

# **DETECTION AND DELINEATION OF SUBSURFACE DNAPL DISTRIBUTION**

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## **INTRODUCTION**

Dense nonaqueous phase liquids (DNAPLs) pose a particular challenge in terms of site investigation and remediation due to complex migration patterns and high residual retention within the aquifer matrix. The presence of DNAPL materials in the subsurface has been noted at numerous industrial facilities, particularly those involved with the use of chlorinated solvents, wood preservatives, coal tar derivatives, and pesticides. Most DNAPLs undergo only limited degradation in the subsurface, and persist for long periods while slowly releasing soluble organic constituents to groundwater through dissolution. Even with a moderate DNAPL release, dissolution may continue for hundreds of years or longer under natural conditions before all the DNAPL is dissipated and concentrations of soluble organics in groundwater return to background levels.

Given the potential long-term impact of DNAPL on groundwater quality, proper detection and delineation of DNAPL materials is critical to the success of groundwater remediation or containment efforts. This paper reviews existing research information regarding DNAPL occurrence and migration patterns and outlines a systematic approach for delineation programs.

## **DNAPL OCCURRENCE AND MIGRATION**

DNAPL fluids can be present in the subsurface either as 1) free-phase mobile liquids or 2) residual liquids retained within the aquifer pore space by capillary forces (see Figure 1). Principal features of these two states of occurrence and factors affecting mobility and dissolution are discussed below.

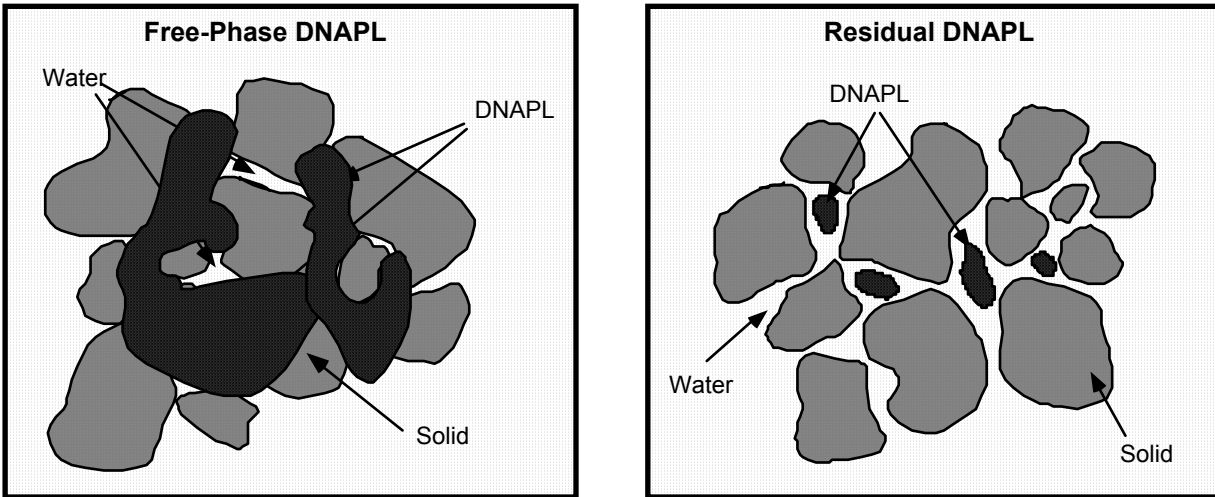


Figure 1. Examples of Free-Phase vs. Residual DNAPL

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### Free-Phase DNAPL Movement

The ability of DNAPL to enter and flow through the aquifer matrix is a function of driving head, fluid viscosity, and soil capillary characteristics. Under sufficient driving head, as in the case of surface spillage or ponding, the DNAPL fluid pressure will exceed the interfacial tension within the aquifer pores, resulting in the DNAPL entry and partial displacement of pore water and air. The principal factors in the migration of this continuous DNAPL mass are the downward fluid density gradient and the large-scale and micro-scale stratigraphic features of the soil or rock material. Groundwater flow gradients do not strongly influence the movement of the DNAPL mass in most cases. Rather, the DNAPL fluid will sink downward through the aquifer media, flowing preferentially in coarse-grained material or through secondary porosity features until a low porosity stratum is encountered such as an unfractured clay or rock layer. DNAPL will accumulate this depth, moving laterally in accordance with the topographic features of the perching layer (see Figure 2).

