 100°C and flowing nitrogen through the sample at the rate of 10 ml/min for a period of 20 hr.
4. Following the nitrogen purge, the in-line activated carbon traps were removed and

each trap was extracted with 2 ml of carbon disulfide and the extract was analyzed by capillary gas chromatography.

Aqueous Samples

Aqueous samples were collected and stored in 40-ml Pierce vials with minimal headspace. A volumetric pipette was used to transfer 20 ml of the aqueous sample to a 125-ml separatory funnel. Three successive liquid-liquid extractions were made with methylene chloride (volume used depended on initial solute concentration in the aqueous sample). Each time the aqueous sample was shaken vigorously with the methylene chloride and the lower methylene chloride layer was drained into a sample vial. The final portion of methylene chloride extract was dried with sodium sulfate. A 1 μ l injection of the methylene chloride extract was made into a Varian capillary gas chromatograph, which was equipped with a flame-ionization detector. A standard curve of the target compounds was run with each set of aqueous samples, and 1-chlorodecane was used as an internal standard.

Activated Carbon Samples

The activated carbon traps were extracted in the laboratory using 1 ml of CS₂. Two internal standards (IS), 1-chlorooctane and 1-chlorodecane, were added at 35 ppb to the CS₂ stock solvent before use. The purpose of the IS was to quantify the sample injection volume—giving a more accurate basis for computing target compound concentration as compared to sample volume estimation from syringe interpolation.

MEASUREMENT OF GASOLINE COMPONENTS

Gasoline components were analyzed using a Varian 3700 high-resolution GC with a flame ionization detector (FID). Chromatographic separation was achieved on a 30-m, Supelco SPB-1 fused-silica capillary column with splitless injection and temperature programming: the initial temperature was held at 35°C for 8 minutes, and then programmed to 175°C at a rate of 6°C per minute. The injector temperature was set at 285°C and the

FID was set at 300°C; and the helium carrier gas flow rate was 1.7 ml per min. If hydrocarbon vapors were not detected by GC analysis, the samples were concentrated under a gentle stream of nitrogen gas to 0.1 ml and rerun under the same GC conditions.

Field samples required gas chromatography/mass spectroscopy (GC/MS) to provide a tentative identification of the components of gasoline. The mass spectrometer was a VG Micromass 12-250 quadrupole with a VG 11-250 data system. Electron ionization (EI) was employed (70 electron volt source potential) with a scan range of 40 to 500 atomic mass units. Identification was by library spectral matching.

SELECTION OF TARGET COMPOUNDS

Target compounds were chosen on the basis of their prevalence in gasoline. The percentages of the target compounds do vary considerably, depending on the type of gasoline, the manufacturer, and the season. A group of "target" compounds was selected from among those identified by the GC/MS library spectral matching procedure. The criteria for selection were that each compound be present in high concentration and sorb well onto activated carbon. The latter criterion was necessary because the methodologies for recovery of gasoline components from both the vapor phase and the subsurface solids involved use of activated carbon at some stage for preconcentration. The drawback to the target compound approach is that the mass of gasoline in the sample cannot be calculated unless all components were to be analyzed. Nevertheless, the selection of target compounds is the only practical way to deal with a mixture that may contain over one-hundred compounds. These target compounds provide "markers" that describe the extent of subsurface contamination. Standard curves of peak area vs. mass injected for each target compound were generated. Response factors generated from these curves were used to convert peak area responses to mass measurements.

Figure 10 is a GC/MS total ion chromatogram for vapor-phase sample BB collected at Marine Corps Base Camp Lejeune (see section on Site Description for location of sam-

ples). Table 1 lists 27 major components that have been identified. Mass spectral analysis revealed that toluene and an aliphatic hydrocarbon—trimethyl pentane (TMP)—coeluted. A comparison of the TMP spectrum (Figure 11) to library spectra tentatively identified this compound as 2,3,3 trimethyl pentane. A chromatographic technique was used to separate toluene from TMP. Three samples (from locations AA, BB, and W) were re-analyzed in duplicate, first on a Supelco SPB-1 (non-polar) and then on a J&W Scientific DB-5 (slightly polar), 30-meter capillary column. While toluene and TMP coeluted on the non-polar column, the retention time of toluene was increased on the slightly polar, DB-5 column due to the slightly polar nature of toluene. Thus the contribution of toluene to the total was calculated. The chromatographic response factors, which are relative measures of FID response to a known mass of analyte, were 1.07 and 1.0 for toluene and TMP, respectively (Dietz, 1967) so that peak area response for the two compounds was calculated with no more than 7% additional error.

Table 1. Major Components of Gasoline Detected by GC/MS Analysis of Vapor-Phase Sample BB.

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

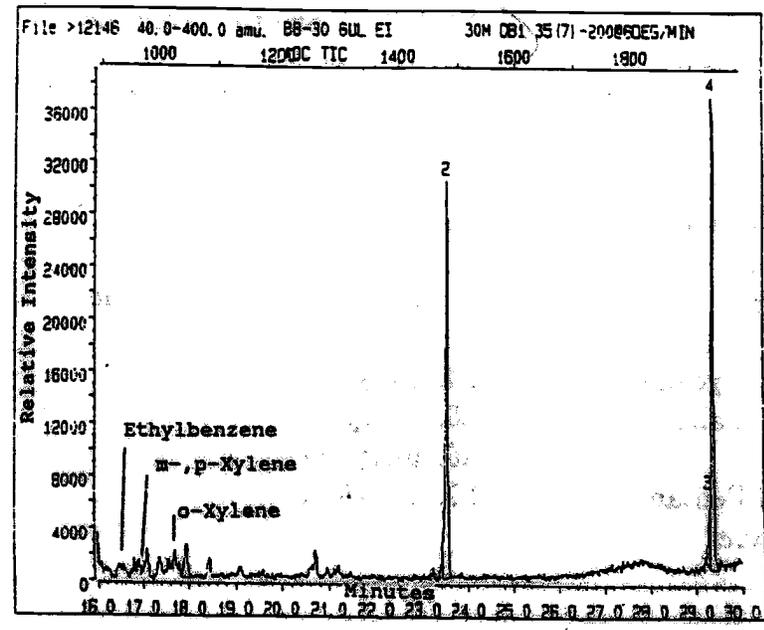
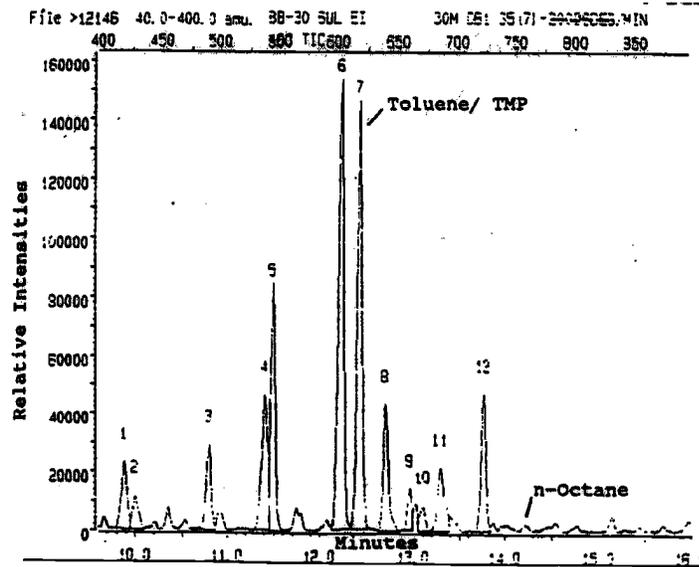
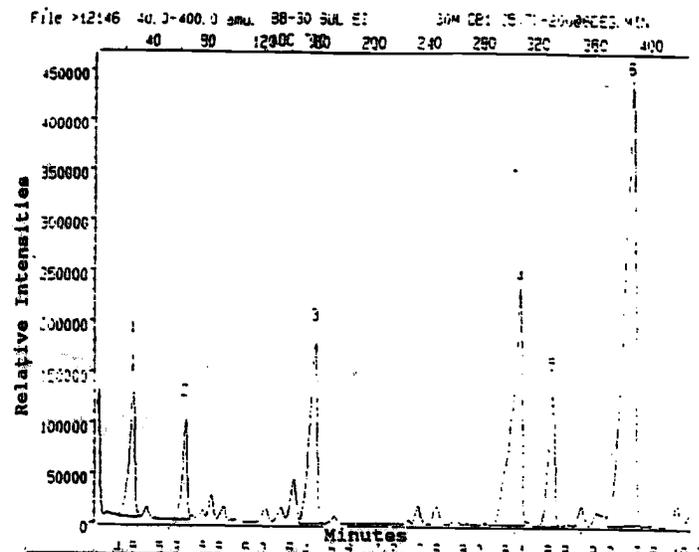


Figure 10. GC/MS total ion chromatogram from vapor-phase sample BB.

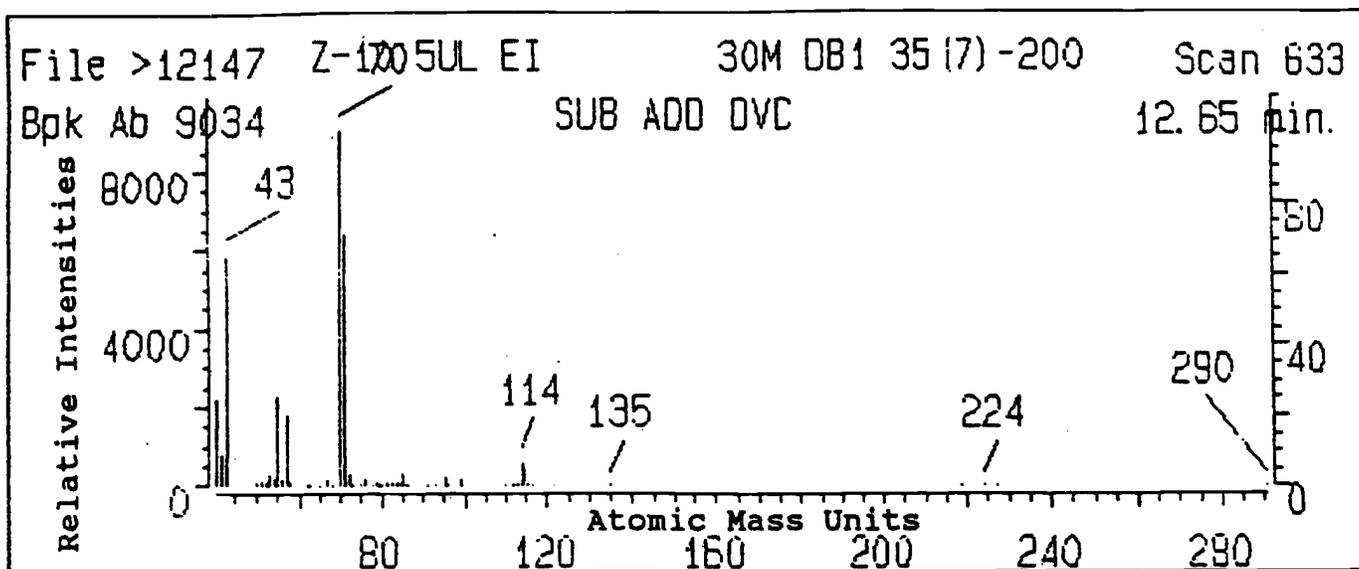


Figure 11. Comparison of TMP spectrum to library spectrum.

The target compounds selected after GC/MS analysis were: toluene (taken together with TMP), octane, ethylbenzene, m,p-xylene (taken together), and o-xylene. Their physical and chemical properties are listed in Table 2. The concentration of each target compound in the vapor phase, expressed as $\mu\text{g/l}$ of vapor, was calculated by:

$$C_V = \frac{M_{sol}}{Qt} \quad (1)$$

where M_{sol} is the solute mass measured by GC analysis; Q is the flow rate of the sampler; and t is the sampling time. For the core samples, concentrations were computed based on solute mass measured by gas chromatography normalized by the mass of solid phase after drying.

Table 2. Physical and Chemical Properties of Target Compounds

Compounds	Mol Wt. ¹ g/mol	Boiling ¹ Pt. °C	Log K_{ow}^2	Density ¹ g/ml	Water Sol. ³ mg/l
Toluene	92.14	110.6	2.46	0.8669	515.
Octane	114.23	125.7		0.7025	0.06
Ethylbenzene	106.20	136.2	3.15	0.8670	152.
o-Xylene	106.17	144.5	3.12	0.8802	175.
m-Xylene	106.17	139.1	3.20	0.8642	200.
p-Xylene	106.17	138.3	3.15	0.8611	198.

¹ Weast (1986)

² Hansch and Leo (1979)

³ Verschueren (1983)

LABORATORY RECOVERY EXPERIMENTS

Recovery of Contaminants from Cores

The extraction methods presented in the previous section were investigated in the laboratory to determine a theoretical recovery. The ultrasonication recovery was tested using the following procedure.

1. The sand to be used in the spiking and recovery experiments was dried overnight at 105°C in an oven.
2. A 20-g sand sample was placed in a 40-ml Pierce vial and hydrated with 5 ml of distilled, deionized water for 1 hr.
3. A target compound stock standard was prepared by adding 5 μ l each of the target solutes (toluene, octane, ethyl benzene, and o,m,p,-xylenes) to 25 ml of acetone in a volumetric flask.
4. Three different masses of the target solutes were spiked onto three different hydrated sand samples by adding 0.5, 1.0, and 1.5 ml of the target stock standard to the Pierce vials. The vials were then capped with Teflon-lined screw caps and allowed to equilibrate at 4°C for 16 hr before extraction.
5. Extraction and analysis were performed using the ultrasonication procedure detailed in the previous section. Comparison of solute mass added and solute mass measured by extraction yielded the bases for computation of the theoretical recovery.

The nitrogen-purge method recovery was tested using the following procedure.

1. The sand to be used was dried overnight in an oven at 105°C.
2. The dry sand (about 615 g) was packed into a 2.5-in diameter, 6-in long brass core and attached to brass inlet and outlet caps.
3. An aqueous solution was prepared by adding 3.8-g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ per 1 l of distilled, deionized water—giving a 0.1 M borate buffer. The aqueous solution was further amended by adding 0.5% by weight of sodium azide to the distilled water to prevent

microbial degradation of the test compounds.

4. The prepared aqueous solution was recirculated through the sand column using a magnetic drive Micropump for 24 hr to hydrate the sand.
5. A spiked solution was prepared by adding 50 μl of each target solute to 1 l of the prepared aqueous solution. The spiked solution was shaken vigorously, and stirred for 30 min to ensure complete dissolution of the target compounds in the water.
6. A 10 ml aliquot of the spiked solution was taken, and liquid-liquid extraction was performed 3 times using 10 ml portions of methylene chloride each time. Samples were analyzed by using 1 μl subsamples of the extract and capillary gas chromatography—yielding a measured initial concentration of each compound.
7. The spiked solution was circulated through the sand column for 48 hr using the set-up schematically shown by Figure 12 (a). All fittings and tubing in the set-up were either Teflon or glass to minimize sorption of the target compounds to materials other than the sand.
8. After a 48-hr period of recirculation, a 10-ml aliquot of the circulated solution was taken, liquid-liquid extracted with methylene chloride, and analyzed by capillary gas chromatography—yielding a measure of the final spiked solution concentration. The difference between the final mass of solutes and the initial mass of solutes was the theoretical amount of the solutes sorbed to the sand.
9. Core extraction and analysis were performed using the nitrogen purge procedure detailed in the previous section. Comparison of solute mass added and solute mass measured by extraction yielded the bases for computation of the theoretical recovery.

