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DNAPL SITE CHARACTERIZATION

Office of Emergency and Remedial Response
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Quick Reference Fact Sheet

INTRODUCTION

Dense nonaqueous phase liquids (DNAPLs), such as some chlorinated solvents, coal tar wastes, creosote based wood-treating oils, and some pesticides, are immiscible fluids with a density greater than water. As a result of widespread production, transportation, use, and disposal of hazardous DNAPLs, particularly since 1940, there are numerous DNAPL contamination sites in North America. The potential for significant long-term groundwater contamination by DNAPL chemicals at many sites is high due to their toxicity, limited solubility (but much higher than drinking water limits), and significant migration potential in soil gas, groundwater, and/or as a separate phase liquid. DNAPL chemicals, particularly chlorinated solvents, are among the most prevalent groundwater contaminants identified in groundwater supplies and at waste disposal sites. For these and other reasons, it is important to investigate for DNAPLs (Table 1).

Table 1. Why Investigate DNAPL?

- To facilitate early removal action (e.g., if the DNAPL zone is still expanding)
- To adequately account for it in performing a risk assessment
- To evaluate possible cosolvency effects (e.g., NAPL mobilizing immobile chemicals)
- Because DNAPL transport principles and properties differ from those associated with solutes
- To adequately characterize the source area
- To characterize mass loadings and mass-in-place (e.g., most mass will be in the DNAPL)
- To adequately account for the dissolution of DNAPL (e.g., can persist for decades; effluent changes over time leaving behind a residual that may be more difficult to remediate)
- To avoid spreading contamination via characterization and/or remediation

INVESTIGATION STRATEGY

Site characterization, a process following the scientific method, is performed in phases (Figure 1). During the initial phase, a hypothesis or conceptual model of chemical presence, transport and fate is formulated using available site information and an understanding of the processes that control chemical distribution. Based on the initial hypothesis, a data collection program is designed in the second phase to test and improve the site conceptual model and thereby facilitate risk and remedy assessment. After analyzing the newly acquired data within the context of the initial conceptual model, an iterative step of refining the hypothesis is performed using the results of the analysis, and additional data may be collected. As knowledge of the site increases and becomes more complex, the working hypothesis may take the form of either a numerical or analytical model. Data collection continues until the hypothesis is proven sufficiently. During implementation of a remedy, the subsurface system is stressed. This provides an opportunity to monitor and not only learn about the effectiveness of the remediation, but to learn more about the subsurface. Therefore, remediation (especially pilot studies) should be considered part of site characterization, yielding data that may allow improvements to be made in the conduct of remediation.

NOTE:

Characterization should be conducted in a phased, evolutionary manner starting with review of available data. Early field work should focus on areas beyond the DNAPL zone and use noninvasive methods in the DNAPL zone. Each characterization activity should be designed to test the conceptual model in a manner that will increase the capacity to perform risk and remedy analysis.

To limit the potential for promoting contaminant migration, avoid: (1) conducting unecessary field work; (2) drilling through capillary barriers beneath DNAPL; (3) pumping from beneath DNAPL zones; and, (4) using invasive characterization or remediation methods without due consideration for the potential consequences.

