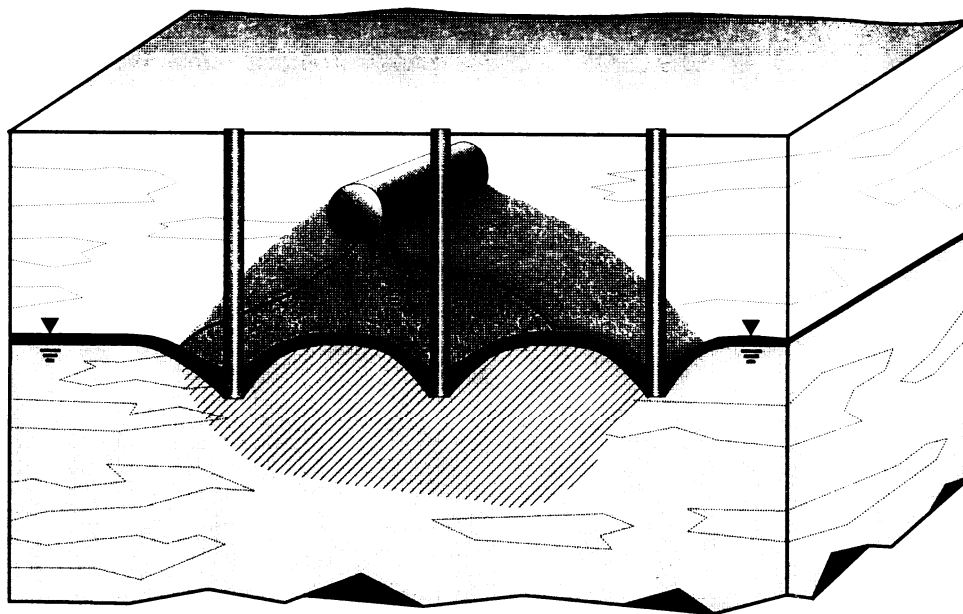




How To Effectively Recover Free Product At Leaking Underground Storage Tank Sites

A Guide For State Regulators



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United States Environmental Protection Agency
Office of Underground Storage Tanks, OSWER
National Risk Management Research Laboratory,
ORD

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CHAPTER I

INTRODUCTION

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INTRODUCTION

Background

Over 315,000 releases from leaking underground storage tanks (USTs) were reported by state and local environmental agencies as of March 1996¹. EPA's Office of Underground Storage Tanks (OUST) anticipates that at least 100,000 additional releases will be confirmed in the next few years as tank owners and operators comply with the December 22, 1998, deadline for upgrading, replacing, or closing substandard USTs. Each release represents a potential threat to human health and the environment; appropriate remedial steps must be taken to assess the risk and minimize the impact. The Federal regulations (40 CFR 280.64) state that at UST sites where investigations indicate the presence of free product, owners and operators must remove free product to the maximum extent practicable as determined by the implementing agency. Typically, the implementing agency is represented by the state environmental agency or local fire prevention office. Where the threat is imminent (*e.g.*, seepage of free product into basements or parking garages) an appropriate response would be immediate emergency action to prevent explosion or fire. Even where the consequences of the release are not immediately hazardous (*e.g.*, contamination of groundwater resources) expeditious recovery of free product will contribute to minimizing the costs and time required for effective corrective action.

The decision-making process for determining the most appropriate corrective action is intended to develop a remedy to mitigate risks. Typically, the remedial approach is described in a corrective action plan (CAP) or other report along with target clean-up levels to be achieved in an appropriate period of time. The corrective action specified in the CAP may include a combination of alternative techniques (*e.g.*, bioremediation, soil vapor extraction [SVE]), traditional remedial methods (*e.g.*, free product recovery, excavation, pump-and-treat), institutional controls (*e.g.*, deed restrictions), and natural attenuation. At most sites where significant volumes of petroleum have reached the water table, free product recovery is the first step of the remedial approach. Because free product recovery may be initiated prior to implementing long-term corrective action using alternative or traditional technologies, this critical step may not be included in a CAP. The written strategy for recovering free product may

¹EPA O.U.S.T. Semi-Annual, FY96 UST Activity Report

be presented in a variety of different formats; this guide will refer to such a document as a free product recovery plan.

Releases of petroleum products may occur above ground (*e.g.*, spills, leaks from exposed piping) or below ground (*e.g.*, leaks from tanks or piping). Recovery of product above the ground is relatively routine, and effective methods for cleaning up these releases from the ground surface, surface water bodies, or sewers and other underground conduits are well established. Recovery of product from below the ground is usually much more difficult, more costly, and less effective. Released product first soaks into the soil, and only if the volume of release is large enough will free product accumulate at the water table. The soil will retain a significant portion of the product, but as this portion is immobile, it does not contribute to that portion termed “free product”.

This manual addresses recovery of free product below the ground surface. A few standard technologies are typically used to recover free product under these conditions. These methods include the following:

- ! Simultaneous withdrawal of vapor (air and vapor phase hydrocarbons) and fluids (groundwater and free product).
- ! Collection of free product using skimming equipment in wells, trenches, or excavations.
- ! Pumping of free product by depressing the water table to enhance migration of free product to a well or drain.

The design of any of the above remedial systems requires an understanding of the site hydrogeological conditions and characteristics, the types, extent, and distribution of free product in the subsurface, and the engineering aspects of the equipment and installations.

Purpose

The purpose of this manual is to provide you—state and local regulators—with guidance that will help you review strategies for recovery of free product from beneath the ground surface. The manual does not advocate the use of one technology over another; rather it focuses on appropriate technology use, taking into consideration site-specific conditions.

The manual is designed to enable you to answer the following three basic questions when reviewing a free product recovery plan.

- ! Is recovery of the free product necessary?
- ! Has an appropriate method been proposed for recovering the free product?
- ! Does the free product recovery plan provide a technically sound approach to remediating the site?

Scope And Limitations

This manual is intended to provide technical guidance to state and local regulators who oversee cleanups and evaluate free product recovery plans at petroleum release sites. It does not represent the issuance of formal policy or in any way affect the interpretation of the regulations.

The text focuses on scientific and engineering-related considerations for evaluating various technologies for the recovery of free product from the subsurface. It does not provide instruction on the design and construction of remedial systems and should not be used for designing free product recovery plans. In addition, this manual should not be used to provide guidance on regulatory issues, such as securing permits and establishing cleanup standards, health and safety issues, state-specific requirements, or cleanup costs.

This document is not intended to be used as the sole reference for review of free product recovery plans. Rather, it is intended to be used along with published general references (*e.g.*, EPA, 1995; Newell *et al.*, 1995; API, 1989, 1996; and ASTM, 1995), guidance from technical experts, information from training courses, and current journals.

The material presented is based on available technical data and information and the knowledge and experience of the authors and peer reviewers.

How to Use This Manual

EPA's OUST encourages you to use this manual at your desk as you review free product recovery plans. We have designed the manual so that you can tailor it to meet your state's or your own needs. The three-ring binder allows you to insert additional material (*e.g.*, state-specific guidance on permitting and technology relevant to free product recovery) and remove certain tools (*e.g.*, flow charts, checklists) for photocopying.

The wide margins in this manual were provided to enable you to add your own notes to the text.

The manual contains the following four chapters that address the major considerations necessary for reviewing plans for recovering free product.

- | | |
|-------------|--|
| Chapter II | <i>The Corrective Action Process</i> is an overview of free product recovery actions. This chapter contains information that is used in determining the complete remedial action or interim action, the remedial objectives, and the technology evaluation process. |
| Chapter III | <i>Behavior of Hydrocarbons in the Subsurface</i> is an overview of important properties of hydrocarbons and geologic media that must be considered when designing a free product recovery system. |
| Chapter IV | <i>Methods for Evaluating Recoverability of Subsurface Hydrocarbons</i> . This chapter contains discussions of the methods used both to characterize the extent of free product at a site as well as to estimate the volume of free product at the water table and the rates at which it can be recovered. |
| Chapter V | <i>Hydrocarbon Recovery Systems/Equipment</i> . This chapter contains descriptions of alternative recovery technologies and it addresses applicability, system design, and monitoring requirements. |

As appropriate, the discussion in each chapter has illustrations, comparative tables, example calculations, flow charts, and a list of selected key references. An appendix, a glossary of relevant terms, and a comprehensive list of references appear at the end of the manual.

At the back of the manual, a step-by-step checklist is provided to facilitate your review of a proposed free product recovery system. This checklist can help you determine whether or not the free product recovery plan contains the necessary supporting information to approve the free product recovery system. The checklist is also designed to verify that an appropriate technology and design have been selected for free product recovery.

CHAPTER II

THE CORRECTIVE ACTION PROCESS

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THE CORRECTIVE ACTION PROCESS

Releases from underground storage tanks and piping caused by leaks, spills, or overfills may result in a subsurface accumulation of a separate phase liquid (“free product” or “free phase”) that will flow into wells or excavations. Other terms that are sometimes used to refer to free product include; phase separated hydrocarbons (PSH), liquid hydrocarbons (LHC), liquid phase hydrocarbons (LPH), and nonaqueous phase liquids (NAPL). These alternative terms also refer to separate phase liquids in the subsurface that are not present in an amount sufficient for them to flow readily into wells or excavations. In this situation, the petroleum hydrocarbons represent a separate residual phase, but not a “free product” phase.

Confirmation of a release from an underground storage tank (UST) and/or its associated piping initiates the corrective action process. At sites where free product is present in the subsurface, free product recovery will be part of most corrective actions, although it may precede development of a formal corrective action plan (CAP). Before addressing the corrective action process, a brief overview of hydrocarbon releases to the subsurface is presented.

Hydrocarbon Releases To The Subsurface

The release of hydrocarbons from an UST can occur under a wide range of operational conditions and environmental settings. The extent of any threat to human health and the environment will depend on these release-specific conditions. Factors that significantly determine the level of risk include the following:

- ! Type of petroleum hydrocarbon(s) and the contaminants of concern.
- ! Volume and age of the release.
- ! Contaminant migration pathways (*e.g.*, utility trenches, sewers, drinking water supplies) to reach receptors.

- ! Proximity of receptors to the site of the release. Receptors include human and animal populations, as well as environmental receptors (*e.g.*, groundwater resources, surface waters, buildings, residences).
- ! Receptor exposure pathways (*e.g.*, ingestion of water or soil, inhalation of vapors).

The hydrocarbons associated with UST releases are usually fuels, oils, or lubricants and almost all are less dense than water, therefore they float on top of the water table. Liquid phase hydrocarbons (residual and free) that are less dense than water are also referred to by the acronym LNAPL (light nonaqueous phase liquids). A nonaqueous phase liquid that is more dense than water is called DNAPL (dense nonaqueous phase liquid). DNAPLs sink throughout the saturated zone to accumulate at the bottom of the aquifer where their movement is dictated by gravity and the topography of the subsurface geologic layers. Solvents such as trichloroethylene and other chlorinated hydrocarbons are DNAPLs. Some of the non-hydrocarbon fuel additives (*e.g.*, MTBE, ethanol) are extremely soluble and dissolve into, and can be transported over long distances by, flowing groundwater.

The volume and the age of the release are the factors that largely control the potential extent of contamination in the subsurface. Small volumes of hydrocarbons or releases detected soon after release tend to be located near the source and can be remediated by direct removal. Large volumes or older releases may lead to more extensive subsurface contamination. The extent of contamination is also controlled by the potential pathways of migration. For example, free product or dissolved hydrocarbons may move rapidly through coarse-grained subsurface materials or in utility beddings. If the contamination extends to points where groundwater is used or discharged to surface water, then the risk of potential exposure is present. The hydrocarbon vapors can pose an explosive risk or health risk where high vapor concentrations migrate to residences, buildings, or accessible subsurface utilities.

Hydrocarbons released to the subsurface partition into one or more of four phases:

- ! Vapor - Gaseous state; occurs primarily in the unsaturated zone.
- ! Residual - Adsorbed to soil particles and trapped within soil pores; occurs above or below the water table.

- ! Aqueous - Dissolved in groundwater and soil moisture.
- ! Liquid - Free product; held up by buoyancy at the water table and capillary fringe, or perched above low permeability lenses in the unsaturated zone.

If a sufficient volume of petroleum hydrocarbons is released into the subsurface, then all four phases are generally present. As each of these phases behaves differently, remediation will typically require a combination of corrective action technologies. Recovery of free product is an especially important aspect of site remediation because improper recovery techniques can cause reduced effectiveness and transfer significant portions of the contaminant mass into other phases.

Vapor phase hydrocarbons are found mixed with air and water vapor in the unsaturated zone. This phase tends to be the most mobile phase and can present an immediate threat from explosion or asphyxiation when the vapors migrate into confined spaces such as basements and sewers. Because of the mobility of hydrocarbon vapors, this phase can be effectively remediated using vacuum-air flow technologies. At any given time, the amount of vapor phase hydrocarbons at a site is typically a very small percentage of the total mass present.

Residual phase hydrocarbons typically do not extend great lateral distances from the source of the release, and they tend to be relatively non-mobile. Residual hydrocarbons can persist in the environment, and leaching of the more soluble components can continue to provide a source of groundwater contaminants for a long period of time. As a result of fluctuations in water table elevations, residual phase hydrocarbons can occur either above or below the water table. This effect, known as “smearing”, can result in the immobilization of significant quantities of previously mobile free product. Above the water table, this phase often can be effectively remediated in situ by promoting volatilization and stimulation of natural biological processes. Residual hydrocarbons can occupy more than 50 percent of the total pore space in subgranular sediments. Generally, greater amounts of residual phase hydrocarbons are retained below the water table than above the water table.

Aqueous or dissolved phase hydrocarbons are found in soil moisture above the capillary fringe, in groundwater in the capillary fringe, and below the water table. Despite the relative insolubility of many constituents of hydrocarbon fuels, some constituents (*e.g.*, MTBE) are extremely soluble and can migrate dissolved in groundwater a significant distance from a site. Although dissolved hydrocarbons typically account for a very small percentage of the total mass of hydrocarbons released,

they represent the largest volume of contamination and are spread over the largest area. They also represent the most probable pathway for human and environmental exposure.

Liquid phase hydrocarbons (free product or free phase) are characterized by having sufficient volume to saturate the geologic media such that the liquid hydrocarbons accumulate on the water table and readily flow into wells or excavations. Because it is the sufficiency of volume and not physical or chemical differences that differentiate between the liquid phase and residual phase, these two phases are often referred to as a single phase (*e.g.*, LNAPL). Both free phase and residual phase hydrocarbons can contribute to the contaminant mass in the vapor (gas) phase through evaporation and the aqueous phase through dissolution. Sorption onto soil particles contributes the residual phase. The liquid phase hydrocarbons may also constitute a threat to health and safety.

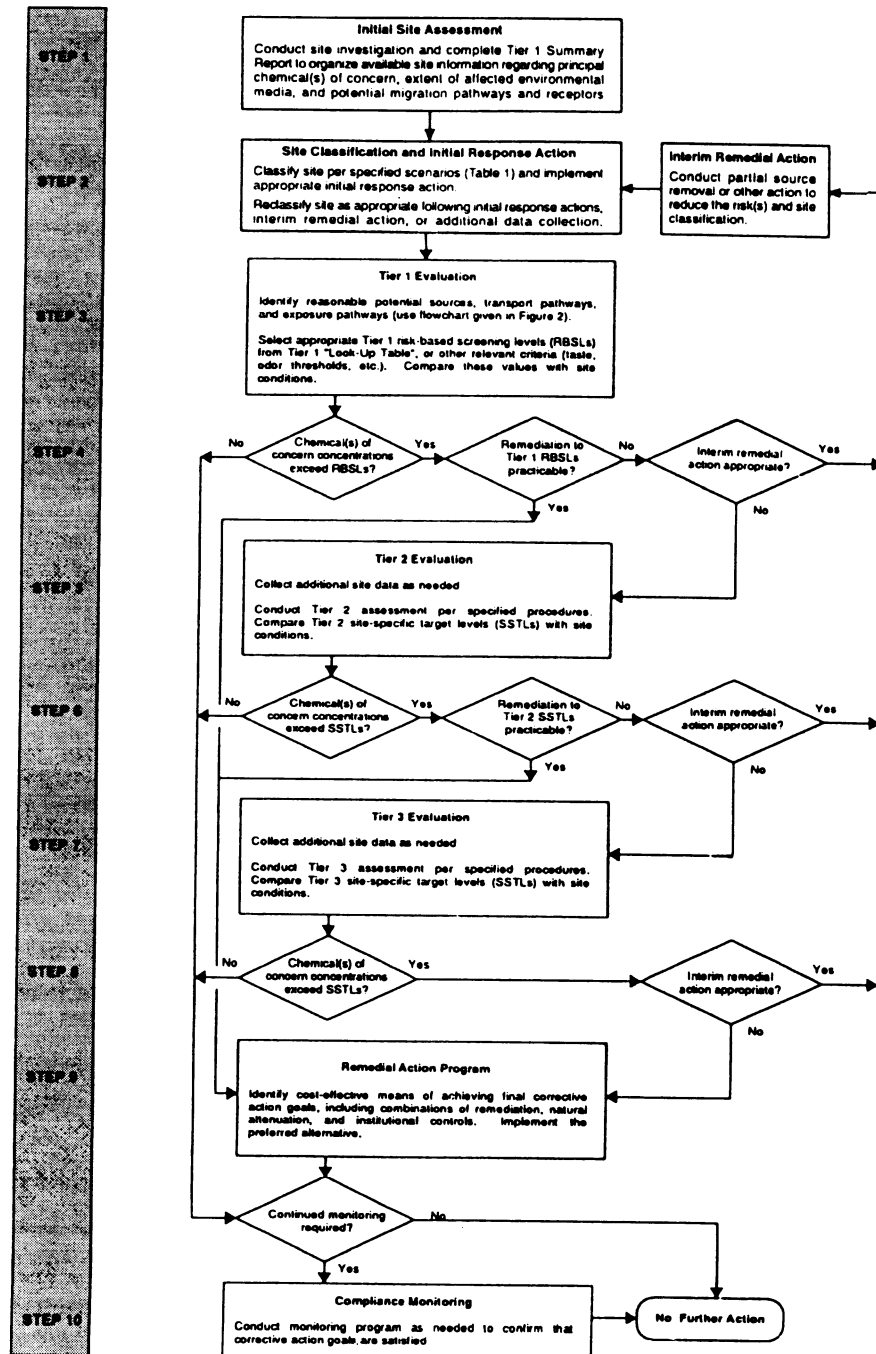
Risk-Based Corrective Action

Confirmation of a release from an UST initiates the corrective action process. The objective of the corrective action process is to assess site conditions and to implement a cost-effective response to protect human health and the environment. Traditional approaches have applied uniform procedures and standards to sites where the subsurface contamination varies greatly in terms of complexity, physical and chemical characteristics, and potential risk. Alternatively, and often more cost effectively, the procedures and remedial objectives can be developed based on a site-specific analysis of risk.

U.S. EPA encourages the use of risk-based decision-making in UST corrective action programs (EPA, 1995; OSWER Directive 9610.17). The American Society for Testing and Materials (ASTM) has issued a “Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites” (ASTM, 1995). The ASTM risk-based corrective action (RBCA; pronounced “Rebecca”) process provides a framework for a consistent decision-making process for the assessment and response to a petroleum release. States generally modify this approach so it is tailored to their individual state needs. The RBCA process uses a tiered approach where corrective action activities are tailored to site-specific conditions and risks. Fundamental to the proper application of this approach is an adequate site assessment. The entire procedure is comprised of ten steps (Exhibit II-1). Free product recovery is typically conducted during steps 2 and 9. Consequently, state and local regulators may need to review free

Exhibit II-1

ASTM Risk-Based Corrective Action (RBCA) Process Flowchart



Source:

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product recovery systems not only as specified in the Corrective Action Plan (CAP) but also in interim actions that may involve free product recovery. States that are adapting the ASTM standard or developing state-specific risk-based procedures need to determine how to review free product recovery plans so that the steps (of the plan) are well integrated into the rest of their program. For more information, please refer to the ASTM standard E 1739-95.

Steps In Reviewing Free Product Recovery Plans

Following are the steps that the state regulator should take when reviewing free product plans (see Exhibit II-2):

- ! Determine if site data are sufficient to evaluate the need for free product recovery and/or recovery design.
- ! Determine if proposed free product approach is consistent with comprehensive CAP and if remedial action objectives are clear.
- ! Determine if active free product recovery is necessary.
- ! Evaluate design of the free product recovery system.
- ! Evaluate operations and monitoring plan.

A checklist based on these steps is presented at the end of the manual.

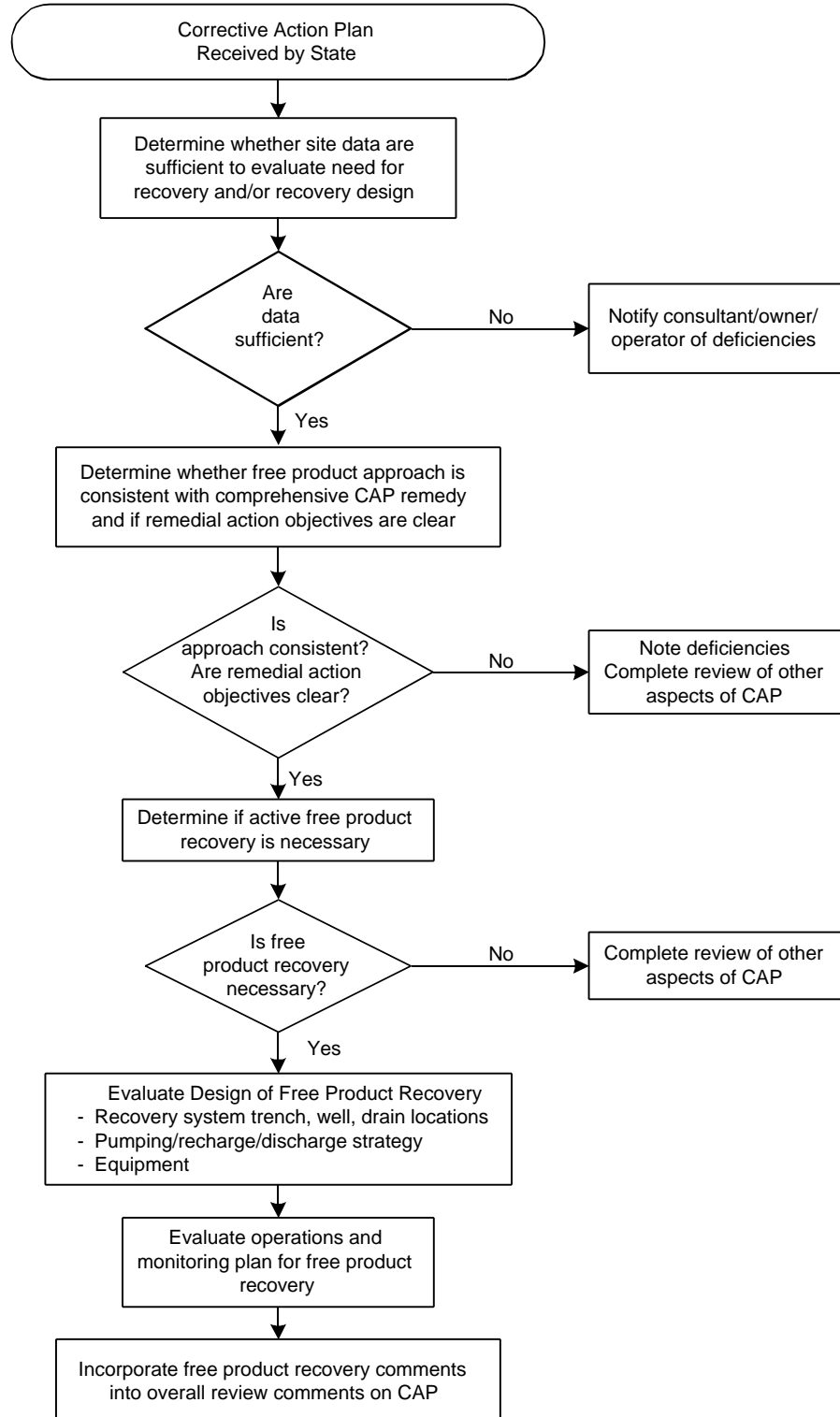
Step 1. Review Data Adequacy

The site information and data that are contained in the free product recovery plan or CAP must provide an adequate basis for making decisions regarding the corrective action. Information required for a CAP is generally more extensive than that required for a free product recovery plan. The need to implement a free product recovery system is typically determined on the basis of site data that indicate that free product is present and recoverable. For a CAP, the need and type of corrective action are based on an evaluation of risks to human health and the environment. The CAP must also consider hydrocarbons present in the vapor phase or dissolved in the liquid phase.

The technical data necessary to evaluate a free product recovery plan include:

Exhibit II-2

Major Steps in Reviewing Free Product Recovery Plans



- ! Description of site.
- ! Description of current and past operations relevant to USTs and piping.
- ! Information on past releases or spills.
- ! Summary of current and completed corrective actions and investigations.
- ! Description of regional and site hydrogeological conditions.
- ! Discussion of hydrocarbon phase distribution in the subsurface.
- ! Listing of the physical and chemical properties of liquid hydrocarbon phase.
- ! Estimates of free product extent (maps and cross sections), free product volumes, and recoverability.

The significance of this information and methods for obtaining it are discussed in Chapters IV and V.

Step 2. Evaluate Remedial Objectives Of The Site

A free product recovery system is often a small part of a comprehensive remedy that also addresses contamination dissolved in groundwater and/or vapors in the unsaturated zone. The remedies proposed for each medium must be compatible. For example, the pumping and treating of contaminated groundwater may result in large drawdowns of the water table. If large drawdowns occur in the vicinity of the free product, then the free product may be drawn to a lower depth where it may become immobilized (*i.e.*, the “smearing” effect) and contaminate previously clean aquifer materials. An example of compatible remedies is the combination of a soil vapor extraction system and free product recovery in moderately permeable soils. Operation of the soil vapor extraction system may actually enhance the effectiveness of a free product recovery system by helping to maintain a higher saturated thickness in the aquifer than would occur with free product recovery only.

Remedial objectives should be clear, achievable, and measurable. A remedial objective of removing all free product may be clear but not necessarily achievable. Many free product recovery systems have the capability to reduce the free product thickness to 0.01 foot or less, however, they may not be cost effective to implement at a site with accumulations on the order of 0.1 foot or less. Minimal amounts of free

product will exist no matter how effective the free product recovery system. Therefore, the remedial objective should also include success measures such as maximum thickness of free product in wells (*e.g.*, less than 0.01 foot or reduction to no more than a sheen) or minimum recovery rates (*e.g.*, 2 gallons per month).

Step 3. Evaluate Need For Active Free Product Recovery

Active free product recovery may not be necessary (or feasible) unless free product is present in sufficient volumes which can be recovered effectively. The necessity for free product recovery should be determined based on an analysis of the feasibility of collecting significant amounts of free product. Feasibility depends not only on site conditions, but also on the chosen technology. For example, although free product is difficult to collect in fine-grained materials, the use of vacuum-enhanced recovery may increase the volume of free product that can be collected.

Factors which would suggest a need for free product recovery include:

- ! Estimates of free product at water table that are moderate to high (greater than 200 gallons).
- ! Permeable aquifer (*e.g.*, sands and gravels) or hydraulic conductivity greater than 10^{-3} cm/sec.
- ! Thick accumulations of free product in wells (greater than 1.0 foot).
- ! Nearby surface water or groundwater use (*i.e.*, close proximity to receptors).

Free product recovery is generally infeasible or otherwise unnecessary at sites where the following factors apply:

- ! Low volumes of free product (less than 50 gallons) at the water table.
- ! Distant (greater than 2,500 feet from free product plume) surface water discharge points and no nearby groundwater use.
- ! Very low permeability media (*e.g.*, silty clay and clay).

- ! Thin accumulations of free product in wells (less than 0.1 foot).
- ! Inclusion in the CAP of other remedial alternatives such as soil vapor extraction or pump-and-treat.

The need (or lack of need) for a free product recovery system may not be clear at all sites (*e.g.*, those with free product volume or free product thickness that fall between the above guidelines). However, as a general rule, where two or more favorable factors (with respect to free product recovery) apply to a given site, the need for free product recovery is indicated; conversely, where three or more unfavorable factors apply, free product recovery is generally not indicated.

Step 4. Evaluate Design Of Free Product Recovery System

It is also necessary to verify that the design of the free product recovery system is likely to be effective. The major design considerations include:

- ! Use of wells or trenches.
- ! Number and location of wells and or trenches.
- ! Fluid production rates, vacuum pressures, fluid elevations to be maintained in wells or trenches.
- ! Design of wells or trenches in terms of construction specifications and depth.
- ! Pumping, skimming, or vacuum equipment.
- ! Pipelines and manifolds.
- ! Instrumentation.
- ! Storage, separation, and treatment facilities (not covered in this guidance).

The rationale for the selection of the recovery approach (skimming, water level depression and collection, or dual phase extraction) should be checked for consistency with remedial objectives. For example, depressing the water table is used when one of the remedial objectives for free product recovery is to contain the free product plume.

The free product recovery plan may include the results of a capture analysis or computer modeling analysis to support the design of the network of wells or trenches and associated pumping rates, fluid elevations and/or vacuum pressures. Simple checks for small systems are suggested in Chapter IV. For complex sites with large volumes of free product, or where sophisticated models have been used in the free product recovery plan, the reviewer should probably seek guidance from an environmental professional with experience in computer modeling.

Step 5. Evaluate Operation, Maintenance, And Monitoring Approach

The free product recovery plan should include an Operation and Maintenance (O&M) plan that describes equipment operation and maintenance and monitoring activities at the site.

Monitoring parameters typically include:

- ! Fluid production rates at wells or drains (both free product and groundwater).
- ! Oil thickness in wells.
- ! Groundwater elevations in wells.

For dual phase recovery systems, vacuum pressures and air flow extraction rates at wells or on the manifold need to be monitored. The O&M plan should specify monitoring points and frequency for each monitoring parameter. The O&M plan should also describe monitoring activities to be continued once the free product recovery system has achieved its remedial objective(s) and associated criteria. The details of an O&M plan depend on site conditions and the free product recovery technology selected (see Chapter V for further discussion).

Primary References

ASTM, 1995. *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*, E 1739-95, Annual Book of ASTM Standards, Philadelphia, Pennsylvania.

EPA, 1995. OSWER Directive 9610.17: Use of Risk-Based Decision-Making in UST Corrective Action Programs, Office of Underground Storage Tanks.

CHAPTER III

BEHAVIOR OF HYDROCARBONS IN THE SUBSURFACE

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BEHAVIOR OF HYDROCARBONS IN THE SUBSURFACE

The purpose of this chapter is to supplement your knowledge of hydrocarbon behavior in the subsurface. This basic information lays the foundation for the principles and concepts used in the design of effective and efficient free product recovery systems.

The fate-and-transport of liquid petroleum products in the subsurface is determined primarily by the properties of the liquid and the characteristics of the geologic media into which the product has been released. Important liquid properties include density, viscosity and interfacial tension. Soil properties that influence the movement of petroleum hydrocarbons include porosity and permeability. Other additional properties, which are functions of both the liquid and the media, include capillary pressure, relative permeability, wettability, saturation, and residual saturation. Site-specific physical conditions (*e.g.*, depth to groundwater, volume of the release, direction of groundwater flow) also contribute to the migration and dispersion of released petroleum products. This chapter contains discussions of each of these factors. To put the following discussion in the context of the types of petroleum hydrocarbons commonly found at UST sites, we begin with a brief description of the classification and composition of hydrocarbons.

Classification And Composition Of Hydrocarbons

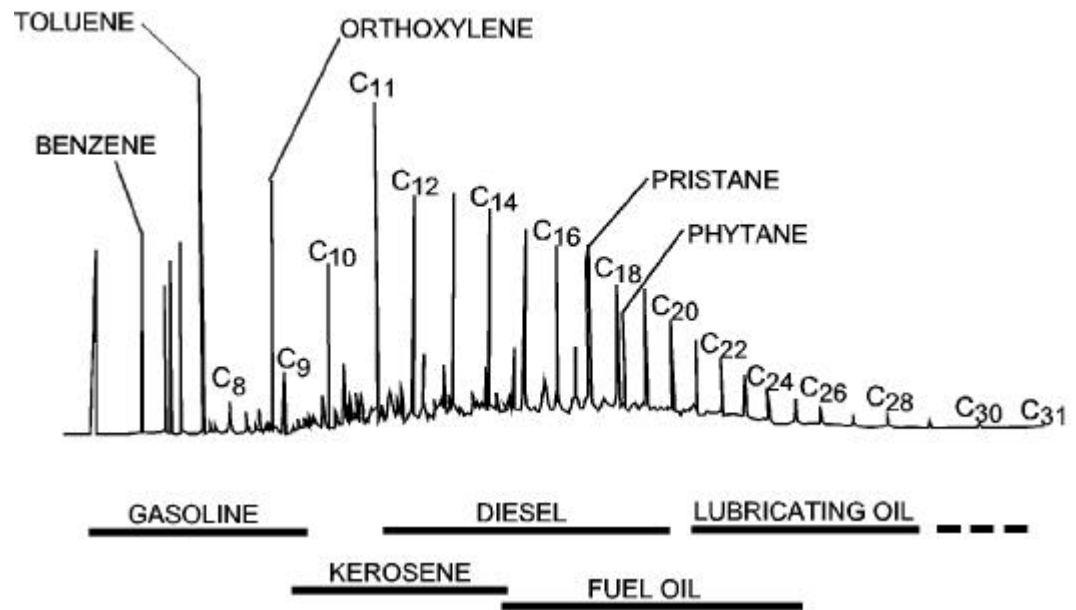
Petroleum hydrocarbons are derived from crude oil, which is refined into various petroleum products by several processes. Like the parent crude oil, refined petroleum products are also mixtures of as many as several hundred compounds. The bulk products may be classified on the basis of composition and physical properties. Products typically stored in USTs include the following main groups:

- ! Gasolines
- ! Middle Distillates
- ! Heavy Fuel Oils

Exhibit III-1 presents a gas chromatogram of a hydrocarbon sample with the approximate ranges in which the various constituents fall. Compounds outside the normal ranges depicted are commonly found as contaminants

Exhibit III-1

Gas Chromatogram Showing Approximate Ranges
For Individual Hydrocarbon Products



Source: Adapted from Senn and Johnson, 1985.

in other products. For example, diesel fuel may contain minor amounts of benzene and other light hydrocarbons.