Activated Carbon Traps

The recovery efficiency of the CS_2 extraction procedure was determined for each of the target compounds sorbed on the carbon traps. The target compounds (76 μg of each) were injected with a 10- μl syringe directly into the open end of a carbon trap (containing 150 mg of activated carbon) and allowed to adsorb. After 24 hr, the trap was extracted

NITROGEN PURGE RECOVERY EXPERIMENT

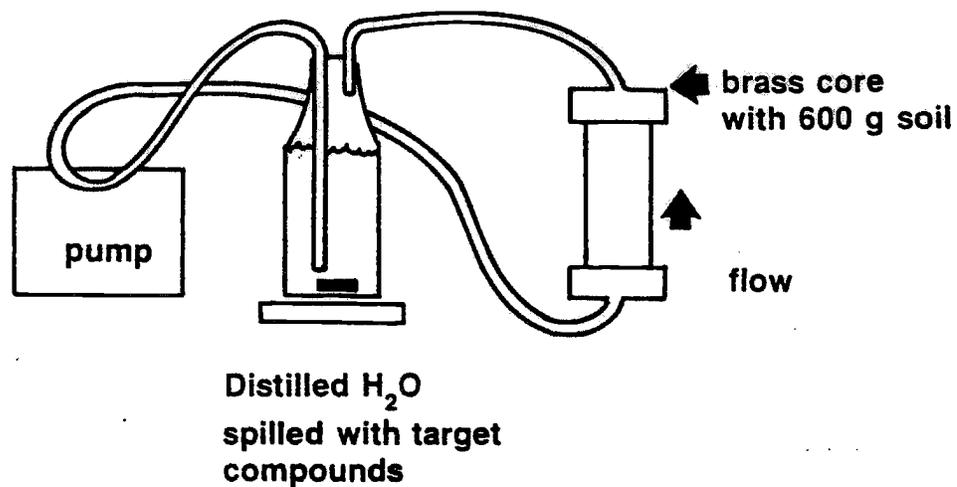


Figure 12 (a). Apparatus for circulating the spiked solution through the core sample to sorb solutes.

NITROGEN PURGE EXTRACTION

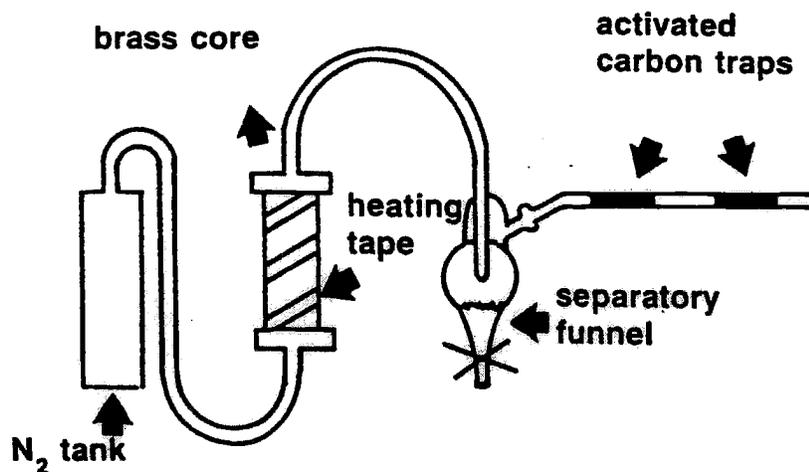


Figure 12 (b). Apparatus to purge sorbed solutes from core sample and concentrate them on activated carbon.

with 2-ml of CS₂. As a control, the same quantity of target compounds was also injected directly into 2-ml of CS₂. Both the carbon trap extract and the control were analyzed by GC as described in a previous section.

One of the advantages of using the carbon trap technique for measuring contaminants in the vapor phase is that samples can be stored before extraction and GC analysis. However, the possibility of desorption of volatile organic compounds during storage was of concern. The five target compounds were added to carbon traps as described for recovery experiments (desorption into 1 ml of CS₂). Enough traps were prepared to have duplicates for analysis after storage periods of 1, 3.5, 6.5, 10, and 15 days at two different temperatures (-13°C and 27°C).

Figure 13 shows the laboratory experiment devised to determine the sorptive characteristics of the carbon trap (100 mg) used in the field vapor-phase sampler. A vapor was generated from a 100-ml sample of unleaded gasoline or mixtures of several target compounds by purging with zero-grade air in a 500- ml, glass washing bottle. This simulated the maximum concentration of target compounds that the trap would be exposed to in field applications, because the vapors were produced from organic solvents undiluted with water. The vapor flow was directed to the carbon trap or to a fume hood. Flow rate was adjusted to match (47 cm³/min) that anticipated for the field sampler. Vapor samples were taken over time at the exit of the carbon trap using a gas-tight syringe to measure breakthrough of the components of interest. If adsorption kinetics are slow or if equilibrium adsorptive capacity is too low, some mass of target compounds could escape the trap thus giving values of $M_{s,oi}$ in Equation 1 that are too low for the actual concentration being measured. The samples collected from the exit stream of the trap were injected directly into the GC for identification by retention time and quantification by standard procedures for calibration.

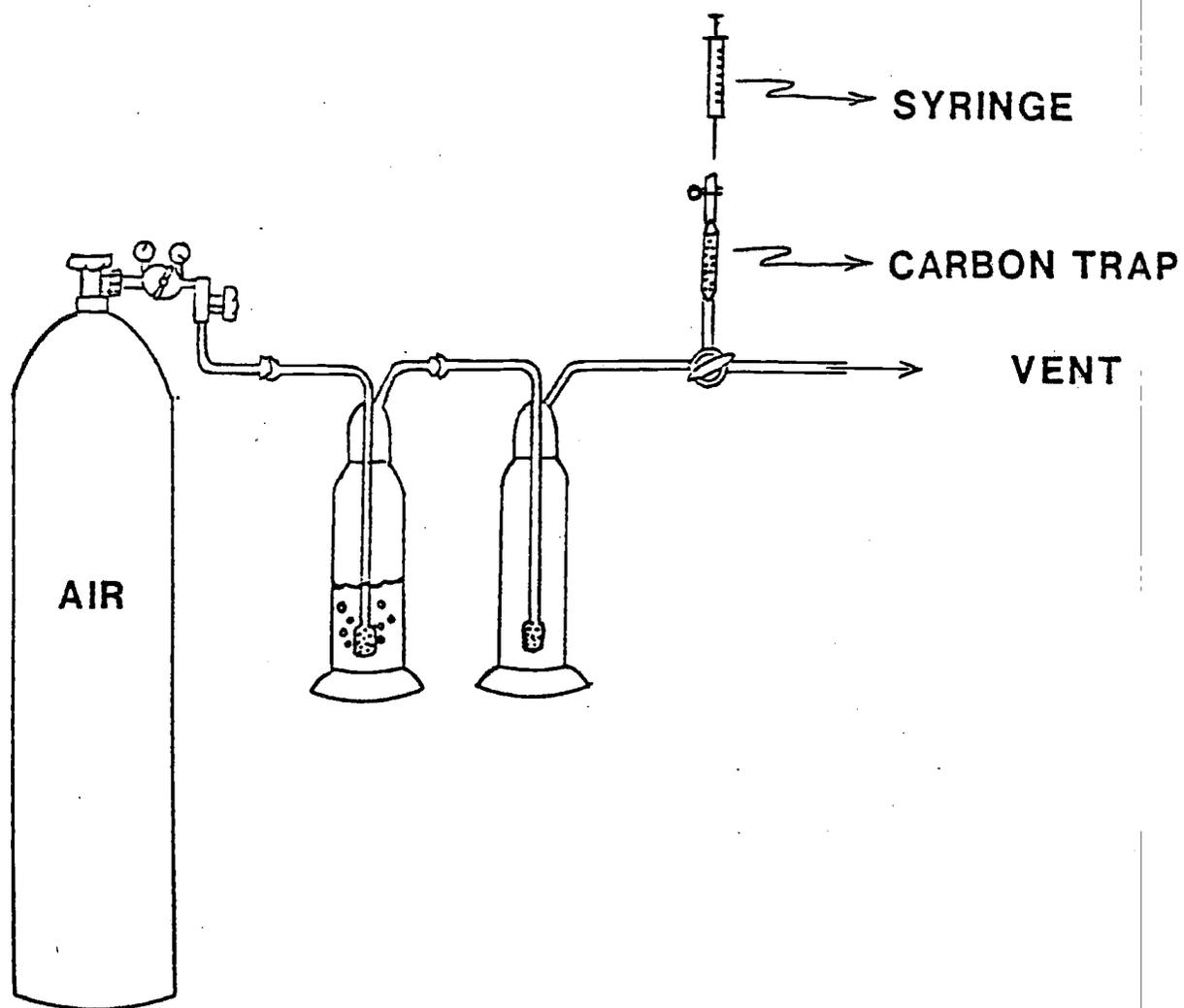


Figure 13. Laboratory apparatus used to determine the adsorption characteristics of the carbon trap.

FIELD INVESTIGATION

SITE DESCRIPTION

The study site is a gasoline station located at Camp Lejeune in Onslow County east of Jacksonville, North Carolina. It is known as the Tarawa Terrace site. The geologic units that water-supply aquifers in the area are: a surficial unit, the Yorktown formation; the Castle Hayne formation; the Beaufort formation; and the Peedee formation—units formed by marine deposition. These and other sedimentary units are about 1,600-ft thick in total in the Camp Lejeune area and are underlain by a basement complex of igneous and metamorphic rocks (LeGrand, 1959).

The only sources of fresh groundwater at Camp Lejeune are the surficial unit and the Castle Hayne formation. The Yorktown formation is not present in the Camp Lejeune area, and the Beaufort, Peedee, and Black Creek formations contain salty water there. The surficial unit is composed of sands, with beds of sandy clay and shells. The Castle Hayne formation is composed of semi- and completely-consolidated limestones, shell beds, sand, and minor amounts of clay. The Castle Hayne formation is the most widely used unit for water supply at Camp Lejeune. The formation thickness exceeds 300 feet in some areas and typical yields for supply wells are 200–250 gallons per minute (gpm). Specific capacities of wells drawing from the Castle Hayne range from about 18–25 gpm per foot of drawdown (LeGrand, 1960).

All sediments below the phreatic surface are completely saturated with water. The phreatic surface lies within 10–20 feet of the land surface in most places and is found in the sands of the surficial unit. Beds of clay and some marl tend to separate the more permeable sand and limestone beds so that several artesian zones can occur. There is considerable leakage of water between the zones where a significant hydraulic gradient occurs, due to the fact that the clayey confining beds are not completely impermeable and are somewhat

lenticular (LeGrand, 1959). The surficial aquifer unit is well connected with the Castle Hayne formation.

The channels of the major streams of the area are cut into the surficial and Castle Hayne units, and the water table and potentiometric surface are both higher than the stream levels. The streams are discharge areas for both these units in this area and groundwater moves through them to the surface streams.

The gasoline station at Camp Lejeune is shown on the Figure 14. The character of the geologic materials of the Tarawa Terrace area was summarized by LeGrand (1959) as follows:

- From the land surface to a depth of about 50–60 ft, a white to light gray medium-grained sand is the chief material.
- Between depths of about 50–85 ft one or more limestone beds occur. The limestone varies in degree of hardness and is commonly less than 20-ft thick.
- Sand underlies the limestone zone and extends to a depth of more than 200 ft. The sand varies from fine to very fine in grain size.

Various well driller reports, geophysical logs, and geologic reports concerning the area have been collected and interpreted. These materials indicate that a clay layer extends from the surface to 10–30 ft below the ground surface, followed by a medium-grained sand mixed with varying amounts of clay, which extends to about 200-ft below ground surface. A clay layer of approximately 15 ft in thickness is found below the sands. Also, an inconsistent clay stringer is found in the sands at about 95-ft below ground surface. This lithology is in conflict with that noted above (LeGrand, 1959) and will be assumed to be more representative of conditions at the research site in question.

A soil survey conducted in 1923 indicates that most of the area is overlain by sandy loams, with patches of purer sands. The loams consist of at least 45% silts and clays and extend at least 3-ft below the ground surface throughout the area (Juney et al., 1923). The consistency of the loams and the amount of asphalt covering the research site suggest

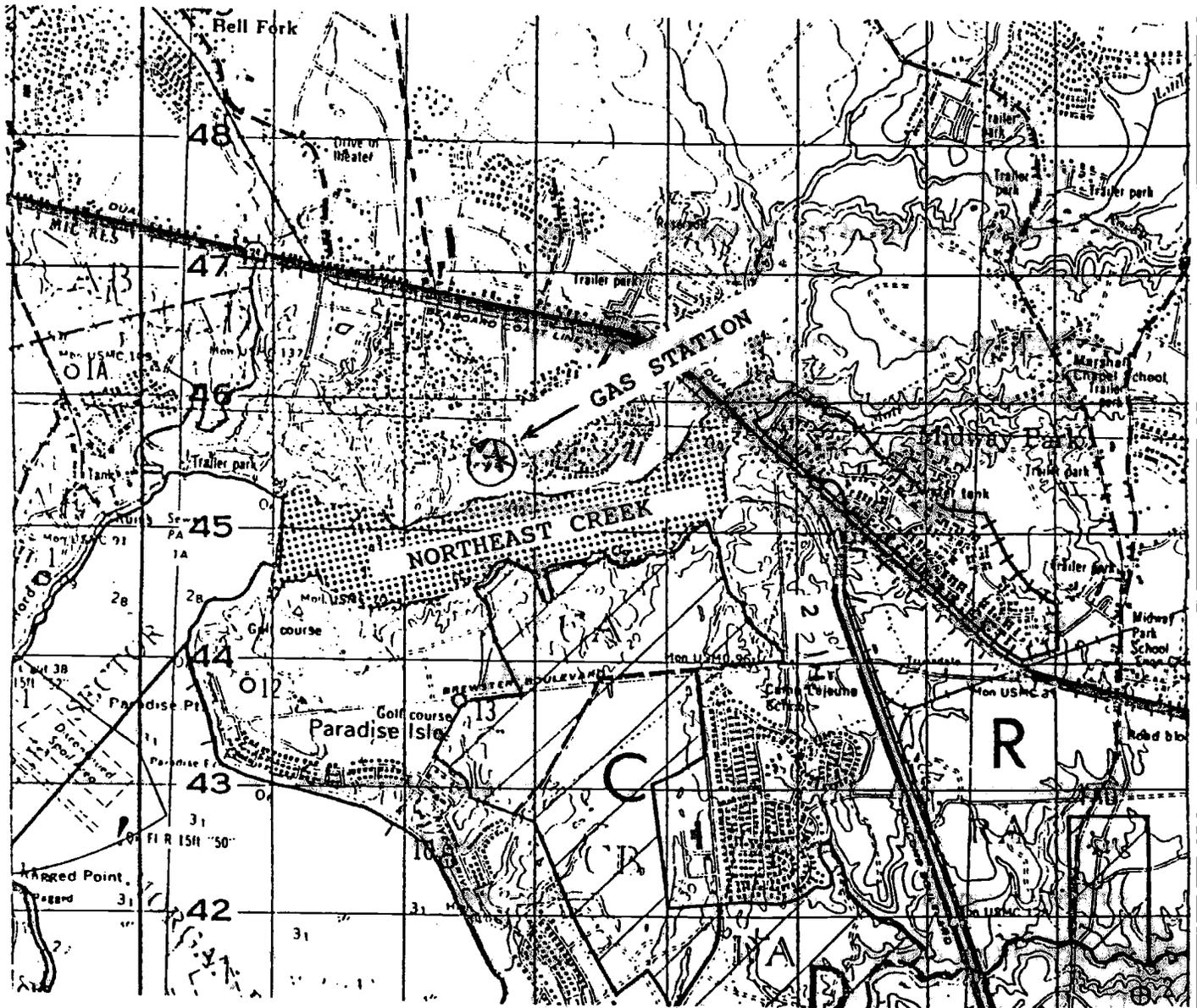


Figure 14. Location of Tarawa Terrace site at Camp Lejeune, Jacksonville, North Carolina.

that recharge from precipitation is small in the study area. However, the surficial-Castle Hayne aquifer system has been observed to rapidly respond to precipitation events— - indicating recharge occurs readily in most locations in the Camp Lejeune area (informal communication, North Carolina Geological Survey, 1988).