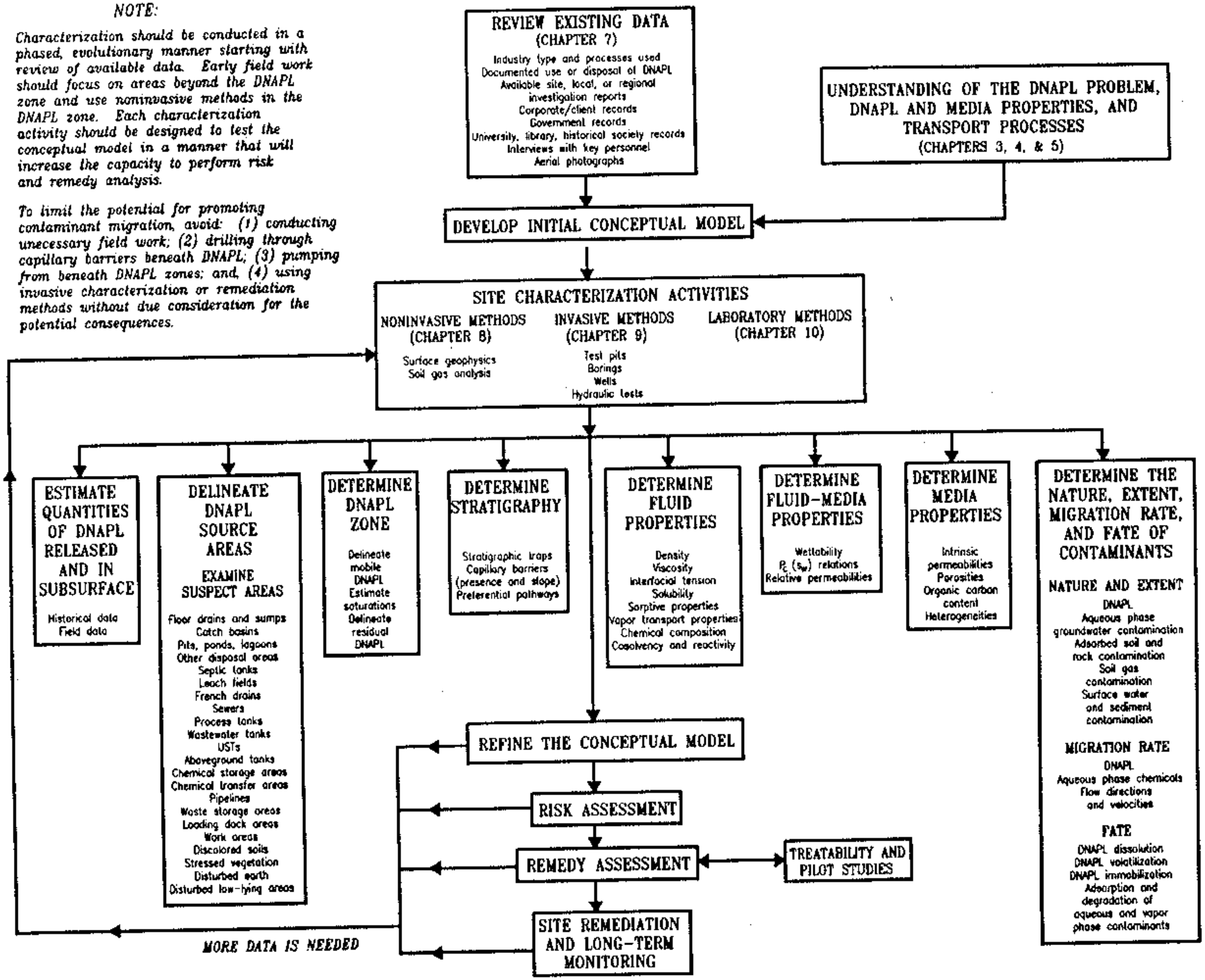


Figure 1. DNAPL site characterization flowchart (modified from Cohen and Mercer, 1993).

SITE CONCEPTUALIZATION

The subsurface movement of DNAPL is controlled substantially by the nature of the release, the DNAPL density, interfacial tension, and viscosity, porous media and capillary properties, and usually to a lesser extent, hydraulic forces. Below the water table, non-wetting DNAPL migrates preferentially through permeable pathways such as soil and rock fractures, root holes, and sand layers that provide relatively little capillary resistance to flow. There are several conceptualizations that can be made for DNAPL sites; two are illustrated in Figure 2. As shown, DNAPL chemicals can migrate in the subsurface as volatiles in soil gas, dissolved in groundwater, and as a mobile, separate phase liquid. Depending on how they are released, DNAPLs may be fairly widespread throughout the subsurface (Figure 2a) or they may have a limited distribution (Figure 2b), making detection difficult. Several relatively simple quantitative methods for examining DNAPL presence, migration, containment, dissolution, and mobilization within the context of various conceptual models are described by Cohen and Mercer (1993).

DNAPL SITE CHARACTERIZATION OBJECTIVES

The objectives of DNAPL site characterization include: (1) to determine DNAPL properties, (2) to identify DNAPL release/source areas, (3) to define stratigraphy, (4) to delineate DNAPL distribution, and (5) to minimize investigation risk. DNAPL and media properties control DNAPL migration in the subsurface; Table 2 lists these properties. It is also important to identify stratigraphic barriers and traps, and to determine migration pathways, including man-made features. As part of the DNAPL distribution, a distinction needs to be made between mobile versus DNAPL at residual. Visual detection of DNAPL in soil and groundwater samples may be difficult where the DNAPL is colorless, present in low saturation, or distributed heterogeneously. These factors confound characterization of the movement and distribution of DNAPL even at sites with relatively homogeneous soils and a known, uniform DNAPL source. The difficulty of characterization is further compounded by fractured bedrock, heterogeneous strata, multiple DNAPL mixtures and releases, and other complicating factors.