Gasolines

Gasolines are mixtures of petroleum hydrocarbons and other non-hydrocarbon chemical additives, such as alcohols (*e.g.*, ethanol) and ethers (*e.g.*, methyl tertiary-butyl ether, or MTBE). Gasolines are more mobile than either the middle distillates or the fuel oils. The higher mobility of gasoline is primarily due to the fact that its components tend to have lower molecular weights; hydrocarbon compounds usually found in gasoline have between 4 and 10 carbon atoms per molecule. The lower molecular weight results in lower viscosity, higher volatility, and moderate water solubility. Fresh gasolines contain high percentages of aromatic hydrocarbons (*i.e.*, those with a 6-carbon benzene ring), which are among the most soluble and toxic hydrocarbon compounds. The most frequently encountered aromatic compounds are benzene, toluene, ethylbenzene, and xylene (BTEX). Because of their relatively high volatility, solubility, and biodegradability, BTEX compounds are usually among the first to be depleted from free product plumes. At sites of older gasoline releases, the free product plume may contain relatively little BTEX, being instead enriched in heavier, less soluble, and less readily biodegradable components. As a consequence, the product will be more viscous, slightly more dense, less volatile, and less mobile than fresh product. The non-hydrocarbon additives (*e.g.*, ethanol, MTBE) are readily soluble and preferentially dissolve into groundwater, which diminishes their concentration in the free product, but results in formation of longer dissolved plumes. MTBE also moves away from the source faster than free product and because it is relatively non-degradable, it is difficult to remediate. Discussion of methods to remediate dissolved plumes are beyond the scope of this manual.

Middle Distillates

Middle distillates (*e.g.*, diesel fuel, kerosene, jet fuel, lighter fuel oils) may contain 500 individual compounds, but these tend to be more dense, much less volatile, less water soluble, and less mobile than the compounds found in gasolines. The major individual components included in this category of hydrocarbons contain between 9 and 20 carbon atoms each. Lighter aromatics, such as BTEX, are generally found only as trace impurities in middle distillates, and if initially present, they are generally not present in plumes at older release sites, because they have biodegraded, evaporated, and dissolved into groundwater.

Heavy Fuel Oils

Heavy fuel oils and lubricants are similar in both composition and characteristics to the middle distillates. These types of fuels are relatively viscous and insoluble in groundwater and are, therefore, fairly immobile in the subsurface. Most of the compounds found in heavy fuel oils have more than 14 carbon atoms; some have as many as 30. Like the older releases of middle distillates and gasolines, the lighter end components are present only in trace amounts as they are more readily biodegraded and dispersed.

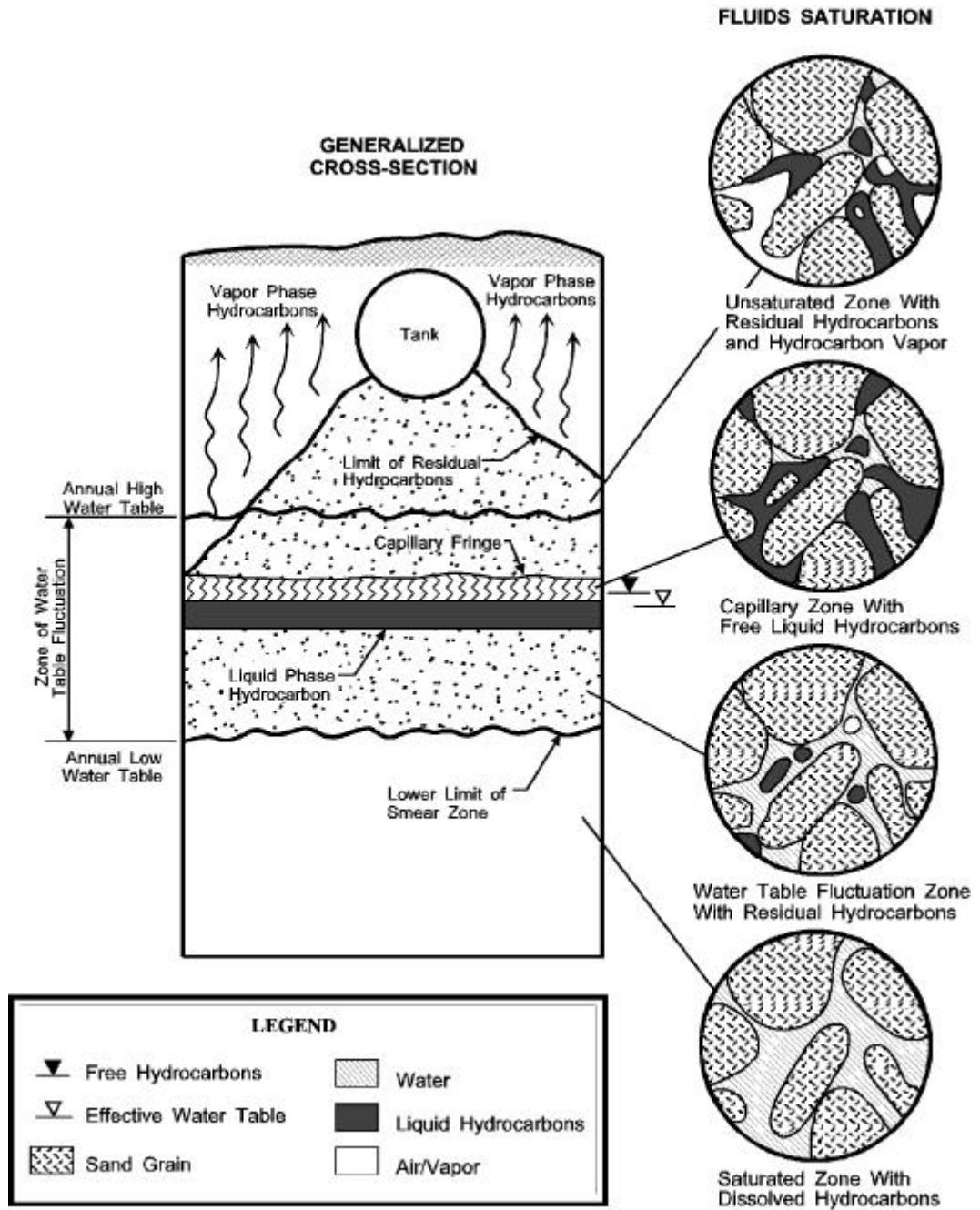
Phase Distribution In The Subsurface

The petroleum hydrocarbon constituents that comprise free product may partition into four phases in the subsurface—vapor (in soil gas), residual (adsorbed onto soil particles including organic matter), aqueous (dissolved in water), and free or separate (liquid hydrocarbons). Exhibit III-2 illustrates the distribution of the hydrocarbon phases in the subsurface from a leaking UST. The partitioning between phases is determined by dissolution, volatilization, and sorption.

When released into the subsurface environment, liquid hydrocarbons tend to move downward under the influence of gravity and capillary forces. The effect of gravity is more pronounced on liquids with higher density. The effect of capillary forces is similar to water being drawn into a dry sponge. As the source continues to release petroleum liquids, the underlying soil becomes more saturated and the leading edge of the liquid migrates deeper leaving a residual level of immobile hydrocarbons in the soil behind and above the advancing front. If the volume of petroleum hydrocarbons released into the subsurface is small relative to the retention capacity of the soil, then the hydrocarbons will tend to sorb onto soil particles and essentially the entire mass will be immobilized. For petroleum hydrocarbons to accumulate as free product on the water table, the volume of the release must be sufficient to overcome the retention capacity of the soil between the point of release and the water table. Without sufficient accumulation of free product at the water table, there is no need for a free product recovery system. However, in either case, there may be a need for appropriate remedial action to mitigate the residual (sorbed) phase so that it does not continue to act as a lingering source of soluble groundwater contaminants or volatile, and potentially explosive, vapor contaminants. Exhibit III-3 illustrates the progression of a petroleum product release from a leaking UST. Frame A shows the hydrocarbon mass before it reaches the capillary fringe. If the release were to be stopped at this point, there would

Exhibit III-2

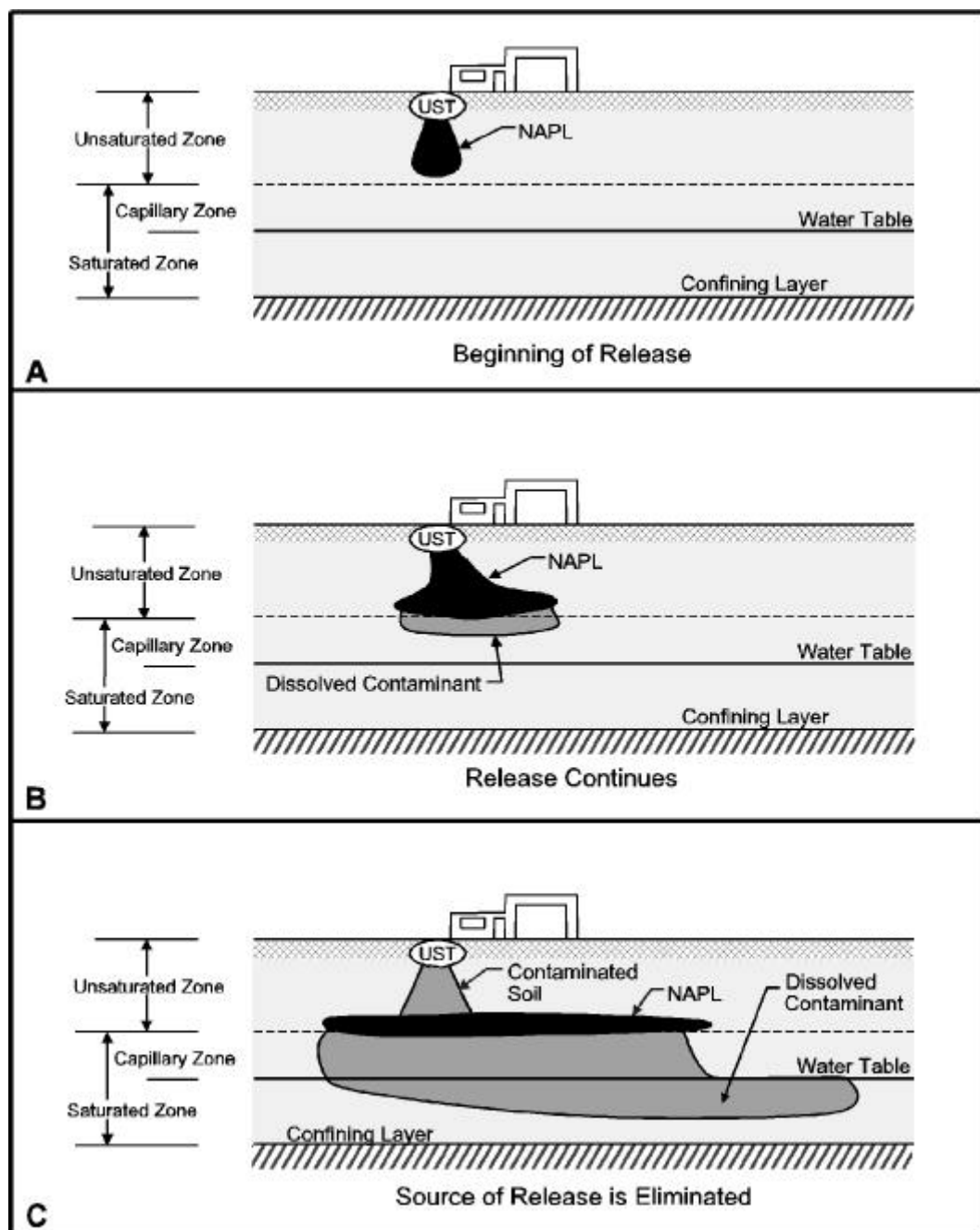
Vertical Distribution Of Hydrocarbon Phases



Source: Modified from Lundy and Gogel, 1988.

Exhibit III-3

Progression Of A Typical Petroleum Product Release From An Underground Storage Tank



Source: EPA, 1990

probably be no accumulation of free product. In Frame B, the release has continued and the volume of the release is sufficient for free product to begin accumulating on, and displacing, the capillary fringe. The free product is beginning to displace the capillary fringe and some of the soluble constituents are dissolving into the groundwater. The source of release has been stopped in Frame C. Residual hydrocarbons remain in the soil beneath the UST. The free product plume has spread laterally, and a plume of dissolved contaminants is migrating downgradient.

Portions of the hydrocarbon mass from both the residual and free phases will volatilize (evaporate) and solubilize (dissolve) to become components of the soil vapor and groundwater, respectively. Volatilization and solubilization of the lighter fractions tend to make the remaining hydrocarbon mass more dense and even less mobile. Hydrocarbons that are in the vapor phase are much more mobile and can migrate relatively great distances along preferential flow paths such as fractures, joints, sand layers, and utility line conduits. Accumulation of vapors in enclosed structures (*e.g.*, basements, sewers) potentially can cause fires or explosions. The more soluble components of the hydrocarbon mass will dissolve into groundwater, both above and below the water table. The dissolved hydrocarbons move with the flowing groundwater and can contaminate drinking water supplies. Also, if groundwater is recovered as a result of pumping or skimming, it may require treatment or disposal if the concentration of dissolved hydrocarbons is higher than the applicable groundwater or drinking water standard. Vapors may be released from the groundwater or be drawn directly from the subsurface if vacuum-enhanced free product recovery systems are employed. These vapors may require treatment to mitigate fire or explosion potential and to comply with air quality criteria.

Exhibit III-4 presents estimates of phase distribution from a gasoline release into the subsurface consisting of medium sand. Most of the amount spilled (64 percent) remains in the free phase; however, the volume contaminated by residual phase and dissolved phase hydrocarbons represents nearly 99 percent of the total contaminated volume. Perhaps the most important point to note is that a very small quantity of petroleum hydrocarbons (1 to 5 percent of the original release volume) can contaminate a significant amount of groundwater (79 percent of the total contaminated volume). Hence, recovery of as much free product as possible is important, but only a portion (up to 50 percent) of the free phase hydrocarbon is actually recoverable with the balance remaining in the residual phase acting as a continuous source of groundwater contamination. Where a water supply is threatened by a release, recovery of free product may be only the first step. An adequate remedial action may require aggressive remediation of the residual phase as well.

Exhibit III-4

Phase Distribution At A 30,000-Gallon Gasoline Spill Site In An Aquifer Of Medium Sand

Phase	Contaminant Volume (gal)	% of Total	Contaminated Volume (yd ³)	% of Total
Free Phase	18,500	64	7,100	1
Residual Phase	10,000	35	250,000	20
Dissolved (Water)	333	1	960,000	79

Source: Modified from Wilson and Brown, 1989.

Properties Of Geologic Media

The extent and rate of petroleum hydrocarbon migration depends in part on the properties of the subsurface medium in which it is released. The subsurface medium may be naturally occurring geologic materials (*e.g.*, sedimentary, metamorphic, or igneous rock or sediments) or artificial fill that has been imported to the site by human activity. In order to design effective and efficient free product recovery systems, you need to characterize both the type and the distribution of geologic media (or fill material) so that you can determine the likely migration routes and travel times.

In the context of fluid flow in the subsurface, geologic media can be classified on the basis of the dominant characteristics of pore space, fractures, or channels through which fluids move. In porous media, fluids move through the interconnected voids between solid grains of soil. Fractured media are those in which fluids migrate readily through fractures rather than the adjacent soil or rock matrix. Fracturing is usually associated with consolidated materials, but it can also occur in unconsolidated clays due to desiccation. Karst media are those in which fluids flow through solution features and channels (*e.g.*, caves associated with carbonate rocks such as limestone).

Porosity and permeability are the two most important media-specific properties of a natural geologic material. Porosity characterizes the ability of media to store fluids, and permeability characterizes the ability of the media to transport fluids. Exhibit III-5 summarizes the

EXHIBIT III-5

Functional Characteristics Of Geologic Media Properties

Property	Significance
Porosity	Porosity is required for calculation of the amount of free product and immobile (residual) product. The relevant parameter for determining recoverable free product is the “drainable” or “effective” porosity, which is always less than total porosity.
Permeability	Permeability controls the rates of groundwater flow and free product migration. It is also used to calculate pumping rates required for hydraulic control.
Anisotropy	Anisotropy is a condition of the geologic media in which measurement of a property (e.g., hydraulic conductivity) depends upon the direction of measurement. Anisotropy can cause groundwater flow to not be in the same direction as the hydraulic gradient.
Heterogeneity	Heterogeneous media often provides preferential pathways for fluid migration—these pathways are difficult to locate and to characterize.

significance of geologic properties and their relevance to free product recovery.

Porosity

Porosity, or more specifically effective (“drainable”) porosity, is an important factor to be considered in the evaluation of a free product recovery system. Calculation of the amount of free and immobile product in the subsurface requires a value or estimate of effective porosity.

Porosity defines the storage capacity of a subsurface media. All rocks and unconsolidated media contain pore spaces. The percentage of the total volume of an unconsolidated material or rock that consists of pores is called porosity. Porosity is classified as either primary or secondary. Primary porosity, which is created when sediments are deposited (or crystalline rocks are formed), depends on the shape, sorting, and packing of grains. Primary porosity is greatest when grains are nearly equal in size (i.e., are well graded or sorted) and nonspherical in shape. Unconsolidated sediments that contain a wide range of grain sizes (*i.e.*, are

poorly graded or sorted) tend to have a low primary porosity because smaller grains fill the pore spaces between the larger grains.

Secondary porosity develops after rocks have been formed or sediments deposited. Examples are joints, foliations, fractures, and solution openings. Also included in this category are animal burrows, root holes, and desiccation cracks in clay soils. While the latter examples typically facilitate free product migration only very locally, the former examples can exert a much more regional influence. Characterization of the flow of groundwater and free product through solution channels, fractures, and joints can be especially problematic. Wells completed at sites underlain by these features may not accurately (or completely) define flow directions or rates. The flow of groundwater and free product through the larger openings can sometimes even be under conditions of open channel flow. Once free product enters these larger openings, it can migrate undetected over relatively great distances (miles in some cases) in a matter of weeks or months. Although it would potentially be easier to recover free product in such a setting, it is much more difficult (and in many cases impossible) to locate recoverable accumulations.

Total porosity is based on the volume of all voids (primary and secondary), whether or not the pores are connected. When pores are not connected and dead-end pores exist, groundwater cannot move through the rock or sediments. Effective porosity is the term that characterizes the ratio of the volume of interconnected pores to the total volume of unconsolidated materials or rock.

There is no direct correlation between effective and total porosity. Effective porosity is approximated by drainable porosity and can be significantly less than total porosity. In general, the smaller the grains in the rock, the smaller the effective porosity (and the greater the retention capacity or residual saturation). For example, clays and limestones can have an upper range of total porosity that is in excess of 55 percent (see Exhibit III-6), but a lower range of drainable porosity of 1 percent or less.

Permeability

Permeability is one of the most critical properties to be considered in the design of any recovery system for free product recovery. The rates of groundwater flow and free product migration are related directly to permeability. The rate of free product migration also depends on other parameters, but permeability exhibits the greatest range in values (varying over 5 or 6 orders of magnitude for common geologic media).

Exhibit III-6

Porosity Of Various Geologic Materials

MATERIAL	NO. OF ANALYSES	RANGE	ARITHMETIC MEAN
Total Porosity			
Sedimentary Materials			
Sandstone	65	0.14 - 0.49	0.34
Siltstone	7	0.21 - 0.41	0.35
Sand (fine)	243	0.26 - 0.53	0.43
Sand (coarse)	26	0.31 - 0.46	0.39
Gravel (fine)	38	0.25 - 0.38	0.34
Gravel (coarse)	15	0.24 - 0.36	0.28
Silt	281	0.34 - 0.61	0.46
Clay	74	0.34 - 0.57	0.42
Limestone	74	0.07 - 0.56	0.30
Metamorphic Rocks			
Schist	18	0.04 - 0.49	0.38
Drainable Porosity			
Sedimentary Materials			
Sandstone (fine)	47	0.02 - 0.40	0.21
Sandstone (medium)	10	0.12 - 0.41	0.27
Siltstone	13	0.01 - 0.33	0.12
Sand (fine)	287	0.01 - 0.46	0.33
Sand (medium)	297	0.16 - 0.46	0.32
Sand (coarse)	143	0.18 - 0.43	0.30
Gravel (fine)	33	0.13 - 0.40	0.28
Gravel (medium)	13	0.17 - 0.44	0.24
Gravel (coarse)	9	0.13 - 0.25	0.21
Silt	299	0.01 - 0.39	0.20
Clay	27	0.01 - 0.18	0.06
Limestone	32	0.00 - 0.36	0.14
Metamorphic Rocks			
Schist	11	0.22 - 0.33	0.26

Source: Modified from McWhorter and Sunada, 1977 (Original Reference Morris and Johnson, 1967).

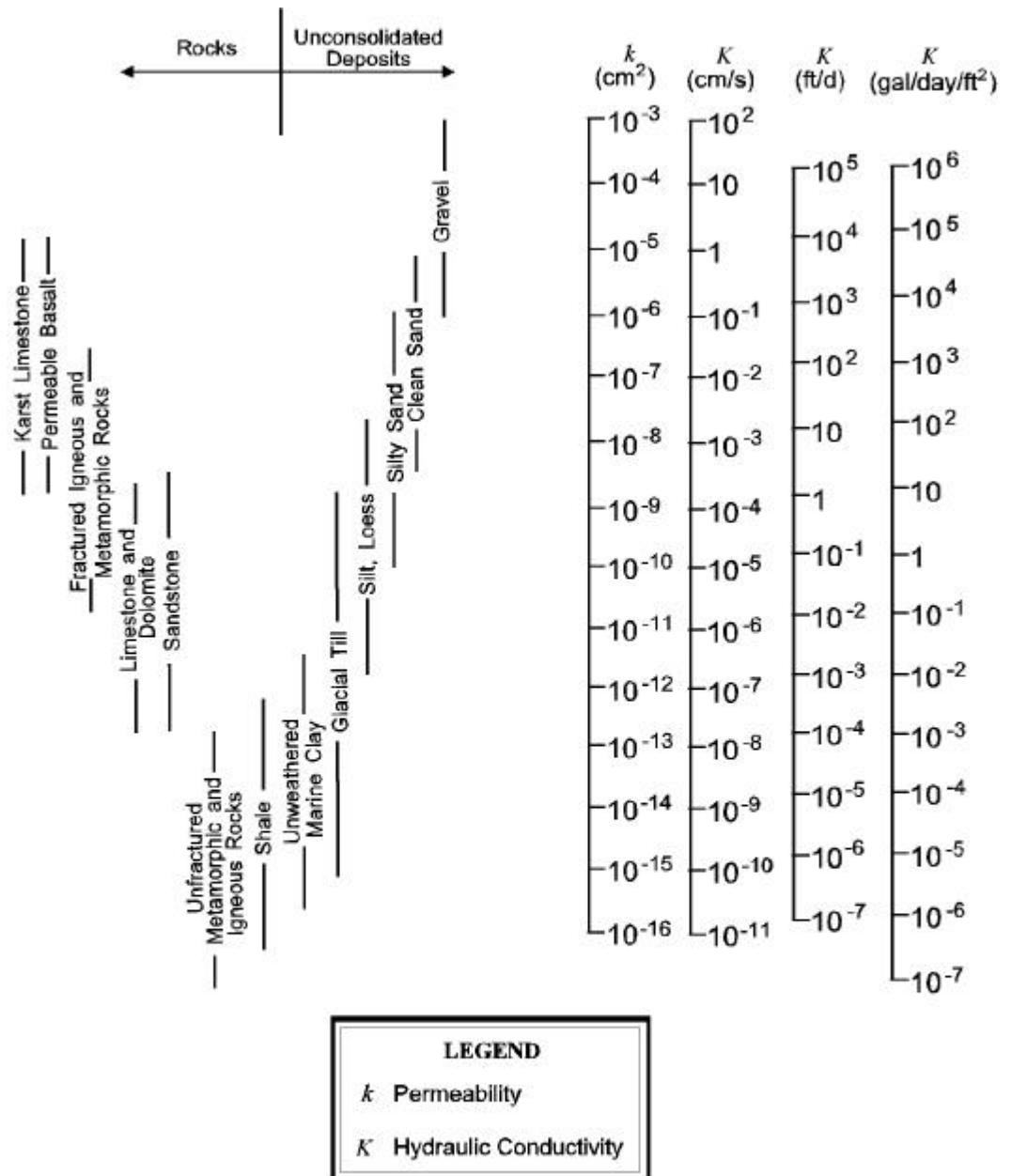
The intrinsic permeability of the geologic media is independent of the nature of the fluid flowing through the media. Intrinsic permeability is related to hydraulic conductivity, which is a measure of the ability of the geologic medium to transmit water, but the terms are not interchangeable. Hydraulic conductivity is a function of properties of both the media and the fluid. Although confusing, hydraulic conductivity is often referred to as simply “permeability”. Geologic media with high hydraulic conductivities are highly permeable and can easily transmit non-viscous fluids, especially water and many types of petroleum products. Various geologic media tend to have hydraulic conductivity values within predictable ranges (Exhibit III-7).

A geologic medium is described as “isotropic” if the measured permeability is the same in all directions. Flow through an isotropic medium is parallel to the hydraulic gradient. This condition might exist in a uniform, well-graded sand. The permeability of a geologic medium is often observed to vary depending upon the direction in which it is measured. Known as “anisotropy”, this condition can cause the flow of groundwater and free product to occur in a direction that is not necessarily the same as the principle direction of the hydraulic gradient. Because of anisotropy, a cone-of-depression formed around a pumping well may be asymmetrical (*e.g.*, elliptical) rather than circular. Sediments that are comprised of a high proportion of flat, plate-like particles (*e.g.*, silt, clay) which can pack tightly together and foliated metamorphic rocks (*e.g.*, schist) often exhibit anisotropy. Anisotropy may occur in three dimensions. For example, in flat-lying sedimentary units, horizontal permeability is usually much greater than vertical permeability.

The nature of geologic processes results in the nonuniform deposition and formation of rocks and sediments. Geologic media often are characterized by the degree of uniformity in grain size and properties such as permeability. Geologic media with uniform properties over a large area are referred to as being homogeneous. By contrast, geologic media that vary in grain size from place to place are called heterogeneous. In nature, heterogeneity is much more common than homogeneity. Soil properties (*e.g.*, permeability, texture, composition) can be dramatically different over short distances. These changes strongly influence the direction and rate of the flow of groundwater, free product, and vapor through the subsurface. For example, free product may migrate farther and faster than it would in homogeneous media because hydrocarbons tend to move through the most permeable pathways and bypass extremely low permeability zones. Fine-grained fractured media are heterogeneous in the extreme. Migration distances in fractured media can be large because of the very small storage capacity of the fractures.

Exhibit III-7

Range Of Values Of Hydraulic Conductivity And Permeability



Source: Modified from Freeze & Cherry, 1979

Properties Of Fluids

The physical properties of fluids that are most significant to free product recovery and migration are density and viscosity. Density determines the tendency of free product to accumulate above the water table or to sink to the bottom of the aquifer. Common petroleum hydrocarbons tend to accumulate above the water table because of their low density. Viscosity is a factor controlling the mobility and recoverability of liquid hydrocarbons. Petroleum hydrocarbons with low viscosity are more mobile and are more easily recovered than those with high viscosity. A third fluid property is interfacial tension, which is important because it determines how easily a geologic media will be wetted with a fluid and also controls (with pore size) the height of the capillary rise in a porous media. All three properties are inversely related to temperature. Exhibit III-8 summarizes the significance of fluid properties and their relevance to free product recovery.

Density

Density, which refers to the mass per unit volume of a substance, is often presented as specific gravity (the ratio of a substance's density to that of some standard substance, usually water). The densities of petroleum hydrocarbons typically found in USTs are less than 1.0 and typically range from 0.75 g/ml to as high as 0.99 g/ml. Density varies as a function of several parameters, most notably temperature, however, in most subsurface environments the temperature (and hence the density) remains relatively constant. The density of water is about 1.0 g/ml at normal groundwater temperatures. Densities of some common petroleum hydrocarbons are presented in Exhibit III-9. For a more detailed list of hydrocarbons and their properties, see Eastcott *et al.* (1988).

Petroleum hydrocarbons that are less dense than water will float; these are also referred to as light non-aqueous phase liquids, or LNAPLs. It is important to know the density of free product at a release site because water levels measured in monitor wells that also contain free product must be corrected to account for the different densities of water and the product and the thickness of the product layer. The correction procedure is demonstrated in Exhibit III-10. Density is also a required parameter for some volume estimation methods, which are discussed in Chapter IV and in the Appendix.

EXHIBIT III-8

Functional Characteristics Of Fluid Properties

Property	Significance
Density	Density values are used to determine whether free product will float on top of water or sink through it. Products that float are called LNAPLs (light non-aqueous phase liquids). Most fuel hydrocarbons are LNAPLs. Water levels measured in monitor wells containing free product must be corrected to account for the density and thickness of the product layer (see Exhibit III-10).
Viscosity	Viscosity is a measure of how resistant a fluid is to flow—viscous fluids resist flow. Higher viscosity fluids are more resistive to flow than lower viscosity fluids. For example, gasoline, which is less viscous than diesel fuel, flows faster than diesel fuel. Diesel fuel, which is less viscous than fuel oil #2, flows faster than the fuel oil.
Interfacial Tension	Interfacial tension is responsible for the capillary rise exhibited by fluids in fine-grained media. Interfacial tension is inversely related to the size of the pores. Fine-grained media retain more free product (residual saturation) than coarse-grained media.

Viscosity

Viscosity, which describes a fluid's resistance to flow, is caused by the internal friction developed between molecules within the fluid. For most practical applications, viscosity can be considered to be a qualitative description in that the higher a fluid's viscosity, the more resistive it is to flow. Fluids with a low viscosity are often referred to as "thin", while higher viscosity fluids are described as "thick". Thinner fluids move more rapidly through the subsurface than thicker fluids. This means that a thinner petroleum product (*i.e.*, gasoline) is generally more easily recovered from the subsurface and leaves a lower residual saturation than a thicker petroleum product (*e.g.*, fuel oil). Viscosity is inversely proportional to temperature: As the temperature of the fluid increases, the viscosity decreases. The efficiency of free product recovery may be reduced at sites in northern areas if temperatures in the shallow subsurface decrease significantly during the winter months. The viscosity of free product in the subsurface environment typically changes over time, becoming thicker as the thinner, more volatile components evaporate and dissolve from the liquid hydrocarbon mass.

Exhibit III-9

Density And Dynamic Viscosity Of Selected Fluids

Fluid	Density, ρ (g/ml)	Dynamic (Absolute) Viscosity, μ (centipoise, cP)
Water	0.998	1.14
Automotive gasoline	0.729	0.62
Automotive diesel fuel	0.827	2.70
Kerosene	0.839	2.30
No. 5 jet fuel	0.844	
No. 2 fuel oil	0.866	
No. 4 fuel oil	0.904	47.20
No. 5 fuel oil	0.923	215.00
No. 6 fuel oil or Bunker C	0.974	
Norman Wells crude	0.832	5.05
Avalon crude	0.839	11.40
Alberta crude	0.840	6.43
Transmountain Blend crude	0.855	10.50
Bow River Blend crude	0.893	33.70
Prudhoe Bay crude	0.905	68.40
Atkinson crude	0.911	57.30
LaRosa crude	0.914	180.00

Notes: all measurements at 15°C.
g/ml = grams per milliliter
C = Celsius

Source: API, 1996. A guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted courtesy of the the American Petroleum Institute.

Exhibit III-10

In Wells Correction To Compute Hydraulic Head Containing Free Product

Equation: To obtain a corrected hydraulic head value when free product (liquid hydrocarbon) is present in a well:

$$h_c = h_m + (H_o \frac{\rho_o}{\rho_w})$$

where:

h_c	=	hydraulic head corrected (ft)
h_m	=	measured elevation of hydrocarbon-water interface (ft)
H_o	=	thickness of hydrocarbon layer (ft)
ρ_o	=	hydrocarbon density (g/ml)
ρ_w	=	water density (g/ml); usually assumed = 1.0

Example: The distance from the well head to the hydrocarbon-air interface is 15.00 feet. The hydrocarbon-water interface is measured at 19.75 feet. The elevation of the top of the well head is 100.00 feet above sea level. The density of the hydrocarbon is 0.73.

What is the hydraulic head in this well?