In the past, lateral groundwater flow in the surficial and Castle Hayne units in the area has been controlled by water supply well withdrawals and by the boundary conditions imposed by Northeast Creek. However, withdrawals from the water supply wells in the area have been suspended since March 1987.

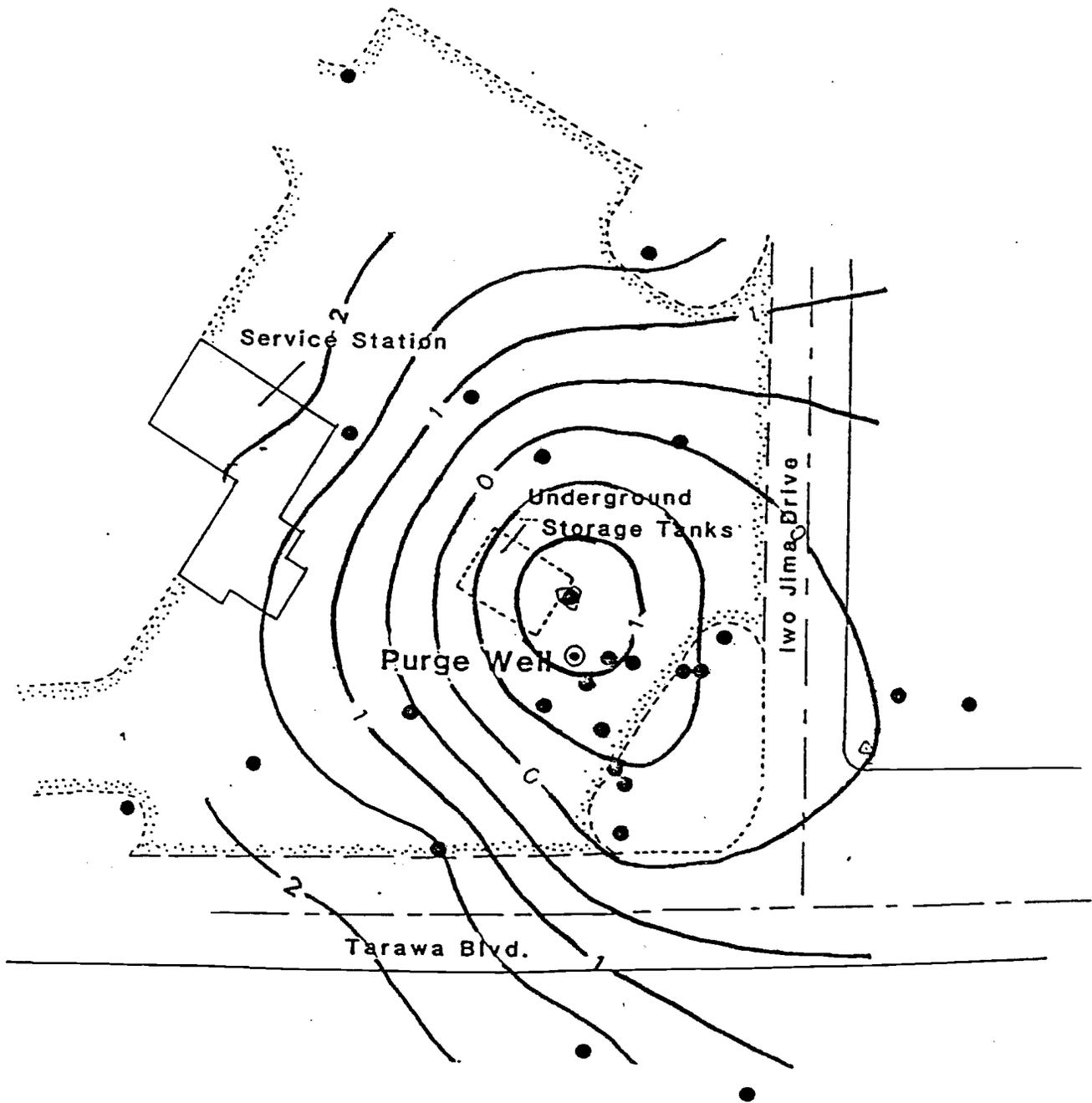
Discussion of the hydrogeology at the research site shall be restricted to the unconfined surficial unit, which is most relevant to movement of any contaminants. At the site, medium-grained sand lies beneath approximately 8 ft of sandy clay and extends to a depth of at least 60 ft below the land surface (Industrial Marine Services, 1985).

Groundwater flow in the surficial unit at the site is currently dominated by the cone of depression created by a recovery system—shown by Figure 15. However, data collected before the recovery effort began and during periods of pump shutdown indicate a slight gradient in the southeast direction, toward the discharge area—Northeast Creek. Preliminary results from aquifer tests performed in the surficial unit at the site indicate transmissivities of approximately 7,000 gal/day/ft (Industrial Marine Services, 1985).

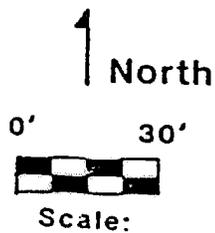
The chronology of groundwater contamination and cleanup events at the Camp Lejeune Tarawa Terrace site are summarized in Table 3. Figure 16 shows a contour map of apparent product thickness measurements collected from the monitoring well network.

CORE SAMPLING

Subsurface core samples were collected during June 1987 when 16 additional monitoring wells were installed at the Tarawa Terrace site by private contract. The location of these wells is depicted by Figure 17. Subsurface core samples were collected during the drilling process according to a scheme shown by Figure 18. The sampling was accomplished



Data collected 4 May 1987. Contour interval in feet above mean sea level.

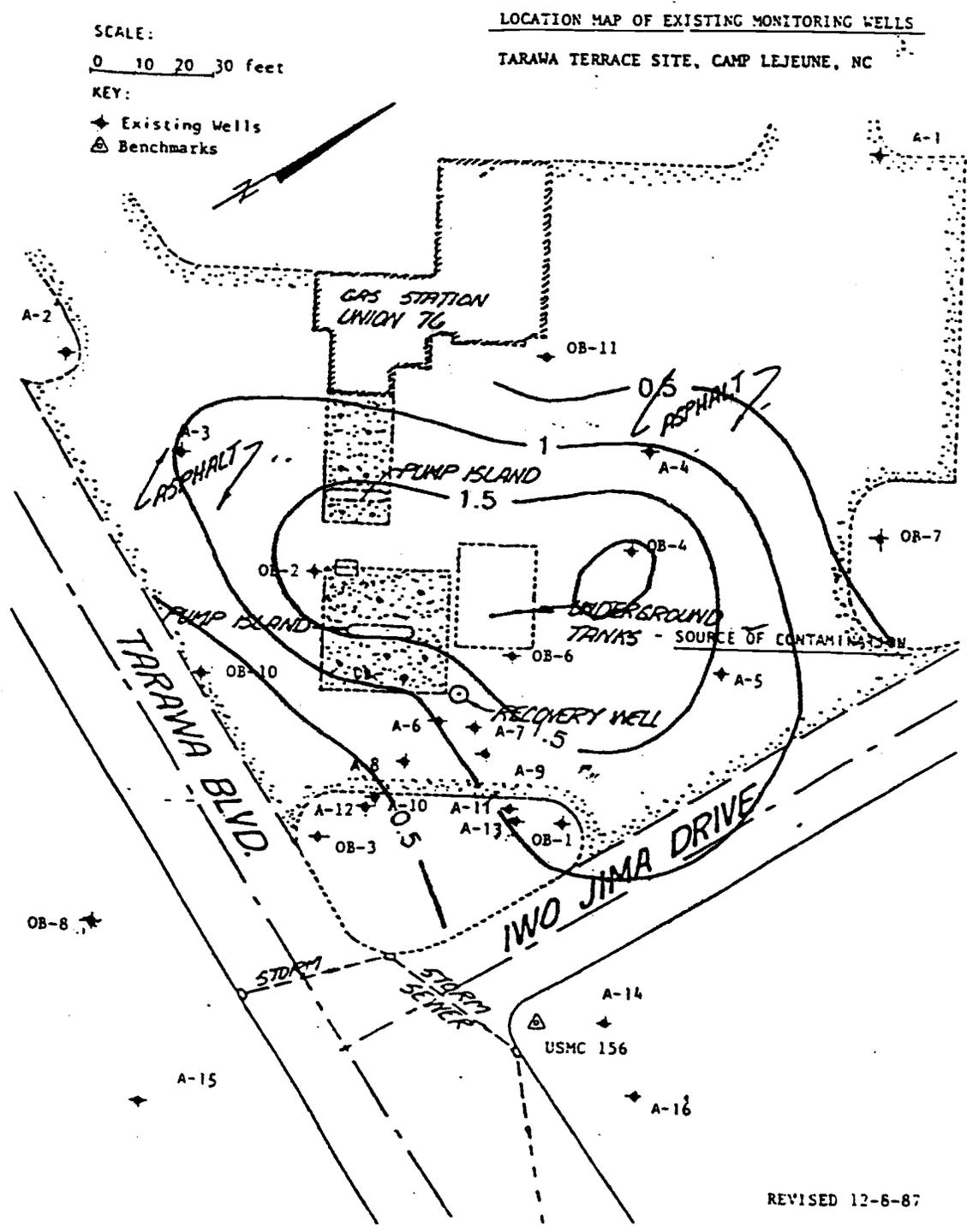


- Monitoring Well
- ⋯ Asphalt

Figure 15. Piezometric head distribution resulting from operation of the purge-well recovery system.

Table 3. 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 gallons 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 permanently.
• May 1987	All underground storage tanks excavated, and removed from the site.



Data collected 4 May 1987. Contour interval in feet of product thickness.

Figure 16. Contour map of apparent product thickness measurements collected from the monitoring well network.

using the following procedure.

1. A hollow-stem, continuous-flight auger was used to drill to the desired depth.
2. A set of 3 brass sleeves (2.5-in diameter by 6-in long) was inserted into the sampler, and the sampler was assembled by screwing the ends in place.
3. The split-spoon sampler was inserted into the hole and hammered down 1.5 ft into the virgin material and removed. This yielded 3, 6-in long cores of subsurface material.
4. At each of the 16 locations sampled, one set of samples was obtained at 10–11.5 ft below the ground surface by this procedure, and a second set of samples collected at 20–21.5 ft. These locations were selected to provide a range of depths that was above the phreatic surface yet below the overlying clay layer. For each set of samples, the upper two brass cores were immediately capped (intact) with polyethylene caps and stored on ice. They were extracted at a later date in the laboratory by the nitrogen purge method discussed in the laboratory methods section.
5. The lead core sample—the deepest sample—was used to collect three 20- to 50-g subsamples. These subsamples were transferred to 40-ml Pierce vials. In order to minimize volatilization losses, the vials containing the subsamples were filled with distilled water so that there was no headspace, tightly capped, and stored on ice for subsequent extraction by the ultrasonication method discussed in the laboratory method section.
6. At wells A6, A7, and A9, 11 subsamples were taken from the bottom brass sleeve in order to statistically evaluate the variability of the field samples analyzed by the ultrasonication method.

Precautions were taken in the field to prevent cross contamination and loss of analyte. All glassware was acid washed, rinsed repeatedly with distilled water and dried at 105°C before being used in the field. The brass sleeves and polyethylene caps were also washed with hot water, distilled water, and dried at 105°C before use.

Several efforts were made to prevent cross contamination and volatilization losses.

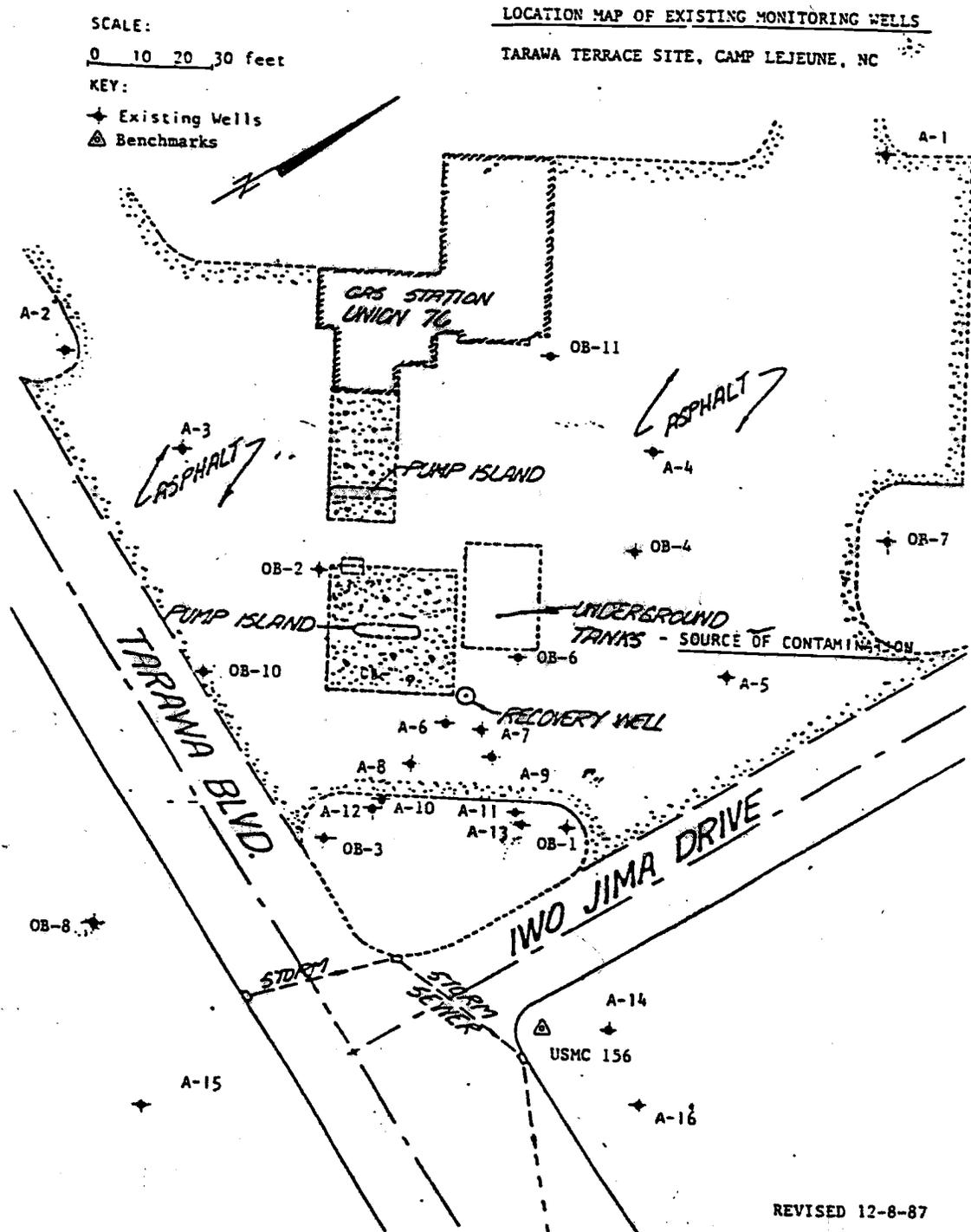


Figure 17. Location of monitoring wells at Tarawa Terrace site at Camp Lejeune, Jacksonville, North Carolina.