NONINVASIVE METHODS

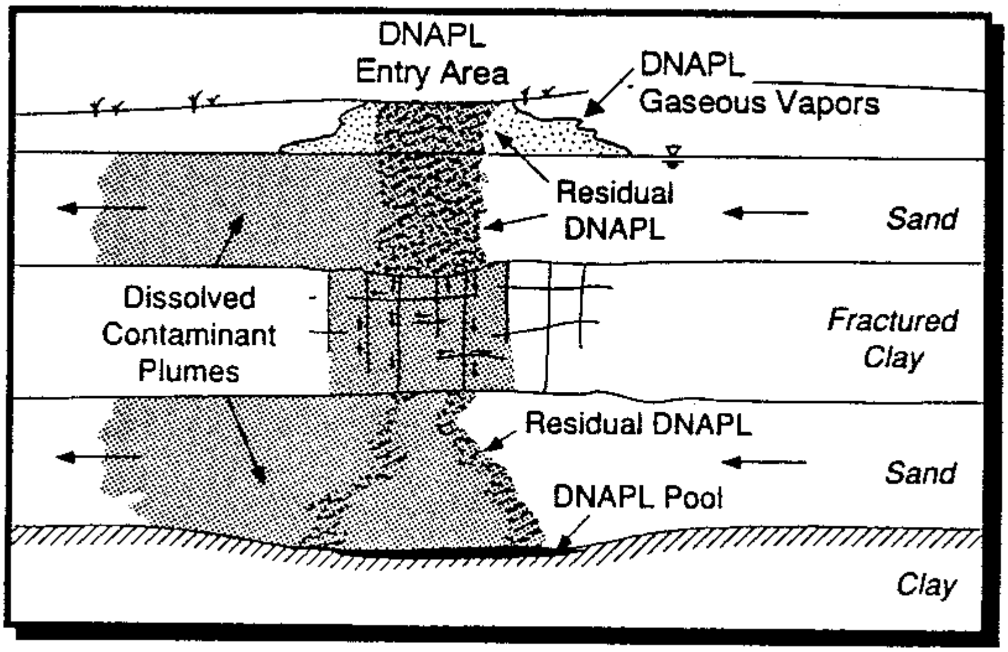
Noninvasive methods can often be used during the early phases of field work to optimize the cost-effectiveness of a DNAPL site characterization program. Specifically, surface geophysical surveys, soil gas analysis, and photointerpretation can facilitate characterization of contaminant source areas, geologic controls on contaminant movement (i.e., stratigraphy and utilities), and the extent of subsurface contamination. Conceptual model refinements derived using these methods reduce the risk of spreading contaminants during subsequent invasive field work.

Surface Geophysics

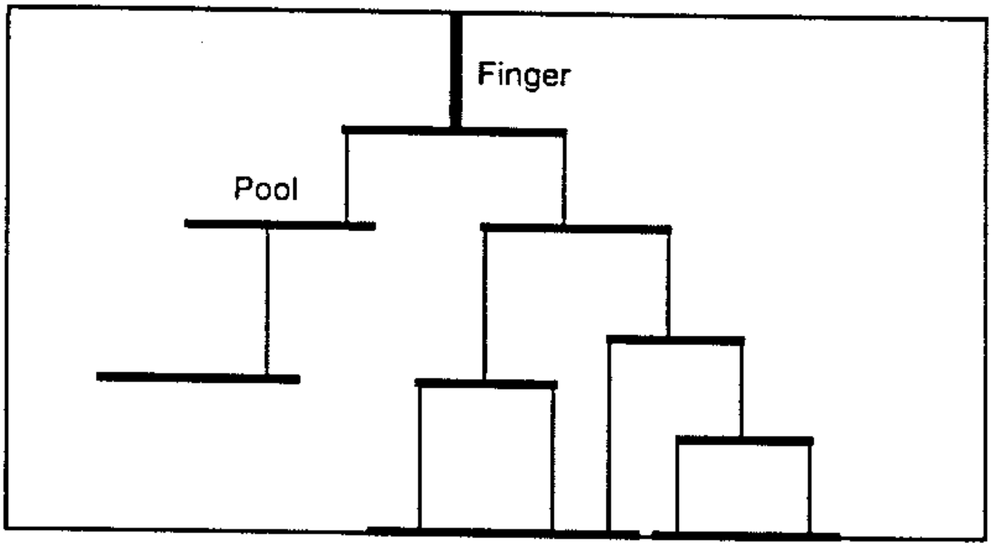
At contamination sites, geophysical surveys are usually conducted to: (1) assess stratigraphic and hydrogeologic conditions; (2) detect and map electrically conductive contaminants; (3) locate and delineate buried wastes and utilities; (4) optimize the location and spacings of test pits, borings, and wells; and (5) facilitate interpolation of subsurface conditions among boring locations. Surface geophysical methods that potentially may be used at DNAPL sites are identified in Table 3. Subsurface DNAPL is generally a poor target for conventional geophysical methods. Although ground-penetrating radar, EM conductivity, and complex resistivity have been used to infer NAPL presence at a very limited number of sites, direct detection and mapping of non-conductive subsurface DNAPL using surface geophysical techniques is an unclear, and apparently limited, emerging technology. The value of surface geophysics at most DNAPL sites will be to aid characterization of waste disposal areas, stratigraphic conditions, and potential routes of DNAPL migration.

Soil Gas Analysis

Many DNAPLs, including most halogenated solvents, have high vapor pressures and will volatilize in the vadose zone to form a vapor plume around a DNAPL source. Volatile organic compounds (VOCs) dissolved in groundwater can also volatilize at the capillary fringe into soil gas. Thus, soil gas surveys may be used to help identify contaminated zones for further study. Table 4 presents characteristics of various contaminants and their



(a) DNAPL chemcials are distributed in several phases: dissolved in groundwater, adsorbed to soils, volatilized in soil gas, and as residual and mobile immiscible fluids (modified from Huling and Weaver, 1991; WCGR, 1991).



