United States
Environmental Protection
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Research and Development

Soil-Gas and Geophysical Techniques for Detection of Subsurface Organic Contamination

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Project Summary

Soil-Gas and Geophysical Techniques for Detection of Subsurface Organic Contamination

Ann M. Pitchford, Aldo T. Mazzella, and Ken R. Scarborough

From 1985 through 1987, the Air Force Engineering and Services Center (AFESC) funded research at the U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV) through an interagency agreement. This agreement provided for investigations of subsurface contamination at Air Force installation Restoration Program sites. The purpose of these investigations was to demonstrate and evaluate inexpensive and relatively rapid reconnaissance techniques which can detect and map subsurface organic contamination. This information can reduce the number and improve the placement of wells required in an investigation, resulting in significant savings in terms of costs and time.

The methods chosen for demonstrations included active and passive soil-gas sampling and analysis, and the geophysical techniques of electromagnetic induction (EM), and d.c. resistivity. Field studies were performed at four Air Force Bases: active soil-gas measurements were performed at all sites; d.c. resistivity and EM measurements were performed at three sites; and passive soil-gas sampling was performed at two sites. The techniques of ground-penetrating radar and complex resistivity were included in the evaluations using experiences at other locations. Based on this limited set of cases and information from published literature, general guidelines on the application of these techniques for detecting organic contamination were developed.

The active soil-gas sampling technique successfully mapped solvents, gasoline, and JP-4 contamination at the four bases where it was used. The passive soil-gas technique was successful in some cases, but not as successful as the active technique, and further research on the performance of the technique is recommended before the method is used widely. The geophysical methods were successful for site characterization, but the EM and d.c. resistivity techniques did not detect gasoline and jet fuel number 4 (JP-4) contamination when it was present. The use of EM and d.c. resistivity for direct detection of hydrocarbons appears to be a subtle technique which depends on a thorough understanding of background information at the site, the skill of the instrument operator, and may depend on the length of time the spill has been present. The ground-penetrating radar and complex resistivity techniques were used successfully at a number of locations for detecting organic contamination. This work was conducted from January 1985 to October 1987.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully

documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In 1984, the U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV) and the Air Force Engineering and Services Center (AFESC) entered into an interagency agreement concerning investigations of subsurface contamination at Air Force Installation Restoration Program (IRP) sites. Organic contamination was emphasized in these studies. The traditional approach to these site investigations involves the installation of wells and analysis of ground-water samples, This approach provides a direct measurement of the contamination at the locations sampled. However, information about the extent and degree of contamination may be limited by the number, cost and possible locations of the wells. If inexpensive, and relatively rapid reconnaissance techniques could be used as an aid to selecting the well locations, the number of wells could be reduced. This would save money and time.

The interagency agreement initiated studies at four IRP sites to demonstrate indirect methods for detecting and mapping organic contamination in ground-water and soil. The methods chosen for evaluation were soil-gas and geophysical measurements. These measurement results then were compared to ground water data obtained during the same study. This made it possible to evaluate the performance of the soil-gas and geophysical techniques. However, because of the wide variety in contaminants and geological conditions, care must be used when applying the conclusions developed from these site-specific studies to other locations. To help to extend the results from these studies to other site conditions, additional examples were assembled from the literature. Using all this information, general guidelines were developed for the use of these techniques in investigations of organic contamination of soil and ground water.

Approach

The overall approach to the project was divided into two parts with activities in each proceeding concurrently. These parts consisted of working with a panel of experts to broaden the ideas, approaches and experiences being used as a basis for developing the guidelines; and performing site investigations to demonstrate the soil-gas and geophysical techniques. The Air Force Bases (AFBs) selected are listed in Table 1. Each AFB provides differing geology, climate, depth to water table, and contaminants, thus representing a variety of situations for performing the comparisons.

This series of studies was intended to help formulate a hierarchy of techniques which could be logically adapted and applied to detect contamination for a variety of site conditions. However, the results from the field studies fit better into a framework of broad guidelines rather than into a detailed strategy which ranks techniques,

Field Study Results

The methods chosen for demonstrations included active and passive soil-gas sampling and analysis, and the geophysical techniques of EM and d.c. resistivity. Active soil-gas measurements were performed at all sites; resistivity and EM measurements were performed at three sites; and passive soil-gas sampling was performed at two sites. Key results from these investigations are summarized in Table 2.

The active soil-gas sampling technique successfully mapped solvents, gasoline, and JP-4 contamination at all four bases where it was used. Results from Robins AFB demonstrated that the choice of sampling depth can influence the measurements obtained. At this AFB, initial sampling at 1 meter revealed very little contamination as shown in Figure 1, while additional sampling at 2 meters located more contamination, which is shown in Figure 2. Thus, it is important to perform depth profiles at a number of locations during the initial phase of a study, preferably in regions of known (quantified) ground-water contamination, in order to select the sampling depth. Sampling depth is particularly important at sites where relatively old fuel spills have occurred, because chemical or biological oxidation of the petroleum hydrocarbons can remove fuel constituents from the aerobic soil horizons. The real-time nature of this method also represents a significant advantage over more time-consuming techniques since the choice and number of sampling locations can be evaluated as data are obtained.

Two of the sites investigated with active soil-gas techniques were also investigated by a passive technique which used adsorbent charcoal badges, At these sites, tests were performed to determine the feasibility of mapping the contamination at these sites by selecting the best exposure times for the badges. Performing feasibility tests with the badges was demonstrated to be very important; an insufficient exposure time may indicate an area is uncontaminated when contamination actually is present, Alternately, overexposure of the badges may result in saturation of the sorbent which would mask any relative differences in soil-gas contamination at the various sampling locations. This passive soil-gas technique was not as successful as the active technique in detecting contaminated ground water However, contaminated areas were identified successfully in some cases. Further testing of the performance of this technique for a variety of contaminants and geologic conditions is recommended before the method is used widely. If on-site personnel are available to conduct the sampling, the low analytical cost of this method has potential for reducing site investigation costs in some cases.

The geophysical methods were successful for site characterization, but the EM and d.c. resistivity techniques did not detect gasoline and JP-4 contamination when it was present. This was attributed to the natural variations in background

Table 1, Geology, Climate, and Contaminants at&r Force Base Study Sites

Base	*Geology*	*Climate*	*Contaminant*
Holloman AFB	*sand, inter bedded clay*	*arid*	*gasoline, JP-4, solvents*
Phelps Collins ANGTB	*karst*	*humid*	*solvent, JP-4, buried metallic objects*
Robins AFB	*marine sand*	*humid*	*JP-4, solvents*
Tinker AFB	clay	*humid*	*JP-4*

Table 2. Key Results from the AFB Investigations

Site *and contaminants*	*Method*	*Comment*
Ho//oman AFB, *BX Service Station,* **Gasoline**	*Active soil-gas sampling*	*Compares favorably with ground-water data. Demonstrates movement of contaminants* along *utility corridors.*
	EM, d.c. resistivity	Do *not detect organics because of natural variability in soil resistivity. Culture limited extent* of *survey.*
Robins AFB,JP-4 Spill, JP-4	*Active sod-gas sampling*	*Compares favorably with ground-water data in* spite *of 20-year age of spill. Demonstrates importance of depth of sampling.*
	Passive soil-gas sampling	*Preliminary test* has *mixed results* compared *to ground-water data.*
	EM, d.c. resistivity	*Do not detect organics because of natural variability in soil resistivity due to rainfall effects and culture. AFB radar interferes with EM-34 measurements..*
Tinker AFB, Fuel Farm 290, JP-4	*Active soil-gas sampling*	*Compares favorably with ground-water* data; *technique effective in clay soil*
	Passive soil-gas sampling	*Preliminary test has mixed results compared to ground-water data. Technique may be responding to surface contamination at times.*
	EM, d.c. resistivity, complex resistivity	*Were not attempted due to high density of buried pipes and tanks, and fences and pipes on* surface.

resistivity which masked any resistivity anomaly due to the presence of hydrocarbons. Based on these results, the use of EM and d.c. resistivity for direct detection of hydrocarbons appears to be a subtle technique which depends on a thorough understanding of background information at the site, the skill of the instrument operator, and may depend on the length of time the spill has been present. This does not preclude the use of these techniques in site characterization. The techniques of GPR and complex resistivity were not demonstrated at the AFBs, but their successful performance in detecting hydrocarbons has been documented in the literature. Table 3 summarizes the general recommendations for application of the geophysical techniques.

Note that only two techniques, GPR and complex resistivity, are recommended for routine use in detecting organic contamination. GPR is commercially available. Complex resistivity, however, is the subject of several research efforts, and is not widely available. The d.c. resistivity and EM techniques may sometimes be useful at a site for detection of hydrocarbons, but the conditions for which this is true are not now understood. Other techniques with greater likelihood of success should be considered first.

Fundamentals for Planning Site Investigations

To place these results in context, recommendations for planning a site investigation also are presented. These recommendations were prepared in conjunction with members of the panel of experts assembled to provide advice to the project. The recommendations address general considerations in designing an investigation, provide examples and references to similar cases in the literature, list the steps in planning a soil-gas investigation, and list issues to be considered in planning a geophysical investigation. The issues which should be considered are presented in series of questions organized by topic area, including hydrology, the use of isotopes, and water chemistry.

Conclusions

Demonstrations of soil-gas and geophysical techniques at four AFBs provided the basis for the development of broad guidelines for the application of these methods. The active soil-gas sampling technique successfully mapped solvents, gasoline, and JP-4 contamination at the bases. The passive soil-gas technique was successful in some cases, but not as successful as the active technique, and further research on the performance of the technique is recommended before the method is used widely. The geophysical methods were successful for site characterization, but the EM and d.c. resistivity techniques did not detect gasoline and jet fuel number 4 (JP-4) contamination when it was present The use of EM and d.c. resistivity for direct detection of hydrocarbons appears to be a subtle technique which may sometimes be useful at a site for the detection of hydrocarbons, but the reasons for this are not well understood. Other techniques with greater likelihood of success should be considered first. The ground-penetrating radar and complex resistivity techniques have been used successfully at a number of locations for detecting organic contamination.

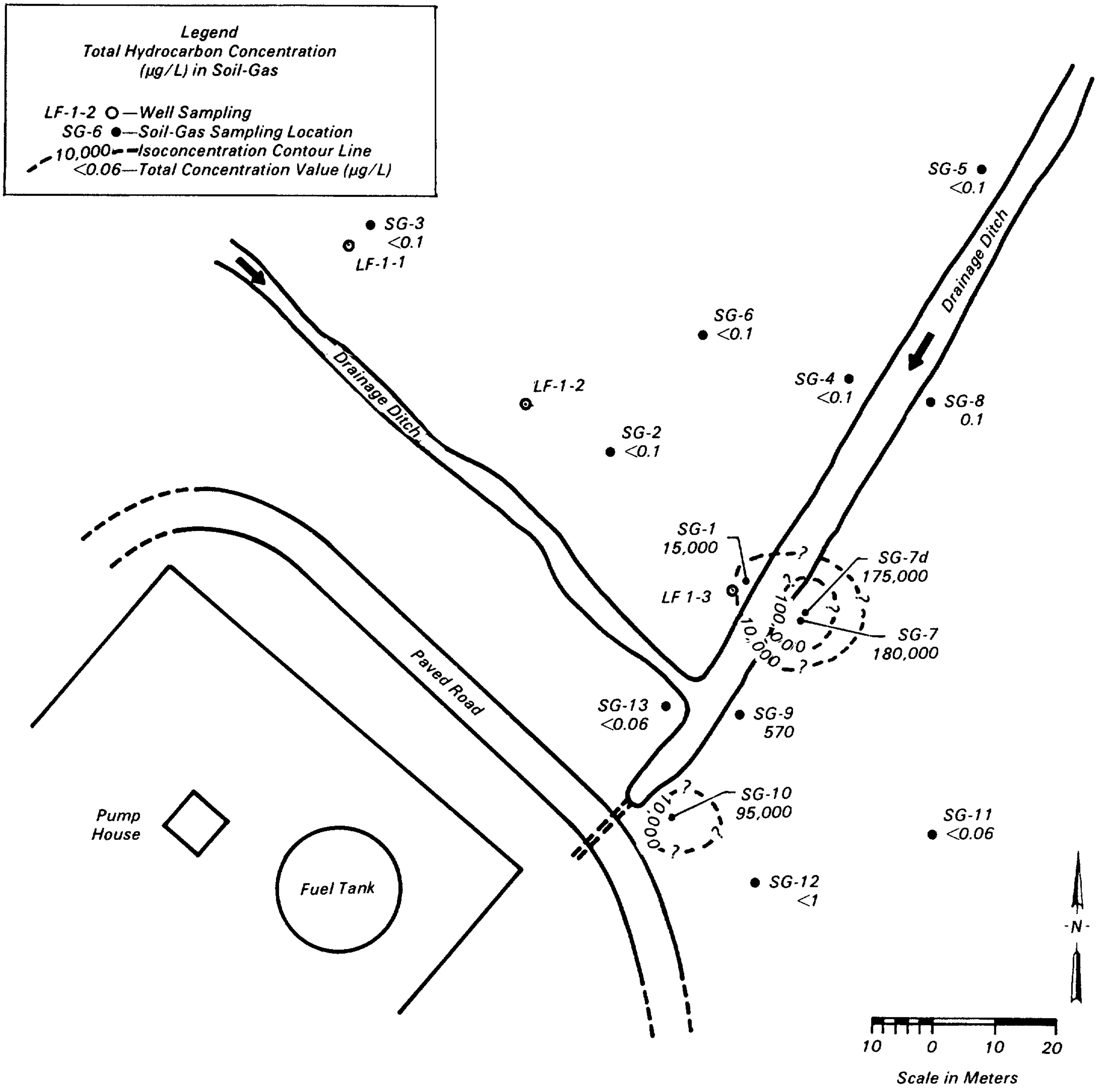

Figure 1. Concentrations of total hydrocarbons in soil gas at JP-4 spill site. Robins AFB, Sampling depth: 1 meter.

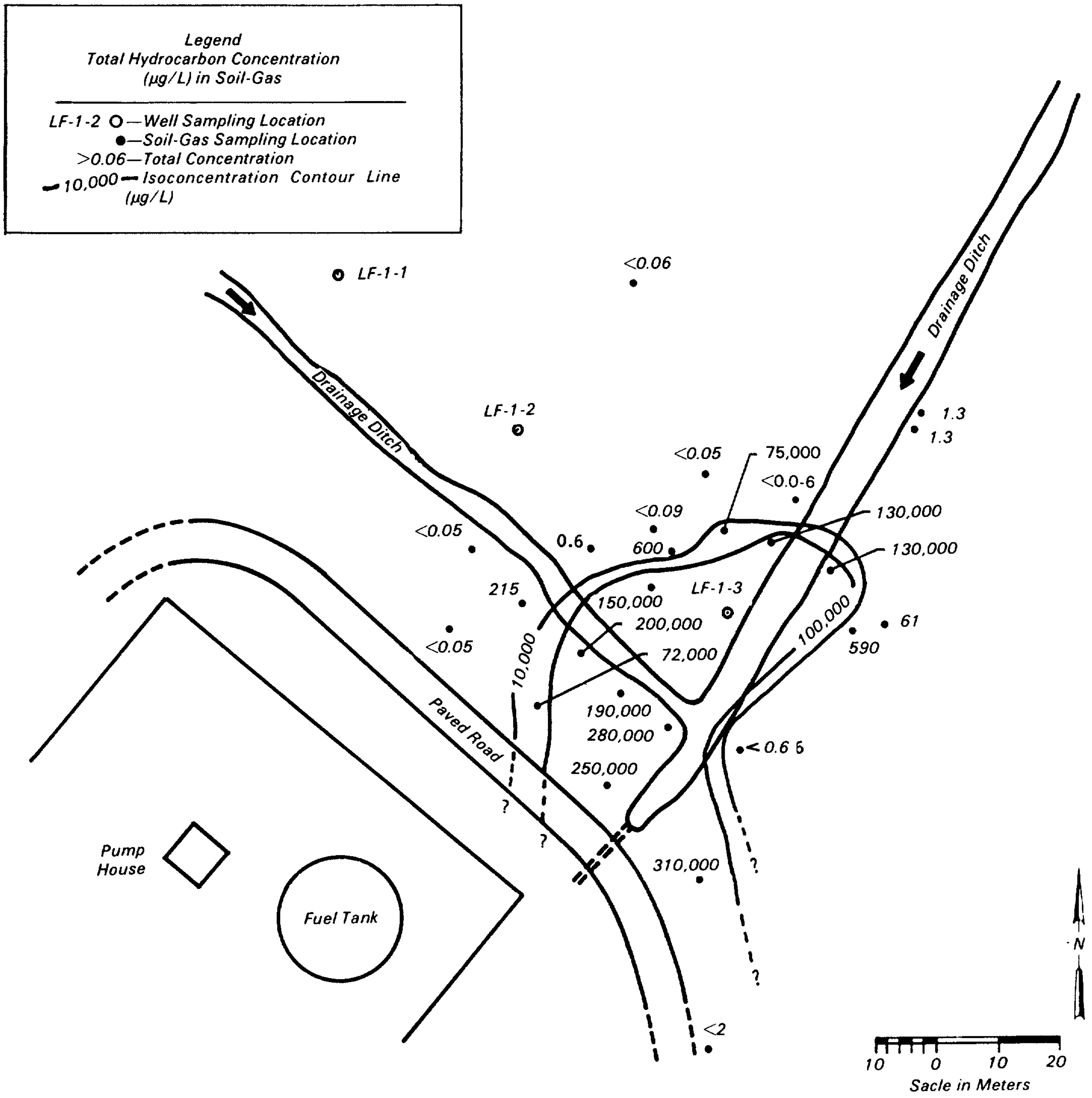

Figure 2. Concentrations of total hydrocarbons in soil gas at JP-4 spill site, Robins AFB. Sampling depth: 2 meters.

Table 3. *Generalized Applications of Geophysical Techniques*

	Application			
Technique	*Site Characterization*	*Conductive Leachate**	*Metal Objects**	*Organic Contamination*
Ground Penetrating Radar (GPR)	*yes*	*yes*	*yes*	*yes*
Electromagnetics (EM)	*yes*	*yes*	*yes*	*possibly*
DC, Resistivity	*yes*	*yes*	*yes*	*possibly*
Complex Resistivity	*yes***	*yes***	*yes***	*yes*
Seismic Refraction	*yes*	*no*	*no*	*no*
Metal Detector	*no*	*no*	*yes*	*no*
Magnetometer	*no*	*no*	*yes****	*no*

**In some cases, the organic contamination will be associated with inorganic contamination: examples include organics in metal drums and mixed organic-inorganic leachate plumes,*

***But* d.c. *resistivity is equally good and much cheaper.*

****Ferrous metals only.*

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Aldo T. Mazzella is also the EPA Project Officer (see below).

The complete report, entitled "Soil-Gas and Geophysical Techniques for Detection of Subsurface Organic Contamination, " (Order No. PB 88-208 194/AS; Cost: $14.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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SOIL-GAS AND GEOPHYSICAL TECHNIQUES FOR DETECTION OF SUBSURFACE ORGANIC CONTAMINATION

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NOTICE

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ABSTRACT

From 1985 through 1987, the Air Force Engineering and Services Center (AFESC) funded research at the U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV) through an interagency agreement. This agreement provided for investigations of subsurface contamination at Air Force Installation Restoration Program sites. The purpose of these investigations was to demonstrate and evaluate inexpensive and relatively rapid reconnaissance techniques which can detect and map subsurface organic contamination. This information can reduce the number of wells required in an investigation, resulting in significant savings in terms of costs and time.

The methods chosen for demonstrations included active and passive soil-gas sampling and analysis, and the geophysical techniques of electromagnetic induction (EM), d.c. resistivity, seismics and magnetics. Field studies were performed at four Air Force Bases where these techniques were used as appropriate. Active soil-gas measurements were performed at all sites; resistivity and electromagnetic induction measurements were performed at three sites, and passive soil-gas sampling was performed at two sites. The other techniques were applied to characterize one study site. The techniques of ground-penetrating radar and complex resistivity were included in the evaluations using experiences at other sites. Based on this limited set of cases and information from published literature, general guidelines on the application of these techniques for detecting organic contamination were developed.

The active soil-gas sampling technique successfully mapped solvents, gasoline, and JP-4 contamination at all four bases where it was used. The passive soil-gas technique was successful in some cases, but not as successful as the active technique, and further research on the performance of the technique is recommended before the method is used widely. The geophysical methods were successful for site characterization, but the EM and d.c. resistivity techniques did not detect gasoline and jet fuel number 4 (JP-4) contamination when it was present. The use of EM and d.c. resistivity for direct detection of hydrocarbons appears to be a subtle technique which depends on a thorough understanding of background information at the site, the skill of the instrument operator, and may depend on the length of time the spill has been present. The ground-penetrating radar and complex resistivity techniques were used successfully at a number of locations for detecting organic contamination. This work was conducted from January 1985 to October, 1987.

