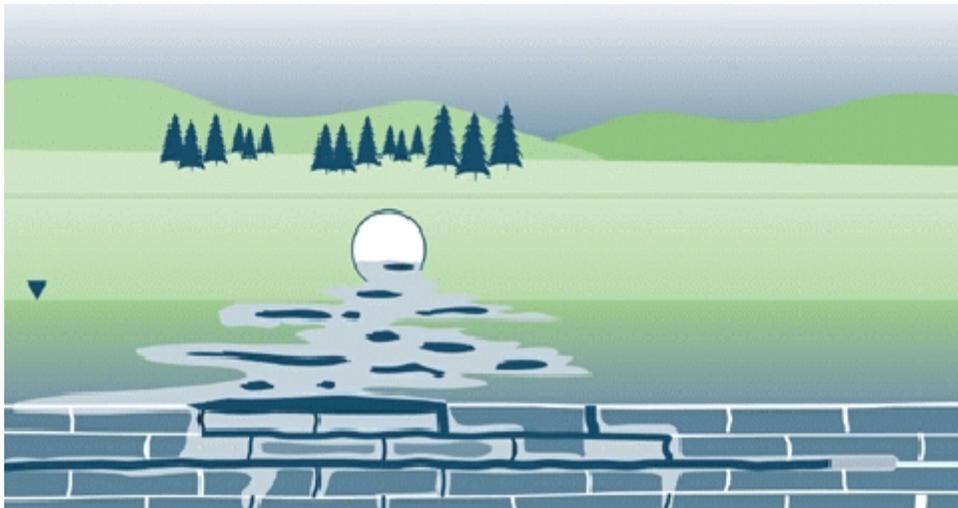**Technology Overview**

# An Introduction to Characterizing Sites Contaminated with DNAPLs

**September 2003**

**Prepared by**
**The Interstate Technology & Regulatory Council**
**Dense Nonaqueous Phase Liquids Team**

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# ACKNOWLEDGMENTS

# TABLE OF CONTENTS

## LIST OF FIGURES

## APPENDICES

Appendix A. List of Acronyms
Appendix B. Innovative DNAPL Characterization and Monitoring Tools Matrix
Appendix C. Case Studies
Appendix D. DNAPLs Team Contacts, ITRC Fact Sheet, ITRC Product List

# An Introduction to Characterizing Sites Contaminated with DNAPLs

## 1.0    INTRODUCTION

The purpose of this document is to discuss scientific approaches and strategies used to characterize sites that are known or suspected to be contaminated with dense, nonaqueous-phase liquids (DNAPLs). This document is written to introduce the fundamental concepts of site characterization strategies as they relate to DNAPLs. It is meant for the reader who is familiar with the principles of contaminant hydrogeology and conventional characterization approaches but may not be well versed in the issues surrounding the characterization of sites contaminated with DNAPLs.

This document is intended to be a primer for characterizing sites contaminated with DNAPLs and to provide some tools for identifying the presence of DNAPL in the subsurface. As such, it does not attempt to fully discuss and describe the physics and complex behavior of DNAPL flow and fate in the subsurface. That information is readily available in the peer-reviewed scientific literature. References to literature describing the multiphase fluid flow concepts required to understand DNAPL physics are included in Section 7.0 of this document.

## 2.0    OVERVIEW OF THE DNAPL PROBLEM

This section presents an overview of the DNAPL problem, provides a general description of DNAPL flow in the subsurface, and describes why conventional approaches to characterizing DNAPL sites can be ineffective.

It is generally agreed that cleaning up sites contaminated with DNAPLs is one of the biggest challenges in the field of environmental remediation. A key aspect of this challenge is the difficulty in adequately characterizing the volume and extent of DNAPL releases to the environment, particularly finding and delineating DNAPL source zones. Investigators are fairly adept at characterizing dissolved-phase contaminant plumes using conventional tools such as monitoring wells. However, due to the extremely complex and therefore relatively unpredictable behavior and heterogeneous distribution of DNAPLs, these liquids often go undetected when conventional tools and investigative strategies designed to characterize relatively homogeneous distributions of contaminants are relied on. Moreover, DNAPLs are commonly present in sufficient amounts to cause significant dissolved phase contamination in the subsurface, but not enough to be readily mapped using standard subsurface investigation methods.

The consequences of a poorly investigated or inadequately characterized DNAPL site are numerous. Improperly conducted environmental site investigations at DNAPL sites can result in an inaccurate assessment of risk, an inadequate remedial design basis, can cause cross-contamination of aquifers, and expand the contaminated area. Moreover, inadequate characterization of a DNAPL source zone can lead to the implementation of costly remedies in an ineffective manner (e.g., treating a much larger volume than needed with an expensive technology). Finally, poor DNAPL site characterization dramatically increases the risk of ineffective remedial performance as a portion of the source may be overlooked and not be treated or controlled.

## 2.1     What Are DNAPLs?

DNAPLs are single or multicomponent liquids that are denser than water and relatively insoluble in water. Common DNAPLs include compounds that have been and are still widely used in industrial and commercial processes. Possibly the most common DNAPLs are halogenated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). These DNAPLs have been used as degreasers in many industrial processes and have frequently been released to the subsurface. Other DNAPLs include, but are not limited to, coal tar, creosote, some pesticides, and polychlorinated biphenyls. Please note that it is common to find metals such as hexavalent chromium dissolved in the halogenated solvents if they have been used in a metal shop. Compounds typically found as DNAPLs can also be found in LNAPLs if these miscible fluids have been co-mingled in the subsurface. Descriptions of the chemical and physical properties of these chemicals are available in Cohen and Mercer (1993), Pankow and Cherry (1996), Dwarakanath et al. (2002), and a variety of other sources.

Although not very soluble in water, many single and multicomponent DNAPLs are soluble enough to present potential risks to human health or the environment. As a result, DNAPLs in the subsurface may become a source of recalcitrant dissolved phase groundwater contamination for many years. Note that, consistent with its name—dense, <u>nonaqueous</u>-phase liquid—DNAPL is a liquid separate from water. While this may seem obvious, unfortunately the phrase "dissolved DNAPL" or "DNAPL plume" is still quite commonly used by some environmental professionals when referring to a chemical dissolved in groundwater. Certainly, DNAPL components can become dissolved in groundwater at concentrations high enough to pose an environmental concern, but the resultant aqueous phase contamination is more properly termed "the dissolved plume" and the components called by their specific chemical names (for example, "a dissolved VOC plume" or "a TCE plume"). This distinction is more than mere semantics. Errors in terminology or misuse of technical language do not foster accurate or effective communication with regard to an already complex and difficult subject, and often reflect or result in a misunderstanding of DNAPL behavior and migration.

While they can be released as a chemical product (as manufactured and sold), DNAPLs are often discharged as spent solvents or wastes that contain appreciable fractions of other organic chemicals. These co-contaminants may represent a wide range of organic (halogenated and nonhalogenated volatiles, and semivolatile compounds such as waste grease and various oils, as well a stabilizers and rust inhibitors) and inorganic chemicals that are miscible with the DNAPL and therefore migrate along with it in the subsurface. These other components can significantly influence the overall chemical and physical properties of the DNAPL and can both aid detection and complicate remediation (Dwarakanath et al., 2002). These compounds can be found above and below the water table at sites where releases of DNAPLs have occurred.

## 2.2     Behavior of DNAPLs in the Subsurface

A brief introduction and discussion of DNAPL behavior and migration in the subsurface is helpful prior to discussing specific DNAPL characterization techniques and strategies.

Dissolved contaminant transport is influenced by groundwater advection, including the effects of mechanical dispersion, molecular diffusion, chemical partitioning between groundwater and porous media, and other chemical reactions (e.g., degradation). Characterizing the behavior, distribution, and transport of the dissolved contaminant phase requires an understanding of the site's groundwater flow characteristics, the physical and chemical properties of the contaminants, and their interactions with the geologic matrix and other contaminants. Finding the source of contamination and understanding the history of contaminant release(s) from the source area or areas including the date/s of release, what was released, and the magnitude of the release if possible, is critical to assessing the ultimate behavior and distribution of the contamination.

Unlike dissolved phase contaminants, DNAPLs migrate through the subsurface under the influence of gravity and capillary effects created by multiphase fluid flow in geologic media. Therefore, DNAPLs can be present in different places than would be expected by simple mapping of the advective flow of groundwater, making them difficult to find and delineate. DNAPLs are commonly present in the subsurface in sufficient volume to cause significant dissolved phase contamination, but not in enough volume to be easily located and identified when performing standard subsurface investigations. Understanding DNAPL flow and behavior allows an adequate site conceptual model to be developed that helps guide characterization efforts. will make remediation more viable both of the DNAPL and the dissolved phase contamination.

It is not the purpose of this document to provide an exhaustive treatise on the physics of DNAPL flow, therefore the reader is referred to the many scientific articles and texts that do provide this level of detail. Among the examples of detailed discussions of DNAPL flow are: Schwille (1988), Huling and Weaver (1991), Cohen and Mercer (1993), Pankow and Cherry (1996), and others. References to these and other articles and texts that discuss DNAPL flow and the physics of DNAPL flow in detail are provided in Section 7.0.

2.2.1    The Concept of Saturation

Residual saturation of NAPL is "the saturation at which the NAPL is immobilized by capillary forces as discontinuous ganglia under ambient groundwater flow conditions." (Cohen and Mercer, 1993, pp. 4–16). Assuming that the gas phase component is negligible in the saturated zone, residual saturation would be equal to the porosity of the matrix less the saturated water content (Kueper and McWhorter, 1991). Residual DNAPL saturation typically ranges between 5% and 15%.

The ultimate distribution of residual DNAPL is not uniform or readily predictable in the subsurface due to minute variations in pore size distributions, soil texture, soil structure, and mineralogy. Although the residual DNAPL is immobile under normal subsurface conditions (unless the equilibrium conditions holding the residual phase DNAPL are changed), it can act as a long-term source for continuing dissolution of contaminants into water or air in adjacent pores.

2.2.2   DNAPL Source Zone

EPA defines the DNAPL zone as "that portion of the subsurface where immiscible liquids (free-phase or residual DNAPL) are present either above or below the water table" (EPA, 1996). The DNAPL source zone encompasses the entire subsurface region in which DNAPL is present at residual saturation, as "pools" of accumulation above confining units, or as mobile DNAPL (Rao, 2001).

2.2.3   Behavior of DNAPLs in Unconsolidated Geologic Materials

Contamination at many DNAPL sites has largely been investigated in the unconsolidated materials comprising all geologic zones above bedrock. Industrial and commercial users of DNAPLs are often located in geologic settings where unconsolidated materials are thickest. The thickness and type of unconsolidated materials may prevent DNAPL releases from reaching bedrock. Therefore, much DNAPL investigation has historically been focused on characterizing DNAPLs in unconsolidated materials. Figure 1-1 is a conceptualization of DNAPL behavior in unconsolidated geologic materials. There may be a significant need to conduct further investigations of the bedrock at some of these sites.



Source: Jackson, 1998

**Figure 1-1. Conceptual model of the migration and fate of DNAPL.**

When a DNAPL is discharged to the subsurface, it can flow downwards through the unsaturated zone. This flow is controlled by the chemical and physical differences and the interactions between the DNAPL and the soil gas, soil moisture, soil matrix, and gravity (Cohen and Mercer, 1993), and the pressure (head) in the DNAPL. Some DNAPL will be retained in the available pore space in the

unsaturated zone, coating the soil matrix (if it is the wetting fluid) or as ganglia—discontinuous accumulations of DNAPL encompassing several soil pores (Cohen and Mercer, 1993). This DNAPL is immobile (trapped by capillary forces), and will act as a source of dissolved phase contamination when recharging water flowing through the contaminated pore space contacts the DNAPL above the water table. If the contaminant is volatile, it will also volatilize in the unsaturated zone. The contaminated soil vapor will migrate through the unsaturated zone and contaminants may partition from the soil gas to recharging waters or directly to the upper surfaces of the water table if the gas comes into contact with the saturated zone.

Many parts of the west and southwestern United States have very deep water tables (some as deep as 1000 feet). The general attributes of DNAPL migration and behavior in thin vadose zones apply in thicker vadose zones, but are magnified and complicated by the increased heterogeneity encountered along the longer flow paths. DNAPL sources which never contact groundwater may exist in thick vadose zones in arid environments, but contaminate groundwater as a result of vapor migration (Korte et al., 1992). DNAPL sources in thick vadose zones may also give rise to "halos" of contamination around sites due to the lateral and downward migration of VOC contaminated soil gas.

As DNAPLs are hydrophobic, there may be significant interfacial tension between the DNAPL and water. Upon reaching the top of the water table, the interfacial tension may prevent the DNAPL from readily moving through the capillary fringe and entering the water table (Cohen and Mercer, 1993). If mobile DNAPL in the unsaturated zone continues to flow downwards, it will form a continuous column of DNAPL "resting" on top of the capillary fringe. Given the presence of sufficient DNAPL, the column will eventually reach a height where gravity acting on the DNAPL will provide enough pressure for the DNAPL to overcome the capillary pressure of the groundwater and displace the water in the pore spaces. This will allow DNAPL to flow into the saturated zone (Kueper and McWhorter, 1991). Matrix heterogeneity caused by subtle variations in the porosity, permeability and grain size will change the height of the column of DNAPL needed to break through the interfacial tension between the water and DNAPL over short distances across the top of the capillary fringe.

DNAPL flow below the water table can be very complex and is influenced by DNAPL mass and physicochemical characteristics (e.g., viscosity, interfacial tension, wettability, etc.). Given sufficient volume of DNAPL discharged to the subsurface, DNAPL can displace some of the groundwater and flow in an apparent continuous mass leaving only a thin film of water surrounding the individual grains of the formation matrix (when water is the wetting fluid). More commonly though, there are smaller amounts of DNAPL discharged to the subsurface. Once a small amount of DNAPL reaches the water table, its flow is highly influenced by the interfacial tension between the DNAPL and groundwater. Depending on the amount of DNAPL released and the characteristics of the DNAPL and the matrix, the interfacial tension will typically prevent DNAPL from spreading evenly throughout the formation and force the DNAPL to follow preferential pathways caused by small changes in the matrix. Schwille (1988) showed this flow characteristic by discharging dyed tetrachloroethylene into tanks of glass beads. Instead of moving in a continuous mass, the tetrachloroethylene broke into thin, threadlike flow patterns that followed tortuous pathways through

the sand based on the amount of DNAPL released, the pore size distribution, and complex interactions between fluids (DNAPL and groundwater) and the matrix.

Whether groundwater or DNAPL is the wetting fluid in the formation, or whether there is mixed wetting of the porous medium can have a major effect on the flow and fate characteristics of the DNAPL in the saturated zone (Dwarakanath et al., 2002). The wetting characteristics of a pure laboratory grade DNAPL may differ significantly from a used DNAPL that is contaminated by its use (such as when a chlorinated solvent is used to degrease mechanical parts). Therefore, it is imperative to collect a sample of the site specific DNAPL if at all possible. Chemical analysis of the DNAPL sample can then be conducted to determine specific solubilities, wetting characteristics, specific gravity, viscosity, etc. of the site specific DNAPL. Experiments have also shown that DNAPL wetting of solids usually increases with time due to adsorption and/or deposition on mineral surfaces of organic matter and surfactants derived from DNAPL or water (Cohen and Mercer, 1993).

It is uncommon to find large pools of DNAPLs in the subsurface unless large amounts of DNAPL were discharged to the subsurface. As DNAPL moves through the subsurface, small droplets of the DNAPL will be left behind in formation pore spaces. These suspended droplets are called "ganglia" (Cohen and Mercer, 1993). At most sites contaminated with DNAPLs, the DNAPL will generally be found as "ganglia" or in very thin lenses. These ganglia are essentially immobile and are "suspended" in the pore space of the formation. The capillary pressure/interfacial tension between the DNAPL and groundwater at the pore space throat is too high for the droplet of DNAPL to move through the formation even though it has a higher specific gravity than the groundwater (Cohen and Mercer, 1993). The size and location of the ganglia will be affected by the wettability characteristic of the DNAPL in the formation (Dwarakanath et al., 2002). Thus, investigators usually do not find DNAPL above residual saturation in soil cores or accumulating in monitoring wells using conventional characterization methods. The lack of observable DNAPL at some sites may lead to the erroneous conclusion that no DNAPL is present when, in fact, it may be present in substantial quantities at residual saturation. The classic experiments of Schwille (1988) provide a valuable illustration of DNAPL behavior. Other helpful references are listed in Section 7.0, References.