### Residual DNAPL Saturation

When the original supply of new DNAPL is exhausted, the pressure on the free-phase DNAPL is removed and small blobs (or "ganglia") of DNAPL "snap-off" or "bypass" the once continuous DNAPL body and become trapped in individual pores or small groups of pores by capillary forces (see Figure 1). These DNAPL ganglia will remain immobilized within the soil or rock pores, serving as a continuing source of contaminant dissolution to passing groundwater. In unsaturated soils, residual saturation of DNAPL fluids, defined as the fraction of the total pore volume occupied by DNAPL under ambient condition, typically ranges from 5% to 20%. In the saturated zone, residual saturation values are typically higher because DNAPL serves as a "non-wetting" fluid when in contact with water, and residual saturation values range from 15% to 50% of the total pore volume (Mercer and Cohen, 1990; Schwille, 1988).

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Figure 2. Surface Map of Top of Clay Unit, Showing Movement of Down Topographic "Valleys"  
Motco Superfund Site, La Marque, Texas

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### **Effect of Fractures and Heterogeneities**

At many sites DNAPL will migrate preferentially through secondary porosity features in the soil/aquifer matrix, i.e. larger fractures, partings, rootholes, slickensides, coarse-grained layers and other micro-stratigraphic features rather than saturating the open pore volume of a porous media. These secondary porosity features permit the DNAPL to penetrate much deeper than

would be predicted from using typical residual saturation values and assuming uniform saturation of the aquifer media (see Figure 3). These results suggest that even small releases on the order of one or two drums of DNAPL chemicals can penetrate tens to hundreds of feet through the vadose zone before reaching the water table (Poulson and Kueper, 1991; and Cherry and Feenstra, 1991).

Clay aquitards that serve as effective "confining units" in the context of groundwater flow may not serve as effective barriers to DNAPL migration because of these micro-scale heterogeneities (Waterloo Centre for Groundwater Research, 1991; U.S. EPA 1992b). Fractures related to clay weathering occur more frequently at shallow depths and in stiff clays, but can extend through existing aquitards and facilitate DNAPL transport deep into the surface. At one Superfund site, for example, large volumes of DNAPL were observed to have moved significant distances (~ 50 ft vertically and ~ 600 ft laterally) in the secondary porosity features of various clay and silt units underlying the site (Connor, Newell, and Wilson, 1989).