Solution: The elevation of the air/hydrocarbon interface is 85 feet above sea level (100.00 feet - 15.00 feet). The elevation of the hydrocarbon-water interface is 80.25 feet above sea level. The hydrocarbon thickness is 4.75 feet (19.75 feet - 15.00 feet). Substituting the appropriate values into the equation:

$$\begin{aligned} h_c &= 80.25 \text{ ft} + 4.75 \text{ ft} \times \frac{0.73 \text{ g/ml}}{1.0 \text{ g/ml}} \\ &= 83.72 \text{ feet} \end{aligned}$$

Note that the hydraulic head elevation (83.72 feet) is significantly different from the measured hydrocarbon-water interface (80.25) and from the measured air-hydrocarbon interface (85.00 feet). Groundwater elevations based on uncorrected measurements are incorrect and flow directions should not be determined using these values. Because the flow directions are incorrect, a recovery system designed based on them would likely be inefficient or even ineffective.

Three different terms are commonly used to describe viscosity: *absolute*, *dynamic*, and *kinematic*. Absolute and dynamic are synonymous terms and are typically reported in units of centipoise (cP). Kinematic viscosity, which is equal to dynamic (or absolute) viscosity divided by density, is typically reported in units of centistokes (cSt). Because viscosity is relative, the term selected for use when comparing viscosities for various petroleum hydrocarbons, does not matter as long as it is the same for all the products being compared. If a flow equation is being solved, be sure to use a term that expressed in units which are consistent with the equation. Absolute (or dynamic) viscosities of common petroleum hydrocarbons are presented in Exhibit III-9.

Interfacial Tension

The characteristics of free hydrocarbon movement are largely determined by interfacial tension that exists at the interface between immiscible fluids (*e.g.*, hydrocarbon, air, and water). Interfacial tension causes a liquid to rise in a capillary tube (or porous medium) and form a meniscus. The height of the capillary rise is inversely proportional to the radius of the tube (or pore spaces), which explains why the capillary rise is greater in fine-grained porous media than in coarse-grained material. In general, higher surface tensions result in higher capillary pressure, which may produce higher residual saturation (Mercer and Cohen, 1990). The interfacial tension between a liquid and its own vapor is called surface tension.

Interfacial tension is the primary factor controlling wettability. The greater the interfacial tension, the greater the stability of the interface between the two fluids. The interfacial tension for completely miscible liquids is 0 dyne cm⁻¹. Water (at 25°C) has a surface tension of 72 dyne cm⁻¹. Values of interfacial tension for petroleum hydrocarbon-water systems fall between these two extremes (Mercer and Cohen, 1990). Interfacial tension decreases with increasing temperature and may be affected by pH, surface-active agents (surfactants), and gas in solution (Schowalter, 1979). Some of the theoretical methods for estimating free product volume in the subsurface and some multiphase flow models require values of interfacial tension as input. Obtaining accurate values is difficult for a couple of reasons. First, measurement of interfacial tension in the field is generally not practical. Second, although values for some petroleum hydrocarbons may be obtained from the literature, these values tend to be for pure compounds under ideal conditions and may not be representative of free product plumes in the subsurface environment.

Properties Of Fluids And Geologic Media

The movement of free product in the subsurface also depends upon several factors which are functions of properties of both the fluid and the geologic media. These factors are capillary pressure, relative permeability, wettability, saturation, and residual saturation. Although all of these factors are interrelated, the most important are capillary pressure and relative permeability. Exhibit III-11 summarizes the most significant properties of both the fluid and the geologic media and illustrates how these properties relate to free product recovery.

Capillary Pressure

Capillary pressure is the difference in pressure observed between two phases (*e.g.*, hydrocarbon liquid and water) that occupy the same pore space. As the result of interfacial tension, the boundary between two immiscible phases is a curved surface, or interface. Capillary pressure is the change in pressure across this curved interface. In the vadose zone capillary pressure is negative (*i.e.*, less than atmospheric) and is referred to as suction or tension. Capillary pressures are larger in fine-grained media (*e.g.*, silt, clay) than in coarse-grained media (*e.g.*, gravel). The capillary fringe above the water table is a familiar consequence of capillary pressure. Because capillary pressure resistance is inversely proportional to pore size, the height of the capillary fringe is greater in finer grained media.

The distribution and accumulation of free product in the subsurface is influenced by capillary pressure. Soil water content and the size and orientation of pore spaces affect the penetration of free product in the vadose zone. Penetration of free product into the subsurface is enhanced by dry soil conditions and facilitated by inclined, relatively permeable pathways such as those provided by secondary permeability features (*e.g.*, fractures, root holes, and bedding plane laminations). Upon reaching the capillary fringe, resistance to downward movement will be increased and hydrocarbons will spread laterally and accumulate above the saturated media. This accumulation is sometimes referred to as a “lens” or “pancake”. As long as there is a sufficient supply of hydrocarbons from above, the lens thickness and downward pressure will continue to increase. Eventually, the petroleum product (the nonwetting fluid) will begin to displace water (the wetting fluid) and enter the largest pores. The pressure required for this to occur is referred to as the “threshold entry pressure” (Schwille, 1988; Cary *et al.*, 1991).

EXHIBIT III-11

Functional Characteristics Of Properties Dependent On Both The Fluid And The Geologic Media

Property	Significance
Capillary Pressure	Capillary forces restrict the movement of free product--movement tends to occur through pathways where capillary pressures are low, as in coarser-grained media. Capillary pressure is inversely related to saturation. It is not practical (or necessary) to measure capillary pressure in the field.
Relative Permeability	Relative permeability is a function of saturation and also controls the mobility of liquids in a porous medium. Relative permeability and saturation are directly proportional. In media with two liquids present, the permeability of the media is reduced for each liquid due to the presence of the other liquid.
Wettability	Most geologic materials are preferentially wet by water as opposed to free product (or air)--this means that water, rather than free product will be more mobile.
Saturation	Saturation controls the mobility of liquids (water and free product) through a porous medium--for a liquid to be mobile, the liquid phase must be continuous and the media must be at least partially saturated. Saturation levels are also used to determine the volumes of free and residual product.
Residual Saturation	Liquids drain from a porous medium until a certain minimum saturation level is reached (for free product this is "residual saturation") and flow ceases.

Similarly, in the saturated zone, hydrocarbons will tend to spread laterally over fine-grained capillary barriers and move through fractures and coarser media wherever possible. The thickness or height of a hydrocarbon column required to develop sufficient hydrocarbon pressure head to exceed capillary force resistance is known as the critical hydrocarbon thickness (or height). Because capillary forces can restrict the migration of free product into water-saturated media, fine-grained layers can act as capillary barriers. That is, before free product can penetrate a water-saturated porous medium, the hydrocarbon pressure head must exceed the resistance of the capillary forces (Schwille, 1988). In heterogeneous media, free product tends to move through pathways where capillary effects are weak, such as lenses of sand and gravel or large fractures.

Although capillary pressure is not measured in the field (it can be measured in the laboratory or estimated from grain size data [Mishra *et al.*, 1989]), the effects of capillary pressure should be considered in the analysis of field data. A commonly measured field parameter is the thickness of product in a well, however, this thickness is usually much greater than the true thickness of free product in the aquifer. This exaggeration is most pronounced in media with strong capillary effects (*e.g.*, fine grained silts and clays) and least pronounced in media with weak capillary effects (*e.g.*, sands and gravels). Exhibit III-12 illustrates this effect, however, the exhibit is not intended to be used to estimate the amount of free product at a particular site. This effect obviously is of great practical significance in the design of a free product recovery system. For example, thick oil accumulations in monitor wells may be caused by either significant amounts of free product or small amounts of free product in fine grained media. A conventional recovery system (*e.g.*, skimmer) may be appropriate in coarser-grained media with thick accumulations of free product. In the case of thinner accumulations in finer-grained media, a vacuum-enhanced recovery system, rather than a conventional recovery system, may be required.

Relative Permeability

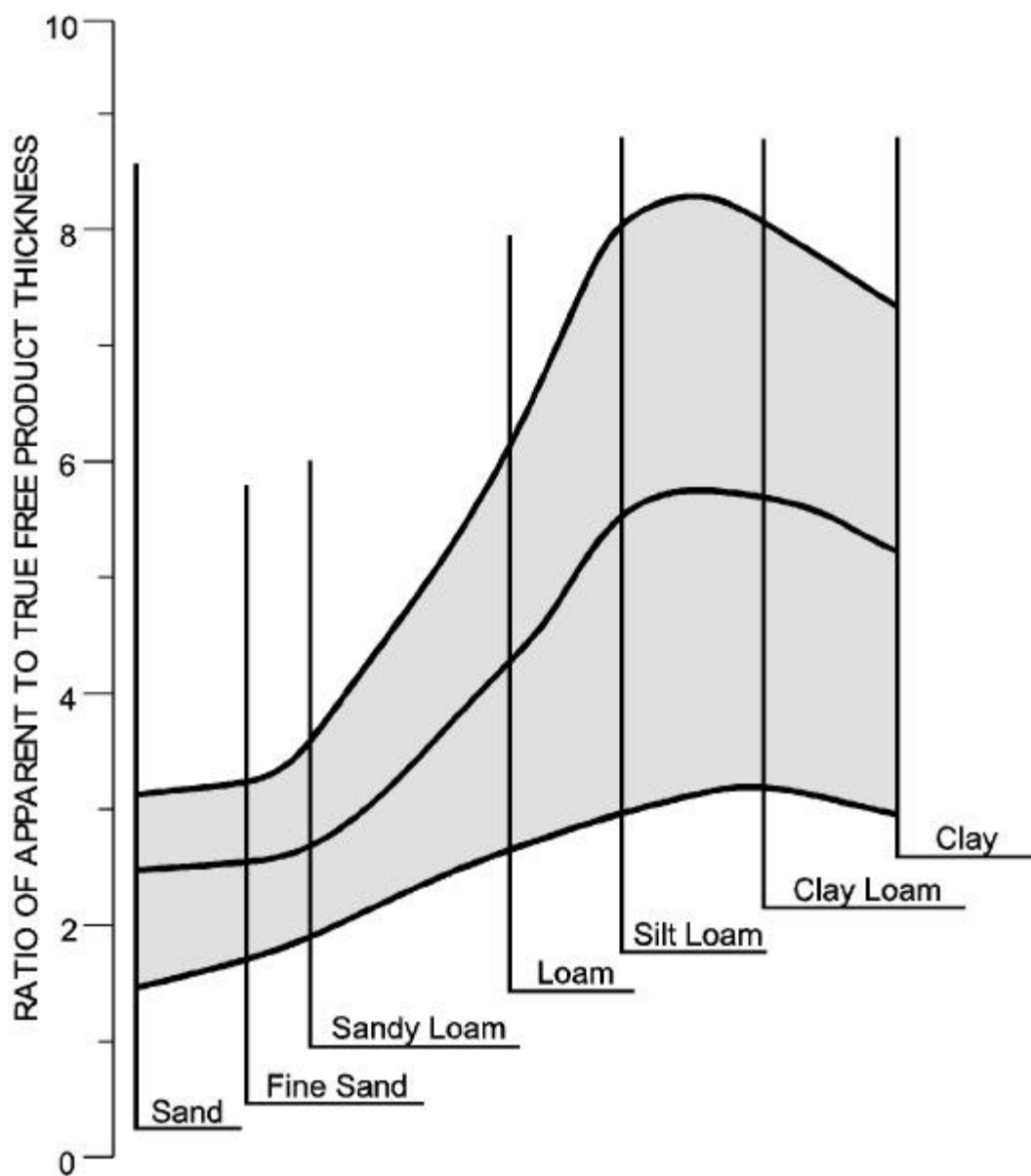
The effectiveness of a recovery system to collect free product depends upon the mobility of the free product through the geologic media. Mobility is strongly controlled by the relative permeability of the petroleum hydrocarbons and water, which in turn is dependent upon saturation. Relative permeability is the ratio of the effective permeability of a fluid at a specified saturation to the intrinsic permeability of the medium at 100-percent saturation (Mercer and Cohen, 1990). The relative permeability of a particular geologic media that is completely saturated with a particular fluid is equal to the intrinsic permeability. When more than one fluid (*i.e.*, air, water, petroleum hydrocarbon) exists in a porous medium, the fluids compete for pore space thereby reducing the relative permeability of the media and the mobility of the fluid. This reduction can be quantified by multiplying the intrinsic permeability of the geologic media by the relative permeability. As with saturation, the mobility of each fluid phase present varies from zero (0 percent saturation) to one (100 percent saturation).

An example of relative permeability curves for a water-hydrocarbon system is shown in Exhibit III-13. The curves representing water saturation and hydrocarbon saturation are contrary to one another and divide the figure into three flow zones. Zone I, where hydrocarbon saturations are relatively high, is dominated by hydrocarbon flow. Water

Exhibit III-12

Ratio Of Apparent To True Free Product Thickness

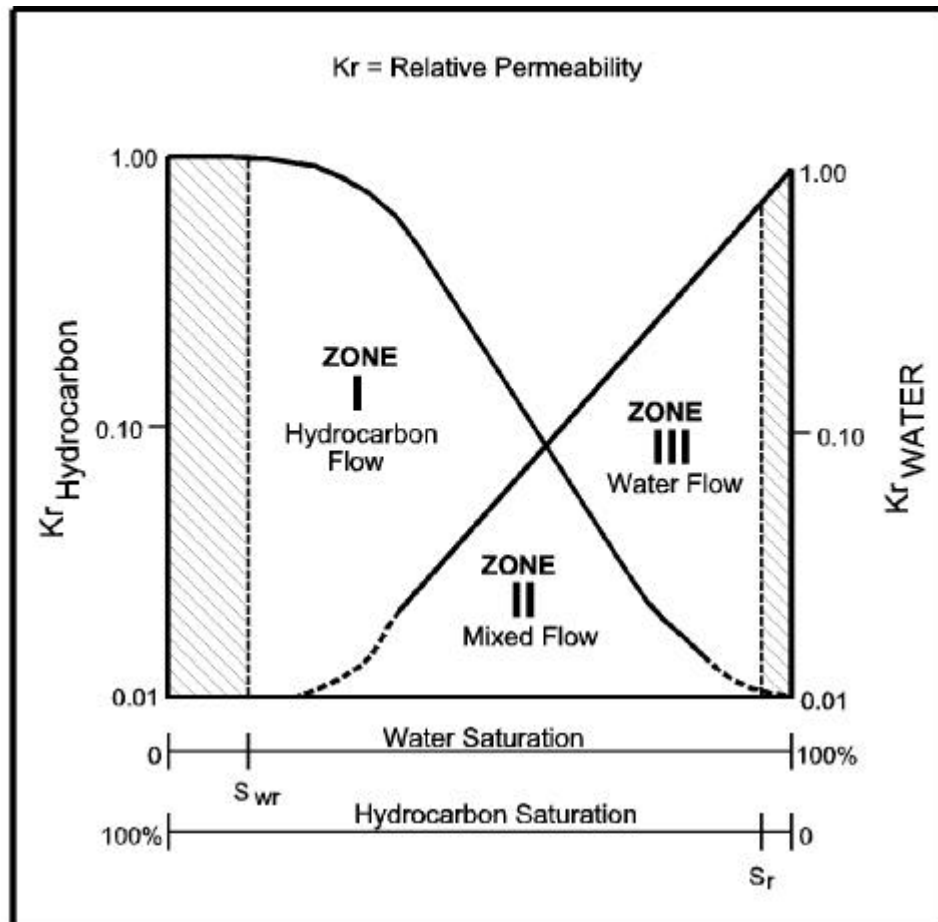
Measured In A Monitor Well For Various Soil Types



Source: EPA, 1990

Exhibit III-13

Hypothetical Relative Permeability Curves For Water And A Liquid Hydrocarbon In A Porous Medium



ZONE

EXPLANATION

- I Liquid hydrocarbon occurs as a potentially mobile, continuous phase and saturation is high. Water is restricted to small pores. The relative permeability of water is very low or zero. Such conditions may be observed within large mobile product accumulations.
- II Both liquid hydrocarbon and water occur as continuous phases, but generally they do not necessarily share the same pore spaces. However, the relative permeability of each fluid is greatly reduced by the saturation of the other fluid. Such conditions may be representative of zones of smaller mobile product accumulations at the water table.
- III Liquid hydrocarbon is discontinuous and trapped as residual in isolated pores. Flow is almost exclusively the movement of water, not LNAPL. Examples of such conditions may be found within zones of residual LNAPL retained below the water table.

Source: Newell et. al., 1995

saturations are relatively high in Zone III, and water flow is dominant. Mixed flow characterizes Zone II. Refer to the exhibit explanation for more details.

Because of the difficulties associated with laboratory and field measurement of relative permeability, alternative theoretical approaches can be utilized to estimate this function from the more easily measured capillary pressure data (Muallem, 1976; Lenhard and Parker, 1987; Luckner *et al.*, 1989; and Busby *et al.*, 1995). Relative permeability relationships can be estimated from grain size data for unconsolidated materials (Mishra *et al.*, 1989).

Wettability

Wettability, which depends on interfacial tension, refers to the preferential spreading of one fluid over solid surfaces in a two-fluid system (Mercer and Cohen, 1990). Because of the dependence on interfacial tension, the size of the pore spaces in a geologic medium strongly influences which fluid is the wetting fluid and which fluid is the nonwetting fluid. The dominant adhesive force between the wetting fluid and media solid surfaces causes porous media to draw in the wetting fluid (typically water) and repel the nonwetting fluid (typically hydrocarbon or air) (Bear, 1972). Liquids (hydrocarbon or water), rather than air, preferentially wet solid surfaces in the vadose zone. In the saturated zone, water will generally be the wetting fluid and displace LNAPL (Newell, *et al.*, 1995). Whereas the wetting fluid (usually water in a hydrocarbon-water system) tends to coat solid surfaces and occupy smaller openings in porous media, the nonwetting fluid tends to be constricted to the largest openings (*i.e.*, fractures and relatively large pore spaces). When a formerly saturated porous media drains, a thin film of adsorbed wetting fluid will always remain on the solid.

The factors affecting wettability relations in immiscible fluid systems include mineralogy of the geologic media, the chemistry of the groundwater and the petroleum hydrocarbon, the presence of organic matter or surfactants, and the saturation history of the media. Sometimes, such factors can lead to the preferential wetting of only a portion of the total surface area; this is called fractional wettability. With the exception of soil containing a high percentage of organic matter (*e.g.*, coal, humus, peat), most geologic media are strongly water-wet if not contaminated by NAPL (Mercer and Cohen, 1990). This means that free product will be less mobile and generally leave a higher residual saturation in the soil, than will water.

Anderson (1986a, 1986b, 1986c, 1987a, 1987b, and 1987c) prepared an extensive literature review on wettability, its measurement, and its effects on relative permeability, capillary pressure, residual hydrocarbon saturation, and enhanced hydrocarbon recovery.

Saturation

The level of saturation possible in a subsurface media has several implications for recovering free product. First, it controls the mobility of fluids; second, it defines the volumetric distribution of petroleum hydrocarbons (discussed in Chapter IV); and third, it is a function of other properties (*e.g.*, capillary pressure, relative permeability). The mobility of a particular phase is reduced with decreasing saturation until flow ceases to occur. Saturation of a porous medium may be defined as the relative fraction of total pore space containing a particular fluid (Newell *et al.*, 1995). The saturation level for each of the fluids ranges between zero (the fluid is not present in the porespace and saturation is 0 percent) and one (the fluid completely occupies the porespace and saturation is 100 percent). Of course, a given pore space can only be filled to a maximum of 100 percent, and the proportions of each phase saturation must sum to 1 (or 100 percent saturation).

The mobility of a liquid through a porous medium is a function of the saturation of the porous medium with respect to that liquid. In order for it to flow through a porous medium, a liquid must be continuous through the area where flow occurs. As liquid drains from the media, the liquid phase becomes discontinuous. The point at which the saturation level for a continuous liquid phase other than water (*i.e.*, petroleum hydrocarbon) becomes discontinuous (and hence immobile) is known as the residual saturation (Newell, *et. al.*, 1995). The corresponding saturation level for water is called the irreducible water saturation. At these low saturations, capillary pressures are very high.

The wetting and draining cycles of a porous media differ from one another as the result of differences in saturation, wettability, and capillary pressure. During drainage, the larger pores drain the wetting fluid (*i.e.*, water) quickly while the smaller pores drain slowly, if at all. During wetting, the smaller pores fill first, and the larger pores fill last. The consequence of this phenomenon is that the vadose zone will retain less residual petroleum hydrocarbon than the saturated zone.

Residual Saturation

Residual saturation refers to the saturation level at which a continuous mass of petroleum hydrocarbons (NAPL) becomes discontinuous and immobilized by capillary forces (Newell, *et al.*, 1995). Residual saturation is important to free product recovery, because it represents the amount of petroleum that cannot be recovered by pumping or gravity drainage. Following a release of petroleum hydrocarbons into the subsurface, the hydrocarbon mass seeps downward into the unsaturated zone. If the volume of the release is enough to sufficiently saturate the soil, the leading edge of the hydrocarbon mass continues to move deeper into the subsurface. Behind and above the leading edge, a significant portion of the hydrocarbon mass is retained in pore spaces by capillary forces. The amount of hydrocarbon that is retained against the force of gravity is referred to as the residual saturation. The corresponding term for water is irreducible water saturation.

Generally, the finer-grained the soil, the higher the residual saturation. Residual saturation for the wetting fluid is conceptually different from that for the nonwetting fluid. When the wetting fluid (*i.e.*, water) drains from a porous media, even at the level of the irreducible water saturation, there is a thin, continuous layer of water occupying the smallest pores and coating the grains of the media. As the nonwetting fluid (*i.e.*, petroleum hydrocarbon or NAPL) drains from a porous media, the pores drain incompletely because of the residual water that remains in the smallest pores. The result is that discontinuous blobs of immobile petroleum hydrocarbon remain in the soil at the level of the residual saturation. More viscous fluids tend to have higher residual saturations than less viscous fluids. Fluids that are more dense for a given viscosity drain to a greater degree under the influence of gravity than do less dense fluids. Fluids that have high interfacial tension also tend exhibit higher capillary pressure, which may result in higher residual saturation. Although field-scale values for residual saturation are difficult to either measure or accurately estimate, in general, residual saturation levels tend to be much higher in the saturated zone (0.15 to 0.50) than in the unsaturated zone (0.10 to 0.20) (Mercer and Cohen, 1990).

Because residual hydrocarbons are both tightly bound and discontinuous in pore spaces, they are essentially immobile and, therefore, not amenable to collection by standard free product recovery methods. However, the residual phase often represents a potential long-term source for continued groundwater contamination. Although some portion of the residual mass will be slowly diminished (*i.e.*, will naturally attenuate) over time as the result of dissolution, volatilization, and biodegradation,

more aggressive remedial action may be required to mitigate this source within a reasonable amount of time.

Groundwater Flow Conditions

The subsurface can be divided into two zones based on water content: The unsaturated zone and the saturated zone. The movement of petroleum hydrocarbons in the subsurface is fundamentally different in the unsaturated and saturated zones. The boundary between these two zones is commonly accepted to be the water table, which is the surface where water pressure equals atmospheric pressure. Below the water table, in the saturated zone, all pore and void spaces are filled with water and water pressure is greater than atmospheric pressure. Water pressures above the water table, in the unsaturated zone, are less than atmospheric pressure, and the water may be considered to be under tension or suction. Directly above the water table is a relatively thin zone—the capillary fringe—that is saturated with water but the water pressure is less than atmospheric pressure. The capillary fringe is thicker in fine-grained media and thinner in coarse-grained media. Above the capillary fringe in the unsaturated zone, voids and pore spaces are filled primarily with air and varying amounts of water as either liquid or vapor.

Petroleum hydrocarbon migration is strongly affected by essentially the same factors that govern groundwater flow. In general, liquid hydrocarbons move in the same direction as groundwater but at a reduced rate because of the higher viscosity of the hydrocarbons (except for gasoline) and the lower relative permeability of the porous medium. Important characteristics of the groundwater flow system that influence free product are depth to water and hydraulic head variations across the site. Direct measurements of depth to water and water table elevations/head are necessary to design or evaluate most free product recovery systems. Exhibit III-14 summarizes the characteristics of the groundwater flow system that are most relevant to free product recovery.

Depth To Water Table

The depth to water table is an important factor that affects how the free product migrates and how its recovery should be approached. Except for very deep water tables, the depth to the water table can be determined through relatively inexpensive borings or monitoring wells (or well points). The depth to water table will indicate the potential for petroleum hydrocarbons to reach the water table, where the free product can then be collected in wells or trenches. All other factors being equal, a greater

EXHIBIT III-14

Functional Characteristics Of Groundwater Conditions

Property	Significance
Depth to Water Table	Mass of free product required to reach the water table increases with depth; options to recover free product become more limited (e.g., depth must be less than 20 feet for trenching); costs to recover free product increase with depth.
Groundwater Elevation	Groundwater elevation (hydraulic head) determines hydraulic gradient and direction of groundwater flow and free product migration—presence of free product requires that measured groundwater elevations be corrected to account for the density and thickness of the free product layer (see Exhibit III-10).

depth to water table requires a greater volume of liquid petroleum hydrocarbons to reach the water table.

The depth to water table, or the top of the free product layer in a well or trench, is a critical consideration in the selection of a recovery approach and equipment specification. For example, excavation depth is constrained by equipment limitations, and excavation costs increase substantially with depth in nearly all cases. Thus, recovery systems utilizing drains or gravel-filled trenches are typically limited to sites with water tables less than 20 feet deep and preferably closer to 10 feet deep. Excavated material may be highly contaminated and require appropriate handling and disposal. In most cases where the depth to the water table is greater than 20 feet, wells must be installed.

Groundwater Elevation (Hydraulic Head)

Measurements of groundwater elevations in wells and piezometers (a well open to a narrow interval) are the basic response data that characterize the direction of groundwater flow. The basic principle of groundwater hydrology is described by Darcy's Law, which relates flow through porous media to the hydraulic gradient. Groundwater flows downgradient; that is, from areas of higher head to areas of lower head. The hydraulic gradient is the change in head per unit distance at a given point and given direction. In an unconfined aquifer, the hydraulic gradient

is defined by the slope and direction of dip of the water table. A common observation at many UST sites is a groundwater mound created by the influence of the tank excavation. These excavations are typically filled with pea gravel which has a much higher permeability than the native soils at the site. As a result, tank excavations tend to accumulate and hold water, usually at a higher hydraulic head than the local water table. This can cause the formation of a localized groundwater mound that can influence the hydraulic gradient at the site, possibly inducing free product to migrate outward in all directions from the source of the release.

Because petroleum hydrocarbons have a density different from that of water, neither the measured elevation of free product nor the measured elevation of water in a well containing free product represents hydraulic head. Measured fluid elevations in monitoring wells must be corrected to determine groundwater flow directions and rates. The equation for this correction and an example calculation are presented in Exhibit III-10.

Relevance To Free Product Recovery

This chapter has presented many factors that influence the occurrence and movement of free product in the subsurface. This section presents a discussion limited to those factors that are most relevant to the recovery of the principal types of petroleum products typically stored in USTs (*i.e.*, gasolines, middle distillates, and heavy fuel oils). A summary of these factors is provided in Exhibit III-15.

The majority of petroleum hydrocarbons stored in USTs are lighter than water, which means that they float. Free product generally moves in the same direction as the flow of groundwater. This movement is strongly influenced by soil heterogeneity and anisotropy, and the design and operation of an effective free product recovery system is dependent upon accurate characterization of the hydrogeologic conditions at the site. It is extremely important to realize that the elevations of liquid surfaces in a monitoring well containing both groundwater and free product is not representative of hydraulic head at that location. The measurement must first be corrected to account for the thickness of the free product and its density. Other critical factors to consider are the total volume of the release and the depth to groundwater. If the volume of release is so small that there is no accumulation at the water table, then recovery of free product is not practical.

Gasolines are significantly less viscous than water. They can move more rapidly through geologic media than water and subsurface accumulations can be relatively easily recovered. Many of the principal

Exhibit III-15

Most Important Factors Influencing Free Product Recovery

Factor	Significance
Soil Heterogeneity and Anisotropy	Controls direction of free product migration and the flow of groundwater
Product Viscosity	Affects mobility, ease of recoverability, and level of residual saturation
Soil Permeability	Controls rate of free product migration and the flow of groundwater
Depth to Water Table	Coupled with volume of release, determines which remedial technologies may be effective at the site
Volume of Release	Coupled with depth to water table, determines whether free product recovery is practical or necessary

components of gasoline are volatile and somewhat soluble. Because of their high mobility and vapor generation potential, recovery measures should be initiated as soon as possible after a gasoline release has been discovered. The lighter components also tend to be more soluble and groundwater supplies can easily be contaminated. Residual soil saturation is lower than for the heavier and thicker petroleum products. Older gasoline plumes will be enriched in the heavier, less volatile fractions; they may behave more like a fresh middle distillate plume. As a result of the absence of the volatile fractions, vacuum technologies will be less effective in recovering petroleum hydrocarbons due to volatilization (evaporation), but vacuum-enhancement may be effective in recovering a greater proportion of the plume than would be possible without the enhancement.

Middle distillates and heavy fuel oils are significantly more viscous than water. Their movement through the subsurface is typically slow. Although not as volatile as gasoline, vapors emanating from middle distillate plumes can create situations in which fire, explosion, or toxicity threatens human health and safety. Because of the higher viscosity and lower volatility, residual soil saturation is higher for plumes comprised of middle distillates and heavy fuel oils than for gasoline plumes.

Recovery of free product to the maximum extent practicable is merely the first step in a typical remedial action. Regardless of what type

of petroleum product was released and the characteristics of the subsurface materials, a significant portion of the total release volume will not be recoverable by any existing remedial technology. Appropriate treatment of the residual hydrocarbon mass may require application of a combination of alternative remedial technologies.

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CHAPTER IV

METHODS FOR EVALUATING RECOVERABILITY OF FREE PRODUCT

CHAPTER IV

METHODS FOR EVALUATING RECOVERABILITY OF FREE PRODUCT

The primary objectives of a free product recovery system are to recover as much free product as possible, as quickly as possible, and with as little expense as possible. In order to design an effective and efficient free product recovery system, you need to answer several questions: “What is the areal and vertical extent of the free product?”, “How much free product has accumulated?”, “How much of the total volume is recoverable?”, and “How quickly can the free product be recovered?”. The answers to each of these questions relate to the recoverability of free product from the subsurface.

Intuitively, the most effective locations for free product recovery devices are those places where the accumulations are the greatest. Early tasks, therefore, include locating those areas where free product accumulations are the greatest and delineating the areal extent of the free product plume (or pools). Knowledge of the areal extent is also necessary to assess whether or not hydraulic containment is required. This information can be obtained from excavations and test pits, soil borings, and monitoring wells or well points.

The volume of free product present at a site should be estimated in order to help evaluate progress during the recovery phase. One of the ways to establish this estimate is to determine the hydrocarbon concentrations in soil and hydrocarbon thickness in wells. Methods used to estimate free product volumes are based on theoretical models, simplified correlations between hydrocarbon thickness in wells, and specific oil volumes. The reliability of volume estimates is typically low, with accuracy within an order of magnitude. Because of the uncertainty, we suggest that more than one method should be used for volume estimation.

The recoverability of free product from the subsurface environment is dependent upon several factors: The physical and chemical properties of the separate phase petroleum hydrocarbons, the transport properties of the geologic media, and the capabilities of engineered recovery systems. The physical and chemical properties of the petroleum hydrocarbons determine how the free product will primarily exist in the subsurface; whether as a vapor, a liquid, or dissolved in groundwater. These properties also affect how fast the free product will move and where in relation to the water

table it will accumulate. Properties of the geologic media influence the rate and direction in which the free product will move. Engineered systems are designed for use within discrete operating ranges, and no one recovery system will be optimally suited for all hydrocarbon release sites. It is also important to realize that only a portion of the total volume of the release will be recoverable. Even under ideal conditions a significant proportion of the free product will remain in the subsurface as immobile residue.

Finally, the rate at which free product can be collected in wells or trenches will influence decisions on the types and number of wells, the type of collection equipment used, and the sizing of the treatment system and/or separators. Recovery rates can be estimated from the results of specialized pumping tests, the projection of initial recovery rates, and the use of theoretical models. As recovery progresses product thicknesses and saturation levels decrease, which affects recovery rates. Other factors, such as fluctuating water table elevations, can also affect recovery rates. As a result, the uncertainty associated with estimates of long-term recovery rates is high.

The relevant properties of petroleum hydrocarbons and geologic media that govern the behavior of free product in the subsurface have been discussed in detail in Chapter III. Engineered free product recovery systems are described in Chapter V. The remainder of this chapter presents methods for: delineating the areal and vertical extent of free product, estimating the volume of free product at a release site, and estimating free product recovery rates. Theoretical models used to estimate hydrocarbon volumes and recoverability are discussed only briefly.

Areal And Vertical Extent Of Free Product

The areal and vertical extent of free product must be delineated before a free product recovery system can be designed. First, the areal extent is defined by determining the free product thicknesses at available observation points. Second, using these data an isopach (thickness contour) map is developed. Locations where free product thicknesses are greatest are usually the best locations for installation of free product recovery equipment. There are several common methods used to identify locations and thicknesses of free product in the subsurface. Used either alone or in combination with one another, these methods include:

- ! Observation/measurement of free product in excavations or test pits.

- ! Observation/measurement or analysis of hydrocarbons in soil samples collected from borings.
- ! In situ measurements using a variety of geophysical and direct push techniques.
- ! Measurement of hydrocarbon thicknesses in wells.
- ! Observations of hydrocarbon seepage in springs or surface water bodies.