When two dissimilar fluids (such as DNAPL and water) are present, the relative permeability of the formation will be less than if a single fluid is present. Pore spaces filled by water will not readily allow passage of DNAPL and vice-versa . Thus, portions of a porous medium saturated with one fluid are less transmissive to a second immiscible fluid (Schwille, 1988).

2.2.4    Behavior of DNAPLs in Bedrock

In bedrock aquifers, DNAPL flow can be even more complex. Bedrock typically includes varying degrees both primary and secondary porosity. Primary porosity is the pore spaces in the matrix of the rock. These are generally small and in some igneous and metamorphic rocks may be essentially absent. Secondary porosity includes structural porosity such as fracture openings and solutions channels. The secondary porosity generally provides the more significant transport pathways for DNAPL migration. Due to the difficulty of delineating bedrock secondary porosity, DNAPL

characterization in bedrock is complex and costly. At some sites, it is also fraught with the substantial risk of enlarging the extent of DNAPL contamination by investigation activities.

Any fracture or solution channel may become a pathway for DNAPL migration, while "clean" fractures or solution channels can be found in very close proximity to the contaminated pathway if not interconnected. Once in a fracture or solution channel, the DNAPL can migrate significantly longer distances than might be expected in unconsolidated materials or the unfractured matrix of the bedrock, as the open spaces are usually larger and more continuous than those found in unconsolidated materials or unfractured rock and will be less likely to "trap" DNAPL in small ganglia. However, irregularly shaped fractures and solution channels or dead end fractures can create structural traps. As the DNAPLs move through the bedrock, they can leave small pools of DNAPL in these structural traps.

DNAPLs in bedrock (and in unconsolidated media) can also diffuse into the formation matrix (Parker, Gillham, and Cherry, 1994), where they will act as another source of dissolved phase contamination. Even if an investigator finds one or more fractures containing DNAPL, it will be difficult to locate all fractures containing DNAPL and the extent of diffusion into the bedrock matrix. Limitations to drilling and sampling methods further hinder the ability to delineate the extent of chemical contamination in bedrock. For example, loss of volatiles as a result of sample handling or drilling, or DNAPL drag-down as a result of drilling may lead to misinterpretations regarding the extent and nature of bedrock contamination.

### 2.2.5    Effects of the Type of Release on DNAPL Occurrence and Migration

The spatial and temporal nature and volume of a DNAPL release will affect its movement and ultimate distribution in the subsurface. If there is a continuous release occurring, such as from a small leak in a chemical pipeline or from an area where chemicals are manually transferred between storage containers, the flow of DNAPL is likely limited to a few vertical pathways. Conversely, a series of smaller discrete spills in different locations will likely result in flow along many different pathways, each based on different localized interactions of the DNAPL with the aquifer matrix. In a discrete spill (single release of a large or small amount of DNAPL), DNAPL will migrate in the subsurface in response to this one release. If another release occurs at the same location, it is likely that the DNAPL will migrate differently than earlier releases as it will encounter different conditions. Each separate release may further complicate the subsurface DNAPL distribution. When there are separate small releases, there is also less of a driving force per release than with one long-term or continuous release.

In an isolated release, the formation of residual phase ganglia should start to occur quickly as there is a finite amount of DNAPL. As the mass of DNAPL moves through the subsurface and is trapped at residual saturation, the driving force for continued DNAPL movement is depleted. In a continuous release, however, the DNAPL (depending on wettability) fills the contiguous pore spaces in the subsurface matrix and flows through the pore spaces as a continuous body, not forming residual ganglia until the release has stopped. The continuous release will maintain a constant flow of DNAPL that will therefore maintain relatively constant conditions in the subsurface. In this case,

once the DNAPL interacts with the formation and displaces groundwater, the flow is likely to be continuous along the same pathways formed by the leading edge of the DNAPL.

If the releases or successive releases occur over time, the characteristics of the DNAPL itself could change (for example, as manufacturing processes change). Changes in DNAPL composition and properties may result in altered flow potential and patterns. A phenomenon, observed at some creosote and manufactured gas plant sites, is that the specific gravity of the DNAPL can change over time due to weathering (i.e., preferential dissolution or other mechanisms). Some of the DNAPL components dissolve or are otherwise lost and the mixture becomes less dense than water. These neutrally buoyant and LNAPL components can migrate with the groundwater (although potentially slower than groundwater depending upon the physical and chemical characteristics of the NAPL. Detailed discussions of the relationship between release history and DNAPL migration and flow patterns are available in Cohen and Mercer (1993); Feenstra, Cherry, and Parker (1996); and others. If possible, multiple samples of the DNAPL on site must be taken in order to understand the varying DNAPL characteristics across the site.


## 3.0    CHARACTERIZING SITES CONTAMINATED WITH DNAPLS

### 3.1    Why Characterizing DNAPL Sites Is Difficult

DNAPLs are thought to most commonly exist as ganglia and to a lesser extent in small, continuous lenses that can be oriented either vertically or horizontally from the original point of entry into the subsurface. These ganglia and small, isolated lenses of DNAPL are very difficult to discover using standard investigation techniques such as soil borings and monitoring wells because of their small size and distribution.

For example, two soil borings spaced only 10 feet (or less) apart might easily miss a discrete ganglia or a lense of DNAPL existing between the bore holes. In addition, because many DNAPL compounds do not appear stained or otherwise distinct from noncontaminated soil, samples taken from non-DNAPL bearing portions of a soil core that intersect a discrete DNAPL lense may not indicate any contamination even though large amounts of groundwater are being contaminated by the residual DNAPL.

Dilution of DNAPL compounds in aqueous samples is a problem exhibited in water quality samples collected from wells with long screens. A monitoring well with a long screen may intersect a subsurface zone containing ganglia or a thin lense of DNAPL. Groundwater flowing into the well from the majority of the screen may significantly dilute (and mask) contaminant concentrations that enter the well from the DNAPL-contaminated zone. Thus, while a long screen may enhance the ability to detect groundwater contamination, it may confuse DNAPL delineation efforts and samples may underestimating the strength of the source. Conversely, if droplets of DNAPL are collected along with an aqueous sample taken from a monitoring well with a long well screen, the analytical results may be show very high concentrations of contamination and a researcher may take this to indicate that the entire screened section of the aquifer is contaminated at these concentrations.

In bedrock, characterizing bedrock fracture geometry and distribution is extremely complex and challenging. DNAPLs have been shown to sink to depths of greater than 200 feet and migrate great distances horizontally via secondary porosity. Once in the secondary porosity, DNAPLs can diffuse into the primary porosity and effectively disappear, in part or entirely (Parker et al., 1994).

In summary, it is difficult to characterize a site contaminated with DNAPL. Because some DNAPLs are colorless or present in minute amounts, they cannot be visually differentiated from the aquifer matrix in which it is contained. Other DNAPLs collected from subsurface environments are discolored, usually from the process in which they were used. Nevertheless, in either case various DNAPL detection techniques (ultraviolet fluorescence, hydrophobic dye tests, photoionization detector screening, VOC analysis, etc.) are needed to detect and confirm the presence of DNAPL in aquifer materials.

The interactions between DNAPL, porous media, and other subsurface fluids are complex and affect the ability to detect DNAPL. DNAPL migration tends to follow small preferential pathways that are very difficult to delineate. The more complex the geology, the more difficult it is to characterize a DNAPL release. A site with complicated geology will generally have a greater number of preferential pathways of varying size as well as more confining layers to trap large and small amounts of DNAPL. Characterizing a DNAPL release can also be difficult even in formations that appear to be homogeneous. Column tests by Schwille (1988) and field tests by Poulsen and Kueper (1992) demonstrated the control on DNAPL migration exerted by preferential flow pathways in what appeared to be homogeneous materials. This is exacerbated in heavily heterogeneous geologic environments, making it even more difficult to determine the location of residual and potentially mobile DNAPL.

Sections 4 and 5 of this document discuss methods of overcoming these difficulties and identifying DNAPLs in the subsurface.

## 3.2    Overview of DNAPL Site Characterization Process

DNAPL sites should be characterized using a dynamic and flexible work plan and real-time analytical methods that aid the development and iterative refinement of a conceptual model. This type of investigative approach has been termed the Triad approach, referring to the three components consisting of systematic project planning, dynamic work plans, and real-time field analytic techniques.

A DNAPL investigation should be designed to collect sufficient data to define the nature and extent of DNAPLs present to the level necessary to assess risk and select appropriate remedial measures. The DNAPL investigation should be based on a strong conceptual model and utilize a combination of investigation techniques that are best fitted to the site and chemicals of concern. Ideally, this should include the ability to obtain real-time chemical analytical results on site for field decision-making purposes. A flexible work plan using real-time analytical methods is the optimum method to characterize DNAPL sites.

The regulator should be involved early on in the design of a work plan to conduct this type of investigation in order to ensure that: (1) the plan will be accepted ; (2) the characterization will gather information acceptable to the regulator; and (3) the regulator will accept the results of the investigation. The investigator should have experience in this type of investigation in order to assure that it is carried out correctly.

More information on the development and use of the flexible work plan approach to site characterization can be found in the references listed in Section 7. These include Crumbling et al., 2001; Kram, et. al., 2001; Robbat, Smarason, and Gankin, 1998; Rossabi et al., 2000; and others.

## 3.3 Establishing Goals and Objectives

Although difficult, it is generally possible to characterize a DNAPL site sufficiently to reduce the level of uncertainty regarding the nature and extent of contamination. Before scoping the investigation and developing a work plan, it is necessary to establish reasonable goals and objectives. The following is a list of some of the more important goals and objectives for a typical DNAPL investigation:

- Determine if the contamination poses a threat to human health and the environment.

- Make decisions regarding the present and future risks caused by the DNAPL.

- Assess the feasibility and potential benefits of DNAPL mass removal.

- Gather information needed to design a remedial system.

## 3.4 Planning and Conducting a DNAPL Site Investigation

Some issues to consider and address when planning a DNAPL site investigation include, but are not limited to:

- **If a DNAPL was used or stored at a site, there is a high potential that a DNAPL release occurred.** Knowledge of previous operations and waste disposal practices at a facility will provide insight and information about whether DNAPL may have been released, and whether it has become a source of groundwater contamination.

- **Standard site investigation techniques do not work well to characterize DNAPLs.** Complex and discrete DNAPL migration patterns can make it very difficult to delineate subsurface DNAPL using standard investigation techniques. DNAPL-specific site investigation techniques are required. The investigator may need to develop strategies to either better locate the DNAPL based on a knowledge of DNAPL-specific fate and transport characteristics, or must make assumptions regarding the subsurface DNAPL distribution. An extensive DNAPL "hunt" will likely be expensive and will probably not

find all of the DNAPL at a site, therefore DNAPL presence and distribution may need to be inferred.

• **DNAPL tends to migrate via discrete preferential pathways.** Since DNAPL follows the path of least resistance, it can migrate in unexpected directions whenever such preferential pathways are encountered. In addition to natural pathways such as thin sand lenses and fracture openings, the investigation needs to consider potential pathways formed by such man-made structures as sewer lines, buried electrical or utility conduits, drainage systems, and areas consisting of historic fill. Being able to predict the DNAPL transport pathways is important since these migration pathways may be put to use as pathways for enhanced DNAPL extraction. As such, the investigation may need to focus on discovering transport pathways to successfully characterize the site and implement an effective remedial action.

• **Effect of DNAPL distribution on groundwater samples.** A long well screen intersecting DNAPL ganglia or a thin DNAPL lense may allow dilution of the groundwater sample and show contamination that does not indicate that the well intersected a DNAPL zone. In addition, monitoring wells can easily miss discrete DNAPL zones and, depending on site-specific conditions, wells drilled very close to subsurface DNAPL may fail to provide a clear indication of the nearby DNAPL mass.

• **Effect of DNAPL distribution on soil samples.** DNAPL confined to small areas can easily be missed by soil borings. If a small amount of DNAPL is collected in a soil core, it can be easily missed when collecting a soil sample from the soil core or even diluted by cleaner soil in the sample container depending upon the sample collection technique. If volatile, too much soil handling or failure to perform field extraction with methanol can allow significant amounts of the DNAPL contaminant to volatilize. Hydrophobic dyes and other visual sample examination techniques may fail to indicate the presence of DNAPL if the ratio of the non-DNAPL soil to DNAPL is too high for easy detection.

• **DNAPL flow counter to the groundwater flow direction can confound delineation of source and dissolved contamination zones.** DNAPL moving counter to groundwater flow may extend contamination source areas and thereby create additional plumes of dissolved phase contamination in unexpected areas. Therefore, there is increased uncertainty regarding the spatial distribution of the source zone. Thus, when monitoring for dissolved contaminants at assumed downgradient locations to delineate the upgradient presence of source (DNAPL) zones and/or the extent of dissolved contamination, an increased degree of monitoring is appropriate. This should include additional samples in assumed upgradient directions to ensure the detection of wandering source zones and associated dissolved contamination plumes.

• **Reasonable precautions should be taken when planning and implementing the DNAPL site investigation.** Reasonable measures should be taken to control the risks of expanding the zone of chemical contamination or developing misleading chemical

concentration data by the use of invasive site characterization methods (e.g., dragdown of residual DNAPL during drilling).

- **The DNAPL found at a site may not have the same composition as the original chemical that was purchased from a chemical supply company.** As DNAPLs are used, they become contaminated with impurities and may not have the same physical and chemical characteristics as the original pure chemical. This needs to be taken into account and samples of the DNAPL should be collected, if possible, and analyzed for parameters that could affect the subsurface behavior. Examples of such parameters include but are not limited to: viscosity, specific gravity, effective solubility, chemical composition, and wetting characteristics.

- **The age of the release and when the chemicals were purchased may be a factor in determining DNAPL composition.** It is important to know the approximate age or time frame of the release and/or chemical purchase since this may provide clues regarding the chemical composition of the DNAPL. Manufacturing processes change over time. Knowledge of the exact chemical composition manufactured during a certain period may help the investigator explain the presence or absence of daughter products in the dissolved phase plume. The date of release can also help the investigator in determining fate and transport related issues including but not limited to source area delineation (release points), liability, discrete/mixed plumes, natural attenuation, etc.

Investigations at DNAPL and potential DNAPL sites should be designed to collect and manage large amounts of data in order to specifically address the above issues. The data collection techniques should be designed to collect data that indicate where the DNAPL may be present in the subsurface, and how it contributes to the aqueous groundwater contamination and unsaturated zone soil gas plumes.

## 3.5    How Much Source Area Characterization Is Enough?

In order to fully characterize a DNAPL site, large amounts of data are usually needed. Even when using field analytical methods and dynamic work plans, large amounts of money can be spent on a DNAPL site investigation without ever determining the precise location of all of the DNAPL mass. Without a clear set of objectives, there can seem to be an almost endless need to keep collecting data and spending large amounts of money to collect these data. There is a need to decide when "enough is enough."

It is imperative that reasonable objectives be established for the project up-front so that the level of uncertainty remaining is acceptable. Central to the decision as to when the source area is adequately characterized is the need to collect sufficient data to: (1) identify risks to human health and the environment; (2) determine what, if any, remediation is necessary; (3) meet requirements specific to the regulatory program overseeing the site investigation and remediation; and (4) attempt to limit any "surprises" that may occur during remediation because the characterization did not allow the designers to accurately assess onsite conditions. Depending on the project goals, it may be

unnecessary (and wasteful) to attempt to locate all DNAPL at the site. To determine this, the investigator will also need to consider risks and contingency measures associated with failure of a remedy that is selected based on the available data.

It is extremely important to include a source area conceptual model within the overall site conceptual model. This will detail the properties of the DNAPL and the environment in which it is located. A clear understanding of the environment the contamination is located in is critical to final remedy selection (although it is possible that a preliminary presumptive remedy may be selected for the purpose of cost estimation based on general site information). The source area conceptual model is a tool that will help the investigation team organize the available data and understand the characteristics of the source.