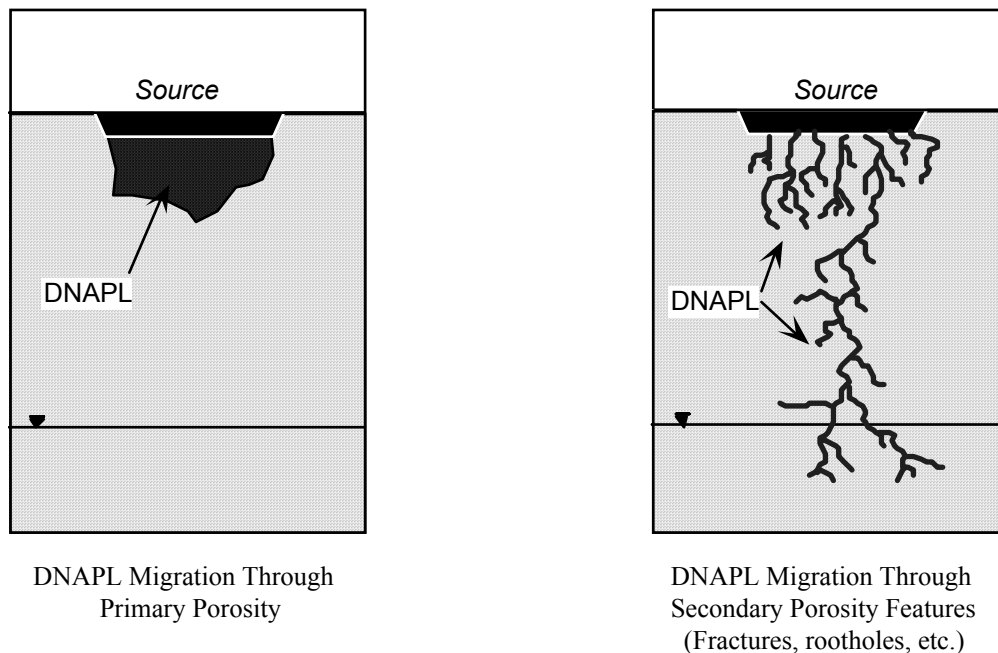


Figure 3. DNAPL Migration Through Primary vs. Secondary Porosity

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### Considerations for DNAPL Detection and Delineation

Conceptual models of DNAPL migration patterns in various hydrogeologic settings are illustrated on Figures 4 to 8. As shown, migration patterns are strongly affected by the source volume, site stratigraphy, and secondary porosity features, resulting in a complex

discontinuous distribution of 1) free-phase DNAPL, 2) residual DNAPL, and 3) dissolution products within the groundwater flow system. The significance of these migration patterns to the formulation of a DNAPL detection/delineation strategy is as follows:

- **DNAPL Mass:** Given the slow release of DNAPL dissolution products to the groundwater flow system, a relatively small mass of subsurface DNAPL may be sufficient to cause a long-term groundwater quality problem. The likelihood of directly encountering a localized DNAPL mass using conventional sampling and testing techniques may be relatively small unless large volumes of DNAPL-related chemicals have been released at the site. Consequently, the site investigation effort should incorporate indirect evidence of DNAPL occurrence, such as historical data or elevated dissolved constituent concentrations.
- **DNAPL Distribution:** Movement of continuous DNAPL fluid within the aquifer is strongly affected by micro-stratigraphic features, such as thin perching seams, fractures, etc. Consequently, stratigraphic measurements and records must be of sufficient resolution to identify such characteristics. Residual DNAPL ganglia are likely to be concentrated as minor droplets within secondary porosity features, rather than uniformly disturbed within the soil or rock mass.
- **DNAPL Pools and Lateral Migration:** Concentrated zones of DNAPL droplets or continuous-phase liquids can accumulate on top of low-porosity, unfractured strata. Characteristics of the surface topography of the perching layer can provide a reliable predictor of lateral DNAPL flow patterns.