(b) DNAPL chemicals in fingers and pools (modified from Anderson et al., 1992).

Figure 2. DNAPL site conceptualizations.

Table 2. Properties of DNAPL and Media that Influence Contaminant Migration (from Mercer and Waddell, 1992).

PROPERTY	DEFINITION	RANGE OF VALUES
Saturation	The volume fraction of the total void volume occupied by that fluid at a point.	0-1
Residual saturation	Saturation at which NAPL becomes discontinuous and is immobilized by capillary forces.	Approximately 0.1-0.5.
Interfacial tension	The free surface energy at the interface formed between two immiscible or nearly immiscible liquids. Surface tension is the interfacial tension between a liquid and its own vapor.	Values of interfacial and surface tensions for NAPL-forming chemicals generally range between 0.015-0.5 N/m.
Wettability	Describes the preferential spreading of one fluid over solid surfaces in a two-fluid system; it depends on interfacial tension.	Determined through contact-angle studies. Commonly, NAPL is the wetting fluid in the vadose zone and the non-wetting fluid in the saturated zone.
Capillary pressure	The difference between the non-wetting fluid pressure and the wetting fluid pressure. It is a measure of the tendency of a porous medium to attract the wetting fluid and repel the non-wetting fluid.	Depends on the interfacial tension, contact angle, and pore size.
Relative permeability	The ratio of the effective permeability of a fluid at a fixed saturation to the intrinsic permeability.	0.0-1.0, depending on the fluid saturation.
Solubility	The maximum concentration of the chemical that will dissolve under a set of chemical and physical conditions.	Varies widely depending on chemical and aquifer conditions.
Volatilization	The transfer of matter from liquid and soil to the gaseous phase.	Depends on organic partitioning between water and air, and NAPL and air.
Density	Mass per unit volume of a substance. Specific gravity is the ratio of a substance's density to that of some standard substance, usually water.	Specific gravities of petroleum products may be as low as 0.7, whereas chlorinated aliphatic compounds can be as high as 1.2 to 1.5.
Viscosity	The internal friction within a fluid that causes it to resist flow.	Varies depending on fluid and temperature.

relation to soil gas surveys. Several chemical characteristics indicate whether a measurable vapor concentration can be detected. Ideally, compounds such as VOCs monitored using soil gas analysis will: (1) be subject to little retardation in groundwater; (2) partition significantly from water to soil gas (Henry's Law constant >0.0005 atm-m3/mole); (3) have sufficient vapor pressure to diffuse significantly upward in the vadose zone (>0.0013 atm @ 20o C); (4) be persistent; and (5) be susceptible to detection and quantitation by affordable analytical techniques.

Studies during the 1980s generally indicated the utility of soil gas surveying for delineating VOC source areas and VOC-contaminated groundwater (e.g., Marrin and Thompson, 1987; Thompson and Marrin, 1987). More recently, well-documented field experiments were conducted at the Borden, Ontario DNAPL research site to investigate the behavior and distributions of TCE in soil gas caused by (1) vapor transport from a DNAPL source in the vadose zone and (2) dissolved transport with groundwater from a DNAPL source below the water table (Hughes et al., 1990a; Rivett and Cherry, 1991). The extent and magnitude of soil gas contamination derived from the vadose zone source was much greater than that derived from the groundwater source. Rivett and Cherry (1991) attribute the limited upward diffusion of groundwater contaminants to the low vertical transverse dispersivities (mm range) which are observed in tracer studies. Soil gas contamination, therefore, is not a reliable indicator of the distribution of DNAPL or groundwater contamination at depth below the water table. Although the vadose zone source produced TCE concentrations in soil gas and groundwater over a much wider area than the groundwater source site, the TCE in groundwater derived from the vadose zone source was less concentrated than at the groundwater source site and was restricted to the upper 5 ft of the saturated zone. Overall, these studies suggest that soil gas contamination will usually be dominated by volatilization and vapor transport from contaminant sources in the vadose zone rather than from groundwater, and that the upward transport of VOCs to the vadose zone from groundwater is probably limited to dissolved contaminants that are very near to the water table.

Air Photo Interpretation

Historic aerial photographs can be analyzed to document waste disposal practices and locations, geologic conditions, drainage patterns, pooled fluids, site development including excavations for pipelines and underground storage tanks, signs of vegetative stress, soil staining, and other factors relevant to assessing subsurface chemical migration. The Earth Science Information Center (ESIC) at the U.S. Geological Survey in Reston, Virginia catalogs and disseminates information about aerial photographs and satellite images available from public and private sources. ESIC will provide a listing of available aerial photographs for any location in the United States and order forms for their purchase.