Once the environment and contamination have been successfully defined such that the risk of remedy failure is acceptable, the next consideration is the volume of media to be remediated. The DNAPL source can be defined either from the outside inwards, or from the inside outwards as is appropriate for the particular site and source area. In order to allow an end point to the investigation, the source area can be considered as a box of media to be remediated.

The source may be considered as a "box" of media so that the mass is defined both laterally and vertically. The extent to which the mass is characterized should ensure adequate definition of contaminant concentrations that exceed regulatory levels, will leach to groundwater, will volatilize at unacceptable concentrations, and/or are a threat to human health or the environment. The size of the area to be remediated will be established by the actual extent of the source plus the cost of remedy. Relatively simple and inexpensive remedies (such as soil vapor extraction) may require less precise source characterization and definition, and cover a larger volume, making it uneconomical and unnecessary to precisely delineate the extent of DNAPL. Remedies that tend to be more expensive per unit volume, generally justify the additional expense to provide more precise data on DNAPL mass, volume, and location. The site investigator can introduce review periods into the work plan to allow time to reassess site information and determine if further investigation is necessary (or if an acceptable remedial system can be designed based on the available data). This will however, result in additional mobilizations and increase the project cost.

Quantification of the entire mass of DNAPL comprising the source zone would be difficult to justify economically, even if it was technically feasible. Mass-in-place and mass-removed estimates can be used as performance metrics to evaluate the effectiveness of a particular remedial action. Remedy effectiveness can be also be measured by comparing field measurements, such as soil gas concentrations, with a predetermined goal based on previous periodic measurements. Samples should be collected such that the impact of the remediation on the source may be accurately assessed. When the remedy has progressed to the stage where field measurements indicate that significant mass is not being removed, a confirmatory investigation in the areas of previous contamination can be initiated to assess the effectiveness of the remedy.

## 4.0     DYNAMIC APPROACH TO DNAPL SITE CHARACTERIZATION

DNAPL site characterization should be carried out using a dynamic approach incorporating a flexible work plan coupled with development and iterative refinement of a conceptual site model. DNAPL site work will benefit from the development of a valid and robust conceptual site model, systematic planning, implementation of a flexible work plan, and expert use of real-time field analytical methods. These strategies can be successful for large sites, such as industrial complexes, and for small sites, such as dry cleaning facilities.

The strategic framework that facilitates this type of investigative approach has been referred to by EPA and others as the Triad approach. The Triad framework encompasses all activities that serve to identify and manage causes of decision errors. Other terms used to describe various components of this strategy are flexible work planning, systematic planning, dynamic field activities, expedited site characterization, and accelerated site characterization.

### 4.1     Introduction to Systematic Planning

The overall goal of a DNAPL site investigation is to collect data sufficient to define the nature and extent of DNAPLs in order to assess risk and select appropriate remedial measures. The DNAPL investigation should utilize a combination of investigation techniques that are most applicable to the site and the chemicals of concern, particularly those methods designed to delineate DNAPLs (residual and free-phase). Ideally, this would include the ability to obtain real-time chemical analytical results on site for field decision-making purposes.

The first step in this investigation strategy is to evaluate available site data and generate a preliminary site conceptual model. The conceptual model should indicate potential contaminant transport pathways and impacts. The second step is to use available site data and the conceptual model to develop a flexible work plan and set goals for the investigation. This work plan should be flexible enough to allow the field activities to change based on site conditions as they are discovered. The third step is to conduct the investigation and include real-time analytical methods as an integral part of the site investigation. Obtaining analytical results in real-time (or near real-time) allows the investigator to immediately revise the conceptual site model in the field based on actual data. As the conceptual model is revised, the field activities are revised to address actual site conditions. This is an iterative process, which can result in a more efficient and less costly site characterization.

### 4.2     Reviewing Site Information and Developing a Conceptual Site Model

In order to characterize a DNAPL site, the investigation strategy must be designed to incorporate DNAPL physics, flow dynamics, and fate. Central to this strategy is the development of an initial conceptual site model that addresses the potential presence of DNAPL. This model will guide the site investigation. The conceptual site model will identify what is and what is not known about the contaminant transport system, will help assure that the investigation team performs the activities

that are necessary to characterize a DNAPL release and will provide the information necessary to make initial decisions regarding human health, ecological risk, and remediation. The conceptual model can also include a conceptual risk model to help focus the investigator on what risks may be caused by the contamination.

4.2.1    Site History

Research into a site's history is an important task when investigating any DNAPL site. An accurate and detailed site history can be used to help guide the site investigation, identify the potential for DNAPL contamination, and help ensure that adequate data are collected to make informed environmental decisions. The investigator needs to determine whether or not there is a likelihood for DNAPL to exist at a site before committing resources to the field. If a DNAPL chemical was used onsite, then there is a significant probability that DNAPL was released to the subsurface. Research into DNAPL use and releases at a site might include the following.

- **Chemical Use.** Identify what chemicals were used onsite. Were DNAPLs used or produced at the site? Review old land use maps, fire insurance maps, and aerial photos. Examine facility records. Research MSDS sheets, chemical invoices, products produced, historic changes in industrial processes, RCRA records, and waste stream information. Check U.S. EPA industry profiles (available at www.epa.gov) for information on what chemicals may have been used or produced at the site. Research previous site owners and prior site use to determine whether DNAPLs were used at the site (e.g., trichloroethylene with metals plating and tetrachloroethylene with dry cleaning operations). Are there known and previously investigated contaminant releases at the site or on adjacent properties?

- **Materials Processing.** Understanding raw material storage and handling procedures, site-specific manufacturing processes, and associated waste generation and disposition, will help indicate the likelihood of DNAPL at a site.

- **Employee Interviews.** Ask employees and former employees what they know about the chemicals used at the site. Were the chemicals disposed of on site? If so, where were the chemicals disposed? This is often the most inexpensive method to locate DNAPL source areas.

- **Past Land Use.** When studying a site with multiple present and past uses, it is important to review each land use for potential releases of DNAPLs. Five or ten gallons of DNAPL in the subsurface can cause significant long-term groundwater contamination.

- **Past Monitoring and Remediation Efforts.** Wells drilled though confining layers before DNAPL was suspected could have created a conduit for downwards DNAPL migration.

4.2.2   Site Environmental Conditions

The next steps in the investigation include reviewing and compiling available information on the hydrogeology beneath the site and any obvious environmental conditions related to past site use. This task might include the following:

- **Locate possible DNAPL release areas.** Use site engineering drawings, fire insurance maps, and aerial photos. Identify tank and pipeline locations, loading/unloading areas, chemical distribution centers, floor drains, sumps, doorways near production areas, onsite landfills, onsite discharge pipes, septic systems, and sewer lines, etc. Conduct interviews with active, former, and retired employees. Interview contractors, waste haulers, etc. Interview neighbors and environmental "watchdog" groups that may be familiar with the site.

- **Conduct a receptor survey.** Determine if there are any receptors presently affected by contamination. This will help determine the need for immediate response to the potential contamination, will help identify the type of contamination, and may provide some general indication of the flow direction of the contamination. Drinking water wells may serve as a starting point in a receptor survey.

- **Conduct windshield surveys and site walk-over.** Identify any clearly apparent DNAPL disposal or spill areas, floor drains, sumps, discharge pipelines, stressed vegetation, etc. Clarify as much as possible the geologic conditions that can be expected onsite. Are there any wetlands or surface waters in the area? Are there any gravel or sand pits in the area?. What role do these play in the local and regional hydrogeology?

- **State and federal records search.** Review state spill response records, solid waste records, and discharge permits (state and federal).

- **Known environmental conditions.** Determine if there are any known environmental problems on or near the site. What is the known problem and what data are available on geology, groundwater flow and depth, and contaminants present in the vicinity of the site? Determine if any known contamination could have a DNAPL source.

- **Hydrogeology and contamination.** Research hydrogeologic and geologic conditions and contamination at and near the site. Review literature and data available from County, state, and federal agencies and from local colleges and universities.

- **Water supply records.** Review any available data on local water wells onsite or in the vicinity of the site. Check health department water supply records if these are available.

4.2.3    Initial Conceptual Site Model

The available data as described above are used to develop the initial conceptual model for the site. The initial conceptual model should summarize in graphics and text the investigator's understanding of the site including the chemical use history, known contaminant types, and the potential for the presence of DNAPL. The conceptual model should also address the role of the local geology and describe its expected effect on contaminant distribution and behavior. The model should include a description of any known contaminant and DNAPL releases, and contemplate the areas where releases may have occurred. The conceptual model should be considered an initial draft document. As the investigation proceeds and data are gathered, the conceptual model must be revised and expanded to include new data. Updating the conceptual model helps to guide and revise the investigation (as depicted in the investigation work plan), and indicates where the field activities need to be focused (ASTM D-6235-98, Crumbling et al., 2001).

**4.3      Developing a Flexible Work Plan**

Due to DNAPL migration characteristics, the "traditional" method of site characterization (multiple iterations of drill, collect and analyze data, evaluate in the office, identify data gaps, go into the field and repeat) is ineffective, inefficient, and expensive. The use of the flexible work plan methods proposed in this document can reduce the costs and number of field investigation phases, and increase site investigation accuracy at sites contaminated by DNAPLs. A flexible work plan is based on the conceptual model and site conditions as known prior to beginning the investigation. Once the investigation is started, real-time analytical data are collected onsite and the conceptual model is updated as these data are generated. When the interpretation of the data begin to explain actual site conditions, the investigation may be changed to fit the actual field conditions. This can save significant funds because the investigation can be based on real site conditions as they are discovered. A flexible work plan allows the investigator to conduct a site investigation that addresses site questions as they arise.

Keys to a successful investigation using flexible work plans include:

- experienced staff capable of interpreting real-time data and making decisions to adjust the investigation;
- necessary equipment to shift priorities in the field, if necessary;
- best possible initial conceptual model;
- clear investigation goals;
- equipment that can collect large amounts of specific point data in reasonable time frames at an acceptable cost;
- real-time data available in the field;
- method of organizing and visualizing the data in the field;
- clear decision points in the investigation process; and
- robust communication and documentation plan to ensure all parties are appraised or relevant site information as it is generated.

Perhaps the single most important factor to a successful project is having someone onsite or readily available who has the knowledge and authority to adjust the work plan and change the direction of the field investigation. If there is a decision team that is responsible for changing the work plan, real-time communication with all members of the decision team is required. When issues arise that the site personnel cannot answer, the site personnel can contact the project manager, explain the situation and the project manager can determine the appropriate step. A preapproved decision tree can be added to the work plan to help guide the in-field staff in the direction to take the investigation.

An investigation at a DNAPL site should ideally be designed to collect sufficient point-specific data to depict the presence and location of DNAPLs, without having to resort to an excessive number of sampling mobilizations. In general, this would include the ability to analyze samples on site for field decision-making purposes. A dynamic work plan using field analytical methods, can provide the data necessary to characterize DNAPL sites adequately to allow regulators to make decisions.

## 4.4     Real-Time Field Analytical Methods: Quantity versus Quality

As mentioned previously, conventional wells drilled reasonably close together can easily miss pockets of DNAPL and may not identify an area where DNAPL ganglia are present. One method to overcome this problem is to collect more data in the area being investigated. In some cases this has been taken to mean drilling and installing large numbers of conventional monitoring wells. This is expensive and may still not answer all the questions. As discussed in Section 5 of this document, there are other methods to characterize a site. It is possible to use innovative subsurface techniques that gather large quantities of both qualitative and quantitative data that will help the investigator determine if DNAPL is present and where it might be concentrated.

A common objective of DNAPL site investigations is to estimate the volume and extent of DNAPL present in the subsurface at the site, as required to assess the human health and environmental risk and implement appropriate remedial tools. By using field analytical techniques that produce near real-time data, the on-site decision maker significantly reduces the uncertainty contributed to the overall investigation from sample location selection. Real-time data coupled with real-time decision making allows rapid iteration to locate and assess contaminant distribution at the site (Robbat, Smarason, and Gankin, 1998; Robbat, Smarason, and Gankin, 1999; Crumbling et al., 2001).

Related to this issue is the concept of data accuracy and validation. Historically, when monitoring is conducted at a site, the environmental samples are sent to an EPA- or state-approved laboratory and analyzed by specific regulatory approved analytical methods (e.g., SW-846 methods). Often, the analytical data are then validated by an independent third party in accordance with rigorous quality assurance protocols. This process is time consuming and expensive, and data are usually not available during the field work phase of the investigation. When implementing a flexible and dynamic work plan, the data should be made available in the field in near-real time to guide the investigation. As there are usually limited funds and time available to collect and analyze data, it may be more effective to collect and analyze more data using potentially less accurate field analytical methods (although many field analytical techniques are just as accurate as laboratory

techniques) that provide the data to the investigator while in the field, than to collect fewer samples and analyze the data using very accurate analytical techniques with post analysis data validation. Please note that data quality objectives must be defined and used to guide the development of proposed analytical methods for any investigation.

In order to justify using potentially less accurate field-generated data at a DNAPL site, consider that the distribution of contaminants will vary greatly throughout the subsurface. As discussed previously, there can be a great deal of heterogeneity in the distribution of DNAPLs and the dissolved phase plume related to the DNAPL. For example, it is possible to take a soil sample from one part of a core, analyze it using exceptionally accurate analytical methods, and detect significantly different contaminant concentrations from a sample taken only one or two inches away in the same core. It seems unnecessary to use an analytical method that is exceedingly accurate if a soil sample taken only two inches away shows significantly different contaminant concentrations. If more samples are taken at a lower but acceptable level of accuracy, the investigator may be able to gain a much better understanding of the distribution of the contaminants in the subsurface.

Large amounts of data are necessary to characterize a DNAPL site. It can be cost prohibitive and time consuming to analyze large numbers of samples with laboratory analytical and data validation. Using a lower cost analytical method allows the investigator to collect and analyze a much greater number of samples. A greater number of samples can provide a significantly better understanding of the contaminant distribution, allowing accurate and prompt adjustments of the conceptual model. Previous investigations have demonstrated that using field based analytical methods allows accurate sample location selection, thus leading to a significant reduction in the uncertainty of the data set produced to assess site conditions (Crumbling et al., 2001).

There are a variety of techniques that can be used to quickly analyze environmental samples. These include field characterization techniques such as field gas chromatography, immunoassay, and direct sampling ion trap mass spectrometry (EPA Method 8265). Screening methods, such as the use of a photo-ionization detector or organic vapor analyzer, can also be useful. Laboratories can also sometimes develop quick and accurate screening techniques to analyze samples. Using these modified analytical techniques allows the investigator to develop a large data base that accurately describes the general site conditions and provides realistic indications of whether or not DNAPL is present and where it might be located. The more data collected during the investigation, the more likely the investigator is to determine if DNAPL is present and to accurately characterize DNAPL source areas.

As implied above, it may be advantageous to utilize less rigorous analytical methods in order to obtain more data for the same or less cost. However, representative data are very important and the dynamic work plan process strives to collect data that are accurately representative of the intended project decisions. The selection of acceptable field-based methods includes understanding the limitations of the techniques and deciding on data accuracy requirements during the early planning stages of any investigation. In the Triad approach, the term "Decision Quality Data" is used to refer to data for which both the sampling and analytical representativeness have been specifically tailored to project decision-making needs. The analytical methodologies must be researched and determined

to be acceptable prior to use (often through a "methods applicability study"), the operator must follow the standard operating procedures (SOPs) developed for the project, the equipment must be calibrated as often as is warranted, and a selection of the samples will be homogenized and split for comparison analysis by more rigorous or selective laboratory methodologies so the analytical bias and precision of field-generated data may be assessed. If the laboratory analyses show that the field methods are unacceptable, the problems with the field method must be solved and more samples will need to be taken and reanalyzed.

One significant advantage to data analysis with on-site analytical methodologies is the ability to recognize and correct data analysis problems as they happen. With traditional data collection methods, the sample is taken, preserved, and sent to a laboratory where analytical results may not be available for weeks. The analytical data are not reviewed until after completion of the field work phase of the site investigation. If there is a problem with the data it may not be feasible to recollect the sample during the investigation, and unexpected data results may not be investigated without a new investigation. With on-site field analytical methodologies, analytical data can generally be available within minutes to hours after the sample is collected and any problems found with the data can be remedied in the field while the investigation is ongoing. Also, if there is a problem noted, it may be possible correct the problem and reanalyze samples prior to expiration of the holding time.