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SECTION 1

INTRODUCTION

BACKGROUND

In 1984, the U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV) and the Air Force Engineering and Services Center (AFESC) entered into an interagency agreement concerning investigations of subsurface contamination at Air Force Installation Restoration Program (IRP) sites. Organic contamination was emphasized in these studies. The traditional approach to these site investigations involves the installation of wells and analysis of ground-water samples. This approach provides a direct measurement of the contamination at the locations sampled. However, information about the extent and degree of contamination may be limited by the number, cost and possible locations of the wells. If inexpensive, and relatively rapid reconnaissance techniques could be used as an aid to selecting the well locations, the number of wells could be reduced. This would save money and time.

The interagency agreement initiated studies at four IRP sites to demonstrate indirect methods for detecting and mapping organic contamination in ground-water and soil. The methods chosen for evaluation were soil-gas and geophysical measurements. These measurement results then were compared to ground-water data obtained during the same study. This made it possible to evaluate the performance of the soil-gas and geophysical techniques for these locations. However, because of the wide variety in contaminants and geological conditions, care must be used when applying the conclusions developed from these site-specific studies to other locations. To extend the results from these studies to other site conditions, additional examples were assembled from the literature. Using all this information, general guidelines were developed for the use of these techniques in investigations of organic contamination of soil and ground water.

OBJECTIVES

The objectives of the interagency agreement are listed below:

- to evaluate techniques, other than directly sampling ground water, for detecting subsurface organic contamination under a variety of conditions;

- to recommend appropriate applications for the alternative techniques based on the field experience; and

- to recommend research that is needed to further the use of these techniques.

The approach for meeting these objectives is described below.

APPROACH

The overall approach to the project was divided into two parts with activities in each proceeding concurrently. These parts consisted of working with a panel of experts to broaden the ideas, approaches and experiences being used as a basis for developing the recommendations; and performing site investigations to demonstrate the soil-gas and geophysical techniques. The reasons the soil-gas and geophysical techniques were chosen are described below.

Soil-gas surveying is an emerging technology for detection of subsurface contamination through the use of near-surface techniques. The techniques of soil-gas surveying are based on the measurement of volatile organic compounds (VOCs) in soil gas to detect contamination in the ground water below. VOCs dissolved in ground water vaporize into the soil atmosphere according to their vapor pressures and aqueous solubilities. In many situations, detectable concentrations of VOCs are present in soil gas above contaminated ground water. Because of this, soil-gas surveying often can be used to map contaminated ground water at a site. Since VOCs are the major components of gasoline, jet fuel number 4 (JP-4), and many industrial solvents, this technology can be very useful for locating commonly-occurring contamination. In these studies, active and passive soil-gas techniques were evaluated. The results were compared to ground-water analyses.

Geophysical techniques, developed for mineral, soil engineering, and oil investigations, are now beinq applied to hazardous waste site investigations. Techniques frequently used include d.c. resistivity, electromagnetic induction (EM), ground-penetrating radar (GPR), magnetics, and seismic methods. These methods, individually or in combination, can often provide information about geohydrologic features, locations of buried metal objects, locations of buried trenches, and mapping of conductive leachates and contaminant plumes. These applications of geophysics are well understood and documented. Electrical geophysical techniques such as EM (terrain) conductivity have been used successfully on a number of occasions to directly detect organic contamination (Germeroth and Schmerl, 1987; Saunders and Cox, 1987; Saunders and Germeroth, 1985; Valentine and Kwader, 1985; and Saunders, et. al., 1983). However, these methods generally have not been accepted for routine use because the physical response occurring is not well understood. The use of GPR and complex resistivity to directly detect organic contamination has been documented for a number of locations (Olhoeft, 1986). Geophysical techniques are subject to interferences from a variety of sources depending on the technique. These interferences, which include the presence of metal objects, pipelines, powerlines, radio transmissions, and ambient noise, may prevent the collection of useful data at a particular location. In this study, all the methods mentioned above except ground-penetrating radar were demonstrated at one or more locations. At most bases, the geophysical techniques were used to determine physical characteristics such as depth to bedrock, or depth to the water table. In some cases, geophysical methods were used to locate buried metal objects. The direct detection of organic contamination was also attempted using EM and d.c. resistivity techniques. In this report, the emphasis will be on using soil-gas and geophysical techniques to directly detect organic contamination.

Panel of Experts

As mentioned earlier, a panel of experts was chosen to provide advice on site investigation approaches. These experts and their fields of expertise are listed in Table 1. Each expert was assigned the task of describing the approach they use for investigations at hazardous waste sites. These approaches were compiled for the entire group to review and later discuss at a 2-day meeting. The resulting information was of value to the field studies in progress, and where appropriate, has been included in this report.

TABLE 1. PANEL OF EXPERTS

Name	Affiliation	Area of expertise
Dr. John Cherry Hydrologist	Geoflow, Limited Waterloo, Ontario, Canada	organics in aquifers, wells, ground-water sampling
Dr. Gary Robbins* Hydrologist	Woodward-Clyde Consultants Santa Ana, CA	organics in aquifers, soil-gas, soil-core head space analysis
Dr. Thomas Spittler Chemist	U. S. EPA, Region 1 Lexington, MA	soil-gas analysis, analytical chemistry
Dr. Dorm Marrin** Hydrochemist	Tracer Research Corp. Tucson, AZ	soil-gas analysis, vapor extraction, aquatic chemistry
Dr. Gary Olhoeft Geophysicist	U. S. Geological Survey Denver, CO	electrical geophysical techniques
Mr. Wayne Saunders† Geophysicist	Camp, Dresser, and McKee, Inc. Annandale, VA	electrical geophysical techniques
Dr. Aldo Mazzella Geophysicist	U. S. EPA, EMSL-LV Las Vegas, NV	electrical geophysical techniques
Dr. Eric Walther‡ Environmental Scientist	Lockheed EMSCO Las Vegas, NV	environmental monitoring programs

*Present affiliation, University of Connecticut, Storrs, Connecticut
**Present affiliation, Consulting and Research Scientist, La Jolla, California
†Present affiliation, Terrascan, Inc., Springfield, Virginia
‡Present affiliation, Versar, Inc., Columbia, Maryland

Selection of Study Areas for Investigation

The other part of the project consisted of field demonstrations and qualitative comparisons of soil-gas and geophysical results to ground-water data. Geophysical techniques also were used as part of the site characterization. Four Air Force bases (AFBs) were chosen for these investigations after review of preliminary information from a total of eighteen. The selection criteria included the following:

- presence of JP-4, gasoline, or solvent contamination from a relatively recent spill (within the last 20 years);
- type of source of contamination; e.g., surface spill, pipeline leak, fire training area;
- depth to aquifer less than 100 meters;
- type of geology, e.g., karst, alluvium, marine sand; and type of soil;
- conductivity of aquifer;
- ease of access both to the study area, and the ground surface; sites with contamination under large paved areas were excluded; and
- number of wells already in place, delineating contamination.

The bases selected are listed in Table 2. Each AFB provides differing geology, climate, depth to water table, and contaminants, thus representing a variety of situations for performing the comparisons. The methods used in the studies are listed and described in Section 3, "Methods." The studies and results are described in detail in individual site reports (Baker et. al., 1987; Pitchford and Scarborough, 1987; and Pitchford et. al., 1987). Results from these site investigations are summarized in Section 4, "Field Investigations."

TABLE 2. GEOLOGY, CLIMATE, AND CONTAMINANTS AT AIR FORCE BASE STUDY SITES

Base	Geology	Climate	Contaminant
Holloman AFB	sand, interbedded clay	arid	gasoline, JP-4, solvents
Phelps Collins ANGTB	karst	humid	solvents, JP-4, buried metallic objects
Robins AFB	marine sand	humid	JP-4, solvents
Tinker AFB	clay	humid	JP-4

This series of studies was intended to help develop a hierarchy of techniques which could be logically adapted and applied to detect contamination for a variety of site conditions. However, the results from the field studies fit better into a framework of broad guidelines rather than into a detailed strategy which ranks techniques. These broad guidelines are provided in Sections 5, 6, and 7, "General Considerations for Site Investigations," "Planning a Soil-Gas Investigation," and "Planning a Geophysical Investigation," respectively.

SECTION 2

CONCLUSIONS AND SUMMARY

From 1985 through 1987, the Air Force Engineering and Services Center funded research at the U.S. Environmental Protection Agency Environmental Monitoring Systems Laboratory in Las Vegas, Nevada through an interagency agreement. This agreement provided for investigations of subsurface contamination at Air Force Installation Restoration Program sites. The purpose of these investigations was to demonstrate and evaluate inexpensive and relatively rapid reconnaissance techniques which can detect and map subsurface contamination. Information from these techniques will reduce the number of wells required in an investigation, resulting in significant savings in terms of costs and time.

The methods chosen for demonstrations included active and passive soil-gas sampling and analysis, and the geophysical techniques of electromagnetic induction, d.c. resistivity, seismics, and magnetics. Field studies were performed at four AFBs; these techniques were used as appropriate. Active soil-gas measurements were performed at all sites; resistivity and EM measurements were performed at three sites; and passive soil-gas sampling was performed at two sites. The other techniques were performed at one site only. The general conclusions about the techniques based on the field work are summarized in Section 4. Briefly, the active soil-gas sampling technique successfully mapped solvents, gasoline, and JP-4 contamination at all four bases where it was used. Results from one site demonstrated that the choice of sampling depth can influence the measurements obtained. Thus, it is important to perform depth profiles at the beginning of a soil-gas study. The real-time nature of this method also represents a significant advantage since the choice and number of sampling locations can be evaluated as data are obtained.

The passive soil-gas technique was not as successful as the active technique in detecting contaminated ground water. However, contaminated areas were identified successfully in some cases. Further testing of the performance of this technique for a variety of contaminants and geologic conditions is recommended before the method is used widely. Because of its low cost, this method has great potential for reducing site investigation costs in some cases.

The geophysical methods were successful for site characterization, but the EM and d.c. resistivity techniques did not detect gasoline and JP-4 contamination when it was present. The natural variations in background resistivity masked any resistivity anomaly due to the presence of hydrocarbons. Based on these results from a limited group of geologic settings, the use of EM and d.c. resistivity for direct detection of hydrocarbons appears to be a subtle technique which depends on a thorough understanding of background information at the site, the skill of the instrument operator, and may depend on the length of time the spill has been present.This does not preclude the use of these techniques in site characterization. The techniques of GPR and complex resistivity were not demonstrated at the AFBs, but their successful performance in detecting hydrocarbons has been documented in the literature.

To place these results in context, recommendations for planning a site investigation were presented next. These recommendations were prepared in conjunction with members of a panel of experts assembled to provide advice to the project. The recommendations address general considerations in designing an investigation, provide examples and references to similar cases in the literature, list the steps in planning a soil-gas investigation, and list issues to be considered in planning a geophysical investigation.

SECTION 3

METHODS

INTRODUCTION

This section serves two purposes. It summarizes the techniques which were applied during the field studies; and it also briefly reviews key characteristics of these techniques, providing references to detailed descriptions in the literature.

SUMMARY OF METHODS USED AT AFBS

A complete summary of the techniques considered for use in the field investigations is provided in Table 3. The goal of applying these techniques was to either characterize the hydrogeology or determine the distribution of contaminants so results from each of the selected techniques could be compared. Soil-gas and ground-water sampling were conducted at all AFBs; the EM and d.c. resistivity measurements were performed at three of the four AFBs.

Some of the techniques listed were not used in the site investigations, although they might have provided useful information. In certain cases, the situations were not appropriate, while in other cases, the equipment could not be obtained easily. For example, because of expense and because sites were chosen with wells already available, no new wells were installed. Similarly, no soil cores were obtained, although normally this technique would be part of an investigation. Ground-penetrating radar and complex resistivity also were not demonstrated in the field. Cost and scheduling problems precluded the use of ground-penetrating radar at Robins AFB where it would have been appropriate. It would be useful to apply this technique at Robins at a later date. Complex resistivity was not appropriate for three of the four study sites. Thick clay was present at the fourth site, Tinker AFB, but the presence of underground pipelines and tanks precluded the use of the technique. Aerial photography would have been used at all the sites if suitable maps and historical information had not been available.

SOIL-GAS TECHNIQUES

Introduction

Soil-gas sampling and analysis services are available commercially. The technique has several common variations, but the key elements include the collection of a sample of vapor from the soil and the detailed analysis of the sample for key compounds which indicate the presence of contaminants. The soil-gas sample can be removed from the soil by inserting a probe and extracting

TABLE 3. INVESTIGATION TECHNIQUES USED AT AIR FORCE BASE STUDY SITES

Technique	Phelps-Collins	Holloman	Robins	Tinker
Sampling ground water from existing wells	yes	yes	yes	yes
Sampling ground water using soil-gas probe	no	yes	yes	no
Soil cores	no	no	no	no
Active soil-gas sensing	yes	yes	yes	yes
Passive soil-gas sensing	no	no	yes	yes
D.C. resistivity	yes	yes	yes	no
Electromagnetic induction	yes	yes	yes	no
Seismic	yes	no	no	no
Ground-penetrating radar	no	no	no	no
Complex resistivity	no	no	no	no
Aerial photography	no	no	no	no

a sample under vacuum with a syringe or by lowering a syringe or sorbent tube into a borehole and collecting a sample in situ. Probes can be inserted into the ground manually or with pneumatic hammers and hydraulic rams, reaching depths of ten meters in some soil types (Lappala and Thompson, 1984; Marrin, 1985a; Eklund, 1985; Kerfoot et al., 1986; Marrin, 1985b; Marrin, 1984; and Devitt et. al., 1987). Alternately, a sample can be collected by burying a collector with an absorbent such as activated charcoal (Kerfoot and Mayer, 1986b and Voorhees, 1984). After allowing a time period for diffusion of VOCs into the sampling manifold and sorption onto the charcoal (e.g. ranging from hours to days), the collector is removed.

Once the sample is collected, it is analyzed using on-site gas chromatography, or transported to the laboratory for VOC analysis. Laboratory analysis is more time consuming because of the additional handling required and cannot provide real-time results.

The detection methods used for analysis of soil-gas samples include:

- Flame ionization detector (FID) for the full range of organic compounds (primarily petroleum hydrocarbons);

- Photoionization detector (PID) for the aromatic hydrocarbons and sulfur species;

- Electron capture detection (ECD) for selective detection of halogenated hydrocarbons;

- Hall Electrolytic Conductivity detector (HECD) for the specific detection of halogenated species, nitrogen-, or sulfur-containing organic species; and

- The flame photometric detector (FPD) for sulfur and phosphorus compounds (Devitt et. al., 1987).

The real-time analysis allows for selection of additional sampling locations so that contamination can be mapped with greater resolution than could be achieved if the same number of sample points were sampled on a regular grid.

Some initial indication of contamination can be obtained using a commercially-available organic vapor analyzer (OVA), but since these field screening devices do not provide compound-specific identification, the results can be confusing if several types of contaminants are present. In addition, these devices are not as sensitive as field gas chromatography (GCs), so it is possible that low-level contamination, which is often associated with plume boundaries, may not be detected.

Soil-gas techniques may be influenced by airborne, surface, and subsurface VOCs. Thus air blanks and vertical profiles should be obtained periodically. Also, variations in the air permeability of soils resulting from utility corridors, clay layers, and fractures will influence the soil-gas results, requiring careful interpretation. Driving gas sampling probes into the ground to depths of 1 to 3 meters (3 to 9 feet) may create a safety hazard if the probes puncture underground utilities or buried drums which cannot be located prior to sampling. Two soil-gas sampling techniques were used in the studies at the AFBs. Both techniques have advantages and disadvantages which are described below.

Active Soil-Gas Sampling

In active (grab) sampling, a hollow pipe is driven into the ground to a prescribed depth and soil gases are pulled up to the surface through it. Alternatively, a syringe or evacuated cylinder may be lowered down a borehole and a gas sample collected in situ. The sample is then analyzed by gas chromatography at or near the sampling location. This method offers the benefit of producing immediate results as the survey progresses, a feature which is attractive because it allows the sampling plan to be changed on the basis of results. In addition, preliminary measurements can be performed which permit investigators to optimize certain survey parameters such as sampling depth and sample volume. An additional advantage of on-site soil-gas analysis is the use of analytical instruments to screen soil and ground-water samples which are produced. The drawback of this approach is that it requires the presence of sophisticated analytical and sampling equipment on site. The presence of this equipment, a specialist to operate and maintain it, and associated support systems such as generators, calibration standards and carrier gases, make the technology somewhat expensive. This technique is most appropriate at sites where plume mapping is the major objective or where relatively low concentrations of VOCs are anticipated in soil gas.

Active soil-gas investigations were conducted at a variety of locations at all four AFBs. In determining the extent of the contaminated areas, the samples were analyzed for methane, benzene, ethyl benzene, toluene, xylene, total nonmethane hydrocarbons, and halogenated organics. The contractor used an analytical field van equipped with two Tracer GCS with FIDs and two computing integrators which permitted real-time sampling and analysis of the soil gas. This van was also equipped with a specialized hydraulic ram mechanism used to drive and withdraw the sampling probes. The probes consisted of 2.1-meter (7-feet) lengths of 1.9-centimeter-diameter (3/4-inch) steel pipes fitted with detachable drive points. A hydraulic hammer was used to assist in driving the probes through hard soil.

Soil-gas samples were collected from depths ranging from 0.6 to 2.4 meters (2 to 8 feet) in the ground. The key features are shown in Figure 1. The above-ground ends of the sampling probes were fitted with a steel reducer and a length of polyethylene tubing leading to a vacuum pump. Some 3 to 5 liters of gas were evacuated with the vacuum pump. Samples were collected by inserting a syringe needle through a silicone rubber segment, just above the reducer, in the flowing evacuation line and down into the steel probe. Ten milliliters (mL) of soil gas were collected for immediate analysis with one of the GCs. The soil gas was subsampled in volumes ranging from 1 microliter (µL) to 2 mL, depending on the expected concentrations of volatiles. The hollow steel probes were used once and discarded; the steel reducers were cleaned and baked after each use. Using the experience at the four AFBs as a guide, the cost for soil-gas sampling and analysis for fifty locations in one area is $7,500. Thus the cost per sample location is approximately $150.

Passive Soil-Gas Sampling

There are at least two passive soil-gas sampling techniques in use. Each technique uses the same sampling technique, i.e., shallow burial in soil, but the collectors and analysis are different. One technique uses a thin ferromagnetic wire coated with adsorbent charcoal. When the sample is returned to the laboratory, the wire is heated in a vacuum and the desorbed compounds are analyzed by Curie point mass spectrometry (Voorhees, 1984). The other technique uses commercially-available, charcoal-adsorbent organic vapor monitor badges (3M™) that were designed to be worn by personnel for occupational exposure monitoring (Kerfoot and Mayer, 1986). These badges cost $7 to $10 each based on the quantity purchased. This method was used at Robins AFB and Tinker AFB to demonstrate the use of this passive sampling technique in sandy and clayey soils, respectively.

To collect a soil-gas sample, the badges were installed in sampling manifolds constructed from clean, 0.95 liter (l-quart) aluminum cans. The sampler and manifold are depicted in Figure 2. The manifold-sampler combination was placed in a shallow hole dug 0.3 meters (1 foot) into the ground, covered with soil, and left in place for a set period of time based on estimated ambient concentrations. Passive samplers should generally be buried 0.6 meters (2 feet)

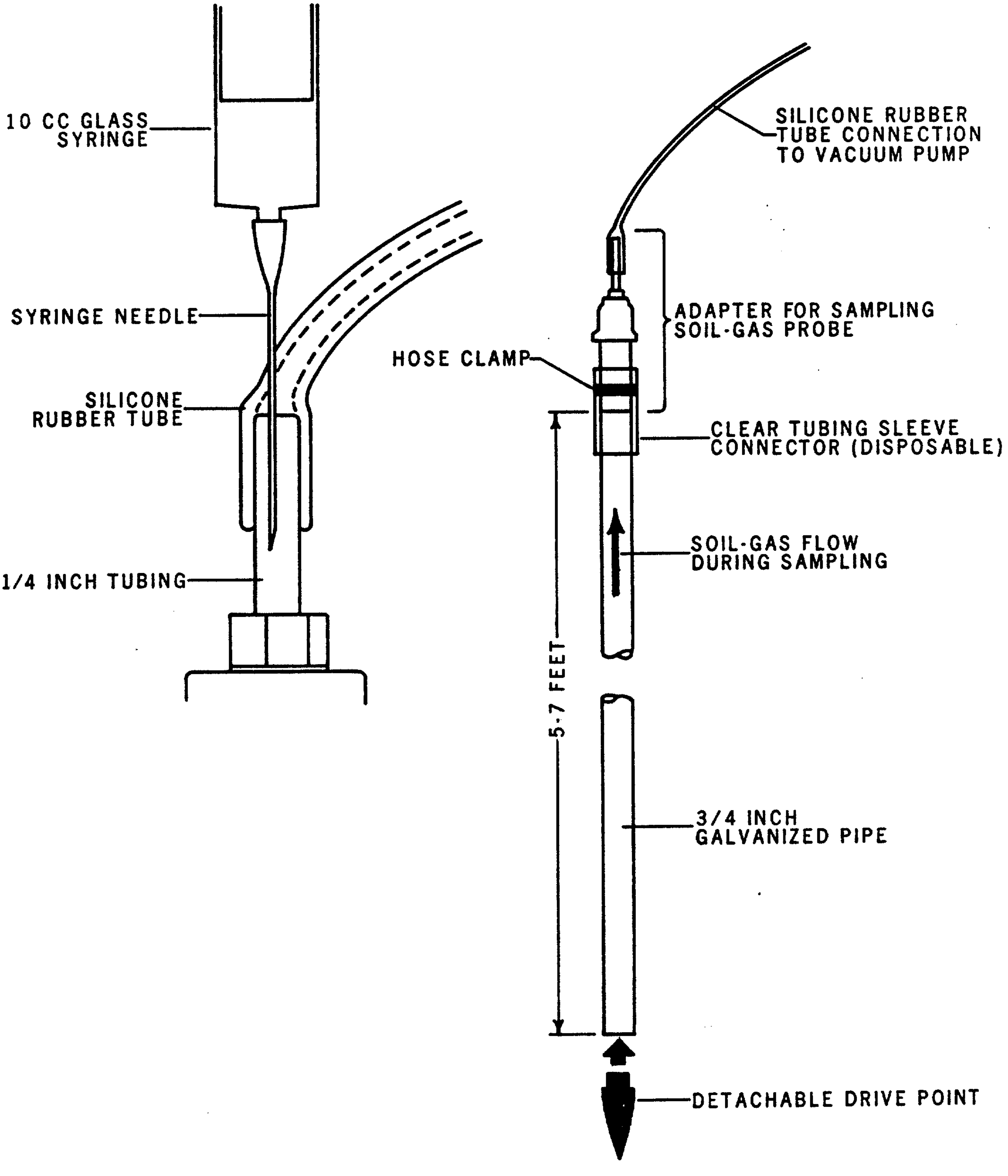


Figure 1. Features of an active soil-gas sampling system (courtesy of Tracer Research Corporation).