At a given site, not all the above methods may be applicable or cost effective, and they each have limitations. Excavations may provide information about free product thickness through measurement of either the thickness of floating product or the thickness of hydrocarbon-saturated soil. In either case, such measurements may not be indicative of the true free product thickness in the soil. For example, the water level in the excavation may not be representative of the ambient water table elevation. Measurements of the thickness of saturated soil should be conducted immediately after the excavation has been dug so that the soil does not have time to drain. Excavations are also generally limited to depths of 20 feet or less.

The process of collecting soil samples results in some degree of disturbance of the sample. For instance, the degree of compaction (which may affect saturation) can change especially if the samples are collected with a split-spoon sampler. The sample collection location relative to the water table and capillary fringe can also affect the degree of saturation and subsequent determination of free product thickness. Various *in situ* methods may be employed to overcome the problems associated with disturbed samples. However, some of the *in situ* methods are geophysical techniques that collect indirect data; that is the response of subsurface materials to an induced stress (*e.g.*, friction) or energy (*e.g.*, electricity, radiation) is measured and the resulting signal is correlated with a particular soil type or characteristic. Their applicability depends to a large degree upon site-specific conditions. The resolution of surface techniques generally diminishes with increasing depth. Borehole techniques require pre-existing wells or boreholes. Direct push techniques enable continuous subsurface data to be collected as well as provide the opportunity to collect samples of both soil and groundwater. The “Soil Borings” section of this chapter provides a limited discussion of direct push methods; a detailed discussion is beyond the scope of this manual. For additional information, please refer to OUST’s soon-to-be published manual on Expedited Site

Assessment Methods and Equipment for Underground Storage Tank Sites, which is anticipated to be available in the late fall of 1996.

Although the thickness of a layer of free product in a monitor well can be measured with high accuracy and precision, the measured thickness is usually larger (sometimes by a factor of as much as 4) than the thickness that exists in the surrounding soil. The reasons behind the limitations of monitor wells in providing accurate information on the thickness of free product in the soil are discussed in greater detail later in this chapter.

In most instances where free product appears in a spring or surface water body, its presence is indicated only as a multi-colored sheen. Rarely is it possible to measure either the thickness of the free product or the rate of flow. However, its presence may provide insight into migration pathways, which can aid in the design of the free product recovery system.

In developing an approach to free product delineation, consideration of each method should lead to the optimal strategy in terms of cost, time, and impact to existing operations at the site. Exhibit IV-1 provides a summary of the features of each of the above methods.

Strategy For Delineation Of Free Product

The strategy for delineating the extent of free product should involve the following steps:

- ! Estimate duration and volume of release.
- ! Evaluate potential to reach water table.
- ! Select methods for identifying locations of free product (*e.g.*, excavation, soil borings, *in situ* techniques, seepage observations, wells).
- ! Evaluate probable direction of groundwater flow and free product migration.
- ! Collect samples, make observations, and install wells/well points, moving outward until areal extent is delineated.

Estimation of the duration and volume of a release is initially based on review of inventory and other records in addition to interviews with site

Exhibit IV-1

Features of Methods for Delineating Extent of Free Product

Method of Data Collection	Data Analysis Method	Data Quality & Reproducibility	Correlation to Actual Free Product Thickness	Maximum Practical Depth	Minimum Free Product Thickness
Free Product Thickness in Excavations	direct measurement/observation	highly variable, but generally low	poor-fair, qualitative (present or absent, much or little)	shallow, less than 20 feet	sheen
Soil Samples					
Chemical Analysis (lab or field methods)	indirect measurement	generally high quality, good reproducibility	good, quantitative	limited only by sample collection method	1 % of saturation of sample; depends on soil type
Direct Observation	direct measurement	highly variable	variable, depends on soil type	limited only by sample collection method	0.01 feet
<i>In Situ</i> Measurement					
Surface Geophysical	indirect measurement	highly variable, depends on method and conditions	variable	up to 100 feet	min. detectable thickness increases with depth
Borehole Geophysical & Direct Push	direct or indirect measurement (depends on method)	generally high, depends on method and conditions	good, quantitative	limited only by the depth of the boring	typically less than 1 foot
Free Product Thickness in Wells	direct measurement	high, very reproducible	poor, qualitative (requires extrapolation)	limited only by depth of well	0.01 feet
Seepage in springs and surface waters	direct measurement/observation	low	poor, qualitative (present or absent, much or little)	not applicable	sheen

personnel. This information may not be credible or available for many sites.

Initial remedial activities often provide direct observations of the depth to water and the presence (or absence) of free product at the water table. Knowledge of the depth to water table is useful in selecting the method of defining the locations of free product. For example, in areas with very shallow water tables (less than 8 feet), test pits excavated by

backhoe may be the most cost effective approach to determining the extent of free product. If the geologic materials are coarse-grained sands or gravels, the test pits may also be used as temporary free product recovery trenches.

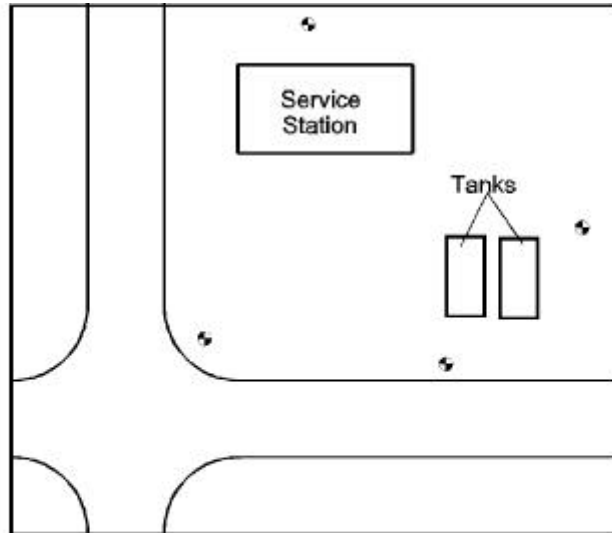
Indirect techniques to identify probable areas of free product may also be useful in focusing the free product investigation. However, these methods (*e.g.*, soil gas surveys, surface geophysical surveys) can be expensive, and the results can be difficult to equate with free product presence. One technique that holds some promise is soil gas monitoring for H₂S, which is associated with anaerobic conditions that may occur with the degradation of free or residual product in the soil (Robbins *et al.*, 1995).

The location of sampling or observation points should be focused in areas in the direction (*i.e.*, downgradient) that groundwater and free product are flowing. This direction may be inferred from the topography and location of surface water bodies (*e.g.*, streams, ponds). In shallow water table aquifers unaffected by pumping, the water table tends to be a subdued reflection of the topography (*i.e.*, groundwater flows from topographically high areas to topographically low areas). This general principle is useful in locating wells to define the direction of groundwater flow. Either traditional wells or well points may be used as locations to measure groundwater elevations. Well points, which are generally less expensive than traditional monitoring wells, can be installed with direct-push equipment during the initial site assessment phase. A minimum of three observation points (well points and/or wells) is required to define the groundwater flow direction. In addition, it is generally recommended that an additional observation point be installed upgradient of the suspected release area. These points must not all be located in the same line. If three points are used, they should be situated in an array that is approximately an equilateral triangle. If four (or more) points are used, they should be arranged in an approximately rectangular array as indicated in Exhibit IV-2. In all cases, whether monitoring wells or well points are installed, the well head or top of casing should be surveyed to establish the elevation.

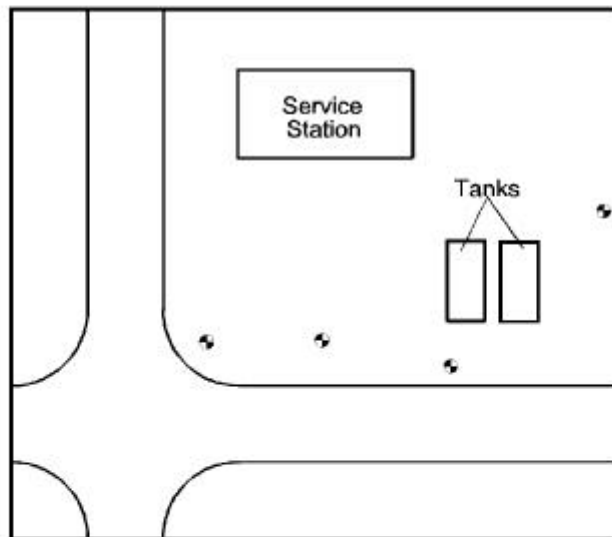
With the groundwater flow direction reliably established, additional sampling points, observation points, or wells/well points can be sited. Well installation and sampling activities generally proceed outward and downgradient from the source area. The areal extent of the plume is adequately delineated when the plume is encircled by a number of observation points (and/or wells/well points) that do not indicate the presence of free product (*i.e.*, no free product is present in the well). The precision of the areal definition of the free product plume depends upon the number of observation points and distances separating the observation

Exhibit IV-2

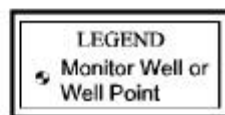
Sample Locations Of Wells/Well Points For Determining Groundwater Flow Direction



(a) Good spread, sensitive to any flow direction



(b) Poor spread, not sensitive to gradient or flow in SE-NW direction



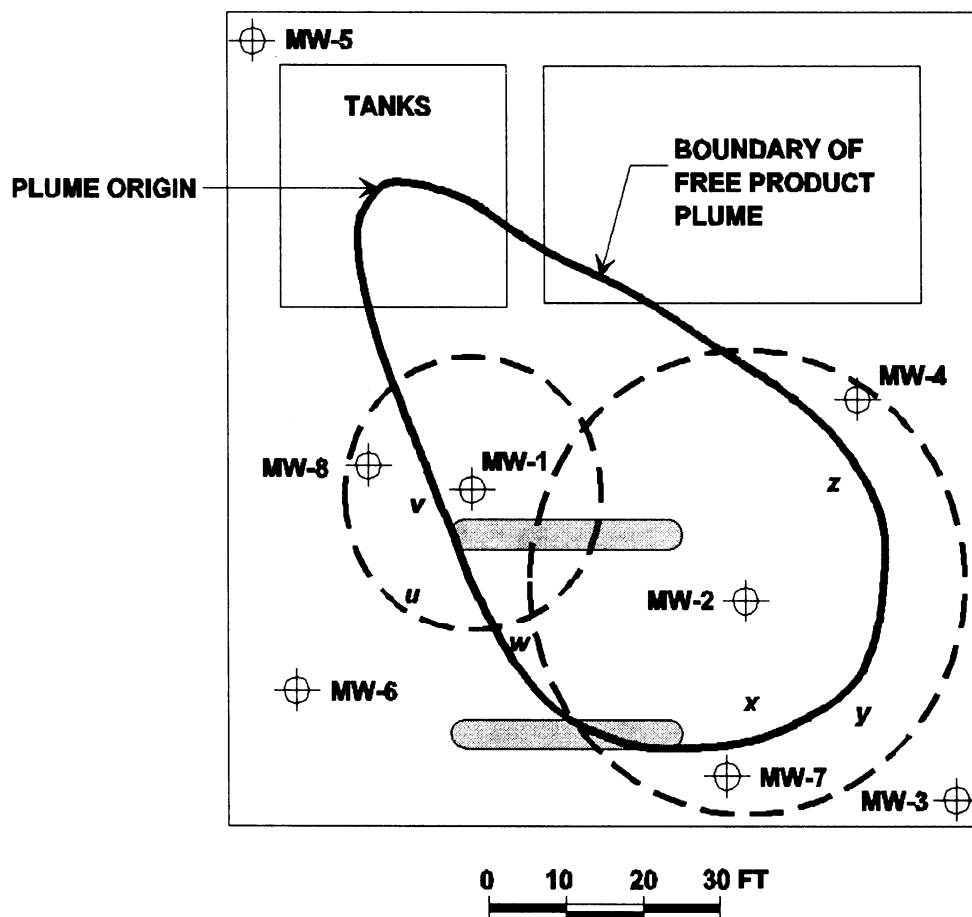
points both inside and outside the boundary of the plume. Although the precise number of observation points must be determined on a site-by-site basis, a sufficient number of observation points should be installed to ensure that no part of the plume is migrating in an unexpected direction. It is also important to realize how soil permeability and retention capacity affect the thickness and extent of the free product plume. For a given volume of free product released into a permeable soil (*e.g.*, sand, gravel), the plume will tend to be flat and relatively broad in extent. The same volume of free product if released into less permeable soil (*e.g.*, silt, very fine sand), will form a thicker plume (especially near the point of release) and the spread will not be as broad. The decrease in plume thickness near the plume boundary is more rapid in tight formations than in permeable formations. The consequence of this is that in tight formations the distance separating inside and outside wells should be less than in permeable formations or the extent of the free product plume is likely to be overestimated.

By its nature, plume delineation is largely a trial-and-error process; the location of each additional observation point is selected based on results of the preceding ones. Because it is not practicable to install an infinite number of observation points, there needs to be a logical and systematic method which can improve plume delineation. First, we will make the assumption that the plume boundary is located half-way between two suitably positioned—one inside the plume and one outside the plume—observation points. For regular-shaped plumes (*e.g.*, circular or elliptical) the accuracy of the delineated plume area will be about ± 40 percent of the actual area. Second, we will introduce a few guidelines for suitably positioning observation points.

The well locations depicted in Exhibit IV-3 are intended to illustrate key points of the following discussion; they are not intended to be interpreted as examples of “ideal” well placement. In general, observation points that are situated within the plume boundaries can be considered to be either interior (*e.g.*, MW-2) or perimeter (*e.g.*, MW-1). For perimeter observation points, the distance between observation points located inside and outside of the free product plume should be less than 40 percent of the distance from the inside observation point to the plume origin. For example, the dashed circle around MW-1 has a radius of 16 feet, which is 40 percent of the distance (40 feet) from MW-1 to the plume origin. Well MW-8 is located within this radius and the mid-point between the two wells (marked as point “v”) is relatively close to the actual plume boundary. Error in the estimated boundary increases with distance beyond this radius. For example, well MW-6 is considerably outside the 16 foot radius and the midpoint (point “u”) significantly overestimates the plume boundary. For interior observation points, these

Exhibit IV-3

Placement Of Observation Points For Delineation Of Free Product Plume



conditions are reversed. Well MW-2 is an internal observation point, which lies 70 feet from the plume origin. The dashed circle around MW-2 has a radius of 28 feet (40 percent of 70 feet). Note that wells either on this radius (MW-4) or inside (MW-7), result in an underestimation of the plume boundary (points “x” and “z”, respectively). The midpoint (point “y”) between wells MW-1 and MW-3 (just slightly outside the 28 foot radius) is reasonably close to the actual plume boundary. If the observation point is too far outside the radius, then the extent of the plume will be overestimated. For both interior and perimeter wells, interpolation accuracy is improved if a straight line between the two observation points intersects the plume boundary at a right angle. Significant deviation from 90° results in increasing error in estimation of the plume boundary. As may be expected, there are exceptions to these guidelines. For instance, the midpoint (point “w”) between MW-2 and MW-6 is reasonably close to the actual plume boundary despite the fact that a line drawn between the two wells intersects the boundary at an angle significantly different from 90°. In spite of the uncertainty in this process, a line beginning at the plume origin drawn so that it connects points v-w-x-y-z and returning to the origin is a reasonable approximation of the actual plume boundary. The approximation could be improved by adding additional observation points to fill in the gaps: Near point “w”, between MW-3 and MW-4, and between MW-1 and MW-4. Exhibit IV-4 shows alternative observation point spacing for free product plumes of various sizes and shapes. In reviewing a free product recovery plan, the adequacy of the delineation of the free product plume is one of the first technical factors to be checked. If the extent of the plume is not defined in all directions from the source area (plume origin), then more site characterization is required. This deficiency frequently occurs when the free product plume is not defined beyond the site property boundary.

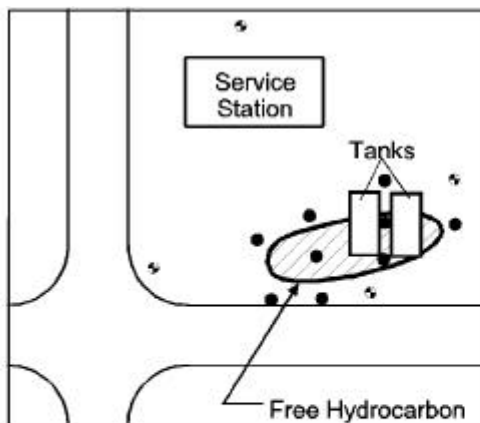
Excavations And Test Pits

Excavation of tanks or pipelines is commonly performed soon after a hydrocarbon release has been confirmed or suspected. These excavations provide for direct observation of the areal and vertical distribution of hydrocarbons. Such observations, if noted and located on a sketch map, can be used to partially identify the extent of free product. However, where the water table is below the maximum depth of the excavation equipment, the extent of lateral spreading at the water table won't be defined.

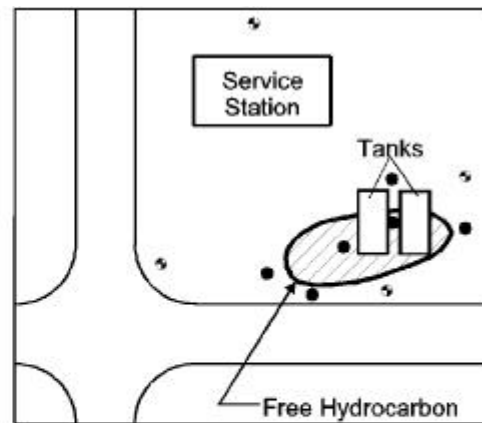
For those sites where the water table is very shallow (*i.e.*, less than 8 feet), excavation of test pits can be a quick and cost effective approach to delineating the extent of free product. Direct observations of the geologic media and potential preferential permeable pathways or barriers can also

Exhibit IV-4

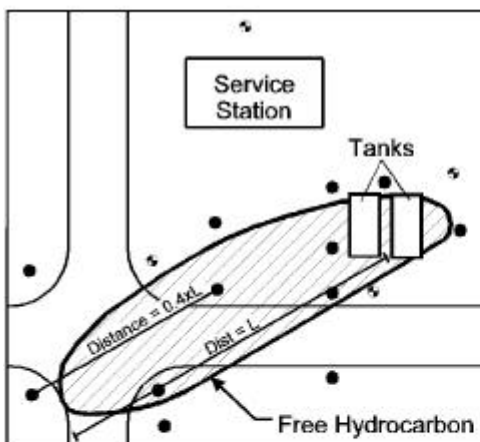
Delineation Of Free Hydrocarbon Plume Extent Using Soil Borings Or Probes And Monitoring Wells



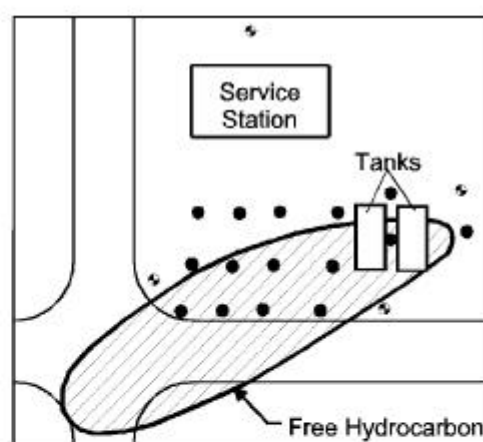
(a) Small plume, well defined in all directions, distance between soil borings about 20 feet



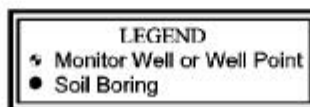
(b) Small plume, not delineated in NW direction



(c) Large plume, defined in all directions, with borings spread at reasonable locations



(d) Large plume, not delineated offsite-unacceptable



be obtained from test pits. The practicality of using of test pits diminishes with depth. Entry into test pits greater than 4 feet requires shoring, a trench box, or sloping of the sides of the excavation to protect workers from cave-in. Such measures although necessary, can be expensive and time consuming to construct or install. In some cases observations can be made from the surface without actually entering the excavation, but visual inspection of deep test pits from the surface is more difficult and less reliable than in shallow test pits. Also, excavated materials, if contaminated, will have to be handled appropriately (*e.g.*, treatment/disposal) which can add to the expense of the investigation.

Soil Borings

The three-dimensional distribution of liquid hydrocarbons can best be determined through a systematic program of soil sampling and free product thickness measurements. These observations may be collected through the use of traditional soil boring and sampling equipment or direct push (DP) technologies. Traditional soil boring techniques include augers (both drill rig-operated hollow-stem and solid stem as well as hand augers) and other rotary drilling methods. Core samples collected by auger rigs are typically obtained using split-spoons and shelby tubes. Direct push technologies, which are also known as “direct drive” and “soil probe” technologies, also include cone penetrometer (CPT) and relatively simple, mechanically assisted push samplers (*e.g.*, impact hammers, hydraulic presses).

DP systems drive, push, and/or vibrate small-diameter steel rods into the ground. These rods may be fitted with specialized tools to collect subsurface samples and data either continuously or over discrete intervals. A wide variety of sampling tools is available for collecting samples of solids (soil), liquids (free product and groundwater) and gas (soil vapor). CPT cones are specially designed to collect continuous lithologic data as the tools are pushed at a constant rate into the subsurface. The presence of free product can be detected using laser induced fluorescence (LIF) technology or other *in situ* analytical screening methods.

DP technologies are generally suitable to depths of up to 100 feet under ideal conditions (*i.e.*, unconsolidated soils free of coarse gravels and cobbles), but at most sites the depth range is between 20 and 60 feet. Deeper penetration typically requires rotary (air or mud) drilling methods. Manual techniques are generally only practical to depths between 0 and 15 feet. None of the DP technologies is applicable for sites overlying bedrock, large cobbles or boulders, or cemented sedimentary rock. Under such circumstances, even augers may not be suitable, in which case rotary drilling/coring techniques may be required.

Direct push techniques offer the following advantages relative to standard soil boring methods:

- ! Ability to collect samples rapidly and obtain a large number of samples.
- ! Capability to collect samples of soil, liquid, and gas.
- ! Little or no generation of soil cuttings.
- ! Deployment vehicles are more mobile and require less overhead clearance than drill rigs.
- ! Lower cost per sample in most settings.

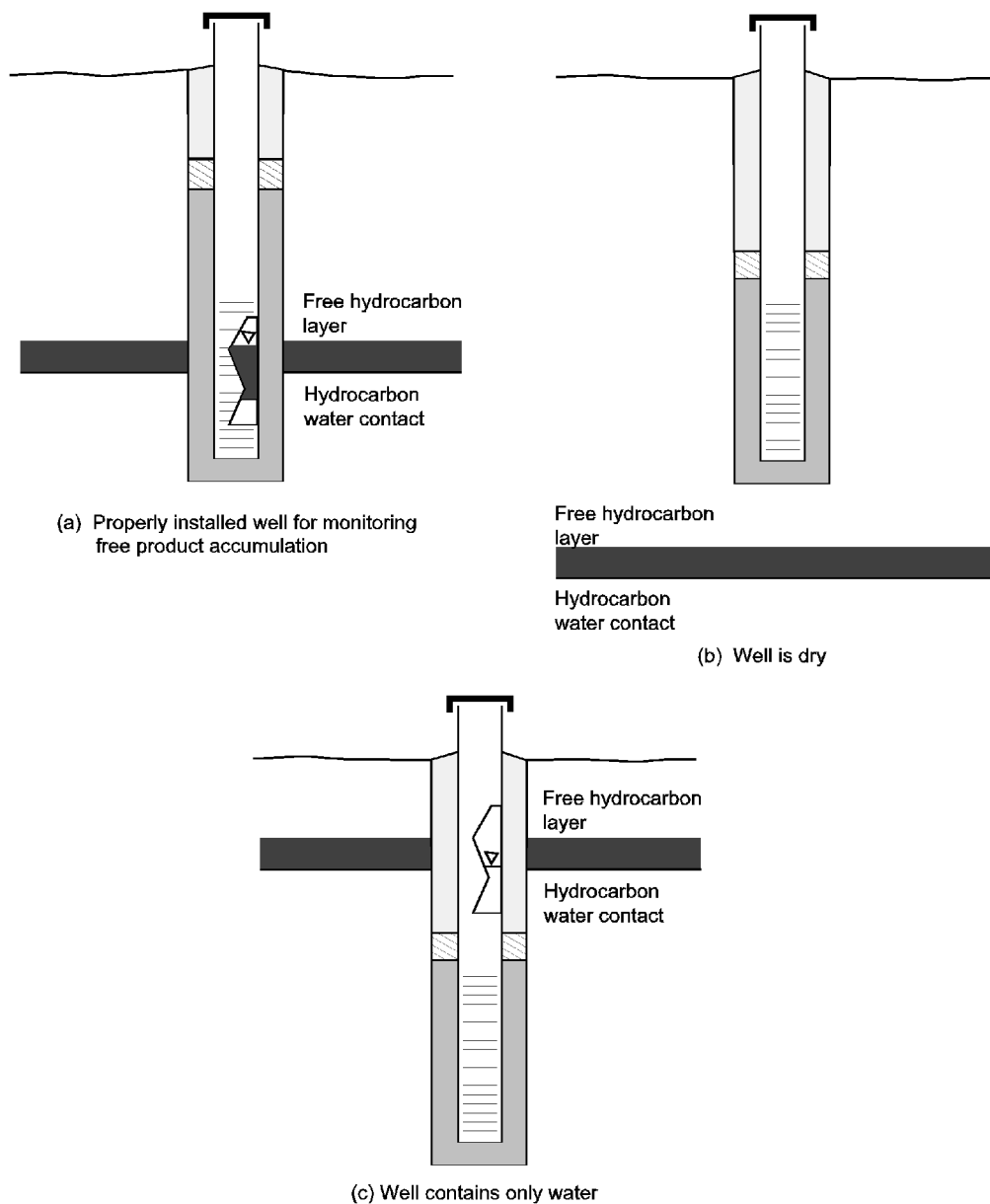
At sites where the use of DP technologies is appropriate, characterization of the subsurface can be more comprehensive than is typically achieved using traditional methods. Where free product recovery (or other remedial alternatives) is required, a more efficient and cost-effective system can be designed for sites that are better characterized. The additional expense of a site characterization conducted using DP technologies can be recovered (possibly many times over) in savings achieved during the remediation phase. However, because the size of the DP borehole is small, installation of free product recovery wells usually must be accomplished with traditional drilling rigs.

Monitor Wells

Properly installed and constructed monitor wells can be used both to delineate the extent of free product and monitor temporal changes in free product accumulations. However, it is also important to realize that monitor wells are subject to significant limitations in their ability to provide accurate measurements of the thickness of free product in the surrounding soil. Free product can accumulate in a well only if the well is open (*i.e.*, screened) across the zone of free product (Exhibit IV-5a). A well screened above the water table will generally be dry (Exhibit IV-5b). A well screened below the zone of free product will collect water but no free product (Exhibit IV-5c). Within a well with a properly positioned screen, the thickness of free product typically fluctuates in response to changes in water table elevation. With each rise (or fall) in water table elevation, the measured thickness of free product also changes, resulting in a different calculation of “actual” thickness in the soil (Durnford, *et al.*, 1991). Where a free product recovery plan relies on wells for free product delineation, the reviewer should check the construction diagram of each well and verify that the open (screened) interval of each well straddles the

Exhibit IV-5

Monitoring Well Installations And Their Ability To Detect Free Product



Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted courtesy of the American Petroleum Institute.

water table. Where wells are initially installed with short screens (*i.e.*, 5 feet or less), changes in the water table elevation may result in a dry well (declining water table) or in a well that is screened below the zone of free product (rising water table). Even in properly constructed wells, the absence of free product may not necessarily indicate that petroleum hydrocarbons (including free product and residual and trapped fractions) are not present in the soil. Similarly to the observation that water may take days or weeks to enter some monitor wells constructed in clayey soil, free product may not initially appear in monitor wells. Such a condition indicates that the relative permeability with respect to free product is very low, hence the mobility of the free product is also low. This may also result in a lower calculated volume of free product.

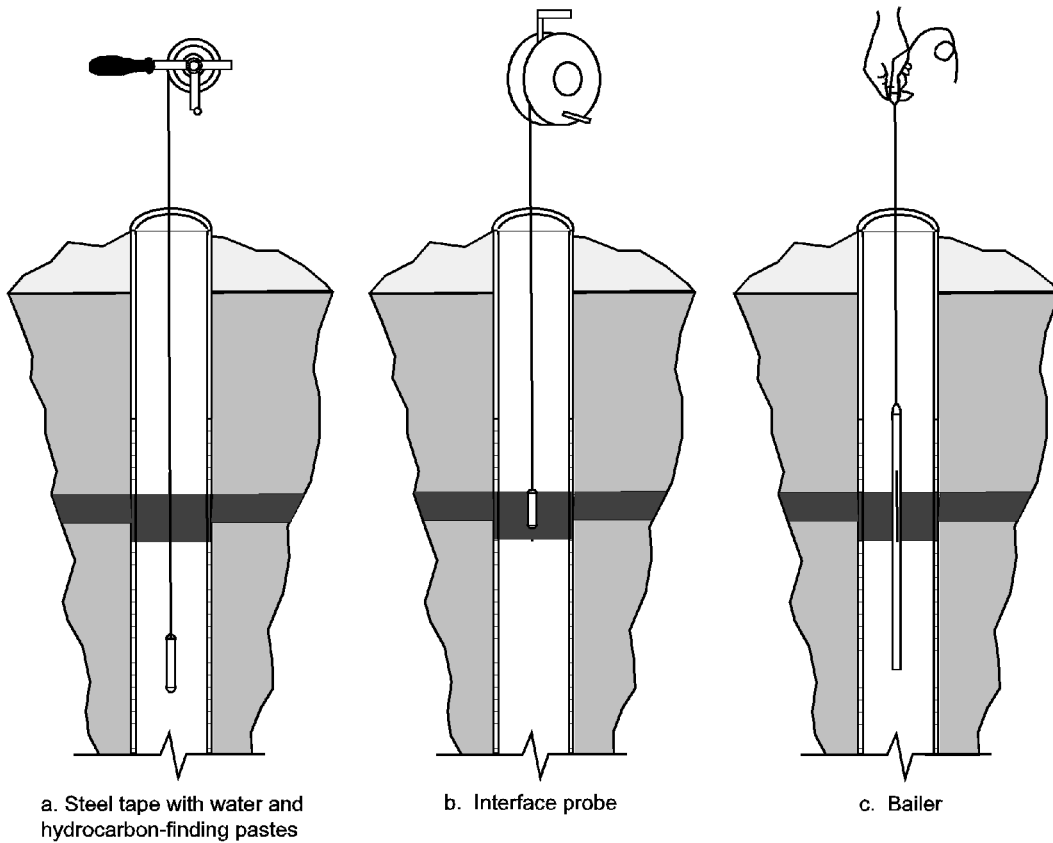
Monitor wells may be installed by any of several methods. (See Driscoll, 1986, and Aller *et al.*, 1989, for detailed descriptions of modern well drilling methods.) For unconsolidated media, hollow-stem augers are used most commonly. The well casing and screen are inserted through the opening in the auger. Depending on the stability of the well bore, the sand pack, sealing, and grout can be placed as the augers are retracted or after the augers have been removed. After the monitor well has been constructed, it should be developed by surging or pumping until water is free of turbidity. The development of new wells in very fine grained materials may not be practical because of its slow recharge rate. For a well with a slow recharge rate, development involves dewatering the well and allowing it to recover for one or more cycles. The development of the monitor well will tend to pull in free product and overcome capillary barriers as a result of the smearing of fine-grained material on the well bore. Without adequate development, free product may accumulate very slowly in the monitor wells (over a period of months). In these cases, initial estimates of the extent of free product may be understated. Product may also enter slowly, or not at all, if the wrong sized sand (filter) pack has been installed. The sand (filter) pack must be four to six times coarser than the aquifer material (Hampton and Heuvelhorst, 1990). The rate of product entry and recovery in wells can be improved by using hydrophobic filter packs (Hampton, 1993).

The presence of free product at a well is indicated by the accumulation of a measurable thickness of hydrocarbons in it. Three following methods (see Exhibit IV-6) are commonly used to measure free product thickness in a well:

- ! Steel tape and paste
- ! Interface probe, and
- ! Bailer.

Exhibit IV-6

Methods For Measuring Accumulations Of Free Liquid Hydrocarbons In A Well



Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted courtesy of the American Petroleum Institute.

The pastes used with the steel tape are sensitive to hydrocarbons and water. Commercially available interface probes sense the presence of both oil and water. The first two methods are accurate to within about 0.01 foot and are convenient for determining the elevation of the air/free product and oil/water interfaces. Whenever possible measurements should be taken using either steel tape and paste or an interface probe. A bailer is a transparent cylinder with a check valve at its base. The bailer method can significantly under- or over-estimate the thickness of free product in the well and should not be used for determining the elevations of air/free product and free product/water interfaces. Disposable bailers, which are commonly dedicated to monitoring wells containing free product, typically collect an unrealistically small product thickness because of the small size of the intake holes. The use of bailers should be limited to verification of the presence of free product in a well or collection of a sample of it. Bailers can be used to remove liquids from monitoring wells during bail-down tests that are designed to determine the rate of free product recovery into wells.