## 5.0    DATA COLLECTION TECHNIQUES AND INTRUSIVE SITE INVESTIGATION METHODOLOGY

The following is a brief discussion of a variety of site investigation tools and techniques that can be useful in characterizing DNAPL sites. This list is not comprehensive and there may be other investigation methods available or presently being developed. As this is a rapidly growing field, there are many new techniques being developed and tested. It is therefore important that personnel responsible for generating site investigation work plans maintain familiarity with recent scientific research.

### 5.1    Geophysics

Although geophysical tools will not be able to identify DNAPL directly (unless it exists as a large pool), these methods can provide significant information about the geology and indicate where DNAPLs may be present. Geophysical techniques such as seismic, ground penetrating radar, or resistivity may provide information on the presence of stratigraphic traps or preferential flow pathways. Ground penetrating radar and electromagnetic surveys may provide information regarding anthropogenic pathways and buried sources of contamination. Secondary porosity may be assessed by very low frequency (VLF) techniques, and structure by gravity surveys.

Once these data are collected and interpreted, they should be used to refine the conceptual model. It is important to stress that results from geophysical instruments can be strongly affected by local geology and anthropogenic activities. In many areas, the geology itself, or the presence of certain utilities, such as overhead power lines, can prevent or limit the successful use of geophysics for site

investigation. The tools utilized for a site investigation must be carefully chosen and account for the local site conditions and geology. Geophysical data may also need to be correlated to a log from an intrusive geological data collection method and ground-truthed since the methods are measuring changes in the matrix, not the matrix itself. The table in Appendix B provides some examples of geophysical techniques useful in characterizing DNAPL sites. The ITRC's technology overview document *Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies* (ITRC, 2000) provides a more detailed discussion of the various geophysical techniques. This document is available for free download on the ITRC Web site at: http://www.itrcweb.org/DNAPL-1.pdf.

## 5.2     Characterizing DNAPLs in Unconsolidated Materials

### 5.2.1    Vadose Zone

The generally preferred strategy for locating sources in the vadose zone is to use active or passive soil gas sampling (where the DNAPL chemical is volatile), to find "hot spots" and then determine the depth of the source through vertical soil gas profiling. It should be remembered that DNAPL may migrate laterally as well vertically, following either natural or man made conduits, and may migrate in different directions at different depths. Soil gas surveys are often first conducted in a grid pattern over a site with a denser grid used in areas where it is expected that DNAPLs were released.

VOC vapor can be far more widespread than DNAPL (depending upon geology), and generally decreases in concentration as a function of distance from the source. Soil gas sampling points, if properly purged and collected in porous and permeable sediments, sample a much larger volume of the vadose zone than can be achieved by soil sampling and will help to locate DNAPL within the vadose zone. Care must be exercised when interpreting the results of soil gas surveys to consider that data may be skewed by natural and anthropogenic features of high air permeability, such as buried stream channels and utility trenches. In addition, pavements and buildings may trap vapors and cause anomalously elevated concentration of VOC vapors in soil gas. As in all environmental site investigations, a detailed understanding of the geology can help tailor the investigation to best fit the geology.

Direct push technologies are commonly used to sample for soil gas but tend to be limited to the shallow portions of the vadose zone by push capacity or lithology (for example: many parts of the west have cobble zones associated with high energy stream deposits, and compacted glacial tills are common in the northeast of the United States). Deeper investigations are usually performed with a combination of drilling, soil gas sampling and soil sampling. Soil sampling alone is discouraged, as the chances of locating a DNAPL source without previous soil gas work is slight, except in the case of massive DNAPL contamination. However, if the DNAPL in the vadose zone is not volatile, it will be necessary to take numerous discrete soil samples to characterize the DNAPL. Vertical profiles of soil samples should be taken in a grid pattern with a tighter grid in areas where DNAPLs are expected.

The use of accurate field analytical techniques for soil gas or soil samples that provide near real-time data can be useful in characterizing a DNAPL release in the vadose zone. The near real-time data will allow the investigator to change the sampling pattern, vertical profile, or sample interval in response to analytic results.

5.2.2   Saturated Zone

DNAPL site characterizations attempt to identify where DNAPLs are located in the subsurface, or at least identify the portion of the site or "box" within which DNAPLs are likely to be located. If feasible, samples of DNAPLs should be obtained. These should be analyzed by conventional laboratory techniques to gain as much knowledge of the site specific characteristics of the DNAPL as possible. As discussed in Section 2.2.2, DNAPL characteristics may vary across the site, therefore, multiple samples of site specific DNAPLs are preferable if possible. However, at many DNAPL sites, it will be impossible to collect a sample of the DNAPL because it is present only as residual phase or in undiscovered pools of DNAPL.

During investigations, it is important to avoid remobilizing the DNAPL. As discussed by Newell and Ross, 1992; Cohen and Mercer, 1993; Pankow and Cherry, 1996; and others, DNAPLs in the subsurface may be static based on the equilibrium between the DNAPL and the groundwater and are immobile because the interfacial tension between the groundwater and the DNAPL prevents the DNAPL from migrating through the subsurface. Drilling through a DNAPL lense or pool can create a preferential pathway that the DNAPL can use to migrate deeper and contaminate a previously uncontaminated portion of the subsurface.

Drilling and field screening techniques must be chosen or developed to avoid remobilizing DNAPLs. When drilling in a suspected DNAPL area, soil samples should be taken preferably continuously and should be immediately screened for the presence of DNAPLs. The field screening technique should be based on the potential DNAPLs at the site and can include hydrophobic dyes and visual screening. Hydrophobic dyes may not work well in instances where there is just a small amount of DNAPL present as there may not be enough DNAPL to allow the colors to be visible in the test vial. However, even in such cases there will be enough DNAPL to contaminate a significant amount of groundwater. Even a simple field screening method such as a photoionization detector (PID) or flame-ionization detector (FID) may indicate signs of DNAPL by exhibiting high concentrations of the contaminant in the soil sample. The PID or FID must be applicable to the contaminant of concern and must have the appropriate lamp in the PID and the appropriate calibration.

Any borehole can become a preferential pathway for contaminant migration. A borehole in a suspected DNAPL area should be pressure grouted immediately after the hole has been drilled and samples collected. If a well must be placed in a DNAPL area, the well should be constructed such that it does not become a conduit for migration. Strategies for constructing a well to minimize the chance for migration include: isolating the well screen in the DNAPL or non-DNAPL area, drilling the borehole only as deep as required for the well screen with no sump , and grouting the annulus of the bore hole above the well screen and sand pack. (if one is used). Care should be taken to use

a grout that will not be affected by the DNAPL present at the site. McCaulou and Huling (1999) discuss this issue in more detail and note that some DNAPLs will prevent bentonite pellets from hydrating.

All field investigation work plans should include steps to be taken to prevent migration of DNAPL if it is encountered. One possible contingency plan is to cease drilling if DNAPL is encountered. Some of the drilling techniques discussed later in this paper may minimize the potential for mobilizing DNAPLs.

Newell and Ross (1992) and others have discussed first drilling in a known DNAPL-free area prior to drilling in areas where DNAPLs are expected or possible. This is done in order to develop a physical and conceptual model of the geology and groundwater flow which may help predict DNAPL locations. They suggest that it may be better to avoid drilling in a DNAPL area in order to avoid remobilizing the DNAPL. Under this technique, investigation can halt when DNAPL is first discovered. This should be considered, but if data on the DNAPL itself is necessary (as may be required to plan for aggressive remediation techniques), new drilling techniques can help minimize the potential for remobilizing the DNAPL. For example, direct push sampling equipment has been modified to include grouting capabilities through the tip of the tools. The hole can be pressure grouted as the tool is removed from the ground, thus limiting the ability of the DNAPL to migrate downwards through the investigation hole (Costanza and Davis, 2000).

### 5.2.3   How to Determine that the Data Collected Indicate DNAPL

DNAPLs will not be readily apparent in water or soil samples at most sites even if DNAPL is present in the subsurface in significant quantities. Determining if DNAPL is present can be a subjective process because as discussed above, in many cases, an investigator could drill directly through DNAPL ganglia and never see concrete indications of the ganglia in the investigation results. One of the most important considerations in determining whether or not DNAPL is present, is whether or not a DNAPL chemical was used, disposed, or manufactured at the site. As discussed above, if a DNAPL chemical can be linked to the site, it is likely that it was released to the environment. The investigator must view all of the available data to determine if there is evidence that indicates the presence of DNAPL.

One potential indication of the presence of DNAPL in the saturated zone in a monitoring well with a long well screen (at least 10 feet long ), is that the concentration of the contaminant is greater than one to ten percent of the compound's effective solubility (Cherry and Feenstra, 1991). The reasoning behind this generalization is that if DNAPL is present, it will generally be present either as a small lense in a small preferential pathway, as residual phase ganglia, or diffused from a preferential pathway into a fine grained matrix. If a ten foot well screen is close to or intersects one of these areas, the area where the DNAPL is present will likely be thin when compared to the full length of the well screen. Therefore, while aqueous phase contamination is dissolving from the DNAPL into groundwater at a concentration close to its solubility limit (please note the DNAPL may be a mixture or used and can have an effective solubility that is different from the solubility of the pure DNAPL chemical), groundwater flow is generally laminar and will not mix quickly with the larger

interval of the formation. The contamination will therefore be diluted in the monitoring well during sampling by the larger screened interval of the formation. Therefore, concentrations of a small percentage of solubility may indicate DNAPL. If well screens are short, there will be less dilution and the contaminant concentration will be a higher percentage of solubility before it indicates DNAPL. This technique is subjective and must be used very carefully. It should be considered only a part of the process used to determine if DNAPL is present, not a method that by itself will indicate the presence/absence of DNAPL. The U.S. EPA has indicated that concentrations of DNAPL chemicals in soil greater than one percent by mass or 10,000 mg/kg may indicate the presence of DNAPL (EPA, 1994).

If long screens are required at a site by regulation, the responsible party, funding that will not allow multiple wells, or for some other reason, discrete groundwater samples taken from distinct intervals in the well screen may give a much better approximation of whether or not there is a DNAPL source. (Please note that a well with a screen longer than a few feet is generally unsuitable for a DNAPL investigation and may among other problems allow cross contamination of the aquifer to occur.). If the well is located near a thin DNAPL source, a profile of the water quality in the well screen can show very high concentrations of the contaminant near the DNAPL source and clean or relatively low concentrations of the contaminant in the rest of the well screen. If the well intersects a dissolved phase contaminant plume however, we would expect to see a more constant contaminant concentration across the entire screened interval. Within a well screen, the groundwater may be flowing up or downwards as per the gradient of the aquifer. This needs to be determined when attempting to understand contaminant concentrations across the length of a well screen. If discrete interval groundwater samples are taken from small discrete intervals of the formation, an even higher percentage of the compound's solubility will be needed to indicate DNAPL because the discrete samples will be less diluted.

In some cases, DNAPL may be present in the water or soil samples. This is unusual and indicates that the sample was collected near the source and/or very large amounts of DNAPL were released at the site. In some cases a discharged DNAPL is colored or includes impurities such as dissolved grease or oil, however it can also be clear and therefore difficult to see in water or soil samples. Hydrophobic dyes that react with the DNAPL may be useful to add to soil samples to assess whether or not DNAPL is present. These only work well if there are relatively large amounts of DNAPLs present. If only a small amount of DNAPL is present, the hydrophobic dye may not render it visible.

The best method used in DNAPL source area determination may be to use the "propensity of data" from site characterization efforts. There is no one particular method available to clearly delineate the presence/absence of DNAPL. All data collected during the site investigations and historical site use surveys need to be collected and viewed as a whole to determine if there is a potential for DNAPLs at the site.

5.2.4  Specific Characterization Techniques for Sites Contaminated with DNAPLs in Unconsolidated Materials

There are a number of site characterization techniques that work well at DNAPL sites. A variety of specific characterization techniques are listed in Appendix B of this document; and the actual use of some of these techniques is discussed in the case studies in Appendix C of this document.

Geophysics can be used to help characterize the geology during the site investigation in order to understand potential preferential transport pathways and stratigraphic traps. Cone Penetrometers (CPT) calibrated to borehole data can be useful to quickly generate geologic profiles of the unconsolidated materials at a site. Techniques capable of combining in situ contaminant sampling with simultaneous collection of geophysical CPT data can rapidly locate contaminants and preferential geologic pathways for contaminant transport (Costanza and Davis, 2000).

Large numbers of discrete interval samples of both soil and groundwater taken for chemical analysis are extremely valuable when characterizing a DNAPL release. If large numbers of samples are taken, there will be a better chance that the distribution of the DNAPL will be understood. Take vertical profiles of soil and groundwater quality and physical parameters in transects across any known plume or plumes and in suspected source areas. Take a large number of discrete samples from the transects to help identify areas of residual phase DNAPL or thin lenses of potentially mobile DNAPL. Be aware the DNAPLs may follow preferential pathways and flow against groundwater flow. Exploration locations should therefore be chosen to investigate many potential preferential pathways and determine if there are other dissolved phase contaminant plumes than ones known at the start of the investigation.

The actual number of samples needed to characterize a site is site dependent and will not become fully apparent until the investigation begins and site specific data are used to adjust the work plan. When planning a site investigation, the budget must reflect that many environmental samples will need to be taken. Costs may be offset by using field analytical methods, but there will still be a large expenditure for sampling and analysis. In the planning stages, the issue of how many samples will be needed may be addressed by preparing preliminary grid patterns for sampling based on what is known about the site. It is possible that these sample locations will be changed as the investigation proceeds, but this will allow an initial indication of the budget needed for sampling and analysis.

The fine resolution data provided by many discrete groundwater samples may indicate best where the small lenses and DNAPL ganglia may be located. These samples should be taken under strict, high quality standard operating procedures that are agreed upon by all parties prior to beginning the investigation. A transect of discrete interval sampling points collected vertically and horizontally can collect more nontemporal data at a lower cost than dozens of monitoring wells.

Soil borings should be advanced collecting continuous cores if the geology will allow this. Discrete soil samples should be taken from multiple locations in the cores in order to discover DNAPL and preferential pathways. Density of sampling in a particular soil core interval may vary during the investigation depending on the results of the field analytical method and the heterogeneous nature

of the site geology. PID or OVA data can be useful in determining where to take soil samples if the contaminant is volatile.

Determining the physical characteristics of the soils (bulk density, fraction organic content, porosity, conductivity, redox conditions, etc) is also an important part of any site investigation as these characteristics will significantly influence how the DNAPL and dissolved plumes interact with the formation matrix. Data on these properties should be gathered early in the site investigation as they can be controlling factors in both aqueous phase and DNAPL contaminant fate and transport. These data should be incorporated into the conceptual model of the site as soon as possible.

If the contaminant is volatile, extreme care are must be taken when drilling and sampling from the soil core to avoid volatilization. If field analytical techniques are used to quantify contaminant concentrations in the soils, the soil samples should be immediately extracted and preserved as appropriate to the analytical method. After the soil samples are taken for chemical analysis, the soil core should be logged and the geology carefully described.

Depending on the geology, it may be simpler to concentrate on groundwater quality versus soil data to identify the location and extent of DNAPLs below the water table. A direct push discrete interval groundwater sampling device can be used for this purpose. As DNAPLs often migrate in small preferential pathways, a large number of groundwater samples taken from small discrete sample locations can provide extremely useful clues as to whether or not DNAPL is present in the subsurface. These transects are drilled solely for the collection of discrete groundwater quality data and are not transformed into monitoring wells. The holes should be pressure grouted during tool removal to avoid remobilizing the DNAPL.

Once the data from the discrete interval soil and groundwater samples are analyzed and integrated into the conceptual site model, the data are used to plan locations and depths of monitoring wells that will intersect areas of the aquifer for long-term monitoring and hydraulic testing. Discrete interval samples provide useful information as they can give accurate water quality data, showing both low and high concentrations of contaminants over small vertical distances. These data can be helpful to identify thin lenses of DNAPL and areas of residual phase ganglia.