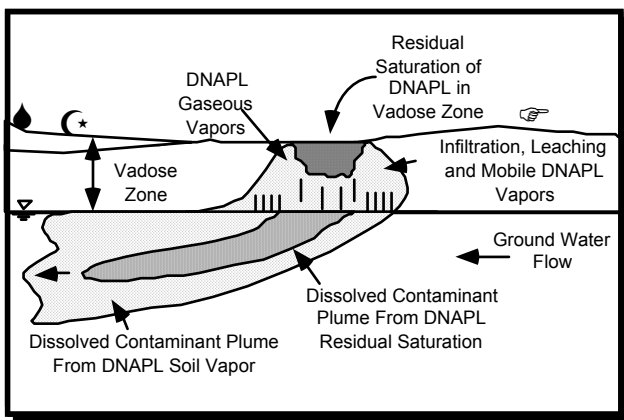


Figure 4: DNAPL Release to Vadose Zone Only

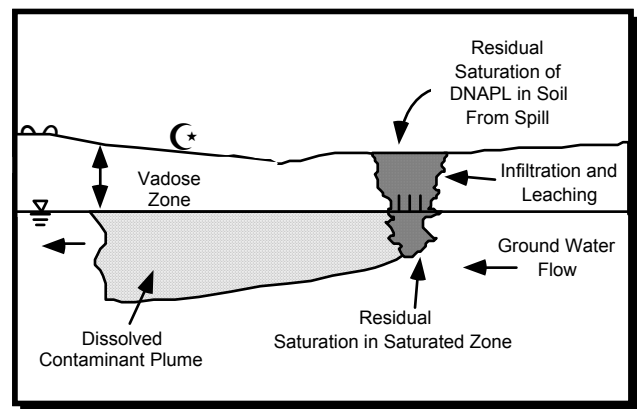


Figure 5: DNAPL Release to Vadose/Saturated Zones

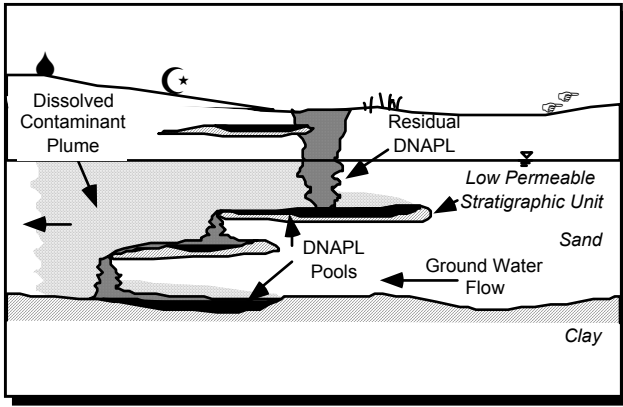


Figure 6: DNAPL Pools and Effect of Low-Permeability Units

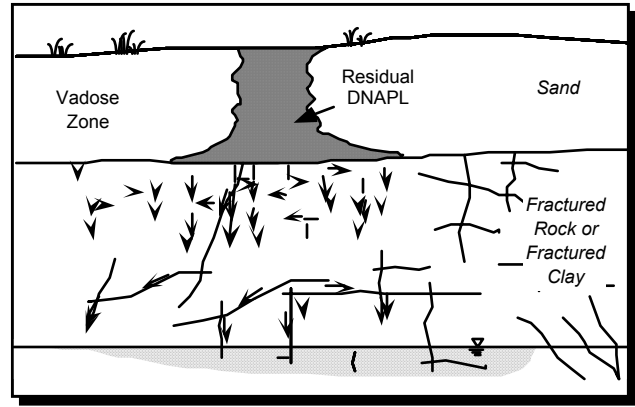
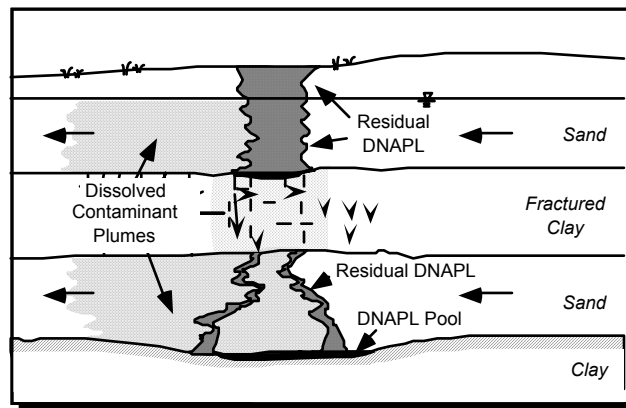


Figure 7: Fractured Rock or Fractured Clay System

(Note: Figures 4 - 7 adapted from Waterloo Centre for Groundwater Research, 1989)

Figure 8: Composite DNAPL Site

(Adapted from Waterloo Centre for Groundwater Research, 1989)



## ESTIMATING POTENTIAL FOR OCCURRENCE OF DNAPL

Procedures for evaluating the potential for DNAPL occurrence at a given site on the basis of indirect evidence have been developed by Newell and Ross, (U.S. EPA, 1992a). This preliminary screening approach, documented in the EPA Quick Reference Fact Sheet

"Estimating Potential for Occurrence of DNAPL at Superfund Sites" (EPA Publication 9355.4-07FS, January 1992), can be employed to determine the need for implementation of a full-scale DNAPL detection/delineation program. Evaluation of low, moderate, or high potential for DNAPL presence involves the following methodology:

#### Step 1: Historical Site Use Information

Certain industries, industrial processes, and chemicals correlate strongly with the presence of DNAPL in the saturated zone and/or the vadose zone at a hazardous waste site. These indicators are incorporated in the historical site use flowchart shown on Figure 9.