Another use of air photos is to perform fracture trace analysis. Fracture trace analysis involves stereoscopic study of aerial photographs to identify surface expressions of vertical or nearly-vertical subsurface zones of fracture concentration. In fractured rock terrain, particularly in karst areas, groundwater flow and chemical transport are usually concentrated in fractures.

Table 3. Surface Geophysical Methods for Evaluating DNAPL Site Contamination (from Cohen and Mercer, 1993).

OBJECTIVE	METHODS
Delineate limits of waste disposal areas.	Following review of historical documentation, interviews, aerial photographs, and available site data, consider use of ground-penetrating radar (GPR), electromagnetic (EM) conductivity, magnetometer, and metal detection surveys.
Delineate buried utility corridors.	Following review of historical documentation, utility records, interviews, aerial photographs, and available site data, consider use of GPR, EM conductivity, magnetometer, and metal detection surveys.
Map stratigraphy, particularly permeable pathways and the surfaces of fine-grained capillary barrier layers and bedrock, to determine potential routes of DNAPL migration and stratigraphic traps.	Following review of aerial photographs and available site, local, and regional hydrogeologic data, consider use of GPR, EM conductivity, electrical resistivity, and high resolution seismic surveys.
Delineate conductive inorganic contaminant plumes that may be associated with DNAPL contamination.	Following review of available data on waste disposal practices, chemical migration, and hydrogeologic conditions, consider use of EM conductivity, electrical resistivity surveys.
Delineate geophysical anomalies that may result from an accumulation of DNAPL.	Consider using GPR to infer DNAPL accumulations at shallow depths in low conductivity soils because DNAPL presence will probably alter the dielectric properties of the subsurface (Olhoeft, 1986; WCGR, 1991). Also consider using electrical methods to infer DNAPL accumulation based on the presence of low conductivity anomalies (Davis, 1991). Note that the use of surface geophysical methods for direct detection of DNAPL presence is an emerging, but limited, technology that may not be cost-effective. Very few geophysicists are experienced in the application of surface survey methods for DNAPL detection. These applications, therefore, should be treated with caution.
Note: Survey results depend on site-specific conditions. At some sites, an alternate method may provide better results.	

Table 4. Characteristics of Contaminants in Relation to Soil Gas Surveying (modified from Marrin, 1987).

GROUP/CONTAMINANTS	APPLICABILITY OF SOIL-GAS SURVEY TECHNIQUES
Group A: Halogenated methanes, ethanes, and ethenes	
Chloroform, vinyl chloride, carbon tetrachloride, trichlorofluoromethane, TCA, EDB, TCE	Detectable in soil gas over a wide range of environmental conditions. Dense nonaqueous phase liquid (DNAPL) will sink in aquifer if present as pure liquid.
Group B: Halogenated propanes, propenes, and benzenes	
Chlorobenzene, trichlorobenzene, 1,2-dichloropropane	Limited value; detectable by soil-gas techniques only where probes can sample near contaminated soil or groundwater. DNAPL
Group C: Halogenated polycyclic aromatics	
Aldrin, DDT, chlordane, heptachlor, PCBs	Do not partition into the gas phase adequately to be detected in soil gas under normal circumstances. DNAPL
Group D: C_1 - C_8 petroleum hydrocarbons	
Benzene, toluene, xylene isomers, methane, ethane, cyclohexane, gasoline, JP-4	Most predictably detected in shallow aquifers or leaking underground storage tanks where probes can be driven near the source of contamination. Light nonaqueous phase liquids (LNAPLs) float as thin film on the water table. Can act as a solvent for DNAPLs, keeping them nearer the ground surface.
Group E: C_9 - C_{12} petroleum hydrocarbons	
Trimethylbenzene, naphthalene, decane, diesel and jet A fuels	Limited value; detectable by soil gas techniques only where probes can sample near contaminted soil or groundwater. DNAPL
Group F: Polycyclic aromatic hydrocarbons	
Anthracene, benzopyrene, fluoranthene, chrysene, motor oils, coal tars	Do not partition adequately into the gas phase to be detected in soil gas under normal circumstances. DNAPL

INVASIVE METHODS

Following development of the site conceptual model based on available information and noninvasive field methods, invasive techniques will generally be required to advance site characterization and enable the conduct of risk and remedy assessments. Generally, these invasive activities include: (a) drilling and test pit excavation to characterize subsurface solids and liquids; and (b) monitor well installation to sample fluids, and to conduct fluid level surveys, hydraulic tests, and borehole geophysical surveys. Invasive field methods should be used in a phased manner to test and improve the site conceptual model based on careful consideration of site-specific conditions and DNAPL transport processes.