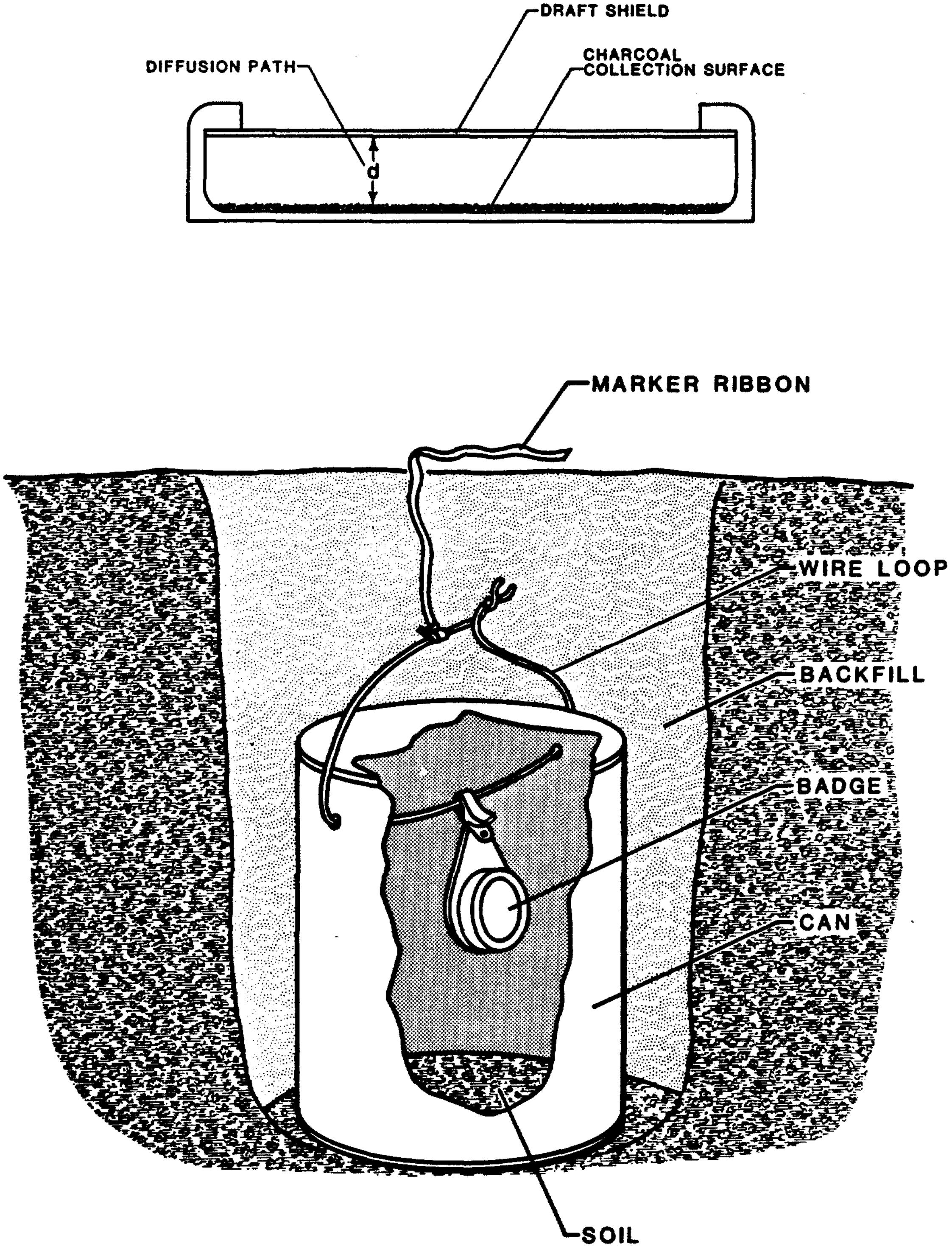


Figure 2. Passive soil-gas sampling badge and manifold (after Kerfoot and Mayer, 1986).

below grade to minimize the effects of atmospheric air dilution of soil gases. Then the samplers were removed, sealed, and returned to the laboratory. At the EMSL-LV laboratory, the VOCs were solvent-desorbed and the resulting solution analyzed by gas chromatography. The procedures used are described in Kerfoot and Mayer, 1986; Mazzella et. al., 1987; and Pitchford and Scarborough, 1987. The estimated cost per analysis for the charcoal badges is $75 to $100, based on this experience. Analytical services for these badges are offered as a service by a number of companies at costs ranging from $48 to $58 depending on the type of analysis requested. Analysis of one to three compounds can be requested.

To perform a full-scale investigation using the passive soil-gas technique, it is desirable to determine an optimum exposure time and depth for the study area. This is accomplished by performing field calibration tests, which are an important part of the study process. Through this procedure, it is possible to assess whether the technique can be used to detect and delineate subsurface contamination at a site.

GEOPHYSICAL TECHNIQUES

Introduction

Geophysical techniques measure a variety of properties of the earth. For example, ground penetrating radar is a reflection technique that measures changes in electromagnetic propagation velocity. Electromagnetic induction measures the electrical conductivity of the subsurface with lower frequency electromagnetic waves. D.C. Resistivity measures subsurface electrical resistivity which is the reciprocal of conductivity. Seismic refraction Involves transmission of sound waves into the ground. Using measurements of the travel time of the waves, the thicknesses and depths of geological layers can be established. Magnetometry measures anomalies in the earth’s magnetic field caused by ferrous objects such as iron or steel. These techniques can be used for defining natural geologic features; locating conductive leachates and contaminant plumes; locating buried trenches and locating metal objects (Benson et. al., 1983). This section briefly reviews the characteristics of these methods.

Electromagnetic Induction

Electromagnetic induction is the most rapid and inexpensive of the geophysical techniques discussed in this report. It is readily available commercially and acquires data for electrical conductivity over a large area. Depth of electromagnetic penetration is a function of coil spacing, frequency, and electrical conductivity. These depths are typically on the order of meters to tens of meters with hand-held instruments. There are a variety of commercially-available instruments that can be used to explore different depths, depending on the conductivity of the surface. Data are acquired by measuring the perturbation in the signal between two coils of wire which is due to the presence of a nearby conducting material (the earth), and which is proportional to the conductivity of the material. If the site relief is greater than one meter, the data may require topographic correction from the surface of the earth to the water table. Nearby utilities, gas pipelines, power and telephone lines, and metal fences and debris can interfere with the measurements. An electrical conductivity map can reflect changes in porosity, water saturation level, salinity of the ground water, or the presence of clay lenses. It can generally illustrate the uniformity of a site subsurface. Basic sources of information about EM include Keller and Frischknecht, 1966; McNeill, 1980; Benson et. al., 1983; and Greenhouse and Harris, 1983.

D.C. and Complex Resistivity

D.C. resistivity is also readily available commercially. Instead of coils of wire which do not touch the earth, the d.c. resistivity method makes physical contact to the earth using shallow (<0.3 meter) electrodes. By injecting current directly into the ground and by measuring the voltage response, the apparent resistivity of the earth is measured. Interpretation of these data can indicate various layers, possibly reflecting the depths of the water table, aquitards, and bedrock. The geometry of the electrode arrays and spacings determines the depth of investigation. The technique requires more time than EM to cover a given area. Resistivity soundings, however, can give more detailed depth profiles than commercially available EM methods. The technique requires topographic correction and may also be subject to interference from utilities. The d.c. resistivity method can be used as described above for the EM method for profiling and mapping. Basic sources of information about d.c. resistivity include Zohdy, 1974; Benson et. al., 1983; and Greenhouse and Harris, 1983.

Complex resistivity is the technique of measuring resistivity in both magnitude and phase as a function of frequency (also called induced polarization). The technique requires costly equipment and more time than conventional resistivity and is thus more expensive. However, the frequency dependent measurement gives information about active chemical processes in the earth as well as the same information acquired by EM or conventional resistivity This technique has shown the ability to detect and map organic materials in the presence of clay by mapping clay-organic reactions. There are few available commercial sources for this technique. Basic sources of information about this technique include Sumner, 1976; and Olhoeft, 1984b, 1985, and 1986.

Ground-Penetrating Radar

Ground-penetrating radar (GPR) is readily available commercially, rapidly provides very high spatial resolution over a large area, can work close to utilities, but is more expensive than EM or resistivity It is cheaper than complex resistivity or seismic techniques. GPR emits transient electromagnetic pulses with energy centered at frequencies in the range of 80 to 1000 megahertz. The wave fronts are reflected when they encounter contrasts in the dielectric constant, such as the water table, bedrock, and clay layers. The reflected waves are plotted as a function of depth, and topographic correction is required. The depth of penetration is controlled by the intrinsic conductivity of the earth, the amount of inhomogeneity in the earth, and the amount of clay and water present (Olhoeft, 1984a and 1986). In clay-free sand with resistivity above 30 ohm-meters, the ground-penetrating radar can map bedding and stratigraphy, water tables, bedrock interfaces, and other features with dielectric contrasts at a resolution of a few centimeters to depths of 30 meters (Wright et. al., 1984). Five to ten weight percent montmorillonite clay will reduce the depth of penetration to less than one meter. As dielectric contrasts do exist between most earth materials and many organic substances, it is possible to detect certain kinds of organics with ground-penetrating radar (Kutrubes, 1986 and Olhoeft, 1986). Basic information may be found in Ulriksen, 1982 and Benson et. al., 1983.

Seismic Techniques

Seismic compressional and shear wave, reflection and refraction techniques are readily available commercially and can be used to determine stratigraphic and lithologic layer thicknesses and depths. This is the most expensive of the geophysical tools discussed in this report. Commercially-available seismographs can plot the arrival times of elastic waves refracted or reflected from these subsurface features. Sources of seismic energy include a sledge hammer striking a steel plate on the ground, specialized shotguns, or explosives. Subsurface velocities are measured or estimated to allow calculation of the depths from the travel times, and topographic correction is required. Seismic refraction works if each successively deeper layer has a higher propagation velocity. Both seismic techniques can provide information at great depths, but they do not easily provide information on features shallower than 3 meters (10 feet). Any nearby loud noise source such as a busy highway or construction may interfere with the survey. Seismic techniques are not as rapid as EM and GPR. The seismic techniques work best in solid materials with no fractures and perform very poorly in loose materials. In clay-free sandy soils, GPR will work better than seismic techniques and with higher resolution. In clay-bearing soils, seismic techniques will work better than GPR. Marine seismic techniques are useful in mapping stratigraphy below rivers and lakes. As there are no acoustic contrasts between geological materials and organic contaminants, seismic techniques cannot directly map organic contamination. Basic information on seismic techniques is in Benson et. al., 1983; Miller et. al., 1986; and Romig, 1986.

Magnetometry

Magnetometry is an inexpensive,readily available technique which measures the intensity of the earth's magnetic field. The presence of ferrous objects such as iron drums creates a perturbation in the local intensity and direction of the earth's magnetic field. The change in intensity is proportional to the mass of the object. Detection of these ferrous objects depends on the mass, magnetic properties, orientation, and depth of the object; the intensity and direction of the earth's magnetic field; and the sensitivity of the magnetometer. A large number of magnetometers are available commercially; two common types are the fluxgate and proton magnetometers. The fluxgate measures a component of the magnetic field and the proton magnetometer measures the total magnetic field. Magnetic field measurements can be made in two ways; the magnetic field can be measured, or a difference (gradient) can be determined between two different points. Total field measurements are more sensitive but are also more susceptible to noise than the gradient measurements (Benson et. al., 1983). Cultural features such as buried pipes; metal buildings; and magnetic properties of the soil may interfere with the measurements. According to Benson et. al., 1983, this technique can detect buried drums, define boundaries of trenches filled with drums or other steel objects; and locate iron pipes or tanks. Basic information about magnetic techniques can be obtained from Mabey, 1974 and Benson et. al., 1983.

Detection of Organic Contamination

A number of physical mechanisms can make the detection of organics by geophysical techniques possible. For example, in most near-surface rocks, the dominant electrical conduction mechanism of current is through the water in the pore spaces of the formation. If the electrolyte is replaced by a high resistivity fluid, such as a petroleum hydrocarbon, the resistivity of the formation may increase. However, the presence of clay minerals and buried metallic objects, such as pipes, can also significantly alter the electrical resistivity of the subsurface. These provide competing mechanisms to the conduction through the pore space. One of the objectives of the studies at Holloman and Robins AFBs was to investigate whether any change in resistivity due to the presence of gasoline or JP-4 was detectable over man-made or naturally-occuring conditions, such as changes in the porosity, saturation level, the presence of clay minerals, or buried metallic objects. For these studies, EM and d.c. resistivity measurements were performed. Other techniques which may be of use for locating subsurface organics are ground-penetrating radar and complex resistivity.

The remainder of this section on GPR and complex resistivity is adapted from Olhoeft, 1986. Dr. Olhoeft is a member of the panel of experts. GPR uses the propagation of electromagnetic energy; thus it is sensitive to relative dielectric permittivity as well as the electrical conductivity. Whereas the electrical conductivity is more sensitive to the presence of inorganic than organics, the dielectric permittivity is more sensitive to organics than inorganic. GPR has the advantage that depth resolution is controlled by the frequency of measurement and is constant with depth, whereas EM for example, has poorer resolution with increasing depth. Organic materials have relative dielectric permittivities that range from 2 to over 40 according to Akadov, 1980. Adding organics to clay may produce no effect or a large effect depending on whether or not the two react. As GPR cannot penetrate clay, it cannot see any effect unless the organics coat the clay and destroy the clay-water interaction without adding a new clay-organic reaction. In this latter case, GPR may map clay-organic processes much like complex resistivity. In one example, a hydrocarbon plume was detected directly by the GPR as the change in contrast between the dielectric permittivity of sand and water compared to the lack of contrast between sand and oil. The dielectric permittivities of sand and water are 4 and 80, respectively; the dielectric permittivity of oil is near that of water, with a value of 2. Dielectric permittivities are unitless ratios. In another example, the plume was inferred by an indirect change due to a soil-organic reaction. GPR is most sensitive to changes in dielectric properties in the unsaturated zone down to and at the water table. Below the water table, GPR cannot see changes caused by water-soluble organics directly, but may infer their presence from changes caused by the organics. Of course, GPR is equally effective in mapping geology above or below the water table.

Complex resistivity acquires the same information as the other methods of measuring electrical conductivity, but also measures the frequency dependence of the electrical properties in terms of magnitude and phase (Sumner, 1976). The added information relates to the chemical activity in the earth, and directly measures the presence of active chemical processes (Olhoeft, 1985). Generally, higher phase and nonlinearity (Olhoeft, 1979 and Olhoeft, 1985) indicate greater chemical activity. Inorganic processes of oxidation-reduction and of cation exchange may be quantitatively observed with complex resistivity. Organic electrochemistry (Baizer and Lund, 1983) suggests a variety of organic processes that may be observable with complex resistivity. To date, only those processes involving reactions between organics and clay minerals have been observed both in the laboratory and at hazardous waste sites. In one example cited, the inhibition of the normal montmorillonite cation exchange process by the organics allowed mapping of the organic plume by complex resistity (Olhoeft, 1984) .

Since the complex resistivity requires clay to map organics through clay organic reactions, and clay severely restricts the penetration of the GPR, the two techniques are complementary. Further, for hydrogeological information, GPR and seismic methods are complementary because increased clay content in loose and sandy soils improves seismic methods.

SECTION 4

FIELD INVESTIGATIONS

INTRODUCTION

This section presents highlights of the field investigations performed at Holloman AFB, Robins AFB, and Tinker AFB. The highlights focus on results of the performance of soil-gas and geophysical measurements for detecting organic contaminants. The results are summarized in Table 4. To construct the table, the site of most interest was selected for each AFB. Methods used to investigate the site were listed along with a brief summary of the result. These results are discussed further below.

DISCUSSION OF SOIL-GAS RESULTS

Four sites were investigated using soil-gas techniques. The site conditions and results of comparisons of soil-gas results to ground-water results are summarized in Table 5. The sites represent a limited set of site-specific and compound-specific parameters. Because of the wide variety of contaminant and geological conditions which may exist at a given site, the conclusions should be extended to other sites only insofar as stratigraphic and contaminant conditions are similar. Some of the more generally applicable conclusions are summarized below.

The comparison portion of Table 5 provides the results from active and passive soil-gas and ground-water sampling conducted at three AFBs. For each site, soil-gas measurements nearest to ground-water sampling locations were selected. Distances between the points of comparison ranged from a maximum of 15 meters (50 feet) at Holloman AFB, to 6 meters (20 feet) at Robins AFB, and 1.2 meters (4 feet) at Tinker AFB. The values were compared qualitatively by classifying the concentrations as background or above background. The cases for which the classifications of the soil-gas and ground-water data agreed were counted and presented as a ratio to the total number of cases. For example, at Holloman AFB, active soil-gas sampling results agreed with ground-water sampling results for 8 of the 12 comparisons. These results are discussed in more detail below.

Active Soil-Gas Sampling

The active soil-gas sampling technique was generally successful at all AFBs in delineating contamination over the areas where contaminants were present in the ground-water. Paired soil-gas and ground-water samples showed agreement at approximately 75 percent of the locations. This percentage might have been higher if the soil-gas sampling locations had been closer to the ground-water

TABLE 4. KEY RESULTS FROM THE AFB INVESTIGATIONS

Base, site, and contaminants	Method	Comment
Holloman AFB, BX Service Station, Gasoline	Active soil-gas sampling	Compares favorably with groundwater data. Demonstrates movement of contaminants along utility corridors.
	EM, d.c. resistivity	Do not detect organics because of natural variability in soil resistivity. Culture limited extent of survey.
Robins AFB, JP-4 Spill, JP-4	Active soil-gas sampling	Compares favorably with groundwater data in spite of 20-year age of spill. Demonstrates importance of depth of sampling.
	Passive soil-gas sampling	Preliminary test has mixed results compared to groundwater data.
	EM, d.c. resistivity	Do not detect organics because of natural variability in soil resistivity due to rainfall effects and culture. AFB radar interferes with EM-34 measurements.
Tinker AFB, Fuel Farm 290, JP-4	Active soil-gas sampling	Compares favorably with groundwater data; technique effective in clay soil.
	Passive soil-gas sampling	Preliminary test has mixed results compared to groundwater data. Technique may be responding to surface contamination at times.
	EM, d.c. resistivity, complex resistivity	Were not attempted due to high density of buried pipes and tanks, and fences and pipes on surface.

TABLE 5. STUDY SITE AND CONTAMINANT CHARACTERISTICS; COMPARISON OF SOIL-GAS AND GROUND-WATER DATA

AFB	Contaminant	Age (years)	Soil type	Depth to ground water feet	Depth to ground water meters	Comparison Active agree/total	Comparison Passive agree/total
Holloman	Gasoline	4	sand/clay	6	2.0	8/12	not available
Robins	JP-4	20	sand	6	2.0	6/8	6/9[a]
Tinker	JP-4	unknown	clay	8	2.6	9/12	5/12

[a] These results for Robins AFB use the data for exposure times of 3 days. The 3-day exposure times provided more consistent results than the shorter times of 1 and 2 days.

sampling locations. For example, the boundary of the contamination at Holloman AFB was very distinct. In one case, the soil-gas and ground-water data did not agree. This discrepancy appeared to result from the relatively long distance between the soil-gas probe and the monitoring well. However, there are other anomalies which cannot be attributed to spatial differences. This pattern of soil-gas anomalies also seemed to be true for the other AFBs. In these cases, the differences between soil-gas and ground-water data have been attributed to local heterogeneities in soil or to sampling difficulties. It is important to rely on the overall pattern indicated by the active soil-gas data, rather than on single values, in estimating the location of ground-water contamination.