Examples of investigation tools that can provide discrete interval groundwater samples include but are not limited to the Geoprobe system, Precision Sampling Multichannel Sampler, Vertek Cone Sipper, passive diffusion bag sampling, and the Waterloo Profiler™ discrete interval sampling device. An alternative to discrete interval groundwater samples is the Membrane Interface Probe™ (MIP) coupled with a cone penetrometer. These can supply direct readings of soil and groundwater quality, soil conductivity and resistivity. The detection limit of the MIP has been shown to be on the order of 100–200 ppb for most analytes (Costanza and Davis, 2000). The MIP is capable of detecting high concentrations of chlorinated solvents in the subsurface. This makes the MIP an idea tool to rapidly screen an area for the potential presence of DNAPL. The MIP can therefore be used to select discrete sampling intervals to confirm or deny the presence of DNAPL by other analytical techniques (field or laboratory based). When DNAPLs are expected in a particular area, a colorimetric device such as the FLUTe Liner™ or ribbon sampler can be installed in open boreholes

to potentially pinpoint where DNAPL lenses are located in the subsurface. Cone penetrometers coupled with laser induced fluorescence can provide useful information about geology and the presence of contaminants that fluoresce. Please note that while many DNAPLs do not fluoresce, some DNAPLs that have been used as degreasers may include enough hydrocarbons to fluoresce. A sample of the on-site DNAPL should be obtained and tested before using this method and it may be possible that in addition to fluorescing DNAPLs, there may also be nonfluorescing DNAPLs present.

Diffusion sampling techniques can be used to collect groundwater quality data in discrete intervals of existing wells with long well screens when subsurface conditions permit. The discrete interval water quality data may indicate presence of a preferential pathway or DNAPL when contaminant concentrations are near solubility limits. The head distribution in the well must be known prior to attempting to collect discrete interval samples with a series of diffusion bags. If there is groundwater flowing in the screen in response to an upwards or downwards gradient, it will not be possible to collect discrete interval samples without using a packer to seal off the interval of interest.

## 5.3    Characterizing DNAPLs in Bedrock

Investigating DNAPL in bedrock is much more difficult than in unconsolidated materials. Characterization must first focus on developing a detailed understanding of the geology and possible contaminant sources and flow paths. Fracture trace analysis coupled with field mapping and geophysics can be helpful to delineate fractures and other preferential pathways. Two geophysical methods that may help delineate subsurface strike and dip of fractures are the VLF (very low frequency radio) technique and high resolution ER (electromagnetic resistivity). It is essential to conduct field work with compass and clinometer to field truth fracture traces, bedding planes, fault lines and other sources of secondary porosity determined from remote sensing or geophysical methods.

In bedrock, DNAPL might be observed or indicated by using borehole geophysical techniques (temperature, resistivity, acoustic logging, digital borehole imaging, etc., see Appendix B) as DNAPLs are chemically different than the surrounding groundwater. Color reactive liner-Ribbon techniques will show DNAPLs if the liner is in contact with the DNAPL. Strings of short diffusion samplers placed in wells may show areas where high concentrations of some contaminants (indicating possible DNAPL) are present.

Pump tests may be necessary to understand the groundwater flow patterns in bedrock. However, aggressive pumping in bedrock may remobilize DNAPL. While this may not normally be the case, care needs to be taken to avoid the possibility.

Samples of the matrix can be taken and analyzed in areas where groundwater quality data or geology indicate the presence of DNAPLs. As discussed above, DNAPLs can diffuse into the matrix of the rock making them difficult to identify. It may be necessary to take core samples in order to conduct this testing. However, if the contaminant is volatile, it is possible that the process of coring and sampling may allow the contaminant to volatilize and escape detection.

Another option is to continuously core the borehole. This will provide specific information regarding the lithology, matrix porosity and permeability, and fracture locations. Discrete interval water quality samples can then be taken from the bedrock by using packers to isolate a section of the bedrock. One method to accomplish this is to isolate the bottom section of the well between each core run. Using a single stage packer avoids the problem of leakage through the bottom packer. Upon completion of the work, the bedrock borehole can be completed as a monitoring well, or tremie grouted closed to prevent the migration of contaminants through the borehole to other parts of the formation. If the borehole is to be completed as a well, it will need to be drilled such that a well can be completed that will not allow contaminants to migrate to clean portions of the bedrock.

## 5.4     DNAPL Site Characterization as Part of a Full Site Investigation

The discussion of DNAPL site characterization in this document has centered on characterization techniques that will provide knowledge on the distribution and extent of DNAPL at a site. The DNAPL investigation has to be grouped with studies regarding fate and transport of both the aqueous contaminant phase and soil vapor contaminant phase. When a site is studied as a whole, including not only the DNAPL characterization but also aqueous and vapor phase characterization, the site characterization may provide data that are sufficient to allow the regulator to make decisions as to whether or not remediation is possible even if the exact location of all DNAPL is not known.

The characterization must also identify any threats to human health and the environment, as these are an essential part of determining remedial responses.

### 5.4.1   Toolbox Approach

Characterizing DNAPL sites may require the use of innovative techniques and the collection and analysis of many soil and groundwater samples. The overall understanding of DNAPL sites can be made more precise and efficient by using an appropriate combination of innovative and conventional characterization tools and analytical methods. This has been called a toolbox approach to DNAPL site characterization and can add flexibility and help offset some of the limitations to using traditional methods by themselves (Rossabi et al., 2000). Conventional methods of locating DNAPL in the subsurface have included groundwater monitoring wells, multilevel samplers, soil gas measurements, chemical analysis of soil samples, and soil borehole logging to determine site stratigraphy. Although these methods are useful , there is the potential to miss discrete pockets of DNAPL contamination in the subsurface. This can lead to incomplete characterization and inadequate remedial designs. For example, at Hill Air Force Base (AFB), a containment wall was constructed around a DNAPL source area that had not been adequately characterized. Subsequent monitoring showed that much of the DNAPL mass was outside the perimeter of the wall (Brown et al., 1998; USAF, 1999).

This toolbox approach to DNAPL characterization was used by investigators at the Savannah River Site where an integrated suite of traditional and innovative characterization technologies was put to use, providing valuable information on the site geology and distribution of DNAPL in the subsurface (Rossabi et al., 2000). The acceptance of DNAPL investigations that incorporate

innovative characterization approaches is vital to successfully deal with the unique nature and challenges of DNAPL.

In order to conduct an effective DNAPL investigation utilizing innovative characterization technologies, consideration must be given to the applicability of the technology for the particular site, as well as an understanding of the characterization technology, particularly with respect to measurement capabilities and detection limits. Also, the factors controlling the performance of a DNAPL characterization technique, as well as a method for verifying its performance, should be reported along with the results. It is critical to make sure that the objectives for the collection and use of the DNAPL characterization data are attainable.

5.4.2    Partitioning Interwell Tracers

If it becomes necessary to design a full scale aggressive remediation of the DNAPL source area, it will be necessary to have a much more detailed understanding of the mass and volume of the DNAPL. Partitioning Interwell Tracer Test (PITT) tests can provide detailed information on the mass and volume of contaminants in place in the subsurface. Injection and monitoring of conservative and nonconservative tracers in contaminant zone is used to measure the volume and mass of residual phase DNAPL (Meinardus et al., 1999). These data are then used to design effective remedial strategies. Please see Meinardus et al. (1999) for more detailed information on this subject. It should be noted that some researchers have reported problems with this technique for determining free phase NAPL.

6.0    REGULATORY ISSUES

Investigators should make use of innovative DNAPL characterization methods, when appropriate and cost-effective. (Some of these methods are discussed in this document and others in the ITRC document *Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies*, June 2000 (http://www.itrcweb.org/DNAPL-1.pdf ). Due to the unique nature and challenges of locating DNAPLs, traditional site investigation methods have not provided adequate understanding of geosystems involving DNAPL contamination and should be supplemented with more effective tools. In some states however, it may be difficult to incorporate an innovative site characterization with a dynamic and flexible work plan as described in this document. Some of the problems include:

- **Permit Requirements.** Some states require permits for all wells drilled. The state may define a borehole drilled to sample groundwater as a well even if no well is installed and the hole is pressure grouted after the water sample is taken. This will complicate the implementation of a flexible work plan as it will be difficult to change the location of a proposed soil boring or discrete interval sampling transect in the field if data indicate that revisions are required. The investigator may be able to work with the permitting authority to set up a process for a quick review of any proposed changes or incorporate the ability to change borehole locations into the permit. A regulatory agency may also

consider proposing changes to governing statutes or regulations to allow boreholes to be drilled in order to allow flexible work plans instituted under regulatory oversight.

- **Work Plan Approval Process.** Some states may require that a work plan be developed and approved prior to beginning any investigation and may not allow any changes to the field activities while the investigation is on-going. States should consider allowing flexible/dynamic work plans and setting up a process where changes to planed field activities can be made in a short time frame. A method to help allow flexible work plans may include the use of decision trees and specifying flexible end points in the work plan. However, the work plan cannot foresee all site conditions, so decision trees and end points may also need to be revised.

- **Use of Innovative Characterization Tools.** Some states have specific regulations regarding site characterization and what tools are acceptable to use during site characterization. These states should consider allowing innovative technologies to be used during site characterization and consider what type of state review of the innovative technology is needed to allow the technology to be acceptable for use in a site characterization.

- **Acceptance of Field Analytical Methods.** States can require specific approved laboratory analytical methodologies with data validation. These states should consider allowing innovative and field analytical methodologies for site characterization and consider what processes are necessary for the state to accept the analytical results from the innovative or field analytical techniques. The ITRC offers guidance documents on many innovative techniques that can be used to help states determine if a proposed innovative technology is appropriate. States can also consider the U.S. EPA Environmental Technology Verification Program studies of field characterization, monitoring and analytical techniques as a guide (http://www.epa.gov/etv). States may also consider setting up their own process for approving field or innovative analytical techniques. This may include requirements for operator training, calibration and verification of field measurement with approved laboratory analytical methods on certain percentages of samples, and development of QA/QC procedures for the investigator to follow in the field.

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http://www.epa.gov/superfund/programs/dfa/index.htm

# APPENDIX A

# List of Acronyms

# Appendix A.  List of Acronyms

| | |
|---|---|
| AFB | Air Force Base |
| AFCEE | Air Force Center for Environmental Excellence |
| ASTM | American Society for Testing Materials |
| bgs | below ground surface |
| BTEX | benzene, toluene, ethylbenzene, xylene |
| cfm | cubic feet per minute |
| CITT | conservative interwell tracer test |
| CPEO | Center for Public Environmental Oversight |
| CPT | cone penetration test |
| DCE | dichloroethylene or dichloroethylene |
| DNAPLs | dense, nonaqueous-phase liquids |
| DO | dissolved oxygen |
| DoD | Department of Defense |
| DOE | Department of Energy |
| DUS | dynamic underground stripping |
| EIT | electrical impedance tomography |
| EM | electromagnetic |
| EMR | electromagnetic resistivity survey |
| EOL | electromagnetic offset logging |
| ERH | electrical resistive heating |
| ERT | electrical resistance tomography |
| ft | feet or foot |
| GC | gas chromatograph |
| GPR | ground penetrating radar |
| $H_2O_2$ | hydrogen peroxide |
| HPO | hydrous pyrolysis/oxidation |
| ISCO | in situ chemical oxidation |
| ISTD | in situ thermal desorption (or destruction) |
| ITRC | Interstate Technology & Regulatory Council |
| LNAPL | light, nonaqueous-phase liquid |
| mm | millimeter |
| MCL | maximum contaminant level |
| MSL | mean sea level |
| MTBE | methyl tertiary butyl ether |
| NAPL | nonaqueous-phase liquid |
| O&M | operation and maintenance |
| OH• | hydroxyl radical |
| OST | Office of Science and Technology |
| OU | operable unit |
| PAH | polynuclear aromatic hydrocarbon |
| PCBs | polychlorinated biphenyls |
| PCE | tetrachlorethylene *or* perchloroethylene |
| PCP | pentachlorophenol |

**List of Acronyms (cont.)**

| | |
|---|---|
| PID | photoionization detector |
| PITT | partitioning interwell tracer test |
| ppm | parts per million |
| PVC | polyvinyl chloride |
| RNS | Ribbon NAPL Sampler |
| ROI | radius of influence |
| ROST | Rapid Optical Screening Tool |
| SCAPS | Site Characterization and Analysis Penetrometer System |
| SEAR | Surfactant-Enhanced Aquifer Remediation |
| SPH | Six-Phase Heating |
| SRS | source removal system |
| SSLs | soil screening levels |
| SVE | soil vapor extraction |
| TCA | trichloroethane |
| TCE | trichloroethylene or trichloroethylene |
| TOC | total organic carbon |
| TPH | total petroleum hydrocarbon |
| VIP | vertical induction profiling |
| VOA | volatile organic compound |
| VOA | volatile organic analysis or analyte |

# APPENDIX B

## Innovative DNAPL Characterization and Monitoring Tools Matrix

# Appendix B. Innovative DNAPL Characterization and Monitoring Tools Matrix

| Technology | Capabilities and Limitations | Data Quality | Data Usage |
|---|---|---|---|
| **Geophysical Techniques** | | | |
| Ground Penetrating Radar (GPR) | -Subsurface geologic features can be identified.<br>-May determine most likely flow path of DNAPL.<br>-Results can produce two-dimensional vertical profile.<br>-Ability to accurately detect DNAPL unproven.<br>-Inability to produce direct readings or measurements.<br>-Highly dependent on soil moisture and soil type. | -Highly qualitative and requires a high degree of subjective interpretation. -Should be calibrated with a core sample. | -Define subsurface features.<br><br>-Locate preferred DNAPL pathways (underground utilities).<br><br>-Map shallow hydrogeologic interfaces. |
| Cross-Well Radar | -GPR principle applied down-hole.<br>-Effective in saturated zone.<br>-Can be applied down existing monitor wells.<br>-Mostly limited to identifying plume sources.<br>-Distance between monitor wells controls effectiveness. | -Gross characterization technology that requires lab sample confirmation. | -Characterize high concentration of DNAPL.<br><br>-Data should be used in conjunction with dielectric logging and ground "truthing" |
| Electrical Resistance Tomography | -Measures electrical resistivity between boreholes or surface to borehole.<br>-Based on resistively contrast between soil/ groundwater contamination and indigenous material.<br>-Dependent on soil type, degree of saturation, geology.<br>-Results can produce 3-dimensional geologic profile.<br>-Possible interference from steel monitor wells, pipelines or underground utilities. | -Highly qualitative and requires a high degree of subjective interpretation. -Should be calibrated with a core sample. | -Characterize high concentration of DNAPL.<br><br>-Map shallow hydrogeologic interfaces.<br><br>- Is good at detecting change therefore can be used to visualize dynamic remediation activities such as steam. |
| Vertical Inductive Profiling | -Surface to borehole configuration can measure the resistivity contrast between DNAPL and groundwater.<br>-Can produce 3-dimensional profile of lateral and vertical configuration of contamination.<br><br>-Effective in PVC cased or open holes only. | -Highly qualitative and requires a high degree of subjective interpretation. Should be calibrated with a core sample. | -Characterize high concentration of DNAPL .<br><br>-Map shallow hydrogeologic interfaces. |

# Appendix B. Innovative DNAPL Characterization and Monitoring Tools Matrix

| Technology | Capabilities and Limitations | Data Quality | Data Usage |
|---|---|---|---|
| High Resolution 3-D Seismic Reflection | Produces acoustical waves that detect subsurface density changes.<br>Not specific for DNAPL detection.<br>Resolution will be affected by geologic and anthropogenic features | -Requires background information on-site conditions for proper interpretation of data. | -Provides 3-dimensional map of subsurface features.<br>-Define subsurface anomalies and boundaries. |
| High Resolution Electromagnetic Resistivity Survey | -Surface to borehole configuration.<br>-Produce surveys capable of identifying high resistivity anomalies representative of DNAPL.<br>-Tunable transmitter and receiver can overcome deployment barriers and electrical noise. | -Gross characterization technology that requires lab sample confirmation. | -Detection of fractures and channels that serve as preferred DNAPL pathways. |
| Very Low Frequency (VLF) | -Can provide indications of bedrock fracture strike, dip, and depth.<br>-Is affected by anthropogenic activities such as power lines.<br>-May be dependent upon other sources of VLF radio waves to work unless investigator has own radio source. | -Can provide detailed information on fracture strike, dip, and depth. | -Detection of fractures and channels that serve as preferred DNAPL pathways. |
| **Intrusive Site Characterization Techniques** | | | |
| Cone Penetrometer (CPT) coupled with laser induced fluorescence | - Useful when deployed with sampling devices and sensors.<br>-Can provide continuous real-time data on soil stratigraphy and contaminant distribution.<br>-Relatively quick, cost effective, minimally invasive.<br>-Limited by surface features and extreme subsurface. conditions (bedrock, boulders, and saturated fine sands).<br>-Laser fluorescence cannot specifically detect chlorinated DNAPL.<br>-Use of CPT is limited to unconsolidated materials that the CPT can penetrate. | -Qualitative screening of the presence of NAPLs.<br>-Typically requires calibration with geologic bore hole data for accurate interpretation of stratigraphy. | -Delineation of stratigraphy and identification of potential preferential pathways.<br>-Delineation of gross contamination and NAPL. |