#### Step 2: Site Characterization Data

Both direct measures of DNAPL presence and indirect indicators are included in the site characterization flowchart shown on Figure 10. Example data that is used includes evidence of DNAPL accumulation in wells, concentrations of groundwater samples, and concentrations of soil samples.

#### Step 3: DNAPL Detection Decision Matrix

Following completion of the historical site use and site characterization data flowcharts, the DNAPL decision matrix shown on Figure 11 can be employed to defined the potential for DNAPL presence in site soil or the underlying groundwater system. If a confirmed,





high potential, or moderate potential for DNAPL occurrence is identified, a DNAPL detection/delineation field program should be implemented at the site.

		<b>Do Characterization Data Indicate Presence of DNAPL? (see Figure 10)</b>		
		<b>No</b>	<b>Maybe</b>	<b>Yes</b>
<b>Does Historical Use Indicate Presence of DNAPL? (see Figure 9)</b>	<b>Yes</b>	<b>MODERATE</b> Potential for DNAPL at Site	<b>HIGH-MODERATE</b> Potential for DNAPL at Site	<b>CONFIRMED OR HIGH</b> Potential for DNAPL at Site
	<b>Maybe</b>	<b>MODERATE-LOW</b> Potential for DNAPL at Site	<b>MODERATE</b> Potential for DNAPL at Site	<b>CONFIRMED OR HIGH</b> Potential for DNAPL at Site
	<b>No</b>	<b>LOW</b> Potential for DNAPL at Site	<b>MODERATE</b> Potential for DNAPL at Site	<b>CONFIRMED OR HIGH</b> Potential for DNAPL at Site

Figure 11. DNAPL Detection Decision Matrix  
(from U.S. EPA, 1992a)

## PROCEDURES FOR DNAPL DETECTION / DELINEATION FIELD PROGRAM

### Special Considerations for DNAPL Sites

Special precautions are required to avoid inadvertent creation or enhancement of DNAPL migration pathways during the course of hydrogeologic investigations conducted at DNAPL-contaminated sites. Given the ability of DNAPL materials to move downward through very small fractures (e.g. 20 microns) within the soil mass, conventional grouting procedures may not prove effective for soil borings or wells drilled directly through a DNAPL perching stratum and into an underlying, clean unit. In developing a DNAPL detection / delineation workplan, the following concepts should be applied:

- "Outside-In" Approach: Prior to penetrating a suspected DNAPL zone, critical stratigraphic features should first be identified by investigations conducted outside of the area of concern. These preliminary data should be analyzed to identify potential perching strata or "safety nets" beneath the DNAPL zone. All drilling subsequently conducted within the area of DNAPL occurrence must be terminated at the depth of the uppermost, continuous "safety net" stratum. In thick, fractured rock settings such perching strata may not be present, and the risks associated with drilling inside the DNAPL zone must be carefully weighed against the need for vertical delineation data.
- Soil Borings and Wells: To avoid inadvertent penetration of perching layers within DNAPL zones, soil borings should be sampled continuously with depth and terminated at or near the surface of such confining strata. For detection of free-phase DNAPL, observation wells must be screened across the upper surface of a perching layer. However, under no conditions should the well boring penetrate the full thickness of the base stratum. Wells should be constructed with short screen sections and double-cased through the depth of any overlying DNAPL -contaminated sections.
- Non-Invasive Site Investigation Techniques: Where applicable, non-invasive techniques should be employed to indicate DNAPL presence or characterize site stratigraphy. Geophysical methods can be applied to define the presence and topography of perching strata. In addition, shallow soil gas sampling above the zone DNAPL occurrence has proven a useful indicator of DNAPL presence in some cases.