The depth of sampling can be very important as shown by the results at Robins AFB. At this AFB, initial sampling at 1 meter revealed very little contamination as shown in Figure 3, while additional sampling at 2 meters located significant contamination, which is shown in Figure 4. It is important to perform depth profiles at a number of locations during the initial phase of a study, preferably in regions of known (quantified) ground-water contamination, in order to select the sampling depth. Sampling depth is particularly important at sites where relatively old fuel spills have occurred, because oxidation (chemical or biological) of the petroleum hydrocarbons can remove fuel constituents from the aerobic soil horizons.

The real-time nature of the active soil-gas sampling was a significant factor in the success of the investigations at each of the AFBs. At Robins AFB, real-time results allowed an immediate change in sampling depth when discrepancies were discovered. The availability of results soon after samples were collected offered the opportunity to choose sampling locations and depths based on the best information available.

At Tinker AFB, the active soil-gas technique did not appear to be affected by the presence of clay except at a few locations. It was possible to determine when the probe was inserted into impermeable clay by observing the vacuum

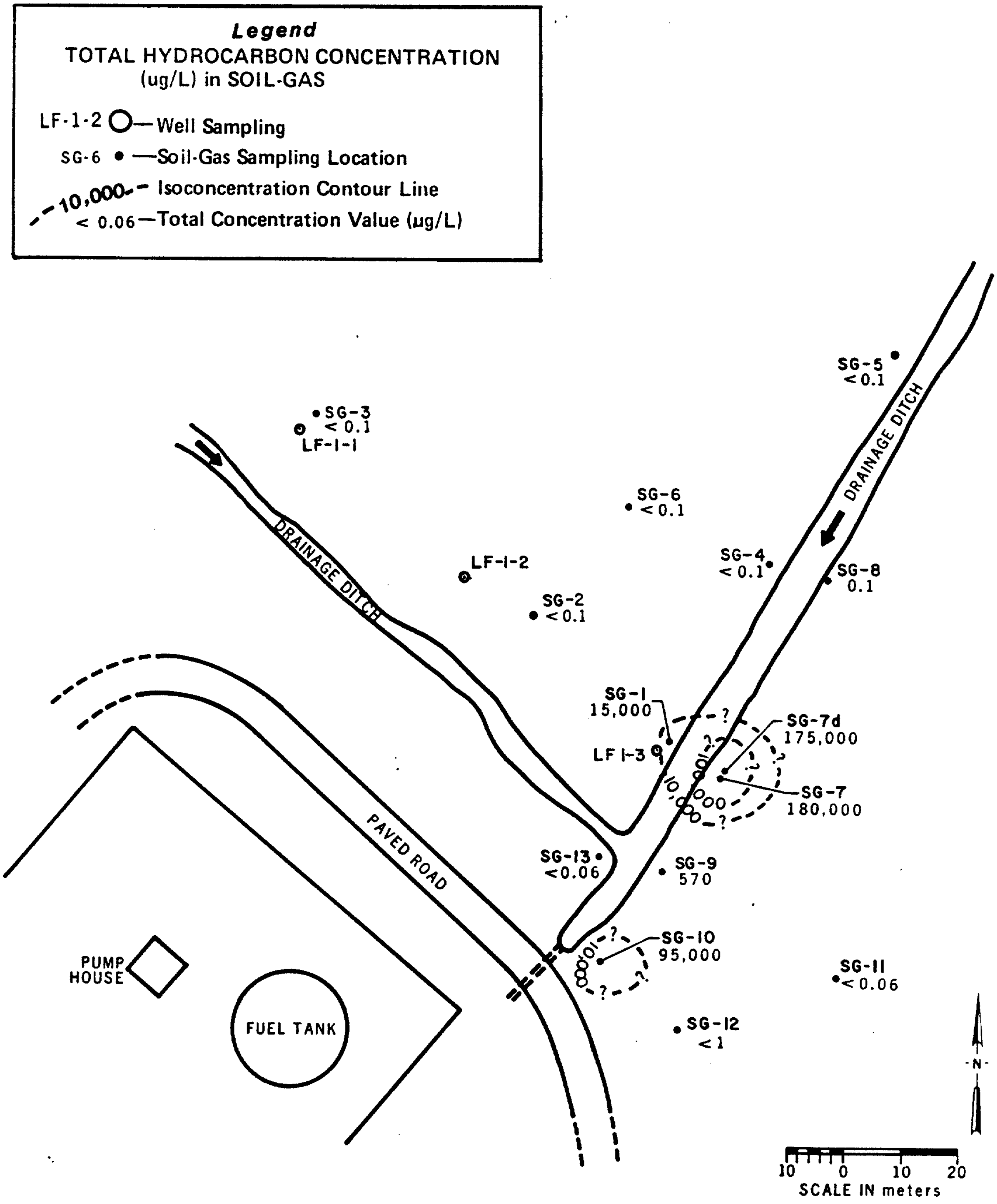


Figure 3. Concentrations of total hydrocarbons in soil gas at JP-4 spill site, Robins AFB. Sampling depth: 1 meter.

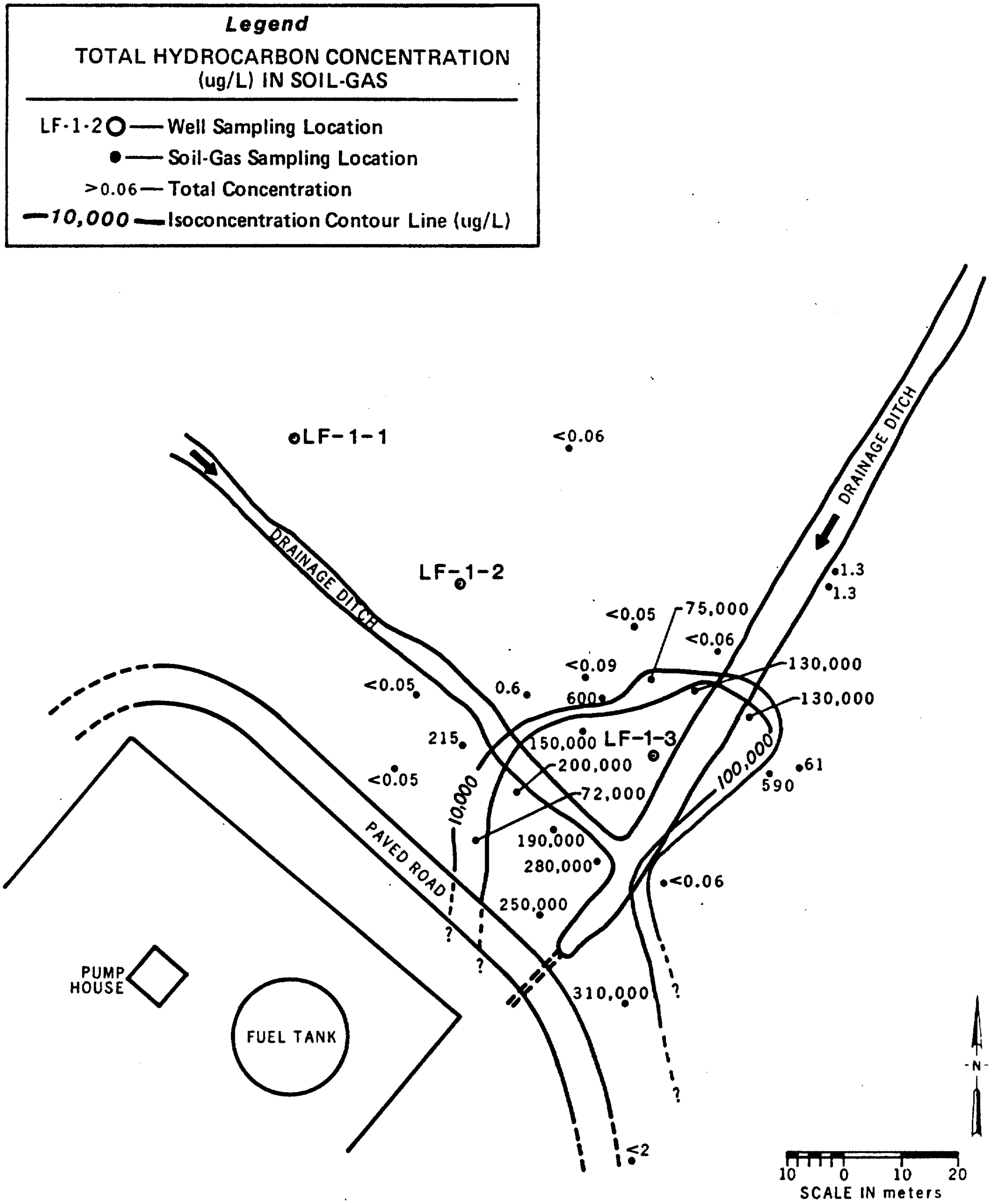


Figure 4. Concentrations of total hydrocarbons in soil gas at JP-4 spill site, Robins AFB. Sampling depth: 2 meters.

pressure necessary to extract a sample. The sampling depth could then be adjusted to avoid the impermeable strata. In some cases, it was not possible to avoid the impermeable strata and the sampling location was changed. Originally, it was anticipated that the soil-gas technique would not work well at this site because of the clay. However, the active sampling technique performed well. Either the permeability of the clay was adequate for soil-gas sampling due to the presence of coarse-grained sediments, or the clay itself had been contaminated by gas-phase VOCs or by infiltration of product.

The use of the soil-gas probe for collecting ground-water samples proved effective in confirming the soil-gas results in a timely way. This approach is not a substitute for the standard procedure of installing and sampling wells, but is useful in field survey activities when the goal is estimating the extent of the contamination. This ground-water sampling approach may not work when the soil is very hard, or when the depth to ground water is greater than approximately 3 meters (10 feet).

Passive Soil-Gas Sampling

Two of the sites investigated with active soil-gas techniques were also investigated using passive techniques. At these sites, only feasibility tests were performed. The purpose of these tests was to determine the feasibility of mapping the contamination at these sites and to select the best exposure times for the badges. Performing feasibility tests with the badges is very important; an insufficient exposure time may indicate an area is uncontaminated when contamination actually is present. For the exposure times used at Robins AFB, the contaminated zone was successfully identified one out of two times for a 1-day exposure, two out of three times for a 2-day exposure, and three out of three times for a 3-day exposure. This emphasizes the importance of carefully selecting an exposure time. Over-exposure of the badges may result in saturation of the sorbent which would mask any relative differences in soil-gas contamination at the various sampling locations.

The passive soil-gas sampling data showed varying degrees of success in qualitative comparisons with ground-water data. For the longest exposure time of 3 days at Robins AFB, the badges successfully identified one area as contaminated and one area as uncontaminated. These results were consistent with the ground-water data. A third area of intermediate contamination was not detected by the badges. It is possible that the location assumed to have intermediate contamination was actually outside the zone of ground-water contamination and was influenced by VOCs diffusing laterally. At Tinker AFB, the badge data matched the ground-water data for 5 out of 12 cases. In some of these cases, the badges may have been responding to near-surface contamination, rather than to the ground-water contamination. These data suggest that the depth of sampling may be as important a consideration for passive sampling as it is for active sampling. Overall, the data obtained from passive soil-gas sampling with badges showed less agreement with ground-water data than did the active soil-gas method.

The choice of which soil-gas technique to choose depends on the nature of the investigation. At this time, there are a number of issues which need further study before the passive soil-gas method should be used widely. Because of its low cost, this technique offers great promise for some sites. The issue of greatest concern is understanding the conditions under which the passive badge technique does not detect existing ground-water contamination. The use of a feasibility test to establish exposure times, sampling depths, and agreement with areas of known subsurface contamination at a specific site is strongly recommended. Passive samplers should generally be buried at least 2 feet below grade to minimize the effects of atmospheric air dilution of soil gases.

As was indicated by the results from the AFB various sites, the active soil-gas results and ground-water data generally show good agreement. For this reason, the active soil-gas method is recommended for routine use. Depth profiles should be used at the beginning of a study to determine optimum sampling depth. In a clay environment, consideration should be given to using vacuum values as a criterion for assessing the validity and representative nature of samples. Moisture and organic carbon content of soils can also affect the predictive capability of soil-gas techniques even if field sampling can be performed without difficulty.

GEOPHYSICAL RESULTS

A number of limited geophysical studies were conducted for the direct detection of subsurface hydrocarbon contamination. At Phelps-Collins ANGTB, the suspected concentration of organic contamination was so low (<100 parts per billion) (Baker et. al., 1987) that geophysical surveys were not attempted for direct detection. At Tinker AFB, the amount of cultural interference from tanks and pipelines was so great that geophysical surveys also were not attempted.

D.C. resistivity and shallow EM surveys were conducted at Holloman and Robins AFBs. These surveys were not successful at either AFB for the direct detection of subsurface hydrocarbon contamination. At Holloman AFB, the resistivity anomalies due to the presence of substantial gasoline contamination could not be distinguished reliably from the naturally-occurring resistivity variations in the soil of the area. At Robins AFB, where substantial JP-4 contamination was present, resistivity anomalies in the d.c. resistivity or EM results could not be distinguished from the natural background resistivity variations in the area. A change in the near-surface resistivity properties due to recent rainfall further tended to complicate and mask any detection. In Saunders and Cox, 1987, the resistivity anomalies attributed to the hydrocarbon contamination are represented by decreases in conductivity on the order of 30 to 50 percent from background values. It may be difficult to separate a signal of this magnitude from background variations in many circumstances. For example, at Robins AFB, background conductivities were low, approximately 3 to 5 millimhos. The measurements performed did not have the sensitivity to separate relative changes on the order of 1 to 2 millimhos from the background variations.

Based on this experience and the results of two cases reported in the literature (Saunders and Germeroth, 1985 and Saunders and Cox, 1987), the use of d.c. resistivity or EM measurements for detection of subsurface hydrocarbons appears to be subtle techniques which depend on a thorough understanding of background information such as near-surface geology and potential interferences, the skill of the instrument operator, and may depend on the length of time the spill has been present. This does not preclude the use of these techniques for site characterization to obtain basic information on the electrical resistivity properties of an area.

GPR was not used in the current studies. However, other reports and studies described in Olhoeft, 1986 indicate direct detection of subsurface hydrocarbon contamination by GPR surveys has been successful. The use of GPR is limited to sites that are relatively clay free and have resistivities greater than about 30 ohm meters. The use of initial reconnaissance EM surveys can help define whether a GPR survey should be attempted at a site.

When clays are present at a site and the resistivities are less than 30 ohm meters, the emerging technology of complex resistivity appears to have some potential for the direct detection of subsurface organic contamination (Olhoeft, 1986) . At the present time, further research is needed to fully evaluate the complex resistivity method.

SECTION 5

GENERAL CONSIDERATIONS FOR SITE INVESTIGATIONS

This section describes broad and general considerations for a site investigation. The role of a conceptual model and the types of technical concerns which should be considered are addressed. Following these general guidelines, nine examples are presented. These examples serve to illustrate the capabilities of the various techniques; references to actual cases are provided.

The type of organic compounds present at a site with subsurface contamination will determine how an investigation is to be conducted and whether the various techniques are likely to be successful. For convenience, the organic contaminants have been categorized into groups which have similar physical properties. These groups, listed below, were developed by Dr. Dorm Marrin, a member of the panel of experts. The group designations will be used in discussions in this section and in Section 6. More specific recommendations for the application of soil-gas and geophysical techniques are provided in Sections 6 and 7, respectively.

Halogenated Methanes, Ethanes, and Ethenes

These compounds include chloroform, carbon tetrachloride, trichlorofluoromethane (Freon-n), 1,1,1-trichloroethane (TCA), 1,2-dibromoethane (EDB), vinyl chloride, and trichloroethene (TCE).

Halogenated Propanes, Propenes, and Benzenes

These compounds include 1,2-dibromo-3-chloropropane (DBCP), 1,2-dichloropropane, 1,3-dichloro-l-propene, chlorobenzene, and trichlorobenzene.

Halogenated Polycyclic Aromatics

These compounds include polychlorinated biphenyls (PCBS) and organochlorine pesticides such as aldrin, chlordane, heptachlor, and dichloro-diphenyl-trichloroethane (DDT).

C_1-C_8 Petroleum Hydrocarbons

These compounds include benzene, toluene, xylene isomers, methane, pentane, cyclohexane, isooctane, and complex products such as gasoline and JP-4.

C_9-C_{15} Petroleum Hydrocarbons

These compounds include trimethylbenzene, tetramethylbenzene, napthalene, dimethylnapthalene, nonane, decane, and complex products such as diesel and Jet A fuels.

Polycyclic Aromatic Hydrocarbons

These compounds include anthracene, benzopyrene, fluoranthene, benzofluorene, chrysene and complex products such as motor oils and coal tars.

Low Molecular Weight Oxygenated Compounds

These compounds include acetone, ethanol, formaldehyde, methyl ethylketone, tetrahydrofuran, and phenol.

This section, except for Parts D, J, and Table 6, was adapted from materials provided by Dr. John Cherry, a member of the panel of experts listed in Section 1. Part D was adapted from materials provided by Dr. Gary Robbins, another member of the panel. Part J was initially developed during discussions by the panel, but is presented in an amplified form which was first documented in Walther et. al., 1986.

CONCEPTUALIZING THE PROBLEM

The first step in any site investigation, and one of the most important steps overall, is the conceptualization of the problem. To conceptualize the problem to a useful degree, some information must be available on the nature of the contaminant source and on the hydrogeology of the site. Useful information on these topics is nearly always available before a site investigation begins and therefore it is usually possible to develop a useful conceptualization before drilling programs and monitoring networks are designed. For the conceptualization, it is desirable to know if the source of contamination has organic floaters or organic sinkers (i.e., halogenated organic liquids) or simply miscible contaminant source liquids. Table 6 lists the density and aqueous volubility of common organic contaminants and classifies those which are insoluble in and less dense than water as “floaters” and those which are insoluble in and more dense than water as “sinkers.” Those which are soluble in water are termed “mixers.”

The presence, or possible presence, of organic sinkers is a particularly important issue requiring attention in the conceptualization because the organic liquids can sink deep into aquifers along pathways usually controlled by geologic features. The sinking and final position are rarely influenced much by the rate and direction of ground water flow at the site. If it is known or suspected that halogenated solvents were at some time used on the site property or disposed of on the site property, it is appropriate to evaluate the possibilities for a significant mass of the solvent to exist in pockets or pools at some depth beneath the property. The pockets or pools may be the long-term cause of ground-water contamination. Depending on the depth at which they are located, the pockets or pools may control the depth and extent of contaminant plumes emanating from the site.

TABLE 6. CLASSIFICATIONS OF COMMON ORGANIC CONTAMINANTS

Name	Aqueous volubility g/m^3[a]	Density	Classification
GROUP A			
Chloroform $CHC1_3$	8,000	1.4832	sinker
Carbon Tetrachloride CCl_4	800	1.5940	sinker
1,1,1 Trichloroethane, TCA	720	1.4714	sinker
Trichloroethene TCE, $C1CH:CCl_2$	1,100	1.4642	sinker
Ethylene Dibromide EDB $BrCH_2CH_2Br$	4	2.1792	sinker
Methylene Chloride CH_2Cl_2	20,000	1.3266	sinker
GROUP B			
Chlorobenzene C_6H_5Cl	500	1.1058	sinker
1,2-Dichloropropane CH_3CHClH_2Cl	2,700	1.1560	sinker
1,2 Dibromo-3-chloropropane (DBCP)	1,000	2.080	sinker
1,2,4-Trichlorobenzene $C_6H_3Cl_3$	25	1.4542	sinker

(continued)

TABLE 6. (Continued)

Name	Aqueous volubility g/m^{3a}	Density	Classification
GROUP C			
Polychlorinated biphenyls, PCBS	0.04 - 0.2	>1	sinker
Dichloro, diphenyl, trichloroethane DDT	0.003	>1	sinker
Aldrin	0.01	>1	sinker
Chlordane	0.056	>1	sinker
GROUP D			
Benzene C_6H_6	1780	0.87865	floater
Toluene C_7H_8	515	0.8669	floater
Xylene isomers C_8H_{10}	162 - 185	0.8802 to 0.8611	floater
Methane CH_4	24	0.5547 0°C	(gas)
n-Pentane $CH_3(CH_2)_3CH_3$	38.5	0.6262	floater
n-Octane $CH_3(CH_2)_6CH_3$	0.66	0.7025	floater
GROUP E			
1,2,3-trimethyl benzene C_9H_{12}	75	0.8944	floater

(continued)

TABLE 6. (Continued)

Name	Aqueous volubility g/m^{3a}	Density	Classification
1,2,4,5-tetramethyl benzene $C_{10}H_{14}$	3.5	0.8875	floater
Naphthalene $C_{10}H_8$	34	1.4003	sinker
1,4-dimethylnaphthalene $C_{12}H_{12}$	2.4	1.0166	sinker
Nonane $CH_3(CH_2)_7CH_3$	0.12	0.7176	floater
Decane $CH_3(CH_2)_8CH_3$	0.052	0.7300	floater
Tetradecane $CH_3(CH_2)_{12}CH_3$	0.0022	0.7940	floater
GROUP F			
Benzopyrene	0.003	>1	sinker
GROUP G			
Acetone CH_3COCH_3	infin	0.7899	mixer
Ethanol C_2H_5OH	infin	0.7893	mixer
Formaldehyde HCHO	infin	0.815	mixer
Tetrahydrofuran C_4H_8O	infin	0.888	mixer

[a] All numeric solubillty data are from MacKay and Shiu, 1981; all other data are from Weast, 1969-1970, or Verschueren, 1983. Density values are for 20°C unless noted otherwise.

infin = infinitely soluble
na = not available

CONTAMINANT SOURCE SIZE

Knowledge of the size of the contaminant source is important because without it, there is not much basis for deciding on the spacing of monitoring locations. The plume of contamination emanating from a contaminant source which is small in areal extent is normally narrow. Narrow plumes require close lateral spacing of measurement locations for detection or delineation. Although the literature on dispersion contains much controversial and problematic information, there is sufficient data now to conclude that in many aquifers, dispersion in the transverse lateral direction is weak and that plumes often do not spread much laterally as they increase in length. In other words, long narrow plumes should be viewed as the rule rather than the exception. The implications of this generalization are great. It means that the lateral spacing of monitoring wells or other measurement locations must be significantly less than the width of the contaminant source. At some sites, such as those that have a local leak in a liner or those that have had leaks from tanks or hazardous liquid supply lines, the small dimensions at the source present a formidable difficulty.