# Appendix B. Innovative DNAPL Characterization and Monitoring Tools Matrix

| Technology | Capabilities and Limitations | Data Quality | Data Usage |
|---|---|---|---|
| Cone Penetrometer (CPT) coupled with Hydrosparge | - A small port in near the tip allows groundwater to enter the penetrometer where helium gas is used to sparge volatiles from the groundwater these gases are analyzed on the surface ion trap mass. Spec or GC mass spec.<br>- Is only useful with volatile contaminants.<br>- Has limitations of cone penetrometer described above.<br>-Use of CPT is limited to unconsolidated materials that the CPT can penetrate. | -Quantitative analysis of chemicals dissolved in groundwater.<br>-Typically requires calibration with geologic bore hole data for accurate interpretation of stratigraphy.<br>- Can have very low detection limits. | -Delineation of stratigraphy and identification of potential preferential pathways.<br>- Delineation of contamination in groundwater. |
| Direct Push Membrane Interface Probe | Can provide continuous real-time data on contaminant distribution.<br> Can be coupled with CPT to compare stratigraphy to contaminant distribution.<br>Cannot detect contaminants at low concentrations (<100-200 ppb).<br>Limited by surface features and subsurface conditions (bedrock, boulders, and clays).<br>-Strong tool for DNAPL source characterization when coupled with on-site, near real-time analytical method in a dynamic work plan investigation. | Qualitative to quantitative screening of contamination. | Delineation of gross contamination, source identification. |
| Direct Push Discrete Interval Groundwater Sampling | Can provide continuous real-time data on contaminant distribution.<br><br>Limited by surface features and subsurface conditions (bedrock, boulders, and tight clays).<br><br>Strong tool for DNAPL source characterization when coupled with on-site, near real-time analytical method in a dynamic work plan investigation. | Quantitative screening of contamination. | Delineation of contamination and DNAPL, source identification. |

# Appendix B. Innovative DNAPL Characterization and Monitoring Tools Matrix

| Technology | Capabilities and Limitations | Data Quality | Data Usage |
|---|---|---|---|
| **Other DNAPL Site Characterization Techniques** | | | |
| Ribbon NAPL Sampler | -Continuous direct sampling device applied down boreholes.<br>-Provides detailed depth discrete mapping of NAPLs.<br>-Sampling membrane must be in contact with NAPL.<br>-Effective for pure phase hydrophobic contaminants only. | -Colorimetric qualitative screening. | -Positive/ negative indicator for the presence of NAPL. The stained area can be preserved for chemical speciation. |
| Partitioning Interwell Tracer Test | -Injection and monitoring of tracers in contaminant zone used to measure the volume of DNAPL.<br>-Based on large-scale application of chromatography.<br>-Injection of tracers may have regulatory implications.<br>-Not appropriate for quantifying free phase DNAPL.<br>-May be less effective in silts and clays and interbedded matrices. | -Quantitative for residual DNAPL in the targeted zone. | -Quantify and locate residual DNAPL contamination.<br>-Allows detailed planning for remediation. |
| UV Fluorescence | - Can show the presence of NAPL in soil samples.<br>-Is limited to certain classes of chemicals.<br>-May not be able to show the presence of small amounts of NAPL in soil. | -Qualitative. | -Positive/Negative indicator for the presence of NAPL. May give false negative depending on the amount of NAPL in the soil. |
| Sudan IV Dye | -Can show the presence of NAPL in soil samples.<br>- May not be able to show the presence of small amounts of NAPL in soil. | -Qualitative. | -Positive/Negative indicator for the presence of NAPL. May give false negative depending on the amount of NAPL in the soil. |

# APPENDIX C

# Case Studies

**Case Study I. Site Investigation of a DNAPL Site Using a Flexible Work Plan, Alternative Analytical Methods, and Discrete Interval Groundwater Sampling Techniques**

**Setting**

The site is a small industrial park located in Williston, VT. Most of the historical use of the Industrial Park has been commercial, with only two buildings known to ever contain manufacturing (Figure C-1). The site is bounded to the north, west and southwest by residential development. The land to the south, east and southeast was open fields and a wetland area in the 1980s and early 1990s. This area is presently rapidly developing as a commercial center with warehouses, a car dealer, and other commercial development. There is a small un-named stream located on the eastern side of the Industrial Park. This is the eastern boundary of the Industrial Park. The stream flows south, south-west, ultimately discharging into Muddy Brook which in turn discharges into the Winooski River.

**Geology**

The unconsolidated materials at this site are silty fine sand underlain by silt which is underlain by a laterally continuous layer of clay at an approximate depth of 40 feet below ground surface. The clay is approximately 20 feet thick, and is underlain by a dense glacial till that is found from approximately 60 to 100 feet below ground surface. The till is underlain by metamorphic carbonate bedrock.

**Hydrogeology**

There are several stratigraphic layers in which groundwater is found at this site. There is an upper, unconfined or "water table" aquifer found in the surficial unconsolidated silty fine sand and silt deposits (0 to 40 feet below land surface). This is a productive aquifer and has been utilized for domestic water supplies in the past. The water table aquifer is the contaminated aquifer at this site. The water table surface is generally found between 4 and 10 feet below land surface depending on where it is measured and the time of year. The vertical gradients are generally nearly flat to slightly downwards. Adjacent to the stream at the eastern edge of the Park, gradients in the water table aquifer are slightly upwards where the groundwater discharges into the stream.

The clay below the silt and sand aquifer is saturated but of such low hydraulic conductivity that it can be considered an aquiclude. Therefore, it is unlikely that the lower glacial till is in hydraulic contact with the upper unconsolidated water table aquifer. Below the till is the Bedrock aquifer. This is also likely not in hydraulic contact with the water table aquifer. The bedrock aquifer has an upwards gradient within the Industrial Park. One well drilled into the bedrock flows slightly.

The general regional groundwater flow direction in the upper unconsolidated aquifer is to the south-west. In the Industrial Park however, there is a groundwater flow divide with some of the groundwater flowing southwest and some flowing east-southeast to the un-named stream on the eastern boundary of the Industrial Park. This stream acts as a groundwater discharge zone. The groundwater flow divide is located between the Industrial Park and the residential development

directly west of the Industrial Park. The groundwater flow pattern is reflected in contaminant plume geometry.
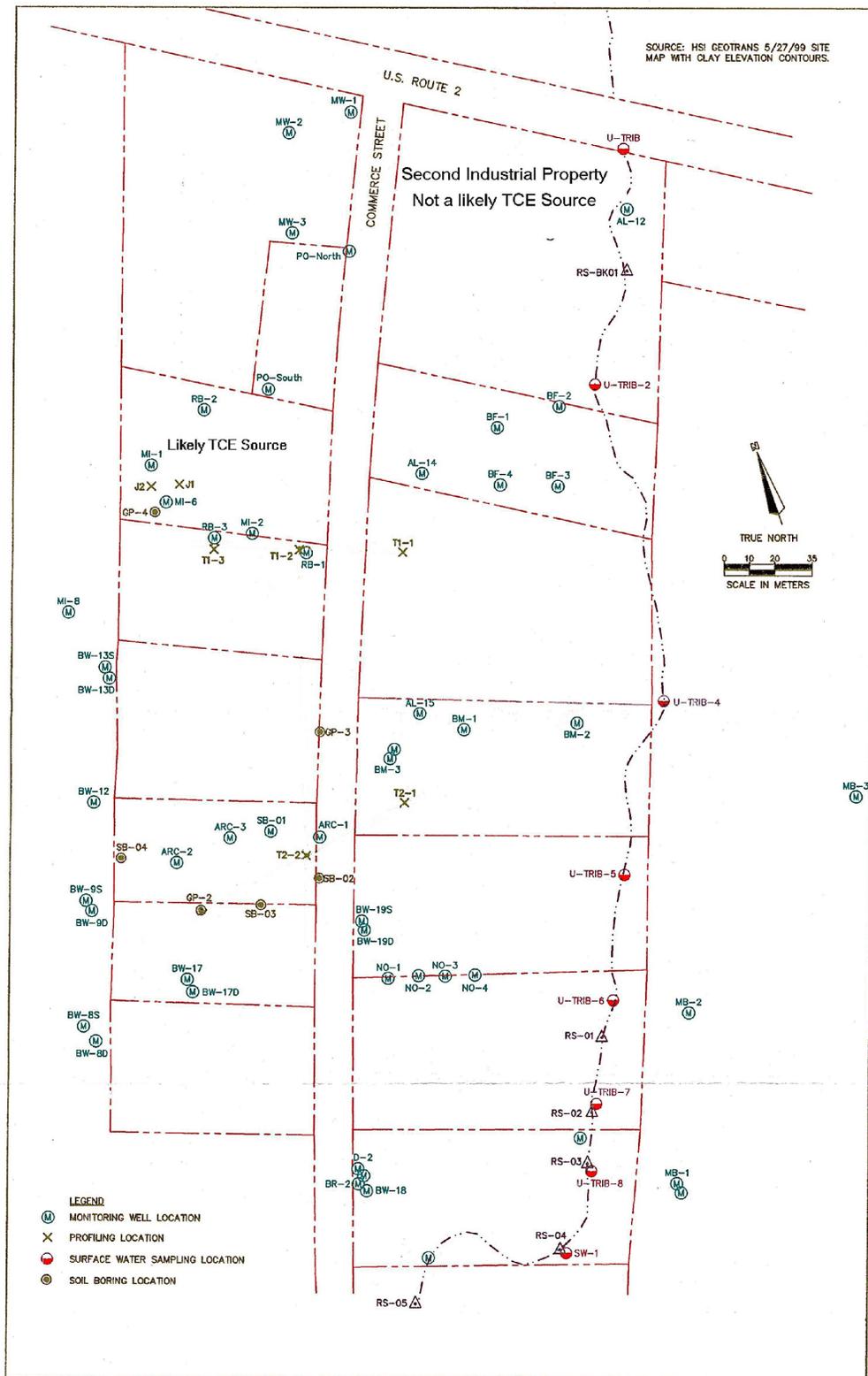
**Figure C-1. Site map.**

**Contaminants**

The groundwater at the site is contaminated with cadmium, chromium, and trichloroethylene (TCE). The metals contamination, while above groundwater enforcement standards, is minimal and confined to a small area of the site. TCE contamination however, is wide spread and likely includes significant quantities of residual phase DNAPL and possible small pools and lenses of potentially mobile DNAPL. The investigations detailed in this case study focused on the TCE contamination.

**Site Investigations**

In 1995, an environmental consultant conducting an investigation for a real estate transaction in the Industrial Park discovered TCE in groundwater at concentrations indicating possible DNAPL contamination. In late 1995, the State of Vermont determined that it was necessary to identify the source of the contamination, to estimate the degree and extent of the contamination, and to determine if the contamination posed any threat to human health and the environment. In order to accomplish these goals, it was determined that a site investigation was necessary. The State of Vermont had only limited funds available for the investigation.

**Flexible Work Plan**

Due to its limited funds, and the need to quickly answer questions as to the source of the contamination, its degree and extent, and whether or not it posed a threat to human health or the environment, the state decided to try a flexible work plan. The state was concerned that if it followed the standard investigation practice of a "concrete" work plan that did not allow flexibility in the investigation, that it could spend significant money on various investigation phases. The state wanted to avoid multiple investigation phases and answer the questions regarding the source of the contamination and possible threats to human health and the environment as soon as possible.

In order to conduct the site investigation at this site using a flexible work plan, the state had a hydrogeologist on site during the site investigation to direct all work and make immediate decisions. The state hired a contractor to collect exploratory groundwater and soil samples using a Geoprobe™. In addition, under the supervision of the state hydrogeologist, the contractor sampled soil gas, sampled the stream adjacent to the Industrial Park, sampled indoor air in the residential development located directly west and southwest of the Industrial Park, and installed three permanent 40 ft deep (+/-) monitoring wells. The work plan was flexible to allow determination of drilling locations to be made in the field based on sampling results. In order to accomplish this, it was necessary to review soil and groundwater quality data in "real time" in the field.

**Alternative Analytical Methods**

In developing the strategy for the investigation, the state determined that the reported concentrations of TCE in the groundwater were high enough to cause concerns about the possible presence of Dense Non Aqueous Phase Liquid (DNAPL). The state realized that it might need to take and analyze many samples in order to investigate potential DNAPL. The state also needed to be able to review the analytical results in "real time" as much as possible in order to be able to pick drilling locations in the field.

Standard laboratory analytical techniques are too slow to allow real-time review of data. Photo Ionization Detectors could not provide the numerical accuracy necessary to make informed decision as to contaminant concentrations. While field gas chromatographs (GCs) are commonly used to analyze data in the field, at this site, site specific testing indicated they were not always very accurate in analyzing soil samples for chlorinated solvents. Therefore, the state needed an alternative method of analyzing soil and groundwater samples that would provide accurate data in a reasonable time. The state talked to a local laboratory to see if they had any available alternatives. They offered to analyze the soil and groundwater samples using a laboratory screening method using an HP 767 ™ GC with a flame ionization detector. This Lab screens all samples with this method with a heated head-space analysis prior to running them on the standard laboratory GC/MS. Using this equipment, the laboratory could provide the same detection limits and nearly the same accuracy as with analyzing the soils by EPA Method 8010, for $50.00 versus $80.00 for EPA Method 8010, and provide analytical results within 5 hours of receipt of samples, versus the typical two weeks turn for chlorinated solvent analysis.

**Results of the 1995 Investigation Using a Flexible Work Plan and Alternative Analytical Techniques**

During the investigation the state received accurate soil analytical results in less than one day of taking the samples. This allowed change to the investigation work plan while in the field. The changes in direction of the investigation allowed by the quick but accurate analytical results allowed meeting investigation goals without multiple drilling phases. The investigation was a success. The state collected enough data to determine:

1) the most likely source of the contamination and a Potentially Responsible Party (PRP);
2) the general distribution of the TCE plume;
3) that TCE could be found in surface water as high as 1,100 $\mu$g/l;
4) how far TCE was distributed in surface water;
5) that DNAPL is likely present at the site;
6) which houses could be affected by the plume and needed indoor air quality tests, and
7) that TCE was present in the indoor air in one house at concentrations exceeding health based risk levels, and test sump water, soil gas and soils around this house, allowing the development of a remedial plan for the house.

The investigation also demonstrated that there were no readily apparent risks to human health or the environment other than the indoor air problems. (The indoor air testing locations were determined by the contaminant data collected during the investigation.) The cost of the investigation was less than $50,000.

**1999 State and PRP Investigations**

The work conducted in 1995 allowed the state to identify the likely source of the contamination and a potentially responsible party (PRP). After several years of negotiations, the PRP agreed to conduct a large scale site investigation and feasibility study of remedial alternatives under state oversight. The state, the PRP, and their consultant were interested in using a flexible work plan and innovative investigation techniques during the investigation. Also, the likely presence of DNAPL at the site

indicated that standard investigation techniques should not necessarily be followed. The goals of this investigation were to map out the plume distribution, determine possible DNAPL distribution, determine contaminant fate and transport, conduct a formal risk assessment, further define the source of the contamination, and collect enough data to allow a feasibility study to be conducted without multiple phases of intrusive investigations.

**Geophysical**

Prior to conducting any intrusive investigatory work, the PRP contracted a geophysical firm to complete an extensive seismic survey over much of the industrial park during the spring of 1999. The purpose of this survey was to delineate the surface of the clay layer. The results of the seismic survey provided a detailed map off the elevation of the clay surface indicated several depressions that could act as traps for DNAPL.