Volume Estimation

Knowledge of the volume of hydrocarbons in the subsurface is useful for evaluating the performance of a free product recovery system in terms of both total volume recovered and time required for recovery. In some instances the original release volume may be unknown but can be estimated by calculating the volume of free product present in the subsurface. Several methods can be used to estimate hydrocarbon volumes. These include:

- ! Compilation of historical information on release events and from inventory records.
- ! Soil sampling and analysis for total petroleum hydrocarbons.
- ! Correlation of the thickness of free product measured in monitoring wells to total volume of free product.
- ! Evaluation and projection (extrapolation) of free product recovery data.

The first two approaches yield estimates of total hydrocarbons—residual and free—present in the subsurface. The last two methods—product thickness measured in monitor wells and recovery data—provide estimates of the volume of free product. None of these four methods are entirely precise in most settings because of limited and uncertain data. Even where

substantial data are available and several estimation methods used, volume estimates with an uncertainty of minus 50 percent to plus 100 percent are the best that can be expected. Exhibit IV-7 presents a brief summary of the salient points of each of these four methods.

The relative mass present as free and residual liquid hydrocarbons is large compared to the mass of dissolved or vapor phase hydrocarbons in most subsurface settings. Residual hydrocarbons may represent as much as 50 to 80 percent of the total volume that was originally released. Recoverable free product typically represents 20 to 50 percent of the total. The ratio of free product to residual liquid hydrocarbons tends to decrease with time as plume migration and other processes occur that trap free hydrocarbons (*e.g.*, rising or falling water table). The relative permeability (and mobility) of the free product decreases as more of the free product is recovered and the level of liquid hydrocarbon saturation decreases. When the saturation approaches the residual saturation of the geologic medium, free product will stop flowing readily into monitor/recovery wells. At this point, the recovery well or recovery system should be switched to operate intermittently or possibly turned off altogether. Small quantities of liquid hydrocarbons may continue to slowly drain into wells, but the rates of drainage are usually not sufficient to justify continuous operation of the recovery system.

Volume Estimates Based On Release History

Historical records of release events and hydrocarbon inventories can be used to estimate the total amount of hydrocarbons lost. When accurate inventory or release data are available, the amount lost is likely to be greater than the amount in the subsurface as a result of volatilization and biodegradation. The reliability of historical data ranges widely, but generally, the older the information, the less reliable it is. Furthermore, historical data generally cannot be used to characterize phase distribution in the subsurface.

Even though volume estimates based on release and inventory data may have limited reliability, these estimates are useful in at least two important ways. First, the volume estimate based on historical data can be compared with volume estimates obtained with other approaches to provide a check on the other methods. Second, historical information on when releases began can provide a basis for initial estimates of the extent of free product migration that can be used to assist in locating sampling points and wells for site characterization.

Exhibit IV-7
Methods For Volume Estimation

Method	Approach & Results	Advantages	Disadvantages
Release History	Review inventory records to determine volume(s) and date(s) of release(s).	Relatively simple and statistically accurate if accurate historical data are available.	Data rarely accurate given numerous potential error sources (e.g., measurement technique, volume changes due to temperature)
TPH Concentration in Soil Samples ¹	Convert TPH concentrations in soil samples to saturations and integrate these values over the area of contamination.	Data are relatively easy to collect; several methods are available for data integration.	Calculations required are relatively complicated; requires a lot of data to reduce uncertainty associated with calculated volume; results may differ among various methods for data integration; TPH analysis may not be representative of actual petroleum hydrocarbon saturations.
Product Thickness in Wells	Measure the thickness of the accumulated layer of free product in all monitoring wells.	Free product thickness measurements in monitor wells are routinely collected on a regular basis; the thickness of the free product layer in the monitor well can be measured quite accurately; several methods are available for data analysis.	Product thickness in wells usually exaggerates the thickness in the aquifer--this effect is more pronounced in finer-grained geologic materials; none of the methods that correlate product thicknesses measured in wells to actual product thickness in the soil are reliable either in the field or in the laboratory.
Extrapolation of Recovery Data	Sum the cumulative product recovery volume and an estimate of the residual volume.	Recovery data are routinely collected.	Works best during later stages of recovery; many factors can bias recovery (e.g., smearing); requires two types of data.

¹ The U.S. Air Force is currently working on an alternative method of using TPH values based on examination of TPH fractions. EPA will release information on this process after peer review has been completed.

Volume Estimates Based On Soil Samples

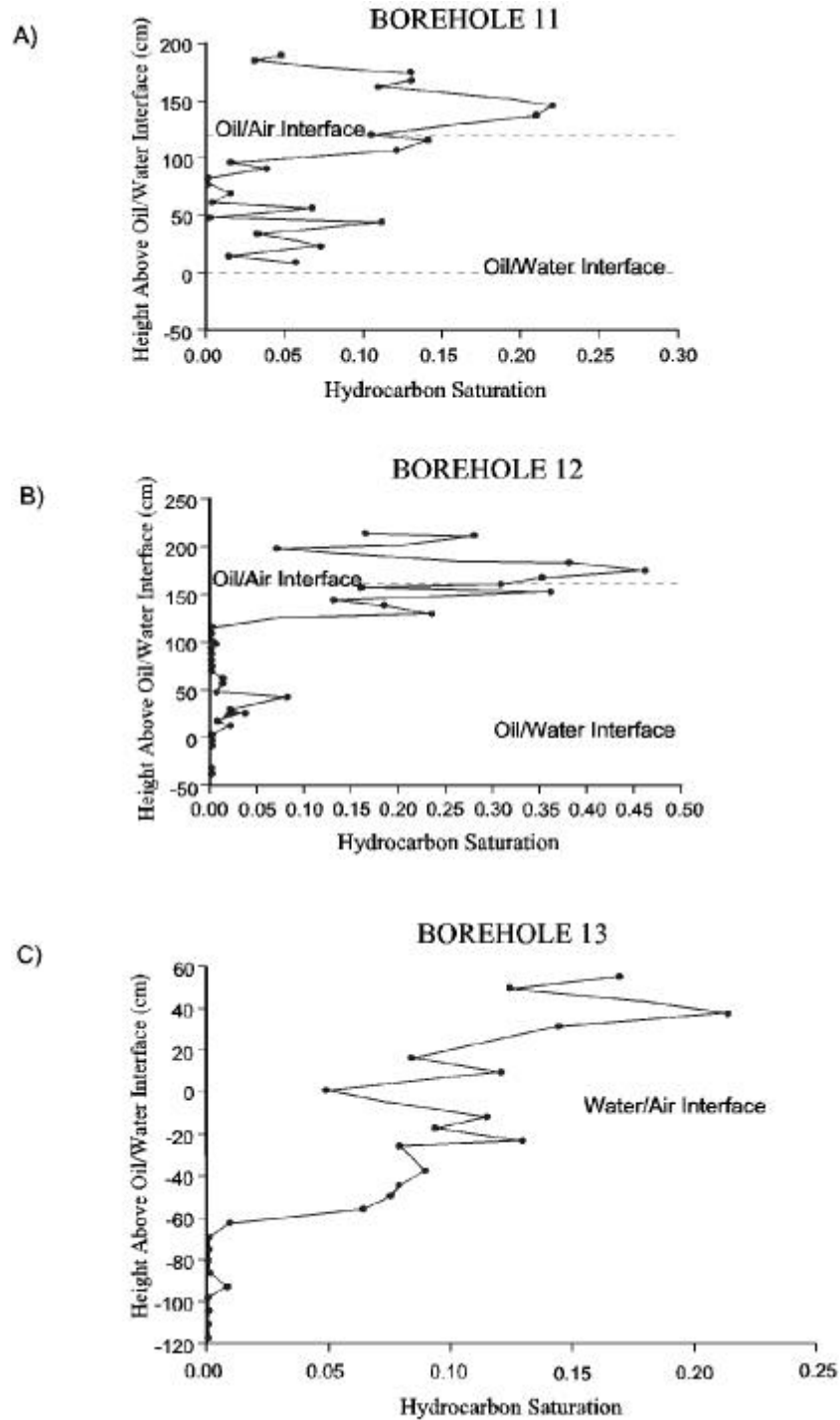
Estimation of the volume of free product in the subsurface based on soil sample data first requires the collection of soil samples and their subsequent analysis for hydrocarbon content. Hydrocarbon content in soil samples can be measured by a variety of standard laboratory methods. These methods include solvent extraction, solvent extraction with distillation, and centrifuging (Cohen and Mercer, 1993; Cohen *et al.*, 1992). The total petroleum hydrocarbons (TPH) analysis commonly used in site assessments is based on solvent extraction. For sites where sufficient TPH data are available, volumes of hydrocarbons in the unsaturated and saturated zones can be estimated. One limitation of TPH data is that it does not distinguish between individual petroleum hydrocarbons or between petroleum hydrocarbons and other non-petroleum organic matter that may be present in the soil sample.

The estimation of hydrocarbon volumes based on soil sample data is subject to significant uncertainty because of the sparseness of the data and the often extreme variability in hydrocarbon concentration within the soil. Exhibit IV-8 shows how variable hydrocarbon saturation can be within the same boring and between three different borings at a typical site. The detail shown in Exhibit IV-8 is much greater than that obtained during most site characterization investigations, but even with this amount of detail at one or more boring, there is still tremendous uncertainty about concentrations in the soil between the borings.

The procedure for estimating liquid hydrocarbon volumes from TPH data involves two calculation steps: (Step 1) TPH results are converted to saturation values at each point, and (Step 2) the volume of liquid hydrocarbons is determined by integrating point saturation data over the volume of subsurface where hydrocarbons are present. The conversion calculation (Step 1) is straightforward and is illustrated in Exhibit IV-9. Integration of the total hydrocarbon volume (Step 2) can be accomplished using standard interpolation and integration techniques. As a simple example, TPH (saturation) results are plotted at their collection locations on a site map. Contours of equal saturation are drawn on the map. The area and volume represented by each contour level is then calculated. Integration is merely the summation of the individual volumes. There are a number of more sophisticated techniques, including computer software, but discussion of these is beyond the scope of this manual. It is also important to recognize that interpolation and integration methods yield only approximations of what is actually present in the field and different methods using the same data set can result in volume estimates that range from minus 30 percent to plus 50 percent. In general, as the number of data points increases the error associated with the method decreases.

Exhibit IV-8

Measured Hydrocarbon Saturation Profiles At Three Boreholes Showing Variability Due To Vertical Heterogeneity



Source: From Huntley, et. al., 1992

Exhibit IV-9

Calculation Procedure To Convert TPH Data From Soil Samples To Hydrocarbon Saturations

TPH analysis results for soil samples may be converted to hydrocarbon saturation by the following equation:

$$S_o = \text{TPH} \times \frac{(1 - \phi) \rho_{gr} \times 10^{-6} \frac{\text{kg}}{\text{mg}}}{\phi \rho_o}$$

where:

- S_o = total hydrocarbon saturation (dimensionless)
- TPH = total petroleum hydrocarbon concentration in mg/kg
- ρ_{gr} = grain density (typically 2.65 g/cm³)
- ϕ = porosity (dimensionless)
- ρ_o = density of the hydrocarbon, liquid (g/cm³).

This equation applies to both the unsaturated and saturated zones.

The amount of free hydrocarbon present can be calculated if residual hydrocarbon saturation is known or estimated. Usually residual saturations are not known or measured, but literature values (*e.g.*, Mercer and Cohen, 1990) can be used as estimates. The free hydrocarbon saturation is given by:

$$S_{of} = S_o - S_r$$

where:

- S_{of} = free hydrocarbon saturation
- S_r = residual hydrocarbon saturation.

Volume Estimates Based On Product Thickness In Wells

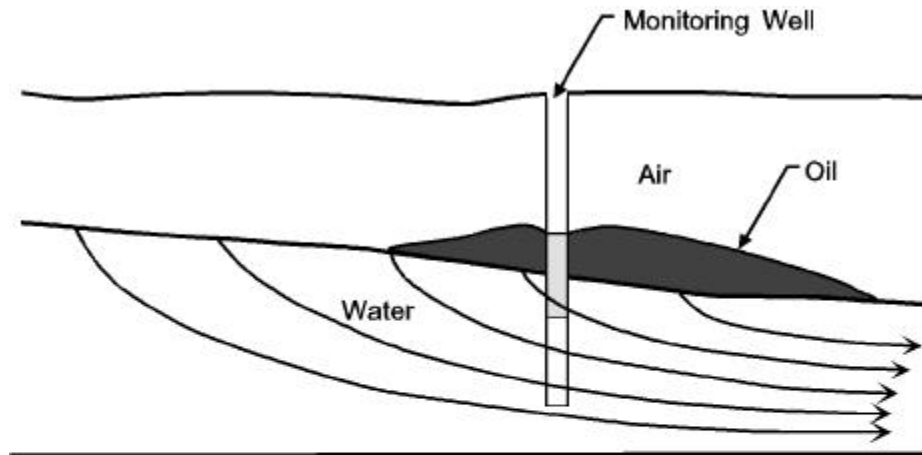
The limitations of monitor wells in providing representative measurements of free product thickness in the adjacent soil are well documented. Fluctuations in the water table can result in large differences in measured hydrocarbon thickness even though the in situ volumes are not significantly changed. Increases in hydrocarbon thickness are commonly observed with declining water tables. API (1989) attributes the thickness increase to drainage from the unsaturated zone. As the water table falls, hydrocarbons previously trapped as a residual phase can become remobilized and enter into wells. Kembrowski and Chiang (1990) relate the changes to preferential fluid flow through the well (Exhibit IV-10).

Many investigators have tried to develop methods to explain how small amounts of mobile hydrocarbons can lead to exaggerated thicknesses of hydrocarbons measured in wells. Hampton and Miller (1988) and Ballesterio *et al.*, (1994) provide comprehensive reviews of the methods used to estimate the thickness of free product in the adjacent soil from measurement in monitor wells. A comparison of the predictability of these alternative methods indicates an order of magnitude accuracy of the predicted versus the measured free product thickness among the methods. These investigations can be grouped into two primary approaches: (1) Derivation of empirically-based correlations--typically based on fluid density differences, grainsize of the geologic media, or height of the water capillary fringe, and (2) development of models based on idealized capillary pressure-saturation curves. In spite of the intense attention that has been focused on developing a correlation between free product thickness measured in wells and volume of free product in the soil, none of the available methods has been particularly reliable when tested either in the field (Durnford *et al.*, 1991; Huntley *et al.*, 1992; and Ballesterio *et al.*, 1994) or even in the laboratory (Hampton and Miller, 1988). Durnford *et al.*, (1991) summarize the limitations of the methods developed to relate the free product thickness measured in monitor wells to the volume of free product in the soil as follows:

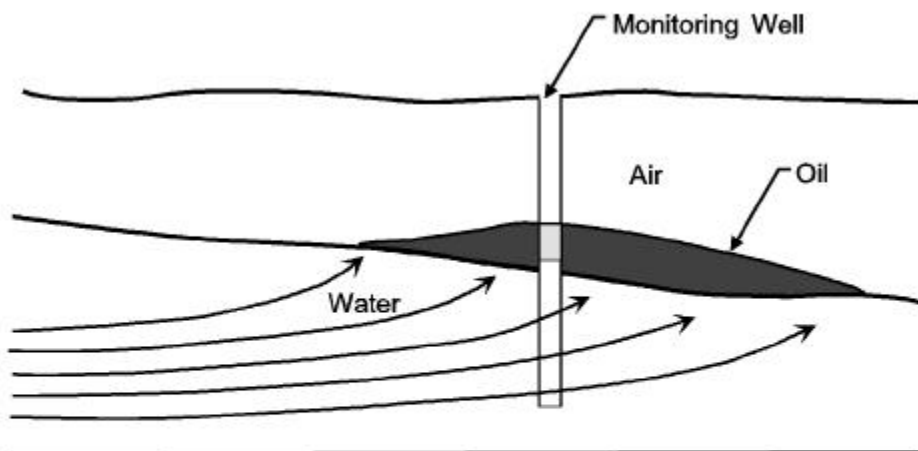
- ! Free product thicknesses observed in monitoring wells change over time as the water table fluctuates. Each different measured thickness of free product results in a different calculation of free product in the aquifer, even if the actual volume of free product (including residual and trapped) hasn't changed.

Exhibit IV-10

Effects Of Falling Or Rising Water Table
On Hydrocarbon Thicknesses Measured In Wells



(a) Hydrocarbon thickness increase for falling water table



(b) Hydrocarbon thickness decrease for rising water table

Source: Kemblowski and Chiang, 1990

- ! None of the estimation methods accounts for residual and trapped petroleum hydrocarbons—a portion of these fractions can be returned to the free product fraction as the water table moves up or down.
- ! Methods that are based on measurement of soil and fluid properties require measurements (*e.g.*, curves of capillary pressure vs water saturation) that are difficult to obtain in the field, and laboratory-derived measurements may not accurately represent field conditions.
- ! None of the methods account for spatial variability (heterogeneity) of aquifer parameters. The movement of free product is strongly dependent upon aquifer heterogeneities, which are rarely represented adequately by “average” properties.

Despite the drawbacks with these volume estimation methods, they are frequently used in practice. To illustrate how some of these methods are used, we present a comparison of seven methods reported in Ballesterro *et al.*, (1994). The seven different approaches can be grouped into the following four categories:

- ! Correlation based on the density of the liquid hydrocarbon (de Pastrovich *et al.*, 1979);
- ! Correlation based on properties of the geologic medium (Hall, *et al.*, 1984);
- ! Correlation based on the height of the water capillary fringe (Blake and Hall, 1984; Ballesterro *et al.*, 1994; and Schiegg, 1985); and
- ! Models based on idealized capillary pressure relationships for homogeneous porous media (Farr *et al.*, 1990; and Lenhard and Parker, 1990).

Exhibit IV-11 summarizes the results of calculations for each of the different methods listed above using data from laboratory experiments reported by Abdul *et al.*, (1989), with additional parameter values acquired (where necessary) from the individual papers. A more complete presentation (including the equations, variable descriptions, input data and discussion of the salient features) is included in the Appendix. It is

Exhibit IV-11

Comparison Of Seven Alternative Methods For Correlation Of Product Thickness Measured In A Monitor Well To Actual Thickness In The Soil

Calculated Results (Hydrocarbon Thickness in Soil)

Measured hydrocarbon thickness in the soil (cm)	de Pastrovic h <i>et al.</i> (1979)	Hall <i>et al.</i> (1988)	Blake and Hall (1984)	Ballestero <i>et al.</i> (1994)	Schiegg (1985)	Farr <i>et al.</i> (1990)	Lenhard and Parker (1990)
---	1.1	-6.5	-16	-16	-28	2.3	7.1
1	12	50.5	1.1	1.1	29	24.3	74.3
3	13	55.5	4.4	4.4	34	26.2	80.2
7	13.9	60.5	9.7	9.7	39	28.1	86.1
13	16	71.5	13.4	13.4	50	32.4	99.1

Note: All values in centimeters except those for Farr *et al.* (1990) which are volume in cm³/cm².

This comparison is based on a study published by Ballestero *et al.* (1994) using data published in Abdul *et al.* (1989). Additional data required for the methods of Lenhard and Parker (1990) and Farr *et al.* (1990) were obtained from their respective papers. Note that the results presented above are only applicable for the data specified in this example. The use of different data may alter the relative performance of the methods. Refer to the Appendix for a more complete presentation of the individual equations used in this comparison.

important to realize that the relative performance of these methods is dependent upon the specific experimental conditions. Given another set of data obtained from a different experiment using different soil (with different grainsize, porosity, and residual saturation) and different liquid hydrocarbon, the relative performance may be radically different. To reiterate from the opening paragraph in this section, none of the available methods has been particularly reliable when tested in either the field or the laboratory. For any given site, it is probably not likely that the method that will ultimately yield the closest match to conditions in the field can be chosen *a priori*. However this is not to say that there is no point in using these methods to estimate free product volumes. On the contrary, free product thickness data collected from monitor wells is typically plentiful, easily collected, and is usually accurate. In many instances these data may be all that are available. What is most important is to not rely too heavily on one method over another. The best approach is to use more than one method so that a probable range of volumes can be calculated.

Volume Estimates Based On Extrapolation Of Free Product Recovery Data

The difference between the volume of free product released and the volume recovered equals the volume remaining in the subsurface. Often the volume of the release is not known, but in theory it can be determined if the volume of free product that has been (or is anticipated to be) recovered and the volume remaining (or is anticipated to remain) in the subsurface is known. Knowledge of any of these three volumes is associated with a degree of uncertainty, and it is usually not possible to quantify the error associated with estimates of these volumes. Many factors contribute to this uncertainty. Some of the components of the types of petroleum hydrocarbons typically stored in USTs are volatile and/or soluble, and are therefore not likely to be measured as residual hydrocarbons. Biodegradation may further decrease the amount of hydrocarbons present in the subsurface. As was discussed previously, hydrocarbon saturations in soil borings are highly variable in both the vertical and horizontal directions. Samples with anomalously high or low saturations can bias estimates of total residual hydrocarbons remaining in the subsurface. Also, it is important to recognize that the rate of free product recovery typically exhibits a logarithmic decrease with time. The rate of decrease can be quite variable even on the same site due to heterogeneities in the soil which influence residual saturation and relative permeability. The estimate of product remaining in the subsurface as either free or residual changes constantly with time as recovery progresses. Despite these limitations, this method may offer the best (or only) means

for estimating volumes at a particular site. Although this method works best late in the recovery phase (after the cumulative recovery curve levels off), it can be used at any time with the understanding that volume estimates based on early recovery data will be associated with a higher degree of uncertainty. Methods to estimate free product recovery rates are presented in the following sections.

Estimation Of Recovery Rates

An important design consideration for free product recovery is the rate at which liquid hydrocarbons can be collected by pumping or skimming techniques. The rate of recovery will depend on the design of the recovery system, the type(s) and distribution of free product in the subsurface, and the hydrogeological conditions. Expected recovery rates are used to size the free product storage tanks and oil/water separators, and, to a lesser degree, to select and size recovery equipment and treatment equipment. Not only is it important to estimate the initial recovery rates but also to predict how the recovery rates will change with time after recovery starts. Estimates of recovery rates can be obtained from field tests (*e.g.*, bail down tests, pumping tests) or from multiphase flow analysis. Usually, recovery rates of free product decline after startup because wells and trenches are located in areas where the volumes of free product are highest. In some settings where wells or trenches pull free product from some distance, recovery rates may increase for a significant duration before declining.

Bail Down Test And Pumping Tests

A bail down test involves removing the free product from a well by bailing and measuring the thickness of and depth to free product in the well as it recovers. These tests have been used to estimate free product thickness by some investigators (Hughes *et al.*, 1988; Wagner *et al.*, 1989; and Gruszczenski, 1987) with limited success. These tests can easily provide estimates of initial recovery rates for a skimming type operation (see Exhibit IV-12, Method 1). In order for the results of a bail down test to be applicable, the free product recharge rate should be slow relative to the rate of groundwater recharge. Where free product recharges the well in less than a few minutes, it is difficult to accurately monitor recovery rates (Hampton, 1993).

Exhibit IV-12

Sample Calculations For Estimating Initial Free Product Recovery Rates

Method 1. Bail down testing (Applicable to skimming-type recovery systems).

Inside Diameter of Well Screen = 4 inches
Radius = 2 inches
= 0.166 foot

1. Maximum thickness from table. = 1.15 feet
2. 80% x maximum thickness recovery.
(0.8 x 1.15) = 0.92 foot
3. Time corresponding to 80% of recovery interpolated from table.
3 hours 24 min = 204 min
4. Compute gallons per foot of oil thickness in well screen.

$$\frac{\pi \times (\text{well radius in ft})^2 \times (\text{conversion factor in gal/ft}^3)}{\pi \times (0.166)^2 \text{ ft}^2 \times 7.48 \text{ gal/ft}^3} = \text{gal/ft}$$

$$= 0.65 \text{ gal/ft}$$
5. Compute average recovery rate to 80% recovery.

$$0.65 \text{ gal/ft} \times 0.92 \text{ ft} / 204 \text{ min} = 0.003 \text{ gal/min} = 4.2 \text{ gal/day}$$

Field Data

Recovery Time	Free Product Thickness (ft)
2 min	0.01
4 min	0.03
10 min	0.12
30 min	0.30
1 hour	0.51
2 hours	0.85
4 hours	0.95
8 hours	0.98
24 hours	1.15
48 hours	1.10

Method 2. Constant rate pump test (Applicable to free product recovery with water level depression).

Pumping Rate = 10 gal/min

1. Compute average hydrocarbon recovery rate from table for 24 hours.

$$\frac{52.1 \text{ gal/24 hours}}{24 \text{ hours}} = 2.17 \text{ gal/hour}$$

$$= 0.0361 \text{ gal/min}$$
2. Compute

$$\text{Hydrocarbon Recovery Ratio} = \frac{\text{Hydrocarbon Recovery Rate}}{\text{Total Pumping Rate}}$$

$$\frac{0.0361 \text{ gal/min}}{10 \text{ gal/min}} = 0.00361 = 0.361\%$$

Field Data

Time Since Pumping Started	Cumulative Hydrocarbons Collected
10 min	0.0 gal
20 min	0.3 gal
40 min	0.8 gal
1 hour	2.5 gal
2 hours	5.8 gal
4 hours	14.6 gal
8 hours	23.8 gal
24 hours	52.1 gal

For systems where free product will be collected by active pumping of groundwater and product, a pumping test can be used to estimate initial free product recovery rates (see Exhibit IV-12, Method 2). Pumping tests (or aquifer tests) are usually performed to determine groundwater flow properties such as hydraulic conductivity and transmissivity. Estimates of free product recovery rates can be obtained by collecting additional data in conjunction with a standard (groundwater) pumping test or by conducting a specialized pumping test or pilot test.

A standard pumping test involves pumping groundwater at a constant rate and monitoring changes in groundwater elevations in the pumping and nearby wells during the test. If free product is present in the vicinity of the well, the pumped fluid will contain both free product and groundwater. The ratio of free product recovered to total fluid recovered can be determined at different times during the test by collecting samples of pumped fluid. These samples may show considerable variability, so as many samples as practicable should be collected during the test. Where the ratios of recovered product to total fluid are more than a few percent, simple volume measurements of the separated liquids may be used to determine the recovery ratio (see Exhibit IV-13). Usually the recovery ratio of free product to total fluid is less than a few percent, in which case the ratio may be determined by a standard TPH or oil and grease analytical method.

Estimates of free product recovery rates can also be obtained from pilot tests or records of free product pumping that may have been performed as an interim or emergency removal action. Information from pilot tests or prior free product recovery systems provide the best estimates of expected free product recovery rates because the duration and rates of pumping are usually much greater than those of bail down or pump tests.

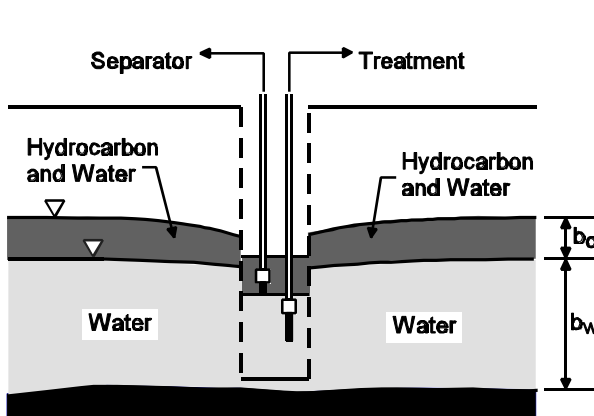
Multiphase Flow Analysis

The theory of multiphase flow in porous media has been widely used in petroleum reservoir engineering for over 50 years. During the past decade, these same theories have been applied to analysis for environmental applications. Because multiphase flow theory results in complex non-linear partial differential equations, few simple solutions to practical problems are available. One such solution is presented in the preceding section (see Exhibit IV-13). Commonly, the governing equations are solved by a variety of sophisticated numerical techniques using computer models.

Exhibit IV-13

Computational Procedure For Determining Ratio Of Free Product Recovery To Total Fluid Recovered From A Single Recovery Well

Basic Equations:



$$\text{Mobility of Water} = \frac{k k_{rw} \rho_w g}{\mu_w}$$

$$\text{Transmissivity of Water } T_w = \frac{b_w k k_{rw} \rho_w g}{\mu_w}$$

$$\text{Mobility of Free Product} = \frac{k k_{ro} \rho_o g}{\mu_o}$$

$$\text{Transmissivity of Free Product } T_o = \frac{b_o k \bar{k}_{ro} \rho_o g}{\mu_o}$$

where:

k is the intrinsic permeability (L^2)

k_{rw} is the relative permeability of water (dimensionless)

k_{ro} is the relative permeability of free product (dimensionless)

\bar{k}_{ro} is the average relative permeability of free product layer (dimensionless)

ρ_w is the density of water (ML^{-3})

ρ_o is the density of free product (ML^{-3})

g is the gravitational constant (LT^{-2})

μ_w is the viscosity of water ($ML^{-1}T^{-1}$)

μ_o is the viscosity of free product ($ML^{-1}T^{-1}$)

b_o is the thickness of free product layer (L)

b_w is the thickness of aquifer below free product layer (L)

Assumed: Water transmissivity of free product layer is negligible

Exhibit IV-13 (continued)

Computational Procedure For Determining Ratio Of Free Product Recovery To Total Fluid Recovered From A Single Recovery Well

General Equation:

$$\text{Ratio} \left(\frac{\text{Free Product Recovery Rate}}{\text{Total Fluid Recovery Rate}} \right) = \frac{Q_o}{Q_o + Q_w} = \frac{T_o}{T_o + T_w}$$

$$= \frac{b_o \bar{k}_{ro} \rho_o / \mu_o}{b_o \bar{k}_{ro} \rho_o / \mu_o + b_w \rho_w / \mu_w}$$

where:

Q is volumetric flowrate of free product (o) or groundwater (w)

Assumed: Same hydraulic gradients exist in free product layer and groundwater

EXAMPLE:

A 2-foot-thick hydrocarbon layer has an average hydrocarbon saturation of 0.5, a viscosity of 4 centipoise, a density of 0.9 g/cm³. The average relative permeability for a free product saturation of 0.5 is assumed to be 0.25. The pumping well is screened across the hydrocarbon layer to the base of the aquifer which has a saturated thickness of 20 feet including the hydrocarbon layer.

$$\frac{Q_o}{Q_o + Q_w} = \frac{T_o}{T_o + T_w} = \frac{2\text{ft} \times 0.25 \times 0.9\text{g/ml} / 4\text{cp}}{2\text{ft} \times 0.25 \times 0.9\text{g/ml} / 4\text{cp} + 18\text{ft} \times 1\text{g/ml} / 1\text{cp}}$$

$$= \frac{0.1125}{0.1125 + 18} = 0.0062$$

For a total fluid production rate ($Q_o + Q_w$) of 2 gallons per minute, determining free product recovery rate, Q_o .

$$Q_o = \text{Ratio} \times (Q_o + Q_w) = 0.0062 \times 2 \text{ gpm} = 0.0124 \text{ gpm}$$

Calculations Of Initial Free Product To Total Fluid

Recovery Ratio. A straightforward calculation based on the relative mobility of free product and water can be used to determine the ratio of free product to total fluid production under pumping conditions in a single well. This procedure is described and illustrated in Exhibit IV-13, which shows that for thin hydrocarbon layers and moderately high viscosities, the recovery of free product will be a small portion of the total fluid production in the well.

Use Of Computer Models. In theory, computer models based on multiphase flow concepts can be used to predict free product recovery rates. Selection of a model for a particular site must be made carefully because all models are not appropriate for all sites. Factors to be considered include; complexity of site geology, availability of input data, and special features of the site (*e.g.*, pumping wells, fluctuating water table). Some of the numerous multiphase flow models that have been developed include:

- ! Simplified models simulating downward migration of liquid hydrocarbons through the unsaturated zone, radial transport of a hydrocarbon lens in the watertable, and radial migration of hydrocarbons to a recovery well (El-Kadi, 1992; El-Kadi, 1994; Weaver *et al.*, 1994; and Charbeneau and Chiang, 1995).
- ! Complex numerical models (finite-difference and finite-element) of immiscible multiphase flow in porous media in cross-section or three-dimensional (Faust *et al.*, 1989; Kaluarachchi and Parker, 1989; Katyal *et al.*, 1991).
- ! Complex numerical models of areal hydrocarbon migration in unconfined aquifers simplified from 3-D to 2-D (Kaluarachchi *et al.*, 1990).

Despite the seemingly wide variety of models that are available, in practice the usability of models for reliable prediction of free product recovery rates is limited for a variety of reasons. Many of the models require data that are not measurable in the field (*e.g.*, relative permeability-capillary pressure relations). Mishra *et al.* (1989) present one solution to this problem; they developed a model to estimate relative permeability-capillary pressure relations from grain-size curves, which can be developed relatively easily from soil samples. The problem is that each soil sample would yield a different grain-size curve, and hence, different relative permeability-capillary pressure curves. As even subtle

heterogeneities can radically influence the movement of free product in the subsurface, no single curve is likely to be adequate to characterize the entire site. Collection of a sufficiently large number of samples may be prohibitive. Assumptions such as vertical equilibrium and vertical uniformity, which are usually required by the simpler two-dimensional models, are not generally applicable.

More often than not model simulations are very accurate only over the period for which field data are available. Models are calibrated given a set of field data (*e.g.*, water table elevations, volume of product recovered) collected over a specified period of time. Model parameters are then adjusted so that the simulated results as closely as possible match the field data. As more field data are collected, model parameters are adjusted so that the simulation results once again closely match the field data. This process is typically repeated every time additional data are available. Often the final set of model parameters is quite dissimilar from the initial set. If the initial parameters are used over the entire simulation period, then the match is usually best during the early stages and worsens as the simulation progresses. Conversely, if the final parameters are used to simulate the behavior measured in the field, the match is typically poor during the initial stages, but improves as simulation time progresses up to the point in time that the latest data are available. It is reasonable to expect that the simulation results would begin to worsen as the simulation continued to progress into the future.