The lack of detailed information on the location and size of contaminant sources, as is the case for many sites, presents the greatest obstacle to the efficient development of site investigation plans. To achieve a good probability of detecting zones of ground-water contamination at these sites, it is wise to consider soil-gas and geophysical techniques for mapping the contamination rather than installing many more monitoring wells or soil sampling holes.

COMPONENTS OF SITE INVESTIGATIONS

The goal of investigations of sites that are known to be or suspected to be contaminated by organic materials is to determine the extent and severity of soil and ground-water contamination and to concurrently determine environmental parameters useful for planning remedial action. Once the extent of the problem is known, and pertinent environmental parameters are determined, plans for remedial action and long-term ground-water monitoring can be developed concurrently.

Many investigative techniques are available from which to select those appropriate for the particular site under consideration. Techniques can be selected from the following categories.

- geological
- hydrological
- geochemical
- environmental isotopes
- mathematical models
- soil-gas sampling and analytical chemistry
- geophysical

The challenge in any site study is to select the most appropriate combination of techniques for the specific site. This section will discuss many of these approaches. However, the details of planning soil-gas and geophysical investigations will be discussed separately in Sections 6 and 7, respectively.

Geological techniques such as drilling and sampling of borehole materials will be included in nearly all site studies because in situ sampling is necessary to confirm the degree and extent of contamination indicated by other techniques.

Hydrological techniques such as the use of monitoring wells for permeability tests and for hydraulic-head monitoring are also an important component of nearly all site studies where organics occur. Permeability measurements and ground-water elevation monitoring determine the ground-water flow pattern if the geologic framework of the site is also known. Without adequate knowledge of the geology of the sites, determination of the hydraulic head distribution will normally not provide for a good interpretation of the flow net. Most types of monitoring wells can be used for three purposes: permeability tests, head measurements, and acquisition of water samples. In recent years, however, there have appeared several dedicated monitoring devices that provide ground-water samples but that are not useful for permeability testing or head monitoring. Thus, hydrological studies of a site are not necessarily an integral part of the monitoring phase of an investigation.

In this report, environmental isotopes refer to those isotopes in the ground water that can be used to assist in the determination of ground-water age or origin. The isotopes of primary interest are tritium, oxygen-18, deuterium and carbon 14 and 13. Of these, tritium is by far the most useful in studies of sites of organic contamination. Tritium can be used to identify ground water that is less than about 30 years in age.

Mathematical models have a potential to aid in the development of hydrological or transport interpretations. Such models offer a formal means of displaying or assessing conceptualizations of the conditions at the site. Mathematical models are rarely a means of reducing much of the need for site data. Instead, they offer possibilities for making better use of the data that are obtained. Ground-water flow models very commonly serve a useful and often essential component in site studies. However, solute transport models that include the combined effects of advection, dispersion and retardation rarely serve an essential role in a site investigation.

In the development of a strategy for an investigation of organic contamination at a site, all of the various investigative techniques or tools should be considered to better select those particular items with potential or expected usefulness. The planned investigation should be formulated in several phases. The phases should generally be sequential in the earliest stages. The approach should allow for extensive feedback as phases are completed so the new information can be applied to improve the investigation strategy.

PRELIMINARY INFORMATION

Before beginning a study, information in a number of categories is essential to aid in the choice of monitoring techniques, the design of survey grids, the procedures for using the instruments,and the interpretation of the data. As mentioned earlier, this list was compiled with the assistance of Dr. Gary Robbins, a member of the panel of experts listed in Section 1. The categories listed have been divided into broad groups: hydrogeology; soil, surficial geology, and bedrock; site layout; and contaminant source information. Sources for this information include local consulting engineers, county offices, state geological and water surveys, U.S. Geological Survey reports and maps (Handman, 1983), the National Climatic Center, the Soil Conservation Service, construction and foundation reports for structures on site. The information described in the list will be helpful in choosing techniques and planning survey grids. Without this information, there will probably be a need for application of additional techniques to provide confidence that the contamination has been detected successfully and completely.

Hydrogeology

a. Existing wells.

   (1) Locations
   (2) Uses, past and present
   (3) Quality of ground water, presence of contamination, for different aquifers
   (4) Well logs and driller's logs
   (5) Construction specifications
   (6) Typical pumping rates, hydrologic parameters such as specific capacity, transmissivity, hydraulic conductivity, storage coefficients or storativity and the extent of pumping influence.

b. Altitude of the water table.

   (1) Regional and on-site (elevation and depth)
   (2) Seasonal fluctuations, if available

c. Thickness and distribution of aquifers and aquitards; existence of perched aquifers.

d. Ground-water flow velocity or gradient, both local and regional.

e. Soil porosity, moisture, and lithology.

f. Recharge and discharge areas.

9. Basic climatic information, including annual precipitation, and monthly temperatures.

h. Nature of drainage conditions, and flooding.

Soil, Surficial Geology, and Bedrock

a. Types, thickness, and lateral distribution of strata.

b. Properties of soil including color, density, porosity, infiltration rates, hydraulic conductivity, soil suction relations, grain size distribution, Unified Soil Classification System (USCS) classification, moisture content, soil chemistry, and organic content

c. Type and extent of fill if present.

d. Boring logs for nearby construction.

e. Stratigraphy and lithology.

f. Location and Type of Bedrock.

   (1) Mass properties (faulting, fracturing, layering, dips, and strikes)
   (2) Geologic maps
   (3) Regional geology
   (4) Regional gravity and magnetic data
   (5) Depth to bedrock

<u>Site Layout</u>

a. Historical and current aerial photographs.

b. Present and past use of site.

c. Topography and nature of surface, in terms of woods, vegetation, bare soil, outcrops.

d. Location of buildings, other facilities such as runways, and survey markers.

e. Nature and location of roads for access.

f. Nature and location of pipelines, utilities, and underground facilities which may be conduits for contamination, obstacles to investigation activities, or both.

9. Location of power, water, and lighting which may be needed in investigation activities.

h. Nature of pavement including type, thickness, and reinforcement.

i. Nature of activities on site which may influence subsurface conditions, such as irrigation, pumping wells, dewatering systems, septic fields, etc.

j. Nature and location of safety hazards.

Contaminant Source Information

a. Identity of organic contaminants.

b. Locations of spills and leaks (tanks, sumps, dumps, pipelines, impoundments, etc.).

c. Amounts spilled or leaked; past problems of similar nature.

d. Time or duration of events.

e. How problem was discovered.

f. Depth of contamination.

g. Characteristics of problem such as odors, seepage, or a contaminated well.

h. Actions to clean up problem to date.

i. Contamination due to other sources, including chemicals, concentrations, extent of problem, time frame of problem, remedial actions being performed.

Status of Early Knowledge

In any site investigation for contaminant migration, determination of the geological conditions is a key task. A good monitoring strategy cannot be developed until a considerable amount of information is obtained on the geology of the site. If very little is known about the geology of the site before the investigation begins, then an important early step in the investigation should be a preliminary geological investigation.

The Zone of Relevance

In most site studies, it is usually determined that there is a depth controlled primarily by geological conditions below which contaminants have not penetrated. The entire zone above this depth can be referred to as the zone of relevance. For example, if the site is situated on an unconfined sand aquifer with an aquitard of fractured clay, the sand would constitute the zone of relevance. It is obvious that the site study should focus primarily on the zone of relevance. But to determine where the bottom of the zone of relevance is located, a component of the site study must extend beneath the bottom of the zone. If the bottom of the zone of relevance can be located early in the site study, the remainder of the study can proceed with greater efficiency. Often, drilling to determine the geological conditions provides appropriate information to draw a tentative conclusion regarding the bottom of this zone. The presence of tritium can be used to help define the zone of relevance. This conclusion can then be assessed by other means such as ground-water monitoring.

GEOLOGICAL TECHNIQUES AND ISSUES

When selecting the geological techniques of drilling and coring for a site investigation, many questions should be addressed. The following is a list of questions which may be useful to consider. The order of the questions is not significant.

- What type(s) of drill rig(s) should be used?
- Can the use of drilling mud or other drilling additives be avoided and if so, how?
- What type of soil or rock sampling methods should be used?
- What soil or rock sampling interval should be selected?
- How should the soil or rock samples be stored?
- Should an organic vapor analyser be used in the field to screen the soil and rock samples?
- To what depth should the boreholes be drilled?
- Should the boreholes be used for installation of monitoring wells or should they be plugged?
- What techniques should be used to plug the holes?
- If it is expected that fractures are the main route for contaminant migration, should angle boreholes be drilled as well as vertical holes?
- Has a geologist with specific knowledge or experience pertaining to the local geology been consulted in the development of the preliminary geological interpretation of the site?
- To what depth is it reasonable to expect root holes, animal burrows and desiccation cracks to penetrate from the ground surface?
- When boreholes are drilled and sampled, to what depth are weathering features identifiable?
- If it is known or suspected that dense immiscible liquids have been used/spilled/buried at the site, what geological contact or layer would most likely have acted as a barrier to the sinking of the liquid?
- If possible geological barrier beds or contacts can be identified, what is the dip of the surface along which dense immiscible liquids might move?
- What procedures should be used to prevent further spread of contamination if this barrier is penetrated?

HYDROLOGICAL TECHNIQUES AND ISSUES

When selecting hydrological techniques for a site investigation, many questions should be addressed. The following list of questions can help to better define the important decisions to be made for a given site investigation:

- Can the available geological knowledge of the site and the general hydrological setting be used to develop a preliminary estimate of the ground-water flow pattern?
- Is the depth to the water table relevant information? How should it be determined?
- Should a network of monitoring wells be used to determine the ground-water flow pattern?
- What techniques would be best for determination of ground-water velocity?
- What type of aquifer test should be used?
- Is there a need to use pumping tests to establish the degree of hydraulic connection between one part of the site and some other part?
- Are there aquitards at the site and if so, do they act as barriers to contaminant migration?
- Should laboratory permeameter tests be done on core samples?
- If fractured clayey deposits occur at the site, has drilling caused smearing of the fractures in the borehole, thereby changing the hydraulic properties?
- Are the ground-water flow conditions observed now at the site the same as those that existed when ground-water contamination began to occur?
- If contaminant migration is occurring at the site, does it occur by porous media transport or fractured media transport?
- If it is expected that the fractured media transport of contaminants occurs, how can estimates of the bulk fracture porosity be obtained for velocity estimates?
- If the mode of flow and transport is via fractures, what is the porosity of the blocks between the fractures?
- At what depths or in what zones do the critical solute-transport paths occur?
- Should detailed vertical profiles of hydraulic head be obtained to assist in the identification of depths of critical flow paths?

- How much annual infiltration is expected to occur at the site?

- In the zone in which contaminant migration is most likely to occur, what is the degree of heterogeneity and what dispersion tendencies are expected?

- What are the locations and yields of water supply wells in the area?

- How does the potentiometric surface respond to precipitation and what does this indicate with respect to the ground-water flow system?

- Is the geology of the site suitable for use of multilevel monitoring devices in single boreholes or is it necessary to drill many holes to different depths at each location in order to monitor at many depths?

GEOCHEMICAL TECHNIQUES AND ISSUES

When selecting geochemical techniques for a site investigation, numerous questions should be addressed.

- What are the redox conditions in the ground-water zone and is it likely that these conditions will affect transformations or degradation of organic contaminants?

- What is the weight percent of solid phase organic carbon in the geologic materials and what degree of contaminant retardation would it be expected to cause?

- Is there evidence of transformations (i.e., biodegradation, hydrolysis)?

- If the geological media allow contaminant transport via fractures, what will be the influence of the matrix diffusion effect?

- Can inorganic parameters such as major ions or electrical conductance be used as indicators of transport paths or contamination?

- Would it be useful to measure parameters such as pH, Eh, CH_4 and dissolved oxygen when sampling monitoring wells?

- Do samples of water from monitoring wells contain H_2S and if so, what does this mean?

- Are there clay-rich aquitards at the site and are they such that molecular diffusion is the dominant influence on solute transport?

- Do core samples from the geologic deposits show evidence of chemical weathering and if so, what does this indicate regarding the development of fractures?

- Should diffusion coefficient measurements be made on core samples?

ISOTOPIC TECHNIQUES AND ISSUES

The presence of tritium can be used to help define the zone of relevance. If the contamination has occurred more recently than 1953, then the presence of tritium may be a useful indicator of the possible extent of the hydrocarbons. However, if organic chemicals which are more dense than water have been used at the site, then tritium is generally not a good indicator of the expected zone of contamination. This is the case because contaminants which are more dense than water can sink through the aquifer into zones much deeper than tritium moves under the influence of ground-water flow alone. References for this technique include Payne, 1972; Freeze and Cherry, 1979; and Cherry, Farzolden, and Frind, 1983. Tritium analyses are commercially available from the University of Miami Tritium Laboratory.

When selecting isotopic techniques for site investigation, several questions should be addressed. These are listed below. The order of the questions is not significant.

- Is it likely that the site became contaminated after 1953 and if so, should tritium be used as an indicator of the zone of active ground-water movement that is susceptible to post-1953 contamination?
- Is there evidence that organic contamination exists in ground-water samples that have no tritium?
- If it appears appropriate to use tritium in the site investigation, what detection limit and precision is appropriate to request in the tritium analyses?
- Should tritium profiling be used to determine whether or not an aquitard beneath the site is leaky?
- Should water samples for tritium analysis be acquired from monitoring wells or by extraction of water from cores?
- Can the mapping of tritium in ground water at the site serve as a means of delineating the zone of relevance for site monitoring?
- Is it likely that organics as dense immiscible liquids have travelled in a manner that would mean that tritium is not a good travel-path or travel-time indicator?
- Is it likely that isotopes in addition to or other than tritium can play a useful role in the site study?
- If the contamination is known to have or suspected to have originated from a lagoon or pond, is it likely that oxygen-18 and deuterium will serve as an indicator of the source water?

LITERATURE REVIEW

Numerous studies of subsurface organic contamination have been conducted and reported in the literature. This discussion provides a series of examples of contaminant and geology combinations along with references to studies of that type in the literature. Each of the cases is meant to represent a broad category of contaminated sites and to serve as an aid to visualizing the distribution of the contamination. With some idea of the likely behavior and features of the contamination, it is easier to plan the investigation. A brief discussion of indirect monitoring techniques which may be appropriate for each case also is provided. These conceptual drawings were developed and techniques selected during the 2-day meeting of the panel of experts.

The characteristics of the cases include sand and gravel, clay, fractured bedrock, and karst limestone; shallow and deep aquifers; and fuel, solvents and landfill leachate. Actual site conditions usually would be more complex than these hypothetical cases (Mackay and Roberts, 1985), but complexity alone would not dictate a different choice of techniques. Instead, complexity will increase the number of techniques necessary for complete understanding of the contaminant location.

Nine hypothetical cases have been developed to represent common combinations of sources, contaminants, and hydrogeology. The hydrogeological medium for six of the nine cases is sand and gravel. Clay was assumed to be present in the sand and gravel, but at low enough proportion to not affect the organic contaminant migration. The remaining three cases deal with the complexities of clay, crystalline fractured rock, and karst terrain.

Fuel Leak Over Unconsolidated Sand and Gravel Aquifer

In this example, shown in Figure 5, gasoline or other non-alcohol fuel has leaked from some surface or near-surface source continuously or frequently for several years. The fuel, which is of lower density than water, floats on top of the water table. Some fuel is trapped in the unsaturated zone as coatings on soil particles; and some constituents dissolve in the ground water, while others volatilize and diffuse away from the fuel pool. The horizontal transport distance will depend on the volume of the leak, ground-water velocity, and other parameters. Soil-gas techniques are likely to be successful in this situation; and if the resistivity of the soil is greater than 30 ohm-meters, GPR may be useful . For a discussion of an actual example with attendant complexities, Hult, 1984 describes an investigation of a crude oil leak at Bemidji, Minnesota. Marrin, 1985 describes a gasoline leak over a sand and gravel aquifer.

Solvent Leak Over Sand and Gravel Aquifer

This case, shown in Figure 6, is similar to Case 1 except that trichloroethylene and other common chlorinated solvents are denser than water and sink through the unconfined aquifer until an aquitard is reached. The solvent may pool in depressions on the aquitard. Each pool of solvent then acts as a secondary source contaminating the ground water, possibly for many years after the surface source is removed. When performing the investigation, the aquitard should not be penetrated unless appropriate drilling precautions are applied.

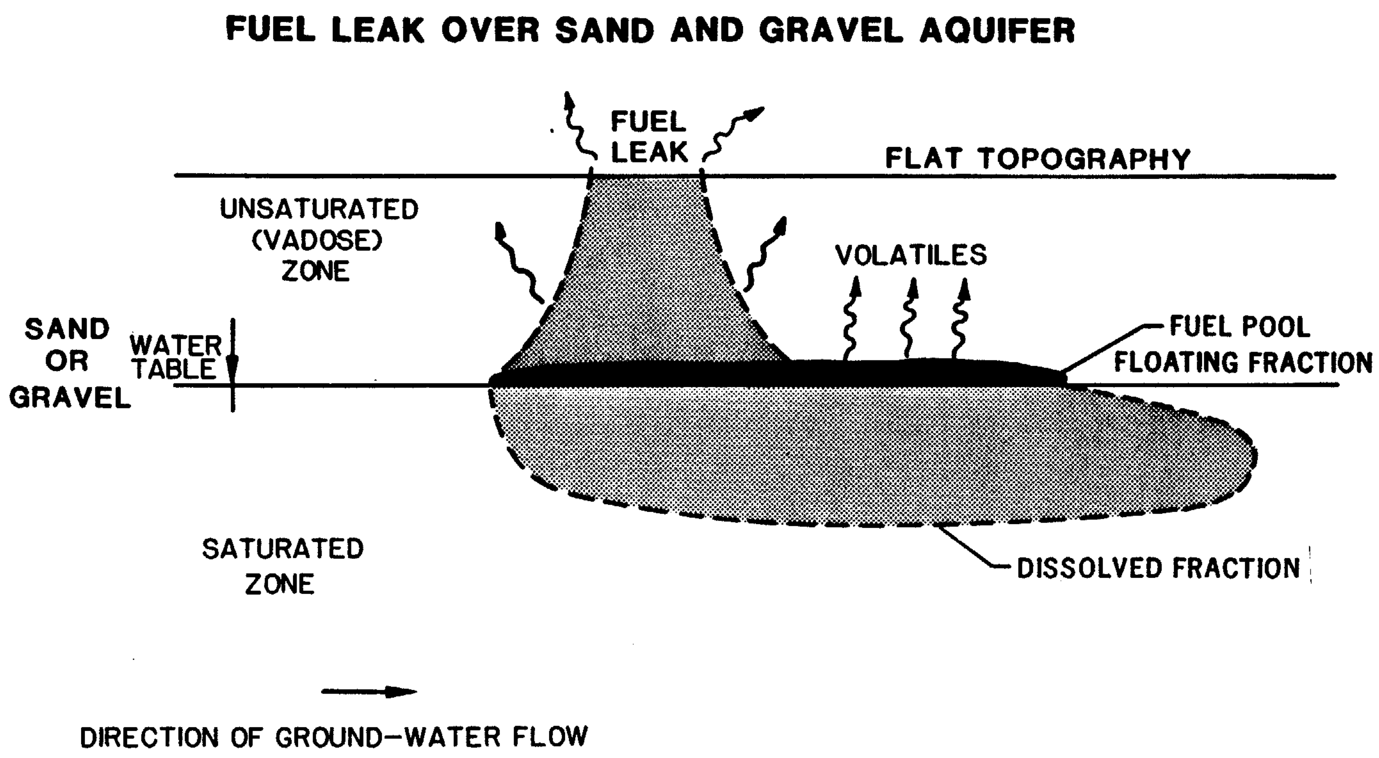


Figure 5. Fuel leak over unconsolidated sand and gravel aquifer.