Invasive Method Risks

The risk of enlarging the zone of chemical contamination by use of invasive methods is an important consideration that must be evaluated during a DNAPL site investigation. Drilling, well installation, and pumping activities typically present the greatest risk of promoting DNAPL migration during site investigation. Drilling and well installations may create vertical pathways for DNAPL movement. In the absence of adequate sampling and monitoring as drilling progresses, it is possible to drill through a DNAPL zone without detecting the presence of DNAPL (USEPA, 1992). Increased hydraulic gradients caused by pumping may mobilize stagnant DNAPL. Pumping from beneath or adjacent to the DNAPL zone can induce downward or lateral movement of DNAPL, particularly in fractured media due to the development of relatively high fluid velocities. In general, groundwater should not be pumped from an uncontaminated aquifer directly beneath a capillary barrier and overlying DNAPL zone. If the risks cannot be adequately minimized, alternate methods should be used, if possible, to achieve the characterization objective; or the objective should be waived.

Drilling Methods

Conventional drilling methods have a high potential for promoting downward DNAPL migration (USEPA, 1992). Specific conditions that may result in downward DNAPL migration include: an open borehole during drilling and prior to well installation; an unsealed or inadequately sealed borehole; a well screen that spans a barrier layer and connects an overlying zone with perched DNAPL to a lower transmissive zone; an inadequately sealed well annulus that allows DNAPL to migrate through the well-grout interface, the grout, the grout-formation interface, or vertically-connected fractures in the disturbed zone adjacent to the well; and, structural degradation of bentonite or grout sealant, or well casing, due to chemical effects of DNAPL or the groundwater environment.

To minimize the risk of inducing DNAPL migration as a result of drilling, site investigators should: (1) avoid unnecessary drilling within the DNAPL zone; (2) minimize the time during which a boring is open; (3) minimize the length of hole which is open at any time; (4) use telescoped casing drilling techniques to isolate shallow contaminated zones from deeper zones; (5) use high-quality continuous sampling procedures (e.g., coring or split-spoon sampling) in a potential DNAPL zone and carefully examine subsurface materials brought to the surface as drilling progresses to avoid drilling through a barrier layer beneath DNAPL (i.e., stop drilling at the top of the barrier layer); (6) consider using a dense drilling mud (i.e., with barium sulfate additives, also known as barite) or maintaining a high hydrostatic head with water to prevent DNAPL from sinking down the borehole during drilling; (7) use less-invasive direct-push sampling methods where appropriate (e.g., cone penetrometer, Geoprobe®, and HydroPunch techniques); (8) select optimum well materials and grouting methods based on consideration of site-specific chemical compatibility; and (9) if the long-term integrity of a particular grout sealant is questionable, consider placing alternating layers of different grout types and sealing the entire distance between the well screen and surface to minimize the potential for vertical migration of DNAPL.

The risk of causing DNAPL migration generally increases where there are fractured media, heterogeneous strata, multiple release locations, large DNAPL release volumes, and barrier layers that are subtle (e.g., a thin silt layer beneath sand) rather than obvious (e.g., a thick soft clay layer beneath sand). At many sites, the DNAPL zone can be adequately characterized by limiting drilling to shallow depths. Characterization of deeper units can be accomplished by deeper borings and wells beyond the edge of the DNAPL zone. The "outside-in" approach whereby invasive activities are conducted beyond suspected DNAPL areas to improve the conceptual model before drilling in the DNAPL zone also is used to reduce risks associated with DNAPL site characterization (USEPA, 1992).

Well Construction

The design and construction of wells at DNAPL sites require special consideration of (1) the effect of well design and location on immiscible fluid movement and distribution in the well and near-well environment; (2) the compatibility of well materials with NAPLs and dissolved chemicals; and (3) well development options. Based on experiments, field experience, and the principles of DNAPL movement, it is apparent that the following factors may cause the elevation and thickness of DNAPL in a well to differ from that in formation and/or lead to vertical DNAPL migration.

(1) If the well screen or casing extends below the top of a DNAPL barrier layer, a measured DNAPL pool thickness may exceed that in the formation by the length of the well below the barrier layer surface.

(2) If the well bottom is set above the top of a DNAPL barrier layer, the DNAPL thickness in the well may be less than the formation thickness.

(3) If the well connects a DNAPL pool above a barrier layer to a deeper permeable formation, the DNAPL elevation and thickness in the well are likely to be erroneous and the well will cause DNAPL to short-circuit the barrier layer and contaminate the lower permeable formation. The height of the DNAPL column at the well bottom will tend to equal or be less than the critical DNAPL height required to overcome the capillary resistance offered by the sandpack and/or formation.

(4) DNAPL which enters a coarse sandpack may sink to the bottom of the sandpack rather than flow through the well screen. Small quantities of DNAPL may elude detection by sinking down the sandpack and accumulating below the base of the well screen.

(5) Similarly, if the bottom of the well screen is set above the bottom of the sandpack and there is no casing beneath the screen, small quantities of DNAPL may elude detection by sinking out the base of the screen and into the underlying sandpack.

(6) Hydrophilic (e.g., quartz) sandpacks generally should be coarser than the surrounding media to ensure that mobile DNAPL can enter the well. Screen or sandpack openings that are too small may act as a capillary barrier to DNAPL flow. Laboratory experiments (Hampton et al., 1991; Hampton and Heuvelhorst, 1990) indicate that (a) NAPL flows more readily into wells with uniform coarse hydrophilic sandpacks than wells with finer-grained and/or nonuniform hydrophilic sandpacks; and (b) NAPL recovery can be optimized using a hydrophobic sandpack material (such as teflon chips or made by applying a water-repellent coating to sand) with angular grains and a nonuniform grain size distribution.