**TARAWA TERRACE SAMPLING SCHEME FOR
GASOLINE COMPONENTS IN AQUIFER MATERIAL**

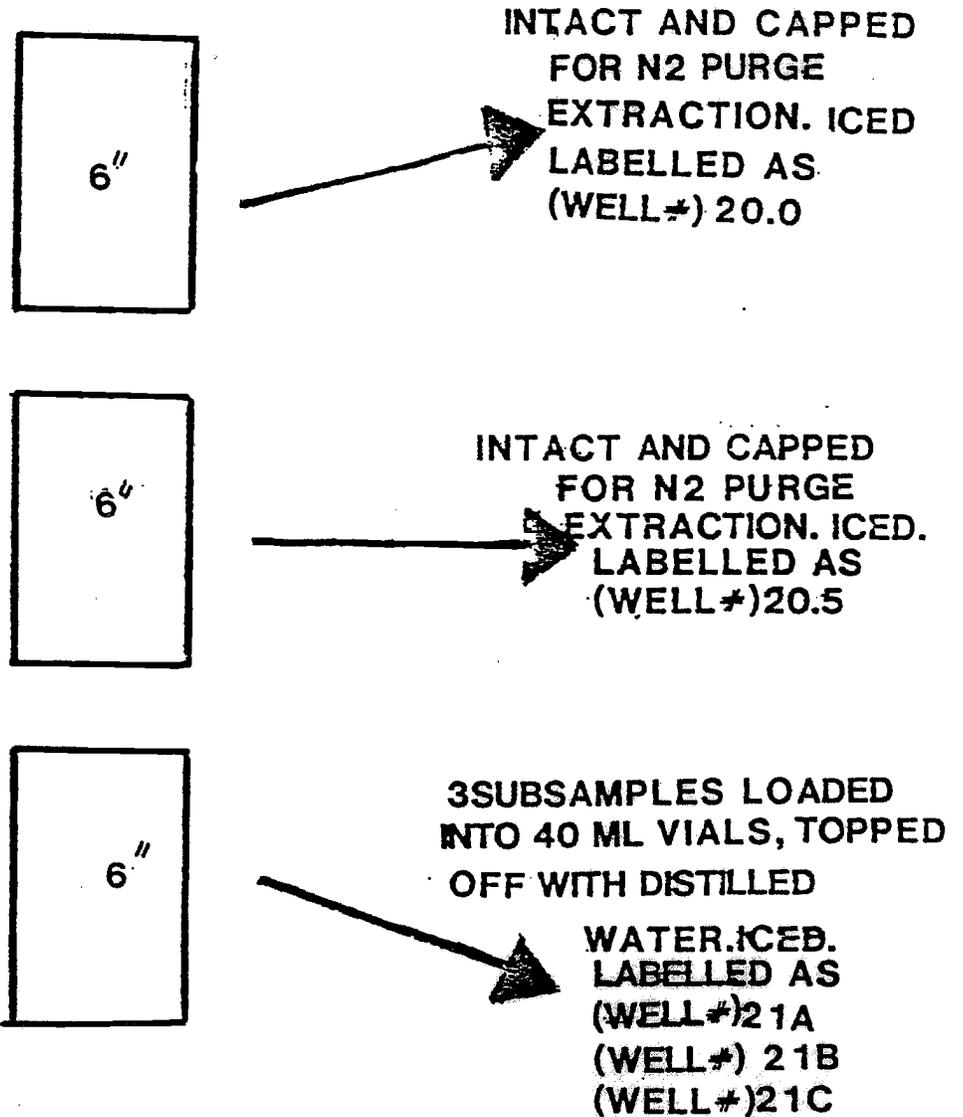


Figure 18. Subsurface core sampling scheme.

Methylene chloride was used to rinse the split-spoon core sampler between sampling points to further avoid cross contamination. The ultrasonication subsamples were topped off with distilled water to prevent volatilization losses. Goodman (1985) had reported up to 95% loss of PCE by storing the solids samples in a closed jar over a 1-wk period. However, storing the spiked solid samples in an aqueous media and refrigerating showed no recovery losses of volatile organic compounds over a period of 10 days. Samples were stored on ice as soon as possible after retrieval from the aquifer.

VAPOR-PHASE SAMPLING

Sampling began by augering a 1 1/8-in pilot hole to 1.5 ft above the intended sampling depth. The DGP was then dropped into the hole and hammered the remaining distance. After removing the inner rod and connecting to the sampling assembly, a flow rate of 47 cm³/min was used to collect a vapor sample. Sampling times during this investigation varied from 5–30 min, thus allowing for collection of from 235–1,410 cm³ of vapor. The traps were capped to await desorption and GC analysis in the laboratory. To prevent carry over of contaminants from one sample to the next, the probe was rinsed with acetone after each use and then purged with ambient air for 1–2 minutes. A total of 26 locations was sampled, which covered the general area of the site as shown in Figure 17.

RESULTS

LABORATORY RESULTS

Recovery of Contaminants from Cores

The final protocol for the ultrasonication method outlined in the methods section and shown schematically in Figure 9 was the result of the three slightly different laboratory procedures investigated. A brief review of the recovery results from the initial and final designs along with a description of the method evolution is summarized below.

The initial ultrasonication recovery experiments performed were extracted once with varying solvent combinations. Samples of 20 g of sand, which had been dried at 105°C overnight were rehydrated with 5 ml of distilled water and spiked with the target compound stock standard at levels of 8.5 $\mu\text{g}/\text{ml}$, 17 $\mu\text{g}/\text{ml}$, and 34 $\mu\text{g}/\text{ml}$. Recovery efficiency was determined by computing mass recovered through GC analysis—using an external calibration curve of the target compounds—and comparing to solute mass injected. The external calibration curve was run with each set of standards and typically yielded correlation coefficients of >0.999 .

Ultrasonication experiments U-I and U-II used a similar procedure—a 1:1 acetone:pentane solvent mixture, and 50% of maximum output of the 500 watt ultrasonic horn for U-I, while 100% of maximum output was used for U-2. The results are listed in Table 4.

Due to low recoveries in experiments U-I and U-II, experiment U-III used a 1:1 acetone:methylene chloride solvent pair in an attempt to increase the recovery of the target compounds. The results are given in Table 4 and show that recoveries for this solvent pair were much lower than the recoveries achieved with the acetone:pentane solvent pair.

The low solubility of octane in water (0.6 mg/l) and its high vapor pressure may have accounted for the consistently lower recovery of this compound compared to the other

Table 4. Mass-Recovery Results by Ultrasonication

Experiment	Compound	Spike Concentration (mg/l)	Recovery (%)
U-I	Toluene	8.6	32
		17.3	41
		34.6	49
	Octane	7.1	34
		17.1	17
		28.2	24
	Ethylbenzene	8.6	27
		17.3	50
		34.6	49
	m,p-Xylene	8.8	35
		17.6	61
		35.2	60
	o-Xylene	8.8	49
		17.6	67
		35.2	60
U-II	Toluene	17.3	28
	Octane	19.1	16
	Ethylbenzene	17.3	21
	m,p-Xylene	17.6	25
	o-Xylene	17.6	37
U-III	Toluene	17.3	26
	Octane	19.1	9
	Ethylbenzene	17.3	25
	m,p-Xylene	17.6	25
	o-Xylene	17.6	25
U-IV	Toluene	8.6	87
		17.3	106
	Octane	7.1	111
		14.1	53
	Ethylbenzene	8.6	111
		17.3	83
	m,p-Xylene	8.8	101
17.6		113	

target compounds. However, volatilization losses of the target compounds from the open centrifuge bottles during the ultrasonication procedure were also suspected.

During experiments U-I, U-II, and U-III, the sonic horn was lowered directly into the open sample in the centrifuge bottle, in order to provide greater contact with the sand-solvent slurry. For experiment U-IV, the acetone:pentane solvent pair was used, but the ratio of acetone:pentane was changed to 3:10. The sand was extracted an additional time with 100 ml of pentane, and the centrifuge bottles were Teflon-stoppered, and placed in a water bath equipped with a sonic horn—rather than direct open sonic disruption. Samples were run in duplicate, and the percent recoveries are shown in Table 4.

It is evident from the increased recoveries in experiment U-IV that the changes in the procedure reduced the loss of the target compounds. Sealing the samples reduced volatilization losses, and placing the samples in an ultrasonication bath equipped with a sonic horn, at 100% maximum output (500 watts) increased the number of samples processed at one time from one to six. This modification alleviated concerns about the sonic horn spreading contamination from sample to sample.

The development of the nitrogen purge protocol outlined in the laboratory methods section followed a four-step evolution, similar to the ultrasonication procedure. In experiment N-I, the final solution concentrations contained twice as much contaminant mass as the initial solution after recirculating through the sand column for 48 hrs (see Figure 12 for description of apparatus). The target compounds had been spiked into the water at 50 $\mu\text{g}/\text{ml}$ (well below their solubility limit, except for octane). The initial spiked water sample was taken after the 30 min stirring period. The data indicate that dissolution of the target compounds took longer than the half-hour stirring period. The results are shown in Table 5.

In experiment N-II, the initial solution was stirred for 1 hr before an aliquot was taken for analysis. A series of three activated carbon traps was added to the effluent of the purge apparatus to determine if solute breakthrough was occurring. The results shown in Table

Table 5. Mass-Recovery Results by Nitrogen Purge

Experiment	Compound	Initial Aqueous-Phase Mass (μg)	Final Aqueous-Phase Mass (μg)	Mass Sorbed (μg)	Mass Recovered (μg)	Percent Recovered
N-I	Toluene	26,918	48,677	—	2,180	—
	Octane	24,744	46,101	—	12,554	—
	m,p-Xylene	23,148	19,980	3,168	1,177	37
	o-Xylene	70,230	67,260	2,970	2,700	91
N-II	Toluene	29,640	23,350	6,290	484	8
	m,p-Xylene	19,990	17,900	2,090	629	30
	o-Xylene	23,660	20,430	3,230	384	12
N-III	Toluene	26,530	19,824	6,800	5,714	84
	Ethylbenzene	15,252	14,831	421	4,048	—
	m,p-Xylene	17,730	17,597	133	4,953	—
	o-Xylene	19,790	19,007	783	4,858	—
N-IV	Toluene	32,846	23,075	9,771	10,099	103
	Octane	900	< DL	900	612	68
	Ethylbenzene	30,378	20,020	10,358	8,931	86
	m,p-Xylene	33,244	21,324	11,920	10,676	87
	o-Xylene	34,327	23,876	10,451	10,128	97

5 indicate that recoveries from this experiment were low. However, most of the solute was retained on the first carbon trap and no target compounds were found on the third carbon trap. Apparently, breakthrough was not responsible for the losses. The carbon traps were wet from collected interstitial pore water from the sand core.

Even though no solute was measured on the third carbon trap, it was thought that perhaps water was competing with the target compounds for sorptive sites on the traps. A mixed train, consisting of two Tenax adsorbent traps, followed by three activated carbon traps, was employed in experiment N-III. Also, a heating tape was wrapped around the brass core. It was operated at 60°C for the duration of the purge experiment. The data shown in Table 5 indicate recoveries greater than the mass added, except in the case of toluene. Possibly, contamination of the glassware resulted in an artificially high concentration. In any case, heating the sand core improved the desorption process. An extraction was made of a 30-g sample of the sand after purging by the ultrasonication method and only 0.18–1% of the target compounds remained on the sand.

The procedure for nitrogen purge experiment N-IV was modified from experiment N-III in regard to aqueous sample preparation, heating tape temperature, and moisture trapping. The initial aqueous solution was shaken vigorously for 10 min after spiking the target solutes. The solution was then stirred for 10 min with a magnetic stirrer. The temperature of the heating tape was raised to 100°C, and a separatory funnel was added between the sand core and the carbon traps. The carbon traps had been chosen over the Tenax tubes since most of the target compounds collected in experiment N-II had passed through the Tenax tubes, and onto the carbon traps. Also, the Tenax tubes are more expensive than the activated carbon tubes. The results of experiment N-IV shown in Table 5 demonstrate the excellent recovery achieved with the final design.

Vapor-Sampling Method Development

All of the target compounds were recovered in controlled experiments with solvent

extraction efficiencies approaching 100%. Therefore, no correction was necessary for mass detected by GC after solvent extraction.

The effect of carbon trap storage at -13°C and 27°C on recovery of the 5 target compounds is shown in Figures 19 and 20, respectively. The mass (ng) of each target compound measured after solvent extraction and injection into the GC did not change appreciably over 15 days of carbon trap storage at either temperature.

Figure 21 shows the breakthrough of toluene, benzene and xylenes (o-, m- and p-) present in gasoline. The concentration scale is normalized by the feed concentration, C_o , as determined at the start of the experiment. The ordering of adsorbability is apparent from the shape and position of the breakthrough curves. Similar behavior was noted when vapors from these compounds were generated using pure solvents instead of gasoline. Toluene and benzene are much more poorly adsorbed than the xylenes. Displacement of weakly adsorbed components is apparent but further interpretation of the shape of the curves is impossible because C_o was not constant over time. The evidence for this anomaly is the failure of the benzene and toluene breakthrough curves to reach $C/C_o = 1$ as must occur when sorptive capacity is exhausted. The results nevertheless suggested that the best target compounds were xylenes because these did not breakthrough the trap in 40 min of sampling; toluene can also be measured accurately if sampling time is limited to about 10 min.