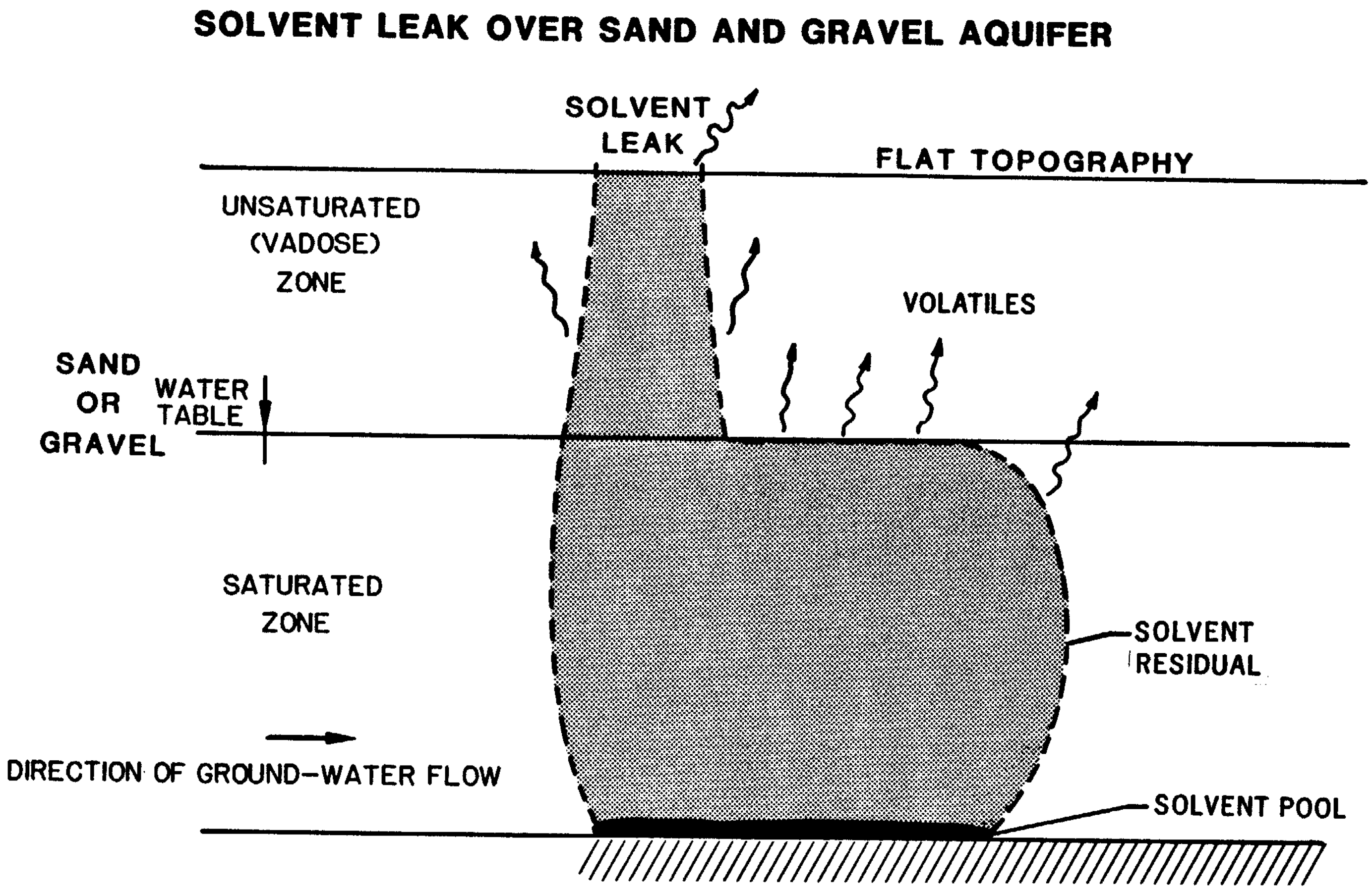


Figure 6. Solvent leak over sand and gravel aquifer.

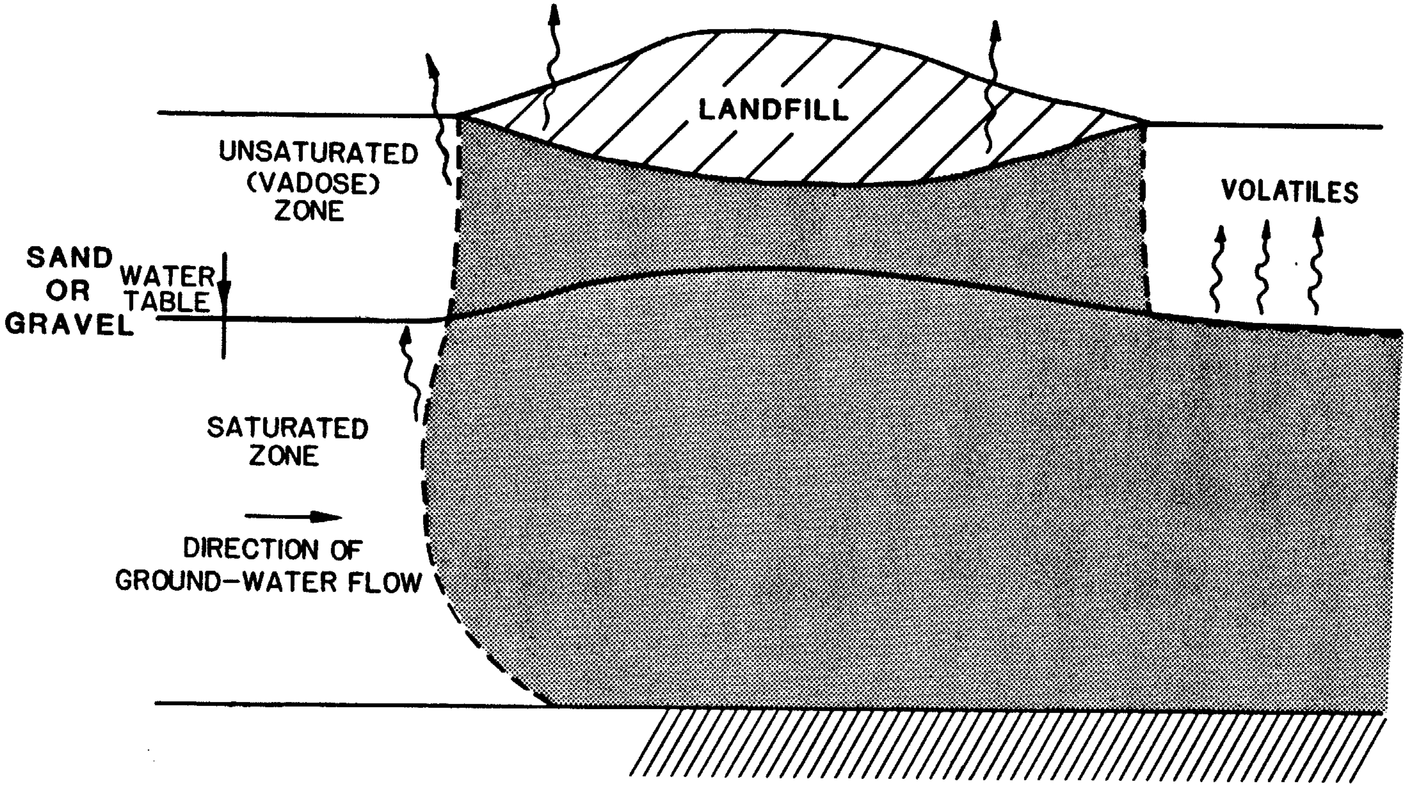
It is important that the well not provide a conduit for the solvent to contaminate lower aquifers. As in the previous case, soil-gas techniques are expected to be successful and GPR may be useful, if the resistivity of the soil is greater than 30 ohm-meters. For an extensive discussion of an actual case in Pensacola, Florida, where the investigation of creosote contamination including phenols was complicated by the presence of clay lenses, see Mattraw and Franks, 1984. Bradley, 1980 and Marrin and Thompson, 1987 discuss an investigation of soil gas above TCE-contaminated ground water. Walther et. al., 1983 describes a site with a soil consisting of a mixture of sand, gravel, and clay, and chlorobenzene and benzene contamination in ground water at Pittman, Nevada.

Landfill Over Unconsolidated Sand and Gravel Aquifer

A landfill, shown in Figure 7, is a much larger area source than most fuel and solvent spills, usually covering acres of land. The permeability of landfills is usually higher than the surrounding soil, and this leads to ground water mounding beneath the landfill after rainfall. Such a mound is a dome in the topography of the water table, whose height and permanence depends on the frequency and intensity of rainfall. Landfills usually leach organic and inorganic contaminants. The inorganic contaminants may be roughly colocated with the organic contaminants, although the two contaminant types migrate at different speeds. In this case, the inorganic plume may be useful for locating the organic contamination. Landfills generally produce gases which can vary in composition according to the age of the fill. These constituents include nitrogen and hydrogen which may be released for brief periods on the order of 2 to 3 months and carbon dioxide and methane which may be released for several years after the placement of the fill. Soil-gas sampling for carbon dioxide, methane, or VOCs may be useful for locating the contamination. If the depth to the aquifer is less than 8 meters., and a conductive ground-water plume is present, EM, resistivity, or GPR may be useful for detecting the inorganic contamination. Measurements using EM, GPR, and magnetics on top of the landfill can locate the the presence of metal trash. Cherry, 1983 describes an actual case at Borden landfill in Ontario, Canada. Seitz et. al., 1971 describes the effect of a landfill on the hydrogeologic environment.

Sewage Leach Field Over Unconsolidated Sand and Gravel Aquifer

A centralized sewage leach field, shown in Figure 8, typically covers a large area, similar to a landfill. The sewage water causes a ground-water mound beneath the sewage leach field. The concentrations and presence of the organic contaminants will be variable because some of the sewage is biodegradable. If the water table is less than 30 meters (98 feet) in depth, the EM and resistivity techniques may detect a conductivity increase caused by the presence of inorganic constituents such as ammonia and nitrates. Soil-gas sampling for methane may be ineffective if soil moisture beneath the leach field reduces the effective porosity to less than five percent (Marrin, 1984). Seismic techniques can be considered for determining the depth of the water table when it is greater than 30 meters. LeBlanc, 1984 describes the investigation of such a case at Cape Cod, Massachusetts.



LANDFILL OVER SAND AND GRAVEL AQUIFER

Figure 7. Landfill over unconsolidated sand and gravel aquifer.

SEWAGE LEACH FIELD OVER SAND AND GRAVEL AQUIFER

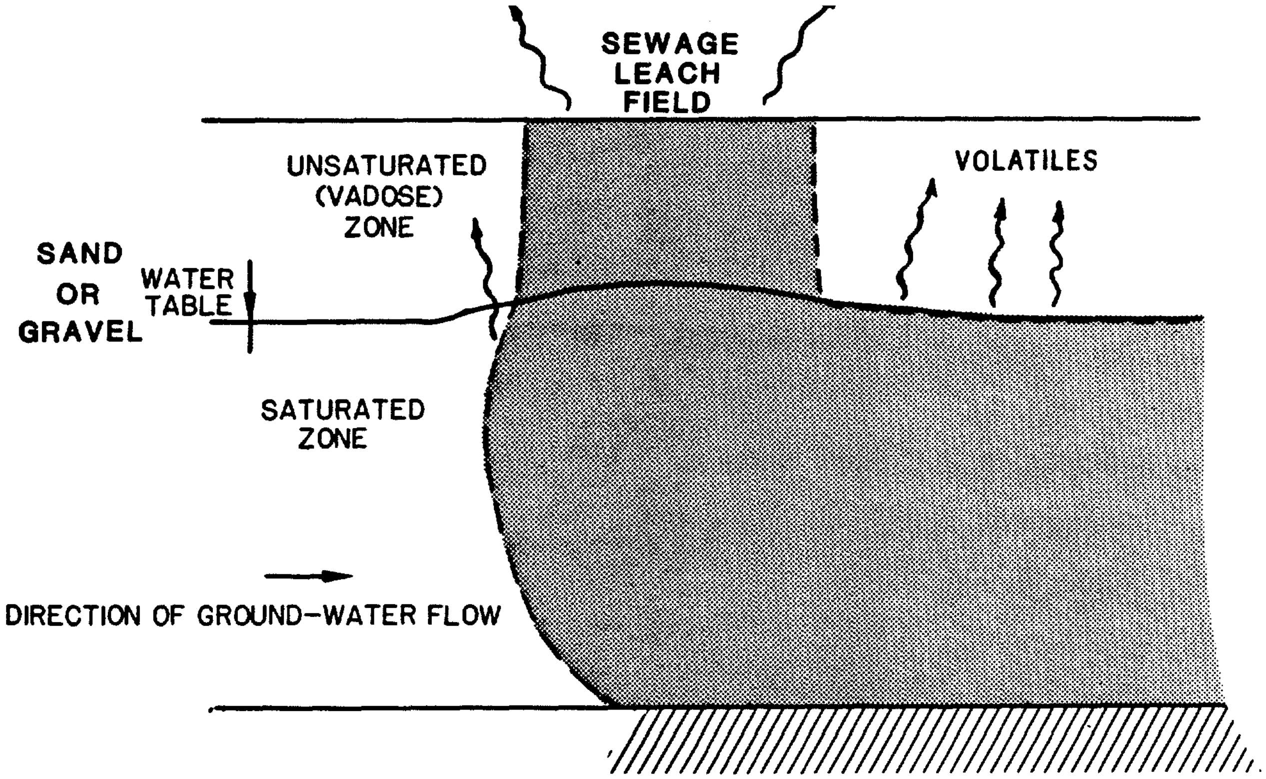


Figure 8. Sewage leach field over unconsolidated sand and gravel aquifer.

Leak Over Deep Aquifer

In this case, shown in Figure 9, there is reason to suspect that the fuel, solvent or landfill leachate has not reached the water table. This may be due to the volume of the leak or the depth to the aquifer. Other reasons this may occur include degradation, volatilization, sorption onto clay and soil particle surfaces, impermeable layers of clay, moisture barriers, or low infiltration rates. The leak will descend in a narrow, vertical column unless clay lenses or variations in permeability redirect the flow. Analysis of soil gas near the source can determine the lateral diffusion of the volatile organic contaminants. Core sampling can establish the vertical extent and actual concentration of the contaminant. When performing the investigation, care should be used to avoid breaching confining layers, thereby allowing new migration paths for the contaminant. This case is similar to a study of contamination in the unsaturated zone from low-level radioactive hospital waste containing organic solvents and carriers (Nichols, 1986 and Beers and Morey, 1981).

Fuel and Solvent Leak Over Two Interconnected Aquifers

This case, shown in Figure 10, provides more structural complexity. Fuel will float on top of the unconfined aquifer, while solvent will form pools on top of both aquitards. Some solvent will dissolve in the fuel, and some fuel components will dissolve in the solvent. The ground water may flow in different directions in the two aquifers. Therefore, detecting the plume in the unconfined aquifer does not locate the plume in the confined aquifer. The silt/clay aquitard between the aquifers acts as a barrier to the upward migration of organic vapors and to the penetration below the unconfined aquifer of electrical current as might be used in a geophysical survey. Resistivity can provide information on the hydrogeology, possibly identifying the depth of the water table and both aquitards. Resistivity is more likely to determine the complex structure than is EM. Seismic techniques can also be used to help determine these depths. Soil-gas techniques can map the contamination in the upper aquifer. The drilling of monitoring wells must proceed carefully. The aquitards should not be penetrated unless appropriate drilling precautions are applied. It is important that the drilling not provide a conduit for the contaminants to move between aquifers, yet it is the only method to obtain information on the lower aquifer. An actual example of a case with multiple aquifers is the St. Louis Park study (Ehrlich et. al., 1982).

Fuel Leak Over Crystalline Fractured Rock

This case, shown in Figure 11, illustrates the complexity of contaminant migration where the presence and orientation of the fractures dictates the pathways followed by the organic contaminants. Aerial image analysis can find major fractures or fracture patterns; field mapping should be used to check these results. This information may suggest where to install wells. GPR, with its continuous profiling capability, may locate fractures if the resistivity of the rock is greater than 30 ohm-meters. Otherwise, seismic or resistivity techniques should be used. Resistivities for many rock types are given in Benson et. al., 1983. Soil-gas sampling at locations of fractures indicated by the earlier techniques can be used to develop further information regarding the presence and type of contamination in the fractures. Monitoring wells may have

LEAK OVER DEEP

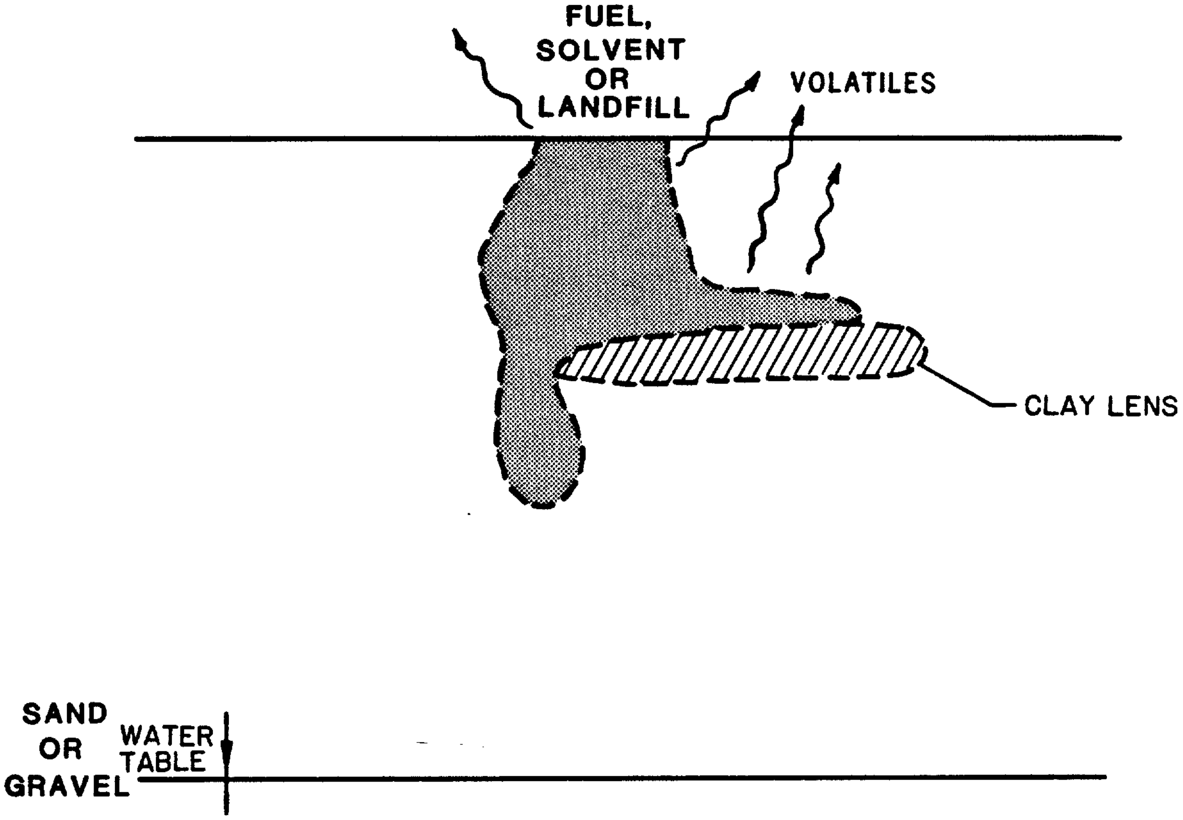


Figure 9. Leak over deep aquifer.