(7) If the well screen is located entirely within a DNAPL pool and water is pumped from the well, DNAPL will upcone in the well to maintain hydrostatic equilibrium causing the DNAPL thickness in the well to exceed that in the formation.

(8) The elevation of DNAPL in a well may exceed that in the adjacent formation by a length equivalent to the DNAPL-water capillary fringe height where the top of the pool is under drainage conditions.

(9) DNAPL will not flow into a well where it is present at or below residual saturation or at negative pressure.

A well that is completed to the top of a capillary barrier and screened from the capillary barrier surface to above the DNAPL-water interface is most likely to provide DNAPL thickness and elevation data that are representative of formation conditions. Well development should be limited in wells containing DNAPL to gentle pumping and removal of fine particles to minimize DNAPL redistribution. Measurements should be made of immiscible fluid stratification in the well prior to and after development.

Fluid Thickness, Elevation, and Sampling Surveys

Fluid elevation and thickness measurements are made in wells to assist determination of fluid potentials, flow directions, and immiscible fluid distributions. With knowledge of DNAPL entry areas, the surface slope of capillary barriers, hydraulic data, and other observations of DNAPL presence, well data can be evaluated to infer the directions of DNAPL migration. Interpretation of fluid data from wells containing NAPL may be complicated by several factors related to the measurement method, fluid properties, well design, or well location. DNAPL in wells, therefore, should be evaluated in conjunction with evidence of geologic conditions and DNAPL presence obtained during drilling.

While conducting immiscible fluid level and thickness measurements, care should be taken to slowly lower and raise the measuring device within the well to avoid disturbing the immiscible fluid equilibrium and creating emulsions. Similarly, measurements should be made prior to purging and sampling activities. The cost of purchase and decontamination of the measuring device should be considered when selecting a measurement method, particularly given uncertainties involved in interpreting NAPL thickness and elevation data. Measurements are typically made using interface probes, bailers, hydrocarbon-detection paste, or other methods (e.g., with a weighted cotton string).

Fluid sampling surveys should be conducted at potential DNAPL sites to examine wells for the presence of LNAPLs and DNAPLs. NAPL samples can be tested for physical properties and chemical composition. Various sampling devices can be employed to acquire fluid samples from the top and bottom of the well fluid column. Villaume (1985) recommends use of a bottom-loading bailer or mechanical discrete-depth sampler for collecting DNAPL samples. Huling and Weaver (1991) suggest that the best DNAPL sampler is a double check valve bailer which should be slowly lowered to the well bottom and then slowly raised to provide the most reliable results. DNAPL can be sampled from wells with a shallow water table (<25 ft deep) with a peristaltic pump and from depths to approximately 300 ft using a simple inertial pump. An advantage of the peristaltic and inertial pumps is that fluid contact is confined to inexpensive tubing (and a foot-valve with the inertial pump). The cost to decontaminate or replace DNAPL-contaminated equipment is usually a major factor in selecting a sampling method.

Determining DNAPL Presence

DNAPL presence can be: (1) determined directly by visual examination of subsurface samples; (2) inferred by interpretation of chemical analyses of subsurface samples; and/or (3) suspected based on interpretation of anomalous chemical distribution and hydrogeologic data. Methods to visually detect DNAPL in subsurface samples are identified in Table 5. Indirect methods for assessing the presence of DNAPL in the subsurface rely on comparing measured chemical concentrations to effective solubility limits for groundwater and to calculated equilibrium partitioning concentrations for soil and groundwater. Chemical data indicative and/or suggestive of DNAPL presence are given in Table 5.

Table 5. Determinant, Inferential, and Suggestive Indications of DNAPL Presence (modified from Cohen and Mercer, 1993, Cherry and Feenstra, 1991; Newell and Ross, 1992; and Cohen et al., 1992).