The detection limit of the procedure was estimated to be 0.04 ppbv (parts per billion by volume) based on a flow rate of $47\text{ cm}^3/\text{minute}$ and a sampling time of 30 min (the GC detection limit is assumed to be 0.5 ng). This compares to 5 ppbv reported by Kerfoot (1987) in vapor-phase sampling of chloroform using the direct injection technique. Evans and Thompson (1986) reported a much lower detection limit (0.01 ppbv) for direct injection (2-ml sample) of gasoline components; however, this requires a GC capable of measuring 70 picograms of the compound, a very low value for ensuring peak resolution from baseline for petroleum hydrocarbons solute mixtures.

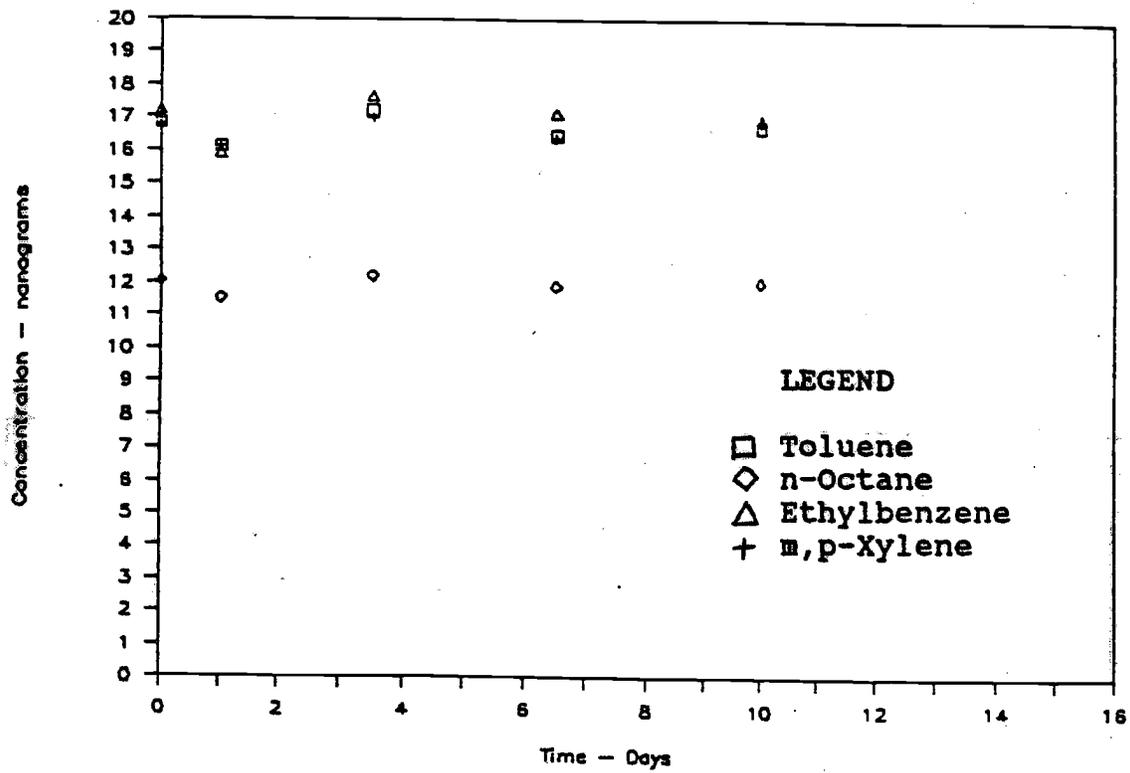


Figure 19. Effect of storage of carbon trap at -13°C.

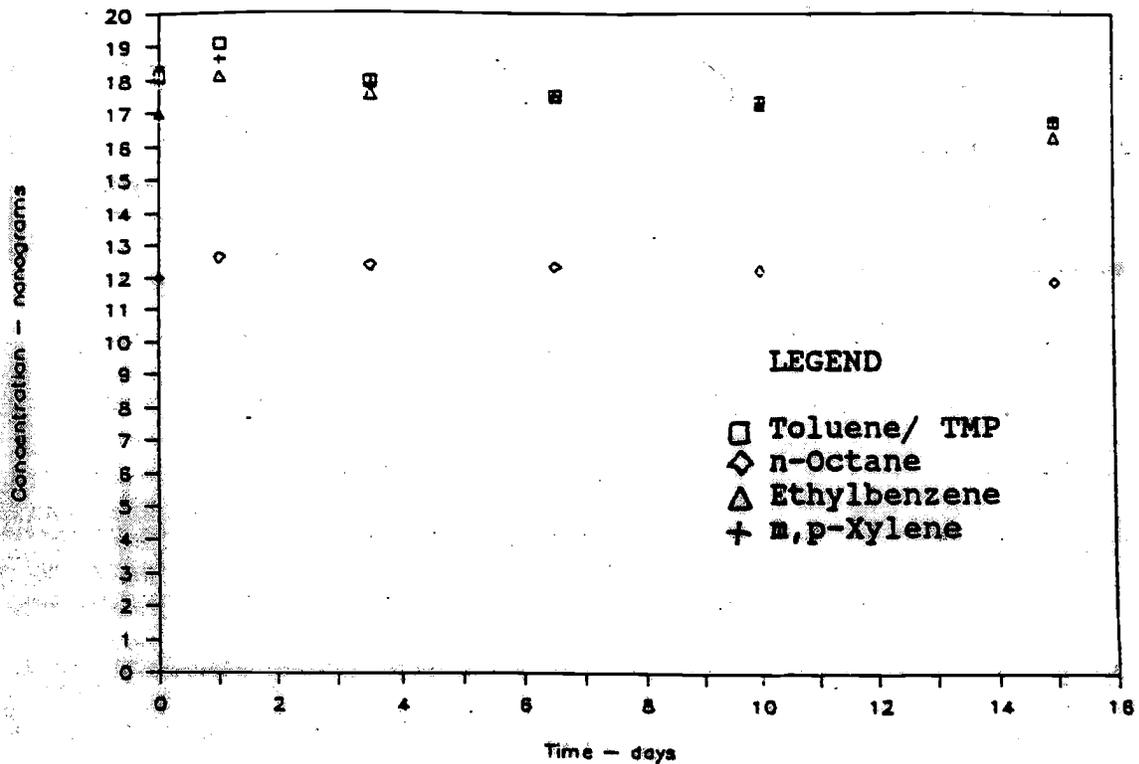


Figure 20. Effect of storage of carbon trap at 27°C.

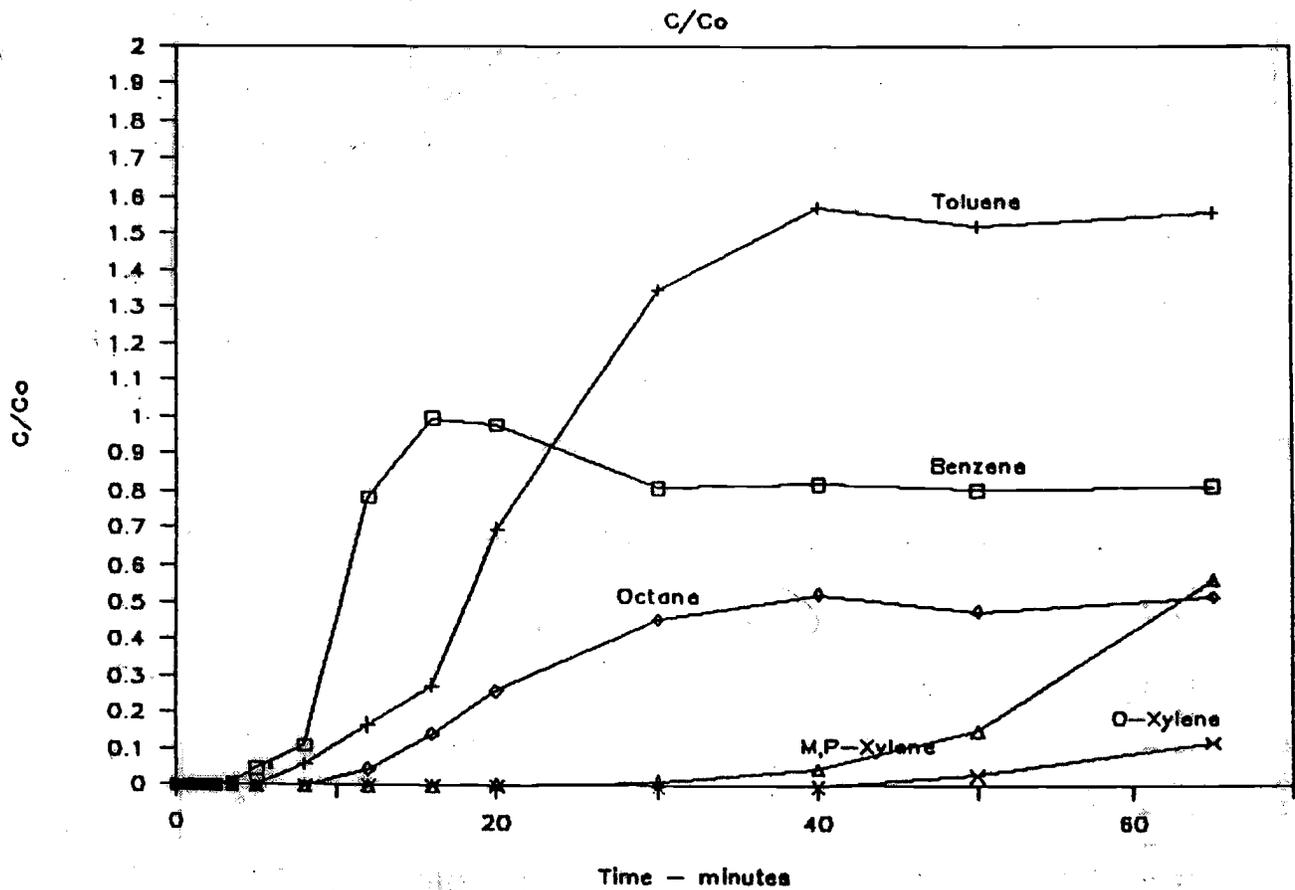


Figure 21. Breakthrough curves for target compounds from a gasoline vapor mixture.

FIELD RESULTS

Core Sampling and Extraction

Core samples were taken from 16 horizontal locations shown on Figure 17 where monitoring wells were installed (A1-A16). At each horizontal location samples were collected from 10-11.5 ft and 20-21.5 ft below ground surface. However, due to the large number of samples collected and the analytical effort involved in sample analysis, the analyses performed were concentrated on wells closest to the leaking underground tank area—wells A6 to A13. Since many of the samples collected at 10 ft contained a significant portion of clay, analytical preference was given to the 20 ft samples.

The target compound concentration results ($\mu\text{g}/\text{kg}$) of the nitrogen purge extractions are shown in Table 6. It was anticipated (based on the laboratory study experiments) that the nitrogen purge samples at 10, 10.5 and 20, 20.5 ft respectively would be replicates, which could be compared to the ultrasonication results from the corresponding well and depth. In addition, it was expected that the nitrogen purge samples would yield a more representative measure of solute concentrations because of the large sample size. This was not found to be the case. The duration of the field sample collection, subsequent storage for about 30 days, microbial degradation, and volatilization of the target compounds were attributed to the lower concentration obtained.

In general, target compound concentrations increased slightly with a lower depth in the aquifer, except where clay in the sample confounded the nitrogen purge method, or where the split-spoon sampler delivered a core which was less than full. In the latter case, volatilization losses are the most likely explanation for the low concentrations observed.

Although it was expected that the most heavily contaminated samples would be obtained from wells A6, A7 and A9, it is possible that contaminant concentration around those wells was reduced by the recovery system, which lies closest to A6, A7 and A9. As can be noted from Table 6, target compound concentration levels dropped off to below

Table 6. Nitrogen-Purge Mass Recovery From Field Samples

Well	Depth (ft)	Toluene ($\mu\text{g}/\text{kg}$)	Octane ($\mu\text{g}/\text{kg}$)	Ethylbenzene ($\mu\text{g}/\text{kg}$)	m,p-Xylene ($\mu\text{g}/\text{kg}$)
06	10.0	8.5	0.8	1.4	2.2
	10.5	12.3	<DL	0.9	9.0
	20.0	24.5	1.1	3.1	9.4
	20.5	55.1	1.8	3.6	28.3
07	10.5	2.4	1.0	<DL	3.7
	20.0	54.5	1.5	4.6	30.3
	20.5	7.4	1.8	0.6	6.8
08	10.0	28.3	0.6	1.0	7.4
	20.0	18.0	<DL	0.8	5.5
	20.5	36.6	<DL	2.4	15.3
09	10.5	4.2	<DL	<DL	8.3
	20.0	<DL	<DL	<DL	5.3
	20.5	14.9	<DL	1.3	10.2
09A	10.0	2.1	<DL	0.6	6.6
	10.5	12.2	<DL	0.4	7.2
	20.0	2.2	<DL	<DL	10.8
	20.5	7.5	<DL	0.4	7.4
10	20.0	66.8	1.0	3.5	19.8
	20.5	46.2	1.2	4.2	24.4
11	20.0	11.6	<DL	<DL	6.5
	20.5	83.7	1.2	7.3	9.8
12	20.0	21.7	1.3	5.3	42.4
	20.5	57.5	<DL	3.8	19.8
13	20.0	22.8	0.9	1.3	13.7
	20.5	78.6	0.8	7.0	85.3
14	20.0	2.4	0.4	<DL	15.0
	20.5	1.8	<DL	<DL	7.3
15	20.0	<DL	<DL	<DL	3.3
16	20.0	<DL	<DL	<DL	7.3

detection levels at a distance of 70–90 ft from the site of the leaking underground tanks (A14, A15, and A16).

During the extraction of the sample cores by the nitrogen purge method, the sample water collected in a separatory funnel, which was placed in line between the sample core oven and the carbon traps. In this way, most of the moisture associated with each discrete core was trapped, and measured at the conclusion of the extraction. Table 7 charts the volume of water present in each core analyzed and the corresponding target compound concentrations. These results generally indicate that as the moisture content increased, so did the concentrations of toluene and m,p-xylenes. Octane and ethylbenzene were below detection levels in many cases.

Table 8 lists the results of the 20–50 g subsamples which were extracted by the ultrasonication method. In the cases where 8–11 subsamples were taken, the mean was used as the target compound concentration (ug/kg) for that location. According to these results the maximum target compound concentrations are around A6, A7, A8, and A9 and start to drop off to the southeast of those wells.

If the ultrasonication method concentration data are compared with the nitrogen purge data, it is evident that the concentrations were within the same order of magnitude, but the nitrogen purge concentrations were generally lower. Also significant is that the points at which the highest contaminant concentrations occurred were different. The maxima points would probably have been in more agreement had not clay caused a problem with wells A7 and A9 nitrogen purge samples. Figure 22 shows a comparison of the results for the two extraction methods for analyses performed on samples collected between 20–21.5 ft below ground surface.