Appropriate use of models generally requires that they be used by persons experienced in the use of models. As the complexity of the site and the selected model both increase, so must the sophistication of both the modeler and the computer. Adequately trained modelers command relatively high hourly billing rates. A single simulation using a complex, multi-phase model may take 24 hours or more to run even on today's fastest desk top computers. Often clients are billed for computer time as part of the overall cost for computer modeling. Between the labor rates and the computer usage rates, several simulations of even a small site can result in a large invoice.

Because of limited reliability and expense of use, multiphase computer models are seldom used to estimate recovery rates for a free product recovery plan. For sites with large spills or large volumes of free product in the subsurface, the expense and effort associated with these models may be warranted if it can help significantly reduce the cost of recovery or improve the effectiveness of free product recovery. Where models have been used to design free product recovery systems, the

analysis is likely to contain significant uncertainty that should be explicitly addressed in the model description.

Recoverability Of Free Product

Chapter IV has presented several methods for evaluating the volume and recoverability of free product. This section presents a discussion limited to those factors that are most relevant to the recovery of the principal types of petroleum products typically stored in USTs (*i.e.*, gasolines, middle distillates, and heavy fuel oils).

It has been established that the thickness of free product measured in wells usually exceeds the thickness that is present in the surrounding soil. Volume estimates based strictly on measured thickness in wells are erroneous and are often significantly greater than the volume of product that was released. Many methods have been developed to correlate the measured thickness to volume in the soil, but none of the available methods is reliable at all sites. Different methods applied to the same site may yield radically different volume estimates. It is, therefore, important not to rely on the estimate of any single method. Comparison of several estimates may provide a reasonable range for the estimated volume. This range may span an order of magnitude.

The steps involved in estimating the volume of free product in the subsurface include measurements of thicknesses in wells, borings, and excavations; determination of the direction(s) of groundwater flow and free product migration; and estimation of the retention capacity of the soil. Once the probable extent and realistic thicknesses of the free product plume (or pool) have been determined, a variety of techniques are available to calculate the total volume of the release. Under the most favorable conditions, only a fraction of the total release will be recoverable. Recoverable volumes typically range from 20 to 50 percent of the total release. Factors that influence the recoverable percentage include water table fluctuations (which can create a “smear zone”), depth to water table, and soil properties (*e.g.*, heterogeneity, pore size, layering).

The initial rates of product recovery are best estimated from bail down tests and pumping tests. Knowledge of the expected recovery rates are important in sizing components of the treatment process. Often the recovery of product declines significantly from initial rates, especially for wells located where free product volume is highest. Various computer models can, in theory, be used to predict future rates of free product recovery. However, these models are expensive to use and have limited reliability.

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CHAPTER V

HYDROCARBON RECOVERY SYSTEMS/EQUIPMENT

CHAPTER V

HYDROCARBON RECOVERY

SYSTEMS/EQUIPMENT

The selection of a hydrocarbon recovery system and its associated equipment is based on specific remedial objectives, design constraints, and site conditions. Hydrocarbon recovery systems are chosen to satisfy remedial objectives involving the control of petroleum hydrocarbon migration, maximum free product recovery, and simultaneous free product and vapor phase collection. Design constraints governing the selection of recovery systems may be site specific, such as limited access to wells. Other constraints may involve conflicts between free product recovery and other aspects of the corrective action; for example, a pump-and-treat remedy may adversely affect free product recovery by smearing the zone of free product.

The general site conditions affecting product recovery are the volume of the free product, its type and areal extent, and the depth at which it is located. Hydrogeologic conditions such as permeability and groundwater flow also influence the selection and design process of recovery systems.

Four general techniques or approaches are used to recover free product:

- ! Free product removal/skimming systems.
- ! Free product recovery with water table depression.
- ! Vapor extraction/groundwater extraction.
- ! Dual phase (liquid and vapor) recovery.

A description and applicability for each of these techniques is summarized in Exhibit V-1. Further detailed discussion on the applicability of these methods is provided later in this chapter. Exhibit V-2 provides a comparison of the general features of these techniques.

Each of these methods involves the installation of recovery equipment (*e.g.*, skimmers, pumps, filters, or absorbent materials) in wells, trenches, or excavations. Other aspects of free product recovery systems consist of phase separation, storage, and treatment processes. In addition,

Exhibit V-1

General Approaches To Free Product Recovery

Free Product Recovery Approach	Description	Applicability
Skimming Systems	Free product is recovered from a well or trench without recovering groundwater.	Small volumes of free product are removed because of limited area of influence in open trenches or excavations. Often used during emergency or short-term remedial actions.
Free Product Recovery With Water Table Depression	Free product is recovered from a well or trench along with groundwater. Groundwater is pumped to create cone of depression in water table to expand area of influence.	Requires moderately permeable to permeable subsurface materials (silts, sands, and gravels). Can be used in settings with deep water tables. Often used in long term (>1 year) remedial actions. Produced groundwater can be expensive to treat.
Vapor Extraction/ Groundwater Extraction	Vacuum is applied to well(s) above water table to recover vapor phase and residual hydrocarbons and to help maintain high water table. Free product and/or groundwater is recovered from wells by pumps.	Low to moderately permeable materials (silts, silty sands). Often used to enhance recovery of hydrocarbons.
Dual-Phase Recovery	Both liquids and vapors are recovered from same well. Groundwater production is minimized, and water table is stabilized.	Generally low permeability materials (clay, clayey silts, silts, silty/clayey sands). Requires surface seal (either naturally occurring clay or man-made) to prevent short-circuiting of vacuum.

EXHIBIT V-2

Comparison Of General Features Of Free Product Recovery Systems

System	Provide Hydraulic Control	Install in Excavations	Require Specialized Wells	Provide Fluid Separation	Produce Ground water	Product Recovery Rate	Capital Costs	Operation and Maintenance Costs
Skimming	No	Yes	Depends on diameter of skimmer	Yes	No	Low	Low -med	Low
Water Table Depression	Yes	Yes	No	Yes—dual-pump systems No—single pump systems	Yes	Low-high depends on volume of recoverable free product and formation characteristics	Low-high depends on number of pumps and complexity of system	Low-high depends on number of pumps and complexity of system
Vapor Extraction/ Groundwater Extraction (VE/GE)	Yes	No	Yes	No	Yes	Low-high depends on volume of recoverable free product and formation characteristics	Med-high	Med-high
Dual-Phase Recovery	Yes	No	Yes	No	Yes	Low-high depends on volume of recoverable free product and formation characteristics	High	High

groundwater pumped in conjunction with free product recovery must be discharged. Collection and treatment equipment must also be monitored and maintained during operation.

This chapter describes each of the four recovery approaches with respect to its applicability, general design considerations, required equipment, system operation and maintenance, and the monitoring and termination of recovery activities.

Free Product Removal/Skimming Systems

The goal satisfied by skimming systems is the collection of free product with little or no recovery of water. In general this approach involves using skimming devices to remove product floating on the water table in excavations, gravel-filled trenches, and wells. This type of system is commonly used in interim remedial actions.

Applicability

Free product removal using skimming equipment is applicable in settings where long-term hydraulic control of the dissolved hydrocarbon plume is not required. In most settings skimmer operations will not control the liquid hydrocarbon plume. The most common use of these systems is inclusion in an interim action where free product has entered open excavations. In general, skimming systems are applicable to settings in which the amount of free product is small and exists in permeable conduits such as utility bedding or buried underground open structures. The hydraulic conductivity should be greater than 10^{-4} cm/s to ensure a sufficient influx of free product to the skimmer. Skimmers may also be used in conjunction with other free product removal programs such as in monitoring and extraction wells for water table depression methods.

General Design Considerations

When hydraulic control of the contaminated region is not necessary, then skimmers are typically located in permeable conduits where significant free product is present. Skimmers are available for installation in wells from 2 inches in diameter up to several feet in diameter. Skimmer equipment may also be used in excavations and

trenches which may be open for very short term or emergency operations. For long-term operations, skimmers are placed in wells and in gravel-filled trenches with sumps. Recovery may be enhanced by use of hydrophobic gravel packs in wells. Field studies by Hampton *et al.* (1992) have shown that gravel packs constructed from hydrophobic materials allow for free product to enter wells and sumps more rapidly. Recovery rates for long-term operations are generally very low, with the exception of skimmers that are used in open excavations where rates of a few gallons per minute are feasible.

If hydraulic control of the contaminated region is deemed necessary, then skimmers should be located in trenches along the full width of the plume at its downgradient edge. The trench should be excavated several feet below the seasonally low water table to allow for fluctuations over time. For longer term operations, the trench should be filled with gravel or sand, as shown in Exhibit V-3. An impermeable partial vertical liner at the downgradient side of the trench will also prevent migration of the product contaminant plume. A sump should be located at areas where free product is present and at low water table elevations.

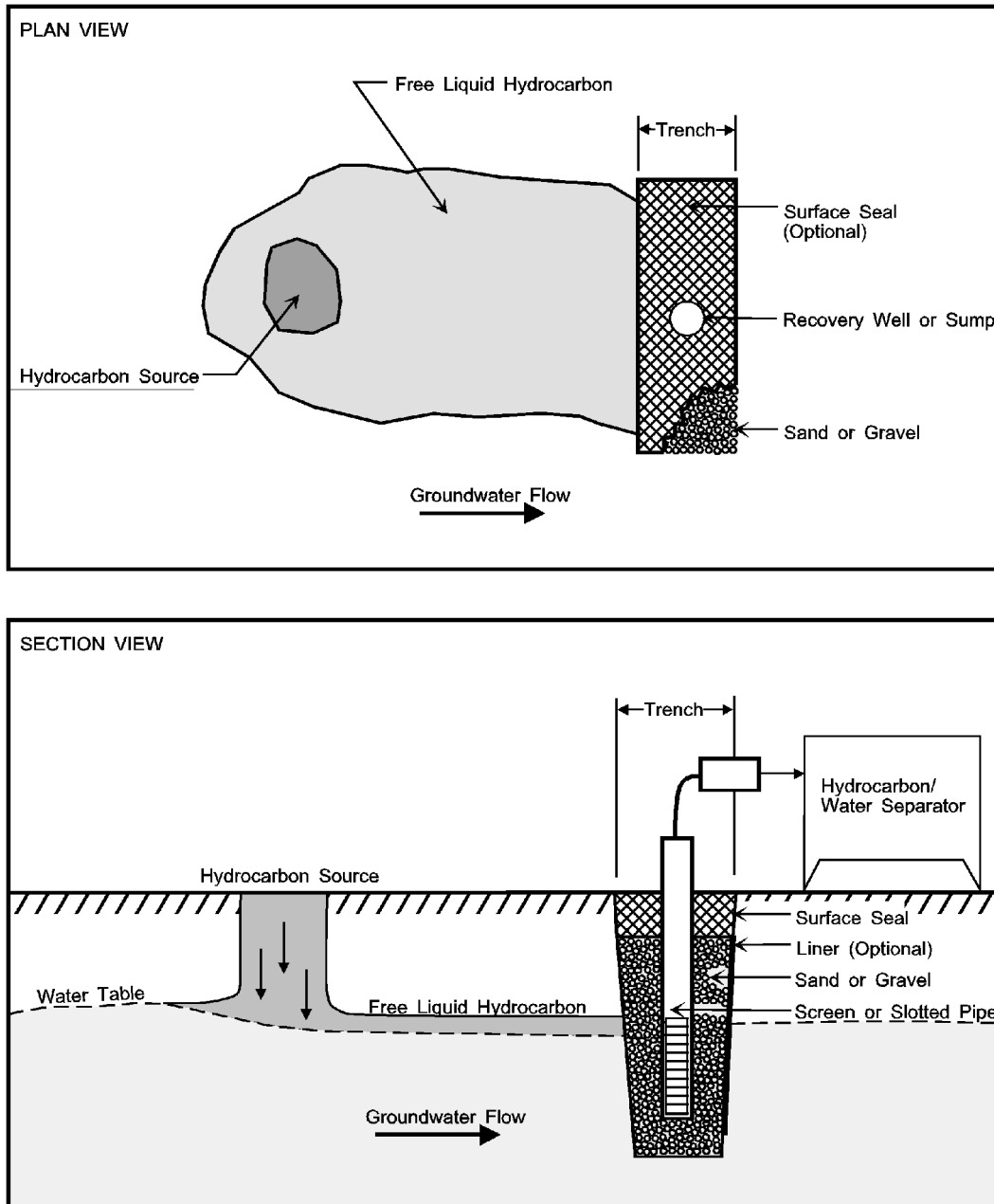
Equipment Description

The selection of skimming equipment will be based primarily on the size of the recovery installation (well, trench, excavation) and expected rate of recovery of free product. Two types of skimming equipment are available. Mechanical skimming equipment actively extracts free product from recovery initiation, whereas passive skimming equipment accumulates free product over time. Exhibit V-4 summarizes the applicability, advantages, and disadvantages of the common types of skimming systems.

Mechanical Skimming Systems. Mechanical skimming systems rely on pumps (either surface mounted or within the well) or other motors to actively extract free product from the subsurface. The more common forms of mechanical skimming systems are:

- ! Floating (large)
- ! Floating (small)
- ! Pneumatic Pump
- ! Belt Skimmer

Exhibit V-3
Interceptor Trench With Skimming Equipment



Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted Courtesy of the American Petroleum Institute.

Exhibit V-4

Applicability of Skimming Systems

	Recommended Minimum Well Diameter	Relative Capital Costs	Relative Operating Costs	Relative Maintenance Costs	Potential For Product Removal	Product Recovery Rate	Advantages	Disadvantages
Mechanical Skimmers								
Floating Large Saucer	36"	M-H	M	M	M	L-H (depends on volume of recoverable free product and formation characteristics)	No water produced; skims thin layers; moves with fluctuating groundwater tables	Limited radius of influence; clogging of screen; limited to shallow (less than 25 ft.) applications
Small Float	4"	M-H	M	M	M	L-M		
Pneumatic Pump	4"	M includes compressor	M	M	M	L-M	Can be adjusted so that very little water is produced; skims very thin layers; pumps are durable	Limited radius of influence; requires manual adjustments; clogging of screens and intake valves
Belt Skimmer	2"	M	M	L	L	L	Skims very thin layer; simple operation and maintenance	Belts have limited capacity; low removal rates
Passive Skimmers								
Passive Bailer/Filter Canister	2"	L	L	L	L	L	Low capital cost; simple operation and maintenance	Low removal rates
Passive Absorbent Bailer	2"	L	L	L	L	L	Low capital cost; simple operation and maintenance	Must be replaced manually; low removal rates

L - Low; M - Moderate; H - High

Large floating skimmers can remove product at a fairly high rate (up to 5 gpm). Each skimmer has a large hydrophobic screen that allows only product into the pump body. These skimmers are generally limited to shallow applications (less than 20 feet) and may require a well or sump that has a 24-inch-diameter or greater. Small float systems require 4-inch or larger wells for operation. They are limited to depths of 30 feet or less. This type of skimmer typically uses a floating screen inlet to capture the product and is contained in a pump device or bailer. A variation on floating skimmers employs a floating (or depth-controlled) intake equipped with conductivity sensors that activate surface mounted pumps when liquid hydrocarbons have accumulated to a sufficient thickness. Belt skimmers use a continuous loop of hydrocarbon absorbent material that slowly cycles down into and out of the well, soaking up product as it moves through the water surface. These skimmers are simple mechanical systems that can operate in 4-inch or larger wells, but they are perhaps best suited for skimming sumps. Pneumatic skimming systems may have a top intake that allows skimming of fluids from the liquid hydrocarbon/water interface (as in Exhibit V-5), or they may have a density-sensitive float valve that permits the passing of water before the valve seats.

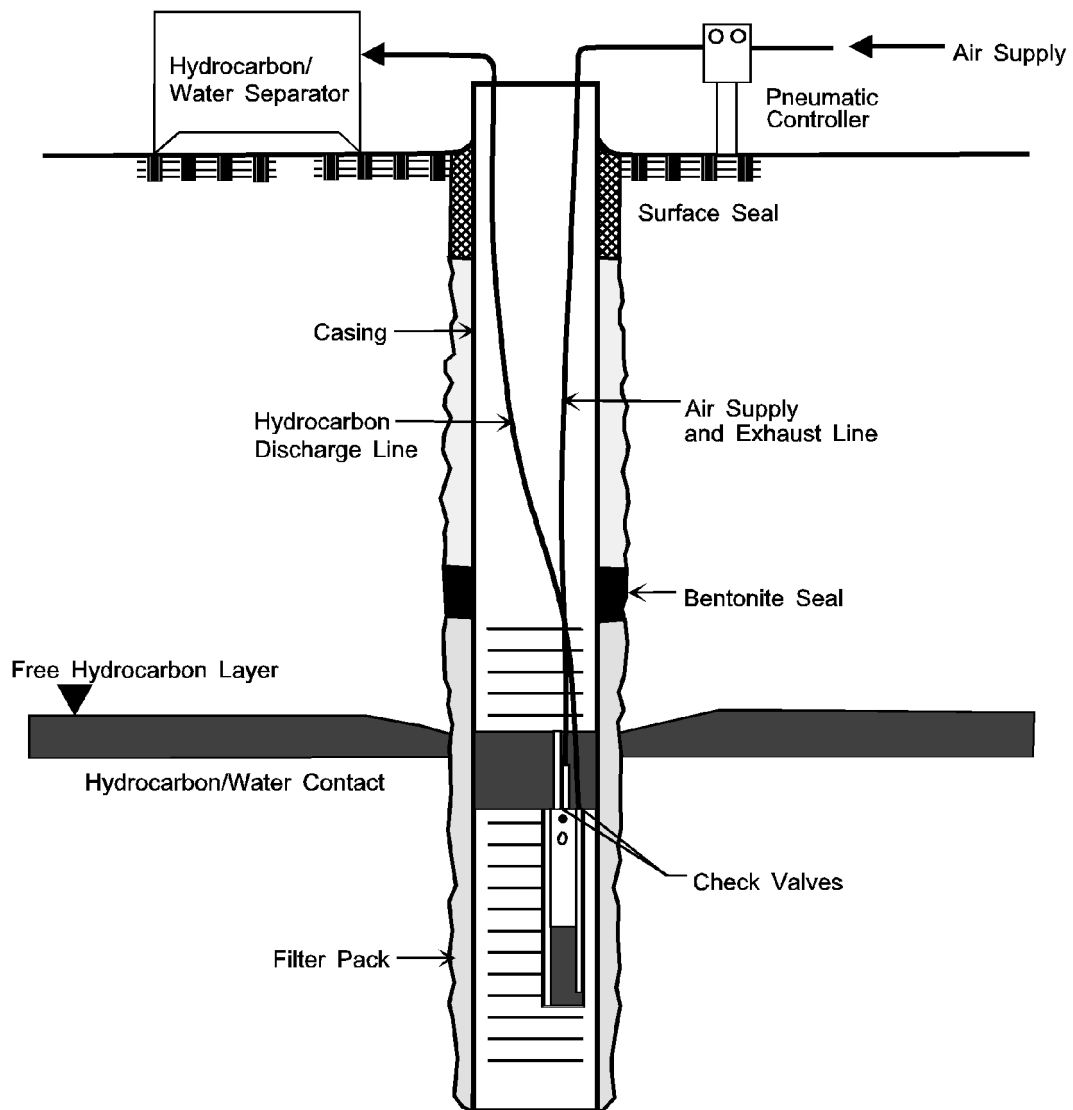
Passive Skimming Systems. Passive skimming systems do not actively pump free product; instead they slowly accumulate it over time. There are two basic forms of passive skimmers:

- ! Filter canisters
- ! Absorbent bailers

Filter canisters are lowered into 2-inch or greater diameter wells so that they contact the layer of free product floating on top of the water surface. The filter is constructed of a hydrophobic material which allows only free product to enter. Gravity causes the liquid hydrocarbons to trickle through the filter and then flow into the bottom of the canister where the product is stored. Canisters can store between 0.5 and 2 gallons of free product. The product can be removed automatically by a suction pump or manually by pulling up and emptying the canister (EPA, 1992). Absorbent bailers are simple skimming devices which are suspended in the well across the surface of the free product layer. Attached material absorbs product from the water surface and must be periodically removed and disposed.

Exhibit V-5

Pneumatic Skimmer In A Single Well



Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted Courtesy of the American Petroleum Institute.

System Startup

The startup operations for skimmer systems, not including treatment systems, are relatively straightforward and of short duration (a few days). The following activities are applicable, in general:

- ! Set the skimmer equipment at proper levels in each well or sump.
- ! Inspect all mechanical and electrical components of skimmers and collection system, and oil/water separator.
- ! Monitor the recovery rate of fluids.
- ! Sample the fluids collected and inspect them for water content and/or emulsification. Modify skimmer settings as necessary to minimize water production.

After the startup activities have been completed, a brief startup summary report should be prepared.

Operations And Maintenance

After the startup activities have been completed, normal operations and maintenance (O & M) activities begin. These activities include:

- ! Measure the thickness of free product and water and product elevations in monitor and skimmer wells or sumps.
- ! Record the amount of product collected at all recovery points.
- ! Inspect all electrical and mechanical components of skimming and collection systems and oil/water separator.
- ! Maintain and repair all equipment as necessary, or as recommended by equipment vendor.

Typically, these activities are performed every two weeks. Most states require reporting at least quarterly.

Termination Criteria/Monitoring

The free product skimming system should be operated until it is no longer recovering significant amounts of hydrocarbons (*e.g.*, less than 2 gallons per month). After the system operations have been suspended, the free product thickness levels should be monitored on a monthly or quarterly basis to ensure that significant accumulations of product do not return to the wells. A threshold level of hydrocarbon thickness (*e.g.*, 0.1 foot) may be used as an action level to restart the recovery system. The termination criteria should also specify the period during which thickness should be monitored (*e.g.*, 2 years of quarterly monitoring) with no exceedance of threshold hydrocarbon thickness.

Free Product Recovery With Water Table Depression

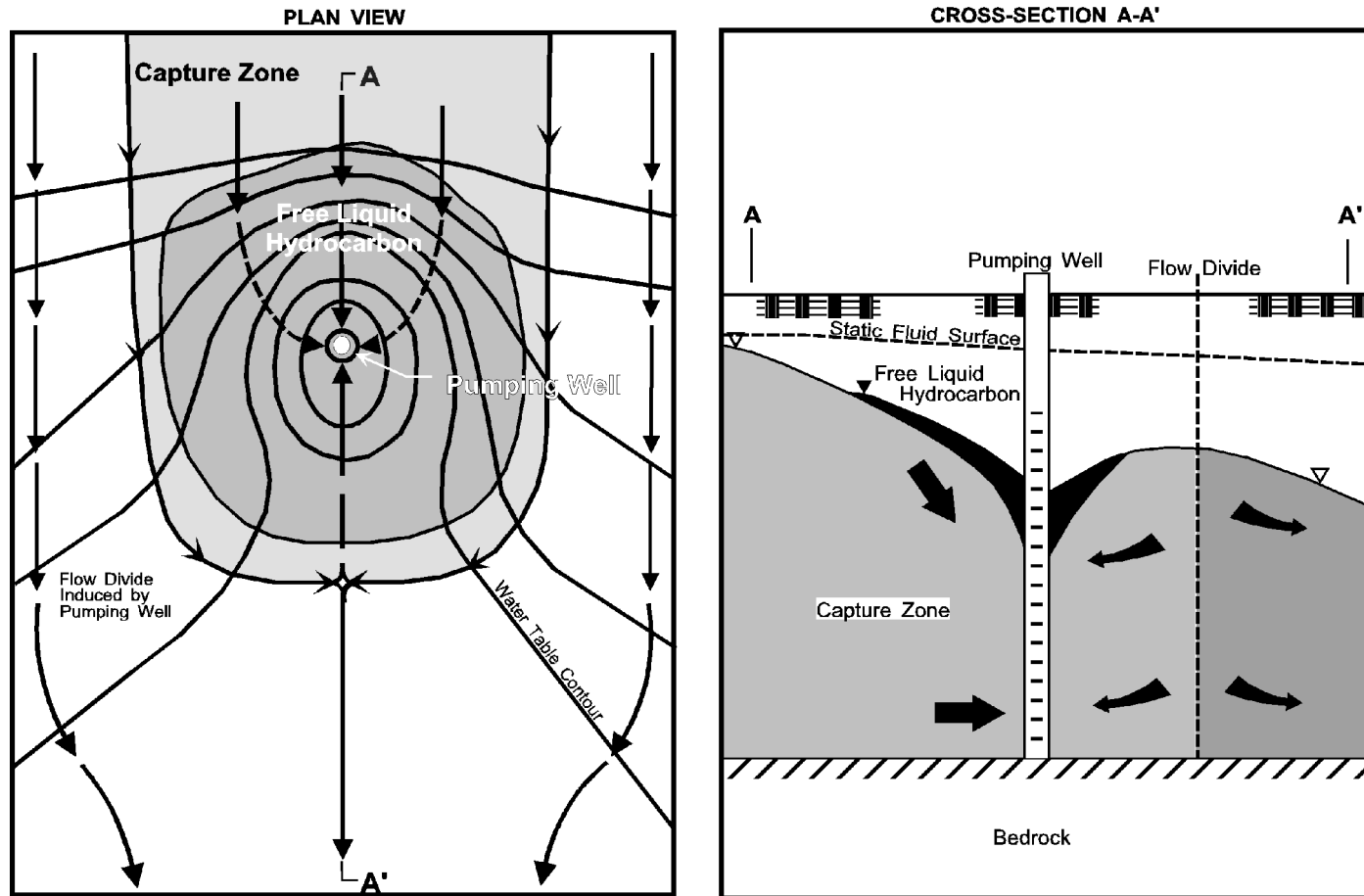
This method of recovery creates a depression of the water table so that any free product is directed toward pumping wells within the plume area. Both free product and groundwater are produced during recovery operations. The design of these systems is constrained by the need to minimize drawdown of the water table. Minimizing drawdown will reduce both the volume of coproduced water as well as the smearing of free product along the drawdown surface. Exhibit V-6 shows a pumping recovery system capture zone.

Applicability

Product recovery systems utilizing water table depression are most applicable when hydraulic control of the hydrocarbon plume is necessary. These systems can operate in a wide range of permeability values and geologic media. However, because of the costs associated with the separation and treatment of dissolved hydrocarbons, these systems are better suited for formations of moderate to high permeability (greater than 10^{-4} cm/s). Typically, free product recovery with water table depression is used in long-term operations of greater than one year.

Exhibit V-6

Pumping Recovery System Capture Zone



Source: Modified from API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted Courtesy of the American Petroleum Institute.

General Design Considerations

The major design components of a free product recovery system using water table depression consist of:

- ! Number, location, and depth of wells and drains
- ! Pumping rates or fluid control levels
- ! Disposition of treated groundwater (discharge)
- ! Pump selection

The primary constraints on the design include the need to minimize pumping rates and drawdowns but still provide hydraulic control of at least the free product plume. At some sites, discharge of treated groundwater to surface water may not be possible because of state or local regulations. At these sites, the design needs to address the impact of subsequent recharge to the aquifer.

Recovery Well/Drain Network Design

The success of a free product recovery system using groundwater depression depends upon selecting the number and location of wells and setting pumping rates or fluid control levels in a manner such that the system pumps as little groundwater as necessary while collecting as much free product as possible as quickly as possible. Design of a recovery system can be based on the results of a simplistic basic analysis or a more sophisticated modeling analysis.

Basic Analysis. The basic analysis requires knowledge of the most fundamental groundwater principles and equations. Typically such an analysis can be conducted using nothing more sophisticated than a hand-held calculator. This approach to the design of a system for free product recovery with water table depression is applicable to simple hydrogeologic settings with small free product plumes. Probably the most significant limitation of this method is that, because it considers only groundwater flow rates, it does not provide an estimate of the time that will be required to recover free product present at a site. The basic approach involves four steps:

1. Determine the amount of groundwater flowing through the plume area.

2. Set the total pumping rate of recovery system, usually 50 percent or 100 percent greater than the groundwater flow through the plume.
3. Determine the number of wells from which to extract groundwater, but minimize drawdown in areas of free product.
4. Locate wells to maximize recovery of free product.

Determining the amount of groundwater flowing through the free product plume requires site-specific information: Dimensions of the plume, hydraulic gradient, aquifer saturated thickness, and hydraulic conductivity. An estimate of the groundwater flow rate through the plume is calculated using Darcy's Law.

To account for uncertainty in the site data and to provide a margin safety should the actual groundwater flow rate be higher than the estimate, the total pumping rate is typically set at 50 percent to 100 percent higher than the estimated groundwater flow rate.

Once the total pumping rate is determined, the next consideration is the minimization of drawdown. Large drawdowns in the free product plume are undesirable because they can result in free product being drawn to lower elevations in the aquifer where it may become immobilized and not subject to recovery (smearing). Simple equations for steady-state flow can be used to estimate flow to a well (or drain) for a desired drawdown. These calculations will determine the number of wells or size of drains.

After the required number of wells has been determined, their locations must be determined. For hydraulic control, the wells are best placed near the downgradient end of the free product plume. Other considerations in locating the wells include the amount of free product at the proposed location and accessibility. If the optimal well locations are in areas having small amounts of recoverable free product, then it may instead be advantageous to place additional wells in the areas where free product can be recovered at higher rates. Terrain and land use may limit accessibility to optimal locations. Proximity to fragile environments (*e.g.*, wetlands) or underground utilities may preclude siting of a recovery well(s) in the optimal location.

An example of the basic analysis used to determine the number of wells and the total pumping rate is presented in Exhibit V-7. In this example, the Theim Equation is used to compute drawdowns at the

Exhibit V-7

Procedure To Determine Number Of Wells And Total Pumping Rate Using Water Table Depression

Setting: Free product plume is 100 feet wide in an aquifer 25 feet thick with a hydraulic conductivity of 5 feet per day and a hydraulic gradient of 0.006 feet per foot.

Step 1: Determine groundwater flow through the plume using Darcy's Law.

$$Q_{gw} = W \cdot B \cdot K \frac{\Delta h}{\Delta L}$$

where:

W = width of the plume
B = saturated thickness of the aquifer
K = average hydraulic conductivity
 $\Delta h/\Delta L$ = hydraulic gradient (the difference in groundwater elevation between two points in the direction of flow, divided by the distance between those two points)
 $Q_{gw} = 100 \text{ ft} \times 25 \text{ ft} \times 5 \text{ ft/day} \times 0.006 \text{ ft/ft}$
 $= 75 \text{ ft}^3/\text{day} = 0.39 \text{ gallons per minute}$

Step 2: Set the design total pumping rate at $Q_{gw} + 100\% Q_{gw} = 150 \text{ ft}^3/\text{day}$.

Step 3: Determine the maximum pumping rate for single well without interference using Theim Equation.

$$Q_{max} = \frac{S_{max} (2\pi BK)}{\ln (W/r_w)}$$

where:

the radius of influence is assumed to be the width of the plume (W)
 r_w = the well radius
 S_{max} = maximum allowable drawdown to minimize smearing (assume 1 ft)
 $Q_{max} = \frac{1 \text{ ft} (2 \times 3.14 \times 25 \text{ ft} \times 5 \text{ ft/day})}{\ln (100 \text{ ft}/0.166 \text{ ft})} = 123 \text{ ft}^3/\text{day}$

For a desired maximum drawdown next to the well, the maximum pumping rate is about $123 \text{ ft}^3/\text{day}$, which is less than the total pumping rate of $150 \text{ ft}^3/\text{day}$. Two pumping wells should be used at this site.

pumping well. This equation does not consider the combined drawdown of several wells: The water levels within the overlapping cones-of-depression would be lower as a result of well interference. If several wells are determined to be necessary, the number determined using the Theim Equation should be considered as the minimum; however, because of well interference and increased drawdown, the pumping rates will need to be reduced somewhat to minimize smearing.