### **Methodology for DNAPL Detection and Delineation in the Field**

The presence and distribution of DNAPL within an aquifer system can be defined using a direct sampling approach developed and applied by Groundwater Services, Inc. (1991). Principal steps in this work program are as follows: This approach is based on an outside-in strategy, where drilling outside the zone of contamination is conducted to help develop a conceptual model of the site. Prior to drilling in potential DNAPL zones, a continuous bottom perching stratum is identified that serves as a "safety net" for any DNAPL that is accidentally mobilized during the drilling process. While in the DNAPL zone, no drilling is permitted within the perching stratum to ensure that the integrity of the safety net is never comprised.

The drilling program is conducted in several stages to ensure that adequate time is allowed to interpret data and to receive laboratory results. Overall, the DNAPL detection/delineation program is conducted in three steps:

### Step 1: Detailed Characterization of Stratigraphic Profile

Prior to drilling through known or suspected zone of DNAPL occurrence, a sufficient number of soil borings should be drilled and continuously sampled outside the area of concern to provide a detailed characterization of both principal and micro-stratigraphic features. In unconsolidated sediments, cone penetrometers can provide a cost-effective alternative to conventional drilling techniques, providing a continuous detailed record of minor sand, silt, and clay strata. Geologic data should be analyzed to identify the uppermost stratum serving as a "safety net" for prevention of downward DNAPL migration (e.g., a laterally continuous clay stratum greater than 2 ft in thickness). Subsequent investigations conducted in the zone of DNAPL occurrence must be designed to prevent artificial penetration of this base confining layer.

### Step 2: DNAPL Detection Sampling

To detect or confirm the presence of residual or free-phase DNAPL within the suspected zone of occurrence, a series of soil borings and observation wells should be completed over the depth interval determined in Step 1 above. Soil borings should be drilled and continuously sampled to the depth of the base perching layer, with caution exercised to minimize breaching of any overlying perching strata. If DNAPL is encountered within the soil column, observation wells should be screened across the surface of the base perching stratum to detect pool accumulation. Sampling and testing procedures should include the following:

Visual Inspection of Soil Cores: In the field, soil cores must be inspected for visual evidence of DNAPL presence. Particularly emphasis is placed on inspecting secondary porosity features; in some cases DNAPL will weep out fractures while the core is being inspected. Although the presence of DNAPL is obvious in some cores, small amounts of residual DNAPL are often difficult to see. To increase the chance of observing small amounts of DNAPL, the soil material may be mixed with water in a sample jar, and the water inspected for an immiscible liquid film or droplets. Alternatively, a soil/water mixture may be run through a paint filter, and inspected for the presence of a free-phase liquid or film.

Organic Vapor Analyses: The concentration of organic vapors on the soil core should be measured in the field with a portable vapor monitoring instrument, using sample jar or headspace techniques. High organic vapor concentrations can be indicative of volatile DNAPL in the soil matrix.

Laboratory Analyses: Selected soil samples, particularly samples with organic vapor concentrations, are analyzed for gross indicators of contamination, such as Total Petroleum Hydrocarbons, as well as specific organic constituents. Soil samples containing greater than 10,000 mg/kg of hydrocarbon contamination (1% of soil mass) commonly contain DNAPL (Feenstra, MacKay, and Cherry, 1991). However, it is important to note that gross indicator analyses may not provide adequate sensitivity to detect residual DNAPL concentrations on the soil mass. For this purpose, compound specific analyses for major components of the DNAPL source material should be conducted using ppb-level analytical methods and the results evaluated in accordance with the partitioning procedure discussed below.

Partitioning Calculation: On the basis of laboratory data, a partitioning calculation, evaluating the potential for dissolved-phase vs. separate phase organic constituent occurrence, can be used to evaluate the presence/absence of residual mass. By using the concentration of organics on the soil and the partitioning calculation, a theoretical pore-water concentration of organics in ground water is determined. If the theoretical pore-water concentration is greater than the estimated solubility of the organic constituent of interest, then DNAPL may be present at the site. A method proposed by Feenstra, MacKay, and Cherry (1991) is summarized in a worksheet shown on Figure 12 (U.S. EPA, 1992a).