In an effort to determine the precision of the ultrasonication extraction method at the field scale, 8–11 subsamples from the 21 ft sample were taken from A6, A7, and A9. The sample results from A6 were widely variable due to water contamination of the ultrasonic solvent-solvent extraction process and resultant analyte losses and emulsions. However,

Table 7. Comparison of Target Solute Concentrations and Moisture Content for Samples Analyzed Using the Nitrogen-Purge Method

Well	Sample Depth (ft)	Water Content (ml)	Toluene ($\mu\text{g}/\text{kg}$)	Octane ($\mu\text{g}/\text{kg}$)	m,p-Xylene ($\mu\text{g}/\text{kg}$)
06	10.0	33	8.5	0.8	2.2
	10.5	42	12.3	<DL	9.0
	20.0	40	24.5	1.1	9.4
	20.5	60	55.1	1.8	28.3
07	10.0	115	—	—	—
	10.5	75	2.4	1.0	3.7
	20.0	60	54.5	1.4	30.4
	20.5	48	7.4	1.8	6.8
09	10.5	25	4.4	<DL	8.3
	20.0	10	<DL	<DL	5.3
	20.5	40	14.9	<DL	10.2
09A	10.0	63	2.1	<DL	6.6
	10.5	50	12.2	<DL	7.2
	20.0	—	2.2	<DL	10.8
	20.5	28	7.5	0.6	7.4
14	20.0	33	2.4	0.6	15.0
	20.5	10	1.8	<DL	7.3

DL Detectable Limit

the results from A7 and A9 were more informative and are shown in Table 9. Toluene, ethylbenzene, and m,p-xylene, varied approximately 10% from the mean concentrations of the samples that were analyzed, indicating that the ultrasonication method of extraction is a reliable procedure for analyzing volatile organic analytes from natural solids, even after a storage period of about 45 days. The octane concentration results were more variable in these same samples, and octane's high volatility is a possible explanation of the variability.

Table 8. Target Solute Concentrations From Ultrasonic Analysis of 20-g Field Samples Collected at Depth of 21 Feet Below Ground Surface

Well	Toluene ($\mu\text{g}/\text{kg}$)	Octane ($\mu\text{g}/\text{kg}$)	Ethylbenzene ($\mu\text{g}/\text{kg}$)	m,p-Xylene ($\mu\text{g}/\text{kg}$)
06	32.5	82.8	<DL	24.2
07	23.2	86.4	17.4	105.2
08	50.8	23.6	<DL	<DL
09	60.2	97.4	<DL	205.4
09.5	31.2	88.5	12.4	35.8
10	37.4	84.0	<DL	76.45
12	19.3	52.7	*88.1*	<DL
13	24.8	39.5	168.4	28.0
14	<DL	<DL	<DL	*132.0*
15	10.9	60.0	<DL	<DL

DL Detectable Limit

* Potential Interference

Vapor-Phase Sampling

The tip of DGP was driven below the clay layer to obtain vapor samples; depths ranged from 6.5–11.5 ft. The vapor concentrations of each target compound were added together to produce a “total” concentration for mapping the extent of contamination at the site.

The contour lines of “total” vapor concentration, expressed in logarithmic units of μg of the target compounds per liter of vapor, are presented in Figure 23. Contour lines were obtained by interpolating the total concentration data obtained at each of 26 sampling locations (sampling locations are shown on Figure 23), using a commercial universal kriging and plotting that assumes a linear variogram (Surfer, Golden Software). Data presented

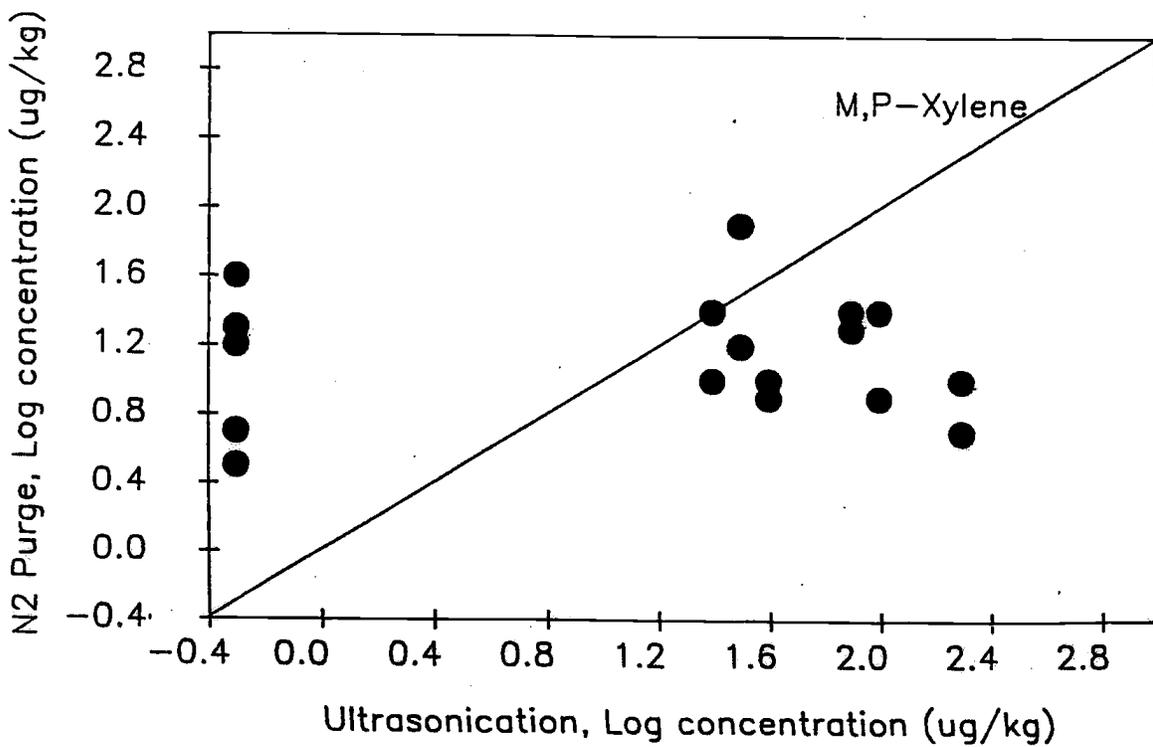
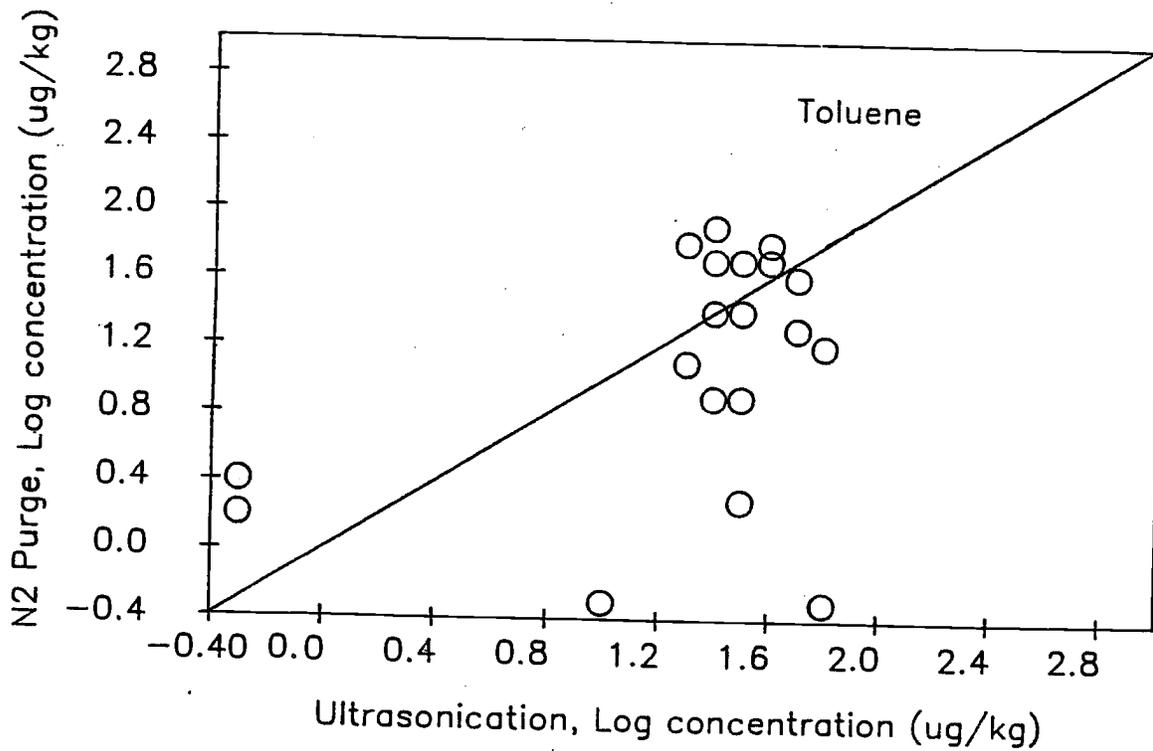


Figure 22. Comparison of nitrogen purge and ultrasonication analyses for samples collected between 20–21.5 ft below ground surface.

Table 9. Comparison of Concentrations From Multiple Ultrasonication Analyses Performed on Samples Collected at 20.5 Feet Below Ground Surface.

Sample	Toluene ($\mu\text{g}/\text{kg}$)	Octane ($\mu\text{g}/\text{kg}$)	Ethylbenzene ($\mu\text{g}/\text{kg}$)	m,p-Xylene ($\mu\text{g}/\text{kg}$)
US721a	24.6	126.8	17.0	112.6
US721b	25.6	96.4	13.3	-
US721e	24.2	72.8	19.7	104.6
US721f	28.4	78.6	13.9	96.3
US721g	22.5	89.4	14.3	97.2
US721i	19.5	74.4	16.9	112.1
US721j	21.8	78.8	15.1	104.5
US721k	18.9	74.2	15.9	108.8
\bar{x}	23.2	86.4	15.8	105.1
σ	2.9	17.1	2.1	6.1
US921a	59.7	59.2	<DL	187.3
US921c	74.7	124.4	<DL	170.3
US921d	57.3	100.9	<DL	215.4
US921e	57.2	90.5	<DL	186.7
US921f	60.3	112.1	<DL	139.7
US921g	57.1	86.2	<DL	123.5
US921h	66.8	121.6	<DL	231.7
US921i	63.6	87.0	<DL	248.6
US921k	52.3	61.8	<DL	182.9
US921l	57.7	130.0	<DL	173.1
\bar{x}	60.2	97.4	—	190.9
σ	6.3	23.7	—	30.6

DL Detectable Limit

in Figure 23 were obtained on three different sampling days over four months, so there is some concern that vapor concentrations changed with time. In fact, as shown in Table 10, samples taken from several locations at the beginning and end of the study did show variations in concentration of individual target compound concentrations ranging from -74-+349%. In addition to experimental error of the sampling method, the recovery operation and movement of the NAPL may have influenced these results. The fact that the contours were in a circular pattern suggests influence from the cone of depression created by the recovery wells.

Table 10. Temporal Variation in Contaminant Concentrations Expressed as Percent Change Between 1 April 1987 and 18 June 1987

Sample Location	Toluene	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%

While there is some error in time averaging of the target compound concentrations, the contour intervals in Figure 23 are broad enough to still have meaning. These contours cover concentrations ranging from 10,000 $\mu\text{g/l}$ near the underground storage tank to less than 10 $\mu\text{g/l}$ of vapor about 150 ft away from the tank. The shaded area of Figure 23 shows the region where a NAPL layer exists on top of the phreatic surface—as interpolated from measurements taken from nine monitoring wells—lies within the region of highest vapor-phase solute concentration. High vapor-phase concentration was expected here due to vertical diffusion of gasoline components from the NAPL. As important, however, was the measured amount of gasoline-origin solutes found in the vapor-phase in regions beyond the

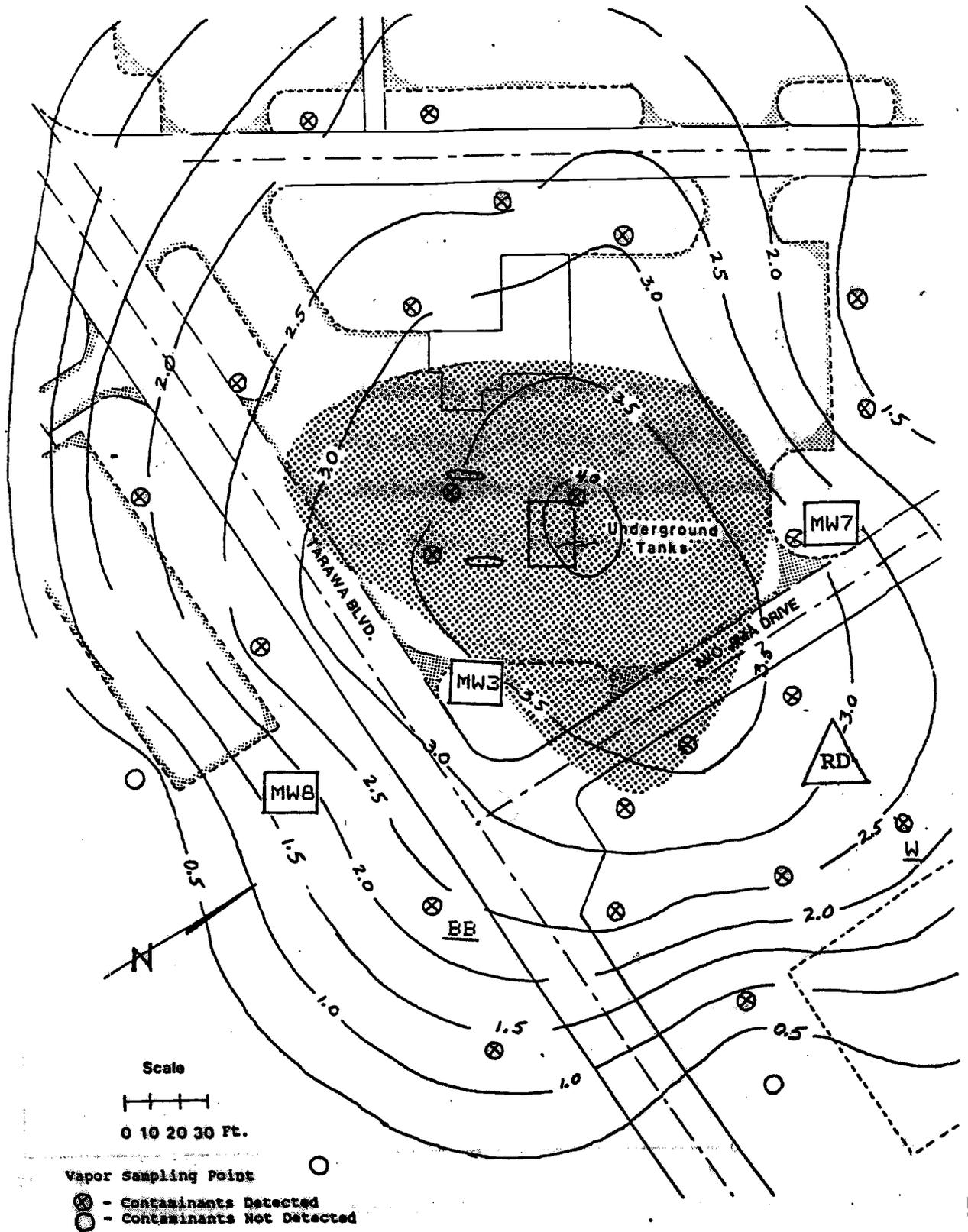


Figure 23. Estimated, vapor-phase concentration distribution based on 26 discrete measurements and universal kriging interpolation.