**Groundwater/Surface Water Interface Diffusion Sampling**

In the 1995 investigation, the state measured TCE in the unnamed stream that borders the eastern side of the Industrial Park. Concentrations as high as 1100 µg/l were seen in surface water. TCE was present in the surface water at 9 µg/l almost two miles downstream from the Industrial Park. The PRP's contractor conducted surface water sampling in December 1997 that confirmed these results. The state and the PRP determined that it would be necessary to determine where the contaminated groundwater flowed into the stream and whether or not the stream sediments create a pathway that allowed contaminated groundwater to flow below the stream in the sediments. Instead of drilling wells along the side of the stream, or installing piezometers in the stream bed, the PRP and the state used passive diffusion sampling techniques to determine water quality in the sediments below the stream and use this as an indication of groundwater quality and the flux into the stream.

Diffusion samplers have been studied at length by the U.S. Geological Survey (Vroblesky, Lorah, and Trimble, 1991; Vroblesky, Rhodes, and Robertson, 1996a; Vroblesky and Robertson 1996b). Diffusion samplers have been filled with inert gas or a sorbent such as carbon, and with deionized water (Vroblesky and Hyde, 1997 and personal communications between the PRP's consultant and Don Vroblesky in 1998). Passive diffusion samplers as used in this application are essentially 40 ml VOA vials filled with deionized water and covered with a VOC permeable membrane ("plastic wrap") instead of the vial cap. As described by Vroblesky and Hyde (1997) and Vroblesky, Rhodes, and Robertson (1996a) and Vroblesky and Robertson (1996b), these sampling devices allow the diffusion of contaminants from groundwater across a VOC permeable membrane into a sample container.

The diffusion samplers were buried approximately six inches below the streambed at various locations along the stream. These were left in place three weeks. As the passive diffusion samplers sat buried in the streambed, groundwater flowed past the samplers as it discharged in to the stream. Where VOCs were present in the groundwater, they diffused through the plastic into the deionized water until a concentration equilibrium was reached across the plastic membrane. When the samplers were collected, the vials were sealed with a standard VOA vial cap placed over the plastic membrane. The vials were sent to a laboratory to be analyzed for VOCs by standard laboratory methods.

The analytical results from the streambed diffusion samplers worked well to delineate where contaminated groundwater was discharging into the stream. As this work was conducted early in the investigation process, it helped clarify where to drill wells to determine the extent of the plume. It did show that the groundwater was not traveling below the stream for any significant length and allowed the investigators to rule out drilling in certain areas. The data were confirmed with wells during the investigation.

**Groundwater Quality Profiling**

The 1995 state investigation discovered that there was very little organic carbon in the soils and consequently, soil samples could not help significantly in determining contaminant distribution. Some soil boring work was needed to determine stratigraphy, but gathering data on groundwater quality and hydraulic conditions was more important. Instead of drilling many wells at varying depths, the investigation looked for a method to profile groundwater and hydraulic data other than by standard soil boring and monitoring well installation techniques. The PRP's consultant and the state choose "discrete interval sampling" as an accurate and quick method for collecting significant quantities of groundwater quality data to determine contaminant degree and extent and to help identify the locations where permanent monitoring wells were needed.

A field GC was used to provide "real-time" analytical data in the field. The laboratory screening method used in the 1995 investigation was used to check the field GC work and did note when there were problems with the field GC. As the laboratory was able to provide near real-time data confirmation, the PRP's consultant was able to correct the field GC problems quickly enough that duplicate samples could be analyzed concurrent with that phase of the investigation and the problems corrected without losing valuable field time. Confirmatory laboratory analysis with EPA Method 8260 was conducted on about ten percent of the samples.

Discrete interval groundwater sampling is a methodology where a collection device is pushed or driven into the subsurface and groundwater samples are taken at specific, discrete intervals. The discrete sampling interval can be very small (as little as ¼ inch) or much larger depending upon the equipment used. The results provide a vertical profile of groundwater quality.

Advantages of this investigation method include that the method provides large amounts of data in a short time frame at generally much lower costs than gathering these data by drilling a monitoring well to each depth sampled; and that the method will allow vertical profiling of groundwater quality at whatever resolution is needed to characterize the site conditions. This vertical profiling is an advantage at a DNAPL site where the DNAPL can travel following very small preferential pathways. The discrete interval sampling can potentially indicate the locations of these pathways. With standard drilling techniques at DNAPL sites, there can be significant concerns that drilling can create a migration pathway for DNAPLs to sink deeper into the subsurface. With the discrete interval sampling however, this is much less of a concern. The sampler is only in the ground for a short period of time and the hole can be pressure grouted as the sampler is removed, lessening concern about possible downwards migration of DNAPL. Groundwater samples taken with a small discrete interval sampler avoid the problem with dilution that is seen when a longer well screen is installed where the contamination is only in a thin portion of the aquifer.

Once the data are collected with a discrete interval sampling device, the investigator can determine where to install permanent monitoring wells and at what depths well screens should be placed. This type of investigation will help avoid the issue common at many sites where monitoring wells are drilled that will not provide the necessary groundwater quality data.

The discrete interval groundwater sampling was conducted at this site by two different methodologies. Most of this groundwater sampling was done by a PRP subcontractor with a small hand built drill rig. This was an all terrain six wheeled vehicle that had a small mast mounted on the back. Using the mast, the contractor could drive $^{7}/_{8}$" o.d. steel water pipe. The pipe was in ten foot sections. The lower five feet of the pipe had a five foot section that had vertical .015" laser slots with a pointed stainless steel drive point at the end of the pipe. This was driven into the ground by an electric percussion hammer. Groundwater samples were taken with a peristaltic pump every five feet as the pipe was driven into the ground. In order to drive the pipe deeper, new sections of un-slotted pipe were connected by steel collars hydraulically clamped around each pipe. Each groundwater sample taken sampled groundwater from a five foot section of the aquifer due to the length of the slots on the driven pipe. With shorter slots, a thinner portion of the aquifer could be sampled. The sampling device was known as Checkwells™.

The discrete interval sampling results provided a detailed characterization of the groundwater quality over a large area. The PRP's contractor working with one driller and one or two field geologists to oversee the work and operate the field GC, conducted discrete interval sampling at 32 locations with over 170 discrete groundwater samples collected in less than three months during the summer of 1999. While the discrete interval samples can be considered "grab" samples, and do not allow measurement of water quality over time, these are essentially equivalent to drilling over 170 conventional monitoring wells and taking one sample from each well. Please note that during this time period, the contractor using the same field staff was also conducting other work such as installing permanent monitoring wells and investigating surface water quality.

Using field GC, we received analytical groundwater quality data almost concurrent to the collection of the groundwater quality samples. These data allowed the state and the PRP to adjust the work plan as the investigation progressed, planning new sampling locations based on the recently collected water samples, and collecting groundwater samples and installing monitoring wells where the data showed they were needed.

Due to the length of the groundwater sample interval in the PRP discrete interval sampling (5 feet) any concentration above 1% of solubility was assumed to indicate DNAPL. A smaller sample interval might use a higher percentage of solubility to determine the presence of DNAPL because there would be less dilution from a small lense into the screened interval.

The second discrete interval sampling technique used on site was conducted by two contractors to the state who both used a Waterloo Profiler™ sampling device. The Waterloo Profiler™ sampler (Figure C-2) has a stainless steel drive point installed into a short section of stainless steel pipe with a number of approximately $^{1}/_{4}$" diameter, screened holes (sampling ports) circling the sampler and connected inside the drill pipe to $^{1}/_{8}$" diameter stainless steel or polyethylene tubing. (The sampling ports can be located horizontally around the pipe such that the sampler samples groundwater from only a $^{1}/_{4}$" interval of the aquifer, or can be also stacked vertically such that the sampler samples

groundwater from a thicker interval of the aquifer.) The drill pipe is driven into the ground and groundwater samples are collected from the sample ports at the desired depths by a peristaltic pump attached to the tubing. The state conducted transects with 1.5 feet between the sampling locations. The sampling ports sampled are spaced horizontally around the sampling tip and collected groundwater from a $1/4$" interval of the aquifer. The state conducted the discrete interval sampling directly downgradient of two potential source areas and in one suspected "hot" zone. The purpose of this sampling was to test the 1995 determination of the source area and to determine if there was DNAPL present in preferential pathways.
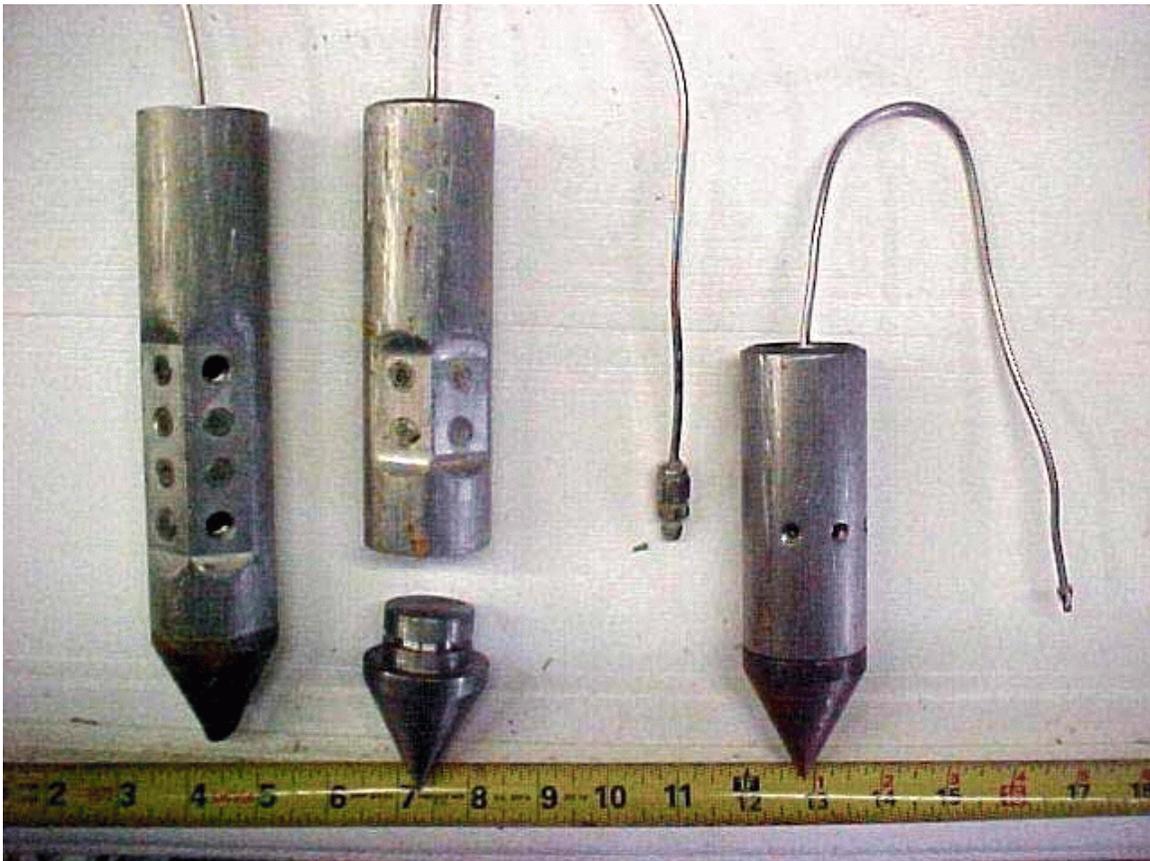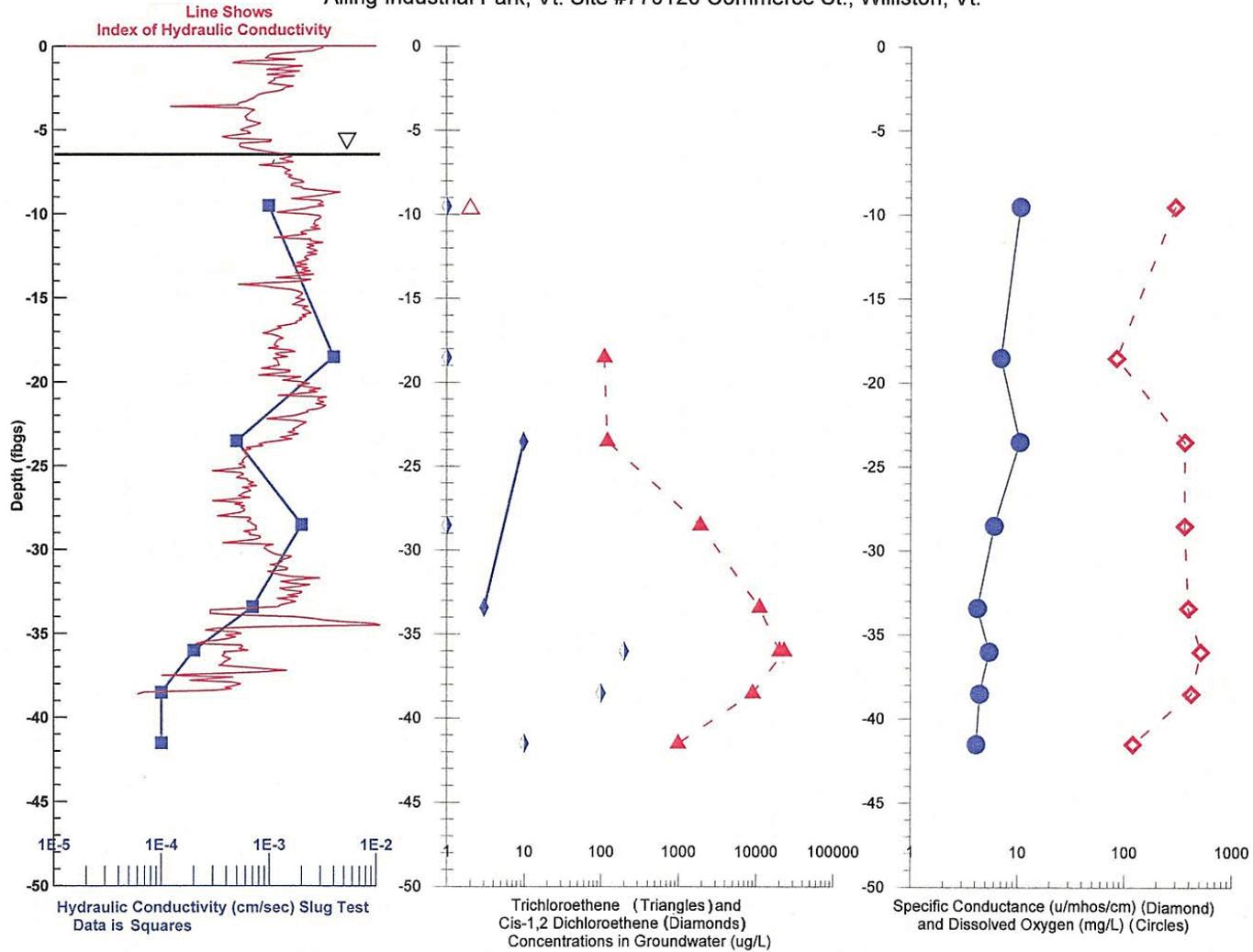


**Figure C-2. Waterloo Profiler™ tip configurations.**
(Source: The Johnson Company Inc., Montpelier, VT)

One contractor used a profiling sampler configuration they had developed with which they could determine a measure of relative hydraulic conductivity of the formation as the sampler drove through the ground. They do this by pumping deionized water through the tubing into the ground as the profiler tip is advanced and measuring how much water the aquifer accepts compared to time. How much water the aquifer is able to accept is dependent upon the hydraulic conductivity of the aquifer. Therefore, by tracking how much water they pump over time compared to the drilling rate, they are develop a graph that shows the relative hydraulic conductivity of the aquifer. They were also able to conduct a slug type test at sampling locations. When graphed compared to the analytical results, these data helped show possible transport pathways (Figures C-3a and C-3b). This contractor could also determine hydraulic head at each sampling point.