Installation of Observation Wells: The final element of the DNAPL detection program is installation of observation wells on top of the bottom perching layer. These wells are constructed to 1) minimize the volume of gravel pack and unscreened well section below the screens, and 2) have the bottom of the screened section set as close as possible to top of the perching layer. This well construction methodology will help ensure that at least some of the DNAPL accumulates in the well rather than in the well/gravel pack.

### Step 3: DNAPL Zone Delineation

Once DNAPL has been detected at a site, the DNAPL zone is delineated to the best degree possible using the following procedure.

Free-phase DNAPL Zone: The topography of the base perching layer should be further defined with additional borings or, where applicable, with cone penetrometers. In some cases, the presence or absence of an oil sheen within the return flow of grout tremied into each penetrometer hole can be used to determine the presence of DNAPL (Connor, Newell, and Wilson, 1989). Based on this surface definition, additional borings or observation wells should be completed in the topographic lows of the principal perching layer(s) to detect and delineate DNAPL pools. The apparent depth of DNAPL accumulation atop the base perching layer may be estimated using either an electronic hydrocarbon probe, a double check-valve bailer, or a weighted cotton string. Although this information provides a qualitative estimate of the volume of DNAPL in the subsurface, accurate quantitation is

frustrated by uncertainties regarding where the DNAPL is coming from, where the well is screened in relation to the DNAPL pool, and other unknowns (Waterloo Centre for Groundwater Research, 1991).

Residual DNAPL Zone: To define the lateral extent of the residual DNAPL zone, a series of step-out borings are made from the source area. Samples are collected and observed visually, analyzed for organic vapors, and analyzed for chemical constituents and gross contaminant indicators in the laboratory. Additional step-out borings are made in an iterative fashion until an apparent clean zone (i.e. no DNAPL) is identified and confirmed with laboratory samples. To define the vertical extent of the residual



DNAPL zone, each boring is sampled continuously until either a) no further DNAPL is observed visually or from vapor monitoring data or b) the bottom perching stratum is reached.

## SUMMARY

This paper reviews existing research information regarding DNAPL occurrence and migration patterns and outlines a systematic approach for delineation programs. First, general DNAPL detection procedures are outlined based on historical site use information, existing site characterization data, and a DNAPL detection decision matrix. If there is a confirmed, high, or moderate potential for the occurrence of DNAPL at a site then the DNAPL detection/delineation field program described below should be implemented.

The DNAPL field program is based on an “outside-in” approach, where a stratigraphic model of the is developed first by drilling outside the potential DNAPL zones. Once a safe perching stratum or “safety net” is identified, a DNAPL detection sampling program is initiated, consisting of visual inspection of cores, organic vapor analyses, laboratory analyses of soil samples, application of partitioning relationships, and installation of observation wells. If DNAPL is detected, a companion field program is implemented to delineate both free-phase and residual DNAPL zones. The overall DNAPL detection/delineation program is summarized below:

### DNAPL Detection Using Existing Information

- Step 1. Evaluate historical site use data (industry and process type, type of chemicals)
- Step 2. Evaluate site characterization data (such as DNAPL accumulation data, groundwater monitoring data, and soil sampling data).
- Step 3. Enter DNAPL detection decision matrix. If potential for DNAPL occurrence is confirmed, high, or moderate then implement DNAPL Detection / Delineation field program.

### Field Program for DNAPL Detection / Delineation

- Step 1. Develop detailed stratigraphic profile of site using “outside-in” approach. If “safety net” perching stratum is found, proceed with Steps 2 and 3.
- Step 2. Conduct DNAPL detection sampling program using special precautions for drilling in potential DNAPL zones. If DNAPL is found or indicated then proceed with Step 3.
- Step 3. Delineate free-phase and residual DNAPL zones with additional soil borings and wells.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the following people and organizations for their contributions to several projects that provided the foundation for this paper: Mr. Randall Ross and Mr. Steve Acree of the R.S. Kerr Environmental Research Laboratory, U.S. EPA; Mr. Dale Wilson and Mr. Gary Vandiver of Monsanto Company; and Mr. Bob Lee and Mr. Grant Cox of Groundwater Services, Inc.

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