NAPL. This could be due to: (1) horizontal diffusion of vapor and (2) vertical diffusion from contaminated groundwater.

Evidence for vertical diffusion of vapor is presented in Figures 24–27. A series of four sampling holes, designated collectively as BB in Figure 23, was drilled within a 6-ft diameter. Measurements of toluene (Figure 24), octane (Figure 25), ethlybenzene (Figure 26), m,p xylene (Figure 27) and o- xylene (Figure 28) were then made at three different depths at each hole. There was considerable variability in concentration among the four sampling holes at each of the two lower depths. Nonetheless, taking the average concentration at each depth shows that concentration decreases toward the surface as would be expected if vertical diffusion from the NAPL were important. Another explanation for this pattern, however, is that more biodegradation occurs near the surface where oxygen may not be limiting.

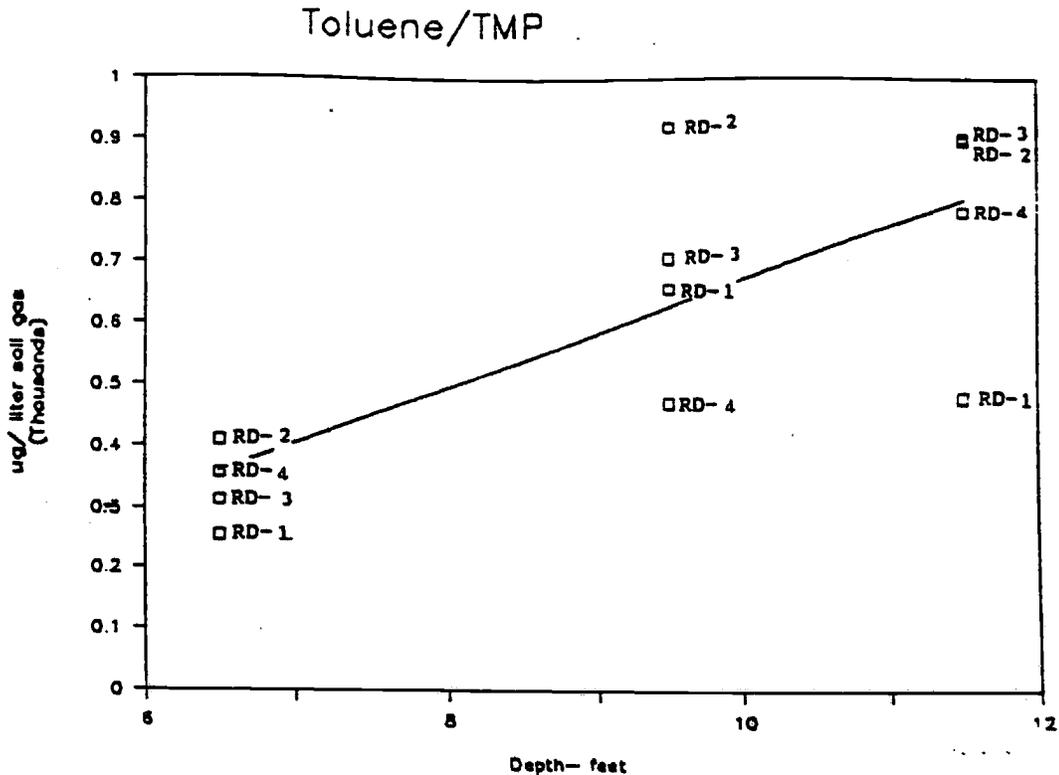


Figure 24. Toluene concentration as a function of depth for the 4 BB sampling locations.

Octane

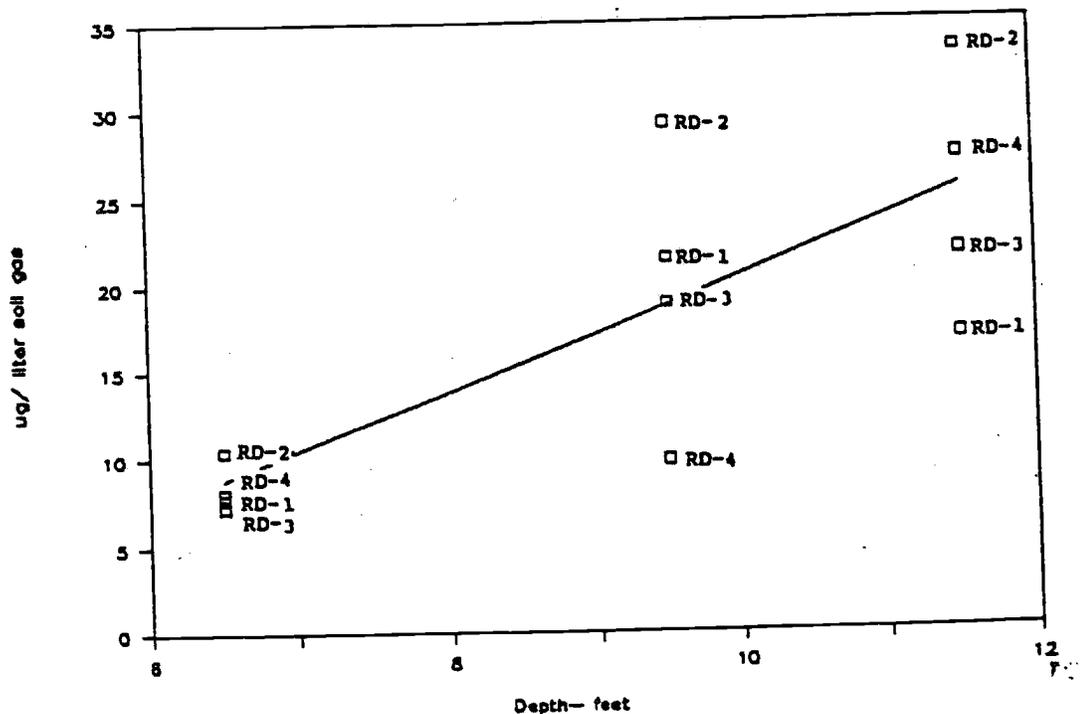


Figure 25. Octane concentration as a function of depth for the 4 BB sampling locations.

Ethylbenzene

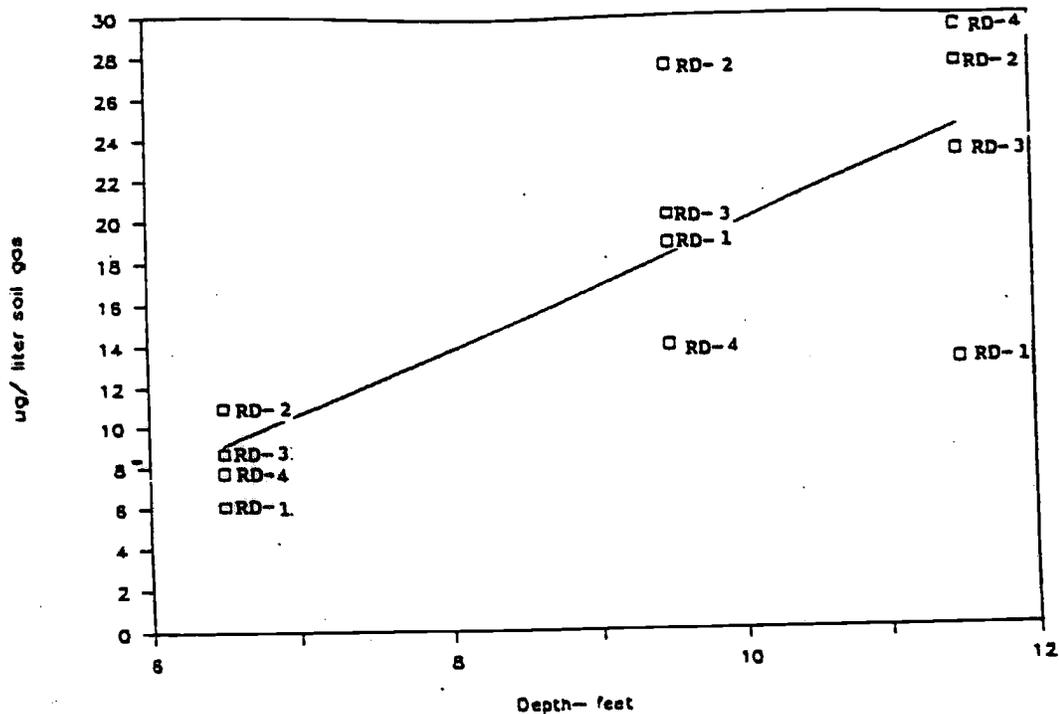


Figure 26. Ethylbenzene concentration as a function of depth for the 4 BB sampling locations.

m,p-Xylene

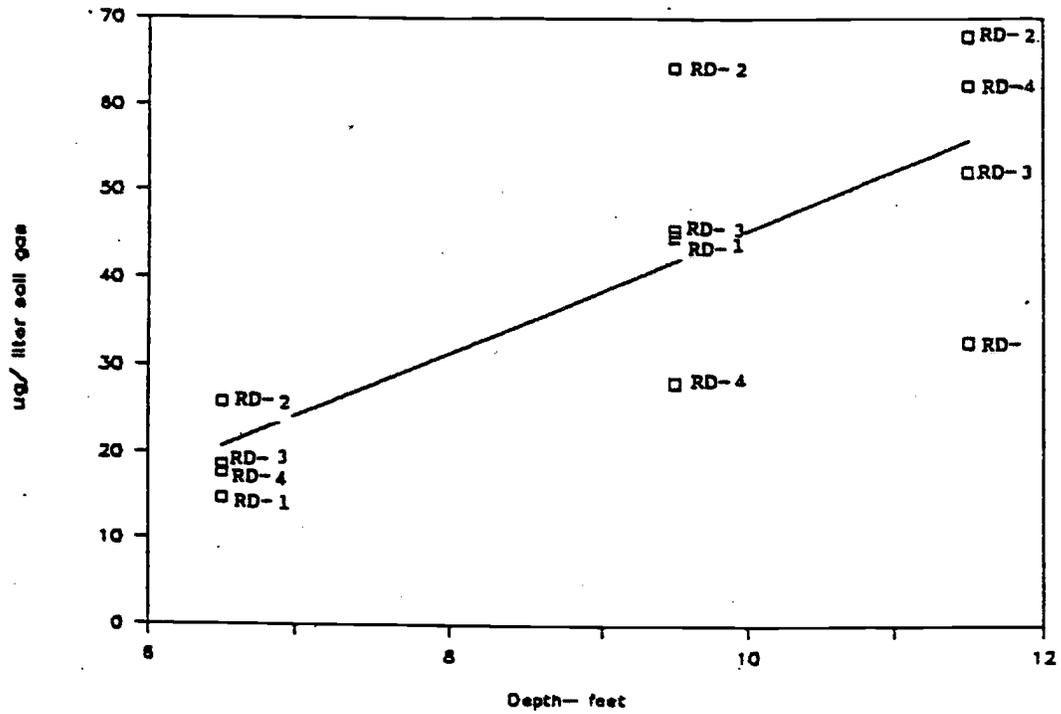


Figure 27. Total m- and p-xylene concentration as a function of depth for the 4 BB sampling locations.

o-Xylene

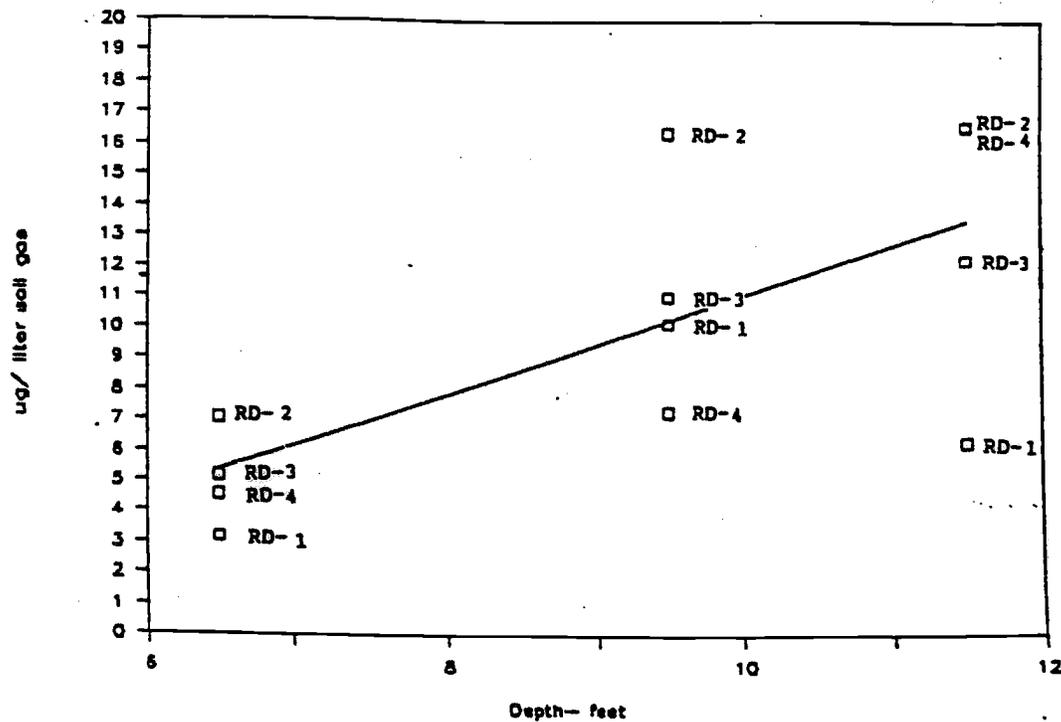


Figure 28. Total o-xylene concentration as a function of depth for the 4 BB sampling locations.

SOLUTE PARTITIONING

Notions of equilibrium partitioning can be used: to assess the distribution of the target solute among the phases present—vapor, aqueous, and solid; and to compare the results obtained from core total-mass measurements to vapor-phase measurements. Such evaluations require information about the relative fractions (mass and volume) of each phase, the assumption of equilibrium among phases, and knowledge of the equilibrium partition coefficients between phases. It can be shown that two solute partition coefficients are sufficient to predict the equilibrium phase distribution. A possible choice for these coefficients is Henry's constant to describe aqueous-vapor phase equilibrium, and an aqueous-solid phase partition coefficient. The former is readily available in the literature, while the latter requires measurement or reliance on relatively rough empirical methods of prediction.