Modeling Analysis. The most reasons cited for not using models to aid in the design of free product recovery systems are complexity of use and cost. However, for large free product plumes and serious contamination problems, the cost of the modeling study may more than pay for itself if the result is a more efficient and cost-effective remedial design than would have otherwise been possible. Because of their speed and flexibility, many models can be used to quickly examine different remedial designs without the time and expense associated with extensive field testing. For example, different well locations can be tested, wells can be added or eliminated, and pumping rates and schedules can be adjusted to achieve an optimal design. Three types of models are available:

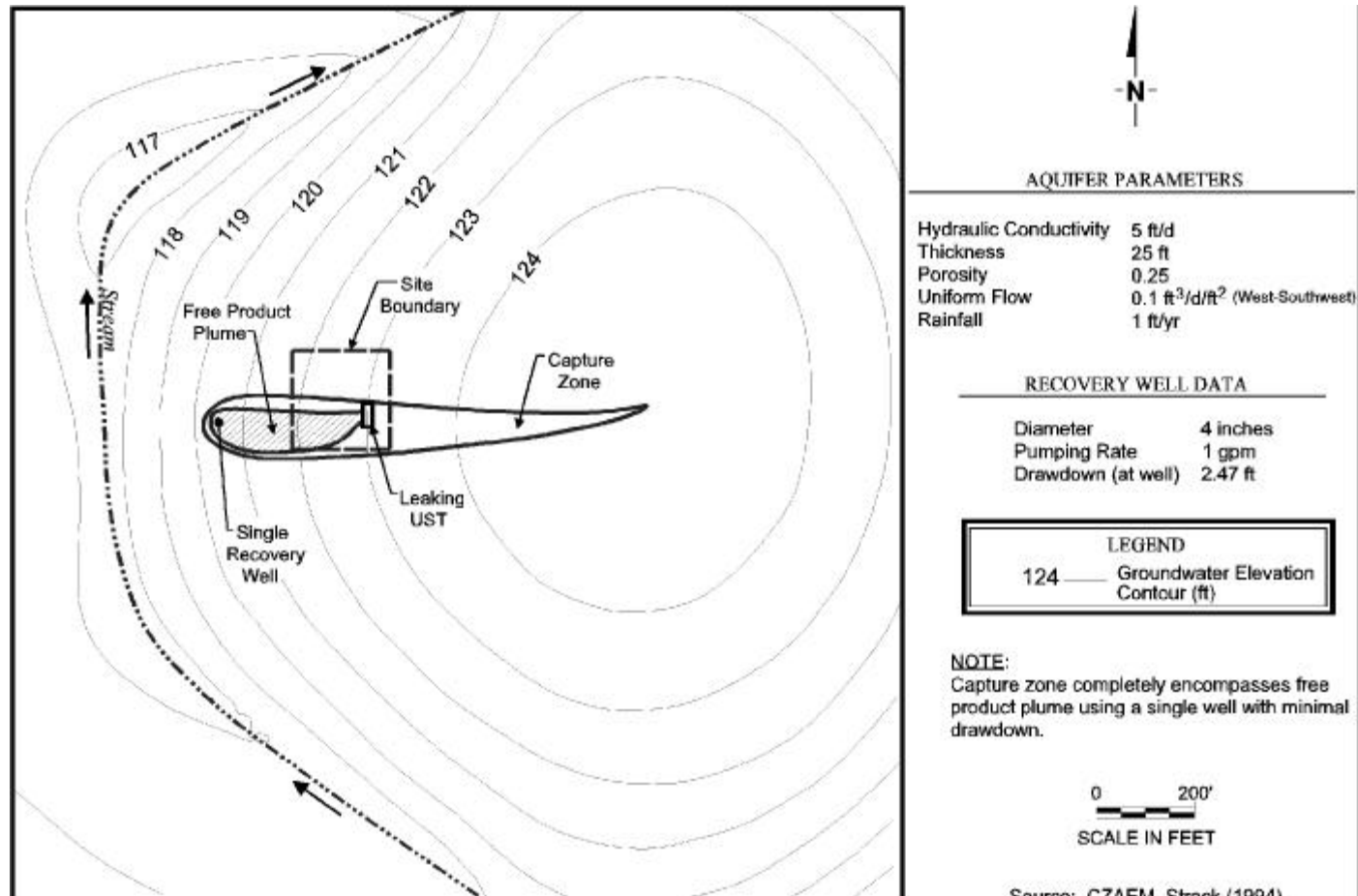
- ! Analytical models of capture analysis based on groundwater flow.
- ! Numerical (finite-difference or finite-element) models for groundwater flow and capture analysis.
- ! Numerical models of multiphase flow.

Analytical groundwater models of capture analysis provide for detailed evaluation of a recovery system design without the expense and complexity of the numerical modeling approach. Analytical methods such as those developed by Strack (1994) may be applied for capture analysis and optimal well and drain placement at smaller sites. The objective is to create a capture zone that completely encompasses the free product plume. An example of such an application is illustrated in Exhibit V-8.

Numerical groundwater flow models may also be used to perform a capture analysis for a recovery system. The USGS model MODFLOW (McDonald and Harbaugh, 1984) is one such model that is frequently applied. A numerical groundwater flow model can simulate three-dimensional flow conditions and heterogeneous conditions that cannot be simulated by the analytical models.

Exhibit V-8

Sample Capture Zone Analysis



Multiphase flow models are capable of simulating the flow of free product as well as groundwater. Ideally, they can predict free product recovery rates and show how the free product plume will evolve over time. The complex models are rarely used in the design of free product recovery systems because they are expensive to run, and they require specialized modeling expertise and data that are generally not available or easily collected at UST sites. However, at sites with large spills or large volumes of free product in the subsurface, multiphase flow models may be useful design tools.

Discharge Of Treated Groundwater

Free product recovery using groundwater depression can generate large quantities of co-produced groundwater. Discharge of water is a necessary element of the free product recovery design. Two options for the disposal of recovered groundwater include:

- ! Surface water or POTW discharge
- ! Recharge to water-bearing geologic formation

Because of the cost of treating contaminated groundwater, discharging it to a publicly owned treatment works (POTW) is preferred (provided the state regulations allow for it and the facility will accept discharges and has the hydraulic capacity). Some pretreatment, such as phase separation, may be required before discharging to the sanitary sewer. Surface water discharges usually require a National Pollutant Discharge Elimination System (NPDES) permit and, thus, have greater treatment demands and costs. Recharge to the aquifer must be considered carefully, as it may directly affect contaminant capture. If water is recharged within the free product plume, it may negate the hydraulic containment provided by pumping. Water recharged to the aquifer outside of the free product plume may alter the migration of the dissolved product plume. Reinjection or recharge may be evaluated using the same methods used for capture analysis.

Equipment

A variety of pumps in one or two configurations will provide water table depression. The types of pumps include diaphragm, centrifugal, submersible, pneumatic, and vacuum. All pumps should be rated for operation in a hydrocarbon environment. The applicability and advantages of the various pump configurations are summarized in Exhibit V-9. There are two common configurations of pumps:

Exhibit V-9

Applicability Of Water Table Depression Equipment

	Recommend d Minimum Well Diameter	Recommend d Minimum Value for K (cm/s)	Relativ e Capital Costs	Relative Operating Costs	Relative Maintenance Costs	Potential For Product Removal	Product Recovery Rate	Advantages	Disadvantages
Single-Pump Systems									
Diaphragm Pump	2"	$> 10^{-4}$	L	L	L	L	L-M	Low cost; low maintenance surface mounted pumps; easy to maintain low flows	Pumps water and product; requires O/W separator; limited to shallow (less than 20 ft.) applications
Centrifugal Pump	2"	$> 5 \times 10^{-3}$	L	L	L	L	L-M	Low cost and maintenance	Level sensor and O/W separator required
Submersible Pump	4"	$> 10^{-2}$	M	M	L	L	L-M	No depth limitation; ease of installation; removes product and water; creates capture zone	Flow usually greater than 5 gpm; requires O/W separator and water treatment; emulsification of product in water
Pneumatic Top Filling	4"	$> 10^{-3}$	M	M	M	M	L-M	Operates over wide range of flow rates; will pump from deep, low permeability aquifers	Requires air compressor system and water treatment; recovered fluids are emulsified
Product Only	4"	$> 10^{-4}$	M	M	M	M	L-M		
Two-Pump Systems									
GWP and PP (separate product and level sensors)	4"	$> 10^{-2}$	H	H	H	H	L-H	Can be set to skim product with little smearing	Proper adjustment can be time-consuming
GWP (steady operation) with PP (with product sensor)	6"	$> 10^{-2}$	H	H	M	H	L-H	Can create large cone-of-depression to expedite recovery	Somewhat larger recovery well required; may require O/W separation
GWP (steady operation) with PP (floating, skimming type)	6"	$> 10^{-3}$	H	H	M	H	L-H	Can create large cone-of-depression to expedite recovery; can skim product	Somewhat larger recovery well required

K - Hydraulic Conductivity; L - Low; M - Moderate; H - High; GWP - Groundwater Pump; PP - Product Pump; O/W - Oil/Water

- ! Single-pump systems or total fluids systems which simultaneously collect both free product and groundwater in each installation.
- ! Two-pump or dual-pump systems consist of one pump which recovers only free product while another pump extracts groundwater and provides the desired level of drawdown.

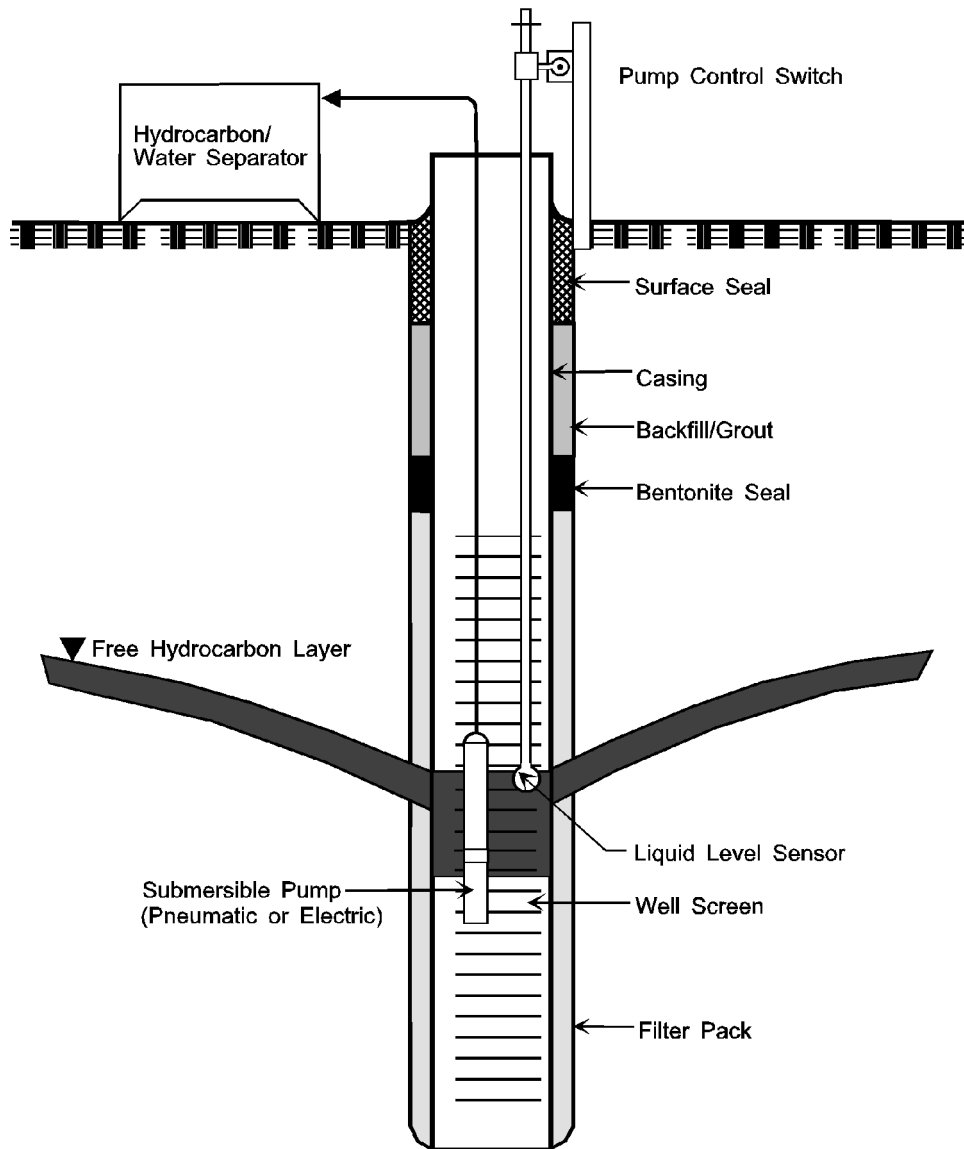
Single-Pump Recovery Systems. Single-pump systems produce both water and hydrocarbons. Depending on the depth to water, the pump may be surface mounted and operated by a suction lift, or it may be submersible. Single-pump systems are most applicable in settings where the soil has low to moderate permeability. The systems are simple to install and consist of a drop tube, the suction lift or submersible pump, a liquid level sensor, and an above ground phase separation unit. A single pneumatic, submersible pump system is shown in Exhibit V-10.

Single pumps may operate well below 5 gpm (as low as 0.1 gpm) to as high as 20 gpm. The pumps usually operate on an intermittent cycle actuated by a liquid level sensor. All pump types have a tendency to emulsify liquid hydrocarbons in water thus increasing the dissolved concentration in the produced groundwater. As a result, above ground separation and perhaps other levels of treatment are necessary components of these systems.

Two-Pump Recovery Systems. The objectives of two-pump recovery systems are to optimize the cone-of-depression to achieve maximum product recovery while minimizing smearing and prevent mixing of free product with water which would then require separation. Three basic configurations of two-pump systems are summarized in Exhibit V-9. All of these systems employ one pump that produces groundwater to create the cone-of-depression and a second pump to collect free product. Groundwater pumping rates can be adjusted to some degree to control the depth of drawdown. This is accomplished by either intermittantly operating the groundwater depression pump, or regulating its pumping rate. Free product recovery is controlled by either a floating skimmer or a hydrocarbon detection probe which activates the pump when there is a sufficient accumulation of free product. By carefully balancing the pumping rates for groundwater and free product, emulsification of oil can be minimized or eliminated, which negates the need for oil/water separation. A dual-pump system that employs a hydrocarbon detection probe is depicted in Exhibit V-11.

Exhibit V-10

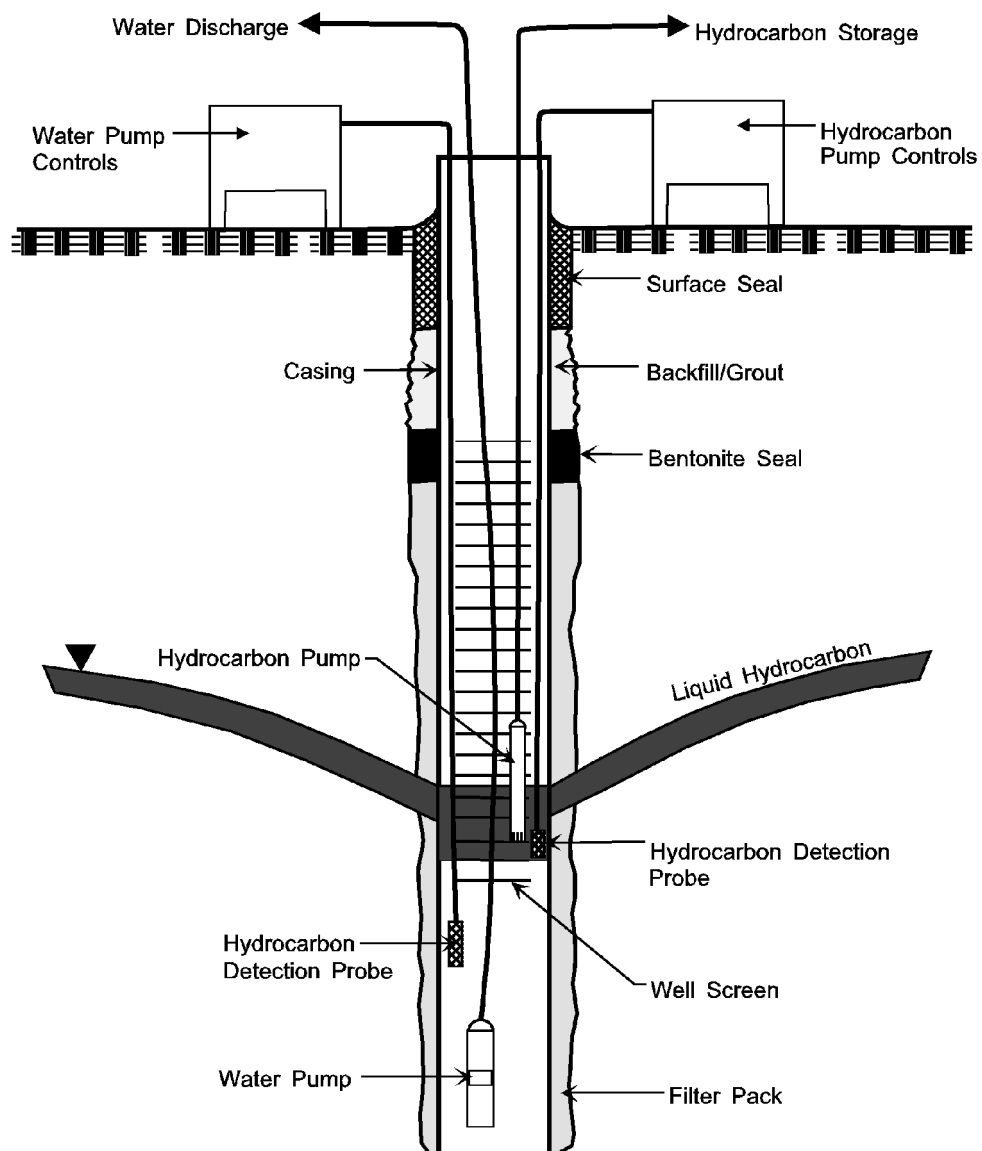
Single-Pump System For Free Product Recovery
And Water Table Depression



Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted Courtesy of the American Petroleum Institute.

Exhibit V-11

Two-Pump System For Free Product Recovery
And Water Table Depression



Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted Courtesy of the American Petroleum Institute.

System Startup

Initial start-up of pumping systems involves the following steps:

- ! Optimize hydraulic control of plume and fluid levels in the system wells.
- ! Calibrate the characteristic drawdown of each well. A flowrate versus drawdown plot will assist in evaluating the effect on other wells.
- ! Determine the operational rate of the pump; select a rate that will minimize drawdown and provide control of plume movement.
- ! Determine a flow rate for each pump that stabilizes the fluid levels and maintains sufficient liquid hydrocarbon/water separation.
- ! Adjust pump rates to meet fluid level and plume containment goals. Set sumps at elevations appropriate for expected drawdowns.

The initial setup, operation, and maintenance are more difficult and time-consuming for two-pump systems. Permits for well installation, discharge, reinjection, and treatment system operation should be secured prior to start-up and full operation of a pumping system.

Operation And Maintenance

Normal O&M activities begin after startup and include:

- ! Measure groundwater elevations and product thicknesses in monitoring wells within the plume.
- ! Calculate amount of free product and water recovered at each well in the pumping network and sample emulsified fluids for total petroleum hydrocarbons (TPH).
- ! Determine the volume of water that separates from the recovered product (or the water to oil ratio).

- ! Measure influent and effluent concentrations of dissolved hydrocarbons to and from the treatment system, respectively.
- ! Inspect all electrical and mechanical components of the recovery and treatment system.
- ! Perform maintenance and repair of equipment and wells when necessary.

Usually these activities are performed once every 2 weeks. Most states require reporting on a quarterly basis.

Termination Criteria/Monitoring

A free product pumping system using groundwater depression should be operated until it no longer produces significant volumes of hydrocarbons. Termination usually requires a total system product recovery at some specified rate (*e.g.*, less than 2 gallons per month or less than 0.02 percent ratio of hydrocarbon recovered to water pumped). In addition, product thicknesses less than a specified thickness at all wells in the monitoring and pumping network is a basis to terminate system operations. After the system is shut down, thicknesses should be monitored on a monthly or quarterly basis to ensure that wells do not contain hydrocarbons in significant amounts. Termination criteria should also consist of a specified period (*e.g.*, 2 years of quarterly monitoring) during which no exceedance of the threshold hydrocarbon thickness (*e.g.*, 0.1 foot) should occur. The threshold thickness should serve as an action level to restart the system if it is exceeded.

Vapor Extraction/Groundwater Extraction

Vapor extraction/groundwater extraction (VE/GE or “veggie”) systems combine conventional water table depression techniques with soil vapor extraction. The systems are designed to expose the smear zone in the capillary fringe by groundwater pumping while simultaneously volatilizing the residual petroleum hydrocarbons in the smear/vadose zone with SVE. VE/GE systems are used after other free product recovery methods have removed as much mobile product as feasible. Then, and only then, is the water table drawn down to expose the smear zone. VE/GE systems have the following favorable characteristics:

- ! Recovery of a larger fraction of total hydrocarbons (*i.e.*, free product and vapor) over shorter time periods.
- ! Increased air flow and groundwater extraction rates.
- ! Recovery of some residual phase hydrocarbons.

These benefits are derived from the fact that volatilization (and biodegradation) is the primary removal mechanism as opposed to the draining and dissolution that results from conventional pumping systems (Peargin, 1995). SVE is ineffective on nonvolatile hydrocarbons, but the increased flow of oxygen may aid in the stimulation of biodegradation.

Applicability

VE/GE systems may be screened on the basis of aquifer hydraulic conductivity, but they are generally most applicable to:

- ! Fine-grained soil types.
- ! Aquifers with moderate to low permeabilities (10^{-3} to 10^{-5} cm/s).
- ! Aquifers with thicker capillary zones (up to several feet).
- ! Settings in which conventional pumping approaches are too costly or ineffective.

The applicability of VE/GE systems is summarized in Exhibit V-12.

General Design Considerations

Recovery wells in VE/GE systems require additional design considerations such as:

- ! Air-tight well caps with an additional connection for air extraction piping.
- ! Well screens extending further into the unsaturated zone for air extraction.

Exhibit V-12

Applicability Of Vapor Extraction/Groundwater Extraction Equipment¹

	Recommend ed Minimum Well Diameter	Recommend ed Minimum Value for K (cm/s)	Relative Capital Costs	Relative Operatin g Costs	Relative Maintenance Costs	Potential For Product Removal	Advantages	Disadvantages
Pneumatic or Electric Submersible Pump Augmented with Vacuum on Well	4"	$< 10^{-3}$	H	H	M	VH	Effective on low permeability aquifers; extracts product from thick capillary fringes; recovers or remediates some residual phase hydrocarbon	Large capital investment; requires vacuum pump or blower; longer initial setup times; usually requires vapor phase and water treatment

¹ See also Exhibit V-10, Single-Pump Systems

K - Hydraulic Conductivity; L - Low; M - Moderate; H - High; VH - Very High

- ! Solid, impermeable annular seals to prevent air short-circuiting from the ground surface to the well screen.

VE/GE well locations may be determined by the same methods used for conventional pumping wells, provided hydraulic containment of the free product plume is desired.

Equipment

The equipment used in VE/GE systems is essentially the same as that involved in conventional pumping and SVE. Exhibit V-13 depicts a VE/GE system in a monitor well. Primary equipment includes:

- ! Surface mounted vacuum pumps or regenerative blowers for air/vapor extraction.
- ! Pneumatic or electric submersible pumps for groundwater extraction.
- ! Air extraction piping.
- ! Contingent vapor treatment equipment (*e.g.*, air/water separator, GAC).
- ! Other equipment such as instrumentation for measuring vacuum pressure and airflow rate.

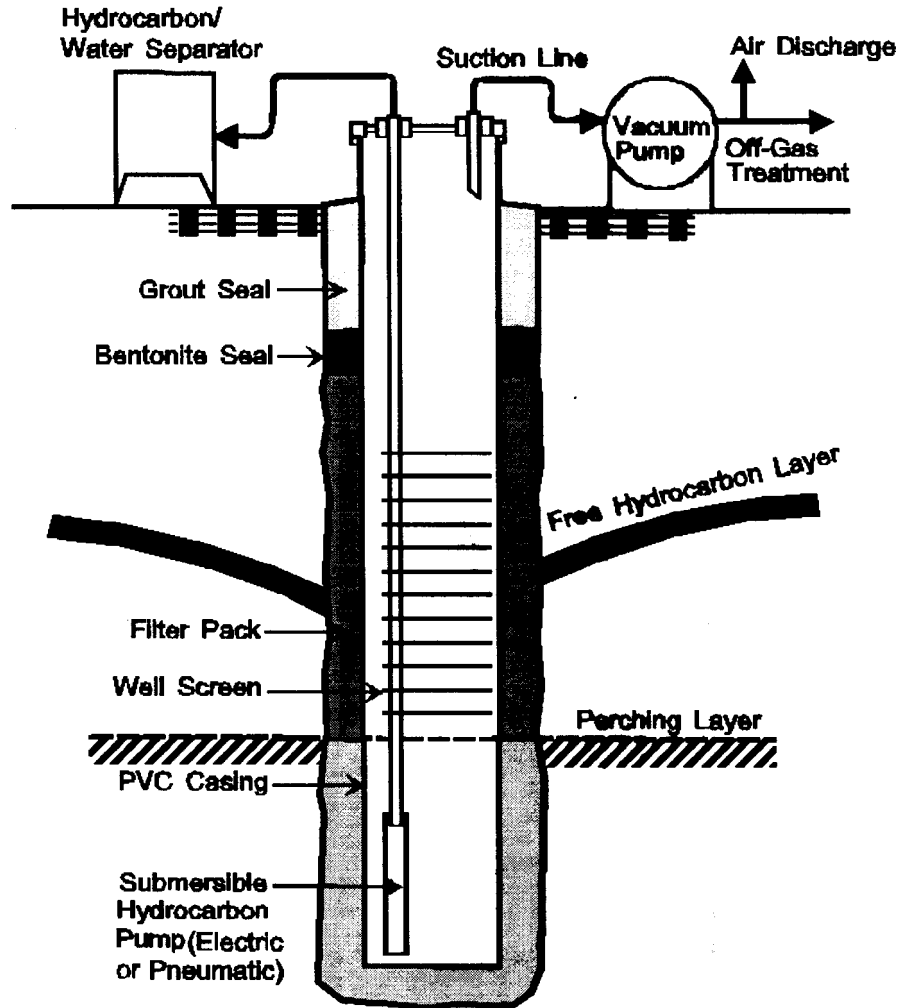
System Setup

The initial setup of a VE/GE system involves the following procedures:

- ! After readily recovered free product is removed by pumping with minimum smearing, increase pumping rate to draw water table down and expose smear zone.
- ! Adjust vacuum and pumping rates in the field such that the recovery of free product is maximized while the recovery of total fluids requiring treatment is minimized.

Exhibit V-13

Vapor Extraction/Groundwater Extraction (VE/GE) Recovery System



Separate Vacuum and Liquids Pump (VE/GE)

Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted Courtesy of the American Petroleum Institute.

- ! Optimize the product recovery while maintaining static fluid levels to avoid unnecessary additional drawdown.
- ! Determine the optimal placement of fluids pump in each well.

Setup times for VE/GE systems are significantly longer than conventional pumping approaches. Adjustment of vacuum pressures and airflow rates will also be necessary during periods of falling background water tables.

Operation And Maintenance

Normal O&M activities of VE/GE systems are equivalent to those of conventional pumping systems. In addition, the following activities are usually performed once every 2 weeks. Most states require quarterly reporting.

- ! Monitor the vacuum applied to each recovery well.
- ! Monitor the vacuum readings at sealed monitoring wells in the vadose zone.
- ! Record the airflow rates, vacuum, and temperature readings at the vacuum pump and air/water separator (if present).
- ! Lubricate and maintain the vacuum pump and check all seals and connections for leaks.
- ! Determine the total volumes of recovered phases and calculate fraction of product recovered from extracted groundwater.

Termination Criteria/Monitoring

A VE/GE may be operated until significant volumes of petroleum hydrocarbons are no longer recovered. Termination criteria are a total free product recovery of less than 2 gallons per month and a free product thickness of less than 0.01 foot at all recovery and monitoring wells. Product thicknesses in wells should be monitored on a monthly or quarterly basis. The free product recovery plan should specify an acceptable time frame (*e.g.*, 2 years of quarterly monitoring) in which no exceedance of the threshold thickness value (*e.g.* 0.1 foot) should occur.

The system should be restarted if the threshold thickness value is exceeded within the specified time frame.

Dual-Phase Recovery

The approach of dual-phase recovery is to extract free product, vapor, and groundwater by vacuum enhanced pumping techniques. In contrast to VE/GE systems, dual-phase systems have a single well point that accomplishes dewatering while also facilitating vapor-based unsaturated zone cleanup (Baker and Bierschenk, 1995). This approach has several benefits relative to other free product recovery methods:

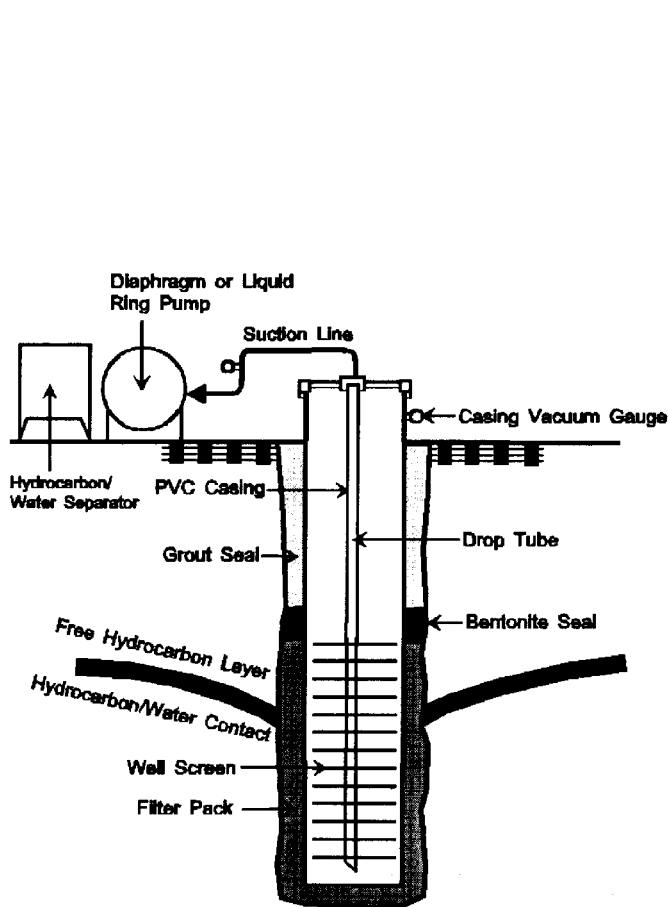
- ! A cone of depression is not formed at the air/oil interface or the air/water interface.
- ! Smearing of the free product zone is minimized.
- ! Aquifer transmissivity near the well is maintained because of the vacuum enhancement even when the water level is drawn down.
- ! Vapor-phase hydrocarbons and mobile free product are collected simultaneously.

There are two main conceptual approaches to dual-phase recovery, although they differ only in the vertical positioning of the pump intake (Exhibit V-14).

- ! Recovery of free product and water by a single vacuum/liquids pump.
- ! Extraction of free product, air, and water with a single pump and a vacuum extraction point set at the air/product interface. This technology is commonly referred to as “bioslurping” (Kittel *et al.*, 1994).

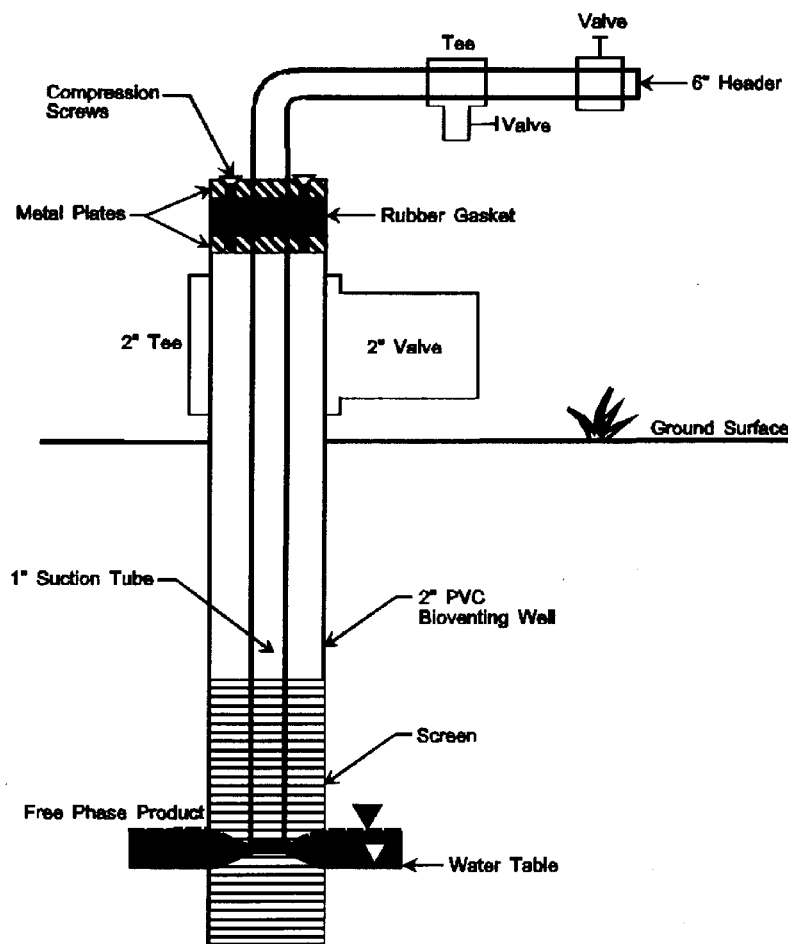
Dual-phase recovery systems may be designed to obtain hydraulic control of the free product plume, depending on the amount of groundwater removed and/or the number and placement of well points.

Dual-Phase Extraction Recovery Systems



(A) Single Vacuum/Liquids Pump

Source: API, 1996. A Guide to the Assessment and Remediation to Underground Petroleum Releases, 3rd edition. API Publication 1628, Washington, DC. Reprinted Courtesy of the American Petroleum Institute.



(B) Biosurping

Source: Kittel, et al., 1994

Applicability

As shown in Exhibit V-15, dual-phase recovery systems are most applicable to:

- ! Medium to low permeable media ($\leq 10^{-3}$ cm/s) or thin (less than 0.5 foot) saturated thicknesses.
- ! Water table depths of 5 to 20 feet (deeper for some designs).
- ! Settings in which conventional pumping approaches or trenches are inappropriate or ineffective (API, 1989).
- ! Free product plumes located under paved or sealed surfaces.