Profile Point T2-1

Alling Industrial Park, Vt. Site #770120 Commerce St., Williston, Vt.
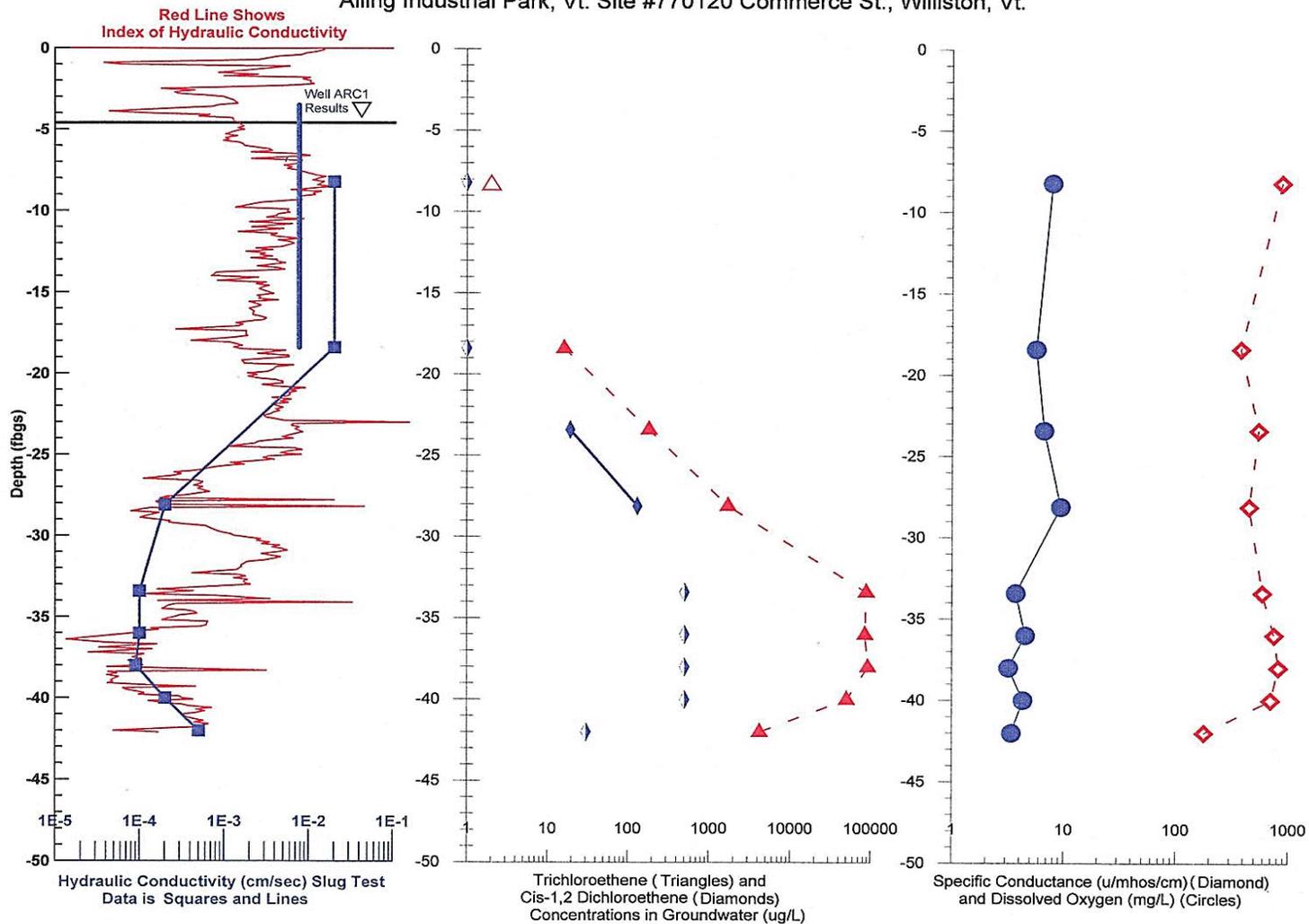
The Johnson Company, Inc. for Vermont DEC Sites Management Section, June 11, 1999 1-2290-1 kchem99.gr1

**Figure C-3a. Profile Point T2-1.**

## Profile Point T2-2
### Alling Industrial Park, Vt. Site #770120 Commerce St., Williston, Vt.

Figure C-3b. Profile Point T2-2.

The work conducted by the state's contractors took slightly longer than seven days total time and provided over 100 groundwater samples taken at 1.5 foot intervals with the Waterloo Profiler ™. At five of the total seven sampling locations, the contractor used the process whereby a hydraulic conductivity was estimated at each sampling location and a relative hydraulic conductivity for the formation generated while driving the sampler (See Figures C-3a and C-3b). The results of this work showed the distribution of the contaminants relative to the stratigraphy as identified by the relative hydraulic conductivity. The data indicated that the release of the TCE was old since the bulk of the contaminant appears to have diffused into the silty material located directly below the silty sand similar to the diffusion of immiscible phase liquid into fractured media as described by Parker et al., 1994. This has significance in determination of remedial strategies. The discrete interval sampling conducted by this contractor cost the state approximately $16,600.

The other two discrete interval locations were drilled in the summer of 2000 in response to a disagreement as to the potential that there was as second source of TCE on the another property in the Industrial Park. This discrete interval sampling conducted with the Waterloo Profiler™ at these locations clearly shows a lack of significant contamination on this other property or directly downgradient of it. When compared to what was already known about the site, these two profiles clearly show that this property is not likely a source of TCE contamination. This work cost the state less than $4,600.

While not temporal in nature, the discrete interval groundwater quality data clearly pointed to the source of the contamination and outlined the extent of the contamination. Monitoring wells were installed based on the discrete interval groundwater quality data. These wells are located such that the well screens intersect the contaminated area of the aquifer and will be useful in tracking long-term contaminant trends. The discrete interval sampling data also precluded the need to collect soil samples while drilling the monitoring wells. Therefore, the wells were installed quickly saving significant time and money.

Geology will limit the use of the discrete interval sampling process. It cannot be conducted in rock or heterogeneous soils such as till that contain many rocks that will cause refusal to the drive points. As the sampling is dependent upon the use of a peristaltic pump, this technique will not work where groundwater head is too deep. Head has to be above approximately 20 feet in order for the suction pump to be able to lift the groundwater.

**Outcome of Investigations**

The investigations conducted by the State of Vermont and by the PRP with state oversight successfully investigated a potential DNAPL site at relatively low cost and in a short time frame.

The state's 1995 investigation using a flexible work plan, quickly clarified the likely source of the contamination, allowed the state to determine where the contamination posed a risk to human health and where the contamination did not pose a risk to human health, and allowed the state to put its resources to work in response to the actual risk. This investigation also established that there is a large contaminant plume with high concentrations of contaminants. The investigation allowed the state to identify a PRP and the results helped in obtaining cooperation from the PRP. The use of a

flexible work plan and alternative analytical methods allowed the state to meet the investigation goals in a short time for a relatively small amount of money.

The 1999 PRP/state investigation was also successful. This investigation allowed the state to develop a detailed understanding of the contaminant plume, the concentration distribution of TCE, the extent of the plume, and provided enough data to allow a formal feasibility study and a formal risk assessment to be conducted. The investigation confirmed the likely presence of DNAPL and discovered dissolved phase concentrations of TCE as high as 90,000 µg/l in groundwater. The investigation confirmed the source of the contamination and the discrete interval sampling results coupled with the seismic data allowed for extremely detailed cross sections of contaminant distribution.

It is important to note that while no actual DNAPL was discovered in the investigations, the weight of evidence from the investigations clearly indicate that DNAPL is present at this site. No DNAPL will be easily recoverable at this site, but the data collected and the behavior of the contaminants indicates DNAPL. The full body of evidence collected during the site investigation phases must be viewed as a whole in deciding whether or not DNAPL is present. The techniques used to investigate this site are an example of what can be used to collect the data needed to make this determination.

Where the state and the PRP disagreed in regard to potential alternate sources for the TCE contamination, the state used the discrete interval sampling to again confirm that the second industrial property in the industrial park was not a likely source of the TCE contamination.

| Comparison of Discrete Interval Sampling Techniques | | |
|---|---|---|
| | Waterloo Profiler™ | Slotted Iron Water Pipe |
| Sample Interval | 0.25 inch | 5 foot (could have been smaller) |
| Sampling Technique | Peristaltic Pump | Peristaltic Pump |
| Automatic Hydraulic Conductivity Testing | Yes (one contractor) | No |
| Automatic Head Measurements | Yes (one contractor) | No |
| Identified preferential pathways | Yes | Partially |
| Allowed a "real-time" comparison of groundwater quality to apparent stratigraphy | Yes | No |

In less than three months working time, the contractor's discrete interval sampling system collected over 170 groundwater samples located in different locations, both horizontally and vertically, without the expense of 170 monitoring wells. The system used by the state, collected over 100 groundwater samples in approximately a week of field work. The state's contractor also provided a detailed study of the relative hydraulic conductivity in each hole drilled. This allowed an analysis of the contaminant distribution.

**Conclusions**

While most of the "alternative" investigation techniques are not extremely new or radical techniques, they served very well to expedite, lower the cost of, and increase the accuracy of the investigations conducted at this site. The discrete interval sampling increased the accuracy and lowered the cost of exploratory drilling allowing us to avoid installing many monitoring wells that could potentially provide no help in characterizing the degree and extent of the contamination. The discrete interval sampling pin-pointed the subsurface source areas where it is likely DNAPL migrated to and helped refine the Conceptual Model of the contaminant distribution. The discrete interval sampling indicated that DNAPLs had migrated through the silty sand unit, leaving behind likely residual phase DNAPL. The data collected coupled with the seismic interpretation of the site also indicated that the DNAPL came to rest on top of the silt units in certain stratigraphic lows. Once the DNAPL rested on these low areas, it apparently diffused into the silt unit.

The use of flexible and dynamic work plans incorporating real-time data allowed more accurate siting of sampling locations and allowed us to save money and time by helping to avoid the need to conduct multiple investigation phases. The diffusion samplers placed in the stream bed allowed a more accurate delineation of where contaminated groundwater discharges in to the surface water than could be accomplished by standard drilling techniques at a low cost. This also helped guide the drilling portion of the investigation at this site and helped the state and PRPs avoid drilling unneeded monitoring wells.

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## Case Study II. DNAPL Site Investigation Study Using a Flexible Work Plan, On-Site Laboratory, and Sudan IV Dye

### Setting

The facility is a New Jersey manufacturer of textile products in operation since 1972. The site comprises approximately 4 acres in a commercial/ industrial area located in the northern part of the state. Historically, the manufacturing operation of textile products included on-site dry cleaning using tetrachloroethylene (PCE). Virgin PCE was stored on site in a 2,000-gallon tank, while spent PCE was recycled on site through a distillation process. Wastewater was discharged to a local stream until 1979. After 1979, wastewater discharge was diverted to a concrete pit located inside the building. A stream lies immediately west of the site. A municipal water supply well is located approximately 500 feet down-gradient of the site. This supply well is contaminated with chlorinated volatile organics, including PCE. Chlorinated hydrocarbons were found in groundwater at the site by NJDEP during 1994 and 1996 site assessments. The facility entered into an Administrative Consent Order (ACO) with New Jersey Department of Environmental Protection (NJDEP) in May 2000.

### Geology

The local area was formerly occupied by Ancient Lake Passaic. The overburden consists of 40 to 50 feet of glacial deposits including lacustrine sediments (fine sand, silt clay), overlying glacial outwash (coarse sand, gravel and cobbles). The bedrock (lower Jurassic age basalt) is at approximately 50 feet below ground surface (bgs).

### Hydrogeology

Two water-bearing zones are evident in the overburden. The Shallow zone (water table at approximately 5 feet bgs) is comprised of fine sand deposits. The deeper zone lies within coarser deposits immediately above bedrock. The two water-bearing zones are separated by 12-18 feet of clay (potential confining unit). Groundwater flow direction is to the west, towards an adjacent surface water body.

### Conceptual Plan

The goal of the project was to complete the delineation in an accelerated fashion while satisfying the following objectives:

- Meet regulatory requirements of N.J.A.C. 7:26E-4, Technical Requirements for Site Remediation
- Delineate product in unsaturated and saturated zone
- Delineate contaminated soil
- Delineate dissolved phase plume
- Evaluate migration pathways
- Obtain sufficient data to implement remedial alternatives

**Method of Investigation**

Conducted in two phases. The initial phase was intended to provide conventional background information, (stratigraphy, and groundwater flow). The fieldwork included the installation of 6 shallow monitor wells, two deep overburden wells and 24 soil borings.

The second phase of the investigation was performed utilizing a flexible work plan concept. The main objective was to determine the extent of product, delineate contaminated groundwater and find the clean zone. The field effort incorporated the following:

- On-site mobile laboratory
- Geoprobe™ drill rig, PID, Sudan IV dye
- 34 soil borings and 56 groundwater samples
- Several groundwater samples from multiple depths

**Flexible Work plan**

The field equipped mobile laboratory was stationed and operated on site for 13 days. Soil samples were collected using a Geoprobe™ with a continuous macro-core for logging soils. Groundwater samples were collected using a Geoprobe™ drive point with a 2-foot screen. Field screening methods, including a PID and Sudan IV dye were used for product identification. The laboratory analyzed approximately 10-15 samples a day, using a GC/MS with a capability of running up to 20 VOC analysis per day. When sample results indicated that a clean zone was reached, confirmatory soil samples were collected and sent for off-site laboratory analysis. The mobile lab allowed rapid turnaround time for aqueous samples, with results available in a matter of hours. The same day analytical results allowed for "real-time" decision making resulting in an expedited delineation and reduced mobilization costs.

**Results of Investigation**

Product (namely chlorinated volatile organics) was identified in 10 borings and one monitoring well, out of a total of 104 borings and 10 wells. The product was typically found sitting on top of the clay-confining unit. Horizontal delineation of contamination was achieved in the shallow water-bearing zone. Clay unit topography was mapped. The vertical delineation of contamination was not completed in this phase due to concerns about breaching the clay unit and introducing contamination to lower aquifer.

Soil sampling results determined that cis-1,2-DCE, TCE and PCE were present in soils at suspected source areas in excess of NJDEP Impact to Ground Water Cleanup Criteria (IGWSCC). The soils delineation was completed during this phase.

Groundwater results indicated that 1,1-DCE, cis-1,2-DCE, TCE, VC and PCE were present in groundwater at levels that exceeded New Jersey Class II-A Ground Water Quality Standards. The shallow dissolved plume was delineated and found to extend to the adjacent surface water body. A zone of free product above the clay layer was confirmed using Sudan IV dye.

**Problems Encountered**

The coordination of the project from the field with all parties was sometimes problematic. The drilling crew often encountered mechanical difficulty resulting in down time for not only the field crew but also the laboratory. The mobile lab's first day on site required most of the day to set up and calibrate equipment. The higher contaminated samples had to be rerun at multiple dilution factors causing delays in sample analysis turnaround. Confirmatory soil samples still had to be sent to an off-site laboratory as required by DEP. The field effort required greater coordination with NJDEP regulators as well as the need for more experienced, higher level field geologist and technician on site for entire fieldwork. The vertical groundwater delineation could not be accomplished during this phase because of concerns of introducing contamination below the confining unit.

**Lessons Learned**

The staffing of a highly experienced field geologist/project manager is critical to the success of the project. Also a good understanding and interpretation of all background information and historical data is imperative. The importance of coordination and understanding of the conceptual plan by regulators, consultant, RP, and contractors (mobile lab and drillers) cannot be underestimated. During the fieldwork it is important to maximize sample collection each day in order to keep up with the capacity of the mobile laboratory. There was very good correlation between results from the Mobile lab and certified off-site lab, however it would be more efficient to prescreen samples to reduce dilution reruns. Also, consideration should be given to using two Geoprobe™ rigs to maximize the capability of the mobile lab. The collection and delivery of field samples rarely exceeded 50% of mobile lab capacity. An effective communication system in the field was essential, which included mobile phones and beepers. A planning meeting was held the end of each day to review results of the day's activities and plan for the following day. Follow-up efforts will be necessary to complete the vertical delineation by installing double cased wells into the deep overburden zone.

**Conclusions**

Significant site characterization of a complex DNAPL site was completed within 13 days. The approach required thorough coordination with all parties and an understanding with regulators (i.e., case manager and geologist) to be available for consultation during fieldwork. The Triad approach requires professional judgment that may at time be inconsistent with more conventional investigative approaches.

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**APPENDIX D**

**DNAPLs Team Contacts, ITRC Fact Sheet, and ITRC Product List**

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