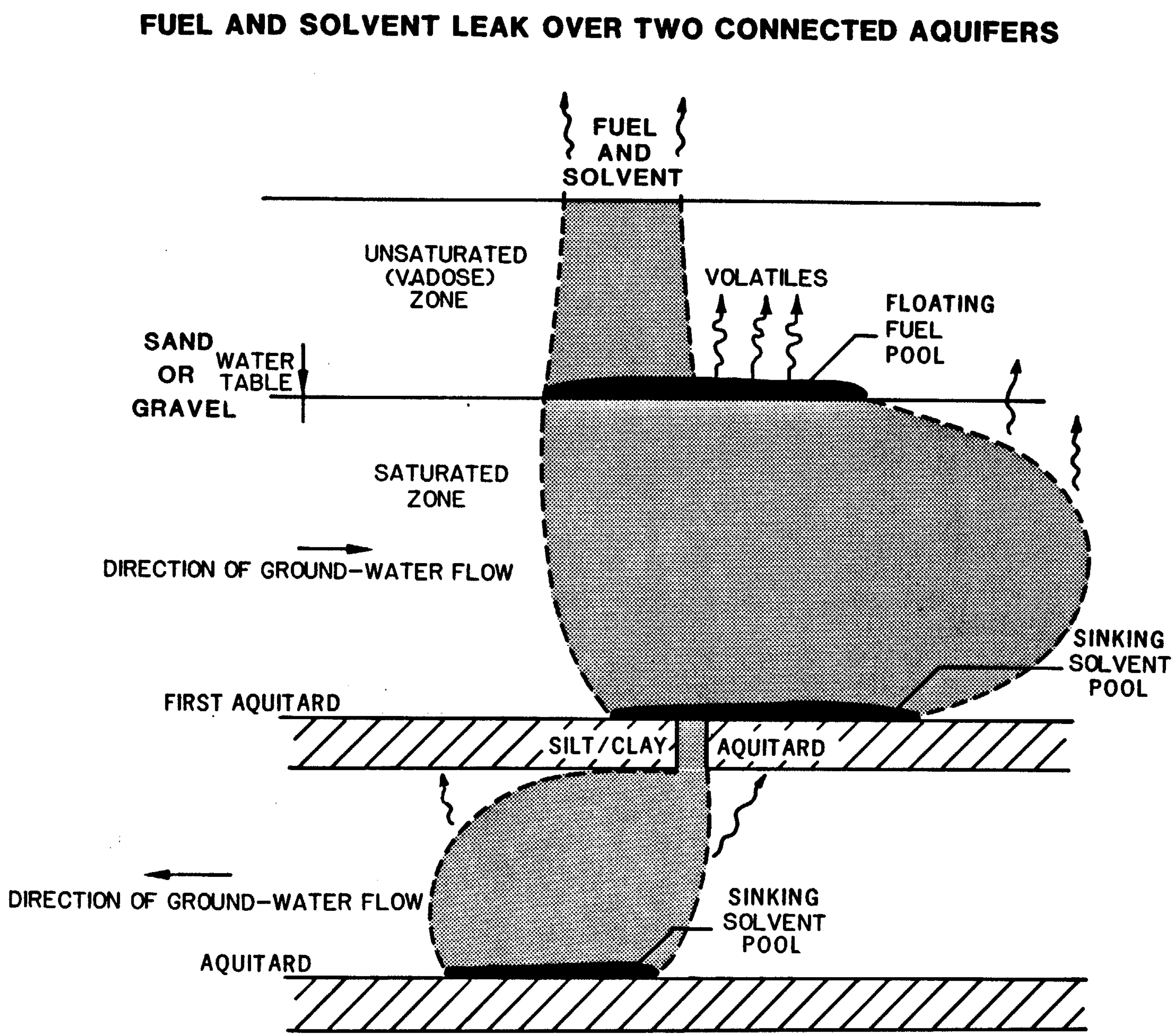


Figure 10. Fuel and solvent leak over two interconnected aquifers.

FUEL LEAK OVER CRYSTALLINE FRACTURED ROCK

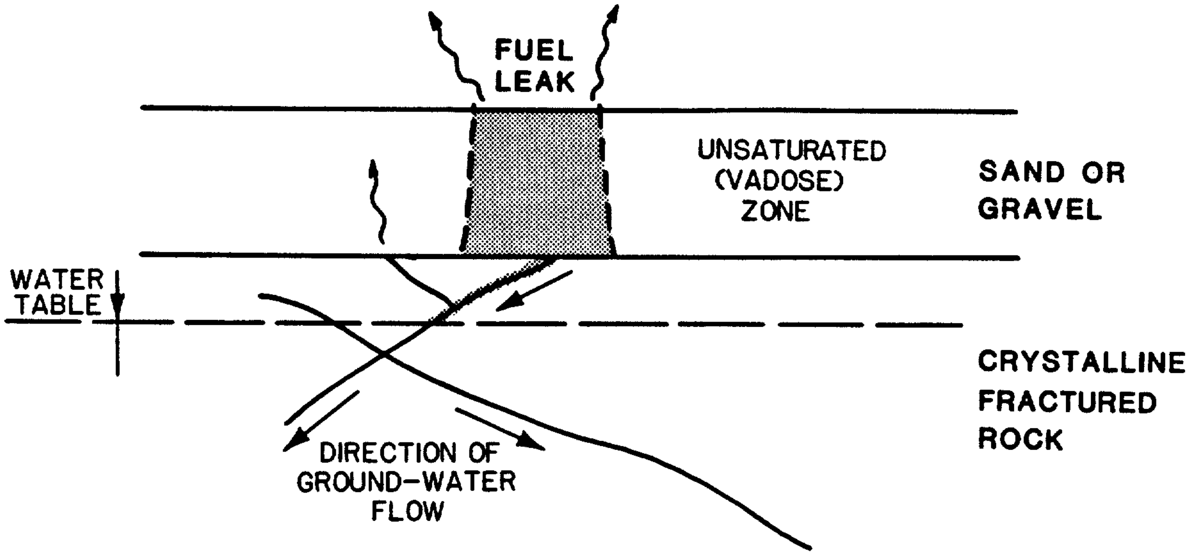


Figure 11. Fuel leak over crystalline fractured rock.

to be angled to intercept the fracture pathways. Taylor, 1984 evaluates methods for measuring hydrological variables in fractured rock units. Examples of geological characterization of waste sites located over fractured rock include Davison et. al., 1982; Olsson et. al., 1984; and Jones et. al., 1985.

Fuel Leak Over Thick Fissured Clay

In this case, shown in Figure 12, the leaked fuel travels along unknown pathways through the clay to the top of the water table. The fuel forms a pool at the water table and the fuel constituents dissolve from that pool into the ground water and travel downgradient. As in the case above, the pathway is unknown. Clay has a high electrical conductivity and it is difficult for the electromagnetic energy of a current field to penetrate. The clay is also a barrier to the upward diffusion of VOCs. Clay layers at any depth above the first aquitard have the same effect. Monitoring wells and soil cores have the highest likelihood of success. It may be worthwhile to have an experienced geophysicist apply the complex resistivity technique. Zehner, 1983 describes a hydrogeological investigation for a site with fractured shale.

Fuel Leak Over Karst Terrain

Karst terrain, shown in Figure 13, usually contains a network of complex fractures, channels, caves, and underground streams which are the migration pathways for contaminants. As in the crystalline fractured rock example, aerial image analysis can be used to find major features of the karst network with field mapping to check the results. Tracers are one of the best methods to determine flow paths. This information may suggest where to install wells. Ground-penetrating radar can be used to locate fractures if the resistivity of the rock is greater than 30 ohm meters. Its capability of continuous profiling is particularly useful in this case. D.C. resistivity should be used instead of GPR if the apparent resistivity of the soil is less than 30 ohm meters. Seismic techniques should be used along with both of these electrical methods to obtain independent information on the location of major geologic features of the karst terrain. Sampling and analysis of soil gas at channel openings can indicate the presence and type of contamination. Monitoring wells may be placed using the results of the surveys. The monitoring wells may have to be angled to find the channels. Quinlan and Ewers, 1985 discuss the complexities of ground-water monitoring in karst terrain and recommend a strategy which monitors existing springs. A description of a site investigation in karst terrain is given by Franklin et. al., 1981.

FUEL LEAK OVER THICK FISSURED CLAY

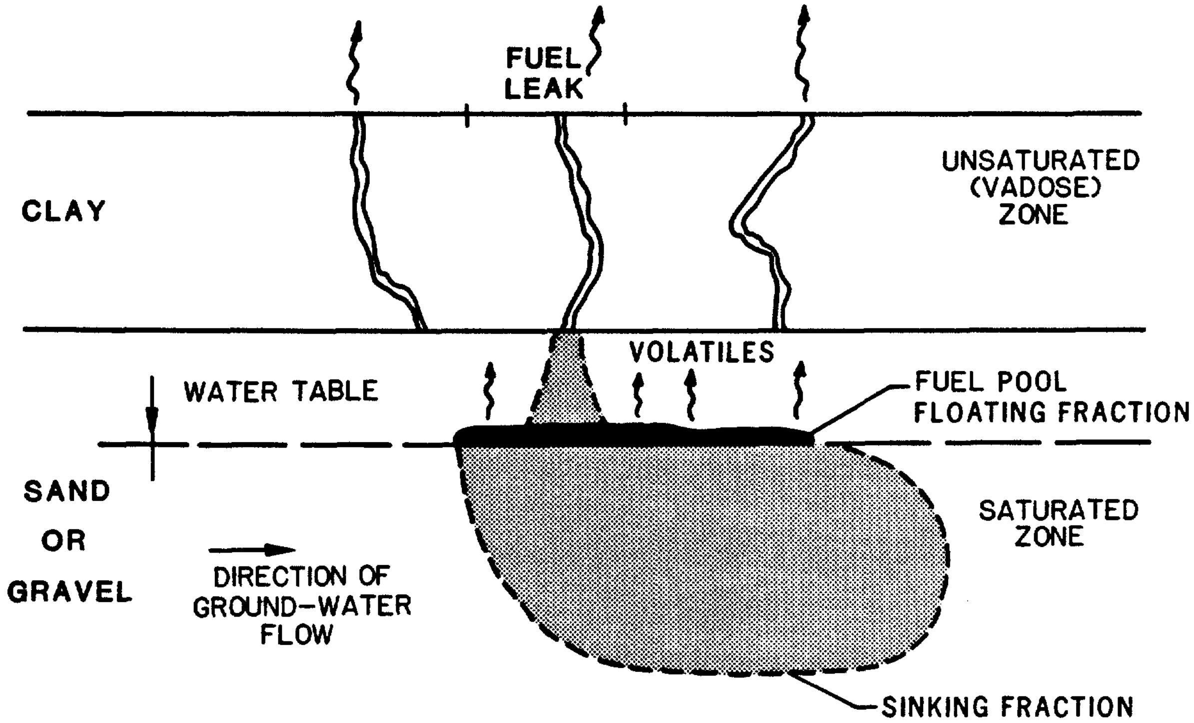


Figure 12. Fuel leak over thick fissured clay.

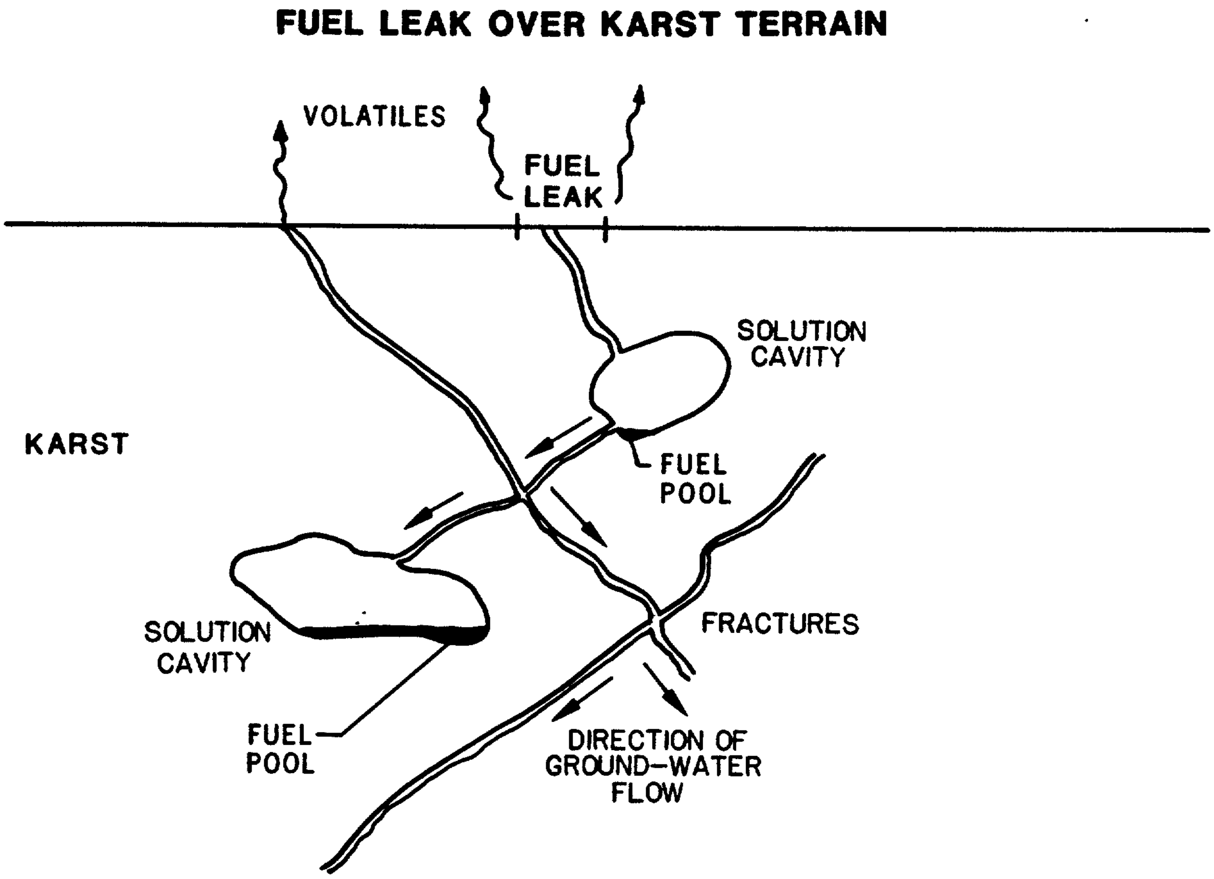


Figure 13. Fuel leak over karst terrain.

SECTION 6

PLANNING A SOIL-GAS INVESTIGATION

INTRODUCTION

This section was adapted from materials provided by Dr. Dorm Marrin, a member of the panel of experts listed in Section 1. The purpose of this section is to identify the types of subsurface contaminant problems which are amenable to soil-gas sampling. Furthermore, it is designed to illustrate environmental conditions under which soil-gas sampling is either not appropriate or subject to misleading interpretations. Soil-gas investigations must be designed and interpreted according to the hydrologic/geologic setting and chemicals which are present at each site. A variety of investigative and interpretive techniques may be used at a single site if there are variable environmental conditions or multiple objectives to fulfill.

The section is organized into two parts; the first assesses the applicability of soil-gas sampling under generalized conditions; and the second develops an investigation plan by presenting a hierarchy of questions addressing the geology, hydrology, contaminant types, and objectives. The first part includes four questions which assess the applicability of soil-gas sampling for common contaminant groups under general subsurface conditions and another four questions which require more detailed site-specific information. These questions provide a basis for estimating the effectiveness and interpretive limits of soil-gas analyses. In the second part are two questions which provide insight into the formulation of an on-site investigation plan.

Questions presented in this section are applicable to all active soil-gas sampling methods. Several of the criteria emphasized here are not directly applicable to passive sampling techniques. The guidance was designed specifically for active soil-gas sampling techniques combined with immediate on-site analysis of the samples. With this approach, the real-time data are produced within a time period which permits the results to be used in selecting subsequent sampling locations.

Questions contained in the two parts are designed to provide users with the necessary criteria to decide whether soil-gas sampling is appropriate for specific subsurface problems.

IS SOIL-GAS SAMPLING APPROPRIATE?

The first question is “What are the contaminants of interest at the investigation site?” This question is fundamental in determining the applicability of soil-gas sampling to a contamination problem. Once specific compounds are identified, their physical properties can be obtained from a variety of chemical references. Generally, soil-gas sampling is most effective for compounds with upper pressures above 1.0 kpa (5.0 mmHg) and Henry's Law constants above 0.1 to 0.5 kpa m^3/mol (Marrin, 1984). If vapor pressures and Henry's Law Constants are not available, then compounds with boiling points below 125°C can probably be detected in soil gas. This information is summarized for common ground-water contaminants in Table 7.

The next question is "Do the contaminants of interest partition adequately into the vapor phase?" Once the compounds of interest are identified and categorized, a determination can be made regarding the likelihood of their presence in soil gas under a variety of environmental conditions. Henry's Law constants are a measure of air-water partitioning and can be calculated from a compound's vapor pressure, aqueous volubility and molecular weight according to Equation 1.

$$H = \frac{VM}{S} \qquad (1)$$

where:

H = Henry's Law Constants $\frac{kpa \cdot m^3}{mol}$;

V = vapor pressure (kpa);

M = gram molecular weight $\frac{g}{mol}$; and

S = aqueous volubility $\frac{mg}{L}$ or $\frac{g}{m3}$.

Vapor pressure and aqueous volubility must be calculated at the appropriate environmental temperatures.

Groups C and F represent high molecular weight compounds which do not partition adequately into the gas phase to be detected in soil gas under normal circumstances. These compounds are of considerable environmental concern, however, they are not amenable to soil-gas detection as described here. All other contaminant groups contain compounds with a significant vapor phase. The success in mapping compounds within these other groups is dependent on a number of site-specific factors.

The next question is "Is the major subsurface contamination present in the soil or the ground water?" The answer to this question determines whether compounds must partition from the aqueous to the gas phase or whether they only have to diffuse in soil gas. This distinction is particularly important for compounds in Group G which have high vapor pressures but which are also very water-soluble. The result is that these compounds diffuse quite readily once in soil gas but tend to remain dissolved in the ground water. Hence, Group G contaminants are amenable to soil-gas detection if they result from a surface or vadose zone spill, but may not be present in soil gas as a result of moderate ground-water contamination.

TABLE 7. USEFUL DATA FOR SELECTED ORGANIC CONTAMINANTS

Name	Group	Boiling point °C	Vapor pressure kpa	Molecular weight g/mol	Aqueous solubility g/m^3	Henry's Law constant kpa m^3/mol
Chloroform $CHCl_3$	A	61.7	25.60	119.4	8,000	0.38
Carbon Tetrachloride CCl_4	A	76.6	15.06	153.8	800	2.3
1,1,1-Trichloroethane TCA	A	74.1	16.53	133.4 (25°C)	720	2.8
1,1,2-Trichloroethene	A	87.0	9.87	131.4	1,100	0.90
1,3-Dichloropropane	B	112.0	4.53	110.97	2,800	0.18
Chlorobenzene	B	132.0	1.58	112.56	500	0.35
Dichloro, diphenyl, trichloroethane DDT	C	185.0	1.34×10^{-8}	354.5	0.003	5.3×10^{-3}
Benzene	D	80.1	12.70	78.11	1,780	0.55
Toluene	D	110.63	3.80	92.13	515	0.67
Methane	D	-164.0	27,260 (25°C)	16.04	24	67.4
n-Pentane	D	36.1	68.4 (25°C)	72.15	38.5	128
n-Octane	D	125.7	1.88 (25°C)	114.23	0.66	325
1,2,3-trimethylbenzene	E	176.1	0.202 (25°C)	120.2	75	0.323
Naphthalene	E	218.0	1.09×10^{-2}	128.19	34	0.043
Benzopyrene	F	311.0	6.67×10^{-13} (25°C)	252.3	0.003	1.4×10^{-7}
Acetone	G	56.2	24.227	58.08	23×10^5	na

Source: Mackay and Shiu, 1981, except for acetone, from Lucius, 1987.
All values are for 20°C unless another value is noted.
na = not available

It is also appropriate to ask “What is the depth to contaminated soil or ground water?” This question is applicable to Groups B and E which have very low aqueous solubilities and readily partition out of the ground water. Once in the gas, however, these compounds tend to remain near the water table or the original zone of soil contamination. Low vapor pressures and gas diffusion coefficients make Group B and E compounds amenable to soil-gas analysis only where probes can be placed near contaminated soil or ground water. Since soil-gas probes are normally driven to a depth of 1 to 3 meters below ground surface, there are obvious limitations to the remote detection of Group B and E compounds using conventional soil-gas techniques.

Group D compounds are also affected by the depth to subsurface contamination sources because of their tendency to be oxidized in the shallow soil. These compounds have high Henry’s Law constants (indicating favorable partitioning out of the aqueous phase) and diffuse rapidly when introduced to the gas phase. Thus, Group D compounds should migrate into the shallow soil gas in any environment which permits subsurface diffusion of volatile organic chemicals (VOCs). The residence time of Group D compounds in shallow soil depends on subsurface redox potentials and microbial activity. Low molecular weight petroleum hydrocarbons are most predictably detected in shallow aquifers or from leaking underground tanks where probes can be driven near the source of contamination.

To summarize, the answers to the first four questions indicate the applicability of soil-gas sampling to broad contaminant groups under general site characteristics. Polycyclic aromatic hydrocarbons, PCBs and organochlorine pesticides (represented by Groups C and F) are rarely, if ever, detected by soil-gas sampling. Volatile oxygenated compounds (Group G) are relatively water-soluble, and therefore are most easily detected as soil, rather than as ground-water, contaminants in close proximity to the source.

Compounds represented by Groups B and E are most often detected as a result of shallow soil or ground-water contamination because they diffuse minimally and tend to partition into aqueous or organic phases in the soil. Low molecular weight petroleum hydrocarbons (Group D) can either be detected in soil gas overlying shallow aquifers (where probes can be driven near the contamination source) or deep aquifers (where probes can be driven below the oxidative zone in soils). C_1 and C_2 halogenated hydrocarbons (Group A) are good candidates for soil-gas detection under a wide range of environmental conditions. These compounds possess low aqueous solubilities, high vapor pressures, high diffusion coefficients and are relatively resistent to degradation processes in most soils. This information is summarized in Table 8.

The next four questions address more specific aspects of the site. The first question is “What are the approximate concentrations of subsurface contaminants?” The concentrations of VOCs in ground water combined with the depth to water can be used to estimate chemical concentration gradients in soil gas. Both contaminant flux rates and soil-gas/ground-water correlations are a function of chemical concentration gradients. Gradients are routinely measured in the field by sampling soil gas in a vertical profile.

Contaminant flux rates are of interest because they provide an estimate of the migration time between contaminated ground water and shallow soil gas.