Equipment

The equipment used in dual-phase recovery systems includes:

- ! Surface-mounted vacuum pumps for air, water, and product extraction.
- ! Vapor and liquid treatment equipment (*e.g.*, phase separators, granular activated carbon [GAC])
- ! Other equipment such as manifolds, suction lines, and drop tubes.
- ! Gauges and other instrumentation for measuring vacuum pressures and airflow rates.

System Setup

The initial setup of a dual-phase recovery system involves the following procedures:

- ! Place wells sufficiently close to achieve measurable pressure drops (*e.g.*, 0.1 psi) at one-half the distance between adjacent wells.

Exhibit V-15

Applicability Of Dual-Phase Recovery Equipment

	Recommended Minimum Well Diameter	Recommended Minimum Value for K (cm/s)	Relative Capital Costs	Relative Operating Costs	Relative Maintenance Costs	Potential For Product Removal	Advantages	Disadvantages
Single Vacuum Pump	2"	$> 10^{-5}$	M	H	M	VH	Effective for medium to low permeability soils; potentially large radius of influence; increases water and product flow by 3 to 10 times while minimizing drawdown;	Large capital investment; requires high vacuum pump or blower; generally limited to applications of less than 20 ft.; requires phase separation and treatment; longer initial startup and adjustment periods
Bioslurping	2"	$> 10^{-5}$	H	H	M	VH	no reduction of transmissivity at the well; extracts product (liquid and vapor) from capillary fringe; significantly reduces remediation time	

K - Hydraulic Conductivity; L - Low; M - Moderate; H - High; VH - Very High

- ! Set well screen intervals at a minimum of 5 feet above and 2 feet below the water table.
- ! Place vacuum extraction points at an elevation just above the air/product interface.
- ! Adjust vacuum and pumping rates in the field such that the recovery of free product is maximized while minimizing the total fluid requiring treatment.
- ! Optimize and control the vacuum applied to each well point.
- ! Seal recovery and monitoring well systems.

Setup times are significantly longer than other recovery alternatives. Adjustments may be necessary to maintain product/water suction for periods when background water tables are falling.

Operation And Maintenance

Normal O&M activities of dual-phase recovery systems include the following activities:

- ! Visually inspect clear tubes for the production of water and product.
- ! Monitor the total system vacuum.
- ! Frequently monitor the vacuum applied at each well point.
- ! Adjust the gate valves on lines at well heads (balance system).
- ! Operate the vacuum pump properly.
- ! Take vacuum and temperature readings at the vacuum pump and air/water separator.
- ! Record airflow rates.
- ! Lubricate vacuum pump.

- ! Check all seals and connections (for leaks).
- ! Monitor vacuum readings at sealed monitoring wells in the vadose zone.
- ! Determine the total volumes of product, water, and air produced as well as the fraction of product recovered from extracted air.

Termination Criteria/Monitoring

Operation of a dual-phase recovery system is complete when it ceases to produce significant volumes of hydrocarbons. Termination criteria may include total free product recovery rates (*e.g.*, less than 2 gallons per month or ratio of hydrocarbons recovered to groundwater pumped of 0.1 percent) and free product thickness in monitoring or extraction wells (*e.g.*, less than 0.01 foot). Thicknesses should be monitored on a monthly or quarterly basis to ensure that wells do not contain hydrocarbons. A time period should be specified in which no exceedance of a threshold hydrocarbon thickness (0.1 foot) should occur (*e.g.*, 2 years of quarterly monitoring). The threshold thickness may also serve as an action level to restart the system if it is exceeded.

A summary of the advantages and limitations of free product recovery systems is provided in Exhibit V-16.

Exhibit V-16

Summary of Advantages and Limitations of Free Product Recovery Systems

SKIMMING		
Floating/Floating Inlet	<u>Advantages</u> <ul style="list-style-type: none"> Removes product to a sheen Minimizes water recovery Requires minimal adjustment since unit moves with fluctuating water table Capable of recovery of up to 5 gpm 	<u>Limitations</u> <ul style="list-style-type: none"> Membranes and screens are prone to clogging and failure and require cleaning Large-diameter units perform better than small-diameter versions Limited radius of influence
Direct Pumping of Product Layer	<u>Advantages</u> <ul style="list-style-type: none"> High recovery rates (>5gpm) are possible 	<u>Limitations</u> <ul style="list-style-type: none"> Removal of product to a sheen requires pumping of some water Requires a minimum product thickness of 1 - 4 inches (~0.08 - 0.30 ft) Frequent adjustment of pump intake required
Absorbent	<u>Advantages</u> <ul style="list-style-type: none"> No water produced Skims product to a thin layer (0.01 ft) Low cost and simple operation and maintenance 	<u>Limitations</u> <ul style="list-style-type: none"> Low recovery rates and limited influence Frequent media replacement/change-out required Requires manual adjustment

WATER TABLE DEPRESSION		
	<u>Advantages</u> <ul style="list-style-type: none"> Capture zone is created which enables hydraulic control of groundwater and product Product recovery rates are enhanced by water table depression, especially in high permeability formations Recovered groundwater can be oxygenated and reinjected for bioremediation 	<u>Limitations</u> <ul style="list-style-type: none"> Recovered fluids usually require treatment Lower permeability formations can require numerous well points Product can be "smeared" across area of depression resulting in greater formation storage Higher permeability formations may require high pumping rates Well network design requires capture zone analysis

Exhibit V-16

Summary of Advantages and Limitations of Free Product Recovery Systems (continued)

VE/GE

Advantages

- Increases free product recovery rates in low permeability settings
- Recovers product from thick capillary fringes
- Decreased residual phase formation or “smearing”
- May be used to recover or remediate residual phase hydrocarbons

Limitations

- Initial startup times are longer than other, conventional methods
- Phase separation is required
- Water and vapor treatment is typically required
- Higher capital costs

DUAL PHASE RECOVERY

Advantages

- Effective for lower permeability formations
- High vacuum increases groundwater and product recovery
- Minimizes drawdown and “smearing” of product
- Expedites site cleanup by recovering all hydrocarbon phases

Limitations

- Usually requires vapor and groundwater treatment
- Phase separation is required
- Longer initial startup time
- Higher capital costs

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APPENDIX

APPENDIX

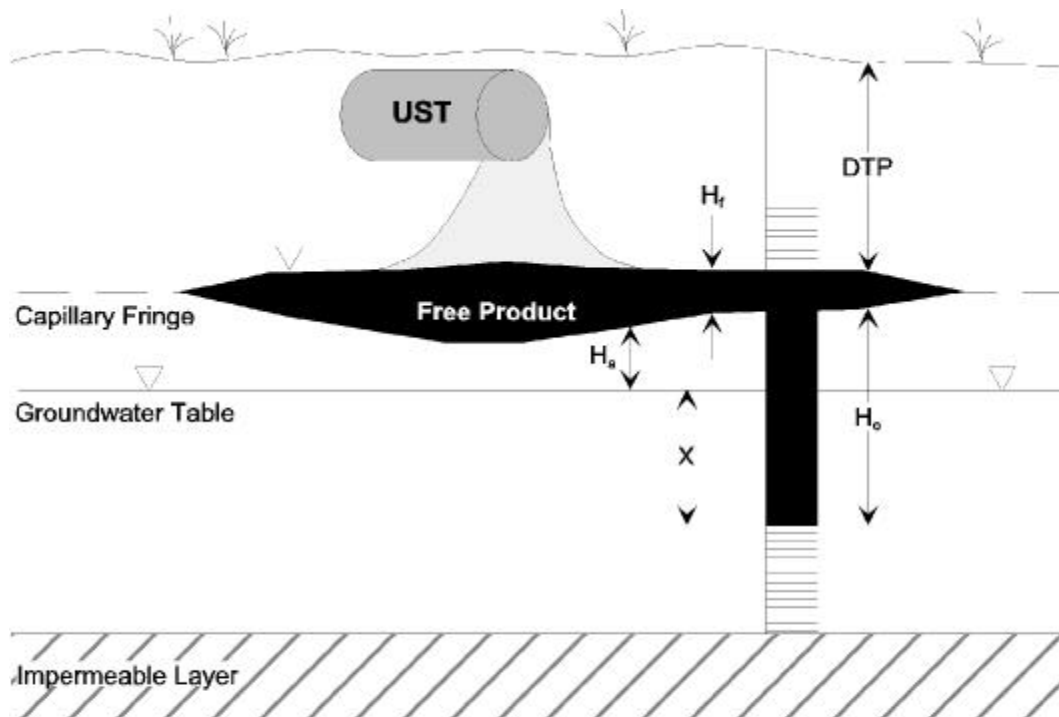
Chapter IV presented various methods for estimating the volume of free product in the subsurface. The results of seven methods were compared for data representative of the same site conditions. Each of these methods are described in greater detail in this Appendix. To facilitate comparison, a uniform terminology has been adopted. Exhibit A-1 lists the variables that appear in the various equations. Exhibit A-2 is a diagram showing the relationship of the variables and characteristics of free product in the vicinity of a monitor well. Experimental data from Abdul *et al.* (1989) and parameter values for the example calculations are presented in Exhibit A-3.

Exhibit A-1
Variables Appearing in Volume Estimation Equations

β_{ao}	=	air-oil scaling factor
β_{ow}	=	oil-water scaling factor
D	=	function of interfluid displacement pressures and hydrostatics
$\Delta\rho$	=	difference in density between water and hydrocarbon ($\rho_w - \rho_o$)
F	=	formation factor
g	=	acceleration of gravity
h_a	=	distance from water table to bottom of mobile hydrocarbon
$h_{c,dr}$	=	average water capillary height under drainage conditions
H_l	=	thickness of mobile hydrocarbon in the adjacent formation
H_o	=	hydrocarbon thickness measured in the well
P_d^{ow}	=	water-hydrocarbon displacement pressure
P_d^{ao}	=	air-hydrocarbon displacement pressure
ρ_w	=	density of water
ρ_o	=	density of the hydrocarbon liquid
V_o	=	volume of hydrocarbon in the adjacent formation per unit area
ϕ	=	soil porosity
σ_{aw}	=	surface tension of water (= 72 dynes/cm @ 20°C)
σ_{ao}	=	surface tension of hydrocarbon
σ_{ow}	=	hydrocarbon-water interfacial tension (= $\sigma_{aw} - \sigma_{ao}$)
S_r	=	residual saturation
x	=	distance from water table to interface between free product and groundwater in the well-- x is equal to the product of the thickness of the hydrocarbon and the hydrocarbon density ($H_o \cdot \rho_o$)

Exhibit A-2

Relationship of Variables and Characteristics of Free Product in the Vicinity of a Monitor Well



Legend

- H_o = apparent (wellbore) product thickness
- H_t = actual formation free product thickness
- DTP = depth to wellbore product level from ground surface
- H_a = free product distance to groundwater table, within formation
- X = interface distance below groundwater table, within well

Modified from Ballesterio *et al.* (1994).

Exhibit A-3

Parameters and Experimental Data Used In Calculating Free Product Thickness Based on Measurements of Free Product in Monitor Wells

Parameters listed in the following table correspond to the variables appearing in the seven equations described previously.

Parameter Values

$\rho_o = 0.84$ gm/cm ³	$\sigma_{aw} = 72$ dynes/cm	$\phi = 0.424$
$\rho_w = 1.00$ gm/cm ³	$\sigma_{ao} = 32$ dynes/cm	$S_r = 0.091$
$F = 7.5$ (med.sand)	$\sigma_{ow} = 40$ dynes/cm	$P_d^{ao} = 5.21$ cm H ₂ O
$h_{c,dr} = 17$	$\beta_{ao} = 2.25$	$P_d^{ow} = 6.51$ cm H ₂ O
$g = 980$ cm/s ²	$\beta_{ow} = 1.80$	$D = 0.035$

The data appearing in the following table are from Abdul *et al.* (1989). Their experiment essentially involved introducing dyed diesel fuel into an acrylic column containing well-graded sand and a miniature monitor well. The cylinder was initially filled with water from the bottom and then allowed to drain until equilibrium was reached. Diesel fuel was then allowed to infiltrate from the surface. The height of diesel fuel in the sand and well was measured and recorded. The experiment was repeated 5 times.

Experimental Data

Trial Number	H _o (cm)	h _a (cm)	x [H _o · ρ _o] (cm)
1	6	17	5.04
2	63	9	52.92
3	68	6.5	57.12
4	73	2	61.32
5	84	0	70.56

Method of de Pastrovich (1979)

$$H_f = \frac{H_o (\rho_w - \rho_o)}{\rho_o}$$

This method depends only upon the density (ρ_o) of the liquid hydrocarbon relative to the density of water. For a hydrocarbon liquid with a density of 0.8, and assuming that the density of water (ρ_w) is equal to 1, the hydrocarbon thickness in the formation (the actual thickness) is only one-fourth the thickness measured in the well (the apparent thickness). Stated another way, the hydrocarbon thickness measured in the well is four times greater than the actual thickness in the formation. The principal weakness of this method is that it does not account for the effects of different soil types. Exhibit III-12 illustrates that in general, the ratio of apparent to true free product thickness increases as soil grain size decreases. Thus, this method may be more accurate in finer grained soil (*e.g.*, silt, clay) than in coarser-grained soil (*e.g.*, sand, loam)

Method of Hall, *et al.* (1984)

$$H_f = H_o - F$$

This method depends upon a “formation factor” (F), which is apparently empirical, and not related to any other type of formation factor (*e.g.*, those found in petroleum literature) (Ballesterro *et al.*, 1994). For a fine sand, F is equal to 12.5 cm; for a medium sand, F is equal to 7.5 cm; and for a coarse sand, F is equal to 5 cm. The principal weakness of this method is in selecting an appropriate value for F , especially when the soil is either not one of the three types mentioned above or is layered. Hall *et al.* (1984) also report that there must be a minimum thickness of hydrocarbon in the well for this method to be valid. For a fine sand, the minimum thickness is equal to 23 cm; for a medium sand, the minimum thickness is equal to 15 cm; and for a coarse sand, the minimum thickness is equal to 8 cm.

Method of Blake and Hall (1984)

$$H_f = H_o - (x + h_a)$$

This method is relatively straightforward, depending only upon measured lengths, however, the parameter h_a is difficult to accurately measure especially in the field. Ballestero *et al.* (1994) indicate that h_a should equal the height of the water capillary fringe when the thickness of hydrocarbon in the formation is relatively small since no pore water is displaced. As the thickness of free product builds up, the water capillary fringe becomes depressed as pore water is displaced and the value of h_a diminishes. When the hydrocarbon lens reaches the water table, the value of h_a becomes zero. At this point, the thickness of hydrocarbon in the formation is equal to the distance between the top of the free product layer and the true elevation of the water table. Both of these measurements can be obtained using the methodology illustrated in Exhibit III-10.

Method of Ballestero *et al.* (1994)

$$H_f = ((1 - \rho_o) \cdot H_o) - h_a$$

This method is essentially equivalent to the method of Blake and Hall (1984) when an actual measurement of their parameter “ x ” is not available, but the product density and thickness of product in the monitor well are known. Recall that x is equal to the product of the thickness of the hydrocarbon in the well and the hydrocarbon density ($H_o \cdot \rho_o$). Rearranging the above equation and substituting x for ($H_o \cdot \rho_o$) yields the same equation. The principal limitation of this method (as well as the method of Blake and Hall) is that the parameter h_a is difficult to measure in the field. When h_a has decreased to zero, the thickness of the free product layer in the soil is equal to the distance between the top of the free product layer measured in the well and the true (corrected) elevation of the water table. Both of these measurements can be obtained using the methodology illustrated in Exhibit III-10.

Method of Schiegg (1985)

$$H_f = H_o - 2(h_{c,dr})$$

This method essentially attempts to correct the exaggerated thickness of free product in a well by subtracting a constant ($2 h_{c,dr}$) that depends on the soil type. The finer the soil, the greater the constant. Typical values of $h_{c,dr}$, as reported by Bear (1972), are 2-5 cm for coarse sand, 12-35 cm for medium sand, and 35-70 for fine sand. The principal weakness of this method is that it relies on a parameter that is difficult to accurately determine. Values for $h_{c,dr}$ vary by a factor of 2 over the range from low to high. Also, it is possible for this method to yield a negative value if there is only a thin layer of free product in the well.

Method of Farr *et al.* (1990)

$$V_o = \phi(1 - S_r) D \left[\left(\frac{H_o}{D} \right) - 1 \right]$$

$$D = \frac{P_d^{ow}}{\Delta \rho g} - \frac{P_d^{ao}}{\rho_o g}$$

This method is dependent upon conditions of static equilibrium. Farr *et al.* (1990) present several variations of this equation for different soil types and different extent of liquid hydrocarbon in the unsaturated zone. The above equation is based on equation #15 in their paper, which is valid for unconsolidated sand with very uniform pore sizes. The principal limitation of this method is in obtaining values for P_d^{ow} and P_d^{ao} , neither of which is easily measured in the field. Ballesterio *et al.* (1994) present and discuss this method, however there is a discrepancy in the formulation of the “D” term, which is not possible to resolve based on the information provided. Ballesterio *et al.* (1994) also mistakenly assume that H_f and V_o are equivalent. The relationship between H_f and V_o is discussed later in this Appendix.

Method of Lenhard and Parker (1990)

$$H_f = \frac{\rho_o \beta_{ao} H_o}{\beta_{ao} \rho_o - \beta_{ow}(1 - \rho_o)}$$

$$\beta_{ao} = \frac{\sigma_{aw}}{\sigma_{ao}}$$

$$\beta_{ow} = \frac{\sigma_{aw}}{\sigma_{ow}}$$

This method is dependent upon conditions of static equilibrium; it assumes a theoretical, vertical saturation profile based on generalized capillary pressure relationships. Extensions of this method allow consideration of residual oil trapped above and below the mobile zone by a fluctuating water table. The principal limitations of this method are that it does not account for dynamic conditions or small-scale heterogeneities, and few of the parameters can be measured in the field. Parameters from published literature for pure compounds may be substituted but it is uncertain how applicable such values are to aged mixtures of petroleum hydrocarbons in the subsurface.

Relationship Between V_o and H_f

Although both the thickness of hydrocarbon in the soil (H_f) and specific oil volume (V_o) can be expressed in dimensions of length [L], they are not equivalent terms. Vertical integration of the hydrocarbon content in the soil yields the volume (V_o) of hydrocarbon in the medium per unit area, whereas H_f is merely the corrected thickness of the free product layer in the geologic formation. V_o actually has dimensions of L^3/L^2 and is commonly expressed in terms of cubic feet per square foot. To determine H_f , V_o must be divided by the effective porosity. In the unsaturated zone, effective porosity is equal to the product of porosity [ϕ] times the quantity ‘one minus the residual saturation’ ($1-S_r$). The length dimension of the V_o term

is equivalent to the height that a specified volume of liquid hydrocarbon would rise in an empty box measuring one unit of length on each side. The length dimension of the H_f term is equivalent to the height that the same specified volume of liquid hydrocarbon would rise in the same box filled with a porous media (*e.g.*, sand) of porosity ϕ and residual saturation S_r . Obviously, the height of the rise in the box filled with a porous media would be higher than in the empty box. To illustrate this point, consider an empty box that measures one unit of length on each side. Take a specific volume of liquid and pour it into the box. The depth of liquid in the box is equivalent to the specific volume of the liquid. Now consider the same box but this time it is filled with marbles that are packed so that the pore spaces represent only 25 percent of the total volume. If the same volume of liquid is poured into this box, the height of the liquid will be four times greater than the height in the empty box.

Relevance To Free Product Recovery

Each of the above methods for determining volume of free product has its strengths and weaknesses. In general, none of the methods is particularly reliable under any given set of conditions either in the field or in the laboratory. Although there have been some creative attempts to compensate for the limitations of some of the methods, it is not usually possible to predict the accuracy. For example, Huntley *et al.* (1992) apply the methods of Farr *et al.* (1990) and Lenhard and Parker (1990) to a stratified system, with each layer represented by its own specific capillary pressure-saturation curves. The profiles generated by the layered model match measured hydrocarbon saturations better than the use of a single “average” layer. However, the study indicates that predicted saturations can be erroneous if the system is not in equilibrium, and hence in violation of the assumption of hydrostatic pressure distribution. These non-equilibrium effects can be caused by rising or falling water table elevations. Unfortunately, like anisotropy, non-equilibrium is most often the rule, and isotropy and equilibrium are the exceptions. To estimate the volume of free product in the subsurface, no one method should be relied on exclusively. Select the methods that are most appropriate to the site conditions and determine a volume using each method. In this way a reasonable range of values can be established.

GLOSSARY

GLOSSARY OF TERMS

Absolute Viscosity:	A measure of a fluid's resistance to tangential or shear stress. Also referred to as dynamic viscosity; see also viscosity. Units are usually given in centipoise.
Air/Oil Table:	The surface between the vadose zone and the oil; pressure of oil in the porous medium is equal to atmospheric pressure.
Anisotropy:	The conditions under which one or more of the hydraulic properties of an aquifer vary with direction.
Aquifer:	A geologic formation, group of formations or part of a formation that contains saturated permeable material that yields sufficient, economical quantities of groundwater.
Aquifer Test:	A test to determine hydraulic properties of an aquifer, involving the withdrawal or injection of measured quantities of water from or to a well and the measurement of resulting changes in hydraulic head in the aquifer.
Biodegradation:	A subset of biotransformation, it is the biologically mediated conversion of a compound to more simple products.
Bulk Density:	The mass of a soil per unit bulk volume of soil; the mass is measured after all water has been extracted and the volume includes the volume of the soil itself and the pore volume.
Capillary Forces:	Interfacial forces between immiscible fluid phases, resulting in pressure differences between the two phases.

Capillary Fringe:	The zone immediately above the water table within which the water is drawn by capillary forces (fluid is under tension). The capillary fringe is saturated and it is considered to be part of the unsaturated zone.
Cone of Depression:	A depression in the groundwater table (or potentiometric surface) that has the shape of an inverted cone and develops around a vertical discharge well.
Darcy's Law:	An empirically derived equation for the flow of fluids through porous media. It is based on the assumptions that flow is laminar and inertia can be neglected, and it states that the specific discharge, q , is directly proportional to the hydraulic conductivity, K , and the hydraulic gradient, I .
DNAPL:	Dense Non-Aqueous Phase Liquid. A liquid which consists of a solution of organic compounds (<i>e.g.</i> , chlorinated hydrocarbons) and which is denser than water. DNAPLs sink through the water column until they reach the bottom of the aquifer where they form a separate layer. Unlike LNAPLs, DNAPLs flow down the slope of the aquifer bottom which is independent of the direction of hydraulic gradient.
Drawdown:	A lowering of the water table of an unconfined aquifer or the potentiometric surface of a confined aquifer caused by pumping of groundwater from wells. The vertical distance between the original water level and the new water level.
Dual-Phase Extraction:	The active withdrawal of both liquid and gas phases from a well usually involving the use of a vacuum pump.
Effective Porosity:	The interconnected pore space through which fluids can pass, expressed as a percent of bulk volume. Part of the total porosity will be occupied by static fluid being held to mineral surface by surface tension, so effective porosity will be less than total porosity.

Extraction Well:	A discharge well used to remove groundwater or air.
Free Product:	Immiscible liquid phase hydrocarbon existing in the subsurface with a positive pressure such that it can flow into a well.
Groundwater:	The water contained in interconnected pores below the water table in an unconfined aquifer or in a confined aquifer.
Interfacial Tension:	The strength of the film separating two immiscible fluids (<i>e.g.</i> , oil and water) measured in dynes (force) per centimeter or millidynes per centimeter.
Henry's Law:	The relationship between the partial pressure of a compound and its equilibrium concentration in a dilute aqueous solution through a constant of proportionality known as the Henry's Law Constant.
Heterogeneity:	Characteristic of a medium in which material properties vary from point to point.
Homogeneity:	Characteristic of a medium in which material properties are identical throughout. Although heterogeneity, or non-uniformity, is the characteristic of most aquifers, assumed homogeneity, with some other additional assumptions, allows use of analytical models as a valuable tool for approximate analyses of groundwater movement.
Hydraulic Conductivity:	A coefficient of proportionality describing the rate at which water can move through a permeable medium. Hydraulic conductivity is a function of both the intrinsic permeability of the porous medium and the kinematic viscosity of the water which flows through it. Also referred to as the coefficient of permeability.
Hydraulic Gradient:	Slope of a water table or potentiometric surface. More specifically, change in the hydraulic head per unit of distance in the direction of the maximum rate of decrease.

Hydraulic Head:	Height above a datum plane (such as mean sea level) of the column of water that can be supported by the hydraulic pressure at a given point in a groundwater system. Equal to the distance between the water level in a well and the datum plane.
Hysteresis:	Phenomenon in which properties such as capillary pressure or relative permeability may differ depending on whether a fluid-fluid interface is advancing (imbibition) or receding (drainage).
Immiscible:	The chemical property where two or more liquids or phases do not readily dissolve in one another, such as soil and water.
Intrinsic Permeability:	Pertaining to the relative ease with which a porous medium can transmit a liquid under a hydraulic or potential gradient. It is a property of the porous medium and is independent of the nature of the liquid or the potential field.
Isotropy:	The condition in which the properties of interest (generally hydraulic properties of the aquifer) are the same in all directions.
Kinematic Viscosity:	The ratio of dynamic viscosity to mass density. It is obtained by dividing dynamic viscosity by the fluid density. Kinematic viscosity is typically reported in units of centistokes (cSt).
LNAPL:	Light Non-Aqueous Phase Liquid. A liquid consisting of a solution of organic compounds (<i>e.g.</i> , petroleum hydrocarbons) which is less dense than water and forms a separate layer that floats on the water's surface.
NAPL:	Non-Aqueous Phase Liquid. See also DNAPL and LNAPL.
Partitioning:	Chemical equilibrium condition where a chemical's concentration is apportioned between two different phases according to the partition coefficient, which is

the ratio of a chemical's concentration in one phase to its concentration in the other phase.

Perched Aquifer: A special case of unconfined aquifer which occurs wherever an impervious (or semipervious) layer of limited areal extent is located between the regional water table of an unconfined aquifer and the ground surface.

Porosity: Ratio of the total volume of voids to the total volume of a porous medium. The percentage of the bulk volume of a rock or soil that is occupied by interstices, whether isolated or connected. Porosity may be primary (formed during deposition or cementation of the material) or secondary (formed after deposition or cementation) such as fractures.

Potentiometric Surface: A surface that represents the level to which water will rise in tightly cased wells. If the head varies significantly with depth in the aquifer, then there may be more than one potentiometric surface. The water table is a particular potentiometric surface for an unconfined aquifer.

Pumping Test: A test that is conducted to determine aquifer or well characteristics. A test made by pumping a well for a period of time and observing the change in hydraulic head in the aquifer. A pumping test may be used to determine the capacity of the well and the hydraulic characteristics of the aquifer. Also called aquifer test.

Radius of Influence: The radial distance from the center of a wellbore to the point where there is no lowering of the water table or potentiometric surface (the edge of its cone of depression). The radial distance from an extraction well that has adequate air flow for effective removal of contaminants when a vacuum is applied to the extraction well.

Relative Permeability: The permeability of the rock to gas, NAPL, or water, when any two or more are present, expressed as a fraction of the single phase permeability of the rock.

Residual Saturation:	Saturation below which fluid drainage will not occur.
Saturation:	The ratio of the volume of a single fluid in the pores to pore volume expressed as a percentage or a fraction.
Saturated Zone:	Portion of the subsurface environment in which all voids are ideally filled with water under pressure greater than atmospheric. The zone in which the voids in the rock or soil are filled with water at a pressure greater than atmospheric. The water table is the top of the saturated zone in an unconfined aquifer.
Solubility, Aqueous:	The maximum concentration of a chemical that will dissolve in pure water at a reference temperature.
Sorption:	Processes that remove solutes from the fluid phase and concentrate them on the solid phase of a medium; used to encompass absorption and adsorption.
Transmissivity:	Rate at which water of the prevailing kinematic viscosity is transmitted through a unit width of the aquifer under a unit hydraulic gradient.
Unconfined:	Conditions in which the upper surface of the zone of saturation forms a water table under atmospheric pressure.
Unsaturated Zone:	The zone between the land surface and the water table. It includes the root zone intermediate zone, and capillary fringe. The pore spaces contain water, as well as air and other gases at less than atmospheric pressure. Saturated bodies, such as perched groundwater, may exist in the unsaturated zone, and water pressure within these may be greater than atmospheric. Also known as “vadose zone.”
Vapor Pressure:	The partial pressure exerted by the vapor (gas) of a liquid or solid substance under equilibrium conditions. A relative measure of chemical volatility, vapor pressure is used to calculate air-

water partition coefficients (*i.e.*, Henry's Law constants) and volatilization rate constants.

Viscosity:	The internal friction within a fluid that causes it to resist flow. Absolute viscosity is typically given in centipoise; kinematic viscosity is the absolute viscosity divided by the fluid density. Kinematic viscosity is typically reported in units of centistokes (cSt).
Viscous Fingering:	The formation of finger-shaped irregularities at the leading edge of a displacing fluid in a porous medium which moves out ahead of the main body of a fluid.
Volatilization:	The transfer of a chemical from the liquid to the gas phase. Solubility, molecular weight, vapor pressure of the liquid, and the nature of the air-liquid interface affect the rate of volatilization.
Water Table:	Upper surface of a zone of saturation, where that surface is not formed by a confining unit; water pressure in the porous medium is equal to atmospheric pressure. The surface between the vadose zone and the groundwater; that surface of a body of unconfined groundwater at which the pressure is equal to that of the atmosphere.
Well Point:	A hollow vertical tube, rod, or pipe terminating in a perforated pointed shoe and fitted with a fine-mesh wire screen.
Wettability:	The relative degree to which a fluid will spread on (or coat) a solid surface in the presence of other immiscible fluids.

CHECKLIST

CHECKLIST: FREE PRODUCT RECOVERY PLAN

This checklist can help you to evaluate the completeness of a plan for free product recovery. As you go through the plan, answer the following questions. If you answer several questions *no*, you probably need additional information or clarification from the plan preparer. This summary should be helpful in answering some of the questions.

1. Data Needed for Review of Free Product Recovery Plan.

Yes No

- | | | |
|--------------------------|--------------------------|---|
| <input type="checkbox"/> | <input type="checkbox"/> | Does plan contain release history and volume estimates? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is the area of the free product plume defined in all directions? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is the depth to water known? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is the volume of free product estimated? |
| <input type="checkbox"/> | <input type="checkbox"/> | Are hydraulic conductivity and thickness of the aquifer known or estimated? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is hydraulic gradient known or presented as water table contours? |
| <input type="checkbox"/> | <input type="checkbox"/> | Are the hydrocarbon type, density, and viscosity known? |

2. Is Free Product Recovery Approach Consistent With Remedial Action Objectives and Comprehensive CAP?

Yes No

- | | | |
|--------------------------|--------------------------|--|
| <input type="checkbox"/> | <input type="checkbox"/> | Are remedial objectives of free product recovery system clearly defined? |
|--------------------------|--------------------------|--|

- | | | |
|--------------------------|--------------------------|---|
| <input type="checkbox"/> | <input type="checkbox"/> | Is applicable approach (skimmer, recovery with groundwater depression, or dual-phase recovery) matched to remedial action objectives? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is the free product recovery approach compatible with comprehensive CAP remedy? |

3. Is Active Free Product Recovery Necessary?

Yes No

- | | | |
|--------------------------|--------------------------|---|
| <input type="checkbox"/> | <input type="checkbox"/> | Is the volume of free product greater 50 gallons? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is the maximum thickness of free product in monitoring wells greater than 0.1 foot? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is the hydraulic conductivity of the soil greater than 10^{-5} cm/s? |

4. Have All The Free Product Recovery System Design Criteria Been Evaluated?

Yes No

- | | | |
|--------------------------|--------------------------|--|
| <input type="checkbox"/> | <input type="checkbox"/> | Are well/drain locations specified? |
| <input type="checkbox"/> | <input type="checkbox"/> | Are construction details for wells/drains specified? |
| <input type="checkbox"/> | <input type="checkbox"/> | Are pumping rates and drawdown levels estimated for wells and drains (groundwater depression)? |
| <input type="checkbox"/> | <input type="checkbox"/> | Are the total rates of groundwater, free product, and vapor production estimated? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is the discharge option for any pumped groundwater specified? |
| <input type="checkbox"/> | <input type="checkbox"/> | Is pumping/skimming equipment specified and appropriate? |

<input type="checkbox"/>	<input type="checkbox"/>	Are the locations of pipelines, manifolds, and separator/treatment system shown on map?
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<input type="checkbox"/>	<input type="checkbox"/>	Are system startup procedures specified?
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5. Is The Operation and Monitoring Plan Complete?

Yes	No	
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<input type="checkbox"/>	<input type="checkbox"/>	Is monitoring of production rates of hydrocarbon and groundwater proposed?
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<input type="checkbox"/>	<input type="checkbox"/>	Are hydrocarbon thickness and groundwater elevations to be monitored?
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<input type="checkbox"/>	<input type="checkbox"/>	Are routine maintenance procedures described?
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<input type="checkbox"/>	<input type="checkbox"/>	Is bi-monthly monitoring scheduled during active recovery?
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<input type="checkbox"/>	<input type="checkbox"/>	Are termination criteria specified?
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<input type="checkbox"/>	<input type="checkbox"/>	Is post-termination (of the recovery system) monitoring specified?
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<input type="checkbox"/>	<input type="checkbox"/>	Are criteria for restarting recovery specified for the post-termination monitoring period?
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