DETERMINING DNAPL PRESENCE BY VISUAL EXAMINATION OF SUBSURFACE SAMPLES	INFERRING DNAPL PRESENCE BY INTERPRETING CHEMICAL ANALYSES	SUSPECTING DNAPL PRESENCE BASED ON ANOMALOUS FIELD CONDITIONS
Methods to detect DNAPL in wells: * NAPL/water interface probe detection of immiscible phase at base of fluid column * Pump from bottom of fluid column and inspect retrieved sample * Retrieve a transparent, bottom-loading bailer from the bottom of a well and inspect the fluid sample * Inspect fluid retrieved from the bottom of a well using a mechanical discrete-depth sampler * Inspect fluid retained ona weighted cotton string that was lowered down a well **Methods to enhance inspection of fluid sample for DNAPL presence:** * Centrifuge sample and look for phase separation * Add hydrophobic dye (such as Sudan IV or Red Oil) to sample, shake, and look for coloration of DNAPL fraction * Examine UV fluorescence of sample (many DNAPLs will fluoresce) * Assess density of NAPL relative to water (sinkers or floaters) by shaking solution or by using a syringe needle to inject NAPL globules into the water column **Methods to detect DNAPL in soil and rock samples:** * Examine UV fluorescence of sample (many DNAPLs will fluoresce) * Add hydrophobic dye and water to soil sample in polybag or jar, shake, and examine for coloration of the NAPL fraction * Conduct a soil-water shake test without hydrophobic dye (can be effective for NAPLs that are neither colorless nor the color of the soil * Centrifuge sample with water and look for phase separtion * Perform a paint filter test, in which soil is placed in a filter funnel, water is added, and the filter is examined for separate phases	**Chemical analysis results from which DNAPL presence ca be inferred (with more or less certainty depending on the strenth of the overall data):** * Concentrations of DNAPL chemicals in groundwater are greater than 1% of the pure phase solubility on effective solubility * Concentrations of DNAPL chemicals on soils are greater than 10,000 mg/kg (equal to 1% soil mass) * Concentrations of DNAPL chemicals in groundwater calculated from water/soil partitioning relationships and soil samples are greater than pure phase solubility or effective solubility * Organic vapor concentrations detected in soil gas exceeds 100-1000 ppm	**Field conditions that suggest DNAPL presence:** * Concentrations of DNAPL chemicals increase with depth in a pattern that cannot be explained by advective transport * Concentrations of DNAPL chemicals increase up the hydraulic gradient from the contaminant release area (apparently due to containated soil gas migration and/or, DNAPL movement along capillary and/or permeability interfaces that slope counter to the hydraulic gradient) * Erratic patterns of dissolved concentrations of DNAPL chemicals in groundwater which are typical of DNAPL sites due to heterogeneity of (1) the DNAPL distribution, (2) the porous media, (3) well construction details, and (4) sampling protocols * Erratic, localized, very high contaminant concentrations in soil gas, particularly located just above the water table (where dense gas derived from DNAPL in the vadose zone will tend to accumulate) * Dissolved DNAPL chemical concentrations in recovered groundwater that decrease with time during a pump-and-treat operation, but then increase significantly after the pumps are turned off (although complexities of contaminant desorption, formation heterogeneity, and temporal and spatial variations of the contaminant source strength can produce similar results) * The presence of dissolved DNAPL chemicals in groundwater that is older than potential contamiant releases (using age dating) suggests DNAPL migration * Deterioration of wells and pumps (can be caused by DNAPL; i.e., chlorinated solvents degrade PVC) * Patterns of dissolved chemicals that may be indicative of pulsed releases associated with recharge events through a DNAPL zone * Plume behavior where most of the plume mass is still near the source area, even after adequate time has passed to allow dissolved transport away from the source area * Mass removed during remediation far exceeds original calculation of dissolved and adsorbed mass-in-place

Where present as a separate phase, DNAPL compounds are generally detected at <10% of their aqueous solubility limit in groundwater. This is due to the effects of non-uniform groundwater flow, variable DNAPL distribution, the mixing of groundwater in a well, and the reduced effective solubility of individual compounds in a multi-liquid NAPL mixture. Typically, dissolved contaminant concentrations >1% of the aqueous solubility limit are highly suggestive of NAPL presence. Concentrations <1%, however, do not preclude the presence of NAPL. In soil, contaminant concentrations in the percent range are generally indicative of NAPL presence. However, NAPL may also be present at much lower soil concentrations. Feenstra et al. (1991) detail an equilibrium partitioning method for assessing the presence of NAPL in soil samples based on determining total chemical concentrations, soil moisture content, porosity, organic carbon content, approximate composition of the possible NAPL, sorption parameters, and solubilities.

INTEGRATED DATA ANALYSIS

There is no practical cookbook approach to site investigation or data analysis. In addition to the site characterization techniques described herein, many additional methods (i.e., using tracers, interpreting chemical distributions and ratios, and conducting hydraulic tests) can be used to enhance site evaluation. Each site presents variations of contaminant transport conditions and issues. Site characterization, data analysis, and conceptual model refinement are iterative activities which should satisfy the characterization objectives outlined in Figure 1 as needed to converge to a final remedy. During the process, acquired data should be utilized to guide ongoing investigations. For example, careful examination of soil, rock, and fluid samples obtained as drilling progresses should be made to identify DNAPL presence and potential barrier layers and thereby guide decisions regarding continued drilling, well construction, and/or borehole abandonment. Geologic, fluid elevation, and chemical distribution data should be organized (preferably using database, CAD, and/or GIS programs) and displayed on maps that are updated periodically to help determine the worth of additional data collection activities. With continued refinement of the site conceptual model, the benefit, cost, and risk of additional work can and should be evaluated with improved accuracy. This is the advantage of a flexible, phased approach to site characterization.

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