TABLE 8. CLASSES OF ORGANIC COMPOUNDS

Group	Group volatility	Class	Examples	Comments
A	High	Halogenated methanes, ethanes, ethenes	$CHCl_3$, CCl_4, TCA, PCE	Diffuse rapidly. Resist degradation.
B	Moderate	Halogenated propanes, propenes, benzenes	DBCP, chlorobenzene	Resist degradation. Moderate diffusion.
C	Very low	Halogenated polycyclic aromatics	PCBs, aldrin, DDT, chlordane	Not good for soil-gas analysis
D	High	C_1-C_8 petroleum hydrocarbons	Benzene, toluene, methane, pentane, isooctane, JP-4, gasoline	Easily oxidized. Diffuse rapidly.
E	Low	C_9-C_{15} petroleum hydrocarbons	Diesel, Jet A, decane, trimethylbenzene	Usually oxidized. Low diffusion.
F	Very low	Polycyclic aromatic hydrocarbons	Motor oil, coal tar, benzopyrene	Not good for soil-gas analysis.
G	High	Low molecular weight, oxygenated	Acetone, tetrahydrofuran, MEK*	Diffuse rapidly. Soluble in soil, water.

*MEK = methyl ethyl ketone.

For the electrical properties of these materials, see Kutrubes, 1986 and Akadov, 1980.

Soil-gas/ground-water correlations are usually determined by placing soil-gas probes near existing monitoring wells. Linear regression analysis can then be used to calculate a correlation coefficient for log-log plots of soil-gas vs. ground-water concentrations. Anomalous concentrations are often indicative of contaminant sources or small-scale geologic/hydrologic heterogeneities in the vadose zone.

Another question is "What is the physical state of subsurface contaminants?" Compounds may exist in the subsurface in several physical states including: (1) dissolved in water, (2) dissolved in another organic phase, (3) adsorbed on soil materials, or (4) present only in the gas phase. The physical state is rarely determined directly but can be estimated on the basis of compound properties, disposal practices, and subsurface conditions. The physical state of a compound determines the degree of phase partitioning, if any, which must occur to permit gas-phase analysis of subsurface contaminants.

Low molecular weight hydrocarbons (Group D) have a density less than that of water and will float as a thin film on the water table. The aromatic components of Group D (e.g. benzene, toluene) are moderately water-soluble and therefore occur as dissolved as well as immiscible contaminants. Many compounds in Group G also have densities less than 1.0 gram/mL, but are seldom encountered as floating product due to their high aqueous volubility. All other contaminant groups have densities greater than 1.0 gram/mL and will sink as immiscible liquids in aquifers. Floating hydrocarbon products can act as a solvent for high-density compounds (e.g. halogenated solvents) and retain them near the surface of the water table. In that case, partitioning between gaseous and organic phases becomes more important than the partitioning between gaseous and aqueous phases. Volatilization of VOCs from organic solvents is determined by the volatility of the solvent and the mole fraction of the solute (VOC) in the solvent. For solvents-other than complex hydrocarbon products, the volatility of VOCs from an organic phase can be estimated by Raoult's Law.

VOCs can be introduced directly to the soil-gas phase without contaminating either soil grains or ground water. Underground utility lines often introduce volatile compounds to soil gas from cracks and/or joints in natural gas and sewer lines. C_1 through C_4 aliphatic hydrocarbons (Group D) can be released from natural gas lines while a variety of solvent and fuel vapors can diffuse from sewers carrying industrial wastes.

The next question is "What are the major hydrologic/geologic features of the vadose zone?" This question is best answered by reviewing detailed lithologic logs prepared by a qualified hydrologist or geologist during the installation of monitoring wells or borings in the investigation area. Of primary interest are clay lenses, perched water, buried foundations, and other potential barriers to the vertical diffusion of gaseous contaminants. Subsurface diffusion barriers often result in soil-gas VOC concentrations which are uncharacteristic of the underlying ground water. Chemical concentration gradients are locally disrupted by diffusion barriers because gaseous contaminants are either absent or present at very low concentrations in soil gas overlying the barrier.

The presence of diffusion barriers does not preclude a soil gas investigation as long as the areal extent of barriers are minimal compared to that of the subsurface plume. However, soil-gas sampling is ineffective in a situation where a clean aquifer overlies a contaminated aquifer because contaminants are unable to diffuse through the unconfined aquifer. Mapping of subsurface plumes via soil-gas sampling is usually not affected by a few anomalous points due to the large number of samples which are collected over an investigation site. However, the location of potential diffusion barriers should be identified prior to the interpretive phase of a soil-gas study.

In addition to gas diffusion barriers, the presence of soil moisture and highly permeable zones (e.g. backfill or utility trenches) locally affect soil-gas samples. High moisture levels reduce the air porosity of soils and inhibit both soil-gas collection and gaseous diffusion. As the number of continuous air-filled pores is reduced (due to increasing water saturation), the mass of VOCs in soil gas also decrease. Representative soil-gas samples are rarely obtained from soils with an air porosity below five percent. Conversely, backfill and gravels have high air porosities which often result in anomalously high VOC concentrations relative to the underlying ground water. These coarse materials are more permeable than the undisturbed soil and can provide a conduit for laterally diffusing gaseous contaminants.

The site may be more complex than anticipated so it is worthwhile to ask, “Are there surface or shallow vadose zone contaminant sources overlying the major subsurface plume?” This question refers to localized contamination sources other than the major ground-water plume. Unknown surface or shallow soil contaminant sources can adversely affect the interpretation of regional soil-gas data. Soil-gas probes can intercept laterally diffusing VOCs from a surface source as well as vertically diffusing VOCs from ground water. Thus, contaminant concentrations in” shallow soil gas can be anomalously high relative to concentrations in the underlying water. A radial distance equal to three times the depth to water has been empirically determined at several sites to be the extent of lateral contaminant diffusion surrounding a source. Soil-gas samples collected beyond this distance are normally representative of the underlying ground water.

If surface sources are not identified prior to a soil-gas investigation, they can be located using several techniques. Contaminant sources within the boundaries of a regional plume are indicated by (1) an abrupt increase in soil-gas contamination compared to surrounding points, (2) a change in chemical composition of the soil gas, and (3) a significant deviation from the soil-gas/ground-water concentration ratio calculated for an overall site. The presence of soil contamination can be confirmed by analyzing a vertical profile of soil gas. Vertical soil-gas profiles completed near a surface spill typically show increasing VOC concentrations down to the depth of maximum soil contamination and then decreasing concentrations toward the water table. Contaminated ground water results in increasing VOC concentrations with depth from the ground surface to the water table.

To summarize, the last four questions identify site-specific factors which determine the subsurface behavior of VOCs. In contrast to the first four questions, these questions require a detailed understanding of the investigation site which may not exist until after a remedial investigation has been completed. Both the planning and interpretation of soil-gas studies are enhanced by the number of the site-specific questions which can be answered initially.

There are no absolute limits for VOC concentrations in soil or ground water below which soil-gas sampling is ineffective. The lower limit is a function of (1) compound properties, (2) analytical detection limits, (3) depth and physical states of the compound, (4) soil properties, and (5) interference from degradation processes or secondary contaminant sources. Soil-gas investigations are also commonly performed as screening or initial assessment procedures where few of the site-specific questions can be answered. Soil-gas sampling can be conducted with a minimal amount of background information, however, the results will generally be more difficult to interpret.

DEVELOPING AN INVESTIGATION PLAN

Two additional questions need to be answered when planning an investigation. The first is "What is the major objective of the soil-gas investigation?" Formulating an investigation plan which specifies the spacing and siting of soil-gas probes requires a clear understanding of the objectives. Delineation of plume edges is most efficiently achieved by establishing a transect parallel to the hydraulic gradient and sampling outward from the suspected source. Once an initial boundary point is identified, subsequent sampling locations are selected on the basis of real-time results. By contrast, locating downgradient contaminant sources is best achieved by sampling soil gas on a pre-determined grid covering the investigation site. Locating primary source areas is accomplished by either grid or real-time sampling, depending on the initial information which is available.

The distance between sampling points is a function of the plume resolution required. Soil-gas samples are commonly collected on 303- to 606-meter (1,000- to 2,000-feet) intervals over large geographic areas where the objective is to identify potentially contaminated regions. Such widely spaced probes cannot provide resolution of individual plume characteristics. Plume definition is accomplished by sampling probes on more closely spaced centers, depending on the specific site.

Soil-gas samples generally should not be collected less than approximately 15 meters (50 feet) apart where high resolution mapping is required. Differences in VOC concentrations between closely-spaced points are as likely to result from small-scale heterogeneities in the shallow soil as from significant changes in the parameter of interest (e.g. contaminant levels in the underlying ground water). Locations of soil-gas samples are also determined by the access to sampling areas and the ability to successfully drive probes into the underlying soil. Generally, the minimum spacing of soil-gas probes is proportional to the depth to ground water.

The other question in this section is "What are the general topography and surface conditions at the investigation site?" This final question is designed to provide additional information for the selection of sampling locations. Topography should be considered if variations in land elevation result in significant differences in the depth to water over an investigation site. The thickness of the vadose zone overlying contaminated ground water affects chemical concentration gradients and thus the comparison of VOC concentrations in soil gas. Topography is a more critical factor for shallow aquifers (less than 6 meters below the ground surface) than for deeper ground water. When sampling above contaminated ground water less than 6 meters deep, probes are often driven to a constant height above the water table rather than to a constant depth below the ground surface.

Surface conditions also influence the location of soil-gas samples over an investigation site. Extremely wet surface conditions caused by ponded water should be avoided because of problems associated with low air porosities in soil. Recently disturbed soils (e.g. plowed or graded) often do not yield representative soil-gas results due to the dilution and mixing of soil gas with atmospheric air. If probes can be driven several feet below the disturbed soil, VOC concentrations in soil gas are usually representative of subsurface contamination.

The presence of man-made pavements covering soil may also affect the results of soil-gas sampling. Asphalt or concrete surfaces can act as a barrier to the gaseous diffusion of VOCs and alter the chemical concentration gradient in shallow soil. Two adjacent probes sampled under exposed soil and pavement, respectively, can yield quite different soil-gas concentrations. Generally, VOC concentrations sampled at the same depth are higher under pavement than under bare soil. This difference can affect data interpretation if soil-gas samples are collected under both surfaces at the same site. Pavement materials vary widely in their ability to restrict the diffusion of VOCs.

To summarize, applicability of soil-gas sampling to a specific site should be determined by answering the first eight questions. The answers to the last two questions are designed to provide information which can be used to optimally design a soil-gas investigation. Information required for the investigation plan can be provided by on-site observations and a clear objective for the soil-gas study. In addition, cost and time constraints usually affect the final investigation plan.

SECTION 7

PLANNING A GEOPHYSICAL INVESTIGATION

INTRODUCTION

The purpose of this section is to provide general guidance in the choice of geophysical techniques to detect organic contamination. Most geophysical techniques are useful in site characterization activities and have been developed for that purpose. Some techniques have capabilities which are useful for the detection of inorganic, while other techniques have capabilities which are useful in detecting organic contaminants. Table 9 reviews the characteristics of seven geophysical techniques, highlighting features of each method. It is intended to provide a capsule summary of the primary technical characteristics of each method, including parameter measured, mode of measurement, depth of penetration, resolution, and raw data format.

Table 10 summarizes common applications of the techniques. The categories listed are general: site characterization refers to detecting layers, depths of soil and rock, and depths to the water table; conductive leachate plumes refers to detecting the vertical and horizontal extent of inorganic leachates; metal objects refers to detecting objects such as drums, trash, pipes, and cables; and organic contamination refers to detecting the vertical and horizontal extent of organics floating on the water table, or present in massive quantities in the soil. This table presents generalizations which are applicable in most cases. However, exceptions exist because of the wide range of site conditions and project objectives.

It is important to realize that techniques will be useful at some types of sites, but not at others. This is chiefly due to the geologic conditions present, but also may be due to instrument capabilities or interferences which affect the performance of the techniques. For example, GPR is not effective in clay soils. All electrical methods are affected by nearby metal objects. D.C. resistivity performs best in resistive soil. Magnetics will not detect copper, stainless steel , or aluminum, but is excellent for ferrous iron. Seismic methods are affected by wind and airport noise, truck and train traffic, and working drill rigs. Seismic methods do not perform well in unconsolidated soil. In addition, interpretation of the data from these techniques is an important part of the process. Topographic corrections may be needed to present the data at a standard distance from the water table. By using mathematical models and supplemental field measurements, it may be feasible to remove the effects of buildings or utilities from the data. However, in complicated geological situations, this may not be possible.

TABLE 9. CHARACTERISTICS OF THE SEVEN GEOPHYSICAL METHODS (MODIFIED FROM BENSON ET. AL., 1983)

Method	Responds to Change in	Mode of Measurement	Depth of Penetration	Resolution	Raw Data Format
1. Ground Penetrating Radar (GPR)	Primarily electrical properties, density and fluid content, but also metallic objects.	Continuous profile at 0.4 km/hr. for detailed survey; 0.8 km/hr for reconnaissance survey. Ground contact not necessary.	One to 30 meters typical--highly site specific. Limited by fluids and soils with high electrical conductivity and by clay.	Most detailed of all six geophysical methods.	Picture-like graphic display. Analog or digital tape.
2. Electromagnetics (EM)	Bulk electric conductivity of soil, rock and pore fluids. Pore fluids tend to dominate,	Continuous profiles to 0.5 to 15 meters depth. Station measurements 15 to 60 meters depth. Some sounding capability. Ground contact not necessary.	Depth controlled by system. Coil spacing 0.5 to 60 meters typical.	Excellent lateral resolution. Vertical resolution of 2 layers. Thin layers may not be detected.	Numerical values of conductivity from station measurements. Strip-chart and/or magnetic recorded data yields continuous profiling.
3. D.C. Resistivity	Bulk electrical resistivity of soil, rock and pore fluids. Pore fluids tend to dominate.	Station measurements for profiling or sounding. Must have ground contact.	Depth controlled by electrode spacing.* Limited by space available for array. Instrument power and sensitivity become important at at greater depth.	Good vertical resolution of 3 to 4 layers. Thin layers may not be detected.	Numeric values of voltage current and dimensions of array. Can plot profile or sounding curves from raw data.
4. Complex Resistivity	Chemical reactions in ground.	Same as d.c. resistivity except measured for specific frequency.	Same as above.	Same as above.	Numeric values of impedance and phase at specific frequencies.
5. Seismic Refraction	Seismic velocity of soil or rock which is related to density and elastic properties.	Station measurements. Must have ground contact.	Depth limited by array length and energy source.*	Good vertical resolution of 3 to 4 layers. Seismic velocity must increase with depth. Thin layers may not be detected.	Numeric values of time and distance. Can plot time/distance graph from raw data.
6. Metal Detector	Electrical conductivity of ferrous and non-ferrous metals.	Continuous. Ground contact not necessary.	Single 55 gal. drum up to 3 meters.** Massive piles 55 gal. drums up to 6 meters.	Very good ability to locate targets.	Relative response from audio/visual indicators. May record data.
7. Magnetometer (MAG)	Magnetic susceptibility of ferrous metals	Continuous total field or gradient measurements. Many instruments are limited to station measurements. Ground contact not necessary.	Single 55 gal. drum up to 6 meters.** Massive piles 55 gal. drums up to 20 meters.	Good ability to locate targets.	Non-quantitative response from audio/visual indicators. Quantitative instruments provide meter or digital display. May record data.

*Depth is also related to equipment capability.

**Depth is very dependent upon instrument used

TABLE 10. GENERALIZED APPLICATIONS OF GEOPHYSICAL TECHNIQUES

Technique	Application Site Characterization	Conductive Leachate	Metal Objects	Organic Contamination
Ground Penetrating Radar (GPR)	yes	yes	yes	yes
Electromagnetic (EM)	yes	yes	yes	possibly
D.C. Resistivity	yes	yes	yes	possibly
Complex Resistivity	no	no	no	yes
Seismic Refraction	yes	no	no	no
Metal Detector	no	no	yes	no
Magnetometer	no	no	yes	no

*In some cases, the organic contamination will be associated with inorganic contamination. Examples include organics in metal drums and mixed organic-inorganic leachate plumes.

Note that only two techniques are recommended for routine use in detecting organic contamination. The successful application of these techniques, GPR and complex resistivity, is discussed in more detail below. The d.c. resistivity and EM techniques may be useful at a site for detection of hydrocarbons, but other techniques with greater likelihood of success should be considered first.

GEOPHYSICAL TECHNIQUES AND ISSUES

When selecting geophysical techniques for a site investigation, many questions should be addressed. The following list of questions can help to better define the important decisions to be made for a given site investigation. Many of the questions have answers which apply to more than one technique. Thus , the questions have been organized into a group of questions which is general in nature, and additional groups of questions which are specific to certain techniques. The questions listed have been selected from an EPA-U.S. Geological Survey computerized expert system now in development.

General

Some of the questions in this category are asked in a different manner in the discussion of preliminary information provided in Section 5. Because of their importance and for logical continuity, they are also included here.

- Was the source of contamination a single event, a continuous leak which has been repaired, or a continuing leak?

- Did the contaminants originate from a surface spill, deep injection, a leaking trench, a leaking landfill, a leaking underground storage tank, a leaking underground pipeline, a land treatment facility, a surface impoundment, or are the contaminants different, like an intact, lost barrel of waste?

- Where are the contaminants now? They may be present on the surface, in the unsaturated zone, in the saturated zone, or in all these areas.

- Is this an areal search, a depth search, or both? This will determine whether profiles or soundings are performed.

- What types of contaminants are present? Are there inorganic contaminants present which may serve as indicators of the presence of organic contamination? If so, geophysical methods for locating conductive plumes may be useful.

- Are there natural organics such as from a farm, forest, or swamp present?

- Are the soils at the site preferentially water-wet or organic wet? A soil is not wet by a liquid if the liquid forms beads on the surface of the soil.

- Are the organics mostly in the water phase, adsorbed on soil solids, or in the gas phase?

- Do the organics and inorganic react in any way? Are the organics being modified by degradation, catalysis, or adsorption?

- Are volatile organics present at the surface? If so, soil-gas techniques should be considered.

- What is the environment at the site? Examples are rural, suburban, urban, industrial, landfill, military base, service station.

- How much of the site is covered by buildings? What type of access is possible? Is it difficult to walk around the site, or is it possible to drive over most of the site with a vehicle such as a van? Is any of the site inaccessible due to property ownership, security reasons, safety hazards, or difficulties such as swampy conditions?

Resistivity, EM, GPR, and Magnetic Techniques

- Are there any metallic objects on or near the site? Metallic objects such as fences, pipelines, and electrical or telephone wires above or below ground may interfere with EM, d.c. or complex resistivity, GPR, and magnetometry. These type surveys may not be possible depending on the amount of the site surface which is covered.

below ground may interfere with EM, d.c. or complex resistivity, GPR, and magnetometry. These type surveys may not be possible depending on the amount of the site surface which is covered.

- Are metallic well casings installed at the site? Casings may also affect EM, d.c. or complex resistivity, GPR and magnetometry measurements.
- Are pipelines catholically protected? If possible, the cathodic protection should be turned off during surveys. Cathodic protection does not affect GPR.
- How much of the area is covered by concrete or asphalt? D.C. and complex resistivity techniques require contact with the ground. Rebar present in the concrete may interfere with EM and magnetic measurements.
- What is the range in topographic relief across the site? If it is greater than 1 meter, then electromagnetic, resistivity, and ground-penetrating radar data should have a topographic correction applied.
- Are radio, television, or radar facilities nearby? Measurements may be affected.

GPR and Complex Resistivity

- Is clay present at the site? How much clay is present? Is it present as layers, lenses, evenly mixed with other soil components, or massive? GPR cannot penetrate clay. However, if the clay is present as lenses, the GPR may be useful between the lenses. The techniques of GPR and complex resistivity are complementary in that complex resistivity requires the presence of clay to be successful.
- Is the zone of relevance above the clay? If so, then GPR may be feasible.
- What are the properties of the contaminants? Are they soluble or insoluble in water? Are they miscible, immiscible, or a mixture of both? What is the density of the contaminants? Are they nonpolar, anionic, cationic or a mixture of these? GPR locates organics that phase-separate, i.e., are immiscible or insoluble, and float.
- What is the average electrical resistivity of the site in ohm meters? If the resistivity is greater than 30 ohm meters, and clay is not present, then the site is a candidate for GPR.

Surface geophysical techniques have the ability to provide useful information at hazardous waste sites. Maps of electrical conductivity variation from EM measurements or resistivity soundings can provide three-dimensional boundary locations for hydrogeological and cultural features as well as direct detection of inorganic contaminants. Direct detection of organics using these techniques may be possible in some cases. Complex resistivity and GPR require more time and expense, but can provide more detailed hydrogeological information and sometimes direct detection of organic contamination. GPR has the highest resolution of any geophysical technique, allowing it to "look" through the gaps in urban and high density utility environments. The data may require modelling to remove the effects of buildings. When most of the precipitation is seasonal, GPR data quality can be improved by performing the measurements during the driest time of the year or during the time when soils are frozen. GPR signals cannot penetrate some types of asphalt or closely spaced rebar or chicken wire. GPR is most useful at sites with no clay, on problems with water-insoluble organics above or floating on the water table. Complex resistivity is most useful at sites containing clay, and on problems with water-soluble organics below the water table. It also may provide an effective noninvasive monitor of the performance of clay barriers around waste sites.

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