An analysis of the fraction of each target compound found in the vapor-phase is given in Table 11. These fractions were calculated from vapor-phase and combined solid-, vapor- and aqueous-phase measurements taken at locations MW3, MW7, and MW8 that are shown in Figure 23. The mass of any target compound in the vapor phase is:

$$M_v = C_v \epsilon_v V_T \quad (2)$$

where C_v is the concentration ($\mu\text{g}/\text{M}^3$) in the vapor phase; ϵ_v , the fraction of voids filled with vapor phase (0.24 has been estimated based on field measurements); and V_T is the total unit volume of solid, vapor and aqueous phases (1 M^3 assumed in Table 11). The total mass, M_T , in all three phases is calculated from measurement of mass in the soil sample:

$$M_T = C_T \rho_s (1 - \epsilon) \quad (3)$$

where C_T is the concentration ($\mu\text{g}/\text{kg}$) of the target compound per dry weight of soil; ρ_s , the density of dry soil ($2.65 \text{ g}/\text{cm}^3$) and ϵ , the void fraction (estimated as 0.35 from field measurements). Thus, the fraction, F , of target compound found in the vapor phase is:

$$F = \frac{M_v}{M_T} \quad (4)$$

The maximum possible value of F is unity when all of the target compound is in the vapor phase. However, Table 11 shows that four values larger than unity were obtained. These anomalous values occurred because F is calculated from two independent experimental measurements—one of the vapor phase directly and the other of the soil sample (including the vapor phase). The value of F for any given target compound was highest at MW3, which is located within the NAPL region; MW7 and MW8 are both outside the NAPL region. However, the amount of each contaminant found in the soil samples was about the same, regardless of the sampling location. This suggests that while the vapor phase may contain the largest fraction of the contaminant within an existing NAPL, it does not rule out the presence of contaminants in the solid and aqueous phases outside the NAPL.

The distribution of target compounds between vapor phase and underlying ground water at these same sampling locations is given in Figure 29. Henry's law describes the equilibrium distribution as:

$$C_v = K_H C_w \quad (4)$$

where C_w is the ground-water solute concentration; K_H , the Henry's constant; and C_v , is as defined previously. Logarithmic transformation gives:

$$\ln C_v = \ln K_H + \ln C_w \quad (5)$$

Table 11. Calculation of Fraction of Target Compound in Vapor Phase Based on Independent Measurements of Vapor Phase and Vapor, Solid, and Aqueous Phases Combined

Target Compound	Well No.	C_v ($\mu\text{g}/\text{m}^3$) $\times 10^{-3}$	C_T ($\mu\text{g}/\text{kg}$) $\times 10^{-3}$	M_V (μg)	M_T (μg) $\times 10^{-3}$	F
Toluene/TMP	MW3	1960	203	470	349	1.35
			233		402	1.17
	MW7	1206	151	289	259	1.12
			168		290	1.00
	MW8	143	221	34	381	0.09
			168		289	0.12
Octane	MW3	98	72	24	123	0.19
			62		108	0.22
	MW7	90	64	22	109	0.20
			74		127	0.17
	MW8	13	63	3	109	0.03
			83		144	0.02
Ethylbenzene	MW3	117	284	28	488	0.06
			291		501	0.06
	MW7	59	388	14	669	0.02
			247		426	0.03
	MW8	3	259	1	447	0.001
			278		479	0.001
m,p-Xylene	MW3	231	35	55	60	0.92
			19		33	1.66
	MW7	73	18	18	32	0.55
			18		31	0.56
	MW8	5	17	1	30	0.04
			ND		ND	

ND None Detected

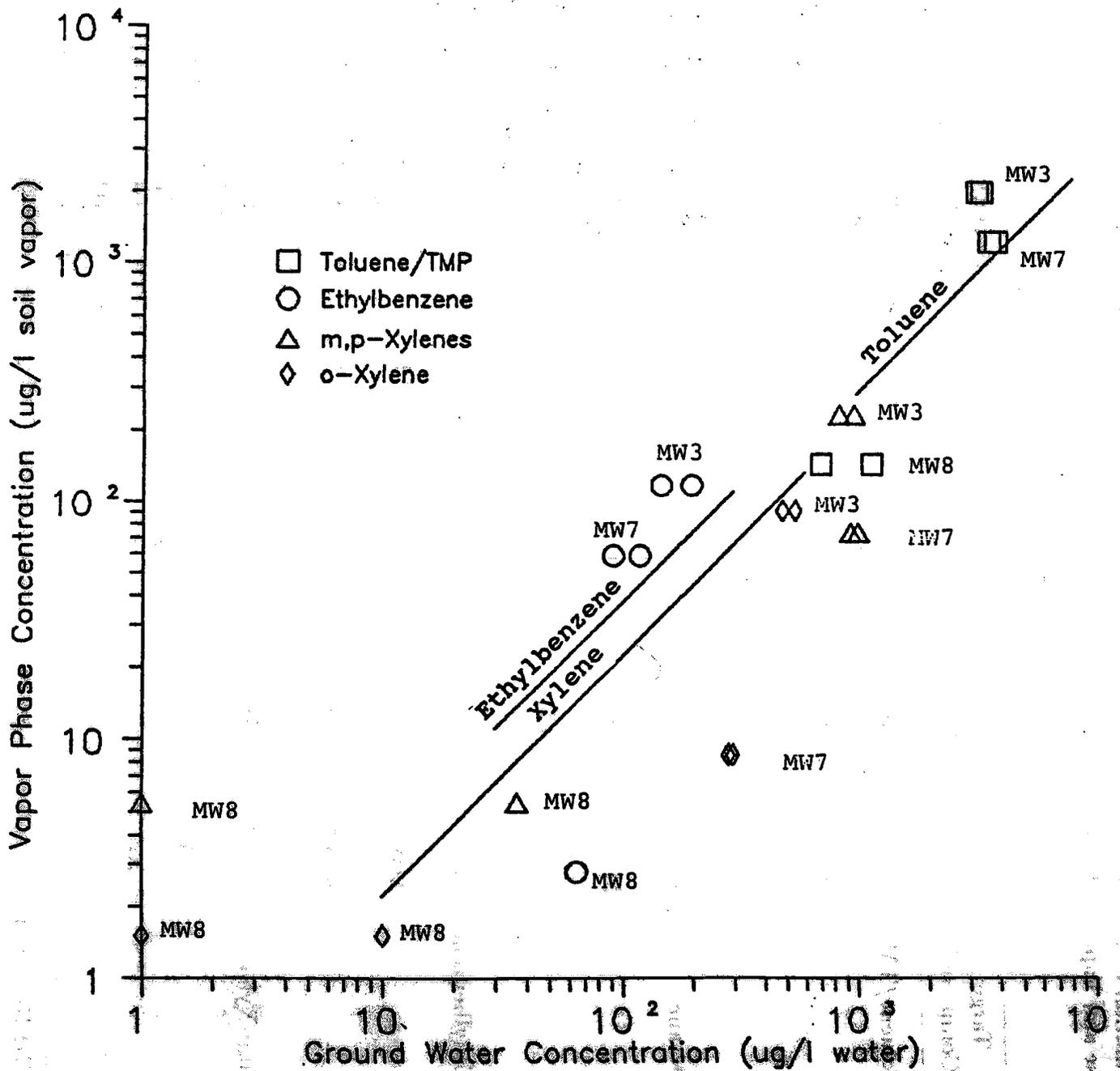


Figure 29. Relationship between vapor-phase and groundwater concentrations for target compounds (in duplicate) at each monitoring well. Solid lines are equilibrium predictions based on Henry's law.

The solid lines in Figure 29 are the resulting predictions of this relationship for each of the target compounds using literature values of K_H (Lyman, Reehl and Rosenblatt, 1982). Duplicate measurements of ground- water solute concentration were made for each vapor phase solute concentration measurement. Most of the data were fairly close to equilibrium predictions, although the logarithmic scales in Figure 29 may distort the extent of agreement in some instances. The most notable discrepancies from equilibrium predictions were for ethylbenzene (at MW7), m,p xylene (at MW8) and o-xylene (at MW7). As shown in Figure 23, these monitoring wells were located on either side of the NAPL while MW3 was within the NAPL region.

REFERENCES

- Chiou, C.T. and T.D. Shoup (1985), Soil Sorption of Organic Vapors and Effects of Humidity on Sorptive Mechanism and Capacity, *Environmental Science & Technology*, Vol. 19, pp. 1196-1200.
- Colenutt, B.A. and D.N. Davies (1980), The Sampling and Gas Chromatographic Analysis of Organic Vapours in Landfill Sites, *International Journal of Environmental Analytical Chemistry*, Vol. 7, pp.223-229.
- Colenutt, B.A. and S. Thorburn (1980), Optimization of a Gas Stripping Concentration Technique for Trace Organic Water Pollutants, *International Journal of Environmental Analytical Chemistry*, Vol. 7, pp. 231.
- Dietz, W.A. (1967), Response Factors for Gas Chromatographic Analyses, *Journal of Gas Chromatography*, February.
- Eklund, B.M. and C.E. Schmidt (1983), Review of Soil Gas Sampling Techniques, In: *Soil Gas Sampling Techniques of Chemicals for Exposure Assessment*, Radian Corporation, Interim Report, EPA-EMSL 68-02-3513, Work Assignment 32.
- Eklund, B. M. (1985), Detection of Hydrocarbons in Groundwater by Analysis of Shallow Soil Gas Vapor, American Petroleum Institute Publication Number 4394.
- Evans, O.D. and G.M. Thompson (1986), Field and Interpretation Techniques for Delineating Subsurface Petroleum Hydrocarbon Spills Using Soil Gas Analysis. In the Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater-Prevention, Detection and Restoration, Houston, Texas, November 12-14, pp. 444-455.
- Goodman, N. L. (1985), Evaluation of Methodology for Analysis of Organic Contaminants in Soil, Master of Science Technical Report, University of North Carolina at Chapel Hill.
- Grimalt, J. C., C. Marfil, and J. Albaighés (1984), Analyses of Hydrocarbons in Aquatic Sediments, *International Journal of Environmental Analytical Chemistry*, Vol. 18, pp. 183-194.
- Hamilton, S.E., T.S. Bates, and J.D. Cline (1984), Sources and Transport of Hydrocarbons in the Green-Buwanish River, Washington, *Environmental Science & Technology*, Vol. 18(2), pp. 72-79.
- Hansch, C. and A. J. Leo (1979), *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley-Interscience, NY, 339 pp.

- Industrial Marine Service, Inc. (1985), Delineation and Proposed Recovery of a Subsurface Fuel Plume, Camp Lejeune, IMS, Inc., Norfolk, VA, 7 pp.
- Jenkins, T. F and C. L. Grant (1987), Comparison of Extraction Techniques for Munitions Residues in Soil, *Analytical Chemistry*, Vol. 59, pp. 1326-1331.
- Johnsen, R. E. and R. I. Starr (1972), Ultrarapid Extraction of Insecticides from Soil Using a New Ultrasonic Technique, *Journal of Agricultural Food Chemistry*, Vol. 20(1), pp. 48-51.
- Juney, R.C., R.E. Devereux, E.H. Stevens, S.F. Davidson, and W.D. Lee (1923), Soil Survey of Onslow County, North Carolina, United States Department of Agriculture, Bureau of Soils, Government Printing Office, Washington, D.C., 127 pp.
- Kerfoot H. B., C. L. Mayer, and M. J. Miah (1986), Evaluation of a Passive Sampling Soil-Gas Survey Technique for Detecting Volatile Organic Compounds, In: Proceedings of the National Water Well Association/American Petroleum Institute Conference on Petroleum Hydrocarbons and Organic Compounds in Ground Water—Prevention, Detection and Restoration, Houston, Texas, pp. 407-419.
- Kerfoot, H. B. (1987), Soil Gas Measurement for Detection of Groundwater Contamination by Volatile Organic Compounds, *Environmental Science & Technology*, Vol. 21, pp. 1022-1024.
- Lapella, E.G. and G.M. Thompson (1983), Detection of Groundwater Contamination by Shallow Soil Gas Sampling in the Vadose Zone. Proceedings of the Characterization and Monitoring of the Vadose (Unsaturated) Zone, Las Vegas Nevada, December 8-10.
- Laseter, J. L., I. R. De Leon, M.A. Maberry, E. B. Overton, C. K. Raschke, P. C. Remele, C. F. Steels, and V. L. Warren (1980), Rapid G.C. Method for the Determination of Volatile and Semivolatile Organochlorine Compounds in Soil and Chemical Waste Disposal Site Samples, *Journal Chron. Science*, 18, pp. 85-88.
- LeGrand, H.E. (1959), Evaluation of Well-Water Supply, Marine Corps Base, Camp LeJeune, North Carolina, 55 pp.
- LeGrand, H.E. (1960), Geology and Ground-Water Resources of Wilmington-New Bern Area, Ground-Water Bulletin Number 1, North Carolina Department of Water Resources, pp. 67-74.
- Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt (1982), Handbook of Chemical Property Estimation Methods, McGraw-Hill Book Company, New York, NY.
- Mackay, D.M., P.V. Roberts, and J.A. Cherry (1985), Transportation of Organic Contaminants in Groundwater, *Environmental Science & Technology*, 19(5), pp. 384-392.

Neglia, S. and L. Faveratto (1962), Study on an Analytical Method for the Execution of Surface Geochemical Prospecting for Petroleum and Natural Gas, Proceedings of the International Meeting on Advances in Organic Geochemistry, Milan, Italy. Vol. 15 pp. 285-295.

Nunez, A.J., L.F. Gonzalez, and J. Janak (1984), Preconcentration of Headspace Volatiles for Trace Organic Analysis by Gas Chromatography, Journal of Chromatography, Vol. 209, pp. 128-163.

Petersen, J. C. and D. H. Freeman (1982), Method Validation of GC-MS-SIM Analysis of Pthalates, International Journal of Environmental Analytical Chemistry, Vol. 12, pp. 277-291.

Radian Corporation (1984), Soil Gas Sampling Techniques of Chemicals for Exposure Assessment, Bonifay Spill Site Data Volume. EPA-EMSL 68-02-3513, Work Assignment 32.

Schwille, F. (1967), Petroleum Contamination of the Subsoil-A Hydrological Problem, The Joint Problems of the Oil and Water Industries, P. Hepple, ed., Institute of Petroleum, London, 1967, pp. 23-54.

Slater, J.P., F.R. McLaren, D. Christenson, and D. Dineen (1983), Sampling and Analysis of Soil for Volatile Organic Compounds: I. Methodology Components, Proceedings of the NWWA/US-EPA Conference on the Characterization and Monitoring of Vadose Zone, pp. 623-58.

Sun, M. (1986), Ground Water Ills: Many Diagnoses, Few Remedies, Science, Vol. 232 pp. 1490-1493, June 20.

Swallow, J.A. and P.M. Gschwend (1983), Volatilization of Organic Compounds from Unconfined Aquifers. Proceedings of the 3rd National Symposium on Aquifer Restoration and Groundwater Monitoring, Columbus, Ohio, May 25-27, pp. 327-333.

Tang, S. (1986), Predicting Equilibria for Gas-Phase Adsorption of Volatile Organic Compounds: The Impact of Relative Humidity and Multi-Component Interactions, Master Thesis, Michigan Technological University.

Thorburn, S., B.A. Colenutt, and S.G. Douglass (1979), The Sampling and Gas Chromatographic Analysis of Gases from Landfill Sites, International Journal of Environmental Analytical Chemistry, Vol. 6 pp. 245-254.

Verschueren, K. (1983), Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, NY.

Voorhees, K. J., J. C. Hickey, and R. W. Klusman (1984), Analysis of Ground Water Contamination by a New Surface Static Trapping/Mass Spectroscopy Technique, Analytical Chemistry, Vol. 56, pp. 2602-2604.

Weast, R. C., ed. (1986), CRC Handbook on Chemistry and Physics, 67th Edition, CRC Press, Inc., Boca Raton, FL.



